

Chemistry of *gem*-Dihalocyclopropanes. IV. Ring Opening of *gem*-Dichlorocyclopropyl Ethers

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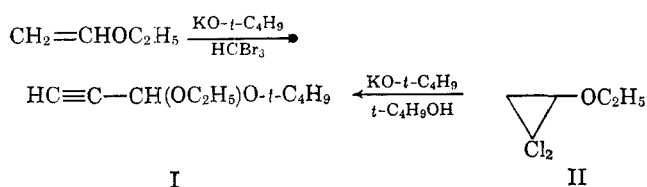
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Thermal reactions of *gem*-dichlorocyclopropyl ethers in alcoholic solvents and in the presence of base results in ring opening with formation of acetals of the general structure, $RR^1C=CClCH(OC_2H_5)OR^2$, in good yields. The ring opening is independent of base, which is only present in order to neutralize the acid formed. Simple kinetic measurements have been carried out by following the consumption of base. The reaction shows first-order kinetics, the rate-determining step being most probably concerted ring opening with loss of chloride ion. Reactions of both *cis*- and *trans*-1,1-dichloro-2-ethoxy-3-methylcyclopropane (IV) gave *trans*-2-chloro-1,1-diethoxy-2-butene (VII). This apparent selectivity is explained on the basis of the selection rules for electrocyclic reactions.

The reactions of *gem*-dibromocyclopropanes with alkyllithium reagents lead in a number of cases to allenes in good yields.^{2,3} As part of a study of this reaction we wanted *gem*-dibromocyclopropyl ethers as starting materials for the synthesis of allenic ethers. Several cases of addition of dichlorocarbene to vinyl ethers, yielding the corresponding cyclopropanes, have been reported;⁴ however, the addition of dibromocarbene to vinyl ethers had not been reported at the time this work was initiated.⁵

The reaction of ethyl vinyl ether with dibromocarbene, generated from bromoform and potassium *t*-butoxide,⁶ gave a mixture of products and no isolable yield of the cyclopropane derivative. The infrared spectrum of this mixture revealed the presence of a compound with an ethynyl group by a sharp band at 3280 cm^{-1} . With an excess of base and more drastic conditions, 1-*t*-butoxy-1-ethoxy-2-propyne (I) was obtained in 53% yield. Apparently the *gem*-dibromocyclopropane derivative was formed as an intermediate in this reaction since the same acetal (I) was obtained in 73% yield from heating 1,1-dichloro-2-ethoxycyclopropane (II) with an excess of potassium *t*-butoxide in *t*-butyl alcohol.



A similar ring opening was reported by McElvain and Weyna⁷ in the pyrolysis of *gem*-dichlorocyclopropanone acetals to give α -chloroacrylic esters or in the presence of an alcohol to yield ortho esters. In addition to this work, the thermal decomposition of bicyclic and polycyclic compounds containing a

gem-dihalocyclopropyl ring has been quite extensively studied, particularly by Parham and Schweizer.⁴

In order to gather some more information about this ring-opening reaction a number of *gem*-dichlorocyclopropyl ethers was prepared by addition of dichlorocarbene to the respective vinyl ether. The latter was either a commercial sample or prepared according to published procedure. A stereoisomeric mixture of propenyl ethyl ether was obtained by acid-catalyzed elimination of ethanol from propionaldehyde diethyl acetal.^{8,9} Gas chromatography showed that 67% *cis* and 33% *trans* isomers were formed, which is close to the equilibrium concentrations.¹⁰ The *cis* isomer was more conveniently prepared by base-catalyzed isomerization of allyl ethyl ether,^{11,12} which has been shown to yield almost exclusively this isomer. Dichlorocarbene was generated by three different methods: the treatment of chloroform⁶ (A) or ethyl trichloroacetate¹³ (B) with base, and the reaction of bromotrifluoromethane with methylithium¹⁴ (C). The results are summarized in Table I. The compounds were

TABLE I
PREPARATION OF *gem*-DICHLOROCYCLOPROPYL ETHERS AND
THEIR RELATIVE RATES OF RING OPENING

Cyclopropane derivative	Method	Yield, % ^a	Relative rate ^b
1,1-Dichloro-2-ethoxy- <i>c</i> (II)	A	50 ^d	1
1,1-Dichloro-2-ethoxy-3-methyl- (IV)	B	67 ^e	
<i>trans</i> -1,1-Dichloro-2-ethoxy-3-methyl- (IV)	C	50	1.5
<i>cis</i> -1,1-Dichloro-2-ethoxy-3-methyl- (IV)	B	61	19
	C	56	
1,1-Dichloro-2-ethoxy-3,3-dimethyl- (V)	B	56	28
1,1-Dichloro-2-ethoxy-2-methyl- (VI)	B	66	2.5
	C	57	

^a Yields are based on olefin when not otherwise stated. ^b Determined at 70° in ethanol with sodium ethoxide as base. ^c See ref 41a. ^d Excess of the ether was used. The yield is based on chloroform. ^e Mixture of stereoisomers.

(1) Presented at the 3rd Annual Metropolitan Regional Meeting of the American Chemical Society, New York, N. Y., Jan 1964.

(2) W. R. Moore and H. R. Ward, *J. Org. Chem.*, **25**, 2073 (1960); **27**, 4179 (1962).

(3) L. Skattebøl, *Tetrahedron Letters*, 167 (1961); *Acta Chem. Scand.*, **17**, 1683 (1963).

(4) For a review, see W. E. Parham and E. E. Schweizer, *Org. Reactions*, **13**, 55 (1963).

(5) Presently, only two examples could be found in the literature: B. T. Gillis and K. F. Schimmel, *J. Org. Chem.*, **27**, 1071 (1962); A. J. Birch, J. M. Brown, and F. Stansfield, *Chem. Ind. (London)*, 1917 (1964).

(6) W. von E. Doering and A. K. Hoffmann, *J. Am. Chem. Soc.*, **76**, 6162 (1954).

(7) S. M. McElvain and P. L. Weyna, *ibid.*, **81**, 2579 (1959).

(8) T. G. Voronkov, *Zh. Obshch. Khim.*, **20**, 2060 (1950).

(9) M. Farina, M. Peraldo, and G. Bressan, *Chim. Ind. (Milan)*, **42**, 967 (1960).

(10) W. H. Snyder, unpublished results, quoted in ref 11.

(11) C. C. Price and W. H. Snyder, *J. Am. Chem. Soc.*, **83**, 1773 (1961).

(12) W. L. Howard, E. C. Jacobsen, and R. A. Newton, *J. Org. Chem.*, **26**, 3574 (1961).

(13) W. E. Parham and E. E. Schweizer, *J. Org. Chem.*, **24**, 1733 (1959).

(14) W. T. Miller and C. S. Y. Kim, *J. Am. Chem. Soc.*, **81**, 5008 (1959). Trichloromethylithium, and not dichlorocarbene, has recently been shown to be the reactive intermediate in this reaction: W. T. Miller and D. M. Whalen, *ibid.*, **86**, 2089 (1964).

TABLE II
 RING-OPENING REACTION OF *gem*-DICHLOROCYCLOPROPYL ETHERS

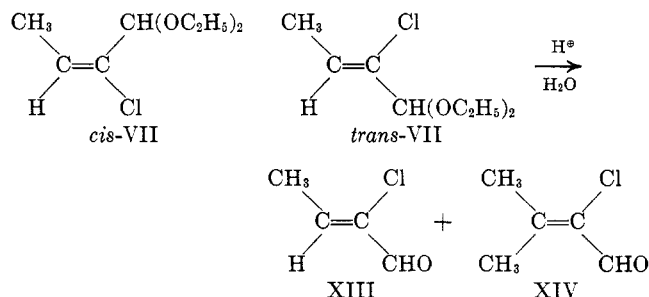
Cyclopropane derivative	Base	Solvent	Product	Yield, %
II	KOC ₄ H ₉ - <i>t</i>	<i>t</i> -C ₄ H ₉ OH	HC≡C—CH(OC ₂ H ₅)OC ₄ H ₉ - <i>t</i> (I)	73
II	NaOC ₂ H ₅	C ₂ H ₅ OH	CH ₂ =CCl—CH(OC ₂ H ₅) ₂ ^a (III)	89
II	Pyridine	C ₂ H ₅ OH	CH ₂ =CCl—CH(OC ₂ H ₅) ₂ ^a (III)	75
IV ^b	NaOC ₂ H ₅	C ₂ H ₅ OH	<i>trans</i> -CH ₃ CH=CCl—CH(OC ₂ H ₅) ₂ (VII)	90
<i>cis</i> -IV	Pyridine	C ₂ H ₅ OH	<i>trans</i> -CH ₃ CH=CCl—CH(OC ₂ H ₅) ₂ (VII)	83
<i>trans</i> -IV	Pyridine	C ₂ H ₅ OH	<i>trans</i> -CH ₃ CH=CCl—CH(OC ₂ H ₅) ₂ (VII)	81
V	KOC ₄ H ₉ - <i>t</i>	<i>t</i> -C ₄ H ₉ OH	(CH ₃) ₂ C=CCl—CH(OC ₂ H ₅)OC ₄ H ₉ - <i>t</i> (VIII)	69
V	NaOC ₂ H ₅	C ₂ H ₅ OH	(CH ₃) ₂ C=CCl—CH(OC ₂ H ₅) ₂ (IX)	86
V	Pyridine	C ₂ H ₅ OH	(CH ₃) ₂ C=CCl—CH(OC ₂ H ₅) ₂ (IX)	82
V	K ₂ CO ₃	C ₂ H ₅ OH	(CH ₃) ₂ C=CCl—CH(OC ₂ H ₅) ₂ (IX)	72
V	NaOCH ₃	Dioxane	(CH ₃) ₂ C=CCl—CH(OC ₂ H ₅)OCH ₃ (X)	77
VI	NaOC ₂ H ₅	C ₂ H ₅ OH	HC≡C—C(OC ₂ H ₅) ₂ CH ₃ (XI)	50
			HC≡C—C(OC ₂ H ₅)=CH ₂ (XII)	15

^a A small amount of the acetylenic acetal was also formed. ^b A mixture of stereoisomers.

characterized by elemental analysis and spectroscopic data. The structures of *cis*- and *trans*-1,1-dichloro-2-ethoxy-3-methylcyclopropane, respectively, were unequivocally established by their nmr spectra. The chemical shifts and relative peak areas were as expected; the magnitudes of the coupling constants for the *cis*- and *trans*-cyclopropyl protons were found to be 8.5 and 4.8 cps, respectively. This is in agreement with theory.¹⁵

The *gem*-dichlorocyclopropyl ethers, when heated under reflux with an alcohol in the presence of a base, underwent ring opening with formation of acetals or, in the case of VI, a ketal. The ease of ring opening appeared to be a function of the structure of the cyclopropane derivative. Reflux (6–48 hr) was used in order to complete the reactions. The reaction also appeared to be independent of type of base since it proceeded equally well with pyridine as with sodium ethoxide. In Table II the results are summarized. The acetals were generally unstable because of the ease with which they hydrolyzed to the corresponding carbonyl compounds. Small amounts of these were occasionally present in the products even after careful isolation procedure; consequently, unsatisfactory analytical data were obtained in some cases. The acetals readily formed 2,4-dinitrophenylhydrazone derivatives, which were identical with those obtained directly from the corresponding carbonyl compounds, described below.

Substantial evidence for the structures recorded in Table II was obtained from their infrared and nmr spectra. The former exhibited in each case very strong bands in the 1200–1000-cm⁻¹ region, characteristic of the carbon-oxygen stretching vibrations of acetals.¹⁶ Interestingly, the reaction of either *cis*- or *trans*-IV with ethanol was stereospecific, yielding in both cases *trans*-2-chloro-1,1-diethoxy-2-butene (VII). The acetal was readily hydrolyzed to the corresponding aldehyde, *trans*-2-chloro-2-propenal (XIII). The configurations of these compounds were established by studying their nmr spectra. Both allylic (1,3) and homoallylic (1,4) coupling are recognized in the acetal spectrum. The former is evidenced by the octet observed for the olefinic proton, the latter by the quartet observed for the methyl group attached to the double bond; furthermore, the allylic proton gives rise to a quintet. In both



cases $J \cong 1.0$ cps. Numerous reports have shown that the magnitude of $J_{1,3}$ and $J_{1,4}$ is in the order of 0.5–2.0 cps;¹⁷ moreover, $J_{1,3}(\textit{cis}) \geq J_{1,3}(\textit{trans})$, although the opposite has been claimed.^{18,19} It has also recently been demonstrated^{20,21} that $J_{1,3}$ is dependent on the angle θ between the plane of the double bond and the direction of the allylic carbon-hydrogen bond; the minimum value is observed for θ equals 0°, and the maximum value when it is close to 90°. Quite similar rules appear to be valid also for 1,4 coupling.¹⁷ Molecular models of *cis*- and *trans*-VII show that only in the *trans* isomer can the dihedral angle θ attain the favorable 90°; consequently, the observed coupling constants indicate that the acetal has the *trans* configuration. The argument becomes stronger by the fact that in 1,1-diethoxy-2-chloro-3-methyl-2-butene (IX), which cannot attain a favorable conformation, the allylic proton indeed gives rise to a singlet; hence, no 1,4 coupling is observed. Perhaps more convincing evidence for the *trans* configuration was obtained by comparing the chemical shift of the methyl group of the aldehyde XIII with those of the aldehyde XIV. Jackman and Wiley¹⁹ have shown that a chlorine substituent deshields *cis*- and *trans*-methyl groups to practically the same extent, while a carbonyl group deshields a *cis*-methyl group considerably more ($\Delta\nu \sim 0.20$ – 0.30 ppm) than a *trans*. The nmr spectra of XIV shows two singlets at τ 7.68 and 7.87 which then accordingly is assigned the methyl group *cis* and *trans* to the carbonyl group, respectively. The methyl group of XIII shows a doublet centered at τ 7.90 and therefore must be *trans* to the carbonyl

(17) J. T. Pinhey and S. Sternhell, *Tetrahedron Letters*, 275 (1963), and references therein.

(18) R. R. Fraser, *Can. J. Chem.*, **38**, 549 (1960).

(19) L. M. Jackman and R. H. Wiley, *J. Chem. Soc.*, 2881 (1960).

(20) E. B. Whipple, *J. Chem. Phys.*, **35**, 1039 (1961).

(21) A. A. Bothner-By, C. Naar-Colin, and H. Günther, *J. Am. Chem. Soc.*, **84**, 2748 (1962).

(15) D. J. Patel, M. E. H. Howden, and J. D. Roberts, *J. Am. Chem. Soc.*, **85**, 3218 (1963).

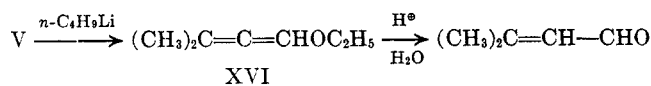
(16) E. D. Bergman and S. Pinchas, *Rec. Trav. Chim.*, **71**, 161 (1952).

group.²² The assignment was confirmed chemically by the formation of 1,1-diethoxy-2-butyne from a reaction of VII with sodium ethoxide.²⁴

The treatment of 1,1-dichloro-2-ethoxy-2-methylcyclopropane (VI) with equimolar amounts of sodium ethoxide in ethanol gave a mixture which consisted of three main components. With an excess of 2 molar equiv of base the higher boiling compound was practically absent in the product. The two remaining compounds were shown to be 3,3-diethoxy-1-butyne (XI) and 2-ethoxy-1-buten-3-yne (XII),²⁶ the former being the predominant product. The higher boiling material, although it was not separated, was probably 2-chloro-3,3-diethoxy-1-butene.

Hydrolysis of either of the acetals VIII, IX, or X gave 2-chloro-3-methyl-2-butenal (XIV) in excellent yields. Without isolation of the acetal, this aldehyde was prepared in 88% over-all yield from the cyclopropane derivative V. In the same way hydrolysis of the acetal III gave 2-chloro-2-propenal (XV), and, as described above, *trans*-2-chloro-2-butenal (XIII) was obtained from *trans*-VII.

Our original goal, *i.e.*, the preparation of allenic ethers, was achieved in one single case. The reaction of V with *n*-butyllithium gave a mixture of compounds and the main component was identified as 1-ethoxy-3-methyl-1,2-butadiene (XVI). It was very readily hydrolyzed by dilute acid to β -methylcrotonaldehyde, characterized as its 2,4-dinitrophenylhydrazone. A similar reaction with IV gave no isolable yield of the expected allene, but the presence of crotonaldehyde in the reaction mixture indicates that it was indeed formed.



Aiming at a better understanding of the mechanism of the reaction some simple kinetic measurements were carried out. Reaction rates of the compounds of Table I with sodium ethoxide in 95% ethanol at 70° were obtained by following the consumption of base by titration. All the compounds gave first-order plots, and their relative rates are given in Table I referring to 1,1-dichloro-2-ethoxycyclopropane (II) as unity. The rates were practically independent of both type and concentration of base but were dependent on the solvent polarity. II reacted about 20 times as fast in 1:1 ethanol-dimethyl sulfoxide as in 95% ethanol, and the rate of V decreased almost threefold when measured in *t*-butyl alcohol.

Discussion

The fact that alkyl-substituted *gem*-dichlorocyclopropanes do not react under the conditions used in the present work clearly demonstrates the importance of

(22) In a *gem*-dimethyl group the replacement of one methyl with hydrogen does not significantly change the chemical shift of the remaining methyl group; see ref 23, pp 50-66.

(23) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press Ltd., London, 1959.

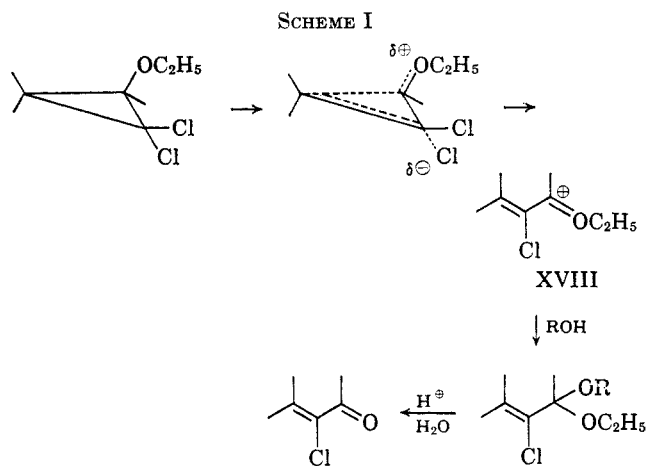
(24) It is not expected that elimination of hydrogen chloride from *cis*-VII would take place under these conditions.²⁵

(25) W. E. Truce and M. M. Boudakian, *J. Am. Chem. Soc.*, **78**, 2748 (1956).

(26) A. A. Petrov and Yu. I. Porfireva, *Dokl. Akad. Nauk SSSR*, **90**, 561 (1953); *Chem. Abstr.*, **49**, 12285 (1955).

the ethoxy group as a driving force, and furthermore that the effect must be essentially polar in nature. One way of explaining the accelerating effect of the ethoxy group involves the ability of the oxygen lone-pair electrons to increase the electron density of the cyclopropane ring, thus polarizing the carbon-chlorine bond. This really means that the electronic effect of the ethoxy group is transmitted through the cyclopropane ring.²⁷ The presence of lone-pair electrons adjacent to the ring appears to increase substantially the rate of ring opening; cyclopropanols²⁸ and cyclopropylamines²⁹ both undergo ring opening readily, and so does also a number of cyclopropylcarbinyl anions.³⁰ Actually, cyclopropylcarbinyl chloride and magnesium gave only allylcarbinylmagnesium chloride,³¹ and cyclopropylcarbinyl lithium³² is only stable at low temperatures.

The mechanism shown in Scheme I is suggested for the reaction. The reaction is depicted as a concerted ring opening with loss of chloride ion to give the allylic cation XVIII. Subsequent reactions of this ion would lead to the observed products. The only difficulty is to explain the exclusive formation of the *trans* isomer of the acetal VII from both the *cis*- and *trans*-cyclopropane IV. Theoretical discussions by Woodward and Hoffmann³³ have resulted in some selection rules



for electrocyclic reactions; in ring opening of a cyclopropyl cation, substituents would move disrotatory, either both inward or both outward. DePuy and co-workers³⁴ have recently extended the rules to concerted ring openings, for which they suggest that substituents *trans* to the leaving group rotate outward. Applying this to the isomers of IV, we propose that in both of these the chlorine atom *trans* to the methyl group leaves preferentially. This is expected in the case of *cis*-IV, since the other choice would cause the groups to rotate inwards, which sterically would be most un-

(27) For a comprehensive review pertaining to the unsaturated nature of the cyclopropane ring, see M. Yu. Lukina, *Russ. Chem. Rev.*, **31**, 419 (1962).

(28) C. H. DePuy and F. W. Breitbeil, *J. Am. Chem. Soc.*, **85**, 2176 (1963).

(29) C. Kaiser, A. Burger, L. Zirngibl, C. S. Davis, and C. L. Zirkle, *J. Org. Chem.*, **27**, 768 (1962).

(30) C. L. Bumgardner and J. P. Freeman, *Tetrahedron Letters*, 737 (1964).

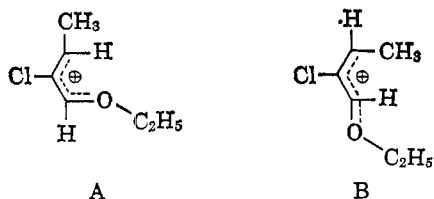
(31) M. S. Silver, P. R. Shafer, J. E. Nordlander, C. Rüdhardt, and J. D. Roberts, *J. Am. Chem. Soc.*, **82**, 2646 (1960).

(32) P. T. Lansbury, V. A. Pattison, W. A. Clement, and J. D. Sidler, *ibid.*, **86**, 2247 (1964).

(33) R. B. Woodward and R. Hoffmann, *ibid.*, **87**, 395 (1965).

(34) C. H. DePuy, L. G. Schnack, J. W. Hausser, and W. Wiedemann, *ibid.*, **87**, 4006 (1965).

favorable. In the case of *trans*-IV, however, it is not that clear. We must assume that of the two possible ions, A and B, the process leading to the former is pre-



ferred. Sterically, at least, this appears reasonable, although it is difficult to understand that it is a sufficient, directive force.

By comparing the relative rates of Table I, it seems evident that the effect of the methyl substituents is essentially steric. This is quite compatible with the above mechanism.

It would be possible to explain the experimental results by a stepwise mechanism involving the formation of a carbanion intermediate with a lifetime long enough for conformational equilibration to occur. Employing the Hammett-Curtin principle,³⁵ the results from the reaction of the isomers of compound IV could be explained. The conditions for employing this principle are hardly fulfilled; the activation energy of the process leading from the carbanion to *trans*-VII is most probably not large compared with the barrier to rotation.³⁶

The above discussion is certainly only valid on the condition that the ion XVIII does not isomerize³⁸ and that the *cis* isomer of acetal VII would retain its configuration during the reaction. Unfortunately, all attempts to prepare *cis*-VII have been unsuccessful.

Experimental Section³⁹

Vinyl Ethers.—Commercial samples of ethyl vinyl ether and 2,3-dihydroxyran were distilled prior to use. A mixture of *cis*- and *trans*-propenyl ethyl ether was prepared in 80% yield from propionaldehyde diethyl acetal.⁸ Gas chromatographic analysis on a 10-ft column of dimethylsulfolane on firebrick at 25° showed the presence of 67% *cis* and 33% *trans* isomers. They were separated on a preparative scale using a 12-ft column of Apiezon J on firebrick, and identified by their infrared and nmr spectra. Isobutenyl ethyl ether was prepared in 82% yield from isobutyraldehyde diethyl acetal. Isopropenyl ethyl ether was prepared in 80% yield by pyrolysis of β -ethoxycrotonic acid.⁴⁰

1,1-Dichloro-2-ethoxycyclopropane (II) was prepared according to Doering and Henderson^{41a} in 50% yield: bp 55° (30 mm) n_D^{20} 1.4450. The nmr spectrum has been analyzed.^{41b}

(35) For a discussion, see E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 149-156; D. Y. Curtin, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **15**, 111 (1954).

(36) Another stepwise mechanism involves anchimeric assistance of the oxygen forming a bridged ion. A similar mechanism was suggested by Schweizer and Parham³⁷ in order to explain the impressive difference in reactivity between the *syn* and *anti* isomers of 7-chloro-2-oxanorcarane. By reversing their structural assignments, however, the results are readily explained by the electrocyclic selection rules discussed above; see also S. J. Cristol, R. M. Sequeira, and C. H. DePuy, *J. Am. Chem. Soc.*, **87**, 4007 (1965).

(37) E. E. Schweizer and W. E. Parham, *ibid.*, **82**, 4085 (1960).

(38) Allylic ions generally retain their configurations: H. L. Goering and R. W. Greiner, *ibid.*, **79**, 3464 (1957); H. L. Goering, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **21**, 109 (1960).

(39) Melting points and boiling points are uncorrected. Infrared spectra were obtained with a Beckman IR 5 or a Perkin-Elmer Model 21 instrument. The nmr spectra were measured with a Varian A-60 instrument, using carbon tetrachloride as solvent and tetramethylsilane as internal standard. The chemical shifts are given in τ values.

(40) M. A. Dolliver, T. L. Gresham, G. B. Kistiakowsky, E. A. Smith, and W. E. Vaughan, *J. Am. Chem. Soc.*, **60**, 440 (1938).

1,1-Dichloro-2-ethoxy-3-methylcyclopropane (IV).—To a stirred slurry of sodium ethoxide, prepared from 6.9 g (0.30 g-atom) of sodium, 19.8 g (0.23 mole) of 1-ethoxy-1-propene, and 150 ml of dry pentane, kept at -60° , was added all at once 44.0 g (0.23 mole) of ethyl trichloroacetate. The reaction mixture was allowed to attain 0° in the course of about 2 hr and was then left stirring at this temperature overnight. Water was added, the organic layer was separated, and the aqueous layer was extracted with pentane. The combined organic layers were dried ($MgSO_4$) and the volatile material was then evaporated. Fractionation through a 40-cm spinning-band column gave 26 g (67%) of compound IV, bp $44-46^\circ$ (12 mm), n_D^{20} 1.4478.

Anal. Calcd for $C_6H_{10}Cl_2O$: C, 42.63; H, 5.96. Found: C, 42.66; H, 5.76.

***cis*-IV.**—A solution of 10.4 g (0.12 mole) of *cis*-1-ethoxy-1-propene, 24 g (0.12 mole) of bromotrichloromethane, and 50 ml of ether was cooled to -70° . To the stirred solution was added dropwise 100 ml of methyl lithium (1.5 M, 0.15 mole) during 50 min. After 1 hr at the same temperature, water was added. The ether layer was separated, the aqueous layer was extracted with ether, and the combined ether layers were dried ($MgSO_4$). The ether was evaporated, and the residue was fractionated through a 40-cm spinning-band column, yielding 11.4 g (56%) of *cis*-IV, bp 44° (12 mm), n_D^{20} 1.4457; gas chromatography showed a purity of more than 98%. The nmr spectrum exhibits the expected resonances due to the methyl and ethyl protons; furthermore, the cyclopropyl hydrogen adjacent to the ethoxy group appears as a doublet centered at 6.64 with $J = 8.5$ cps.

***trans*-IV** was prepared in 50% yield from *trans*-1-ethoxy-1-propene, in the same way as described above for the *cis* isomer: bp 75° (45 mm), n_D^{20} 1.4425. The product was better than 99% pure by gas chromatographic analysis. The nmr spectrum is quite similar to that of the *cis* isomer (see above); however, the doublet for the cyclopropyl hydrogen is centered at 7.02 with $J = 4.8$ cps.

1,1-Dichloro-2-ethoxy-3,3-dimethylcyclopropane (V) was prepared in 56% yield from isobutenyl ether, ethyl trichloroacetate, and sodium methoxide as described for compound IV, bp 57° (13 mm), n_D^{20} 1.4515.

Anal. Calcd for $C_7H_{12}Cl_2O$: C, 45.92; H, 6.61. Found: C, 46.11; H, 6.62.

1,1-Dichloro-2-ethoxy-2-methylcyclopropane (VI) was prepared in 66% yield from ethyl trichloroacetate and sodium methoxide as described for compound IV: bp 68° (30 mm), n_D^{20} 1.4483.

Anal. Calcd for $C_6H_{10}Cl_2O$: C, 42.63; H, 5.96. Found: C, 42.89; H, 5.89.

1-*t*-Butoxy-1-ethoxy-2-propyne (I). **a. From Ethyl Vinyl Ether.**—Dry potassium *t*-butoxide was prepared in the usual way⁶ from 24.0 g (0.6 g-atom) of potassium. A solution of 14.4 g (0.2 mole) of ethyl vinyl ether in 60 ml of pentane was added, and the slurry was cooled in an ice bath. Bromoform (50.6 g, 0.2 mole) was added with stirring during 6 hr, and the reaction mixture was left at room temperature overnight. It was finally heated with reflux for 2 hr, and then water was added. The product was extracted with ether and dried (Na_2CO_3). Fractionation gave 16.5 g (53%) of the acetal I: bp $48-50^\circ$ (10 mm); n_D^{20} 1.4280; ν_{max} 3290, 2130, 1115-1010 cm^{-1} .

Anal. Calcd for $C_8H_{16}O_2$: C, 69.18; H, 10.32. Found: C, 68.86; H, 10.38.

b. From 1,1-Dichloro-2-ethoxycyclopropane (II).—Potassium *t*-butoxide was prepared from 7.4 g (0.19 g-atom) of potassium and 100 ml of *t*-butyl alcohol. The chloride II (24.8 g, 0.16 mole) was added and the solution was heated under reflux and with stirring for 12 hr. Water was added; the product was extracted with ether and dried (Na_2CO_3). Fractionation gave 18.3 g (73%) of the acetal I, bp $40-42^\circ$ (10 mm), n_D^{20} 1.4277. The infrared spectrum was identical with that of the acetal obtained by procedure a.

2-Chloro-1,1-diethoxy-2-propene (III).—Sodium ethoxide was prepared from 3.0 g (0.13 g-atom) of sodium and 50 ml of absolute ethanol. The chloride II (15.5 g, 0.1 mole) was added and the mixture was heated under reflux and with stirring for 48 hr. Part of the ethanol was distilled under reduced pressure through a short Vigreux column, and then aqueous sodium carbonate solution (5%) was added to the residue. The product was extracted with ether and the ether solution was dried (Na_2CO_3). The ether was distilled and the residue was fraction-

(41) (a) W. von E. Doering and W. A. Henderson, *ibid.*, **80**, 5274 (1958); (b) E. B. Whipple and Y. Chiang, *J. Chem. Phys.*, **40**, 713 (1964).

ated to give 12.4 g (75% based on III) of a liquid, bp 70–78° (25 mm), n_D^{25} 1.4210–1.4293. The liquid was mainly the acetal III contaminated with some of the corresponding acetylenic acetal. Refractionation gave the acetal III: bp 78° (25 mm); n_D^{25} 1.4262; ν_{\max} 1630, 1150–1020, 900 cm^{-1} ; nmr, doublets at 4.35 and 4.60 ($=\text{CH}_2$), doublet at 5.20 (CH), multiplet at 6.44 (CH_2), and triplet at 8.92 (CH_3), with peak area ratio 1:1:1:4:6, respectively.

Anal. Calcd for $\text{C}_7\text{H}_{13}\text{ClO}_2$: C, 51.07; H, 7.96. Found: C, 51.67; H, 7.83.

We have not been able to prepare a 2,4-dinitrophenylhydrazone or a semicarbazone from the acetal. With pyridine as base the acetal III was obtained pure in 89% yield.

a. *trans*-2-Chloro-1,1-diethoxy-2-butene (VII) was prepared in 90% yield from a stereoisomeric mixture of chloride IV and sodium ethoxide in ethanol as described above, using 10-hr reaction time: bp 65–67° (12 mm), n_D^{25} 1.4351. A small amount of 1,1-diethoxy-2-butyne was probably formed since the infrared spectrum of the total reaction product shows a weak band at 2250 cm^{-1} .

Anal. Calcd for $\text{C}_8\text{H}_{15}\text{ClO}_2$: C, 53.78; H, 8.46. Found: C, 54.36; H, 8.01.

The acetal readily formed a 2,4-dinitrophenylhydrazone which was recrystallized from ethyl acetate, mp 229–230° dec.

Anal. Calcd for $\text{C}_{10}\text{H}_9\text{ClN}_4\text{O}_4$: C, 42.19; H, 3.19; N, 19.68. Found: C, 42.34; H, 3.37; N, 19.48.

b.—A solution of 16.9 g (0.1 mole) of the chloride *cis*-IV, 10 ml of dry pyridine, and 50 ml of absolute ethanol was heated under reflux for 10 hr. The product was isolated as described above; fractionation gave 14.8 g (83%) of the acetal *trans*-VII: bp 67° (12 mm); n_D^{25} 1.4356; ν_{\max} 1660, 1175–1040 cm^{-1} ; nmr, multiplet at 3.9 ($=\text{CH}$), quartet at 5.22 (CH), multiplet at 6.52 (CH_2), quartet at 8.24 ($=\text{CCH}_3$), and triplet at 8.83 (CH_3).

c.—Heating the chloride *trans*-IV for 24 hr under the same conditions as described under b gave an 81% yield of *trans*-VII, bp 55–56° (6 mm), n_D^{25} 1.4355; the infrared and nmr spectra were identical with those of the product from *cis*-IV.

Reaction of *trans*-VII with Sodium Ethoxide in Ethanol.—Sodium (0.46 g, 20 g-atoms) was converted to sodium ethoxide in 50 ml of absolute ethanol. The acetal (0.71 g, 4 mmoles) was added, and the solution was heated under reflux for 24 hr. The alcohol was partly removed by distillation, and the residue was diluted with water. The product was extracted with pentane and dried (Na_2CO_3). The pentane was evaporated under reduced pressure, leaving 0.4 g of a liquid. The infrared spectrum shows bands at 3250, 2250, and 1960 cm^{-1} indicating that 1,1-diethoxy-3-butyne, 1,1-diethoxy-2-butyne, and 1,1-diethoxy-2,3-butadiene had been formed.

1-*t*-Butoxy-2-chloro-1-ethoxy-3-methyl-2-butene (VIII).—Potassium *t*-butoxide was prepared from 4.7 g (0.12 g-atom) of potassium in 100 ml of *t*-butyl alcohol. To this was added 18.3 g (0.1 mole) of the chloride V, and the mixture was heated under reflux with stirring for 7 hr. The product was worked up as described for compound III. Fractionation gave 15.2 g (69% based on IX) of a liquid, bp 72–76° (7 mm). The infrared spectrum showed that a considerable amount of the corresponding aldehyde, 2-chloro-3-methyl-2-butenal (XXI), was present. Careful fractionation gave practically pure acetal VIII: bp 61–62° (1 mm); n_D^{25} 1.4471; ν_{\max} 1645, 1635, 1195–1020 cm^{-1} .

Anal. Calcd for $\text{C}_{11}\text{H}_{21}\text{ClO}_2$: C, 59.90; H, 9.52. Found: C, 59.15; H, 9.18.

The 2,4-dinitrophenylhydrazone was recrystallized from ethyl acetate: mp 212–214°. Red rhombic crystals were first formed and then needles. The latter, by standing, changed into the rhombic form.

Anal. Calcd for $\text{C}_{11}\text{H}_{17}\text{ClN}_4\text{O}_4$: C, 44.23; H, 3.71; N, 18.75. Found: C, 44.38; H, 3.62; N, 18.58.

2-Chloro-1,1-diethoxy-3-methyl-2-butene (IX) was prepared in 86% yield from the chloride V as described for compound III, with 10-hr reaction time: bp 64–65° (3 mm); n_D^{25} 1.4495; ν_{\max} 1645, 1635, 1150–1020 cm^{-1} ; nmr, singlet at 4.90 (CH), multiplet at 6.50 (CH_2), doublet at 8.13 ($=\text{CCH}_3$), and triplet at 8.83 (CH_3) with peak area ratio 1:4:6:6.

Anal. Calcd for $\text{C}_9\text{H}_{17}\text{ClO}_2$: C, 56.10; H, 8.89. Found: C, 56.10; H, 8.46.

The 2,4-dinitrophenylhydrazone was recrystallized from ethyl acetate, mp 211–213°, and was found to be identical with that obtained from the acetal IX.

The same acetal was prepared in 82% yield using the above procedure, but with dry pyridine as base, while a 72% yield was obtained with sodium carbonate as base.

2-Chloro-1-ethoxy-1-methoxy-3-methyl-2-butene (X).—A mixture of 3.5 g (65 mmoles) of sodium methoxide, 9.15 g (50 mmoles) of the chloride V, and 25 ml of dry dioxane was heated under reflux and with stirring for 8 hr. The product was worked up as described for compound III. Fractionation gave 6.9 g (77%) of the acetal X: bp 81–83° (15 mm); n_D^{25} 1.4576; ν_{\max} 1640, 1150–1000 cm^{-1} .

Anal. Calcd for $\text{C}_8\text{H}_{15}\text{ClO}_2$: C, 53.78; H, 8.46. Found: C, 54.20; H, 8.61.

The acetal formed a 2,4-dinitrophenylhydrazone, mp 212–214°, identical with that prepared from acetal VIII.

Reaction of 1,1-Dichloro-2-ethoxy-2-methylcyclopropane (VI) with Sodium Ethoxide in Ethanol.—Sodium ethoxide was prepared from 8.5 g (0.37 g-atom) of sodium and 100 ml of absolute ethanol. The chloride VI (25.4 g, 0.15 mole) in 10 ml of dimethyl sulfoxide was added and the mixture was heated under reflux with stirring for 8 hr. The product was isolated with ether in the usual way, and the ether was distilled through a 40-cm spinning-band column. The residue was fractionated through the same column, giving two main fractions. Fraction a, 2.2 g, bp 60–67° (40 mm), was shown by gas chromatography to consist mainly of one component. This was obtained pure by preparative gas chromatography and shown to be 2-ethoxy-1-buten-3-yne (XII): bp 103–104°; n_D^{25} 1.4412; $\lambda_{\max}^{n\text{-hexane}}$ 224.5 μ ; ν_{\max} 3260, 2110, 1600, 1270, 1060, and 815 cm^{-1} (lit.²⁶ mp 103.4–103.7°, n_D^{25} 1.4432). Fraction b, 8.2 g, consisted mainly of 3,3-diethoxy-1-butyne (XI): bp 65–67° (40 mm); n_D^{25} 1.4125; ν_{\max} 3260, 2120, 1210–1050 cm^{-1} . It readily formed a 2,4-dinitrophenylhydrazone, mp 181°, $\lambda_{\max}^{\text{CHCl}_3}$ 364 μ (ϵ 24,000) (lit. mp 181°, λ_{\max} 365 μ ⁴³).

In another run, with the same amount of chloride but without dimethyl sulfoxide and a reaction time of 17 hr, 12.1 g of a mixture of compounds XI and XII was obtained, bp 59–66° (25 mm), n_D^{25} 1.4282–4303. This represents a 78% yield when calculated for the ketal XI.

trans-2-Chloro-2-butenal (XIII).—The acetal *trans*-VII (9.5 g, 53 mmoles) and 20 ml of 1 N hydrochloric acid were shaken mechanically for 0.5 hr at room temperature. The product was extracted with pentane and dried (MgSO_4). Evaporation of the pentane and distillation gave 4.85 g (88%) of the aldehyde, *trans*-XIII: bp 57° (20 mm); n_D^{25} 1.4795 (lit.⁴⁴ bp 53–54° (20 mm), n_D^{25} 1.478); ν_{\max} 2785, 1690, 1625 cm^{-1} ; nmr, singlet at 0.60 ($-\text{CHO}$), quartet at 2.87 ($=\text{CH}$), and doublet at 7.90 ($=\text{C}-\text{CH}_3$) with a peak area ratio of 1:1:3.

The 2,4-dinitrophenylhydrazone, mp 229 dec, was identical with that obtained from *trans*-VII.

2-Chloro-3-methyl-2-butenal (XIV) was obtained in 92% yield from the acetal IX by the same procedure as described for XII: bp 64–66° (15 mm); n_D^{25} 1.4976; $\lambda_{\max}^{\text{cyclohexane}}$ 251 μ (ϵ 9300); ν_{\max} 2750, 1680, 1620 cm^{-1} ; nmr, singlets at 0.14 (CHO), 7.68, and 7.87 ($=\text{C}-\text{CH}_3$) with a peak area ratio of 1:3:3, respectively.

Anal. Calcd for $\text{C}_8\text{H}_7\text{ClO}$: C, 50.65; H, 5.95. Found: C, 50.55; H, 5.91.

The 2,4-dinitrophenylhydrazone crystallized from ethyl acetate, mp 213–214°, and was found to be identical with that obtained from the acetal IX.

From V without Isolation of the Acetal.—Sodium ethoxide was prepared from 5.3 g (0.23 g-atom) of sodium in 75 ml of absolute ethanol. The chloride V (36.6 g, 0.2 mole) was added, and the mixture was heated under reflux with stirring for 10 hr. Most of the ethanol was distilled under reduced pressure. The residue was then shaken mechanically with 60 ml of 1 N hydrochloric acid for 0.5 hr at room temperature. The product was extracted with ether and dried (Na_2CO_3). Fractionation gave 20.7 g (88%) of the aldehyde XIV, bp 63° (13 mm), n_D^{25} 1.4972.

2-Chloro-2-propenal (XV) was prepared in 61% yield from the acetal III in the usual way: bp 44° (50 mm); n_D^{25} 1.4710; ν_{\max} 3025, 1580 (C=C), 2810, 1675 (CHO) cm^{-1} (lit.⁴⁵ bp 39–40° (30 mm), n_D^{25} 1.463).

(42) K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946).

(43) G. D. Johnson, *J. Am. Chem. Soc.*, **75**, 2720 (1953).

(44) C. Moureu, M. Murat, and L. Tampier, *Bull. Soc. Chim. France*, [4] **29**, 29 (1921).

(45) C. Moureu and P. Robin, *Ann. Chim. (Paris)*, [9] **15**, 158 (1921).

Reaction of 1,1-Dichloro-2-ethoxy-3,3-dimethylcyclopropane (V) with *n*-Butyllithium.—The chloride V (20.0 g, 0.11 mole) was dissolved in 30 ml of dry ether and cooled to -30° . An ethereal solution (1.3 *M*) of *n*-butyllithium (100 ml, 0.13 mole) was added dropwise with stirring during 1 hr. The reaction mixture was stirred for another 0.5 hr while the bath temperature rose to 10° . Water was added, and the ether layer was separated. The aqueous layer was extracted with a small amount of ether, and the combined ether layers were dried (Na_2CO_3). Evaporation of the ether and fractionation of the residue gave 7.3 g (59%) of impure 1-ethoxy-3-methyl-1,2-butadiene (XVI), bp $55-57^{\circ}$ (65 mm), n_D^{25} 1.4344. Redistillation gave a purer sample: bp 51° (60 mm); n_D^{20} 1.4400; ν_{max} 1960, 1120 cm^{-1} .

Anal. Calcd for C_7H_{12} : C, 74.95; H, 10.78. Found: C, 73.30; H, 10.68.

The allene readily formed a 2,4-dinitrophenylhydrazone, which recrystallized from ethyl acetate as red needles, mp 187° (lit.⁴⁶ mp 179° for the 2,4-dinitrophenylhydrazone of β -methylcrotonaldehyde).

Anal. Calcd for $\text{C}_{11}\text{H}_{12}\text{N}_4\text{O}_4$: C, 50.00; H, 4.58; N, 21.20. Found: C, 49.94; H, 4.66; N, 21.14.

It is also interesting that V underwent a slow reaction with methylithium at room temperature, yielding the allene XVI, as evidenced by the band at 1960 cm^{-1} in the infrared spectrum of the crude product.

Reaction of 1,1-Dichloro-2-ethoxy-3-methylcyclopropane (IV) with *n*-Butyllithium.—The chloride IV was treated with *n*-butyllithium as described for the homolog V. The infrared spectrum of the total distilled reaction product showed no appreciable absorption in the 2000–1900- cm^{-1} region, but strong bands at

2750, 1700, and 1650 cm^{-1} characteristic of an α,β -ethylenic aldehyde.

The mixture gave a 2,4-dinitrophenylhydrazone, mp $187-188^{\circ}$, undepressed on admixture with that of crotonaldehyde.

Kinetic Measurements.—The kinetic runs were carried out in a flask inserted in a constant-temperature bath, accurate within 0.1° . At time intervals aliquots were removed, quenched with water, and titrated with hydrochloric acid using phenolphthalein as indicator. A typical run, as that of the compound V in 95% ethanol with 0.01 *M* sodium ethoxide as base, is given in Table III. The rate constants used for calculations of relative rates were an average value of three or more runs. When the base concentration was varied from 0.01 to 0.5 *M*, the rate constant of V decreased by a factor of 2.

TABLE III

KINETIC MEASUREMENT AT 70°

Time, min	0.01 <i>N</i> HCl, ml	10^3k , min^{-1}
0	5.00	
15	4.50	7.03
60	3.26	7.13
90	2.45	7.92
120	2.06	7.39
150	1.63	7.47
175	1.39	7.32

$$k = (1.23 \pm 0.08) \times 10^{-4} \text{ sec}^{-1}$$

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(46) E. A. Braude and E. R. H. Jones, *J. Chem. Soc.*, 498 (1945).

Study of Epoxy Compounds. VII.^{1,2} Base-Catalyzed Reaction of Substituted Phenyl Glycidyl Ethers with Benzoic Acid

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The base-catalyzed reaction of substituted phenyl glycidyl ethers (PGE) with benzoic acid in the presence of dimethyldodecylamine was studied in various nonaqueous solvents such as xylene and mono- and *o*-dichlorobenzene, and nitrobenzene. The reaction in these solvents was found to be third order, being first order in each of the three reactants. Etherification, hydrolysis, and diesterification did not appear to occur under these conditions. The reaction constant, ρ , is positive and is smaller at higher temperature and larger in the solvents of higher polarity.

A considerable number of ring-opening reactions of epoxides with compounds having an active hydrogen have been studied kinetically. Kinetic studies of various epoxides in basic or neutral solutions have been carried out as for the reactions with water,³⁻⁷ ammonia,⁸⁻¹³ and various amines.^{7,11,13-17} The acid-

catalyzed reactions with water^{3,4,18-21} and amines^{22,23} have been studied for a series of epoxides. Boyd and Marle²⁴ studied the reaction of substituted phenols with ethylene oxide in the presence of corresponding sodium phenoxides in ethyl alcohol, and proposed an ionic mechanism. Patat^{25,26} studied the same reaction

(1) This work was first presented at the 12th Annual Meeting of the Society of Polymer Science, Tokyo, May 1963.

(2) Part VI: Y. Tanaka and H. Kakiuchi, *J. Polymer Sci.*, **A2**, 3405 (1964).

(3) J. N. Brønsted, M. Kilpatrick, and M. Kilpatrick, *J. Am. Chem. Soc.*, **51**, 428 (1929).

(4) A. M. Eastham and G. A. Lathremouille, *Can. J. Chem.*, **30**, 169 (1952).

(5) H. J. Lichtenstein and G. H. Twigg, *Trans. Faraday Soc.*, **44**, 905 (1948).

(6) J. G. Pritchard and F. A. Long, *J. Am. Chem. Soc.*, **79**, 2365 (1957).

(7) L. Smith and T. Nilsson, *J. Prakt. Chem.*, **162**, 63 (1943).

(8) F. Berbé, *Chim. Ind. (Paris)*, **63**, 492 (1950); *Chem. Abstr.*, **47**, 4286 (1953).

(9) P. Ferrero, F. Berbé, and L. R. Flamme, *Bull. Soc. Chim. Belges*, **56**, 349 (1947).

(10) S. Andersson, *Nord. Kemistmötet, Helsingfors*, **7**, 172 (1950); *Chem. Abstr.*, **48**, 7405 (1954).

(11) J. Hansson, *Svensk Kem. Tidsskr.*, **60**, 183 (1948); *Chem. Abstr.*, **43**, 926 (1949).

(12) C. Potter and R. R. McLaughlin, *Can. J. Res.*, **25B**, 405 (1947).

(13) L. Smith, S. Mattsson, and S. Andersson, *Kgl. Fysiograf. Sällskap. Lund, Handl.*, **42**, No. 7, 1 (1946); *Chem. Abstr.*, **41**, 6458 (1947).

(14) N. G. Barker and N. H. Cromwell, *J. Am. Chem. Soc.*, **73**, 1051 (1951).

(15) A. M. Eastham, B. de B. Darwent, and P. E. Beaubien, *Can. J. Chem.*, **29**, 575 (1951).

(16) J. Hansson, *Svensk Kem. Tidsskr.*, **67**, 246 (1955); *Chem. Abstr.*, **49**, 12935 (1955).

(17) J. Hansson, *Svensk Kem. Tidsskr.*, **67**, 263 (1955); *Chem. Abstr.*, **49**, 12936 (1955).

(18) J. G. Pritchard and F. A. Long, *J. Am. Chem. Soc.*, **78**, 2667 (1956).

(19) W. L. Petty and P. L. Nichols, *ibid.*, **76**, 4385 (1954).

(20) L. Smith, G. Wode, and T. Widhe, *Z. Physik. Chem. (Leipzig)*, **180**, 154 (1927).

(21) G. Wode, *Svensk Kem. Tidsskr.*, **40**, 221 (1928); *Chem. Abstr.*, **23**, 2344 (1929).

(22) A. M. Eastham and B. de B. Darwent, *Can. J. Chem.*, **29**, 585 (1951).

(23) A. M. Eastham, *J. Chem. Soc.*, 1936 (1952).

(24) D. R. Boyd and E. R. Marle, *ibid.*, **105**, 2117 (1914).

(25) E. Patat, *Monatsh.*, **83**, 322 (1952).

(26) E. Patat, E. Cremer, and O. Boblester, *J. Polymer Sci.*, **12**, 489 (1954).