

REACTION OF 1-ETHOXYVINYL ACETATE
WITH ALIPHATIC DIAZO COMPOUNDS

by

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A THESIS

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CHAPTER I

INTRODUCTION

The purpose of the experiments described in this thesis was to prepare certain cyclopropane derivatives by the reaction of 1-ethoxyvinyl acetate with various diazo compounds, and to investigate the behavior of the resulting products on hydrolysis. Background information relating to the mechanism of such reactions and previous work in this area is discussed. The preparation of 1-ethoxyvinyl acetate is described, and evidence is presented for its subsequent conversion to ethyl 2-acetoxy-2-ethoxycyclopropanecarboxylate by reaction with ethyl diazoacetate. The infrared spectra of the major products in this synthetic sequence are reproduced and discussed in detail. Other experiments concerned with the attempted reactions of 1-ethoxyvinyl acetate with diazomethane and diphenyldiazomethane, and the hydrolysis of ethyl 2-acetoxy-2-ethoxycyclopropanecarboxylate are described.

CHAPTER II

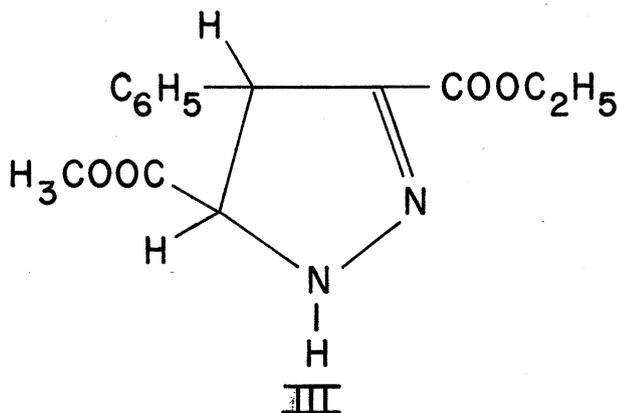
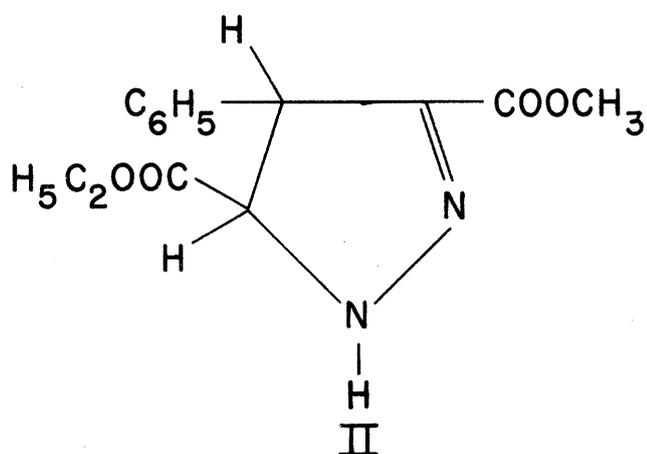
HISTORICAL

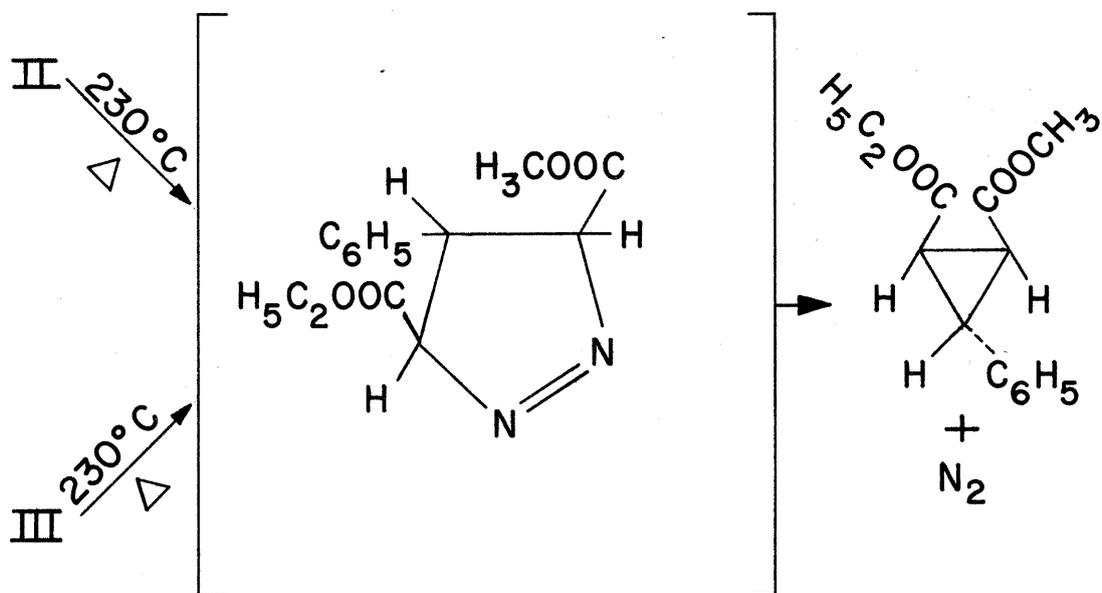
The addition of diazomethanes to olefinic bonds to form either pyrazolines or cyclopropane derivatives is a reaction that has been extensively investigated since the last decade on the nineteenth century. Much work in this area has been done in the last ten years.

The reactions of diazomethanes with unsaturated compounds fall into at least two categories. In one, the diazo compound undergoes ionic addition to a double bond, usually a conjugated one, and the resulting pyrazoline may be converted to a cyclopropane derivative. In the other category the diazo compound is caused to react with a double bond by either photolysis, or heavy metal or heavy metal ion catalysis, yielding directly the cyclopropane derivative and nitrogen gas.

The two general classes of mechanisms that can be applied to these reactions are: first, the electrophilic attack of an electron deficient carbon of the double bond on the carbon-nitrogen double bond of the diazomethane; and second, the addition of a methylene

thermal decomposition of the products to cyclopropane derivatives. It is of interest that Jones was able to isolate both the cis and trans isomers.





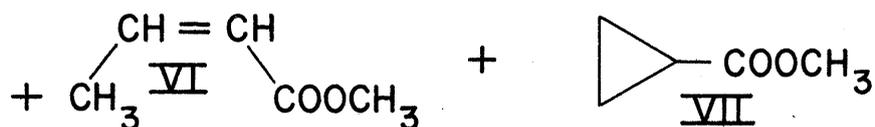
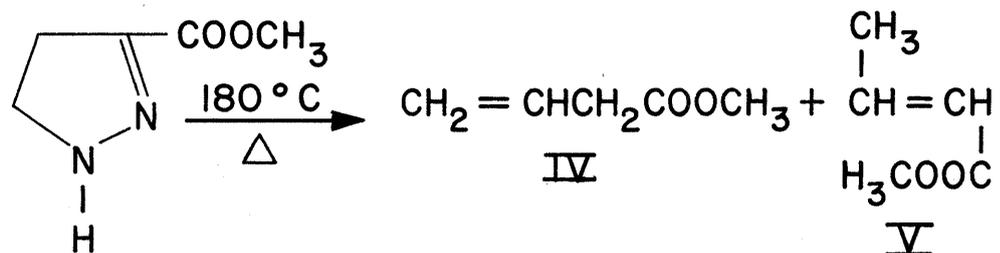
Jones⁵ has also investigated the reactions of diphenyldiazomethane with dimethyl maleate and dimethyl fumarate at high temperatures (180-200°). Both reactions were found to yield the same product: i.e., only the trans-cyclopropane derivative was obtained with no isolable amount of cis-isomer. This work was an investigation of the mechanism of a reaction first reported by Auwers and König⁶.

As further indication of the course of reactions

(5) W. M. Jones, J. Am. Chem. Soc., 81, 3776 (1959).

(6) K. V. Von Auwers and F. König, Ann., 496, 252 (1932).

of diazomethane with conjugated olefinic bonds, the work of McGreer⁷ illustrates the decomposition of pyrazolines to cyclopropanes, and also indicates the complexity of the products obtained. In this study 3-carbomethoxypyrazoline was pyrolyzed at 180° to give a mixture of methyl cis- and trans-crotonate (V and VI), methyl cyclopropanecarboxylate (VII), and a small amount of methyl vinylacetate (IV).

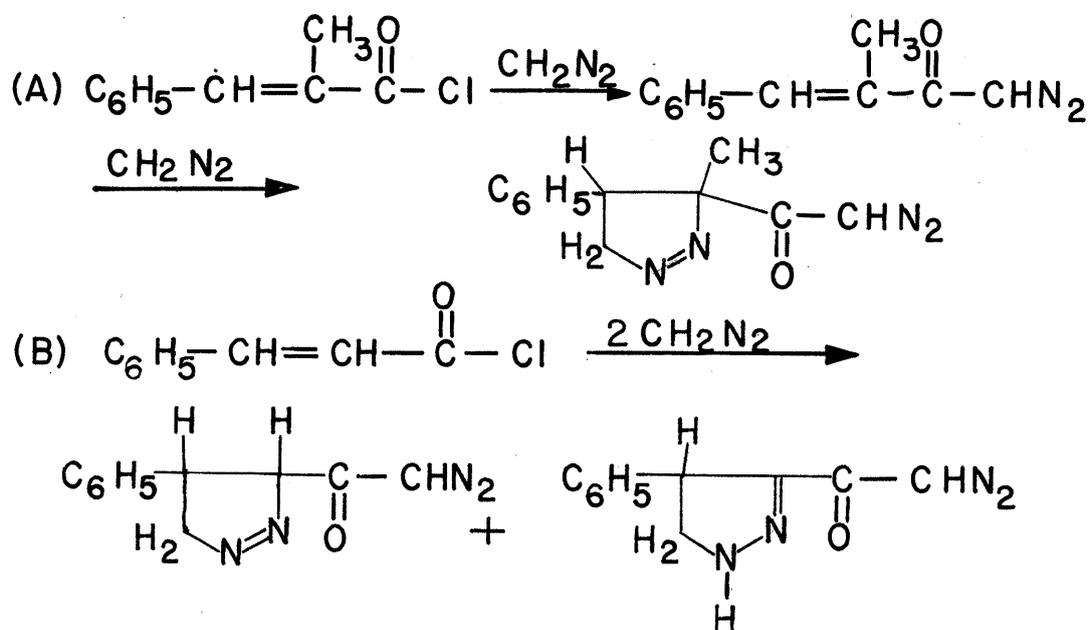


The ratio of products IV:V:VI:VII is 7:30:31:32

Moore⁸ has studied the reaction of diazomethane with various unsaturated acid chlorides and obtained the following results.

(7) D. E. McGreer, J. Org. Chem., 25, 852 (1960).

(8) J. A. Moore, J. Org. Chem., 20, 1607 (1955).

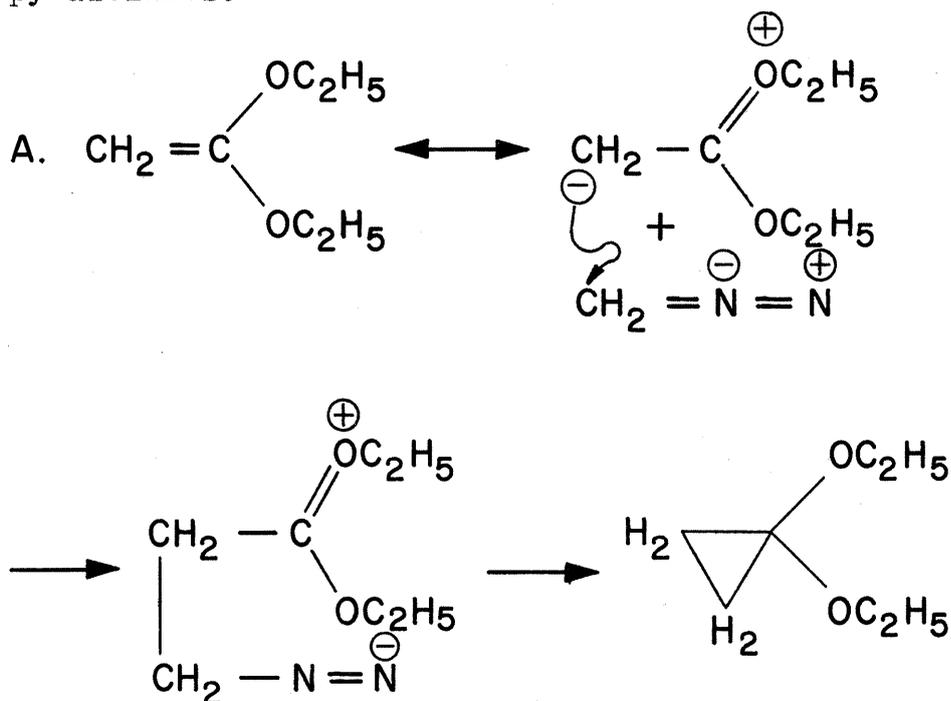


If reactions of diazomethanes with unsaturated molecules are carried out by irradiation with ultraviolet radiation, or in the presence of heavy metals or heavy metal ions, the course of the reaction and the type of products isolated is different.

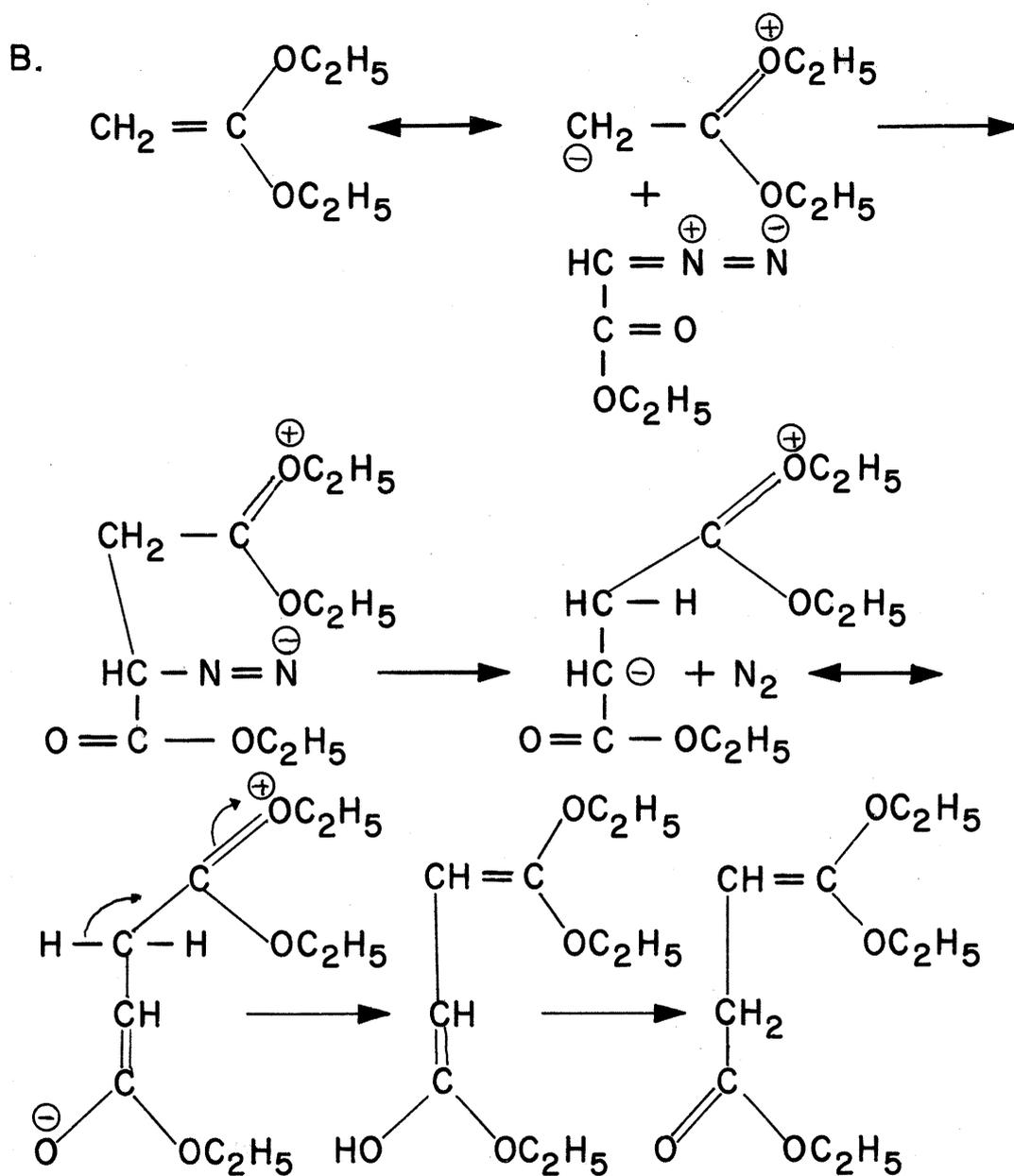
D'yakanov has written many papers on the formation of cyclopropanes by the addition of diazomethanes to double bonds. Of this series one paper is sufficient to demonstrate the point that no pyrazolines are formed. D'yakanov⁹ reacted ethyl diazoacetate with ethyl vinyl ether and obtained ethyl 2-ethoxycyclopropanecarboxylate in good yields without the formation of an isolable pyrazoline.

(9) I. A. D'yakanov *Zhur. Obshchei. Khim.* (J. Gen. Chem.) 21, 893 (1951), ref. cit., (C. A. 45, 7023i).

The work of Dull and Abend¹⁰ is further indication that pyrazolines are not always intermediates in the formation of cyclopropanes. In this work diazomethane and ethyl diazoacetate were reacted with ketene diethylacetal and no evidence of a pyrazoline intermediate was found. In the case with ethyl diazoacetate no cyclopropane derivative was obtained, instead an unsaturated compound was the major product. However, with diazomethane the major product was cyclopropane diethylacetal. The proposed mechanisms do not involve pyrazolines.



(10) M. F. Dull and P. G. Abend, J. Am. Chem. Soc., 81, 2588 (1959).



This second type of mechanism for the addition of diazomethanes to olefins apparently involves the addition of a diradical, either a methylene or a carbene, to the double bond. In the cases previously discussed in which pyrazolines are formed, the reactions are usually carried out with heating or at room temperature, but in the case of the radical addition a catalyst (silver metal, cuprous, or cupric ions) is used, or else the reaction is brought about by irradiation with ultraviolet radiation.

The concept of methylene radicals has been utilized in ever increasing frequency since the late nineteenth century. In 1904 and 1908 Nef tried to explain many types of organic reactions by using intermediates quite similar to the methylene intermediates now proposed.^{11, 12}

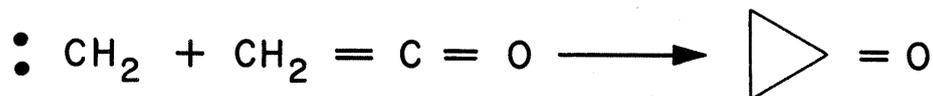
The actual existence of the methylene radical has been demonstrated by several workers utilizing the metallic mirror methods of Paneth. The technique involves decomposition of the parent compound and the removal of the metal mirror by the free radical.

(11) J. U. Nef, J. Am. Chem. Soc., 26, 1549 (1904).

(12) J. U. Nef, J. Am. Chem. Soc., 30, 645 (1908).

This decomposition has been carried out with diazomethane both by thermal and photolytic means. For example, if diazomethane in a stream of ether is decomposed at a temperature of 550° , a tellurium mirror is removed with the formation of telluroformaldehyde polymer, $(\text{HCHTe})_n$.¹³ The half life of the radical was also calculated to be about 5×10^{-3} second.

Other workers have investigated the formation of methylene by photolysis as well as by thermal methods. Pearson¹⁴ and co-workers decomposed ketene by irradiation at $2580\text{--}3130 \text{ \AA}$, and diazomethane by thermal methods and by irradiation at $4200\text{--}4700 \text{ \AA}$. The results of this study agree with those of Rice except that the half life of methylene radicals from the ketene was found to be about ten times greater than that from diazomethane. As an explanation for this difference the reaction



was proposed. The cyclopropanone was assumed to exist

(13) F. O. Rice and A. L. Glazebrook, J. Am. Chem. Soc., 56, 2381 (1934).

(14) T. G. Pearson, R. H. Purcell, and G. S. Saigh, J. Chem. Soc., 409 (1938).

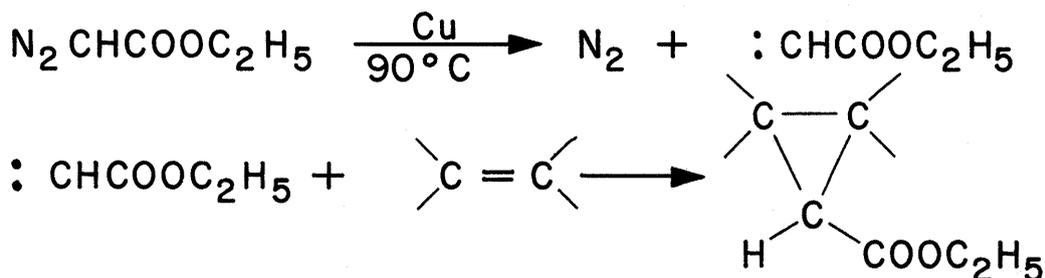
only momentarily, decomposing on contact with the metal mirrors of tellurium and selenium.

Since the proof that methylene radicals could be formed by thermal decomposition or by photolysis, a tremendous amount of work has been done to prove that methylenes exist in solution reactions, and to show the mechanisms by which such reactions take place.¹⁵

It has long been known that diazomethane will slowly decompose at room temperature to yield nitrogen and polymethylene.¹⁶ The early experiments using the metal mirror technique of Paneth had indicated that the methylene radical was the precursor of the polymethylene. It had also been reported that when diazomethane in ethyl ether was irradiated with ultraviolet radiation ethyl propyl ether and ethyl isopropyl ether were formed.¹⁷

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- (15) For studies other than those cited in the following pages the work of P. S. Skell, W. E. von Doering, M. S. Kharasch, and J. Hine may be consulted. A detailed survey of all the works is precluded because of the number of publications.
- (16) E. Baumberger and F. Tschirner, Ber., 33, 956 (1900).
- (17) H. Meerwein, H. Rathjen, and H. Werner, Ber., 75, 1610 (1942).

D'yakonov¹⁸ has made an intensive study of the reactions of diazomethanes and diazoesters with unsaturated compounds. One phase of these experiments involved the addition of ethyl diazoacetate with diazomethane to ethyl vinyl ether. It was reported that ethyl diazoacetate added to ethyl vinyl ether in the presence of copper powder to yield ethyl 2-acetoxycyclopropanecarboxylate, but diazomethane would not add under similar conditions. Also, ethyl diazoacetate added to vinyl acetate to yield ethyl 2-acetoxycyclopropanecarboxylate. D'yakonov proposed the following mechanism for these reactions.



In addition to the above reaction, it was also shown that a portion of the carboethoxycarbene radical dimerized to diethyl fumarate.

(18) I. A. D'yakonov, *Zhur. Obschchei Khim.* (J. Gen. Chem.) 19, 1734 (1949) ref. cit. C. A. 44, 1014a

This paper is one of a series of about thirty papers that were finally compiled in a book on the reactions of diazo compounds with unsaturated compounds.

Kharasch¹⁹ and co-workers made a careful study of the reaction of ethyl diazoacetate with cyclohexanone and with acetone. The cyclopropane derivatives were formed only by secondary reactions, but it is of interest that the mechanisms proposed did involve a carboethoxy-carbene intermediate.

During the period since 1950 much work has been done in efforts to determine the mechanism or mechanisms for these reactions, and to assign orbital structures to the methylenes. Although these studies have not led to a complete elucidation of the problem, some of the pertinent evidence will be presented here.

Doering and co-workers²⁰ studied the reaction of diazomethane with n-pentane, 2,3-dimethylbutane, cyclopentane, and cyclohexene. Dilute solutions of diazomethane in each of the hydrocarbons were irradiated with ultraviolet radiation, and the products and product ratios identified. It was reported that diazomethane yielded methylene radicals that apparently reacted indiscriminately with primary, secondary, and tertiary

(19) M. S. Kharasch, T. Rudy, W. Nudenberg, G. Buchi, J. Org. Chem. 18, 1030 (1953).

(20) W. von E. Doering, R. G. Buttery, R. G. Laughlin, and H. Chardhuri, J. Am. Chem. Soc., 78, 3224 (1956).

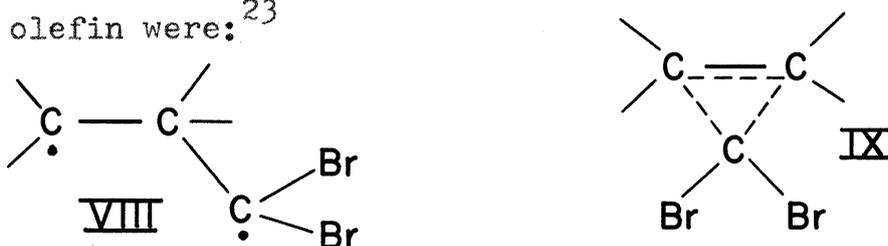
hydrogen atoms to insert a methylene group into the molecule. The hydrogen atoms of cyclohexene were classed as vinylic, allylic, and aliphatic, depending on their relationship with the double bond. Only one of the series of results will be discussed here as it is representative of the rest of the data obtained. n-Pentane has six primary, four secondary hydrogens at the two-positions and two secondary hydrogens at the three-positions. If the methylene radicals reacted in a completely random manner the ratio of products should be n-hexane:2-methylpentane:3-methylpentane 6:4:2(50:33.3:16.2). On analysis of the products of the reaction of diazomethane with n-pentane at -70° and 15° the ratios were 48:35:17 and 49:34:17, respectively. The only exception to the randomness was that norcarane seemed to be slightly preferred over a completely statistical ratio in the reaction with cyclohexene.

However, Frey and Kistiakowsky²¹ reported that methylene radicals produced photochemically from ketene in the gas phase reacted with ethylene, propane, cyclopropane, and n-butane, attacking the secondary hydrogen atoms with a rate about 1.7 times as great for the secondary as for the primary.

(21) H. M. Frey and G. B. Kistiakowsky, J. Am. Chem. Soc., 79, 6373 (1957).

It was also reported that methylene radicals, produced from diazomethane by photochemical means, reacted with in a stereospecific manner was cis- and trans-2-butene in the gas phase.²² At about the same time Skell and Woodward presented evidence that dibromocarbene and methylene radicals reacted with olefins in solution in a completely stereospecific way.^{23, 24}

Skell suggested that the two most likely intermediates for the reaction of dibromocarbene with an olefin were:²³

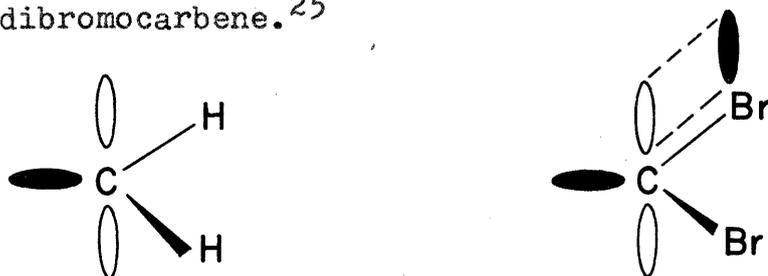


Evidence was presented²⁴ that supported structure IX as the most likely intermediate. The conclusion that IX was the likely intermediate was based on two sets of data. If structure VIII were the intermediate, the relative rates of reaction of dibromocarbene and the monoradical

- (22) W. von E. Doering and P. Laflamme, J. Am. Chem. Soc., 78, 5447 (1954).
- (23) P. S. Skell and R. C. Woodward, J. Am. Chem. Soc., 78, 4496 (1956).
- (24) P. S. Skell and A. Y. Garner, J. Am. Chem. Soc., 78, 5430 (1956).

trichloromethide radical with the same series of olefins should be of the same general order. Rates of the two reactions with a series of olefins were compared and no correlations could be established. Also, if structure VIII were the intermediate, the reaction of dibromocarbene would not be stereospecific as it was found to be.

In the same work it was reported that methylene radicals produced from diazomethane by ultraviolet radiation and carboethoxycarbene from ethyl diazoacetate by copper bronze reacted stereospecifically with olefins. cis-2-Butene produced only cis-dimethylcyclopropane and cis-2-pentene, while trans-2-butene yielded only trans products. On the basis of these results the following orbital structures were assigned to methylene radicals and dibromocarbene.²⁵



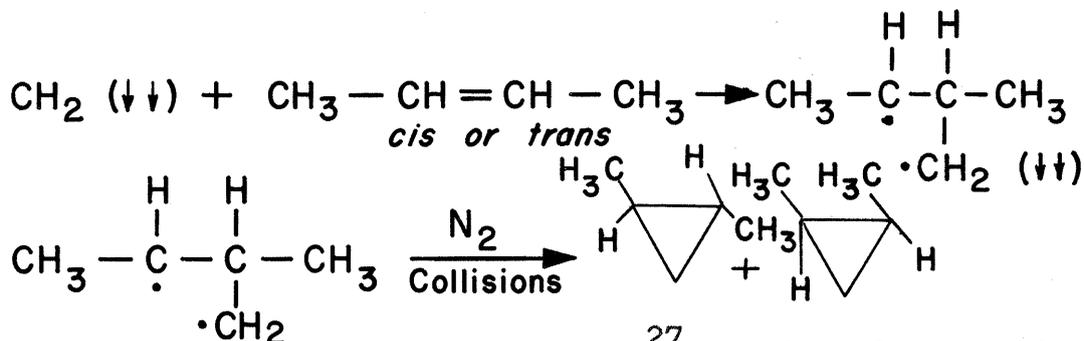
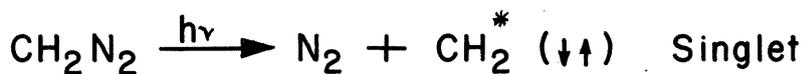
Skell and Etter²⁵ also studied the reaction of carboethoxycarbene with pairs of olefins in competing

(25) P. S. Skell and R. M. Etter, Chem. and Ind. 624 (1958).

reactions. It was found that carboethoxycarbene was much less selective than dibromocarbene, trichloromethide radicals, or bromine radicals. These workers have attempted to formulate orbital pictures to explain this difference in selectivity.

Anet and co-workers²⁶ studied the addition of methylene radicals produced from diazomethane, to olefins at low pressures and in the presence of a large excess of an inert gas. They found that at relatively high partial pressures of the reacting gases the stereospecificity observed by Skell was retained, but that at low partial pressures the results of Doering and LaFlamme were obtained; i.e., the stereospecificity was destroyed. The hypothesis was advanced that the methylene radicals as first formed are in a highly energetic singlet state, but that at low pressures collisions with nitrogen degrade the singlet to the triplet state and that it is this species that produces non-stereospecific results. The postulate of Anet may be summarized:

(26) F. A. L. Anet, R. F. W. Bader, and A. M. Van der Auwera, J. Am. Chem. Soc., 82, 3217 (1960).



Richardson and co-workers²⁷ studied the reaction

of methylene with alkanes both in solution and in the gas phase. It was found that in the solution the methylene reacted indiscriminately with primary, secondary and tertiary hydrogen atoms, but that in the gas phase in a nitrogen atmosphere the attack is preferentially on a secondary hydrogen atom. These results are rationalized using spectral evidence for the singlet and triplet states in methylene radicals obtained by Herzberg.²⁸

The assumption was made that the highly energetic singlet state is the first species formed in solution or gas phase. In solution it is this species

(27) D. B. Richardson, M. C. Simmons, and J. Dvoretzky, J. Am. Chem. Soc., **82**, 5001 (1960).

(28) G. Herzberg, and J. Shoosmith, Nature, **183**, 1801 (1959).

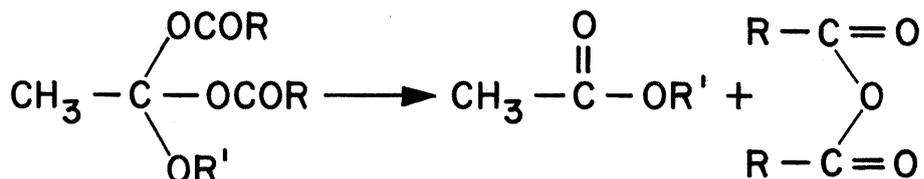
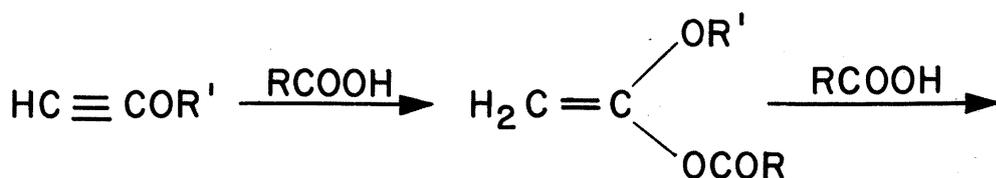
that causes the random attack, because the rate of transition of singlet to triplet is assumed to be less than the rate of random insertion giving rise to the random products. However, in the gas phase there are fewer collisions with the alkane and there is sufficient time for collisions with the inert gas to degrade the singlet to the triplet state, or at least the rate of transition becomes as great or greater than that of insertion. The triplet state species then can abstract a proton to yield methyl radical and an alkyl radical. Since secondary alkyl radicals are more stable than the primary radical this mechanism would then give preferential attack on the secondary hydrogen atoms. Experimental evidence to support this supposition was found in the fact that at low pressures the stereospecificity of addition to olefins is lost and that increasing the relative amount of nitrogen increases the amount of triplet products formed.

In addition to the reactions of diazomethanes, the reactions of alkoxyacetylenes must be included as pertinent to this discussion. Ethoxyacetylene has been

prepared^{29, 30, 31} and its reactions studied.^{32, 33}

Arens and co-workers³⁴ found that alkoxyacetylenes reacted with carboxylic acids to yield acid anhydrides and esters of acetic acid. A mechanism was proposed and unsuccessful attempts were made to isolate the proposed intermediate 1-alkoxyvinyl esters. In particular, the attempt to isolate 1-ethoxyvinyl acetate from the reaction of ethoxyacetylene and acetic acid failed.

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- (29) H. Dykstra, J. F. Lewis, and C. E. Boord, J. Am. Chem. Soc., 52, 3401 (1930).
- (30) T. Jacobs, R. Cramer, and J. E. Hanson, J. Am. Chem. Soc., 64, 223 (1942).
- (31) R. H. Jones, G. Eglinton, M. C. Whiting, and B. L. Shaw, Org. Syn. Vol. 34, p. 16
- (32) R. H. Jones, G. Eglinton, M. C. Whiting, and B. L. Shaw, J. Chem. Soc. 1860 (1954).
- (33) J. F. Arens and P. Modderman, Koninkl Ned. Adad. Wetenshep, 53, 1163 (1950) ref. cit., C. A. 45, 6152 (1951).
- (34) J. F. Arens and H. C. Volger, Rec. Trav. Chem., 77, 1174 (1958).



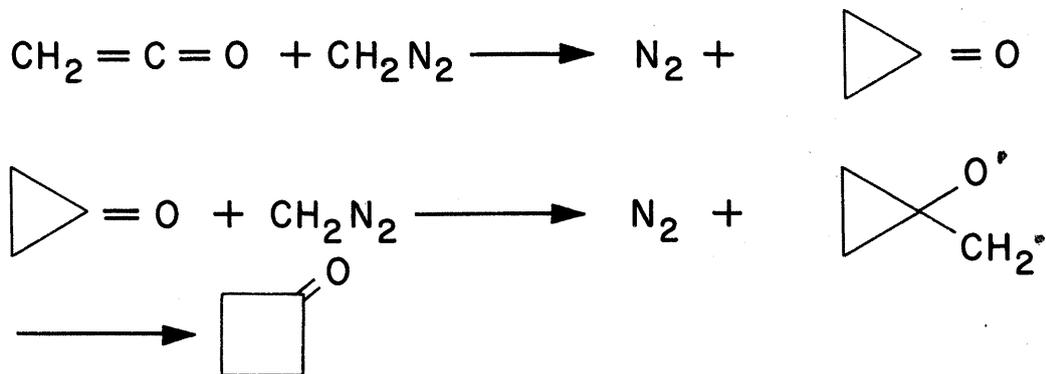
Wasserman and Wharton prepared methoxyacetylene and from this compound they prepared l-methoxyvinyl acetate.³⁵ Wasserman and Garner prepared l-ethoxyvinyl acetate from the reaction of ethoxyacetylene and acetic acid in the presence of mercuric salts.³⁶

The studies in the synthesis of small ring compounds by Roberts have not been considered previously and should be included. The reaction of ketene with diazomethane yields cyclobutanone as the major product. It was suggested by Roberts that the reaction involved a

(35) H. H. Wasserman and P. S. Wharton, J. Am. Chem. Soc., 82, 661 (1960).

(36) H. H. Wasserman and R. H. Garner, unpublished work on alkoxyacetylenes at Yale University.

cyclopropanone intermediate.³⁷ The mechanism proposed was:



The reaction was run with diazomethane prepared from carbon-14 and the resulting cyclobutanone was degraded and the percentage of carbon-14 appearing at the four positions determined. The results indicated that cyclopropanone was probably an intermediate.

The work of Dull and Abend,³⁸ and Roberts and co-workers, in which cyclopropanone intermediates and derivatives are discussed, in conjunction with the works of Wasserman cited above, provided the idea for the experiments described in this thesis.

(37) D. A. Semenov, E. G. Cox and J. D. Roberts, J. Am. Chem. Soc., 78, 3221 (1956).

(38) M. F. Dull and P. G. Abend, loc. cit.

CHAPTER III

EXPERIMENTAL

I. Preparation of Ethoxyacetylene

To 1575 ml. of dry petroleum ether (b.p. 30-60°) in a five-liter flask was added 241 g. (3.57 moles) of ethyl vinyl ether (Eastman Yellow Label). The flask was equipped with a paddle stirrer, addition funnel, and a condenser fitted with a drying tube. The solution of ethyl vinyl ether was cooled to - 40°, and maintained at that temperature with a dry ice-acetone bath.

To the cold solution 530 g. (3.31 moles) of bromine (Reagent grade) was added over a period of 45-60 minutes. As soon as addition of the bromine was complete, 637 g. (6.25 moles) of triethylamine (Eastman Yellow Label) was added. At this time the triethylamine hydrobromide began to precipitate. The flask was then removed to a steam bath and refluxed until the lachrymatory evidence of the dibromide disappeared (about sixteen hours). The solution was filtered with suction

and the precipitate was washed with petroleum ether. The washings and filtrate were combined and the solvent was distilled at atmospheric pressure. The pressure was then reduced to 35 mm. and the beta-bromoethoxyethylene distilled at 48-52°. There was obtained 300 g. of crude bromide, n_D^{25} 1.4680, for a yield of 59%. In other preparations the yield varied from the 59% up to 76%.

A one-liter flask, equipped with a 24-inch Vigreux column and a distilling head leading to a water condenser, was charged with 245 g. (4.37 moles) of powdered potassium hydroxide (Reagent grade). To the potassium hydroxide, 300 g. (1.96 moles) of beta-bromoethoxyethylene was added. The mixture was heated with a Glass-Col mantle until the first visible sign of reaction. At this point heating was discontinued until the initial vigorous reaction had ceased (usually 5-15 minutes). (It is recommended that this reaction be run behind a shield as some alkoxyacetylenes have been known to polymerize explosively.) After the initial reaction subsided, heating was continued and the product distilled at 48-50° at atmospheric pressure. At times during the distillation the temperature rose rather rapidly to about 75°, presumably due to water. The product was dried over potassium hydroxide pellets and redistilled. A yield of 91.9 g. (67%) was obtained. The ethoxyacetylene was

relatively stable and could be stored in a refrigerator for 7-10 days without appreciable decomposition. It was redistilled before use.³⁹

II. Preparation of 1-Ethoxyvinyl Acetate⁴⁰

About 2 g. (0.0006 mole) of mercuric acetate was suspended in 540 ml. of methylene chloride in a one-liter two-neck flask equipped with an addition funnel. The other neck held a condenser fitted with a drying tube to serve as a safety valve. To this suspension 90 g. (1.28 moles) of ethoxyacetylene was added.

The resulting pale yellow solution was cooled in an ice-salt water bath and stirred with a magnetic stirring bar. Then 45 g. (0.75 mole) of acetic acid in 60 ml. of methylene chloride was added slowly (at least 30 minutes for complete addition). As soon as addition was complete the flask was stoppered, equipped with a 24-inch Vigreux column, and the solvent and excess ethoxyacetylene were removed at atmospheric pressure. The pressure was then reduced to 25 mm. The product,

(39) When the ethoxyacetylene was redistilled after storage a small residue of tar remained.

(40) This is a variation of the procedures of Wasserman and Wharton, loc. cit.

b.p. 63-64°, n_D^{25} 1.4148, weighed 77 g. (0.59 mole) for a yield of 79%.

III. Preparation of Ethyl Diazoacetate⁴¹

Ethyl diazoacetate was prepared by the method of Womack and Nelson and the solvent was then removed under reduced pressure.

IV. Reaction of l-Ethoxyvinyl Acetate with Ethyl Diazoacetate

Ten grams (0.077 mole) of l-ethoxyvinyl acetate was placed in a 300-ml. three-neck flask equipped with a by-pass addition funnel and a reflux condenser from which a delivery tube led to a graduated cylinder inverted in water. The delivery tube also contained a drying tube. The third neck of the flask was only stoppered to serve as a safety valve. A suspension of 0.25 g. of cuprous bromide in the l-ethoxyvinyl acetate was stirred with a magnetic stirrer and about 14 g. (0.1 mole) of ethyl diazoacetate was added in small portions, while the flask was heated with a flood lamp.

After a short induction period of about 15 to 30 minutes evolution of nitrogen began and continued

(41) E. B. Womack and A. B. Nelson, "Org. Syn., Coll. Vol. III," p.392.

smoothly⁴² until a volume of about 2400 ml. of nitrogen had been evolved.

The reaction mixture was distilled at 25 mm. pressure. About 5 g. (0.05 mole) of 1-ethoxyvinyl acetate was recovered.

All material boiling from 100-135° was collected and redistilled through a Podbielniak Whirling Heli-Band Mini-Cal. column. The major portion of this material was collected as a 6.5-g. (40% yield) fraction, b.p. 107-109° (25 mm.), n_D^{25} 1.4260, d_{25}^{25} 1.0392, M_r (calcd. for ethyl 2-acetoxy-2-ethoxycyclopropanecarboxylate 51.84, M_r (obsvd.) 53.31, apparent exaltation, 1.47⁴³, molecular weight (calcd. for $C_{10}H_{16}O_5$) 216.2, molecular weight (cryoscopically in nitrobenzene) 190⁴⁴, saponification equivalent, 111. The compound ethyl 2-acetoxy-2-ethoxycyclopropanecarboxylate has not been reported in

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- (42) In one preparation the temperature was allowed to go too high and the reaction went out of control. Evolution of nitrogen was so rapid that the condenser etc. were blown out of the flask. The vapors did not detonate.
- (43) V. A. Slabey, J. Am. Chem. Soc., 76, 3603-4 (1954). Molar refraction of cyclopropanes. Exaltation reported from 0.71 to 1.3 for cyclopropanes.
- (44) M. F. Dull and P. G. Abend, loc. cit. For a cyclopropane of M.W. 206, a result of 234 was obtained in nitrobenzene.

the literature.

Anal.⁴⁵ Calcd. for $C_{10}H_{16}O_5$: C, 55.54%; H, 7.46%. Found: C, 55.44%; H, 7.63%.

This material did not decolorize a carbon tetrachloride solution of bromine even on standing, and decolorized potassium permanganate solution only slowly. The infrared spectrum of this material is discussed later in this thesis. One sample of this material was subjected to vapor phase chromatography by passage through a Perkin-Elmer vapor fractometer. The packing material of the column used was not known. The chromatograph showed two major peaks of areas in the approximate ratio 3:1. Other small peaks accounted for less than 5% of the material. This experiment was repeated on another sample using a Beckman GC-2 Gas Chromatograph fitted with a Beckman 74346 (Silicone) Column, at a column temperature of 190°. In this case the material trailed through the column without showing any distinct peaks.

A small amount of material, b.p. 124-126° (25 mm.) was collected from the distillation of the

(45) E. Thommen, Thannestrasse 45, Basel, Switzerland Sample J-2.

products of the reaction of ethyl diazoacetate with 1-ethoxyvinyl acetate. The infrared spectrum of this material was consistent with that reported for diethyl fumarate.⁴⁶ Diethyl fumarate has been reported as a by-product of other reactions involving ethyl diazoacetate.⁴⁷

V. Preparation of Diazomethane

Diazomethane was prepared by three methods:

(1) from "Diazald"⁴⁸ (N-methyl-N-nitroso-para-toluenesulfonamide) as directed by the manufacturer; (2) by the action of potassium hydroxide on N-methyl-N-nitroso-para-toluenesulfonamide as given in Organic Syntheses^{49, 50}; and (3) from N-methylnitrosourea as described in Organic Syntheses.⁵¹

- (46) D. G. I. Felton and S. F. D. Orr, J. Chem. Soc., 2170 (1955).
- (47) I. A. D'yakonov, Zhur. Obschchei Khim (J. Gen. Chem.), 19, 1734 (1949) ref. cit. C. A., 44, 1014a.
- (48) Aldrich Chemical Company, Inc., 2369 N. 29th Street, Milwaukee 10, Wis.
- (49) J. Deboer and H. J. Black, "Org. Syn." 34, p. 96 (1954).
- (50) The N-methyl-N-nitroso-para-toluenesulfonamide was prepared in one case by Fred Williams of the School of Chemistry, University of Alabama.
- (51) F. Arndt, "Org. Syn. Coll. Vol. II," p. 165 (1943).

VI. Attempted Reactions of Diazomethane
with 1-Ethoxyvinyl Acetate

A. Ten grams (0.077 mole) of 1-ethoxyvinyl acetate was placed in a 250-ml. three-necked flask equipped as described in the reaction of ethyl diazoacetate. About 0.25 g. of cuprous bromide was suspended in the 1-ethoxyvinyl acetate, and the mixture was stirred with a magnetic stirrer.

To this suspension about 4 g. (0.09 mole) of diazomethane in 150 ml. of ether was added. This diazomethane was prepared from N-methyl-N-nitroso-para-toluenesulfonamide and was not free of ethanol.

The addition took place while the flask was heated by a flood lamp. Nitrogen evolution began almost immediately and proceeded smoothly as long as the diazomethane was added. The volume of nitrogen evolved was as calculated for the decomposition of the 4 g. of diazomethane. The starting material was recovered unreacted. The only other product was polymethylene.

B. The diazomethane for this reaction was prepared from "Diazald". This reaction was identical with that above except that the diazomethane solution was prepared in such a way as to be free of ethanol. The starting material was again recovered unreacted.

In addition, the volume of gas liberated in this case was greater than the calculated amount indicating that some ethene may have been formed from the diazomethane.

C. The diazomethane solution for this reaction was prepared ethanol-free by the method used in B. The same weights of reagents were used. The only variation was that the 1-ethoxyvinyl acetate and diazomethane were mixed and then added to the catalyst suspended in a little ether. Results were the same, and again some ethene seemed to have been formed.

D. A pentane solution of diazomethane was prepared from N-methylnitrosourea and also in this case the weight of 1-ethoxyvinyl acetate was changed to 15.6 g. (0.11 mole) so that an excess of the assumed less reactive reagent would be present. In this case not all the starting material was recovered. About 2 g. had reacted but the only product other than the polymer was a tar that resisted distillation even when heated to 180-190° at a pressure of 3 mm.⁵²

(52) In all cases there was a small amount of this tar if the polymer was filtered, but in the reaction in paragraph D there was much more of it than in the other three cases. No product could be extracted from this tar.

VII. Preparation of Diphenyldiazomethane

Diphenyldiazomethane was prepared by the method of Smith and Howard.⁵³ One change was made in that the compound was prepared in two ways: one exactly as described, and another in which pentane was used as solvent.

VIII. Reaction of 1-Ethoxyvinyl Acetate and Diphenyldiazomethane

In a 500-ml. three-necked flask, equipped as previously described, 8 g. (0.06 mole) of 1-ethoxyvinyl acetate was dissolved in 50 ml. of petroleum ether and to this solution was added 0.25 g. of cuprous bromide. To this solution, a solution of diphenyldiazomethane in petroleum ether was added in small portions. The reaction mixture was heated with a flood lamp.

Evolution of nitrogen began within a few minutes of the start of the addition and continued until 900 ml. of nitrogen was obtained (about one-half the expected amount). At this time the solution was still red in color indicating an excess of the diazo compound.

During the evolution of nitrogen a white solid separated. When it was apparent that no more nitrogen

(53) L. I. Smith and K. L. Howard, "Org. Syn., Coll. Vol. III," p. 351.

would be evolved, the reaction mixture was filtered. The white crystals, recrystallized from ethanol, had m.p. 162-163^o, and were identified as benzophenone azine on the basis of melting point and infrared spectrum.

At the end of one day orange crystals had formed in the reaction mixture. They were recrystallized from ethanol and had a m.p. of 175-176^o. An insufficient quantity was obtained for complete characterization although the infrared spectrum was run. The spectrum showed no carbonyl absorption bands. No conclusion was reached as to the identity of this compound.

At the end of three weeks at room temperature the red color of the diazo compound had completely disappeared and upon evaporation of the solvent, a viscous oil was obtained. When this oil was diluted with methanol a white crystalline product was obtained. Recrystallization from ethanol yielded white crystals, m.p. 225-226^o. This compound was identified as tetraphenylethylene on the basis of melting point and infrared spectrum. No starting material was recovered, but some was assumed to remain in the residue after all crystalline products were removed. Yields were not calculated since all the isolated products seemed to have been formed only from the diazo compound and not

the 1-ethoxyvinyl acetate.

IX. Hydrolysis of Ethyl
2-Acetoxy-2-Ethoxycyclopropanecarboxylate

Two hydrolyses were attempted in 10% potassium hydroxide and in a solution containing base and compound in the ratio 3:1. In both cases no crystalline products were obtained. Mostly tars and decomposition products were obtained. There was obtained a small amount (too small for recrystallization) of a white-brown solid which partially melted and partially decomposed from 180-190°. The hydrolysis was also attempted with sodium carbonate in the hope that milder conditions would yield a crystalline product, but the results were the same.

X. Acid Hydrolysis of Diethyl Fumarate

A small amount of the highest boiling fraction, boiling range 124-126° (25 mm.), obtained from the reaction products of ethyl diazoacetate with 1-ethoxyvinyl acetate and thought to be diethyl fumarate, was hydrolysed in concentrated hydrochloric acid. The white solid that separated had m.p. 289° (sealed capillary), and did not depress the melting point of authentic fumaric acid, m.p. 287° (sealed capillary). When the supposed cyclopropane derivative was subjected to the same treatment no fumaric acid was obtained.

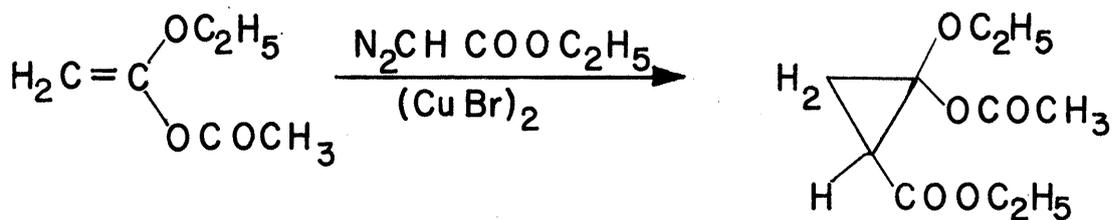
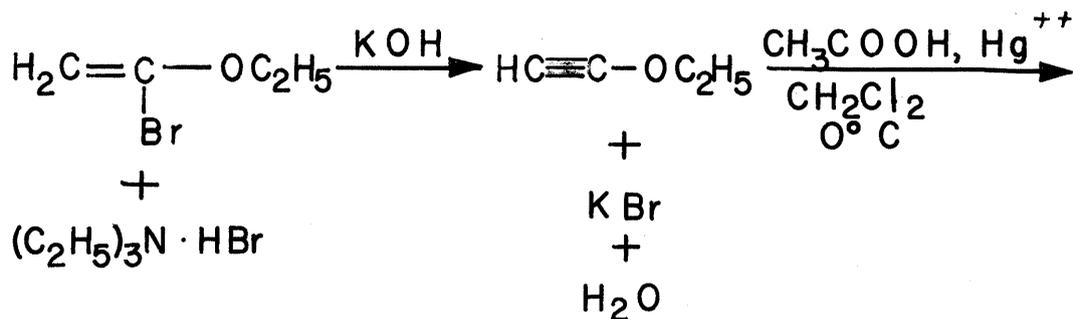
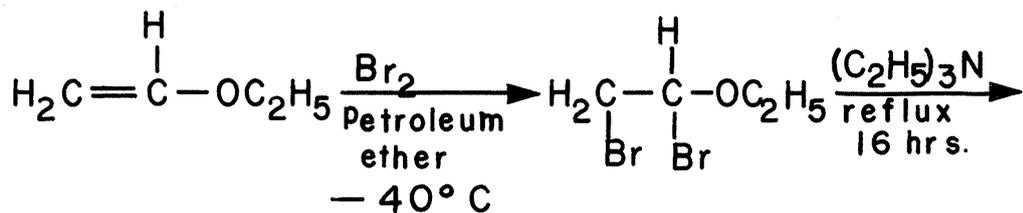
XI. Acid Hydrolysis of Ethyl
2-Acetoxy-2-Ethoxycyclopropanecarboxylate

One gram of the compound was dissolved in 10 ml. of concentrated hydrochloric acid and heated under a nitrogen atmosphere for a period of two hours. The major portion of the product was a brown polymer, a very hard material that adhered to the walls of the flask. No succinic acid was obtained.

CHAPTER IV

DISCUSSION OF RESULTS

The reactions utilized in this work and the products are:



X

XI

Both X and XI are compounds which have not been reported in the literature, although X was prepared by Wasserman and Garner.⁵⁴

No derivatives of compound XI were prepared for identification purposes since all derivatives would represent new compounds, and the complex nature of the material would make the course of any reaction somewhat unpredictable.

It is usually appropriate to hydrolyze esters of cyclopropanecarboxylic acids to the free acid by base, followed by neutralization of the sodium salt to the free derivative. However, since XI is the acetate of the hemiacetal of a cyclopropanone it would seem logical to expect not the cyclopropanecarboxylic acid, but succinic acid as the product of base hydrolysis.

Basic hydrolysis of XI was attempted, but even under a nitrogen atmosphere the majority of the reaction mixture was tars and highly colored material that could not be purified. In one instance a small amount of a water soluble acidic material was obtained, but the quantity of the material was insufficient for recrystallization. This impure substance partially melted and partially decomposed in the temperature range 180-190°.

(54) H. H. Wasserman and R. H. Garner, loc. cit.

Acid hydrolysis of XI would also be expected to produce succinic acid. Acid hydrolysis of the compound was carried out as previously described under a nitrogen atmosphere. The only product was a dark brown polymer. No succinic acid was obtained.

The possibility that compound XI might be only diethyl fumarate was considered. In this connection compound XI was compared with the higher boiling fraction, boiling range 124-126° (25 mm.), obtained from the same reaction. The infrared spectrum of this material was distinctly different from that of compound XI, and was consistent with the reported spectrum of diethyl fumarate.⁵⁵ From the hydrolysis of the high boiling fraction fumaric acid was obtained. On the basis of the spectrum and different behavior on hydrolysis the possibility that XI might be diethyl fumarate was discarded.

The molecular weight of XI was determined cryoscopically in nitrobenzene and was found to be 190. The calculated value is 216.

The infrared spectrum is the major evidence used to decide the structure of XI, and is discussed in detail in the last section of this thesis.

(55) D. G. I. Felton and S. F. D. Orr, loc. cit.

In addition to the physical properties already given, compound XI has one very striking property. When dissolved in benzene (0.005 mole/20 gm. benzene) the resulting solution is very highly luminescent. It was compared with a solution of 2,5-diphenyloxazole of approximately equal concentration. The luminescence is much more intense with XI than with the 2,5-diphenyloxazole. This property was accidentally noticed and no further experimental work was done in connection with this observation. It would seem that this phenomenon would merit further investigation.

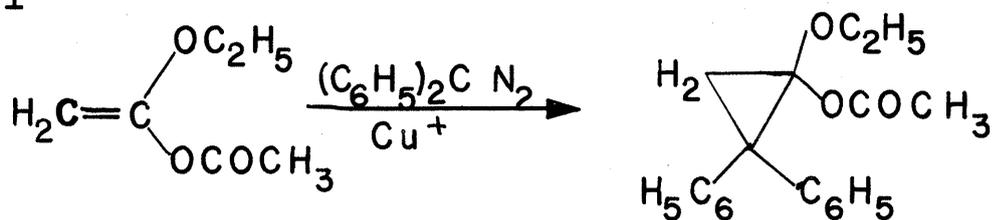
On the basis of the elemental analysis, infrared spectrum, molecular weight, and comparison with diethyl fumarate it is concluded, although not unequivocally, that compound XI is ethyl 2-acetoxy-2-ethoxycyclopropanecarboxylate.

There exists the possibility of cis and trans isomers of the compound, but other than vapor phase chromatography no attempt was made to separate or distinguish between the isomers. One vapor phase chromatograph was made of a sample of ethyl 2-acetoxy-2-ethoxycyclopropanecarboxylate of doubtful purity. The chromatograph had two major peaks with areas in the ratio of 3:1. The two peaks might have represented the cis and trans isomers of ethyl 2-acetoxy-2-ethoxycyclopropanecarboxylate, or the smaller peak might have been

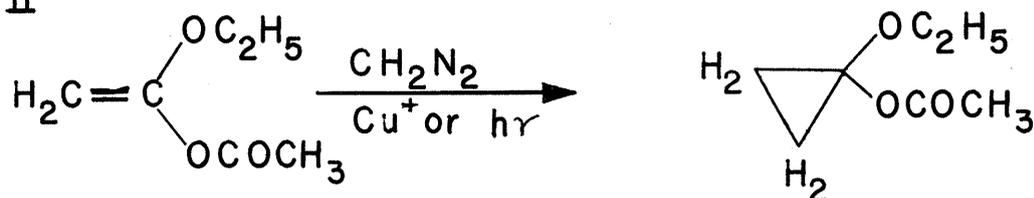
caused by an impurity, probably diethyl fumarate.

Originally three reactions were planned for l-ethoxyvinylacetate with diazomethanes. In addition to the reaction already discussed the following reactions were planned:

I



II



Neither reaction gave any cyclopropane derivative that could be isolated. The two reactions were attempted under varying conditions as was described previously.

In the case of reaction I the volume of nitrogen evolved during normal reaction time (i.e. 1-1.5 hr.) was usually about one-half the calculated amount, and the solution retained the red color of diphenyldiazomethane for a period of approximately two weeks. From this reaction three products were obtained. Two of the three compounds were thought to be benzophenone azine and tetraphenylethylene on the basis of infrared spectra and

melting point. The third product, obtained in very small yield, remained unidentified. The spectrum of this compound does not conform to any rational product arising from 1-ethoxyvinyl acetate.

Diazomethane could not be reacted with 1-ethoxyvinyl acetate under any conditions tried. The reaction was attempted at temperatures for -40° to 40° , in different solvents, and the presence of ultraviolet radiation. This is surprising, but there have been previous cases reported in which diazomethane failed to yield cyclopropane derivatives with olefins, but the corresponding reaction with ethyl diazoacetate was successful.⁵⁶ In all cases only starting material and polymethylene were obtained. In one case a small quantity of tar was obtained.

(56) I. A. D'yakonov, loc. cit.

CHAPTER V

INTERPRETATION OF INFRARED SPECTRA

All spectra were run on a Beckmann I-R7 Infrared Spectrophotometer. The instrument settings were: speed, 200 $\text{cm}^{-1}/\text{min.}$; gain, 2%; period, 2; slit schedule, "select"; ordinate scale, 0-100. The cell thickness in all cases was 0.09 mm. All but one of the spectra were run in solution in carbon tetrachloride.⁵⁷ The solutions were all made in concentrations of 10% by volume. A wedge reference cell filled with the same solvent was first balanced against pure solvent, and then the spectrum of the sample was run.

This discussion will be confined in the most part to the strong bands of the spectrum. In some cases it is necessary to include medium strength bands.

Unless otherwise indicated the basis for assignment of a particular frequency to a specific

(57) For the one spectrum run in the solid state, and for one not included in this thesis I am grateful to Mr. M. Thorpe of Southern Research Institute, Birmingham, Alabama.

vibration is based on information given by Bellamy.⁵⁸

I. The Spectrum of Ethyl Vinyl Ether

The spectrum of redistilled ethyl vinyl ether was run. It is to be expected that a compound containing a carbon-carbon double bond will exhibit an absorption at 1410-1420 cm^{-1} , or at least most double bonds exhibit this band. The carbon-carbon double bond band in this compound is displaced to 1389 cm^{-1} . This spectrum was included to show that the products arising from ethyl vinyl ether will not necessarily show absorption at 1410-1420 cm^{-1} frequency.

II. The Spectrum of Ethoxyacetylene

The band at 3340 cm^{-1} is attributed to the acetylenic carbon-hydrogen stretching vibration. The three bands at 3000, 2950, and 2910 cm^{-1} are assigned to the carbon-hydrogen vibrations at a saturated carbon. These three bands appear throughout the series and will be omitted in further discussion unless thought significant.

The strong band at 2165 cm^{-1} is assigned to the carbon-carbon triple bond stretching vibration for a

(58) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," (Second Edition), John Wiley & Sons, New York. 1958.

mono-substituted alkyne. This value is slightly higher than the usual frequency, but, when considered with the remainder of the spectrum, would seem a valid assignment.

The strong bands at 1105 and 1245 cm^{-1} are assigned to the carbon-oxygen stretching vibrations of the ether linkage. The combination of bands for acetylenic linkage and ether bonding are the only bands in this spectrum that are discussed.

III. The Spectrum of 1-Ethoxyvinyl Acetate

If Spectrum II and this one are compared it will be seen that the two acetylenic bands at 3340 and 2165 cm^{-1} have been completely eliminated from the spectrum, indicating that the triple bond is no longer present in the molecule.

As additional evidence of the structure of this compound, the strong band at 1787 cm^{-1} , which was completely absent in Spectrum II, may be assigned to the carbonyl stretching vibration of a vinyl ester. The band is within the expected range for a compound of this type.

The strong band at 1685 cm^{-1} is important for two reasons. First, it is within the range for the carbon-carbon double bond stretching vibration. In addition, the fact that this band is relatively strong indicates that it arises from a molecule of the type

$RR_1C=CH_2$. 1-Ethoxyvinyl acetate is a compound of this type.

The strong band at 1373 cm^{-1} is attributed to the methylene in plane deformation. If a standard reference on infrared spectra is consulted this vibration is assigned the frequency $1410\text{-}1420\text{ cm}^{-1}$. However, there was not a band at the frequency $1410\text{-}1420\text{ cm}^{-1}$ in ethyl vinyl ether, but a band was present at 1375 cm^{-1} (see Spectrum I).

The two bands, both very strong, at 1275 and 1195 cm^{-1} are considered to be the carbon-oxygen vibrations shifted to higher frequencies than in Spectra I or II.

There is one more band in this spectrum that may be of importance. The medium strength band at 887 cm^{-1} has been assigned to hydrogen out of plane deformation as is found in asymmetric disubstituted ethylenes.

In summary, the infrared spectrum of this compound differs from that of ethoxyacetylene in that the acetylenic bands have disappeared and the characteristic bands for an asymmetric disubstituted olefin have appeared. The ether bands of ethoxyacetylene have remained but have shifted in frequency, while the characteristic band for a vinyl ester has appeared.

IV. The Spectrum of Ethyl
2-Acetoxy-2-Ethoxycyclopropanecarboxylate

The bands of this spectrum are not sharp, but no explanation for this fact can be given since the spectrum was run in the same manner as the previous ones and the material used was pure enough for analysis to be correct. In spite of the weakness of the bands it seems that correlation of spectrum and structure may be attempted, especially in view of the analysis and properties.

There are only two bands in the infrared spectrum that may be assigned to the cyclopropane ring and they sometimes appear in compounds that do not contain the ring. Slabey and others^{59, 60} have reported that in a series of cyclopropanes a band occurs in the range 1048-1017 cm^{-1} , and that the C-H frequencies are usually shifted to the range 3010-3020 cm^{-1} . In this spectrum the C-H frequency is shifted to about 3015 cm^{-1} . Since the band is much weaker and the three bands have blurred, the only comment possible is that the frequency has been shifted to slightly higher wave numbers.

The carbonyl frequency has been reduced to 1765 cm^{-1} , but this is still within the range to be

(59) V. A. Slabey, J. Am. Chem. Soc., 76, 3604 (1954).

(60) J. D. Bartleson, R. E. Buck, H. P. Lankelma, J. Am. Chem. Soc., 68, 2513 (1946).

expected for an ester carbonyl. It would be expected that the frequency be lower since vinyl esters usually have higher frequencies than those of normal esters.

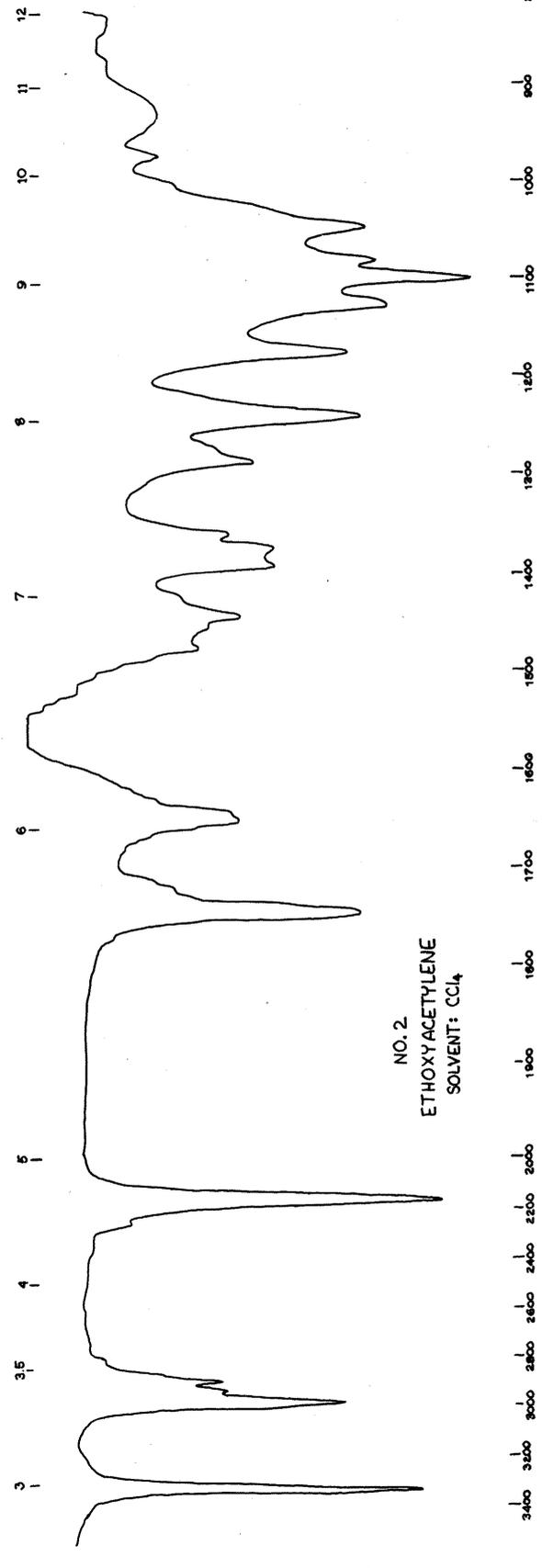
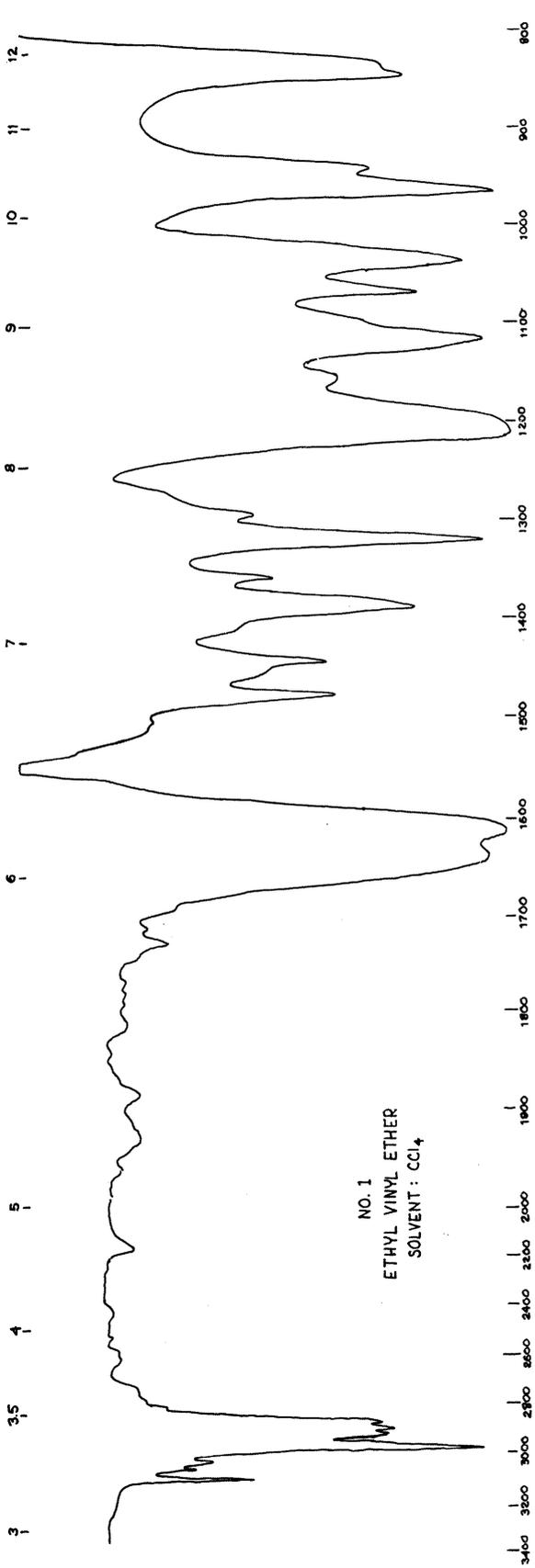
The most important feature of the spectrum involves the absence of three bands. The bands at 1685, 1373, and 887 cm^{-1} have disappeared from the spectrum. Since these bands were attributed to the double bond of the preceding compound their absence in this spectrum indicates that the double bond has been eliminated from the compound. This fact also eliminates the possibility that the compound could have been diethyl fumarate.

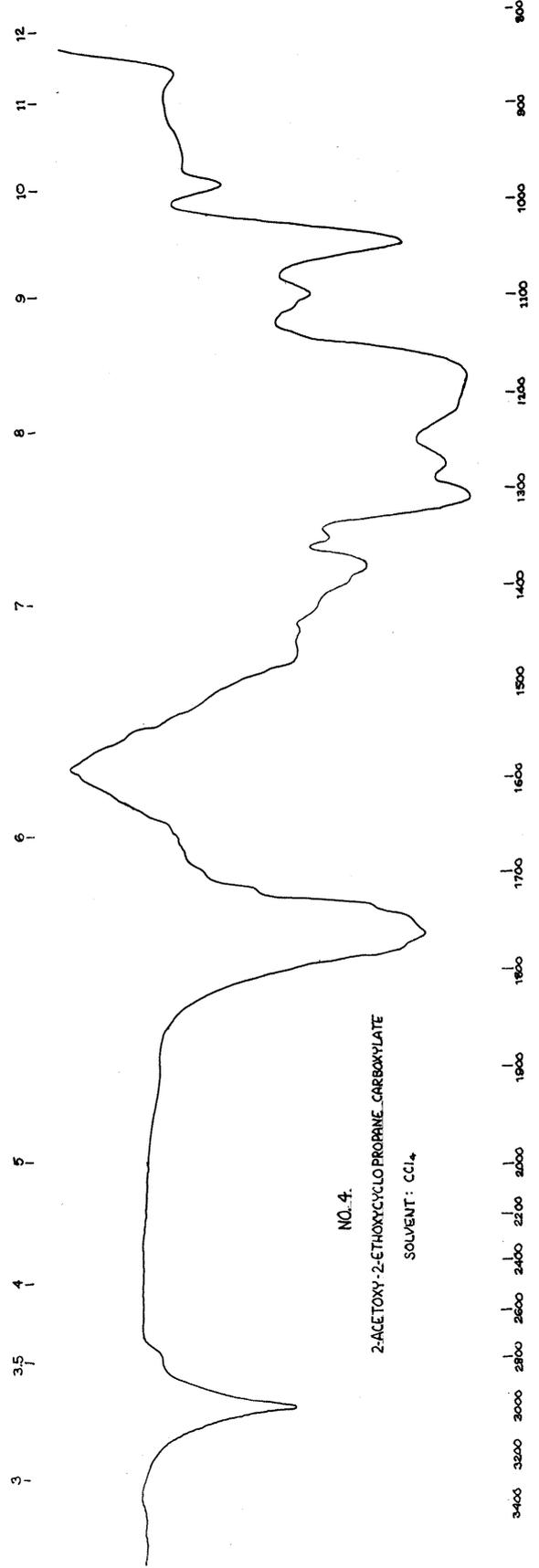
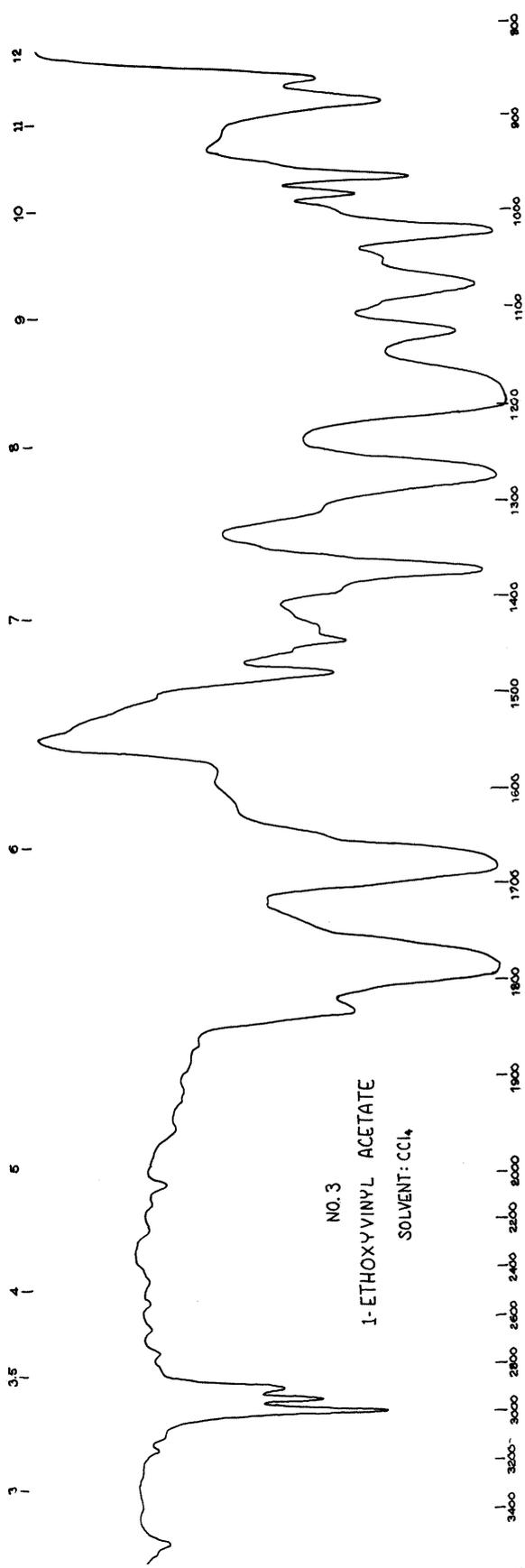
The region of the ether bands in this spectrum is blurred though there are indications of the ether absorptions in the 1100-1200 cm^{-1} range. Possibly the wide absorption is due to the addition of a third carbonyl group to the molecule.

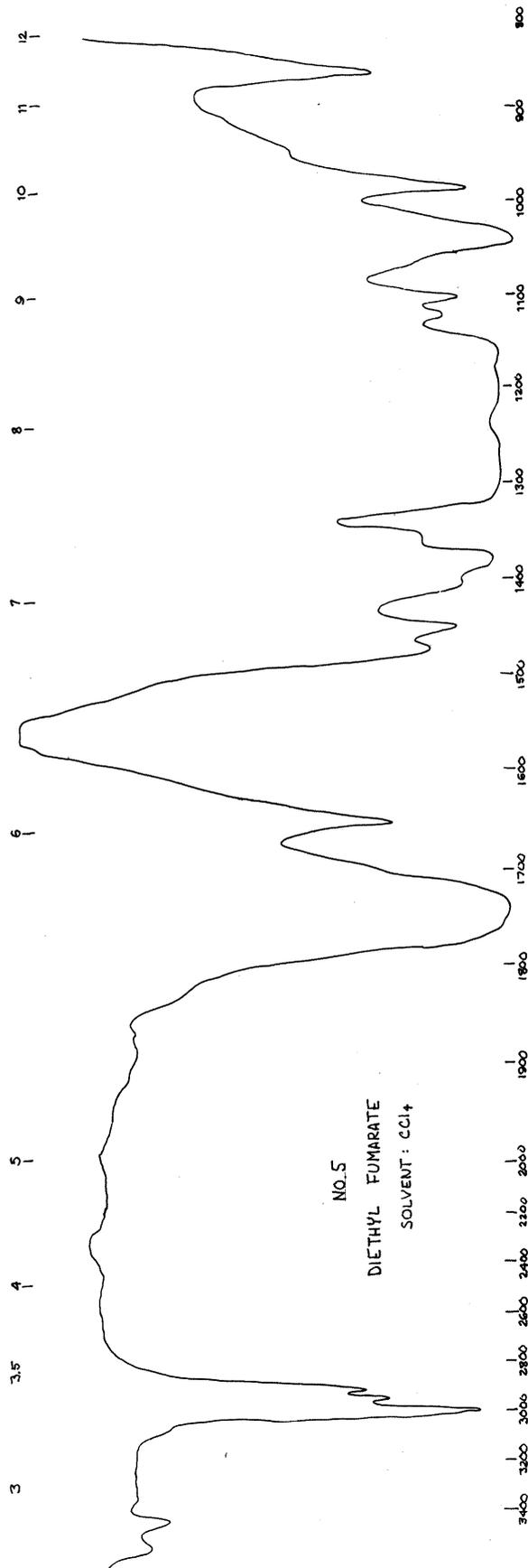
There remains one significant feature of this spectrum and that is the appearance of a band at 1047 cm^{-1} . This band has not appeared in the spectra discussed before and is medium strength when compared with the other bands of the spectrum.

The appearance of the band at 1047 cm^{-1} , the shift of the carbon-hydrogen stretching frequency to 2015 cm^{-1} in combination with the removal of the double bond absorptions, and the broadening of the carbonyl

frequency argue for the addition of ethyl diazo acetate to the double bond of 1-ethoxyvinyl acetate and support the structure ethyl 2-acetoxy-2-ethoxycyclopropanecarboxylate.







NO. 5
DIETHYL FUMARATE
SOLVENT: CCl₄

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