THE PHOTOCHEMICAL BEHAVIOR OF SELECTED OXIME ESTERS

by

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A DISSERTATION

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ACKNOWLEDGMENT

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CHAPTER I

INTRODUCTION

To our knowledge, investigations of the photochemistry of oxime esters have been limited to studies of *syn*-benzaldoxime acetate[1] and pregnolone oxime acetate[2], and these studies were merely tangential to other work. In neither case were photolysis products reported.

The photochemistry of oximes, however, dates back to 1903[3] when photolytically induced geometrical isomerisation about the C=N linkage was reported, and has continued[4,5,6] sporadically until recently when photochemical Beckmann rearrangements have been reported in aldoximes[5] and ketoximes[2]. In particular cyclohexanone oxime[2] has been

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[1] J. H. Amin and P. de Mayo, Tet. Letters, 1585 (1963).

[2] R. T. Taylor, M. Donek, and G. Just, Tet. Letters, 4143 (1966).

[3] G. Ciamician and P. Silber, Ber., 36, 4268 (1903).

[4] R. Stoermer, Ber., 44, 667 (1911).

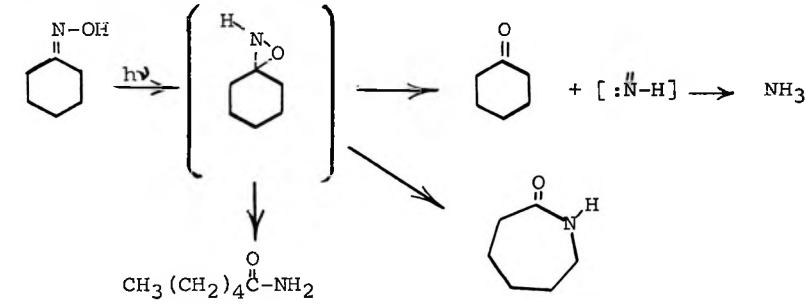
[5] O. L. Brady and F. P. Dunn, J. Chem. Soc., 103, 1620 (1913).

[6] O. L. Brady and G. P. McHugh, J. Chem. Soc., 125, 547(1924).

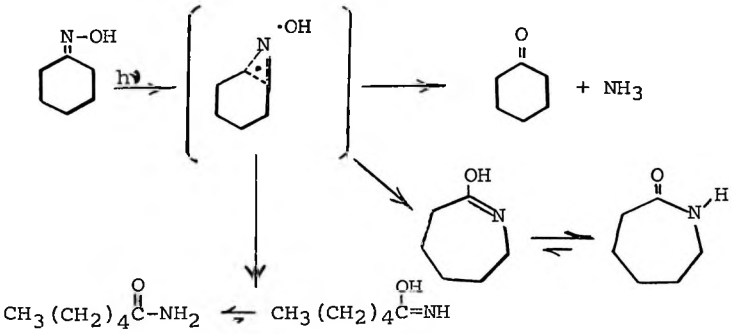
shown to undergo photochemical rearrangement to yield caprolactam, caproamide, and, in addition, cyclohexanone.

Two mechanisms which may be envisioned to account for the reaction of cyclohexanone oxime are Mechanism A and Mechanism B.

Mechanism A:



Mechanism B:



Mechanism A would require the existence of an oxazirane intermediate. The photodecomposition of oxaziranes to give nitrenes is supported by the work of Meyer and Griffin.[7]

Mechanism B would require initial cleavage of the N-O bond. This is quite reasonable since the N-O bond is by far the weakest bond in the molecule, at 53 kcal/mole, and the energy absorbed by the C=N chromaphore is on the order of 136 kcal/mole. One would expect the cleavage and recombination steps of the reaction to proceed within a "cage" system, as suggested by Walling and Gibian[8], and not to undergo mixing of the radical fragments.

It appeared possible to us that oxime esters could undergo rearrangement in the same manner as oximes and the research discussed herein was undertaken to explore that possibility. Mechanism B would be the most attractive in the case of oxime esters since Mechanism A would require an intermediate with separation of charge. Should

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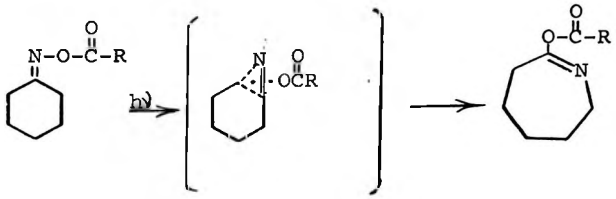
[7] E. Meyer and G. W. Griffin, Angewandte Chemie, 79, 648 (1967).

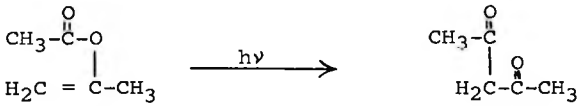
[8] C. Walling and M. J. Gibian, J. Am. Chem. Soc., 83, 2998 (1961).

Mechanism B be operative, the reaction would, of course, stop at the enol, or lactim, stage as shown in equation 1.



(1)

However, the introduction of the carbonyl chromaphore, as well as any chromaphore in the R group, would drastically increase the number of photochemical reaction possibilities. For example, a rearrangement analogous to that of enol esters, reported by Yogev, Gorodetsky, and Mazur[9], might occur. They reported that the irradiation of enol esters produces β-diketones as shown in Equation 2.



(2)

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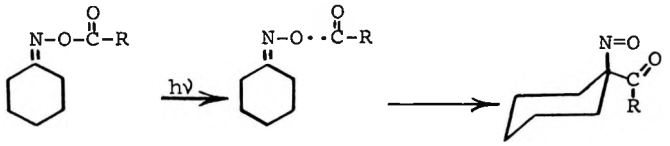
[9] A. Yogev, M. Gorodetsky, and Y. Mazur, J. Am. Chem. Soc., 86, 5208 (1964).

An analogous rearrangement of the oxime ester system would be that shown in Equation 3.



(3)

An interesting sidelight of this reaction is the possibility of creating selective chelating agents by varying the size of the ring and the R group.

There are, of course, myriad other decomposition, recombination, and reduction reactions that might be imagined for the ester moiety.

CHAPTER II

HISTORICAL

The photochemistry of the oximino chromaphore has been under investigation for a number of years. Studies concerning the photolytically induced syn-anti isomerism about the C=N linkage were first published in 1903[1] and have appeared sporadically since that time.[2,3,4]

Amin and de Mayo[5] reported that irradiation of aryl aldoximes in a variety of solvents leads, aside from geometrical isomerism, to the formation of amides. This is the first published evidence of a photochemical Beckmann rearrangement. They suggest that a general system (I), or its vinylogue, may be susceptible to photochemical

$$Ar - A = \overset{C}{\overset{|}{B}} \qquad (I)$$

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[1] G. Ciamician and P. Silber, Ber., 36, 4268 (1903).

[2] R. Stoermer, Ber., 44, 667 (1911).

[3] O. L. Brady and F. P. Dunn, J. Chem. Soc., 103, 1620 (1913).

[4] O. L. Brady and G. P. McHugh, J. Chem. Soc., 125, 547 (1924).

[5] J. H. Amin and P. de Mayo, Tet. Letters, 1585 (1963).

rearrangement, with the overall transfer of C from B to A (or vinylogue). The oxime rearrangement reported by them falls into this class as does that of nitrones.[6]

Just and Pace-Asciak[7] have shown that α-β unsaturated aldoximes rearrange to give the corresponding nitriles.

Taylor, Donek, and Just[8] have investigated the photochemistry of several ketoximes and report that these compounds give Beckmann rearrangement products as well as the ketones corresponding to the starting material. In particular they cite the irradiation of cyclohexanone oxime in methanol and isopropanol as producing caprolactam, caproamide, and cyclohexanone.

The only photolyses of oxime esters that have been published, to our knowledge, have been concerned with *syn*-benzaldoxime acetate[5] and pregnolone oxime acetate.[8] In neither case was a reaction reported.

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[6] J. Splitter and M. Calvin, J. Org. Chem., 23, 651 (1958).

[7] G. Just and C. Pace-Asciak, Tetrahedron, 22, 1069 (1966).

[8] R. T. Taylor, M. Donek, and G. Just, Tet. Letters, 4143 (1966).

CHAPTER III

EXPERIMENTAL

CHEMICALS & REAGENTS

The following is a list of reagents and materials used in this research including the source as well as preliminary preparations where necessary.

Acetic Anhydride, Reagent A.C.S., J. T. Baker Chemical Co., Phillipsburg, New Jersey.

Acetone, A standard solvent which was not further purified.

Acetyl Chloride, Reagent A.C.S., J. T. Baker Chemical Co., Phillipsburg, New Jersey.

Alumina, Chromatographic Grade, F-20, Aluminum Company of America, Bauxite, Arkansas.

Ammonium Acetate, Eastman Organic Chemicals, Rochester, New York.

Ammonium Benzoate, Eastman Organic Chemicals, Rochester, New York.

Aniline, Reagent A.C.S., J. T. Baker Chemical Company, Phillipsburg, New Jersey.

Benzene, A standard which was not further purified.

Benzophenone, Reagent A.C.S., Eastman Organic Chemicals, Rochester, New York.

Benzoyl Chloride, Reagent A.C.S., J. T. Baker Chemical Co., Phillipsburg, New Jersey.

Bromoacetyl Bromide, Practical Grade, Eastman Organic Chemicals, Rochester, New York.

Calcium Chloride, Anhydrous, Reagent A.C.S., Fisher Scientific Company, Fair Lawn, New Jersey.

Carbon Tetrachloride, Spectro Grade, Eastman Organic Chemicals, Rochester, New York.

Chloroform, Spectro Grade, Eastman Organic Chemicals, Rochester, New York.

Cyclohexane, Practical Grade, Eastman Organic Chemicals, Rochester, New York.

Cyclohexane, Specially distilled on spinning band column for photolysis solvent.

Cyclohexanone, Reagent A.C.S., Eastman Organic Chemicals, Rochester, New York.

Cyclohexanone Oxime, Reagent A.C.S., K & K Laboratories, Inc., Plainview, New York.

Cyclohexyl Methyl Ketone, Reagent A.C.S., K & K Laboratories, Inc., Plainview, New York.

Cyclopentanone Oxime, Reagent A.C.S., Eastman Organic Chemicals, Rochester, New York.

Deuterium Oxide, 99.8 mole % D_2O, Bio-Rad Laboratories, Richmond, California.

Dimethylglyoxime, Reagent A.C.S., Eastman Organic Chemicals, Rochester, New York.

Diethyl Ether, Anhydrous, Reagent A.C.S., Mallinckrodt Chemical Works, St. Louis, Missouri.

2,4-Dinitrophenylhydrazine, Reagent A.C.S., Eastman Organic Chemicals, Rochester, New York.

Ethanol, Absolute, a standard solvent which was not further purified.

Ferrous Ammonium Sulfate, Fisher Scientific Co., Fairlawn, New Jersey.

Hydrochloric Acid, Concentrated, Reagent A.C.S., J. T. Baker Chemical Co., Phillipsburg, New Jersey.

Hydroxylamine Hydrochloride, Practical Grade, Eastman Organic Chemicals, Rochester, New York.

Lead Tetraacetate, Fisher Scientific Co., Fairlawn, New Jersey.

Magnesium Sulfate, Anhydrous, Reagent A.C.S., Fisher Scientific Co., Fairlawn, New Jersey.

Methyl Alcohol, Technical Grade, Baker and Adamson, Allied Chemical, General Chemical Division, Morristown, New Jersey, A standard solvent which was not further purified.

Methyl Alcohol, Reagent A.C.S., Eastman Organic Chemicals, Rochester, New York. Specially distilled on spinning band column for photolysis solvent.

p-Nitrobenzoyl Chloride, Practical Grade, Eastman Organic Chemicals, Rochester, New York.

Nonanoic Acid, Sample, Eastman Chemical Products, Inc., Kingsport, Tennessee.

Petroleum Ether, (b.p. 30-60°C), Technical Grade, Baker & Adamson Allied Chemical, General Chemical Division, Morristown, New Jersey. A standard solvent which was not further purified.

1,10-Phenanthroline Monohydrate, Eastman Organic Chemicals, Rochester, New York.

Phenyl Acetyl Chloride, Reagent A.C.S., Eastman Organic Chemicals, Rochester, New York.

Potassium Ferric Oxalate, Reagent A.C.S., K & K Laboratories, Inc., Plainview, New York.

Potassium Hydroxide, Reagent A.C.S., J. T. Baker Chemical Co., Phillipsburg, New Jersey.

Pyridine, Purified, J. T. Baker Chemical Co., Phillipsburg, New Jersey.

Sodium Acetate, Reagent A.C.S., Fisher Scientific Co., Fairlawn, New Jersey.

Sodium Amide, Reagent A.C.S., K & K Laboratories, Inc., Plainview, New York.

Sodium β-Anthroquinone Sulfonate, Reagent A.C.S., Eastman Organic Chemicals, Rochester, New York.

Sodium Benzoate, Eastman Organic Chemicals, Rochester, New York.

Sodium Bicarbonate, Reagent A.C.S., J. T. Baker Chemical Co., Phillipsburg, New Jersey.

Sodium Dithionite, Practical (90%), Eastman Organic Chemicals, Rochester, New York.

Sodium Hydroxide, Reagent A.C.S., J. T. Baker Chemical Co., Phillipsburg, New Jersey.

Sulfuric Acid, Concentrated, Reagent A.C.S., J. T. Baker Chemical Co., Phillipsburg, New Jersey.

Thionyl Chloride, Purified, J. T. Baker Chemical Co., Phillipsburg, New Jersey.

p-Toluic Acid, Cowles Chemical Co., Cleveland, Ohio.

Triethylamine, Reagent A.C.S., Eastman Organic Chemicals, Rochester, New York.

APPARATA & EQUIPMENT

Standard Taper glassware was used through-out the work.

Melting points were determined on a Fisher-Johns block and are uncorrected.

Infrared spectra were obtained with a Perkin-Elmer Model 137b Spectrophotometer, a Perkin-Elmer Model 337 Spectrophotometer, and a Beckman IR-7 Spectrophotometer.

Ultraviolet and visible spectra were obtained with a Perkin-Elmer Model 202 Spectrophotometer, a Beckman D.B. Spectrophotometer, and a Cary Model 14 Spectrophotometer.

N.M.R. spectra were obtained with a Varian HA-100 Spectrometer.

Three analytical gas chromatographic columns were used in this research. Two columns were packed with SE-30; one 15% SE-30 on 60/80 mesh Chromosorb G in 6 feet of ¼ inch O.D. copper tubing, and the other 5% SE-30 on 60/80 mesh Chromosorb W in 6 feet of 1/8 inch O.D. stainless steel tubing. The third column was Poropak Q in 6 feet of 1/8 inch O.D. copper tubing.

The stainless steel column was received as standard equipment with the Varian Aerograph Series 1520 Chromatograph. The other columns were packed by plugging one end of the tubing with pyrex wool and vibrating the column as the packing was introduced. The other end of the tubing was then plugged with pyrex wool and the column was coiled. Standard ¼ inch Swagelok brass fittings were attached to the ¼ inch column and 1/8 to ¼ inch Swagelok adaptors were attached to the 1/8 inch column. The 15% SE-30 column was conditioned for 24 hours at 250° and the Poropak column at 210° for 24 hours under helium gas at 4 p.s.i.g.

Gas chromatographic instruments used in this research were:

(1) Varian Aerograph Model 90-P3 Gas Chromatograph, manufactured by Varian Aerograph, Walnut Creek, California. The recorder was a Sargent Model SR Recorder, manufactured by E. H. Sargent and Co. and equipped with a Disc Chart Integrator Model 201-B manufactured by Disc Instruments Inc., Santa Anna, California.

(2) Varian Aerograph Series 1520 Gas Chromatograph, manufactured by Varian Aerograph, Walnut Creek, California. The recorder was a Sargent Model SR Recorder, manufactured by E. H. Sargent and Co.

Fractions obtained from elution chromatography on alumina were collected with a Rinco Model VE-2002-B24 Automatic Fraction Collector manufactured by Rinco Instrument Co., Inc., Greenville, Illinois.

Conductometric titrations were performed with a Model RC 16B2 Conductivity Bridge manufactured by Industrial Instruments, Inc., 88 Commerce Road, Cedar Grove, New Jersey.

Photolyses were performed with either a Rayonet Photochemical Reactor manufactured by the Southern New England Ultraviolet Co., Newfield Street, Middletown, Connecticut or with a Hanovia 450-W lamp manufactured by Englehard-Hanovia Inc., Lamp Division, 100 Chestnut Street, Newark, New Jersey.

In order to use the Hanovia 450-W lamp it was necessary to construct a transformer box. This box was constructed with components obtained from Englehard-Hanovia Inc. according to the schematic diagram shown in Figure 1.

Selection of the desired wavelength of light for photolyses was accomplished by the use of filters obtained from Englehard-Hanovia Inc. These filters were in the form of sleeves 29 mm in diameter and 282 mm in length and were fabricated from Pyrex 7740, Corex 9700, and Vycor 7910 glass.

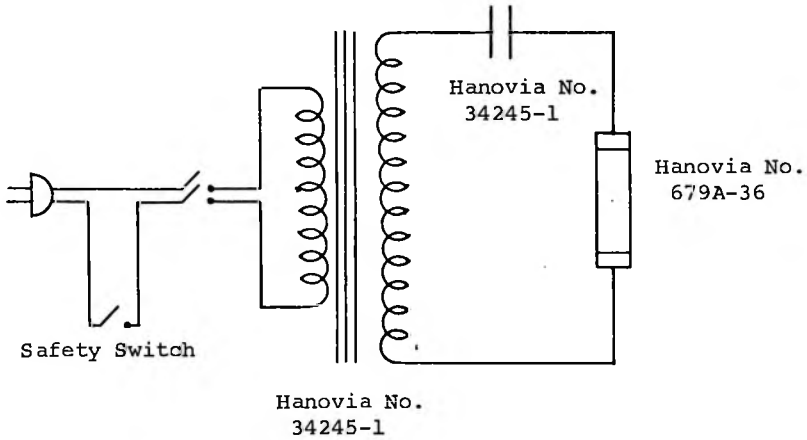

FIGURE 1. Schematic Diagram for Transformer Box (Ballast) Used with the Hanovia 450-W High Pressure Lamp

The absorbance characteristics of these types of glass as well as that of quartz are shown in Figure 2.

A quartz immersion well for use with the Hanovia 450-W lamp was obtained from Englehard-Hanovia Inc. (catalog no. 19434). This well was designed so that a cooling liquid - which could also be used for purposes of light filtering - could be passed between the lamp and the solution being photolysed.

A photolysis vessel was, as shown in Figure 3, fabricated by the glass blower at the University of Alabama. The volume of this vessel was approximately 550 ml with the immersion well inserted.

A switch designed[1] to prevent overheating of the Hanovia 450-W lamp was fabricated by the glass blower according to Figure 4. With this switch the lamp would be extinguished when the cooling liquid flow dropped below a pre-determined flow rate.

To prevent retinal damage to the operator while working with the Hanovia 450-W lamp a pair of safety glasses were

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[1]M. A. Rieman, Rev. Sci. Instru., 37, 681 (1966).

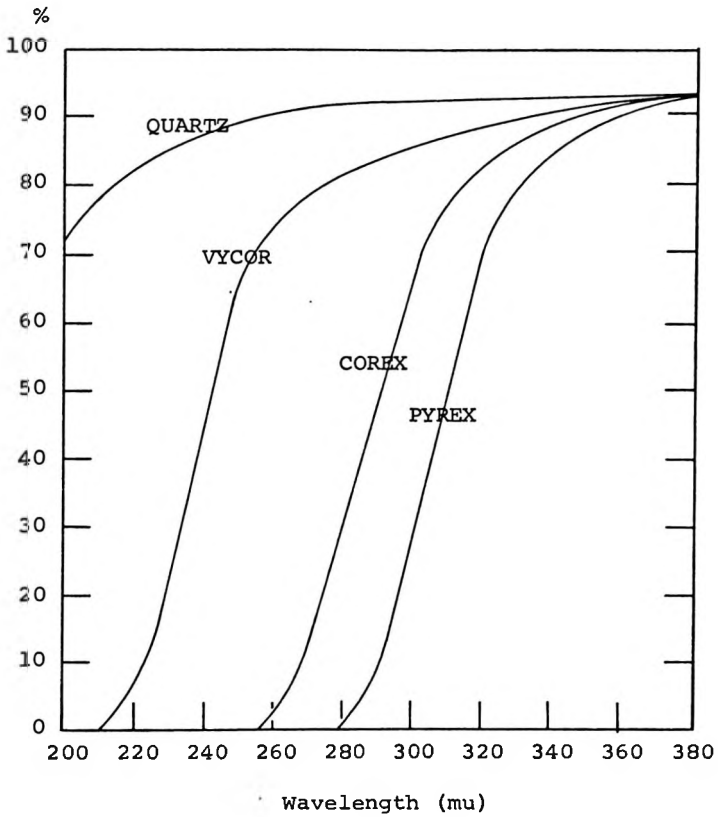

FIGURE 2. Absorbance Characteristics of Filter Sleeves

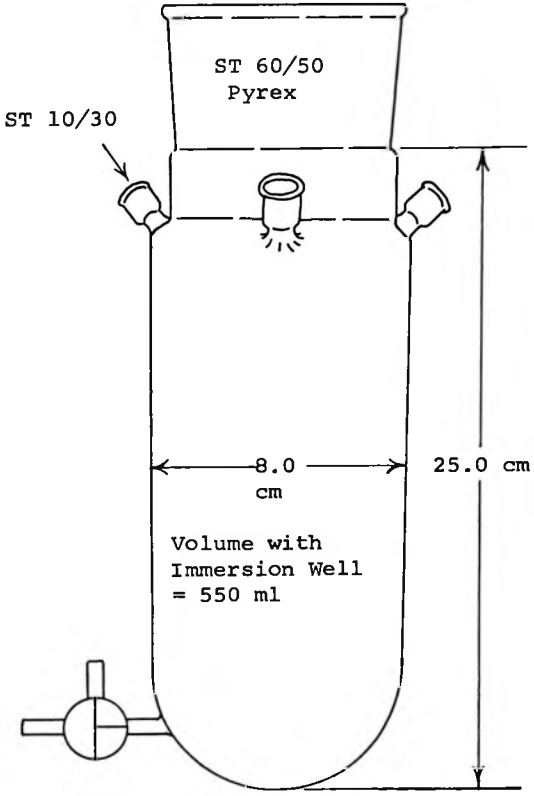

FIGURE 3 . Photolysis Vessel for Use with Hanovia 450-W Lamp and Immersion Well

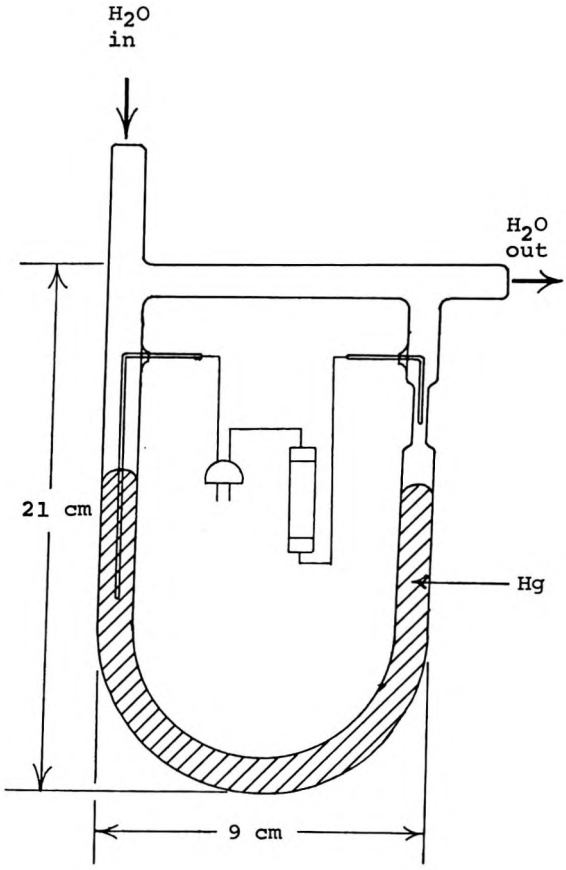

FIGURE 4. Safety Switch to Prevent Overheating of Havovia 450-W Lamp

constructed by superimposing two pair of Cool-Ray polaroid sunglasses at about 89° to each other and taping in place. When these glasses were placed in the sample beam of a spectrophotometer, they showed infinite absorbance from 200 to above 600 mμ. It is probable that enough untra-violet radiation is filtered to prevent retinal damage.

Figure 5 presents the complete experimental apparata used in photolyses with the Hanovia 450-W Lamp.

1. Nitrogen supply
2. Fieser's solution
3. Fieser's solution
4. Lead acetate
5. Drierite
6. Lamp
7. Immersion well
8. Photolysis vessel
9. Cold trap
10. Cold trap
11. Ascarite
12. Transformer box (ballast)

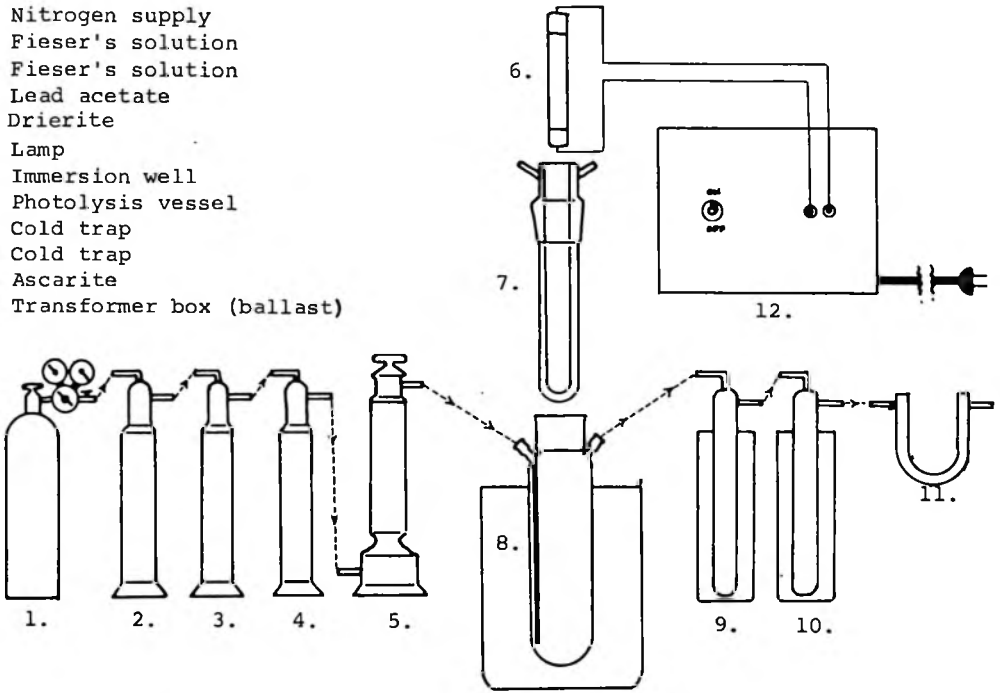

FIGURE 5 . Experimental Photolysis Set-up

ANALYSES

All elemental analyses were performed by the following laboratories:

Midwest Microlab, Inc.
6000 East 46th Street
Indianapolis, Indiana 46226

Dr. H. Trutnovsky
Medizinisch-Chemisches Institut
und Pregl-Laboratorium
der Universitat Graz
A 8010 Graz
Universitatsplatz 2
Austria

Galbraith Laboratories, Inc.
P. O. Box 4187 - Lonsdale
2323 Sycamore Drive
Knoxville, Tennessee 37921

PHOTOLYSES

General Photolysis Procedure

The following general procedure was used in photolyses involving the 450-W Hanovia lamp.

Approximately 500 ml of a 0.1N solution of the material to be photolysed in the selected solvent was degassed for one-half hour by bubbling oxygen-free, dry nitrogen through the solution.

The Hanovia lamp was allowed to come to full intensity (approximately ten minutes) while placed in a shielded, well ventilated enclosure (usually the Rayonet reactor), and then introduced into the reaction vessel. The radiation emitted by the lamp is capable of causing severe eye damage and skin burns; consequently, a face shield, safety glasses (polaroid), and long sleeved clothing were worn while handling the lamp during photolyses.

The photolyses were then allowed to continue for the selected length of time with oxygen-free, dry nitrogen continuously being bubbled through the solution.

When it was necessary to momentarily discontinue the photolyses for sampling purposes, the lamp was not turned off

but removed while still operating and placed in the Rayonet reactor during sampling.

After the selected photolysis time had elapsed, the lamp was turned off and the solution removed for analysis.

Purification of Nitrogen

Dry nitrogen from the tank was passed through two wash towers of Fieser's solution to remove any trace amounts of oxygen which might quench triplet reactions or otherwise interfere, then through a saturated solution of lead acetate to remove any hydrogen sulfide generated in the Fieser's solution, and finally through a drying tower of calcuim sulfate (Drierite - indicating) to remove water.

Preparation of Fieser's Solution[2]

A clear blood-red solution was prepared by dissolving 20 g of potassium hydroxide, 2 g of sodium β-anthroquinine sulfonate, and 15 g of sodium dithionite ($Na_2S_2O_4$) in 100 ml of water.

When the color of Fieser's solution turns form clear red to dull red or brown it should be replaced.

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[2]L. F. Fieser, "Experiments in Org. Chem.", D. C. Heath and Co., Boston, 1957, p. 299.

Example Photolysis

A solution of 5.7 g (0.05 mole) of O-benzoylcyclohexanone oxime in 500 ml of spinning-band-distilled cyclohexane was degassed for 0.5 hours by bubbling through oxygen-free, dry nitrogen.

The Hanovia lamp was allowed to warm up for 10 minutes and was inserted into the photolysis vessel along with the Corex filter sleeve. The lamp was removed at 15, 30, 45, 60, 90, 120, 180, and 240 minutes and placed in a shielded, well-ventilated area (such as the Rayonet Reactor). During these pauses a sample aliquot was removed by syringe and subjected to infrared, ultraviolet, and gas chromatographic analysis. At the same time a pre-weighed ascarite tube - which had been connected to the photoplysis apparatus - was removed and weighed to determine the amount of CO_2 evolved as a function of irradiation time. In addition a qualitative test was made for the presence of ammonia in the gaseous effluent.

The photolysis was continued for 240 minutes. The post-photolysis solution was removed and the reaction vessel washed with 95% ethanol. This ethanolic solution was titrated conductometrically with 0.0569 N HCl. In addition 50 ml of the postphotolysis solution was taken up in 95% ethanol and

titrated. The resulting value was multiplied by ten and combined with the value for the wash solution to give the total yeild of ammonium benzoate. As a check on the value validity of this analysis, known samples of ammonium benzoate were titrated and also a separate photolysis reaction was performed and the ammonium salt carefully isolated and weighed. Reasonable agreement was obtained.

The remaining 450 ml of postphotolysis solution was separated by elution chromatography on alumina and analysed.

PREPARATIONS

O-Acetylbenzophenone Oxime Using Sodium Benzophenone Oximate

A suspension of 10.9 g (0.05 mole) of sodium benzophenone oximate in 300 ml of anhydrous diethyl ether was cooled in an ice-salt bath and 3.8 g (0.05 mole) of acetyl chloride was added dropwise with stirring to the cold etheral suspension under the hood. The stirring was continued for 0.5 hour after complete addition of the acetyl chloride.

The resulting sodium chloride and any unreacted oxime salt was filtered and the remaining etheral solution was washed three times with 50-ml portions of cold, saturated sodium bicarbonate solution and dried over anhydrous calcium chloride.

The solvent was evaporated and the product recrystallized from ethanol to yield 2.24 g (18.7% yield) of very fine white crystals melting at 73.5 - 74°.

Ultraviolet (absolute ethanol) λ_{max}: 207 mμ and 253 mμ; infrared ($CHCl_3$) ν_{max}: 3060-3000 (multiplet), 1770 (C=O), 1600, 1570, 1490, 1450, 1380, 1330, 1305, 1195, 1005, 910, 860, 690, 645 cm^{-1}; NMR (CCl_4): δ7.3 (m, 10), δ4.71 (s, 2) (water of hydration), δ1.95 (s, 3).

Anal: calculated for $C_{15}H_{13}NO_2$: C, 75.31%; H, 5.44%; N, 5.86%; O, 13.39%, Found: C, 74.73%, H, 5.54%; N, 5.72%; O, 14.01%.

O-Acetylcaprolactim by Reaction of O-acetylcyclohexanone Oxime With Acetic Anhydride - Attempted Preparation

A solution of 5 g of O-acetylcyclohexanone oxime in 20 ml of acetic anhydride was refluxed for 23 hours. The acetic anhydride was removed by vacuum distillation and the remaining material was chromatographed on alumina with benzene as eluent. The identifyable fractions appeared to be the starting material and cyclohexanone. It is possible that the lactim was produced, but if so, it was in very low yield.

O-Acetylcyclohexanone Oxime Using Sodium Cyclohexanone Oximate

A suspension of 13.5 g (0.10 mole) of sodium cyclohexanone oximate in 150 ml of anhydrous diethyl ether was cooled in an ice-salt bath and 6.3 g (0.08 mole) of acetyl chloride was added dropwise to the cold etheral suspension with stirring under the hood. The stirring was continued for 0.5 hour after complete addition of the acetyl chloride.

The resulting sodium chloride and excess oxime salt mass was filtered and the solvent evaporated. Some ether was apparently left since the actual yield (103%) was greater than the theoretical yield.

The product was a viscous amber liquid whose infrared spectrum was consistent with the expected product. Infrared analysis indicated that the product was superior in purity to that of the cyclopentanone oxime esters prepared previously.

O-Acetylcyclohexanone Oxime By Direct Reaction

A solution of 22.6 g (0.20 mole) of cyclohexanone oxime and 20.2 g (0.20 mole) of triethylamine in about 200 ml of dry methylene chloride was prepared, and 15.7 g (0.20 mole) of acetyl chloride was added dropwise with vigorous stirring. The reaction was obviously exothermic and caused the solution to reflux steadily.

After the solution had cooled to room temperature, it was washed twice with 500-ml portions of water and dried over anhydrous magnesium sulfate. The solvent was evaporated and any remaining volitile impurities were removed by vacuum distillation at 1 mm Hg pressure to yield 25.8 g (83.3%) of an viscous amber fluid. NMR analysis indicated this material to be at least 99% pure.

Before use the product was chromatographed on alumina with methylene chloride as eluent. Evaporation of the eluent gave a light yellow fluid.

Ultraviolet (absolute ethanol) λ_{max}: 210 mμ, (cyclohexane) 216 mμ; infrared (thin film) ν_{max}: 2940, 2860, 1760, 1640, 1450, 1380, 1290, 1250, 1235, 1200, 1140, 1005, 990, 925, 910, 860, and 845 cm^{-1}; NMR (CCl_4): δ2.48 (m, 2), δ2.28 (m, 2), δ2.06 (s, 3), δ1.65 (m, 6).

Anal. Calculated for $C_8H_{13}NO_2$: C, 61.93%; H, 8.31%; N, 9.04%; O, 20.72%. Found: C, 62.17%, H, 8.62%; N, 9.37%; O, 19.84%.

O-Acetylcyclopentanone Oxime - Sodium Hydroxide Method[3]

A solution of 10 g (0.10 mole) of cyclopentanone oxime in 200 ml of acetone was treated with 50 ml (0.10 mole) of 8% aqueous sodium hydroxide at 0° and then with 7.8 g (0.10 mole) of acetyl chloride, and the mixture was stirred at 0° for 10 minutes.

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[3] J. C. Craig and A. R. Naik, J. Am. Chem. Soc., 84, 3410 (1962).

The acetone was evaporated and the remaining solution was extracted with six 50-ml portions of diethyl ether. The ether was evaporated but no product was obtained.

O-Acetylcyclopentanone Oxime - Pyridine Method[4]

A mixture of 5 g (0.05 mole) of cyclopentanone oxime, 67 ml of pyridine, and 75 ml of 97% pure acetic anhydride was slowly stirred at room temperature for 24 hours. Efforts were made to exclude water from the reaction system.

After stirring, 150 ml of water was added to react with excess acetic anhydride. The aqueous solution was extracted with four 100-ml portions of methylene chloride. The organic phase was then evaporated to 50-ml volume.

An attempt was made to distill the concentrated solution under 10-mm Hg pressure, but the product underwent extensive decomposition at about 35°.

O-Acetylcyclopentanone Oxime Using Sodium Cyclopentanone Oximate

A suspension of 7.2 g (0.06 mole) of sodium cyclopentanone oximate in 300 ml of anhydrous diethyl ether was cooled

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[4]A. Hassner and I. H. Pomerantz, J. Org. Chem., 27, 1760 (1962).

in an ice-salt bath and 3.9 g (0.05 mole) of acetyl chloride was added with stirring to the cold etheral suspension under the hood.

The resulting sodium chloride and unreacted oxime salt mass was filtered and the ether solvent evaporated to yield 7.1 g (80%) of a viscous amber liquid.

Infrared analysis indicated that the material was the expected product but was relatively impure.

Benzoic Anhydride

A suspension of 14.4 g (0.10 mole) of sodium benzoate in about 250 ml of dry chloroform was prepared and 14.0 g (0.10 mole) of benzoyl chloride was added dropwise with stirring. The resulting mixture was refluxed for 4 hours, washed with 500 ml of water, dried over anhydrous calcium chloride, and the solvent evaporated to yield 19.0 g (84%) of a viscous light yellow oil. An infrared spectrum of this material corresponded exactly to that expected for benzoic anhydride. No attempts were made to crystallize this product since it was not necessary to do so.

Infrared ν_{max} (thin film) 1790 cm^{-1} $(C=O)_1$ and 1725 cm^{-1} $(C=O)_2$.

Benxophenone Oxime[5]

A mixture of 100 g (0.55 mole) of benzophenone, 60 g (0.86 mole) of hydroxylamine hydrochloride, 200 ml of 95% ethanol, 40 ml of water, and 110 g (2.76 mole) of powdered sodium hydroxide was refluxed for 5 minutes. The mixture was then added to a solution of 300 ml of concentrated hydrochloric acid in 2 l of water. The product was filtered and washed with 1.5 l of water. The product was then recrystallized from ethanol to yield 84.5 g (78%) of oxime melting at 141-142°. The literature melting point for benzophenone oxime is given as 141-142°.

O-Benzoylcaprolactim by Thermal Rearrangement of O-Benzoylcyclohexanone Oxime - Attempted Preparation

Several grams of O-benzoylcyclohexanone oxime was heated for 4 hours at 100° under a nitrogen atmosphere to yield a brown oil which had the infrared spectrum of O-benzoylcyclohexanone oxime and an obvious odor of cyclohexanone.

The reaction was carried out again with a tiny drop of acetic acid added and the mixture heated for 12 hours. The same results were observed in this case.

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[5]A. Lachman and C. R. Noeller, Org. Syn., 10, 10 (1930).

O-Benzoylcaprolactim by Reaction of O-Benzoylcyclohexanone Oxime with Benzoic Anhydride - Attempted Preparation

A solution of 3 g of O-benzoylcyclohexanone oxime in 10 g of benzoic anhydride was heated under anhydrous conditions at 100° for 7 hours. The resulting mixture was fractionally distilled under 1 mm Hg pressure to yield three fractions. None of these fractions contained the desired lactim. However, a reaction did take place to yield about 1 ml of a material having a carbonyl absorption in the infrared at 1705 cm^{-1} and a ketone-like odor (not cyclohexanone). Since this fraction did not have a C=N absorption in the infrared, it was obviously not the desired product, and its identity was not pursued further.

O-Benzoylcyclohexanone Oxime Using Sodium Cyclohexanone Oximate

A suspension of 13.5 g (0.10 mole) of sodium cyclohexanone oximate in 350 ml of anhydrous diethyl ether was cooled in an ice-salt bath and 11.2 g (0.08 mole) of benzoyl chloride was added dropwise with stirring to the cold etheral suspension under the hood. The stirring was continued for 0.5 hour after complete addition of the benzoyl chloride.

The resulting sodium chloride and unreacted oxime salt mass was filtered. The etheral solution was washed with four 50-ml portions of cold, saturated sodium bicarbonate solution and the solution dried over anhydrous calcium chloride. The solvent was evaporated and the product recrystallized from ethanol--water to yield 4.09 g (23.5%) of a white crystalline solid melting at 61-63°. An infrared spectrum of the product was consistent with the expected compound and indicated a high degree of purity.

O-Benzoylcyclohexanone Oxime by Direct Reaction

A solution of 11.3 g (0.10 mole) of cyclohexanone oxime and 10.1 g (0.10 mole) of triethylamine in 750 ml of anhydrous diethyl ether was prepared and 14.0 g (0.10 mole) of benzoyl chloride was added dropwise with vigorous stirring. The reaction was obviously exothermic and caused a steady reflux of the etheral solution.

After the solution had returned to room temperature it was washed twice with 500-ml portions of water and dried over anhydrous calcium chloride. The solvent was evaporated and the product recrystallized three times from ethanol-water to yield 13.5 g (68%) of very pure white crystals melting at 62-63°.

Ultraviolet (absolute ethanol) λ_{max}: 202 mμ, 234 mμ (e = 18000), 273 mμ, and 281 mμ; (cyclohexane) 229 mμ (e = 12400), 273 mμ (e = 800), and 281 mμ (e = 600), (water) 196 mμ, 236 mμ, and broad shoulder 270-280 mμ; infrared ν_{max} (cyclohexane) 3060, 1760, 1640, 1600, 1590, 1318, 1243, 1180, 1140, 1080, 1060, 1023, 988, 928, 918, 830, and 700 cm^{-1}; NMR (CCl_4): δ7.90 (m, 2), δ7.35 (m, 3), δ2.56 (m, 2), δ2.38 (m, 2), δ1.67 (m, 6).

Anal: Calculated for $C_{13}H_{15}NO_2$: C, 71.89%; H, 6.91%; N, 6.45%; O, 14.75%. Found: C, 71.76%; H, 6.85%; N, 6.28%; O, 15.11%.

O-Benzoylcyclopentanone Oxime Using Sodium Cyclopentanone Oximate

A suspension of 7.2 g (0.06 mole) of sodium cyclopentanone oximate in 250 ml of anhydrous diethyl ether was cooled in an ice-salt bath and 7.0 g (0.05 mole) of benzoyl chloride was added dropwise with stirring to the cold etheral suspension under the hood.

An additional 100 ml of cold anhydrous diethyl ether was added to the solution to insure complete dissolution of the product.

The resulting sodium chloride and unreacted oxime salt mass was filtered. The ether solvent was evaporated and the

product was recrystallized from diethyl ether to yield 3.8 g (37.4%) of a white crystalline solid melting at 51-53°. Infrared analysis indicated that this solid was the expected product and was relatively pure.

O-Bromoacetylcyclopentanone Oxime using Sodium Cyclopentanone Oximate

A suspension of 12.1 g (0.10 mole) of sodium cyclopentanone oximate in 300 ml of anhydrous diethyl ether was cooled in an ice-salt bath and 16.2 g (0.08 mole) of bromoacetyl bromide was added dropwise with stirring to the cold etheral suspension under the hood. Stirring was continued 0.5 hour after complete addition of the acid chloride.

The resulting sodium bromide and unreacted oxime salt mass was filtered and the solvent evaporated yielding 11.7 g (66.5%) of a heavy brown liquid. Infrared analysis indicated that the purity of the product was extremely poor.

Cyclohexylidene Aniline

Five drops of concentrated hydrochloric acid was added to a mixture of 29.4 g (0.30 mole) of cyclohexanone and 23.3 g (0.25 mole) of aniline and the mixture stirred for 2 hours. The bottom of the flask was then covered with potassium hydroxide pellets and left over night.

The mixture was distilled under reduced pressure and the product collected at 180° under the lowest pressure the vacuum pump could attain.

The product was an extremely viscous amber fluid having the consistency of pine resin. The infrared spectrum was consistent with what would be expected for cyclohexylidene aniline.

Ultraviolet λ_{max} (EtOH): 224 mμ and 280 mμ; infrared (thin film) v max: 3060 (multiplet), 2920, 2850, 1660, 1600, 1505, 1450, 1397, 1300-1350 (multiplet), 761, and 704 cm^{-1}.

Cyclopentanone Oxime - Sodium Bicarbonate Method[6]

A mixture of 66.4 g (0.80 mole) of cyclopentanone, 50.0 g of sodium bicarbonate, 300 ml of 10% methanol - water solution, and 50.0 g (0.71 mole) of hydroxylamine hydrochloride was refluxed for 2 hours.

The solution was extracted with four 200-ml portions of diethyl ether and the organic phase placed under a current of air to evaporate.

The product was recrystallized first from benzene, then diethyl ether, and finally from petroleum ether. The

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[6] L. Reyicka, M. Kobett, O. Hafliger, and V. Prelog, Helv. Chem. Acta., 32, 544 (1949).

final yield was only about 30% due to difficulties in recrystallization.

Cyclopentanone Oxime - Pyridine Method[7]

A mixture of 20 g (0.24 mole) of cyclopentanone, 20 g (0.29 mole) of hydroxylamine hydrochloride, 100 ml of pyridine, and 100 ml of absolute ethanol was refluxed for 2 hours.

The solution was then left under a current of air over night to evaporate. The resulting concentrate was diluted with 150 ml of petroleum ether (30-60°) and the solvent was again evaporated. The resulting concentrate was then cooled to 0° and filtered.

The product was recrystallized from petroleum ether (30-60°) to give 8.7 g of oxime representing a 38% yield.

Methyl-(P-Nitro)-Benzoate

A solution of 5 g of p-nitrobenzoyl chloride in excess methanol was refluxed under nitrogen for several minutes with obvious evolution of hydrogen chloride. The solvent was evaporated to give a high yield of very pale yellow

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[7]R. L. Shriner, R. C. Fuson, D. Y. Curtin, "The Systematic Identification of Organic Compounds," 5th ed, John Wiley and Sons, New York, N. Y., p.123.

crystals melting at 94°. Infrared and NMR spectra were those expected and corresponded exactly to those of the product of the photolysis of p-nitro cyclohexanone oxime benzoate.

Nonanoyl Chloride

A mixture of 15.8 g (0.10 mole) of nonanoic acid and 11.9 g (0.10 mole) of thionyl chloride was refluxed for 0.5 hour. Upon refluxing the liquid turned dark brown.

The product was distilled under 22 mm Hg pressure to yield a dark brown liquid boiling at 105-110°.

O-Nonanoylcyclohexanone Oxime Using Sodium Cyclohexanone Oximate

A suspension of 6.8 g (0.05 mole) of sodium cyclohexanone oximate in 300 ml of anhydrous diethyl ether was cooled in an ice-salt bath and 8.6 g (0.05 mole) of impure nonanoyl chloride was added dropwise with stirring to the cold etheral suspension under the hood. Stirring was continued for 0.5 hour after complete addition of the acid chloride.

The resulting sodium chloride and unreacted oxime salt mass was filtered and the solvent evaporated yielding a cloudy, heavy brown liquid. Infrared analysis demonstrated this product to be extremely impure.

O-(p-Nitrobenzoyl)cyclohexanone Oxime by Direct Reaction

A solution of 18.5 g (0.10 mole) of p-nitrobenzoyl chloride in 500 ml of anhydrous diethyl ether was added dropwise to a solution of 11.3 g (0.10 mole) of cyclohexanone oxime and 10.1 g (0.10 mole) of triethylamine in 200 ml of anhydrous diethyl ether. The resulting mixture was refluxed for 0.5 hour, washed once with 500 ml of water, dried over anhydrous calcium chloride, and the solvent evaporated to yield 16.8 g (64%) of pale yellow crystals melting at 104-105°.

Ultraviolet (MeOH) λ_{max}: 208 mμ and 261 mμ; infrared (CCl_4) v max: 3060 (multiplet), 2945, 2870, 1750 (C=O), 1650 (C=N), 1605, 1530, 1450, 1440, 1410, 1345, 1320, 1285, 1260, 1110, 1075, 1020, 920, 850 cm^{-1}; NMR ($DMKd_6$): δ8.30 (d, 4), δ2.70 (m, 2), δ2.41 (m, 2), δ1.71 (s, 6).

O-Phenylacetylbenzophenone Oxime Using Sodium Benzophenone Oximate

A suspension of 10.9 g (0.05 mole) of sodium benzophenone oximate in 300 ml of anhydrous diethyl ether was cooled in an ice-salt bath and 7.7 g (0.05 mole) of phenyl acetyl chloride was added dropwise with stirring to the cold etheral suspension under the hood. The stirring was continued for 0.5 hour after complete addition of the acid chloride.

The resulting sodium chloride and any unreacted oxime salt mass was filtered and the remaining etheral solution was washed three times with 50-ml portions of cold, saturated sodium bicarbonate solution and dried over anhydrous calcium chloride.

The solvent was evaporated and the product recrystallized from ethanol-water to yield 6.12 g (39%) of a white crystalline solid having a strong odor of phenyl acetic acid. Infrared analysis indicated a highly impure product.

O-Phenylacetylcyclohexanone Oxime Using Sodium Cyclohexanone Oximate

A suspension of 5.1 g (0.04 mole) of sodium cyclohexanone oximate in 200 ml of anhydrous diethyl ether was cooled in an ice-bath and 4.6 g (0.03 mole) of phenyl acetyl chloride was added dropwise with stirring to the cold etheral suspension under the hood. Stirring was continued for 0.5 hour after complete addition of the acid chloride.

The resulting sodium chloride and unreacted oxime salt mass was filtered and the solvent evaporated to yield 6.2 g (67%) of a viscous amber liquid having only a very slight odor of phenyl acetic acid.

O-Phenylacetylcyclohexanone Oxime by Direct Reaction

A solution of 56.5 g (0.50 mole) of cyclohexanone oxime and 50.5 g (0.50 mole) of triethylamine in 1500 ml of anhydrous diethyl ether was prepared and 77.0 g (0.50 mole) of phenyl acetyl chloride was added dropwise with vigorous stirring. The reaction was obviously exothermic and caused a steady reflux of the etheral solution. Stirring was allowed to continue for 1 hour.

The solution was washed twice with 1000-ml portions of water, dried over anhydrous calcium chloride, and treated with decolorizing carbon. The solvent was evaporated to yield 92.0 g (80%) of a viscous yellow-green fluid freezing at 2-5° and having a very slight odor of phenyl acetic acid.

Infrared (thin film) ν_{max}: 3060 multiplet, 2940, 2860, 1760 (C=O), 1640 (C=N), 1600, 1500, 1450, 1340, 1280, 1250, 1240, 1220, 1115, 1080, 1030, 990, 905, 825 cm^{-1}; NMR (CCl_4): δ7.12 (m, 5), δ4.53 (m, 2), δ2.2 (m, 4), δ1.48 (m, 6).

Sodium Benzophenone Oximate

A solution of 51.2 g (0.260 mole) of benzophenone oxime in 500 ml of anhydrous diethyl ether was added dropwise to a suspension of 9.2 g (0.246 mole) of sodium amide in 150 ml

of anhydrous diethyl ether with stirring. The stirring was continued for 2 hours after the complete addition of the oxime.

The oxime salt was then filtered, dried, and ground up.

Sodium Cyclohexanone Oximate

A solution of 27.8 g (0.246 mole) of cyclohexanone oxime in 200 ml of anhydrous diethyl ether was added dropwise with stirring to a suspension of 8.9 g (0.228 mole) of sodium amide in 250 ml of anhydrous diethyl ether. Stirring was allowed to continue for 2 hours after the complete addition of the oxime.

The product was filtered, dried, and ground up. Again, as in the case of the cyclopentanone oxime salt, the actual yield (105%) was higher than the theoretical value because of water of hydration.

Sodium Cyclopentanone Oximate

A solution of 21.9 (0.22 mole) of cyclopentanone oxime in 150 ml of anhydrous diethyl ether was added dropwise with stirring to a suspension of 7.9 g (0.20 mole) of sodium amide in 100 ml of anhydrous diethyl ether. The stirring was

allowed to continue for 2 hours after complete addition of the oxime.

The salt was filtered and dried. An anomaly resulted in that the yield of salt was about 18% higher than the theoretical value. This was later shown to be due to water of hydration.

P-Toluoyl Chloride

A mixture of 17.8 g (0.13 mole) of p-toluic acid and 23.8 g (0.20 mole) of thionyl chloride was refluxed for 0.5 hour and the excess thionyl chloride was then boiled off to yield 18 ml of a dark brown liquid having an odor similar to benzoyl chloride. Since it was not necessary, the product was not further purified.

O-(p-Toluoyl)-cyclohexanone Oxime By Direct Reaction

A solution of 14.7 g (0.13 mole) of cyclohexanone oxime and 18.2 g (0.13 mole) of triethylamine in 1000 ml of anhydrous diethyl ether was prepared, and the entire product from the preparation of p-toluoyl chloride (18 ml) was added dropwise with stirring. The stirring was continued for 2 hours. The solution was then washed with 1000 ml of water, dried over anhydrous calcium chloride and the

solvent evaporated. The product was recrystallized from ethanol-water to yield 5.8 g (53%) of pale yellow solid melting at 67-69°.

Ultraviolet (MeOH) λ_{max}: 208 mμ and 242 mμ; infrared (CCl_4) ν_{max}: 3060 multiplet, 2940, 2860, 1750 (C=O), 1643 (C=N), 1610, 1450, 1440, 1400, 1325-1300 multiplet, 1270, 1223, 1185, 1145, 1075, 1025, 990, 930, 922, 890, 868, 690 cm^{-1}; NMR (CCl_4): δ7.80 (d, 2), δ7.12 (d, 2), δ2.53 (m, 2), δ2.34 (m, 5) (multiplet under singlet), δ1.65 (m, 6).

List of Photolyses

The following is a list of the photolyses performed during the course of this research with comments where pertinent:

1.) Crude Photolysis of O-Benzoylcyclopentanone Oxime in Diethyl Ether

The photolysis was performed with pyrex glassware in the Rayonet Photochemical Reactor using lamps with peak intensity at 350 mμ. The irradiation was continued for 22.75 hours. Although a reaction definitely occurred, it was most likely a thermal phenomenon since the ester does not absorb at the incident wavelength and the reaction temperature was around 35-40°.

2.) Crude Photolysis of O-Benzoylcyclohexanone Oxime in Cyclohexane

The photolysis was performed with pyrex glassware in the Rayonet Photochemical Reactor using lamps with peak intensity at 350 mμ. The irradiation was continued for 122.5 hours. Although a reaction definitely occurred, it was most likely a thermal phonomenon since the ester does not absorb at the incident wavelength and the reaction temperature was aroung 35-40°.

3.) Irradiation of O-Benzoylcyclohexanone Oxime in Cyclohexane Through a Pyrex Filter

The photolysis was performed according to the general procedure with the exception that a 3 l vessel was used. The irradiation was continued for 120 minutes and no evidence of a reaction was observed.

4.) Irradiation of O-Benzoylcyclohexanone Oxime in Cyclohexane Through a Corex Filter - Run I

The photolysis was performed according to the general procedure with the exception that a 3 l vessel was used. The irradiation was continued for 370 minutes.

5.) Irradiation of O-Benzoylcyclohexanone Oxime in Cyclohexane Through a Corex Filter - Run II

The photolysis was performed according to the general procedure and the irradiation was continued for 240 minutes. The second run was performed to provide more material for product analysis.

6.) Irradiation of O-Benzoylcyclohexanone Oxime in Cyclohexane Through a Corex Filter - Run III

The photolysis was performed according to the general procedure and the irradiation was continued for 240 minutes.

The third run was performed to provide more material for analysis and to comfirm the results of the first two runs.

7.) Irradiation of O-Benzoylcyclohexanone Oxime in Cyclohexane Through a Corex Filter - Run IV

The photolysis was performed according to the general procedure, and the irradiation was continued for 180 minutes. The fourth run was performed to analyse for carbon dioxide evolution as a function of irradiation time and to follow the decrease in reactant concentration with irradiation time.

8.) Irradiation of O-Benzoylcyclohexanone Oxime in Cyclohexane Through a Corex Filter - Run V

The photolysis was performed according to the general procedure, and the irradiation was continued for 180 minutes. The fifth run was performed to confirm the results of the previous four runs.

9.) Irradiation of O-Benzoylcyclohexanone Oxime in Cyclohexane Containing a Drying Agent Through a Corex Filter

The photolysis was performed according to the general procedure with the exception that 15 g of anhydrous magnesium sulfate was added. The reaction was identical to those

performed without drying agents, indicating that water does not take part in the reaction.

10.) Irradiation of O-Benzoylcyclohexanone Oxime in Cyclohexane With No Filter - Run I

The photolysis was performed according to the general procedure, and the irradiation was continued for 240 minutes.

11.) Irradiation of O-Benzoylcyclohexanone Oxime in Cyclohexane With No Filter - Run II

The photolysis was performed according to the general procedure, and the irradiation was continued for 150 minutes. The second run was performed to confirm the results of the first and to determine if shorter irradiation time would show any product differences.

12.) Irradiation of O-Benzoylcyclohexanone Oxime in Methanol With No Filter - Run I

The photolysis was performed according to the general procedure, and the irradiation was continued for 150 minutes.

13.) Irradiation of O-Benzoylcyclohexanone Oxime in Methanol With No Filter - Run II

The photolysis was performed according to the general procedure, and the irradiation was continued for 150 minutes. The second run was performed to confirm the results of the first and to determine if shorter irradiation time would show any product differences.

14.) Irradiation of O-Acetylcyclohexanone Oxime in Cyclohexane Through a Corex Filter

The photolysis was performed according to the general procedure and the irradiation was continued for 240 minutes.

15.) Irradiation of O-Acetylcyclohexanone Oxime in Cyclohexane Through a Vycor Filter

The photolysis was performed according to the general procedure and the irradiation was continued for 450 minutes.

16.) Irradiation of O-Acetylcyclohexanone Oxime in Methanol Through a Vycor Filter

The photolysis was performed according to the general procedure, and the irradiation was continued for 180 minutes.

17.) Irradiation of O-Acetylcyclohexanone Oxime in Cyclohexane With No Filter - Run I

The photolysis was performed according to the general procedure, and the irradiation was continued for 420 minutes.

18.) Irradiation of O-Acetylcyclohexanone Oxime in Cyclohexane With No Filter - Run II

The photolysis was performed according to the general procedure, and the irradiation was continued for 420 minutes. The second run was performed to confirm the results of the first run.

19.) Irradiation of O-Acetylcyclohexanone Oxime in Cyclohexane With No Filter - Run III

The photolysis was performed according to the general procedure, and the irradiation was continued for 150 minutes. The third run was performed to confirm the results of the previous two runs and to determine if shorter irradiation time would show any product differences.

20.) Irradiation of O-Acetylcyclohexanone Oxime in Methanol With No Filter - Run I

The photolysis was performed according to the general procedure, and the irradiation was continued for 360 minutes.

21.) Irradiation of O-Acetylcyclohexanone Oxime in Methanol With No Filter - Run II

The photolysis was performed according to the general procedure, and the irradiation was continued for 300 minutes. The second run was performed to confirm the results of the first run.

22.) Irradiation of O-Acetylcyclohexanone Oxime in Methanol With No Filter - Run III

The photolysis was performed according to the general procedure, and the irradiation was continued for 150 minutes. The third run was performed to confirm the results of the previous two runs and to determine if shorter irradiation time would show any product differences.

23.) Irradiation of O-(p-Nitrobenzoyl)-cyclohexanone Oxime in Methanol With No Filter - Run I

The photolysis was performed according to the general procedure, and the irradiation was continued for 150 minutes.

24.) Irradiation of O-(p-Nitrobenzoyl)-cyclohexanone Oxime in Methanol With No Filter - Run II

The photolysis was performed according to the general procedure, and the irradiation was continued for 225 minutes.

The second run was performed to confirm the results of the first and to obtain more comprehensive yield data.

25.) Irradiation of O-(p-Toluoyl)-cyclohexanone Oxime in Cyclohexane With No Filter

The photolysis was performed according to the general procedure, and the irradiation was continued for 240 minutes.

26.) Irradiation of Cyclohexanone Oxime in Methanol With No Filter

This photolysis was performed to check the results reported by Just and co-workers.[8]

27.) Irradiation of Ammonium Acetate in Cyclohexane With No Filter

The purpose of this photolysis was to determine the products of the irradiation of ammonium acetate. A solution of 5 g of ammonium acetate in 500 ml of cyclohexane was degassed for 0.5 hour and photolysed for 60 minutes. Qualitative tests were made for the presence of carbon dioxide and ammonia in the gaseous effluent and the amount of carbon dioxide evolved was measured quantitatively.

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[8] R. T. Taylor, M. Donek, and G. Just, Tet. Letters, 4143 (1966).

28.) Irradiation of Ammonium Acetate in Methanol With No Filter

This photolysis was performed in exactly the same manner as that of ammonium acetate in cyclohexane.

ACTINOMETRY OF THE HANOVIA 450-W SOURCE

The Hanovia 450-W Type L High-Pressure mercury lamp has the following specifications:[9]

Lamp code	L
Lamp Cat. No.	679A
Lamp watts	450
Lamp volts	135
Current, amps.	3.6
Arc-length (in.)	4.5

The spectral characteristics of the lamp are given in Table 1.[9]

The spectral intensity of the Hanovia 450-W lamp throughout the ultraviolet and visible region of the spectrum was determined by a modification of the method of Hatchard and Parker.[10]

Preparation of Solutions

The following solutions were prepared and used in the determination of a calibration curve and in the actinometry of the lamp:

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[9] Hanovia Lamp Division, Research Laboratory, Communication, May 1959.

[10] C. G. Hatchard and C. A. Parker, Proc. Royal Soc., A 235, 518 (1956).

TABLE 1

SPECTRAL ENERGY DISTRIBUTION OF RADIATED MERCURY LINES IN THE HANOVIA 450-W LAMP

Mercury lines (angstrums)	Radiated Energy in Watts
13673 (infrared)	2.6
11287	3.3
10140	10.5
5780 (yellow)	20.0
5461 (green)	24.5
4358 (blue)	20.2
4045 (violet)	11.0
3660 (ultraviolet)	25.6
3341	2.4
3130	13.2
3025	7.2
2960	4.3
2894	1.6
2804	2.4
2753	0.7
2700	1.0
2652	4.0
2571	1.5
2537 (reversed)	5.8
2482	2.3
2400	1.9
2380	2.3
2360	2.3
2320	1.5
2224	3.7
Total Watts	175.8

Ferrous Ammonium Sulfate - A solution was prepared by dissolving 0.7022 g of reagent grade ferrous ammonium sulfate and 3 ml of concentrated sulfuric acid in 100 ml of distilled water and diluting this solution to 1000 ml with distilled water. One milliliter of the resulting solution is equivalent to 0.100 mg of iron (II).

1,10-Phenanthroline Monohydrate - A solution was prepared by dissolving 0.125 g of 1,10-phenanthroline monohydrate in 50.00 ml of distilled water.

Hydroxylamine Hydrochloride - A solution was prepared by dissolving 10 g of hydroxylamine hydrochloride in 100 ml of distilled water.

Sodium Acetate - A solution was prepared by dissolving 17 g of sodium acetate in 100 ml of distilled water.

Potassium Ferrioxalate - A 0.006 M solution was prepared by dissolving 8.841 g of potassium ferrioxalate and 9 ml of concentrated sulfuric acid in 3000 ml of distilled water.

Determination of Spectrophotometric Calibration Curve

The absorbance of a series of standard samples of ferrous ammonium sulfate was determined and these values

plotted against concentration of ferrous ammonium sulfate in mg Fe(II) per ml. The various standard samples were prepared by adding the proper amount of ferrous ammonium sulfate solution to 1.25 ml of 1,10-phenanthroline solution, and 1.25 ml of hydroxylamine hydrochloride solution (apparently to reduce any Fe(III) that might be present), adding enough sodium acetate solution to bring the pH up to 3 or 3.5, and then diluting to 25.00 ml with distilled water.

The results were as follows:

SAMPLE	CONC (mg Fe(III)/ml)	ABSORBANCE	CORRECTED ABSORBANCE
0	0	0.018	0.000
1	0.020	0.436	0.418
2	0.040	0.835	0.817
3	0.008	0.173	0.155
4	0.016	0.325	0.307
5	0.032	0.660	0.642

Calculation of the slope of the curve derived from these values indicates that the absorbance of actinometry samples should be multiplied by the factor 0.00484 to determine the concentration of Fe(II) in mg per ml.

Actinometry of the 450-W Lamp Using 0.006 M Ferrioxalate Solution

Two and one-half liters of 0.006 M ferrioxalate solution was placed in a 3 l reaction vessel and degassed for

0.5 hour with oxygen-free dry nitrogen. The solution was then photolysed with the Hanovia 450-W lamp with no filter and samples were taken at 5, 10, 15, 30, 45, 60, and 75 minutes. Since it was later determined that the ferrioxalate solution was at least 93% reacted at 5 minutes, only the 5 minute sample was used. Sampling and analysis were accomplished by removing a 1.00 ml aliquot with a syringe, adding 2.5 ml of 1,10-phenanthroline solution, buffering to pH of 3 to 3.5 with sodium acetate solution, diluting to 100.0 ml with distilled water, and measuring the absorbance of the resulting solution.

The corrected absorbance of a sample after 5 minutes irradiation was determined to be 0.629.

This corresponds to $(0.629)(4.84 \times 10^{-3}) = 3.04 \times 10^{-3}$ mg Fe(II)/ml. Since the sample aliquot was diluted by a factor of 100,

$$(3.04 \times 10^{-3})(100) = 3.04 \times 10^{-1} \text{ mg Fe(II)/ml}$$

which corresponds to

$$(3.04 \times 10^{-1}/56)(10^{-3}) = 5.42 \times 10^{-6} \text{ mole Fe(III)/ml}$$

Since the total volume of ferrioxalate solution was 2500 ml (the total volume is immaterial as long as it absorbs all of the light and there is sufficient Fe(III) to react with all of the light),

$(5.42 \times 10^{-6})(2.5 \times 10^{3}) = 1.36 \times 10^{-2}$ mole Fe(II) = the total amount of Fe(II) generated in 5 minutes, or

$$1.36 \times 10^{-2}/5 = 2.72 \times 10^{-3} \text{ mole/min.}$$

Estimating that the average quantum yield of the actinometry reaction throughout the ultraviolet and visible is 1.00, the total radiation would then be

$$\frac{2.72 \times 10^{-3}}{1.00} = 2.72 \times 10^{-3} \text{ Einsteins per minute}$$

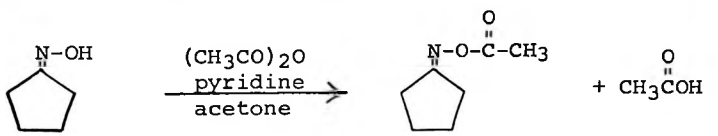
This value represents the total incident radiation throughout the ultraviolet and visible regions of the spectrum.

CHAPTER IV

DISCUSSION

The initial problem in this research was that of the synthesis of the oxime esters to be used as starting materials for the photochemical reactions. It was decided to begin the work with the derivatives of the 5 and 6-membered cyclic ketones.

The first oxime ester prepared was O-acetylcyclopentanone oxime. This was accomplished by the method of Hassner and Pomerantz[1] using the oxime, acetic anhydride, and pyridine as shown in Equation 1:



(1)

Although the desired reaction occurred, the product was an extremely impure liquid. Attempts at vacuum distillation of the product resulted in complete decomposition.

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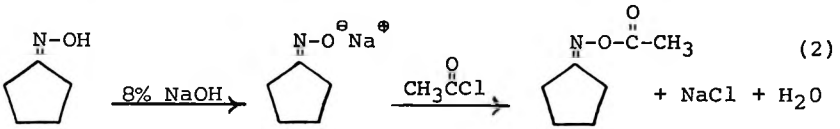
[1] A. Hassner and I. H. Pomerantz, J. Org. Chem., 27, 1760 (1962).

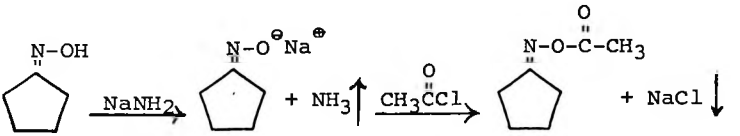
The next method tried was that of Craig and Naik[2] using the oxime, sodium hydroxide, and acetyl chloride as shown in Equation 2:



(2)

This method was equally unsuccessful even though the sodium salt of the oxime appeared to form satisfactorily.

At this time it was decided to substitute sodium amide for sodium hydroxide. With sodium amide the only side products would presumably be ammonia - which could be driven out of solution as a gas - and the sodium halide - which could easily be filtered. This sequence is shown in Equation 3:



(3)

This reaction should then be capable of producing a very pure product.

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[2] J. C. Craig and A. R. Naik, J. Am. Chem. Soc., 84, 3410 (1962).

The sodium salt of cyclopentanone oxime was prepared using sodium amide, isolated, dried, and then put into suspension in ether and reacted with acetyl chloride. The reaction gave the acetate ester, but again the product was a liquid which decomposed upon vacuum distillation.

Since the benzoate ester would likely be a solid, which could be purified relatively easily, it was prepared next. The product was indeed a solid which melted at 51-55°. However, the crude yield was only 37% indicating that there was probably a conflicting reaction occurring.

The acetate ester of cyclohexanone oxime was prepared next via the sodium salt. This acetate was also a liquid but appeared to be of higher purity than that of the cyclopentanone oxime.

The benzoate ester of cyclohexanone oxime was prepared and was a solid melting at 61-62°. However, the yield in this case was only 24%; again indicating a probable competing reaction.

Several other esters of cyclopentanone oxime and cyclohexanone oxime as well as two esters of benzophenone oxime were prepared in the search for a suitable starting material. The oxime esters along with their physical properties are listed in Table 2.

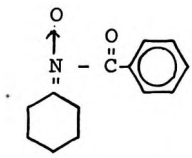
TABLE 2

OXIME ESTERS PREPARED DURING THIS RESEARCH AND THEIR PHYSICAL PROPERTIES

COMPOUND	PHYSICAL STATE	MP or BP
O-acetylbenzophenone oxime	white crystalline solid	73.5 - 74°
O-acetylcyclohexanone oxime	viscous yellow liquid	dec. 35 - 40°/ 1 mm
O-acetylcyclopentanone oxime	viscous yellow liquid	dec. 35 - 40° 1 mm
O-benzoylcyclohexanone oxime	white crystalline solid	62 - 63°
O-benzoylcyclopentanone oxime	white crystalline solid	51 - 53°
O-bromoacetylcyclopentanone oxime	viscous brown liquid	dec. 35 - 40°/ 1 mm
O-nonanoylcyclohexanone oxime	viscous brown liquid	dec. 35 - 40°/ 1 mm
O-(p-nitrobenzoyl)cyclohexanone oxime	light yellow crystalline solid	104 - 105°
O-phenylacetylbenzophenone oxime	white crystalline solid	---
O-phenylacetylcyclohexanone oxime	viscous yellow-green liquid	dec. 35 - 40°/ 1 mm; MP = 2-5°
O-(p-toluoyl)-cyclohexanone oxime	off-white crystalline solid	67 - 69°

O-benzoylcyclohexanone oxime was selected as the first ester to be photolysed because of its relative ease of preparation, its ease of purification by recrystallization, and its simplicity in structure.

During the course of routine preparations of O-benzoylcyclohexanone oxime a second product was isolated in yields varying up to 20%. This product melted at 145-148° and gave an infrared spectrum consistent with that of a nitrone; in particular N-cyclohexylidene benzamide-N-oxide. Elemental analysis of this material agreed satisfactorily with values calculated for the nitrone structure shown below.



It appears then that there was competition between O-acylation - to give the ester - and N-acylation - to give the nitrone. This type of reaction is well known.[3]

In addition to the ester and nitrone products, a green color was occasionally observed in the reaction solution.

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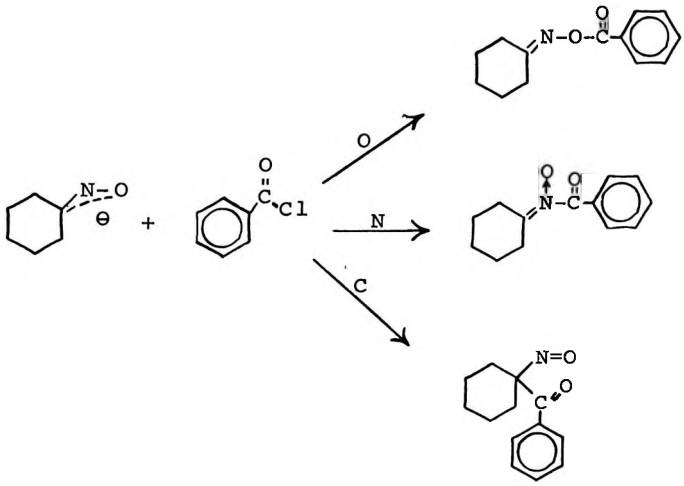
[3]A. S. Peter and J. E. Robertson, J. Am. Chem. Soc., 84, 1197 (1962).

Concentration of the solution and chromatography on alumina yielded an intensely colored, azure blue, lachramatory liquid whose infrared spectrum contained a nitroso group absorption. This compound could not, however, be sufficiently separated from the ester for further characterization.

One possible explanation for the occurrance of a nitroso compound could be that, in addition to N and O-acylation, C-acylation of the oximate anion was occurring as shown in Equation 4:



(4)

The possibility of C-acylation in the reaction of sodium cyclohexanone oximate with benzoyl chloride was further investigated.[4] Since the nitroso compound was not generated in every case, several reaction variables were investigated as possible causes.

Reactions were run at 0, 25, 54, and 69°, but the nitroso product was not observed. The only effect of increasing the temperature was to cause extensive decomposition of the primary ester product.

Since it was determined that the oxime salt readily hydrated upon exposure to air, and that the degree of hydration varied from the trihydrate after a few minutes exposure to the pentahydrate after several days exposure, reactions were run with the anhydrous, trihydrated and pentahydrated salt. In each reaction no nitroso product was observed.

It was felt that the basicity of the solution should have an effect on the reaction, that is, sodium hydroxide resulting from the hydrolysis of sodium amide might facilitate C-acylation. The reaction was run with sodium hydroxide added, but no nitroso compound was generated.

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[4]M. R. Andrews, University of Alabama, personal communication, 1968.

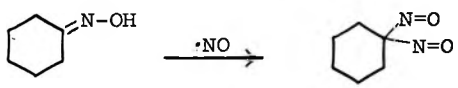
Since sodium amide from an old bottle had been used when the nitroso product was observed, the reaction was run again with the sodium amide from this old bottle. This time the reaction mixture turned a dark green indicating the presence of a nitroso compound.

The solution was concentrated and chromatographed on alumina to yield a deep blue solution. The vapor pressure of the product was such, however, that it could not be sufficiently separated from the solvent for satisfactory analysis. Consequently, the reaction was run in carbon tetrachloride and carbon tetrachloride was used as the chromatographic eluent so that the product would be in a solvent suitable for infrared and NMR analysis.

Analysis indicated that the product did not contain any phenyl or carbonyl functions and that it had approximately the same proton arrangement as cyclohexanone oxime. Nitrosocyclohexane and 1-chloro-1-nitrosocyclohexane were ruled out on the basis of physical properties. Since the product does not dimerize but remains a liquid, the nitroso group must be highly hindered; and since the product does not tautomerize to the oxime, it is likely that there is no hydrogen on the carbon bound to the nitroso group. This is supported by the absence of a methyne proton in the NMR.

It would appear then that the nitroso compound does not arise through C-acylation but is probably generated through reaction of decomposition products of the sodium amide. Sodium amide decomposes upon exposure to the air to give NaOH, Na_2CO_3, $NaNO_2$, as well as several other salts of oxides of nitrogen[5] all of which would be capable of producing nitric oxide.

A possibility for this unknown nitroso compound, for which there is no conflicting evidence, is 1,1-dinitroso-cyclohexane. This could occur by reaction of cyclohexanone oxime with nitric oxide to give oxime to nitroso conversion followed by - or concurrent with - addition of nitric oxide.



Since synthesis of the oxime esters via the sodium oximate gave such low yields another method of preparation was sought. It was found that the simple addition of an acid halide to an etheral solution of the oxime in the presence of triethylamine, as a base to react with the

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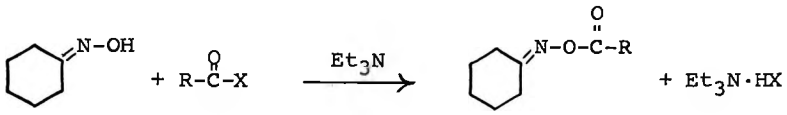
[5]F. W. Bergstrom and W. C. Fernelius, Chem. Reviews, 12, 63, 75, 78 (1933).

hydrogen halide generated, gave excellent yields (60-70% after recrystallization) of relatively pure product.



This method was adopted for further preparations. Attention was now turned to the photolysis experiments.

The first compound irradiated was O-benzoylcyclopentanone oxime, however, this was more or less a practice run to develop technique. O-benzoylcyclohexanone oxime was decided upon for extensive study since the oxime is cheaper and more readily available than cyclopentanone oxime. The infrared spectrum of O-benzoylcyclohexanone oxime in CCl_4 is presented in Figures 6 & 7.

Before beginning the photochemical study with O-benzoylcyclohexanone oxime, a study was made of its ultraviolet absorption spectrum. Absorption spectra were obtained in cyclohexane, ethanol, and water as solvents. The absorption maxima as well as the molar absorptivities - where they could be determined - are presented in Table 3.

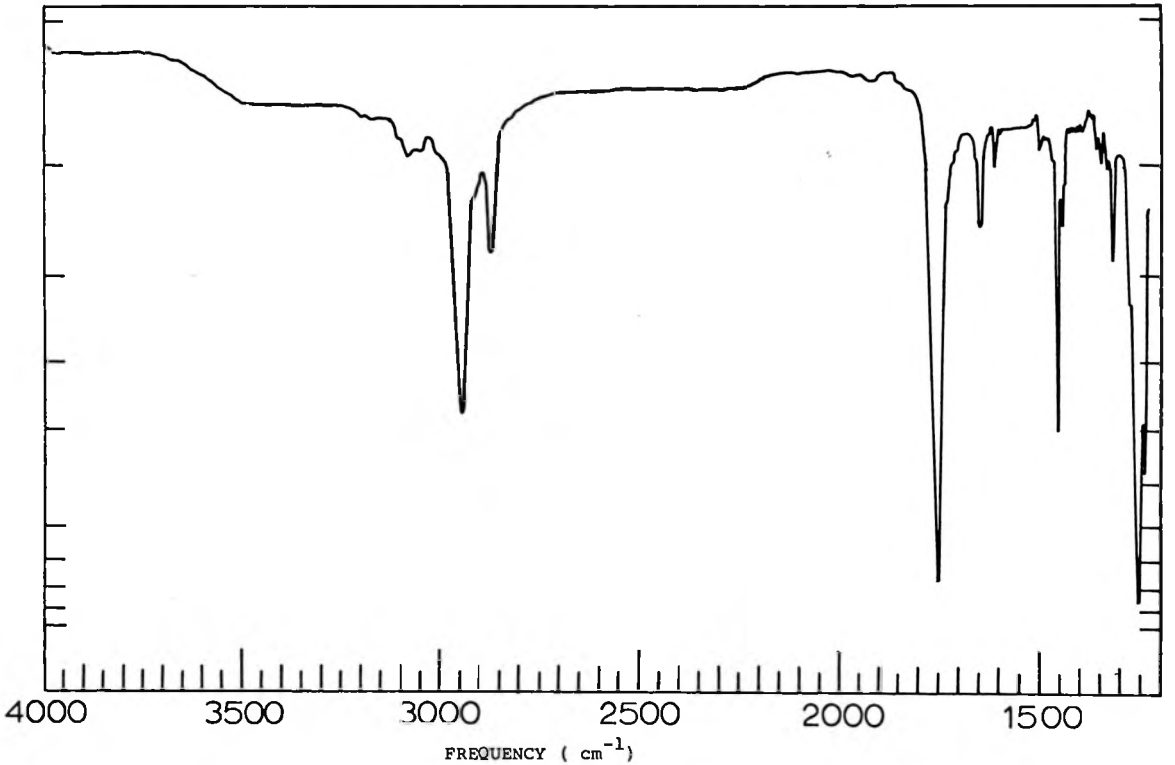


FIGURE 6 . Infrared Spectrum of O-benzoylcyclohexanone Oxime in CCl_4

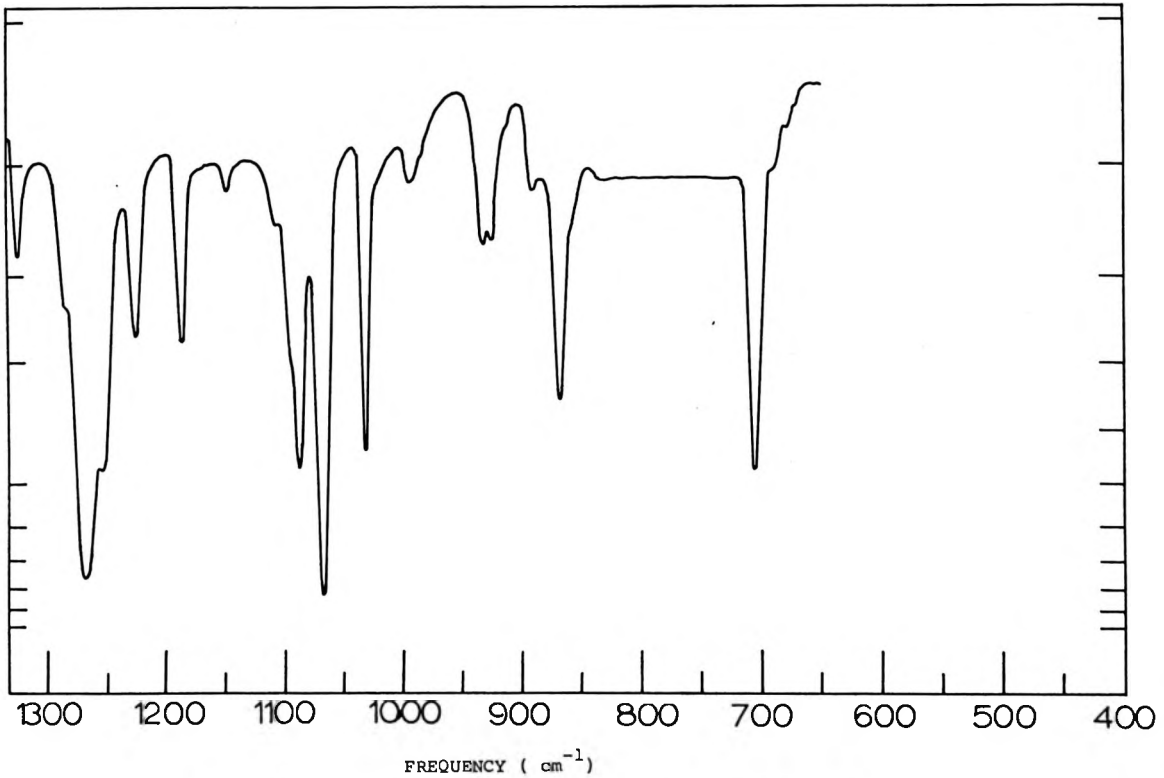


FIGURE 7 . Infrared Spectrum of O-benzoylcyclohexanone Oxime in CCl_4

TABLE 3

ABSORPTION MAXIMA AND MOLAR ABSORPTIVITIES OF O-BENZOYLCYCLOHEXANONE OXIME

cyclohexane		ethanol*		water	
λ_{max}	ε	λ_{max}	ε	λ_{max}	ε
--	--	202 mμ	--	196 mμ	--
229 mμ	12400	234 mμ	18000	236 mμ	--
273 mμ	800	273 mμ	--	broad shoulder	
281 mμ	600	281 mμ	--	broad shoulder	

*These absorption maxima were later determined more precisely (Cary 14) to lie at 200.8 mμ, 233.2 mμ, 273 mμ, and 283 mμ respectively.

The lowest absorption maximum, around 200 mμ, did not follow Beer's Law in any solvent; probably due to its close proximity to the solvent and instrumental cut-off. This absorption appeared to undergo a blue shift with increasing solvent polarity indicating an $n \rightarrow \pi^*$ transition. However, this absorption has been assigned to the $\pi - \pi^*$ transition of the C=N chromaphore[6] and the observed blue shift is possibly a function of the complete lack of adherence to Beer's Law. In any event, this absorption is definitely due to the imine chromaphore since it reoccurs in all the oxime esters, oximes, and imines whose absorption spectra were determined.

The absorption around 230 mμ is the best defined and follows Beer's Law in cyclohexane and ethanol but gives a poor curve in water. This absorption definitely undergoes a red shift with increasing solvent polarity indicating a $\pi - \pi^*$ transition. This absorption is probably the K-band of the phenyl nucleus.

The two absorptions at 273 and 281 mμ are well defined in cyclohexane, but do not follow Beer's Law in ethanol, and

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[6] R. T. Taylor, M. Donek, and G. Just, Tet. Letters, 4143 (1966).

coalesce into a broad shoulder in water. These absorptions do not undergo any descernable shift in going from cyclohexane to ethanol and could be either the n - π^* transition for the carbonyl chromaphore of the B-band for the phenyl nucleus - or both. Possibly the 273 mμ peak is the phenyl B-band and the 281 mμ peak is the carbonyl n - π^* transition. With increasing solvent polarity the 273 mμ peak would undergo a red shift while the 281 mμ peak would move toward the blue. This could account for the fact that the peaks coalesce in water.

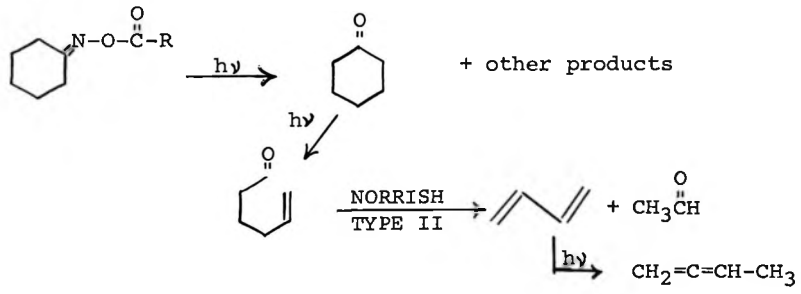
Initial photolyses of O-benzoylcyclohexanone oxime were performed with the Rayonet Photochemical Reactor. However, it soon became apparent that some method of cooling the reaction would be required to prevent thermal reaction of the oxime ester. Since this would require fabrication of rather elaborate quartz glassware for use with the Rayonet apparatus, a Hanovia Type L 450-W lamp and quartz immersion well were obtained. Subsequent photolyses were performed with this apparatus. At first a 3 l reaction vessel was used, but this was found to be too large for routine work and a 550 ml vessel was fabricated and was used thereafter for photolyses.

Cyclohexane was chosen as the initial photolysis solvent because of its spectral transmission characteristics, because it cannot act as a photosensitizer, and because it is a satisfactory infrared solvent and would permit the progress of the reaction to be monitored by infrared spectrophotometry.

It was decided to first irradiate with light of relatively low energy and then to increase the energy in hopes of detecting product differences as a function of wavelength. A pyrex filter was first used, thereby limiting the incident light to above 300 mμ. Since there is no absorption by O-benzoylcyclohexanone oxime above 300 mμ, no photochemical reaction should occur and indeed none was observed. The reaction solution showed no precipitate, change in color or odor, or any other sign of a reaction, and the monitoring infrared spectra were identical throughout the photolysis.

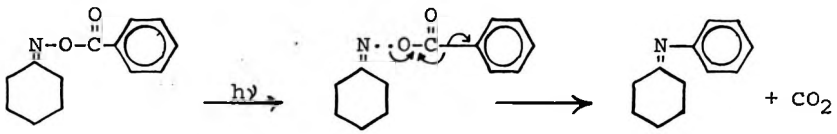
A corex filter was then used thus limiting the incident radiation to above 280 mμ. This reaction was monitored by infrared as well as ultraviolet spectrophotometry, and the irradiation was continued for 370 minutes. No difference was observed in the ultraviolet spectra, but several new peaks appeared in the infrared. Most significant were peaks

at 1720 and 1350 cm^{-1} which appeared almost immediately, reached a maximum at 240 minutes, and then decreased in intensity. During the photolysis the solution took on an amber color and a fine powder precipitated from solution. The postphotolysis solution was concentrated and the concentrate chromatographed on alumina with cyclohexane followed by diethyl ether as eluents. Analysis of the chromatographic fractions indicated a large amount of unreacted oxime ester remaining as well as trace amounts of cyclohexanone. In addition a fraction was isolated having peaks in the infrared at 1950 and 850 cm^{-1}. These absorptions are characteristic <u>only</u> of allenes. A possible explanation for the presence of an allene is as follows:



A positive Tollen's test on the postphotolysis solution confirmed the presence of an aldehyde function.

It seemed that a logical reaction of O-benzoylcyclohexanone oxime under irradiation would be the loss of carbon dioxide and recombination of the radicals to yield cyclohexylidene aniline.



In order to test this possibility, cyclohexylidene aniline was synthesized from aniline and cyclohexanone and a second solution of O-benzoylcyclohexanone oxime in cyclohexane was irradiated through a corex filter for 240 minutes. The infrared spectra monitoring this photolysis were identical to those of the previous photolysis reaction.

The postphotolysis solution and a sample of cyclohexylidene aniline were subjected to gas chromatographic analysis. Although the postphotolysis solution gave a complex chromatogram, the last fraction had a retention time of 9.9 minutes versus 17.2 minutes for cyclohexylidene aniline on the same column under the same conditions.[7]

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[7]column: 1/8" x 6', 5% SE-30 on 60/80 mesh chrom W.

conditions: column temp. - 175°
injector temp. - 230°
detector temp. - 250°
He flow rate - 15% of maximum

It is evident then that cyclohexylidene aniline is not a product of the photolysis of O-benzoylcyclohexanone oxime with radiation above 280 mμ.

It might be well to point out here that although g.l.p.c. would appear to be ideally suited for product analysis in these photolysis reactions, the starting oxime esters are thermally unstable and have such an extremely low vapor pressure that gas chromatograms of any sample containing the starting material are prohibitively complex.

After standing several days a brown oily precipitate settled from the postphotolysis solution. This material was definitely not the starting material but efforts to determine its identity were unsuccessful at this point.

In order to provide more of this unknown material for analysis a third solution of O-benzoylcyclohexanone oxime was irradiated through a corex filter for 240 minutes. As in the previous photolyses, yellow color began to appear in the solution within 5 minutes and an odor characteristic of the reaction was detected at 30 minutes. A light tan powder precipitated during the reaction and was later isolated. Infrared analysis of this material indicated that it contained a benzoate anion and it was observed to evolve ammonia upon basic hydrolysis. Comparison with an authentic infrared

spectrum identified this material as ammonium benzoate. Elemental analysis of this material gave satisfactory agreement with the values calculated for ammonium benzoate.

The postphotolysis solution was concentrated and chromatographed on alumina with diethyl ether as eluent. Infrared analysis of the chromatographic fractions indicated the presence of cyclohexanone, trace amounts of benzoin, and possibly cyclohexanone oxime.

Even though a solution of O-benzoylcyclohexanone oxime decomposed extensively on a gas chromatographic column, it was found that one decomposition product produced an isolated and relatively reproducible peak on a certain column and under certain conditions.[8] Based on the average of five chromatograms for each concentration, values of 38% and 15% were obtained for known 40% and 20% samples (100% = 0.1 N).

A fourth solution of O-benzoylcyclohexanone oxime in cyclohexane was irradiated through a corex filter for 180 minutes so that the decrease in reactant concentration

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[8] column: 1/8" x 6', 5% SE-30 on 60/80 mesh Chrom. W.

conditions:	column temp.	200°
	injector temp.	- 250°
	detector temp.	- 250°
	He flow rate	- 1 ml/sec.
	sample size	- 20 ul

could be followed by gas chromatography. The results of this analysis are presented in Figure 8. In addition to analysing for the concentration of the starting material, ammonia was identified qualitatively in the gaseous effluent, and carbon dioxide evolution was determined by sorption on ascarite to be 15% of the total available carbon dioxide. The yield of ammonium benzoate was determined by conductometric titration with standard hydrochloric acid and was shown to be 4% of the total available ammonium benzoate.

A fifth solution of O-benzoylcyclohexanone oxime in cyclohexane was irradiated through a corex filter for 180 minutes. This photolysis was performed in order to determine the yield of ammonia as well as to check on the results of the previous reactions. The yield of ammonia was determined by sorption on Granusic (granular P_2O_5) to be 3% of the total available ammonia. In this photolysis reaction the carbon dioxide yield was 13%; ammonium benzoate yield was 8%; and there was around 30% of the starting material remaining. Again, as in the previous reactions, infrared evidence as well as odor indicated the presence of cyclohexanone.

Since it was difficult to visualize how cyclohexanone could be generated photochemically, the possibility of water in the reaction was considered. To check this, a

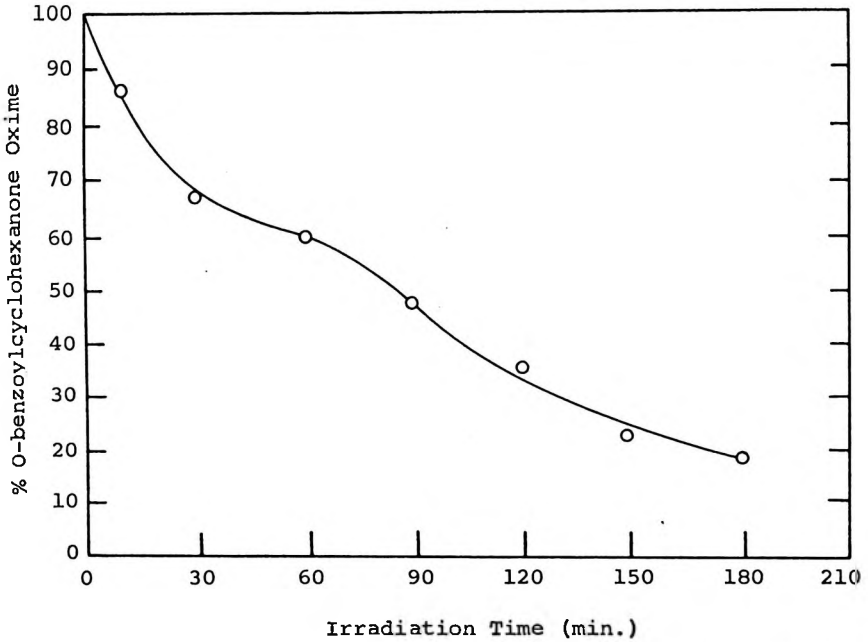

FIGURE 8 . Concentration of Starting Material as a Function of Irradiation Time in the Photolysis of O-benzoylcyclohexanone Oxime in Cyclohexane with a Corex Filter

solution of O-benzoylcyclohexanone oxime in cyclohexane containing 15 g of anhydrous magnesium sulfate in suspension was irradiated through a corex filter for 180 minutes. No difference in the photolysis reaction or in the products was observed, indicating that water does not take part in the reaction.

Before irradiating O-benzoylcyclohexanone oxime with more energetic radiation, it was decided to study another oxime ester under the same conditions and to determine whether the same reaction occurred. The second compound chosen for study was O-acetylcyclohexanone oxime. Although this compound is a viscous liquid, it was found that it could be prepared in a relatively pure form by direct reaction of acetyl chloride with cyclohexanone oxime in the presence of triethylamine; and then, after isolation, could further be purified by distilling away the volitile contaminants and chromatographing on alumina to yield a product of very high purity.

Before undertaking a photochemical study of O-acetylcyclohexanone oxime, its ultraviolet absorption spectrum was investigated. The spectrum showed only one absorption which occurred at 210 mμ in ethanol and 216 mμ in cyclohexane. This absorption is definitely due to the C=N chromaphore,

but, as in the case of the benzoate ester, it underwent a blue shift with increasing solvent polarity indicating a $n - \pi^*$ transition. Again this is in conflict with the previously reported assignment of this band to a $\pi - \pi^*$ transition.[9] Attempts to determine the molar absorptivity of this absorption resulted in a curve with poor adherance to Beer's Law. It was possible only to estimate that the value lies between 1200 and 2300. Even though they are too weak to appear in the spectrum, there should be absorptions due to the carbonyl chromaphore above 270 mμ. The infrared spectrum of O-acetylcyclohexanone oxime as a thin film is presented in Figures 9 & 10.

A solution of O-acetylcyclohexanone oxime in cyclohexane was irradiated through a corex filter for 240 minutes. Although a reaction occurred, indicated by a slight cloudiness in the solution, infrared spectra showed no evidence of a reaction. This is to be expected since O-acetylcyclohexanone oxime does not absorb significantly above 280 mμ.

A solution of O-acetylcyclohexanone oxime in cyclohexane was then irradiated through a vycor filter, which

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[9]R. T. Taylor, M. Donek, and G. Just, Tet. Letters, 4143 (1966).

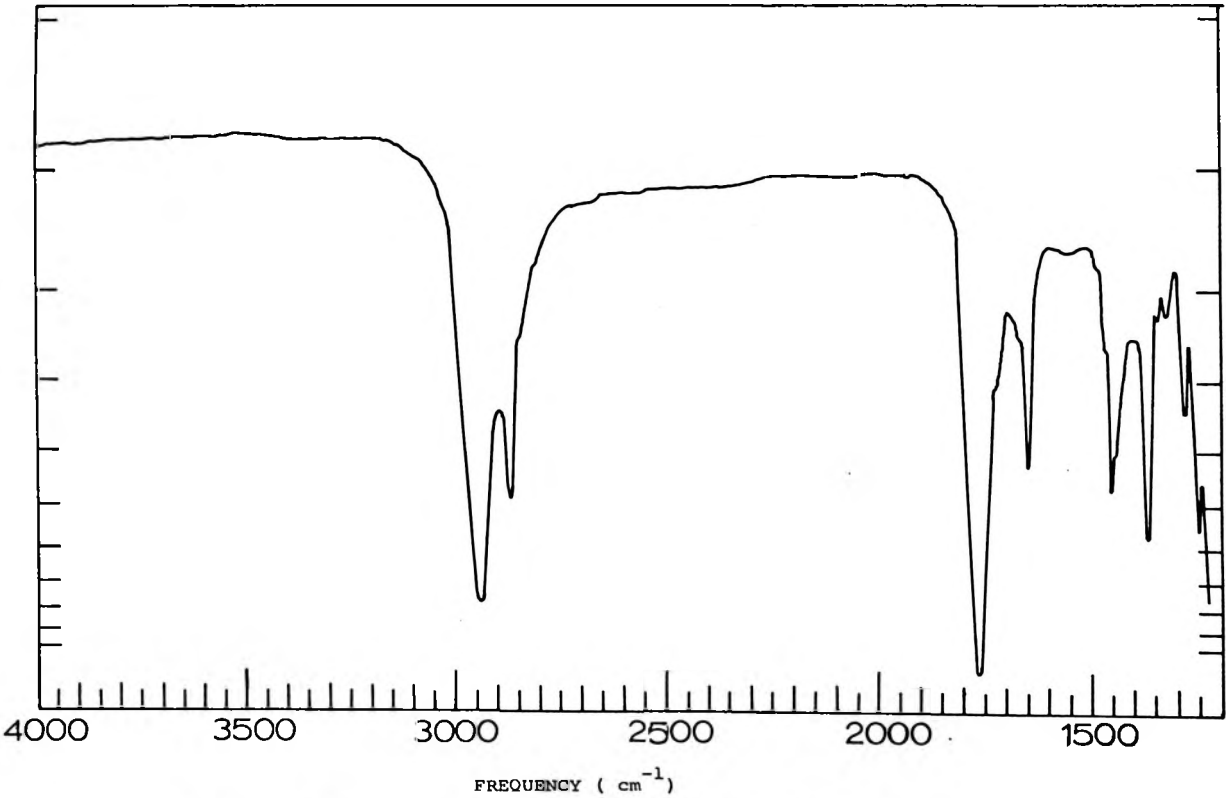


FIGURE 9 . Infrared Spectrum of O-acetylcyclohexanone Oxime as a Thin Film

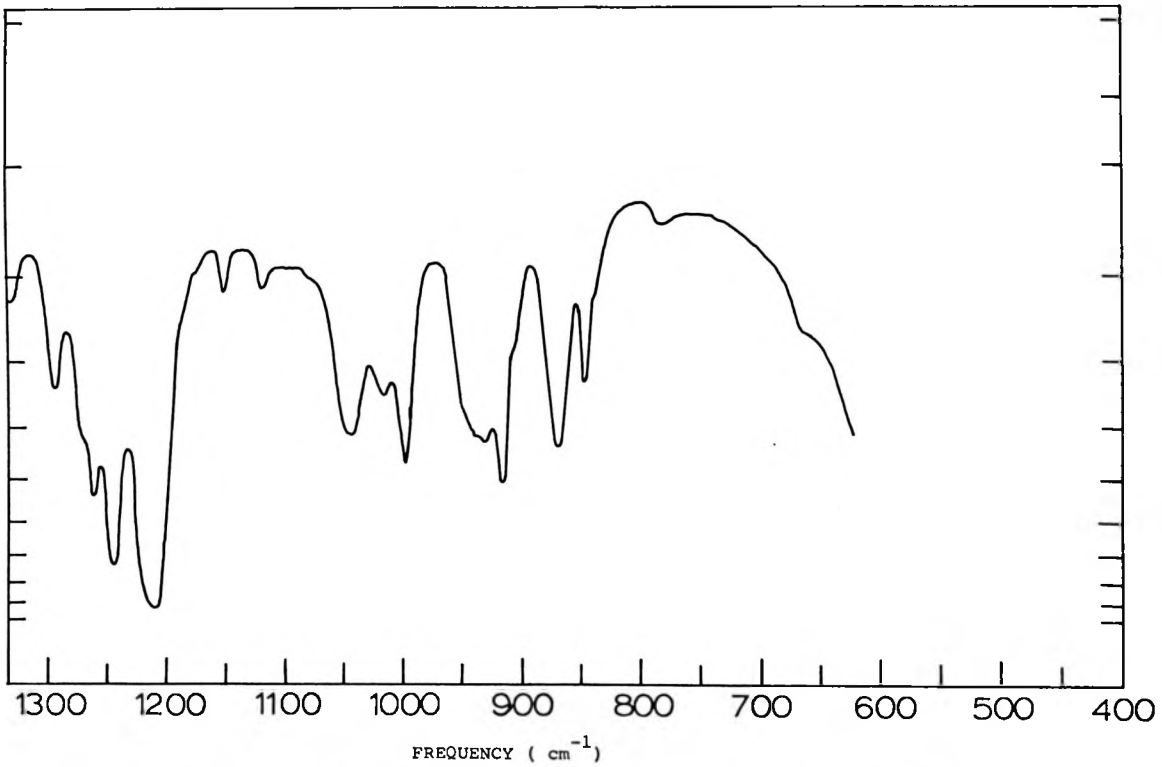


FIGURE 10 . Infrared Spectrum of O-acetylcyclohexanone Oxime as a Thin Film

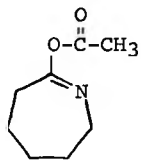
limits the incident radiation to above 230 mμ. After 120 minutes irradiation time a fine powder was observed to precipitate from solution. Infrared monitoring of the photolysis reaction showed new peaks at approximately 3500 and 3200, and at 2800, 2700, 2650, 1720, 1430, 1360, 1250, 1100, 1030, 1005, 890, and 850 cm^{-1} which continued to grow in intensity throughout the reaction of 450 minutes.

A portion of the postphotolysis solution was fractionally distilled under 5 mm Hg pressure. Infrared analysis showed the presence of a carbonyl compound in six of the ten fractions. Comparison with an authentic spectrum and preparation of a 2,4-DNP derivative identified this product as acetone. In addition, the presence of cyclohexanone was detected in the postphotolysis solution.

The concentrated postphotolysis solution from this reaction was extracted with water and the aqueous solution was titrated conductometrically. Although ammonium acetate was not isolated in this reaction, the titration curve was identical in appearance to that of ammonium benzoate and indicated a yield of ammonium acetate of 9%. Considering this, it is reasonable to assume that ammonium acetate is

a product of the photolysis of O-acetylcyclohexanone oxime in cyclohexane.

The concentrated postphotolysis solution was then chromatographed on alumina with diethyl ether as eluent. The first fraction yielded a minute quantity of a yellow, sweet-smelling oil. The infrared spectrum of this material is presented in Figures 11 and 12. Two possible interpretations of this spectrum could be that of the Beckmann rearrangement product, O-acetylcaprolactim,



or an azepine contaminated with cyclohexanone. Unfortunately, there was not enough of this material to permit further analysis.

Analysis of the remaining fractions indicated nothing but the starting material contaminated with an unidentified, foul-smelling, substance.

The next photolysis undertaken was that of O-acetylcyclohexanone oxime in methanol through a vycor filter for 150 minutes. This reaction was performed to determine whether using methanol as a solvent instead of cyclohexane

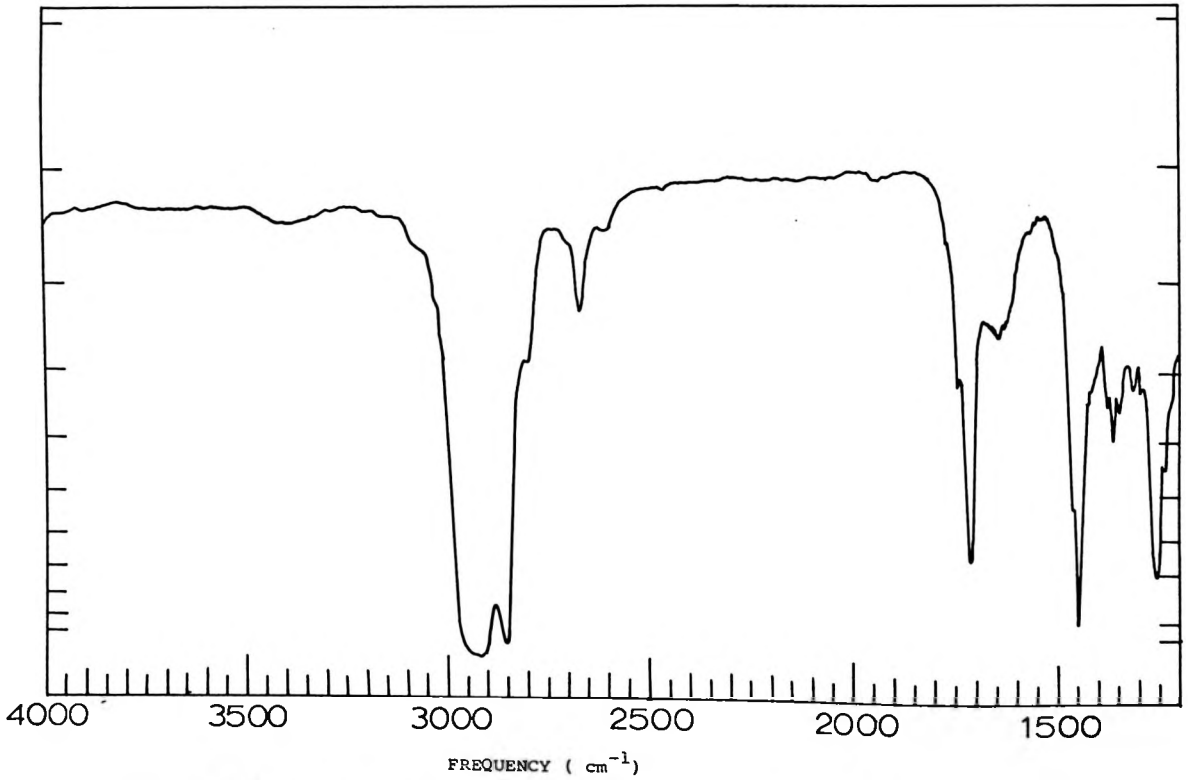


FIGURE 11. Infrared Spectrum of Product Isolated from the Photolysis of O-acetylcyclohexanone Oxime in Cyclohexane Through a Vycor Filter

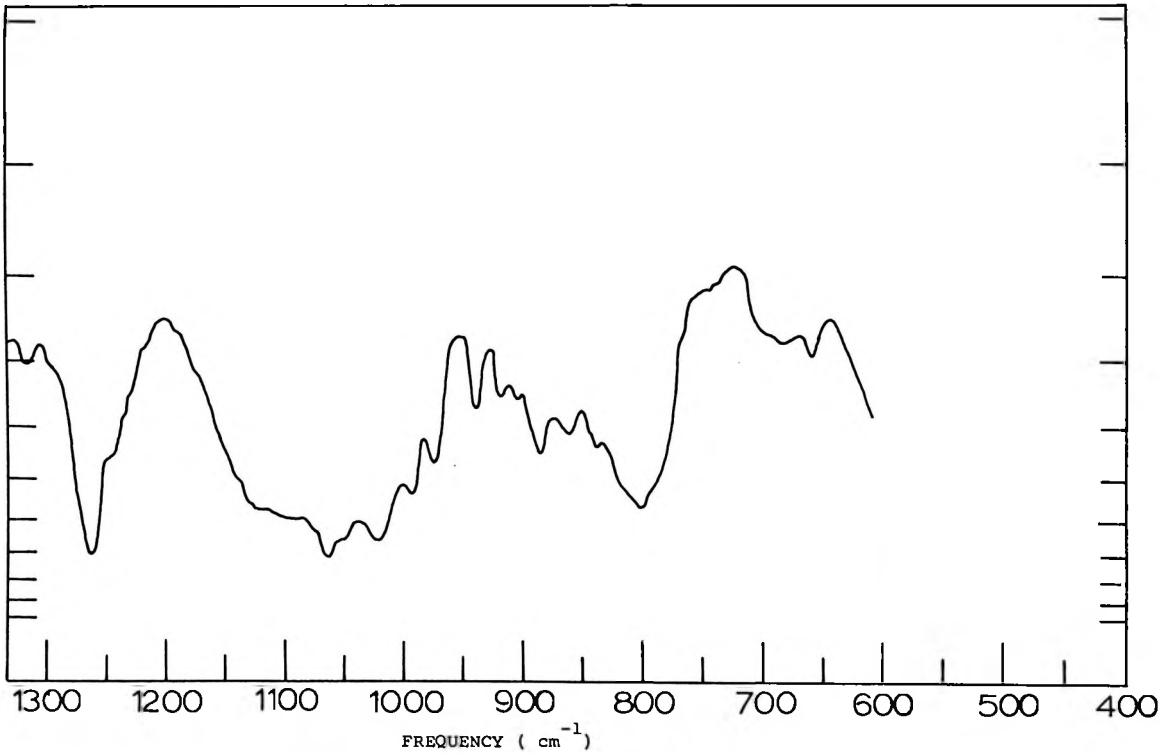


FIGURE 12 . Infrared Spectrum of Product Isolated from the Photolysis of O-acetylcyclohexanone Oxime in Cyclohexane Through a Vycor Filter

would have any effect on the reaction. One would expect methanol to be a better hydrogen atom donor than cyclohexane thereby increasing the possibility of photoreduction. The methanol used in this reaction was distilled on a gold spinning-band column to insure a high degree of purity.

During the reaction there was no precipitate observed and there was much less color imparted to the solution than in the case of the same photolysis in cyclohexane. The yield of carbon dioxide was much higher than in cyclohexane, but in this case there was no ammonia evolution observed. However, addition of potassium hydroxide to a sample of the postphotolysis solution evolved ammonia indicating the probable presence of the ammonium ion. Addition of base to a solution of the starting material did not evolve ammonia. The fact that ammonia was not evolved during the photolysis reaction is probably due to the higher solubility of ammonia in methanol as opposed to cyclohexane.

Conductometric titration of a sample of the postphotolysis solution indicated a total yield of ammonium acetate of 11%.

Since the absorption of the imine chromaphore is at 210 mμ in methanol as opposed to 216 mμ in cyclohexane, it is possible that the reaction in methanol is caused by

absorption by the carbonyl chromaphore only, while reaction in cyclohexane is due to absorption by both the imine and carbonyl chromaphores. This could account for the lack of color in methanol solution. The absence of a precipitate is probably due to the higher solubility of ammonium acetate in methanol.

It was evident at this stage of the research that a reaction occurs in the photolysis of O-benzoylcyclohexanone oxime and O-acetylcyclohexanone oxime to produce carbon dioxide, ammonia, and the ammonium salt of the corresponding acid, and furthermore that this reaction is most likely caused by absorption of the carbonyl chromaphore (as well as the phenyl chromaphore in the benzoate). Since absorption by the imine chromaphore would be necessary cause ring expansion, and since this absorption occurs below 230 mμ in all compounds containing the imine linkage, it was decided to irradiate the oxime esters with unfiltered light.

As in the case of O-benzoylcyclohexanone oxime, it was found that the gas chromatography of O-acetylcyclohexanone oxime in cyclohexane - on a certain column under certain

conditions[10] produced a decomposition product which gave rise to an isolated, relatively reproducible peak. When known concentrations of 100% (0.1 N), 40%, and 20% were chromatographed, the average of five determinations for each concentration gave values of 100%, 47%, and 22%. Again, as in the case of the benzoate ester, the results are not highly accurate but the method should provide a reasonable idea of the extent of the reaction.

A solution of O-acetylcyclohexanone oxime in cyclohexane was irradiated for 420 minutes with no filter ($\lambda >$ 200 mμ). The purpose of this photolysis was two fold: first to determine the effect of irradiating with more energetic radiation; and second, to follow the decrease in reactant concentration as a function of irradiation time. The results of the latter determination are presented in Figure 13.

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[10]column: 1/8" x 6', 5% SE-30 on 60/80 mesh Chrom. W.

conditions:	column temp.	- 128°
	injector temp.	- 250°
	detector temp.	- 250°
	flow rate	- 1 ml/sec.
	sample size	- 20 ul

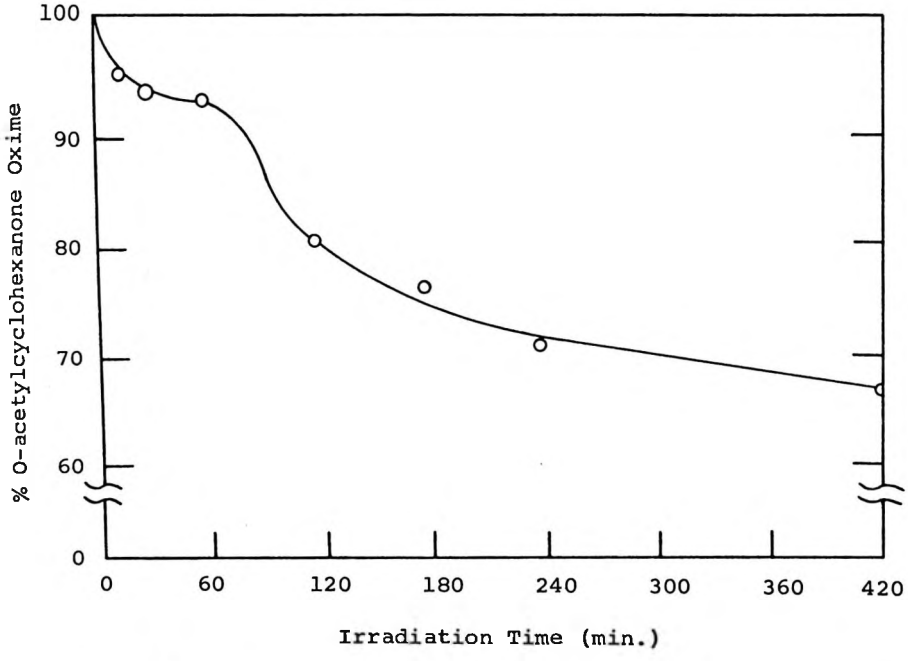

FIGURE 13 . Concentration of Starting Material as a Function of Irradiation Time in the Photolysis of O-acetylcyclohexanone Oxime in Cyclohexane with No Filter

In this reaction the solution became yellow within 5 minutes and became a dark amber within 30 minutes. Infrared monitoring of the reaction showed only one new peak around 1720 cm^{-1} during the photolysis as opposed to the profusion of new peaks in the spectra when monitoring the photolysis of O-acetylcyclohexanone in cyclohexane through a vycor filter.

The yield of ammonia in this reaction was determined quantitatively by absorption on Granusic (granular P_2O_5) to be 5% of the total available ammonia. The total yield of carbon dioxide was determined to be 16%. Conductometric titration of a sample of the postphotolysis solution indicated a yield of ammonium acetate of 10%.

The irradiation of O-acetylcyclohexanone oxime in cyclohexane with no filter was performed a second time so that the evolution of carbon dioxide and ammonia could be followed as a function of irradiation time. This was accomplished by removing the lamp from the photolysis vessel at pre-selected intervals and determining the change in weight of a pre-weighed tube of ascarite which was placed in the gaseous effluent stream of the photolysis. The results of these determinations are presented in Figure 14 and Figure 15. The evolution of ammonia was confirmed

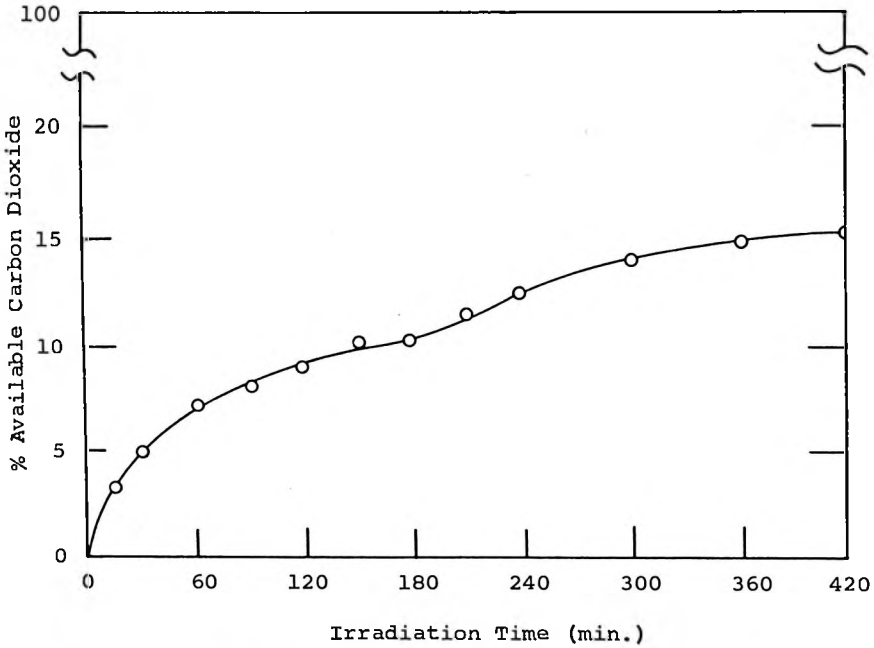

FIGURE 14. Evolution of Carbon Dioxide as a Function of Irradiation Time in the Photolysis of O-acetylcyclohexanone Oxime in Cyclohexane with No Filter

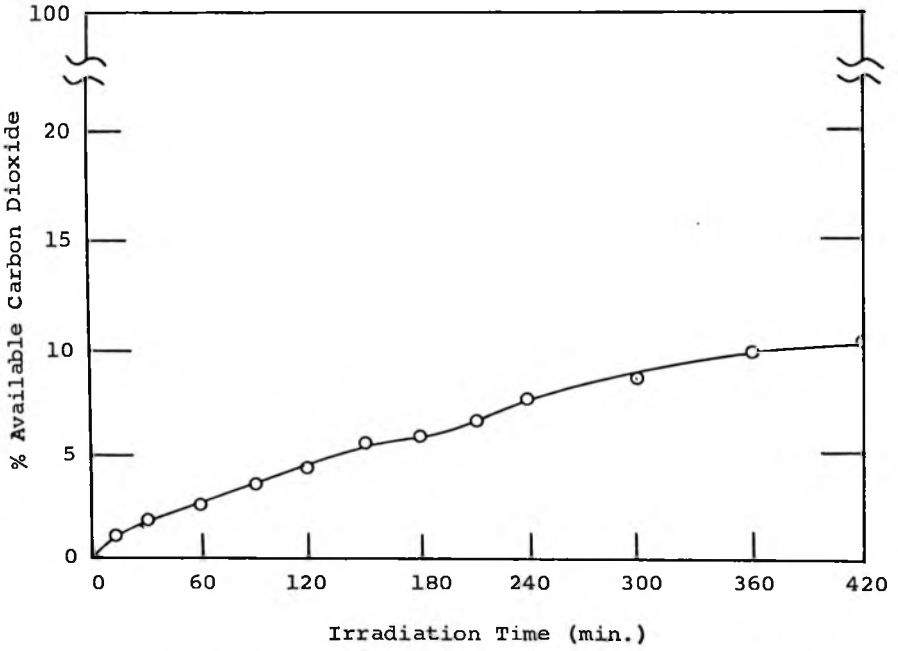

FIGURE 15 . Evolution of Ammonia as a Function of Irradiation Time in the Photolysis of O-acetylcyclohexanone Oxime in Cyclohexane with No Filter

qualitatively by tests with litmus and hydrogen chloride. The yield of ammonium acetate in this reaction was determined by conductometric titration to be 6%.

It is likely that the quantitative determinations of ammonia by absorption on Granusic give results that are too high because of the strongly hygroscopic nature of phosphorous pentoxide.

An attempt was made in this photolysis reaction to again follow the reactant concentration by pyrolysis gas chromatography, however, the analysis peak would no longer separate, and attempts at varying the conditions would not provide the required separation. A second, identical column was prepared but was also unsuccessful in obtaining separation. After repeated unsuccessful attempts to accomplish separation this method of analysis was abandoned.

The yield of cyclohexanone in this reaction was determined by quantitative precipitation with 2,4-dinitrophenylhydrazine[11] to be 8%. This result is somewhat in doubt because O-acetylcyclohexanone oxime itself will give cyclohexanone-2,4-DNP upon addition to an acid solution of

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[11] H. A. Iddles, A. W. Low, B. D. Rosen, and R. T. Hart, Ind. & Eng. Chem., Anal. Ed., 11, 102 (1939).

2,4-dinitrophenylhydrazine. However, this reaction occurs much slower than with cyclohexanone itself; so, if the precipitate is filtered shortly after it forms, it should be due primarily to cyclohexanone and the result should be reasonably valid.

The next photolysis to be conducted was the irradiation of O-acetylcyclohexanone oxime in methanol with no filter for 360 minutes. The evolution of carbon dioxide was determined as a function of irradiation time. The results of this determination are presented in Figure 16. An attempt was made to follow the evolution of ammonia, however, the Granusic must have picked up water since the results reached 117% at 180 minutes.

Comparison of Figure 16 to Figure 14, that is, the evolution of carbon dioxide by the reaction of O-acetylcyclohexanone oxime in methanol to that in cyclohexane, demonstrates graphically that the reaction proceeds much more rapidly in methanol than cyclohexane.

The postphotolysis solution from this reaction was concentrated and chromatographed on alumina with diethyl ether followed by ethanol as eluents.

The first fraction contained a tiny amount of a clear oil with a very sweet, pleasant odor. The infrared spectrum

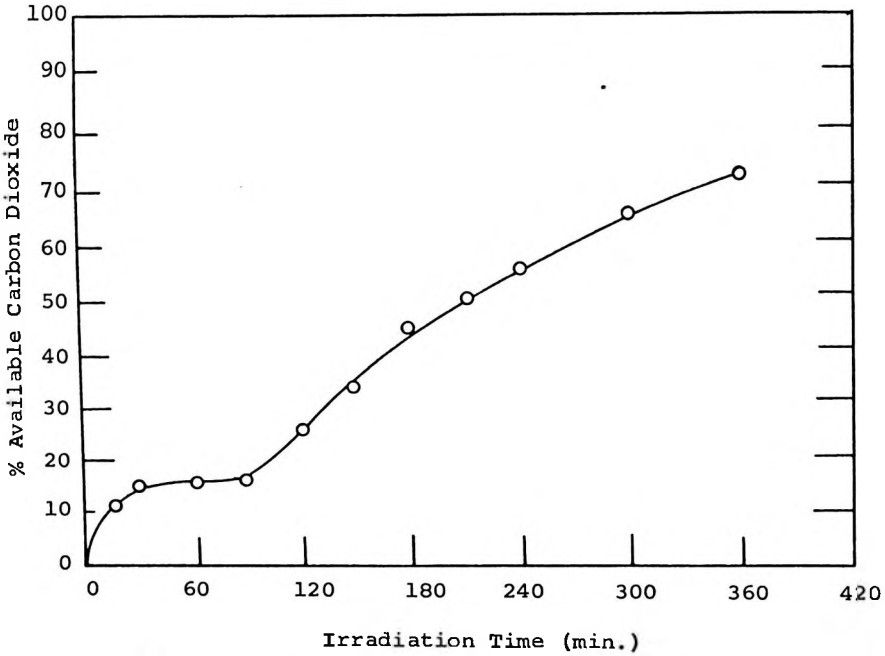
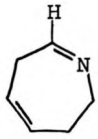


FIGURE 16 . Evolution of Carbon Dioxide as a Function of Irradiation Time in the Photolysis of O-acetylcyclohexanone Oxime in Methanol with No Filter

of this material is presented in Figures 17 and 18. A reasonable interpretation of this spectrum would be that of an azepine with further unsaturation in the ring, for example,



However, there is far too little evidence to confirm this. Unfortunately, there was too little of this material to permit further analysis.

The fifth through the eleventh fractions contained a large amount of a material whose infrared spectrum contained absorptions at 3600 (sharp), 3300 (broad), and 1670 cm^{-1}. Fraction 11 was composed almost entirely of this material and had a melting point of 75-85°. Comparison with an authentic infrared spectrum identified this material as cyclohexanone oxime. With the exception of cyclohexanone and the starting material, no other products could be identified in the chromatographic fractions.

The photolysis of O-acetylcyclohexanone oxime in methanol with no filter was repeated to provide more material for analysis. The postphotolysis solution was

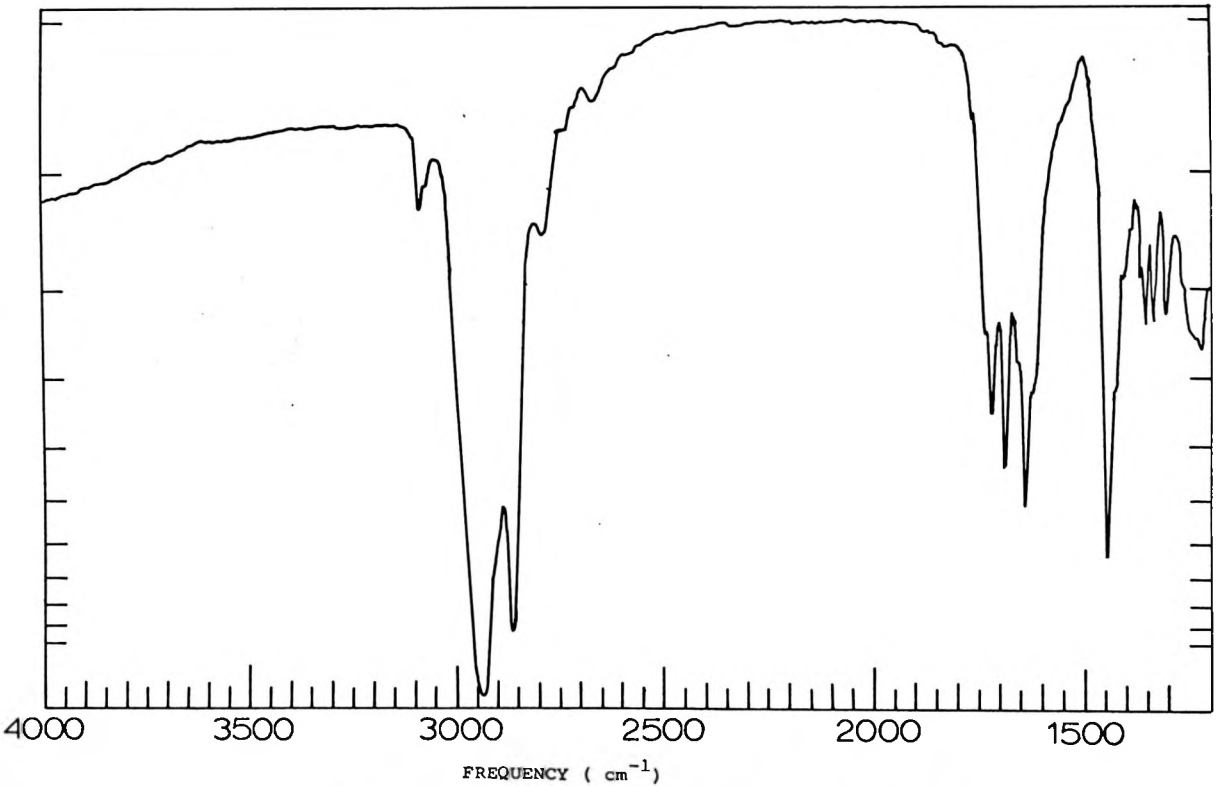


FIGURE 17 . Infrared Spectrum of Product Isolated from the Photolysis of O-acetylcyclohexanone Oxime in Methanol with No Filter

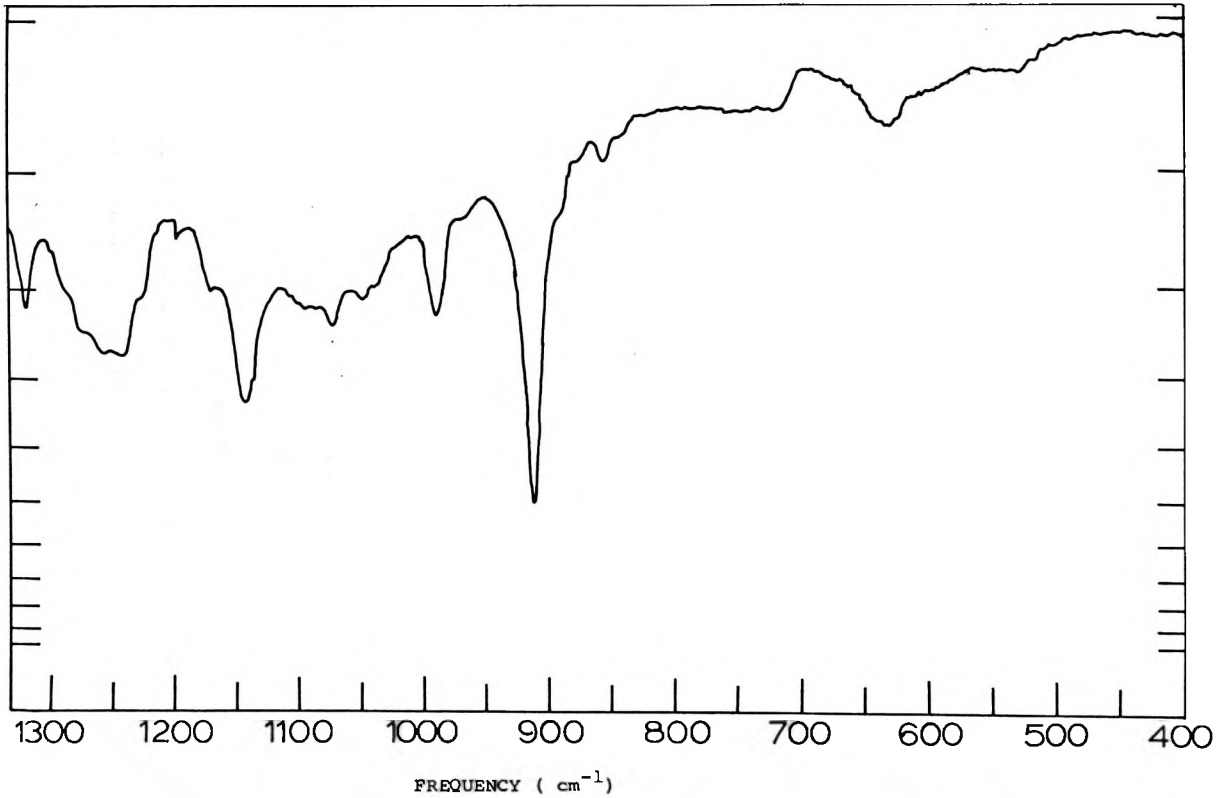


FIGURE 18 . Infrared Spectrum of Product Isolated from the Photolysis of O-acetylcyclohexanone Oxime in Methanol with No Filter

concentrated and chromatographed on alumina with a 50:50 mixture of diethyl ether and methanol. The third fraction was a sweet-smelling oil having approximately the same infrared spectrum as the first fraction in the previous photolysis (Figures 17 and 18). Unfortunately, again there was not enough of this material for further analysis. The presence of cyclohexanone, cyclohexanone oxime, and the starting material was again confirmed.

Since Just and co-workers[12] did not report the generation of ammonia in the photolysis of cyclohexanone oxime, it was decided to repeat their work in part to determine whether the photolysis of cyclohexanone oxime would yield ammonia as well as the reported cyclohexanone, caprolactam, and caproamide. A 1% solution of cyclohexanone oxime in methanol was irradiated for 180 minutes with no filter. Ammonia was definitely detected in the gaseous effluent by odor, litmus, and hydrogen chloride. The other products were the expected amides and cyclohexanone. There was no discoloration of the photolysis solution indicating that the color observed in the photolysis of oxime esters must be a function of the ester moiety.

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[12] R. T. Taylor, M. Donek, and G. Just, Tet. Letters, 4143 (1966).

It was decided at this point to return to O-benzoylcyclohexanone oxime as a reactant in hopes that absorption by the imine chromaphore would lead to more stable and more easily isolated products than in the case of O-acetylcyclohexanone oxime.

A solution of O-benzoylcyclohexanone oxime in cyclohexane was irradiated for 240 minutes with no filter. The solution became yellow within 3 minutes and intensely colored within 7 minutes. The evolution of carbon dioxide was followed as a function of irradiation time and these results are presented in Figure 19. The reaction was monitored by infrared spectrophotometry and showed new peaks at 1720 (probably cyclohexanone), 1700, 680, and 640 cm^{-1}.

The postphotolysis solution was concentrated and chromatographed on alumina with a 50:50 mixture of diethyl ether and methanol as eluent. The first fraction contained an oily material which definitely did not contain a phenyl group and had an infrared spectrum very similar to that of the first fraction in the photolysis of O-acetylcyclohexanone oxime (Figures 17 and 18). It is possible that this material is an azepine contaminated with cyclohexanone. The sixth fraction in this separation contained cyclohexanone

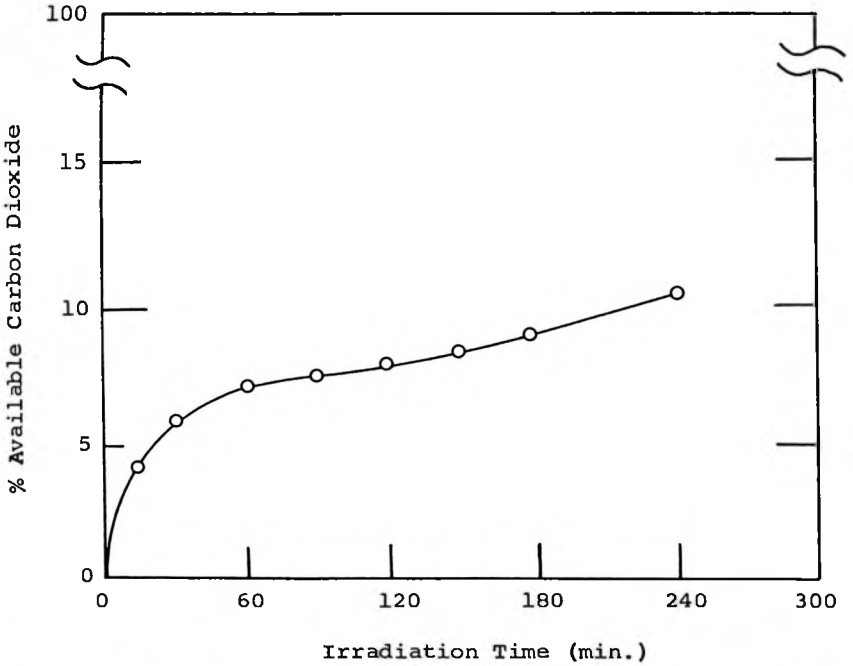


FIGURE 19. Evolution of Carbon Dioxide as a Function of Irradiation Time in the Photolysis of O-benzoylcyclohexanone Oxime in Cyclohexane with No Filter

oxime and an absorption at 1720 cm^{-1}, probably cyclohexanone. The seventh fraction was cyclohexanone oxime only slightly contaminated with a brown color. There was no evidence for any additional products. Ammonium benzoate and any polymeric product would, of course, be expected to remain on the alumina column, and this must account for the phenyl ring moiety since none was observed in the chromatography fractions (with the exception of the starting material).

The next photolysis undertaken was the irradiation of a solution of O-benzoylcyclohexanone oxime in methanol with no filter. In this case the irradiation was discontinued at 150 minutes because the evolution of carbon dioxide had almost ceased after 120 minutes. The results of the determination of the evolution of carbon dioxide as a function of irradiation time are presented in Figure 20. Comparison of the carbon dioxide evolution in the photolysis of O-benzoylcyclohexanone oxime in methanol to that in cyclohexane (comparison of Figure 20 to Figure 19) show that, as in the case of the acetate ester, the evolution of carbon dioxide proceeds much faster, and to a greater extent, in methanol than in cyclohexane.

The photolysis solution became yellow within 3 minutes but did not become as intensely colored as in the same

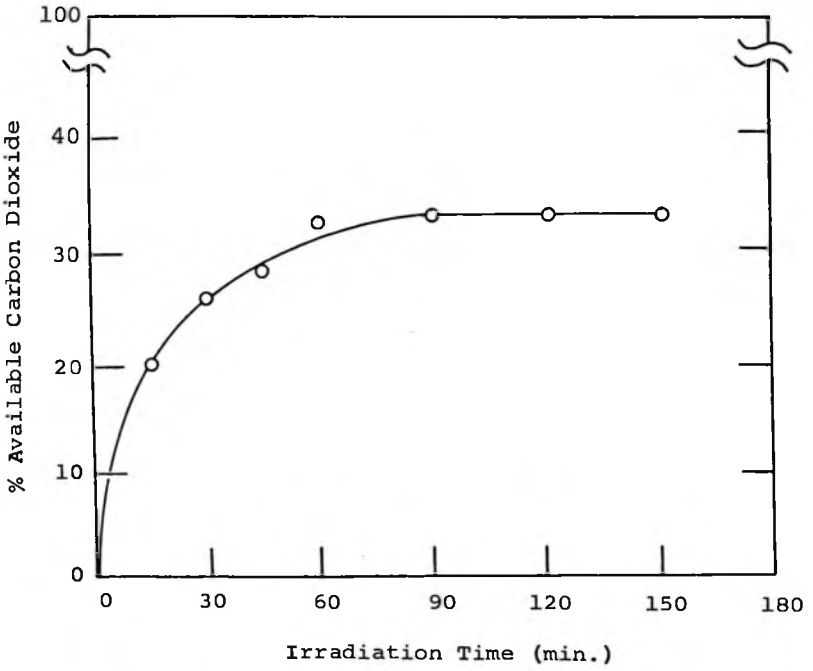


FIGURE 20. Evolution of Carbon Dioxide as a Function of Irradiation Time in the Photolysis of O-benzoylcyclohexanone Oxime in Methanol with No Filter

reaction in cyclohexane. Furthermore, the postphotolysis solution in methanol had a sweet, agreeable odor while that in cyclohexane had a foul, irritating odor.

The postphotolysis solution was concentrated and chromatographed on alumina with methanol as eluent. The only identifiable products were cyclohexanone, cyclohexanone oxime, and the starting material. Infrared spectra showed other materials present in very small quantities, but it was not possible to establish their identity.

There is the possibility that, if a ring expansion reaction occurred, the products might themselves undergo photolysis and would therefore not be detected in the postphotolysis solution. In order to increase the chances of finding these products, if they exist, four more photolyses were performed with no filter for 150 minutes. These four photolyses consisted of both O-acetylcyclohexanone oxime and O-benzoylcyclohexanone oxime in methanol and cyclohexane solution. These photolyses were performed also to provide additional product material for analysis.

The postphotolysis solution from each photolysis was subjected to very careful analysis. The solvent was distilled from the solution and then subjected to fractional distillation, but no photolysis products were found. The

concentrated solutions were chromatographed on alumina with cyclohexane followed by benzene, acetone, and methanol as eluents. A large number of fractions (20 to 60) were collected in each case, and these were carefully analysed by refractive index and infrared spectrophotometry. The only evidence for a previously unobserved product was the isolation of a solid product from the photolysis of O-benzoylcyclohexanone oxime in methanol which melted above 250° and gave a poorly defined infrared spectrum with amide characteristics. This material is apparently polymeric in nature.

Since O-(p-nitrobenzoyl)-cyclohexanone oxime has a higher melting point (104°), and a much lower solubility in all solvents tested than O-benzoylcyclohexanone oxime, it was hoped that the photolysis of this compound would produce products that could be isolated and identified should a ring-expansion reaction occur. The infrared spectrum of O-(p-nitrobenzoyl)-cyclohexanone oxime in CCl_4 is presented in Figures 21 and 22.

A solution of O-(p-nitrobenzoyl)-cyclohexanone oxime in methanol was irradiated for 150 minutes with no filter. The solvent was evaporated and the concentrated solution separated by fractional crystallization. Analysis of the

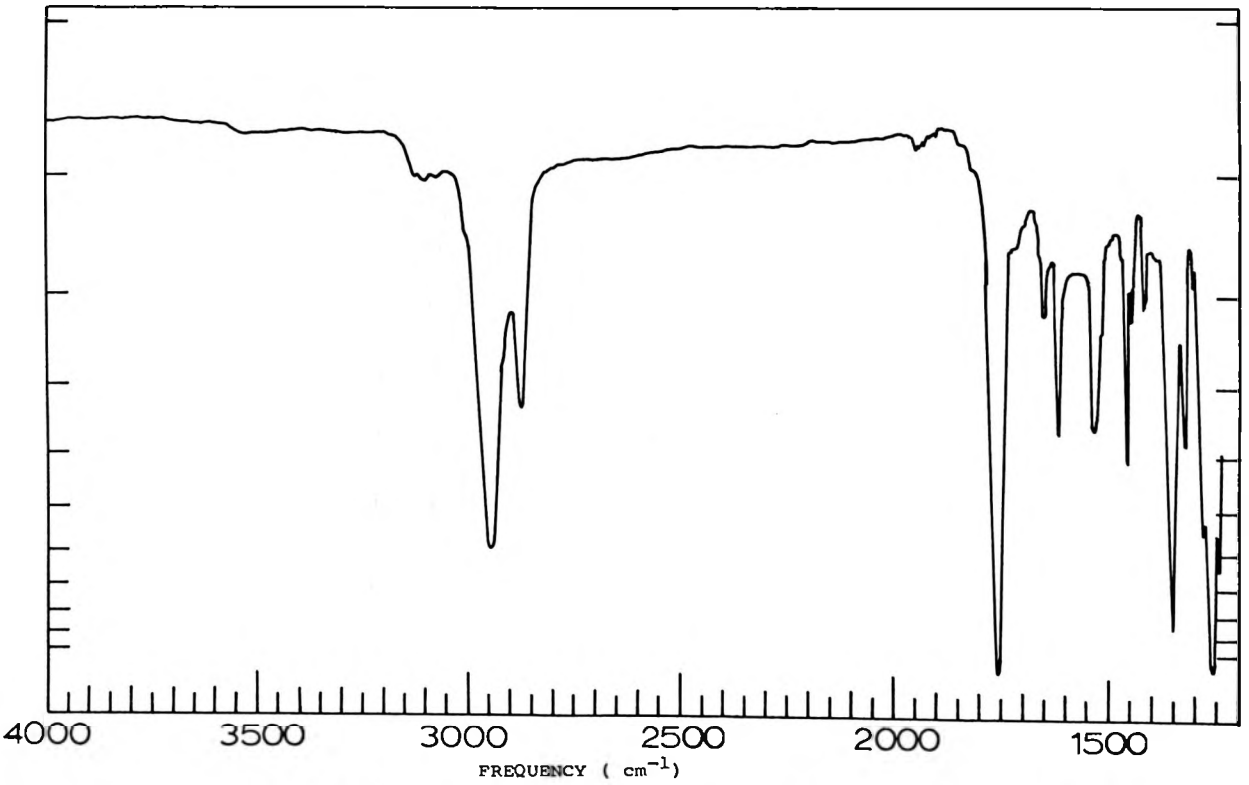


FIGURE 21. Infrared Spectrum O-(p-nitrobenzoyl)-cyclohexanone Oxime in CCl_4

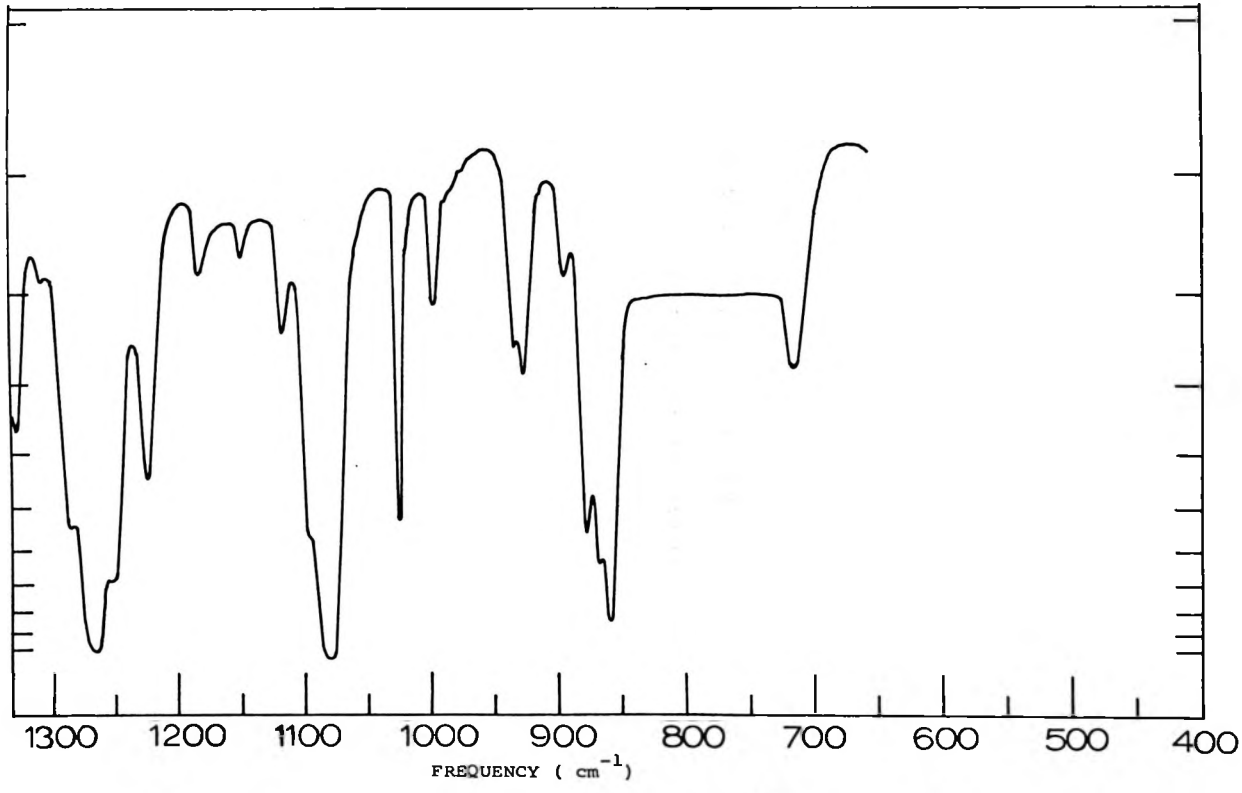
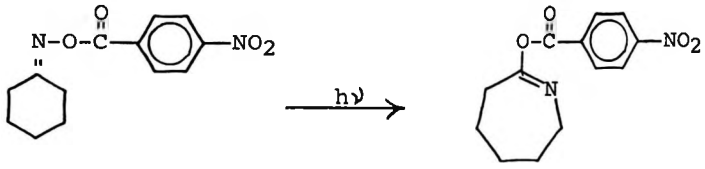


FIGURE 22. Infrared Spectrum of O-(p-nitrobenzoyl)-cyclohexanone Oxime in CCl_4

fractions indicated that a large proportion of the starting material remained unreacted (approximately 50%). The products consisted of cyclohexanone, cyclohexanone oxime, a brown amorphous material, probably polymeric, and an impure yellow solid. After several recrystallizations, this yellow solid still remained contaminated with the starting material and had a melting point of 77-78°. Infrared analysis indicated the presence of a carbonyl group (1740 cm^{-1}), a phenyl group, and an aliphatic group. At this time it was thought that this compound might be O-(p-nitrobenzoyl)-caprolactim and that the Beckmann rearrangement



might be occurring.

In order to provide more material for analysis, better yield data, and to follow the evolution of carbon dioxide, a second solution of O-(p-nitrobenzoyl)-cyclohexanone oxime in methanol was irradiated for 225 minutes with no filter. The evolution of carbon dioxide was followed as a function of irradiation time and the results of this determination are

presented in Figure 23. A sample of the postphotolysis solution was titrated conductometrically with standard hydrochloric acid but resulted in a curve in which there was very little evidence of a break. The best curve that could be drawn indicated a yield of ammonium p-nitrobenzoate of 2%, but the validity of this result is doubtful.

The postphotolysis solution was concentrated and separated by extraction and fractional crystallization. Careful analysis of the fractions resulted in the same products that were observed in the previous photolysis, that is, the starting material, cyclohexanone, cyclohexanone oxime, a brown polymeric material, and the yellow solid. It was found that the yield by weight of the starting material was 44%, that of the polymer was 12%, and that of the yellow solid was 27%. The infrared spectrum of the polymer had amide-like characteristics but was poorly defined. The spectrum did indicate that the nitro group was intact so that polymerization did not occur through the nitro group.

As previously mentioned it had been thought that the yellow solid might be the lactim resulting from Beckmann rearrangement. Further purification enabled a more exhaustive

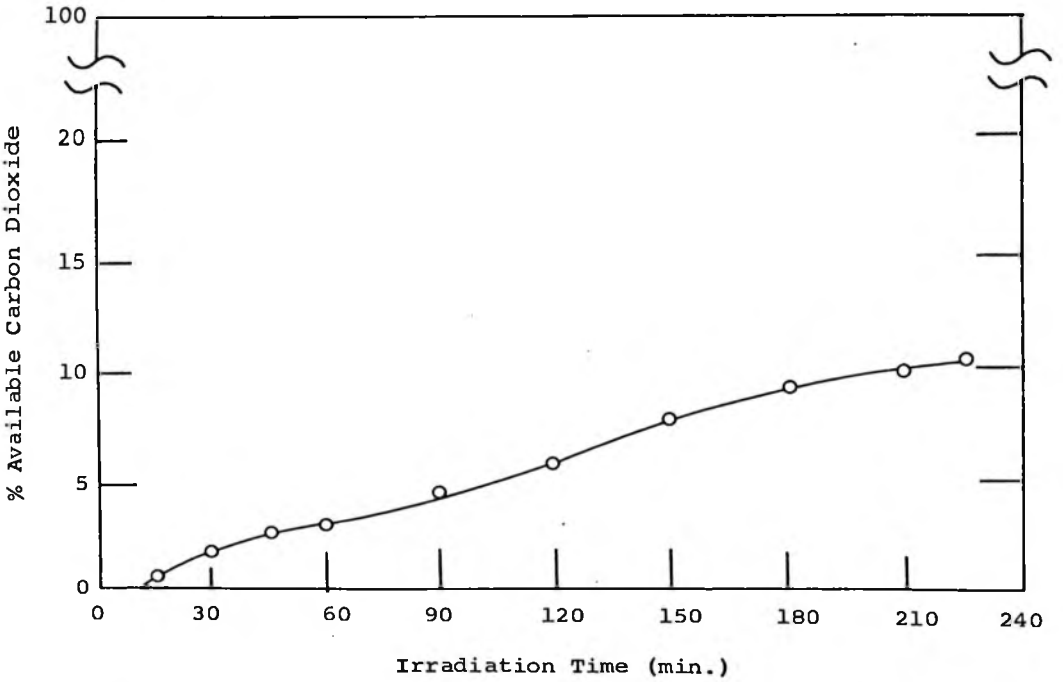


FIGURE 23 . Evolution of Carbon Dioxide as a Function of Irradiation Time in the Photolysis of O-(p-nitrobenzoyl)-cyclohexanone Oxime in Methanol with No Filter

analysis to be made. The NMR spectrum of this product showed only the aromatic protons and a sharp singlet with an intergrated intensity of 3 protons. Synthesis of methyl-(p-nitro)-benzoate and comparison of its spectral and physical properties with those of the product identified the product as methyl-(p-nitro)-benzoate.

At first glance it would appear that the methyl ester probably arises through simple trans-esterification of the starting material with the solvent. To test this possibility a solution of O-(p-nitrobenzoyl)-cyclohexanone oxime in methanol was subjected to the same conditions as in the photolysis but in the absence of light. Trans-esterification did indeed occur, but the yield of methyl ester was less than 1% as compared to 39% (on a molar basis) in the photolysis. It would appear then that the formation of the methyl ester is a photochemical phenomenon, or more likely, the photolytic reaction produces some species which catalyses the trans-esterification reaction.

Heldt[13] has reported the synthesis and the infrared spectrum of O-(p-toluoyl)caprolactim. With this infrared spectrum as a standard of comparison, it was decided to

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[13] W. Z. Heldt, J. Am. Chem. Soc., 80, 5880 (1958).

irradiate O-(p-toluoyl)-cyclohexanone oxime and search for evidence of the Beckmann rearrangement product, O-(p-tolyoyl)-caprolactim. The infrared spectrum of O-(p-toluoyl)-cyclohexanone oxime in CCl_4 is presented in Figures 24 and 25.

A solution of O-(p-toluoyl)-cyclohexanone oxime in cyclohexane was irradiated for 240 minutes with no filter. The evolution of carbon dioxide was followed as a function of irradiation time and the results of this determination are presented in Figure 26. Ammonia was observed in the gaseous effluent throughout the reaction, and yellow color appeared almost immediately and rapidly became a dark amber. In addition the reaction evolved a foul, extremely irritating odor, which definitely made the investigator feel groggy. Attempts to determine the yield of ammonium p-methylbenzoate by conductometric titration were unsuccessful because of instrumental difficulties; so the salt was filtered, identified, and weighed. The yield thus determined was 2% on a molar basis. The postphotolysis solution was concentrated and examined for evidence of O-(p-toluoyl)-caprolactim, but none was observed.

In order to determine whether it was possible that photolysis of the observed ammonium salt could be responsible for the carbon dioxide and ammonia observed in these

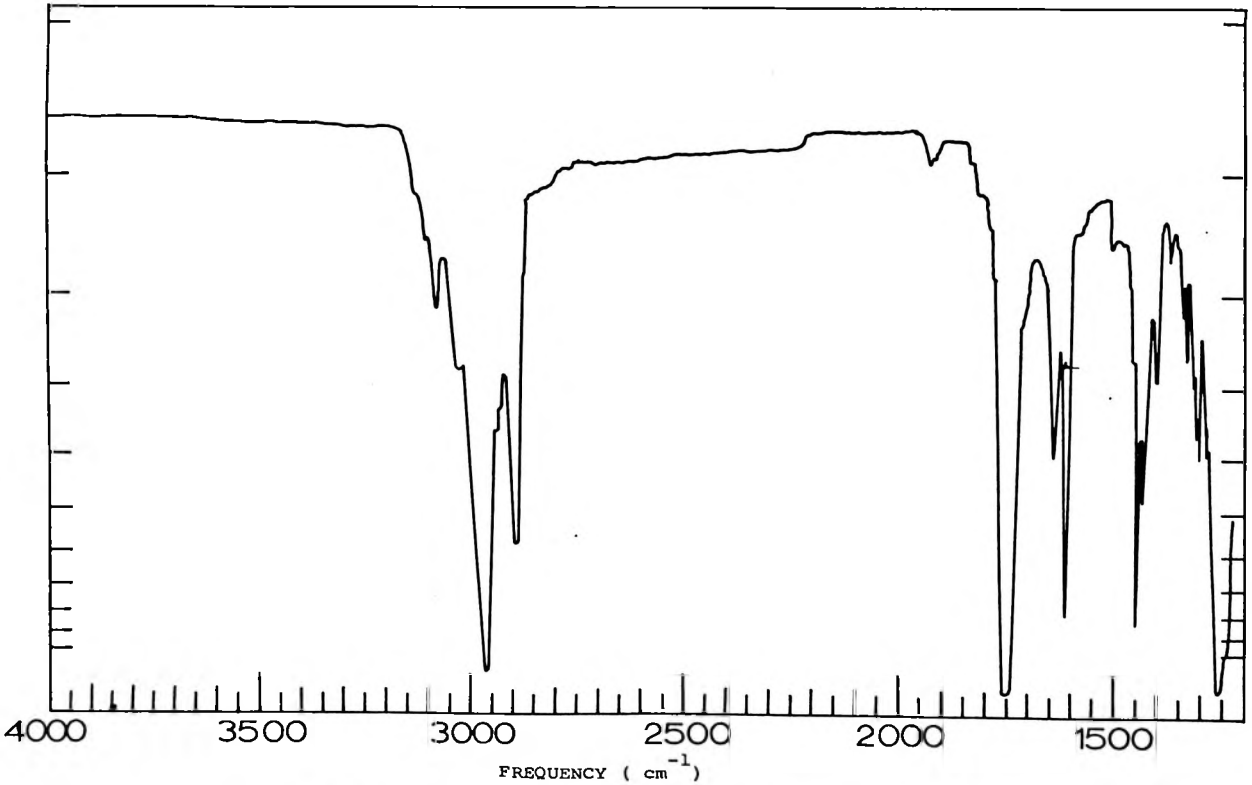


FIGURE 24. Infrared Spectrum of O-(p-toluoyl)-cyclohexanone Oxime in CCl_4

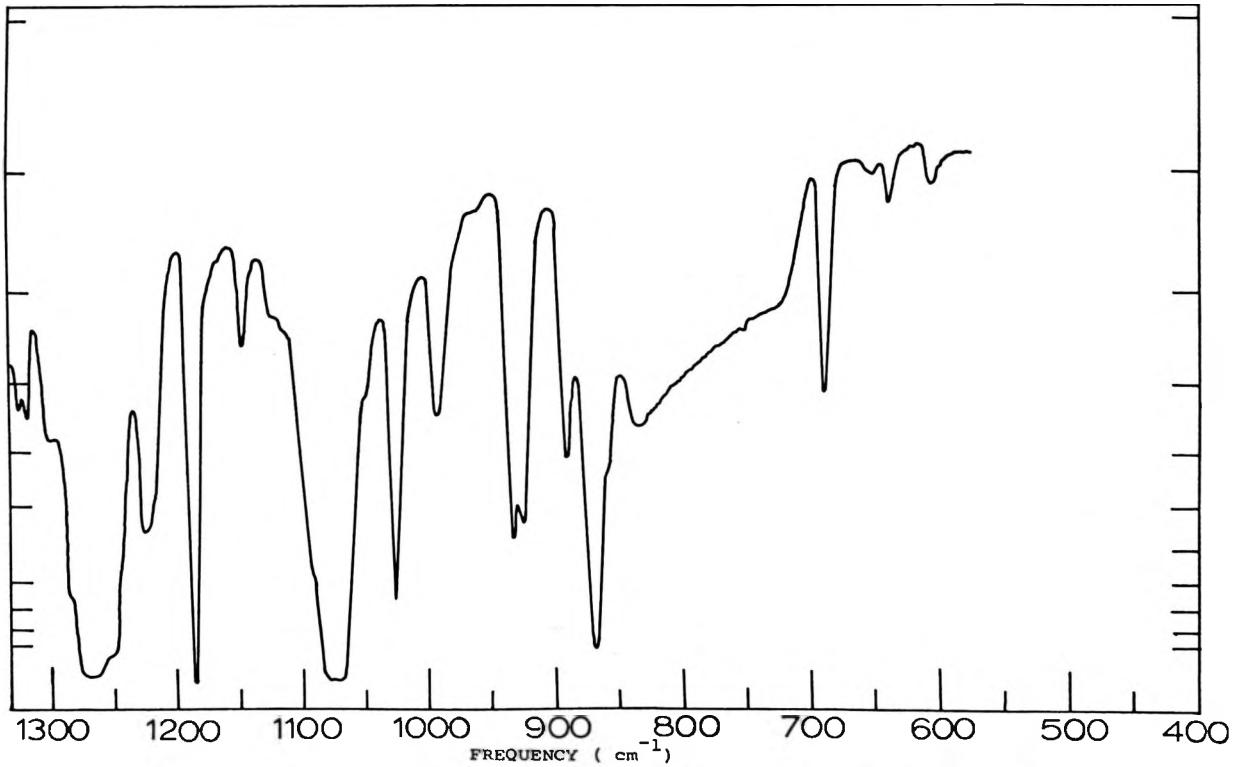


FIGURE 25 . Infrared Spectrum of O-(p-toluoyl)-cyclohexanone Oxime in CCl_4

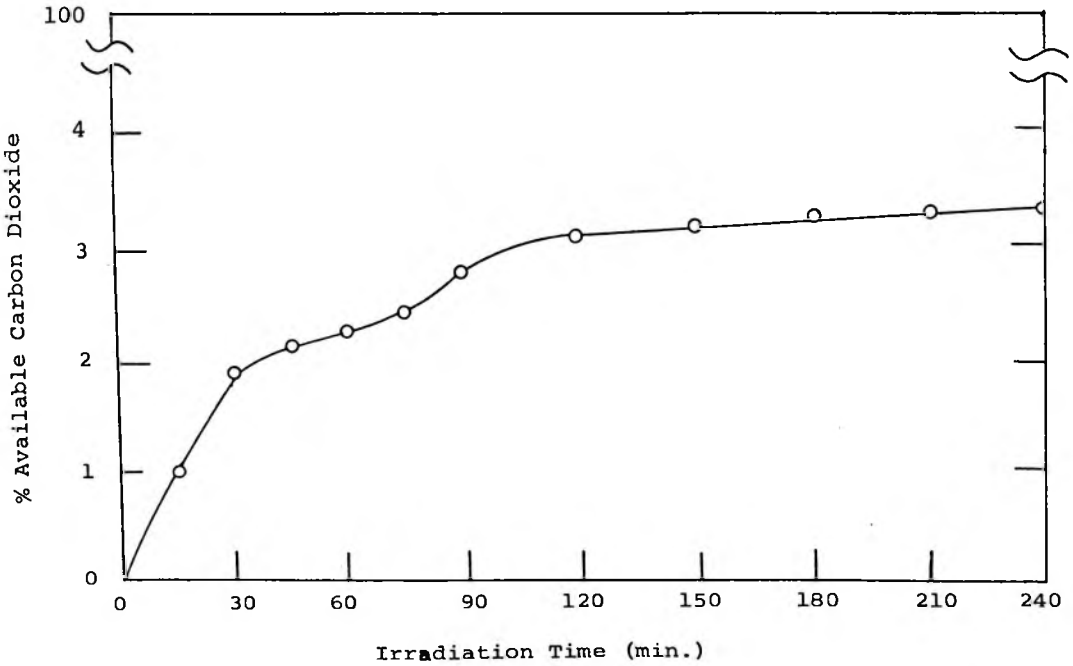


FIGURE 26. Evolution of Carbon Dioxide as a Function of Irradiation Time in the Photolysis of O-(p-Toluoyl)-cyclohexanone Oxime in Cyclohexane with No Filter

reactions, ammonium acetate was irradiated in both cyclohexane and methanol solution for 60 minutes with no filter. In cyclohexane solution ammonia was detected in the gaseous effluent, the solution turned an amber color and had a disagreeable odor, and the yield of carbon dioxide was found to be 0.5%. The irradiation of ammonium acetate in methanol produced ammonia and a 23.4% yield of carbon dioxide. The methanol solution became a very light yellow and had a sweet, ester-like odor.

SUMMARY

The compounds irradiated in this research and the conditions under which the photolyses were performed are presented in Table 4. O-benzoylcyclohexanone oxime was the first compound studied because of its ease of preparation from readily available materials, because it could be easily purified by recrystallization, and because its structure is relatively simple. The other reactants were chosen for various experimental and mechanistic reasons.

The solvents used throughout the research were cyclohexane and methanol. These were chosen because they are transparent throughout the spectral region of interest, because they differ considerably in their ability to donate hydrogen atoms, and because neither can act as a photosensitizer. In addition, cyclohexane is a satisfactory infrared solvent, so that the photolyses in this solvent could be followed by infrared spectrophotometry.

Initial reactions were performed with radiation of relatively low energy, and the energy was later increased in hopes of detecting product differences as a function of wavelength.

TABLE 4

COMPOUNDS PHOTOLYSED AND CONDITIONS OF PHOTOLYSES

Reactant	SOLVENT	WAVELENGTH	TEMPERATURE
O-benzoyl-cyclohexanone oxime	cyclohexane	above 300 mμ	0° and R. T.
	cyclohexane	above 280 mμ	0° and R. T.
	cyclohexane	above 200 mμ	R. T.
	cyclohexane (with $MgSO_4$)	above 280 mμ	R. T.
	methanol	above 200 mμ	R. T.
O-actylcyclo-hexanone oxime	cyclohexane	above 280 mμ	R. T.
	cyclohexane	above 230 mμ	R. T.
	cyclohexane	above 200 mμ	R. T.
	methanol	above 230 mμ	R. T.
	methanol	above 200 mμ	R. T.
O-(p-nitro-benzoyl)-cyclo-hexanone oxime	methanol	above 200 mμ	R. T.
O-(p-toluoyl)-cyclohexanone oxime	cyclohexane	above 200 mμ	R. T.

At first photolyses were carried out at ice-bath temperatures to prevent thermal reactions. However, it was soon determined that reactions at room temperature were identical to those at 0° and thereafter no cooling of the reaction solution was provided.

The effect of solvent upon carbon dioxide evolution in the photolyses of O-acetylcyclohexanone oxime and O-benzoylcyclohexanone oxime in cyclohexane and methanol is shown graphically in Figures 27 and 28.

Ammonium acetate was irradiated for 60 minutes with no filter in both cyclohexane and methanol. Carbon dioxide and ammonia were observed as products, and it appeared that the resulting methyl radical reacted with the solvent. The yield of carbon dioxide after irradiation for 60 minutes with no filter was 0.5% in cyclohexane and 23.4% in methanol.

Concerning experimental procedure, the photolysis solvents were distilled on a gold spinning-band column, and the photolysis solutions were degassed and continuously agitated by bubbling through nitrogen which had been passed through a purification chain. During the photolysis carbon dioxide evolution was monitored by observing the change in weight of a tube of Ascarite (NaOH on asbestos), and ammonia evolution was determined quantitatively by

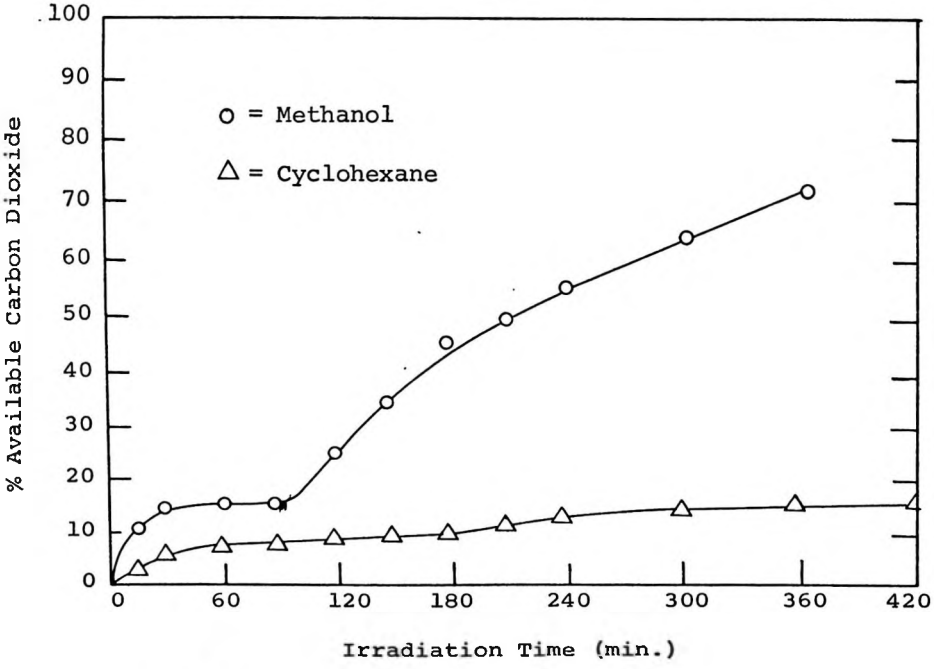


FIGURE 27 . Evolution of Carbon Dioxide as a Function of Irradiation Time in the Photolyses of O-acetylcyclohexanone Oxime in Cyclohexane and Methanol with No Filter

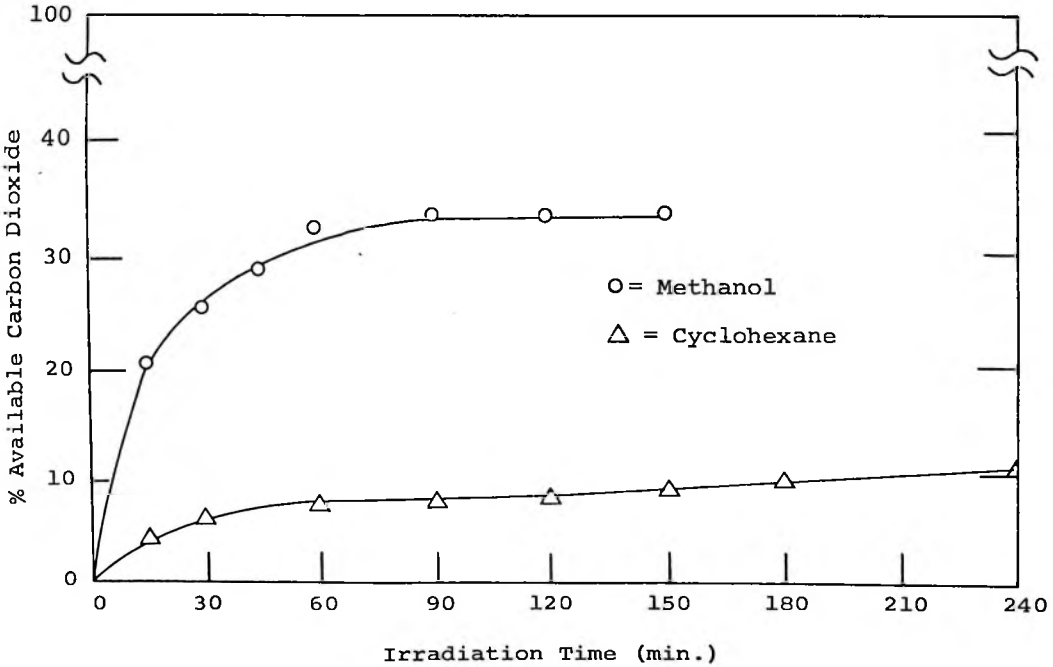


FIGURE 28. Evolution of Carbon Dioxide as a Function of Irradiation Time in the Photolyses of O-benzoylcyclohexanone Oxime in Cyclohexane and Methanol with No Filter

sorption on Granusic (granular P_2O_5). The yield of ammonium salt was determined by conductometric titration with standard hydrochloric acid.

Most of the photolyses carried out in cyclohexane were monitored by infrared spectra. In the case of the acetate and benzoate esters in cyclohexane, the reactant concentration was followed by pyrolysis gas chromatography. It would appear that g.l.p.c. would be ideally suited for product analysis in these reactions, however, the starting esters are thermally unstable and have an extremely low vapor pressure, so that gas chromatograms of any sample containing the starting material were prohibitively complex.

Postphotolysis solutions were separated for analysis by elution chromatography on alumina, fractional distillation, fractional crystallization, and solvent extraction.

The photolysis products, with yield ranges in each solvent, are presented for each compound in Tables 5 through 8. The numbers in parentheses indicate the irradiation time in minutes for which the yield was determined.

TABLE 5

PRODUCTS AND YIELDS FROM THE PHOTOLYSES OF O-ACETYL-CYCLOHEXANONE OXIME IN CYCLOHEXANE AND METHANOL

PRODUCTS	YIELDS	
Major	Cyclohexane	Methanol
Carbon Dioxide	15% (420) 14.6% (360) 10% (150)	72% (360) 34% (150)
Ammonia	10% (420)	qualitative
Ammonium Acetate	6-10% (420)	12% (180)
Cyclohexanone Oxime	5+% (420)	qualitative
O-acetylcyclohexanone Oxime	70% (420)	not determined
Minor		
Cyclohexanone	5-8% (420)	qualitative
Acetone	qualitative	---
an azepine?	trace	---
a lactim?	trace	---
amide (s)	trace	trace

TABLE 6

PRODUCTS AND YIELDS FROM THE PHOTOLYSES OF O-BENZOYL-CYCLOHEXANONE OXIME IN CYCLOHEXANE AND METHANOL

PRODUCTS	YIELDS	
Major	Cyclohexane	Methanol
Carbon Dioxide	10% (240) 8% (150)	34% (150)
Ammonia	qualitative	qualitative
Ammonium Benzoate	4-8% (180)	2% (150)
Cyclohexanone Oxime	5+% (180)	5+% (150)
O-benzoylcyclohexanone Oxime	18% (180) 22% (150)	not determined
Minor		
Cyclohexanone	qualitative	qualitative
Benzoin	trace	---
Allene(s)	trace	---
Amide (s)	trace	trace
Aldehyde (s)	trace	trace

TABLE 7

PRODUCTS AND YIELDS FROM THE PHOTOLYSIS OF O-(*p*-NITRO-BENZOYL)-CYCLOHEXANONE OXIME IN METHANOL

PRODUCTS	YIELDS
Carbon Dioxide	10% (225)
Ammonia	not detected
Ammonium *p*-nitrobenzoate	2% (225)
Cyclohexanone Oxime	trace
Cyclohexanone	qualitative
Methyl-(*p*-nitro)-benzoate	39% (225)
Polymer	12% by weight (225)
O-(*p*-nitrobenzoyl)-cyclohexanone Oxime	44% (225)

TABLE 8

PRODUCTS AND YIELDS FROM THE PHOTOLYSIS OF O-(*p*-TOLUOYL)-CYCLOHEXANONE OXIME IN CYCLOHEXANE

Products	Yields
Carbon Dioxide	3.3% (240) 3.2% (150)
Ammonia	qualitative
Ammonium *p*-methylbenzoate	2% (240)
Cyclohexanone Oxime	qualitative
Cyclohexanone	qualitative
O-(*p*-toluoyl)-cyclohexanone Oxime	90+% (240)

CHAPTER V

CONCLUSIONS

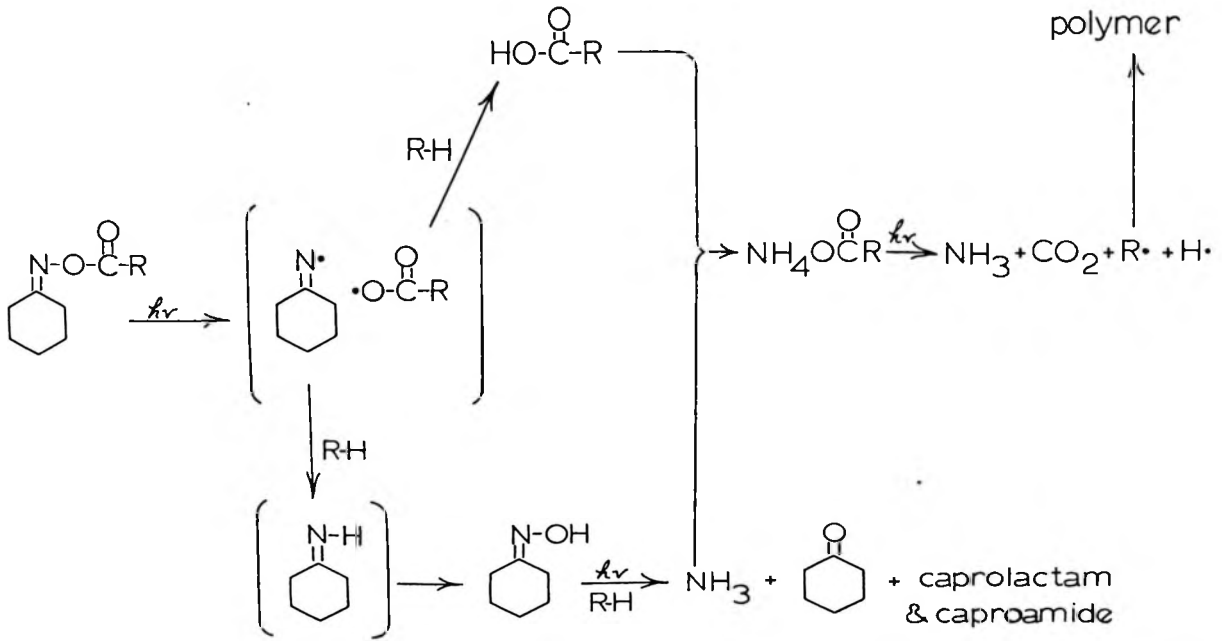
From the evidence presented herein, it appears that the proposed Beckmann rearrangement is not operative in the photochemical reaction of oxime esters; or, if it does occur, the products have only a transient existence.

The evidence indicates that there is a general photochemical degradation of oxime esters and this reaction is well defined in the photolysis of the acetate, benzoate, and p-toluoyl esters of cyclohexanone oxime. A competing reaction, however, predominates in the case of the p-nitrobenzoate ester of cyclohexanone oxime.

The general photochemical degradation of oxime esters has been observed to produce carbon dioxide, ammonia, the ammonium salt corresponding to the ester moiety, cyclohexanone oxime, cyclohexanone, traces of caprolactam, and caproamide, and various other secondary products. In the p-nitrobenzoate ester of cyclohexanone oxime, a transesterification reaction predominates to produce methyl-(p-nitro)-benzoate.

Figure 29 presents a plausible explanation for the origin of the products observed in the general reactions.

FIGURE 29.


N-O-C-R
hν
N•
•O-C-R
R-H
HO-C-R
R-H
N-H
N-OH
hν
R-H
NH3
+
+ caprolactam
& caproamide
NH4OCR
hν
NH3 + CO2 + R• + H•
polymer

No detailed mechanistic investigations on these photochemical reactions were made since this fell outside the scope of the present investigation. Indeed the mechanistic intricacies of these reactions appear to be quite complex, and any completely definitive pathway must necessarily await further experimentation, which is planned for the future. The flow diagram presented in Figure 29 is one plausible explanation for the origin of the observed products.

The initial cleavage of the N-O bond is quite reasonable since this is by far the weakest bond in the molecule with an energy of 53 kcal/mole, which corresponds to the energy of an absorption at 540 mμ. Hence, absorption by even the carbonyl chromaphore would be more than sufficient to cause cleavage of the N-O bond. The observed reaction obviously does not require absorption by the C=N chromaphore (which occurs around 210 mμ = 136 kcal/mole) since the reaction occurs even when the incident radiation is limited to above 230 mμ. This makes it doubtful that the observed reaction passes through the Beckmann rearrangement product as an intermediate since Beckmann rearrangement would presumably require absorption by the imine chromaphore.

Once the N-O bond cleavage has occured, the radical fragments would be expected to react before they have time to diffuse into the solution. That is, they would react within a "cage" system. One obvious possibility would be the loss of carbon dioxide followed by recombination of radical fragments to yield an imine. We have shown that, at least in the case of the benzoate ester of cyclohexanone oxime, this does occur. What appears to happen is that a certain proportion of the radical fragments lose carbon dioxide and go to other products, while the remainder are reduced by hydrogen abstraction from the solvent to cyclohexanone imine - or somehow to cyclohexanone oxime - and the carboxylic acid corresponding to the ester moiety. The reduction of benzoate radicals to benzoic acid has been demonstrated in the photodecomposition of dibenzoyl hydroxylamine[1], however, there has been no confirmation of the existence of free acetate radicals in solution. Walling and Gibian[2] have, however, shown that acetate radicals can indeed exist, and react, in a "cage" system.

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[1] C. Walling and A. N. Naglieri, J. Am. Chem. Soc., 82, 1820 (1960).

[2] C. Walling and M. J. Gibian, J. Am. Chem. Soc., 83, 2998 (1961).

Since the acetate, benzoate, and p-toluoyl esters of cyclohexanone oxime parallel each other in their photochemical behavior, we feel that it is not unreasonable to suspect that the acetate radical, as well as the benzoate and the p-methylbenzoate radical, is reduced to the carboxylic acid in this reaction.

It has been shown in this research that the irradiation of cyclohexanone oxime yields ammonia as well as the cyclohexanone, caprolactam, and caproamide previously reported[3]. The ammonia thus produced could then easily react with the carboxylic acid produced by the reduction of the initial radical fragment to yield the observed ammonium salt.

We have shown in this research that the irradiation of ammonium acetate, in both cyclohexane and methanol, produces carbon dioxide, ammonia, and presumable the hydrocarbon radical and a hydrogen atom. It is probable that the hydrocarbon radical then reacts with another radical like itself and/or with the solvent to produce hydrocarbon and polymeric materials. The proposal that the solvent is

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[3] R. T. Taylor, M. Donek, and G. Just, Tet. Letters, 4143 (1966).

incorporated into the final product is supported by the fact that reactions in cyclohexane and methanol lead to postphotolysis solutions which vary markedly in odor and color. Those reactions in cyclohexane produce amber colored solutions with foul, irritating odors; while the same material photolysed in methanol produces a bright yellow solution with a sweet, agreeable odor. These colors and odors directly parallel those observed in the photolysis reactions of the oxime esters.

It can be observed that breaks appear in the carbon dioxide evolution curves for each photolysis reaction, usually around 90 minutes in methanol solution and around 180 minutes in cyclohexane solution. A possible explanation for this break could be that a reaction occurs initially to produce carbon dioxide and other products as well as the ammonium salt. The ammonium salt could then begin to decompose photolytically and cause an increase in the rate of carbon dioxide evolution.

It is still possible that a Beckmann rearrangement, or ring expansion, occurs in the irradiation of oxime esters, but there is very little evidence to support this. The only evidence we have to offer is an unidentified peak at about 1720 cm^{-1} in the infrared spectra monitoring the photolysis

reactions and rather poor infrared spectra of several trace fractions which could be interpreted as azepines or lactims. The unidentified peak at 1720 cm^{-1} appeared in every photolysis monitored by infrared spectra and usually grew to a maximum intensity and then decreased. The frequency of absorption is correct for the ester carbonyl in a lactim, but unfortunately is also correct for cyclohexanone.

The predominant reaction in the photolysis of O-(p-nitrobenzoyl)-cyclohexanone oxime is a trans-esterification to produce methyl-(p-nitro)-benzoate. It has been shown in this research that this is not a simple trans-esterification reaction, but requires light to produce yields on the order of those observed in the photolysis reaction. It is possible that the trans-esterification is completely photochemical in nature, but a more reasonable explanation is that some species is generated photochemically which catalyses the trans-esterification reaction.