out for 63 hours, and processed as described for II (part B). The neutral fraction weighed 55 g.; the acidic fraction weighed 2 g. and was discarded.

The neutral fraction was chromatographed using 750 g. of activated silica gel in a column of dimensions 2 × 20 inches. Four major fractions were obtained: A, 1.6 g., 16 l. of petroleum ether–benzene (max. ratio 1:2); B, 16.6 g., 5 l. of benzene and 5 l. of 1:1 benzene–chloroform; C, 19.9 g., 26 l. of benzene–chloroform (max. ratio–pure chloroform); and D 17.6 g., chloroform.

Isolation XIIa.—Distillation of fraction B, using a short path distillation apparatus (0.5 mm.), gave 11.5 g. of a yellow oil ($n^{25}D$ 1.5247).

Anal. Calcd. for $C_{20}H_{26}O_3$: C, 76.40; H, 8.34; sapon. equiv., 314. Found: C, 76.47; H, 8.21; sapon. equiv., 311.

This product showed no maximum in the ultraviolet spectrum in the region 220–300 mμ. The infrared spectrum

showed two bands in the carbonyl region: 1720 and 1790 cm.$^{-1}$.

Distillation of fraction C gave an additional 16.6 g. (28.1 g. combined, 47% yield distilled) of XIIa ($n^{25}D$ 1.5218). The ultraviolet and infrared spectra of this material were identical to those obtained from fraction B.

Isolation of XIIb.—Fraction D partially solidified and 1.5 g. of XIIb was obtained which melted at 119–120° after recrystallization from petroleum ether (60–68°)–benzene.

Anal. Calcd. for $C_{20}H_{26}O_3$: C, 76.40; H, 8.34; sapon. equiv., 314. Found: C, 76.36; H, 8.47; sapon. equiv., 314.

This product showed no maximum in the ultraviolet spectrum in the region between 220–300 mμ. The infrared spectrum showed two strong bands in the carbonyl region: 1805 and 1725 cm.$^{-1}$.

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY]

# The Reaction between Diazoacetic Ester and Allylic Halides

By DONALD D. PHILLIPS

Diazoacetic ester reacts with allyl bromide to give ethyl 2-bromo-4-pentenoate (IIa) rather than the expected cyclopropane derivative. Similar results with allyl iodide, methylvinylcarbinyl and allylidene chloride indicate the generality of the reaction. The possibility of rationalizing the formation of these unsaturated esters on the basis of an S_N2' type mechanism is discussed.

An abnormal reaction recently has been reported to occur when allyl bromide is treated with diazoacetic ester,[1a] in that ethyl 2-bromo-4-pentenoate (IIa) is formed instead of the expected cyclopropane (I).[2] Similar findings in these laboratories are in substantial agreement with the Russian work and our extensions of the reaction to substituted allylic halides form the basis for the present communication.
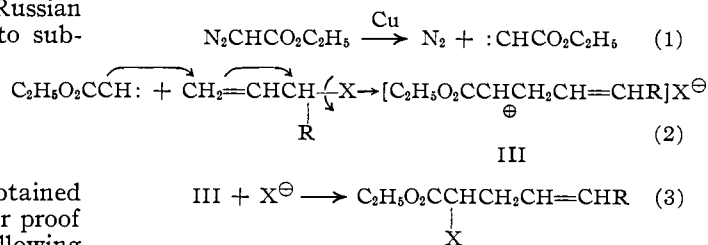
Whereas the degradative reactions reported[1a] in most cases agreed with the assigned structure, IIa the ozonolysis results are sufficiently different from those obtained in our work to merit a brief discussion of our proof of structure. This was based on the following

R——⟋——CH₂X   CH₂=CHCH₂CHCO₂C₂H₅
      | |
   CO₂C₂H₅   X

I, X = Halogen   IIa, X = Br
   R = H or alkyl   b, X = I
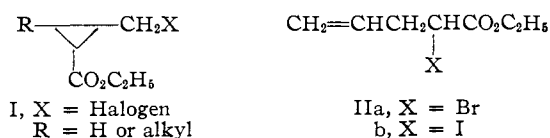
facts: (1) The compound IIa showed a double bond peak in the infrared spectrum at 6.10 μ as well as absorption at 10.07 and 10.85 μ, characteristic of the grouping CH₂=CHR.[3] (2) Reduction with zinc and acetic acid gave ethyl allylacetate. (3) Reductive ozonolysis yielded formaldehyde and ethyl aldehydosuccinate. (4) Reaction with thiourea produced a thiazolidinone, thus confirming the presence of an α-haloester grouping.[4] (5) Lith-

ium aluminum hydride reduced the compound to 4-pentene-1-ol.

A possible mechanism to account for the formation of IIa and other α-haloesters (*cf.* Chart 1) is summarized in equations 1–3.[5]

$$N_2CHCO_2C_2H_5 \xrightarrow{Cu} N_2 + :CHCO_2C_2H_5 \quad (1)$$

$$C_2H_5O_2CCH: + CH_2{=}CHCH{-}X \rightarrow [C_2H_5O_2CCHCH_2CH{=}CHR]X^\ominus$$
$$\underset{R}{\quad} \quad \underset{III}{\overset{\oplus}{\quad}} \quad (2)$$

$$III + X^\ominus \longrightarrow C_2H_5O_2CCHCH_2CH{=}CHR \quad (3)$$
$$\underset{X}{\quad}$$

The formation of the highly reactive "carbethoxycarbene" fragment in equation 1 has been postulated previously.[6,7] Nucleophilic attack at the double bond could then proceed with subsequent ejection of halide ion in a manner closely resembling the S_N2' mechanism.[8,9] Uptake of the halide

(1) (a) I. A. D'yakonov and N. B. Vinogradova, *J. Gen. Chem.*, **21**, 851 (1951); (b) *ibid.*, **23**, 66 (1953).
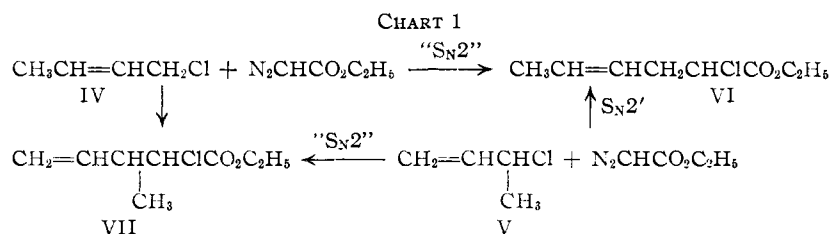
(2) The reaction between diazoacetic ester and suitably activated olefins has long been known as a preparative method for cyclopropanes, *e.g.*, E. Buchner, *Ber.*, **21B**, 2637 (1888); *ibid.*, **23B**, 701 (1890).

(3) N. Sheppard and D. M. Simpson, *Quart. Rev.*, **6**, 1 (1952); and many references contained therein.

(4) B. H. Nicolet and L. F. Bate, THIS JOURNAL, **49**, 2064 (1927).

(5) In view of the results of Gutsche and Hillmann (*ibid.*, **76**, 2236 (1954)) it has been suggested by a referee that an equally plausible mechanism for these reactions would be the initial attack of the "carbethoxycarbene"[6] (:CHCO₂C₂H₅) fragment at the *halogen* atom with synchronous rearrangement to give the observed products. This mechanism fits the benzal chloride case for which it was first suggested because the chlorine represents the only electron-rich center in the molecule. It does not necessarily hold for allylidene chloride (see later discussion) where for both steric and electronic reasons, the double bond represents an equally likely site of attack. However, neither mechanism is unequivocally established at this time and a decision between the two must await further study.

(6) W. von E. Doering and L. H. Knox, Abstracts of Papers, 119th Meeting of the Am. Chem. Soc., April, 1951, p. 2M.

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

(8) G. Stork and W. N. White, THIS JOURNAL, **75**, 4119 (1953), give a brief history of the S_N2', reaction.

(9) The species $C_2H_5O_2CCH$: with its open sextet is unique in

ion by carbonium ion III would proceed instantaneously to give the observed product.[10]
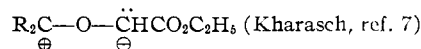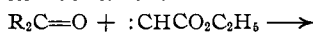
In an effort to minimize the number of mechanisms that can be written for the unsubstituted allylic halides we have investigated the reactions between diazoacetic ester and crotyl and methylvinylcarbinyl chloride. Some of the possible compounds from these reactions are indicated in chart 1.

<div align="center">CHART 1</div>

$$CH_3CH=CHCH_2Cl + N_2CHCO_2C_2H_5 \xrightarrow{"S_N2"} CH_3CH=CHCH_2CHClCO_2C_2H_5$$

IV VI

$$\uparrow S_N2'$$

$$CH_2=CHCHCHClCO_2C_2H_5 \xleftarrow{"S_N2"} CH_2=CHCHCl + N_2CHCO_2C_2H_5$$
$$\underset{CH_3}{|} \qquad\qquad \underset{CH_3}{|}$$

VII V

From the complex mixture obtained when diazoacetic ester reacts with V at the boiling point it was possible to isolate only 10% of the unrearranged product VII, whereas the rearranged product, VI, was formed in greater than 40% yield. That this is not the result of initial rearrangement of V to IV followed by S_N2 attack was evidenced by the stabilities of the two halides, IV and V, when subjected to the conditions of the reaction. Thus V, when heated under reflux in the presence of copper powder, underwent no significant change within three hours, whereas the crotyl isomer IV was approximately 20% isomerized to V under the same conditions.[11] These results, although they indicate a much higher proportion of rearranged product, are consistent with the tendency of V and similar halides to undergo S_N2' reactions to some extent,[12] especially when the nucleophilic reagent is uncharged.[11]
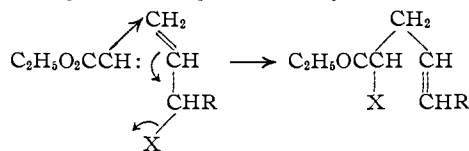
When crotyl chloride (IV) reacted with diazoacetic ester, a mixture resulted in which the unrearranged product VI predominated (ca. 35%) as might be expected on the basis of an S_N2 type reaction.[13] A rather substantial amount (ca. 25%) of

that with ketones it can act as an electrophilic reagent resulting in the formation of a *carbanion*

$$R_2C=O + :CHCO_2C_2H_5 \longrightarrow$$

$$\underset{\oplus}{R_2C}-O-\underset{\ominus}{\overset{..}{C}HCO_2C_2H_5} \text{ (Kharasch, ref. 7)}$$

or with olefins as a possible nucleophilic reagent which results in the formation of a *carbonium* ion as in equation 2. Since it is not known whether the carbethoxycarbene fragment has paired or unpaired electrons it is impossible to say whether bond formation is by one- or two-electron transfers but the final result would be the same in either case.

(10) A cyclic mechanism that would be kinetically indistinguishable from the one postulated in equations 1-3 may also be written

$$C_2H_5O_2CCH: \overset{\nearrow CH_2}{\underset{\searrow X}{\big(\underset{|}{CH}}}_{\underset{CHR}{|}} \longrightarrow C_2H_5OC\overset{CH_2}{\underset{X}{\overset{/ \diagdown}{CH}}}_{\underset{CHR}{\overset{|}{\parallel}}} \underset{CH}{\overset{}{}}$$

This is still basically an S_N2' mechanism but combines equations 2 and 3 in one concerted step.

(11) These results are in agreement with those of Young and co-workers, *e.g.*, R. E. Kepner, S. Winstein and W. G. Young, THIS JOURNAL, **71**, 115 (1949); W. G. Young, I. D. Webb and H. L. Goering, *ibid.*, **73**, 1076 (1951).

(12) P. B. D. de la Mare and C. A. Vernon, *J. Chem. Soc.*, 3555 (1953).

(13) S. Oae and C. A. VanderWerf, THIS JOURNAL, **75**, 2754 (1953).

rearranged product VII was also obtained but its formation cannot be unequivocally explained in view of the complicating isomerization of IV to V described above. However, although there may be appreciable isomerization before reaction in this particular case, the final products VI and VII show no signs of isomerization (probably because the halogens are no longer allylic) so that interconversion of *products* offers no problem in these reactions. It is pertinent to mention at this point that the two halides IV and V yield significantly *different* mixtures of VI and VII, a result that is incompatible with the S_N1' mechanism.

In an effort to find a pair of allylic halides that would yield more clean-cut results, we have also studied the reaction between diazoacetic ester and allylidene chloride (VIII) as well as its allylic isomer, 1,3-dichloropropene (IX).[14] A rapid reaction occurs between VIII and diazoacetic ester, giving as isolable products a mixture of rearranged product X and diethyl fumarate in approximately a 4:1 ratio. Ozonolysis and infrared analysis failed to detect *any* of the unrearranged product XI.

$$ClCH=CHCH_2CHClCO_2C_2H_5$$

X

$$CH_2=CH-CH-CHCO_2C_2H_5$$
$$\underset{Cl}{|} \quad \underset{Cl}{|}$$

XI
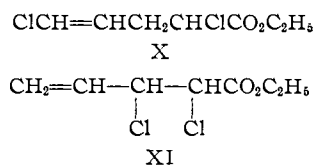
Conversely, the reaction between diazoacetic ester and *trans*-1,3-dichloropropene (IX) was extremely sluggish and over 60% of the halide was recovered unchanged. The distillate was a 1:1 mixture of unrearranged product X and diethyl fumarate. No cyclopropane derivative or rearranged product could be detected. These results suggest that the S_N2' mechanism may be operating in this system, although supporting kinetic evidence is lacking at present.

Infrared analysis played an important role in the proof of structure of VI, VII and X. The characteristic[3] bands of the crotyl group (6.07 and 10.37 μ) in VI, the vinyl group (6.12, 10.08 and 10.84 μ) in VII and of the *trans*-ClCH=CHR[15] group (10.74 μ) in X gave strong support to the assigned structures. Chemical evidence was based on reductive ozonolysis experiments. Thus VI and VII gave as volatile fragments acetaldehyde and formaldehyde, respectively, whereas no volatile component was obtained from V. Although we expected the same large fragment (ethyl aldehydosuccinate) from the ozonolysis of VI and X as was obtained from IIa and b, the product actually identified was that resulting from elimination of the elements of hydrochloric acid, namely, ethyl fumaraldehyde (CHOCH=CHCO_2C_2H_5). Similarly, the β-methyl fumaraldehyde was obtained from VII. Appar-

(14) This selection was made because it has recently been reported that allylidene chloride gives a high proportion of S_N2' product when treated with ethoxide and thiophenoxide ions (P. B. D. de la Mare and C. A. Vernon, *J. Chem. Soc.*, 3325, 3331 (1952)).

(15) R. E. Kitson, *Anal. Chem.*, **25**, 1470 (1953).

ently the chlorine atom in these three compounds is much more inert to simple reduction than is bromine or iodine and β-elimination occurs instead. This facile elimination indicated that the chlorine atom in VI, VII and X must be β with respect to the double bond and hence α to the ester group.

Although the possible mechanistic features of this reaction of diazoacetic ester have been stressed we are also investigating its use as a synthetic method for the preparation of α-aminoacids. In addition, a homogeneous catalyst for the reaction has been found and a study of the kinetics is under way in order to test the validity of the S_N2' mechanism proposed.

Experimental[16]

Starting Materials.—Ethyl diazoacetate was prepared in 90% yield according to Searle's procedure.[17] Allyl bromide and allyl iodide were freshly distilled commercial reagents. Crotyl chloride, b.p. 82–83.5°, n^{23}D 1.4326, and methylvinylcarbinyl chloride, b.p. 64–65°, n^{23}D 1.4148, were prepared from crotyl alcohol in 50 and 21% yields, respectively.[18] Allylidene chloride, b.p. 82–84°, n^{21}D 1.4488, and trans-1,3-dichloropropene, b.p. 111–113°, n^{21}D 1.4720, were prepared from acrolein and phosphorus pentachloride in xylene as inert solvent.[18] Baker reagent grade copper (precipitated powder) was used as catalyst.

Ethyl 2-Bromo-4-pentenoate (IIa).—Allyl bromide (230 g., 1.9 moles) was added to a three-necked flask equipped with stirrer, condenser and dropping funnel and after the addition of 0.5 g. of copper powder was brought to reflux. Over a period of four hours was added a mixture of 41.0 g. (0.36 mole) of ethyl diazoacetate and 30 ml. of allyl bromide. Vigorous nitrogen evolution ensued. After an additional one hour reflux the copper was filtered off, the excess allyl bromide removed at the water pump and the residual red oil fractionally distilled through a 29″ Podbielniak type column. After a small forerun (3.0 g.) there was obtained 52.1 g. (70%) of colorless ester; b.p. 88–90° (21 mm.), n^{20}D 1.4640, $d^{20}{}_4$ 1.307, MRD (obs.) 43.72, MRD (calcd.) 43.49, reported,[2a] b.p. 74–75° (10 mm.), $d^{20}{}_4$ 1.3099; n^{20}D 1.4642, MRD 43.63.

Anal. Calcd. for $C_7H_{11}O_2Br$: C, 40.49; H, 5.35; Br, 38.59; sapon. equiv., 103.5. Found: C, 40.68; H, 5.35; Br, 38.32; sapon. equiv., 102.

Proof of Structure. (a) Zinc and Acetic Acid Reduction. —To 7.3 g. of zinc in 30 g. of acetic acid was added 4.0 g. (0.019 mole) of the bromoester. After the exothermic reaction had subsided, the mixture was allowed to stand for several hours, filtered free of zinc and the filtrate poured into excess water. Ether extraction followed by distillation gave 1.7 g. (70%) of ethyl allylacetate, b.p. 143.5°, n^{28}D 1.4114, identical in infrared spectrum with a sample prepared from diethyl allylmalonate.

(b) Lithium Aluminum Hydride Reduction.—A slurry of 1.6 g. (0.042 mole) of lithium aluminum hydride in 25 ml. of ether was made and to this over 5 min. was added 3.5 g. (0.017 mole) of bromoester. The usual workup gave 1.47 g. (70%) of 4-pentene-1-ol; b.p. 139–140°, n^{28}D 1.4305. The infrared spectrum was identical to that of a sample prepared from tetrahydrofurfuryl chloride.[19]

(c) Reaction with Thiourea.—A solution of 1.14 g. (5.5 mmoles) of bromoester and 0.45 g. (5.9 mmoles) of thiourea in 15 ml. of absolute alcohol containing a trace of sodium acetate was heated under reflux for two hours. Dilution with water followed by crystallization from dilute

(16) Melting points were determined on the Nalge–Axelrod apparatus and are uncorrected. Analyses are by Du-Good Labs., St. Louis 4, Mo., and Geller Labs., Hackensack, N. J. Infrared spectra were determined on a Perkin–Elmer double-beam spectrophotometer, Model 21. Ultraviolet absorption spectra were measured with a Beckman quartz spectrophotometer, model DU. In all cases, the solvent was 95% ethanol.

(17) N. E. Searle, U. S. Patent 2,490,714; C. A., **44**, 3519 (1950). No attempt was made to remove the approximately 5% ethyl chloroacetate contaminant.

(18) W. H. King and H. A. Smith, THIS JOURNAL, **72**, 3459 (1950).

(19) L. A. Brooks and H. R. Snyder, Org. Syntheses, **25**, 84 (1945).

ethanol resulted in the formation of 0.50 g. (58%) of 2-imino-5-allylthiozolidin-4-one as colorless needles, m.p. 179–180°.

Anal. Calcd. for $C_6H_8ON_2S$: C, 46.13; H, 5.16. Found: C, 46.35; H, 5.33.

(d) Ozonization.—A solution of 1.5 g. (7.2 mmoles) of bromoester in 25 ml. of methylene chloride was ozonized at −40° for 30 min. then poured with stirring into 25 ml. of acetic acid containing 5 g. of zinc. The filtered reaction mixture was next distilled from a steam-bath and the distillate collected in a flask containing 2.0 g. (0.014 mole) of dimedon and 2 drops of piperidine in 15 ml. of 60% ethanol. The methylene chloride was removed on the hot plate and on cooling, the residual solution deposited 1.6 g. (76%) of long needles, m.p. 189°, undepressed on admixture with authentic formaldehyde–dimedon adduct, m.p. 189–190°.

To the acetic acid solution was added 1.4 g. (7 mmoles) of 2,4-dinitrophenylhydrazine in 15 ml. of acidified ethanol. Overnight 1.1 g. (51%) of orange plates separated, m.p. 104–107°. Two crystallizations from ethanol resulted in a product, m.p. 109–110°.

Anal. Calcd. for $C_{12}H_{14}N_4O_6$: C, 46.44; H, 4.55; N, 18.05. Found: C, 46.33; H, 4.55; N, 18.10.

There was no depression on admixture with authentic[20] ethyl aldehydosuccinate-2,4-dinitrophenylhydrazone, m.p. 110–112°. The infrared and ultraviolet absorption spectra were identical, the latter having λ_{max}. 358 mμ, log ϵ 4.32.

Ethyl 2-Iodo-4-pentenoate (IIb).—When allyl iodide and diazoacetic ester reacted under conditions similar to those described above for IIa, there was obtained in 50% yield a pale orange liquid; b.p. 83–83.5° (5.5 mm.), n^{20}D 1.5058, $d^{20}{}_4$ 1.5508, MRD (calcd.) 48.53; MRD (obs.) 48.67.

Anal. Calcd. for $C_7H_{11}O_2I$: C, 33.08; H, 4.36; I, 49.95; sapon. equiv., 127.0. Found: C, 32.97; H, 4.25; I, 49.24; sapon. equiv., 130.0.

The infrared spectrum (λ_{max}. 5.80, 6.10, 10.10 and 10.86 μ) was very similar to that of IIa. Ozonolysis produced the same fragments and treatment of IIa with sodium iodide in acetone gave a 77% yield of IIb, thus confirming its structure.

Diazoacetic Ester and Methylvinylcarbinyl Chloride.—To refluxing methylvinylcarbinyl chloride (13.4 g., 0.15 mole) containing 0.5 g. of copper was added over three hours 11.4 g. (0.10 mole) of ethyl diazoacetate. Nitrogen evolution began almost immediately. After an additional hour under reflux the brown solution was filtered free of copper and distilled. There was obtained 1.8 g. of ethyl chloroacetate, b.p. 51–52°· (12.5 mm.) followed by 1.4 g. (A), b.p. 87–90° (12.5 mm.), n^{18}D 1.4439, $d^{20}{}_4$ 1.040; 5.1 g. (B), b.p. 90–92.5° (12.5 mm.), n^{19}D 1.4460, $d^{20}{}_4$ 1.037, and 1.8 g. (C), b.p. 90–93° (7.5 mm.), n^{19}D 1.4487; $d^{20}{}_4$ 1.043. A residue of approximately 4 g. remained.

Anal. Calcd. for $C_8H_{13}O_2Cl$; C, 54.38; H, 7.42; Cl, 20.07; sapon. equiv., 88.3. Found (fraction A): C, 54.33; H, 7.49; Cl, 20.09; sapon. equiv., 89.5; (fraction B): C, 54.38; H, 7.30; Cl, 20.20; sapon. equiv., 90.5.

Proof of Structure. 1. Fraction B (VI).—The infrared spectrum of B strongly suggested that it was the crotyl isomer (VI). Its rather high molar refractivity (45.54 obs. v. 45.24 calcd.) was in line with the exaltation known to prevail among crotyl compounds.[21]

Ozonolysis under the same conditions described for IIa produced a 51% yield of acetaldehyde–dimedon adduct, m.p. 141–142°, identical in all respects to the authentic material, m.p. 142°. The non-volatile aldehyde portion formed a 2,4-dinitrophenylhydrazone, m.p. 155–159°, in 60% yield. One recrystallization from ethanol gave orange plates, m.p. 157–159°; λ_{max}. (log ϵ); 214 mμ (4.27), 235 μ (4.22), 373 mμ (4.51), 380 mμ (4.50).

Anal. Calcd. for $C_{12}H_{12}O_6N_4$: C, 46.72; H, 3.93; N, 18.16. Found: C, 46.64; H, 4.12; N, 18.24.

This material was compared to an authentic sample of ethyl fumaraldehydate 2,4-dinitrophenylhydrazone,[22] m.p. 154–157.5°, and was found to have the same infrared and

(20) S. W. Fox and M. W. Bullock, THIS JOURNAL, **73**, 2754 (1951).

(21) G. H. Jeffery and A. I. Vogel, J. Chem. Soc., 658 (1948), report RD = 2.30 for crotonate double bonds and 1.58 for the normal type.

(22) A. Funke and P. Karrer, Helv. Chim. Acta, **32**, 1016 (1949), report m.p. 153°.

ultraviolet absorption spectrum. Admixture caused no depression in melting point.

2. **Fraction A (VII).**—The lower b.p. and molar refractivity (45.07 obs. v. 45.24 calcd.) suggested that this compound was the vinyl isomer (VII). The infrared spectrum, with peaks at 10.08 and 10.84 μ, supported this conjecture although the band at 10.35 μ indicated the presence of some crotyl isomer as contaminant. Ozonization under described conditions gave a 56% of formaldehyde-dimedon adduct, m.p. 189°. The non-volatile aldehyde fragment formed a 2,4-dinitrophenylhydrazone, m.p. 174–183°, in 40% yield. Crystallization from ethanol resulted in an orange, microcrystalline powder, m.p. 183–185°. The ultraviolet absorption spectrum (214 mμ (4.25), 374 mμ (4.47), 379 mμ (4.47)) was essentially identical to that of ethyl fumaraldehydate-2,4-dinitrophenylhydrazone indicating that this was the methyl analog ethyl β-formylcrotonate 2,4-dinitrophenylhydrazone.

Anal. Calcd. for $C_{13}H_{14}O_6N_4$: C, 48.45; H, 4.38; N, 17.38. Found: C, 48.67; H, 4.37; N, 17.42.

3. **Fraction C.**—The spectrum of this fraction differed only slightly from that of fraction B, but the lower molar refractivity (45.41) and higher density indicated contamination by some of the cyclopropane isomer, although none of the latter could be isolated in the pure state. Ozonolysis gave the same fragments as described for fraction B, but in lower yield.

If one takes into account the fact that ethyl chloroacetate is an impurity in the limiting reagent diazoacetic ester, and that fraction C is made up of at least 50% of the same compound obtained in fraction B, the yields of the S_N2 product (VII) and the S_N2' product (VI) come out to be approximately 10 and 40%, respectively.

Diazoacetic Ester and Crotyl Chloride.—To 16.3 g. (0.18 mole) of crotyl chloride containing 0.5 g. of copper was added under reflux over three hours 14.2 g. (0.12 mole) of diazoacetic ester. Nitrogen evolution began only after an induction period of 30 min. After an additional hour under reflux the mixture was filtered free of copper and distilled. There was obtained 2.9 g. of ethyl chloroacetate, b.p. 52–53° (12 mm.); 3.6 g. (fraction A), b.p. 73–75° (8 mm.), $n^{19}D$ 1.4438, d^{20}_4 1.040; 4.4 g. (fraction B), b.p. 77–79° (6.5 mm.), $n^{20}D$ 1.4462, d^{20}_4 1.038 and 1.5 g. (fraction C), b.p. 83–84° (6.5 mm.), $n^{20}D$ 1.4482. About 5 g. of residue remained.

Fractions A, B and C were identical to fractions A, B and C isolated from the methylvinylcarbinyl chloride reaction as established by ozonolysis and infrared analysis. Based on pure diazoacetic ester, the yields of (VII) (fraction A) and (VI) (fraction B, the S_N2 product) are approximately 25 and 36%, respectively.

Diazoacetic Ester and Allylidene Chloride.—When 18.6 g. (0.17 mole) of allylidene chloride was treated with 13.7 g. (0.12 mole) of diazoacetic ester as described above, nitrogen evolution began immediately. On distillation there was obtained the following fractions: 2.5 g. of recovered allylidene chloride, b.p. 83–84°; 4.1 g. (A), b.p. 94–95° (7 mm.), $n^{20}D$ 1.4578, d^{20}_4 1.150; 3.6 g. (B), b.p. 95–98° (7 mm.), $n^{20}D$ 1.4629, d^{20}_4 1.175; 1.75 g. (C), b.p. 98–99° (6 mm.), $n^{20}D$ 1.4664, d^{20}_4 1.193. A residue of about 7 g. remained.

Proof of Structure. 1. Fraction C.—The strong infrared peak at 10.74 μ (Fig. 1) coupled with the lack of absorption at 10.25 μ suggested that this fraction was essentially free of diethyl fumarate and hence represented the best sample of ethyl 2,5-dichloro-4-pentenoate (X) among the three fractions. This was substantiated by the molar refractivity (45.77 obs. v. 45.52 calcd.) and the analysis.

Anal. Calcd. for $C_7H_{10}O_2Cl$: C, 42.66; H, 5.12; Cl, 35.98. Found: C, 42.78; H, 5.23; Cl, 35.52.

Ozonolysis under described conditions gave no volatile aldehyde but the residual material yielded 60% of a 2,4-dinitrophenylhydrazone, m.p. 157-159°, identical with the

derivative obtained from fraction B in the methylvinylcarbinyl chloride reaction.

2. **Fraction B.**—The infrared spectrum was very similar to that of fraction C with a correspondingly weaker absorption at 10.74 μ and the appearance of a band at 10.25 μ, caused by diethyl fumarate contaminant. The lower refractive index, density and chlorine content (30.10%) are in line with the interpretation that this is a mixture of (X) and diethyl fumarate.

Ozonolysis produced no volatile aldehyde fragment and the only 2,4-dinitrophenylhydrazone formed (45%) was the same one obtained in fraction C. Although some ethyl glyoxalate 2,4-dinitrophenylhydrazone might be expected from the diethyl fumarate contaminant, none could be found in the ozonolysis mixture, probably because the lower m.p. (124°) prevents its isolation under these circumstances.

On the basis of $n^{20}D$ 1.4405 for diethyl fumarate, the mixture was calculated to be 87% compound X and 13% diethyl fumarate. The somewhat less reliable chlorine analysis indicated a ratio of 85%:15%.

3. **Fraction A.**—The appearance in the infrared spectrum of a band at 11.26 μ along with the peak at 10.25 μ suggested the presence of some cyclopropane[23] derivative as well as diethyl fumarate contaminant. None of the pure cyclopropane compound could be isolated, however, and the above assignment is therefore a dubious one.

Ozonolysis gave in 30% yield the same 2,4-dinitrophenylhydrazone obtained in fractions B and C. The failure to obtain a volatile aldehyde fraction eliminated the possibility of any vinyl isomer (XI) in this fraction. On the basis of refractive index, the mixture was approximately 67% (X) and 33% diethyl fumarate. The chlorine content (27.10%) indicated the higher ratio of 75%:25%, suggesting the presence of a third chlorine-containing substance, possibly the cyclopropane.

The total yield of compound X in the three fractions could thus be estimated as 7.6 g. or 31% of theoretical and the ratio of XIII to diethyl fumarate as 81%:19%.

Diazoacetic Ester and *trans*-1,3-Dichloropropene.—The reaction between 17.6 g. (0.16 mole) of *trans*-1,3-dichloropropene and 17.2 g. (0.15 mole) of diazoacetic ester failed to commence immediately even in the presence of larger amounts of copper (1.0 g.). Distillation of the reaction mixture gave 10.6 g. (60%) of unreacted halide, b.p. 110–112° and 4.4 g. of a mixture, b.p. 93–98° (6 mm.), $n^{20}D$ 1.4450-1.4580, d^{20}_4 1.080-1.140. A residue of approximately 6 g. remained.

The mixture had an infrared spectrum similar to fraction A from the allylidene chloride reaction although the much weaker absorption at 10.74 μ coupled with the lower refractive index, density and chlorine content (21.8%) indicated the presence of a much larger proportion of diethyl fumarate. The same calculations used above gave the value of 50%:50% for the ratio of X to diethyl fumarate. Even on the basis of the halide actually consumed, the yield of X was only 17%. This yield and ratio of products is quite different from those described for the allylidene isomer, a fact that is incompatible with an S_N1' mechanism.

Isomerization of Crotyl Chloride.—Twenty grams of crotyl chloride, $n^{20}D$ 1.4340, was heated for three hours under reflux in the presence of 0.7 g. of copper powder. The refractive index of the resultant mixture was $n^{20}D$ 1.4308, indicating 18% conversion to the methylvinylcarbinyl isomer. Distillation gave 3.4 g., b.p. 64–66°, $n^{20}D$ 1.4160 and 2.8 g. of an intermediate fraction, b.p. 66–84°, $n^{20}D$ 1.4250. The total yield of methylvinylcarbinyl chloride from both fractions was 4.8 g. or 24%. This higher figure is probably a result of additional isomerization during the distillation which required two hours.

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(23) R. Suhrmann and H. Luther, *Fortschr. Chem. Forsch.*, **2**, 817 (1953).