2.0 g. (0.053 mole) of lithium aluminum hydride in 100 ml. of anhydrous ether overnight followed by workup in the usual manner lead only to recovered VIII.

1-Formylnortricyclene (IX). The procedure was analogous to that of Lipp.[22] A solution of 5.0 g. (0.04 mole) of VIII in 100 ml. of 10% acetic acid was treated portionwise (10 min.) with 2.7 g. (0.041 mole) of chromic oxide. The mixture was heated on the steam bath for 0.5 hr., made alkaline with potassium carbonate, and steam distilled. The organic layer and ether extracts of the aqueous layer were dried (anhydrous magnesium sulfate) and solvent removed using a Vigreux column. The residue, which distilled at 83–87° (14 mm.), weighed 2.5 g. (50%) and was predominantly the desired aldehyde IX, carbonyl band at 5.95 μ, but was contaminated with some unchanged alcohol VIII. It was not further purified, but a portion was converted to the red 2,4-dinitrophenylhydrazone, m.p. 218–219.5° (recrystallized from 95% ethanol containing some ethyl acetate).

Anal. Calcd. for $C_{14}H_{14}N_4O_4$: C, 55.62; H, 4.67; N, 18.50. Found: C, 55.71; H, 4.77; N, 18.64.

1-Methylnortricyclene (X). The mixture of 20 ml. of diethyleneglycol, 1.9 g. of crude aldehyde (IX), 3 ml. of 85% hydrazine hydrate, and 3.5 g. of potassium hydroxide was refluxed for 1 hr., then distilled until the pot temperature reached 177°. The organic layer of the distillate was dried over anhydrous magnesium sulfate, and gave a single peak in a Perkin-Elmer vapor fractometer, preparative column with didecyl phthalate on firebrick, column temperature 76°. An authentic sample[12] showed identical retention time, and samples thus purified had identical infrared spectra.[13]

2-Chloro-6-(1-hydroxyethyl)norbornane (XIV). To a slurry of 3.7 g. (0.10 mole) of lithium aluminum hydride in 250 ml. of anhydrous ether there was added (2 hr.) a solution of 26.0 g. (0.15 mole) of crude 2-chloro-6-acetylnorbornane (IV), as obtained from the acetylation of nortricyclene, in 250 ml. of anhydrous ether. After 1 hr. of reflux, the mixture was cooled (ice) and hydrolyzed with water and dilute hydrochloric acid. Celite was added, the mixture stirred vigorously, filtered, and ether extracts of the celite-hydroxide residue combined with the organic layer and dried (anhydrous sodium sulfate). After the solvent was removed, the residue gave two main products, 6.8 g. (26%) of 1-(1-hy-

(22) P. Lipp, *Ber.*, **53B**, 769 (1920).

droxyethyl)nortricyclene (XI, *vide infra*), b.p. 55–57° (0.9 mm.), n_D^{25} 1.4858–1.4864 and 13.8 g. (53%) of 2-chloro-6-(1-hydroxyethyl)norbornane (XIV), b.p. 72–77° (0.4 mm.), n_D^{25} 1.5006–1.5040. The latter showed characteristic hydroxyl absorption (2.75 and 3.0 μ) and did not have the characteristic 1-substituted nortricyclene bands at 11.7 and 12.7 μ.

Anal. Calcd. for $C_9H_{15}CCl$: C, 61.88; H, 8.66; Cl, 20.30. Found: C, 62.00; H, 8.63; Cl, 20.35.

Several attempts to convert this chlorohydrin to a tetrahydrofuran (XV), including refluxing with powdered potassium hydroxide, led only to recovered starting material.

1-(1-hydroxyethyl)nortricyclene (XI). Reduction of 1-acetylnortricyclene (VI) with lithium aluminum hydride in the usual manner gave the corresponding alcohol (XI). From 8.0 g. (0.059 mole) of VI and 3.8 g. (0.1 mole) of lithium aluminum hydride in 150 ml. anhydrous ether there was obtained 6.6 g. (82%) of XI, b.p. 63–64° (1 mm.), n_D^{25} 1.4838.

Anal. Calcd. for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.04; H, 10.21.

The hydrochloride of 1-aminomethylnortricyclene (XIII). To a suspension of 0.84 g. (0.0219 mole) of lithium aluminum hydride in 100 ml. of anhydrous ether was added as the solid, in several small portions, 1.0 g. (0.0073 mole) of 1-nortricyclenecarboxamide (XII), and the mixture stirred at room temperature for 3 hr., then hydrolyzed with water and 20% sodium hydroxide according to Gaylord.[23] The ether layer was dried overnight (barium oxide), then treated with anhydrous hydrogen chloride, whereupon the white crystalline hydrochloride of XIII was obtained, 1.05 g. (90%), m.p. 238–239.5° (dec.).

Anal. Calcd. for $C_8H_{14}NCl$: C, 60.19; H, 8.84; N, 8.77; Cl, 22.27. Found: C, 60.21; H, 8.76; N, 8.74; Cl, 22.39.

East Lansing, Mich.

(23) N. G. Gaylord, *Reduction with Complex Metal Hydrides*, Interscience Publishers Inc., New York, 1956, p. 1011.

[Contribution from the Department of Chemistry and Chemical Engineering, Case Institute of Technology]

Addition of Halogens and Halogen Compounds to Allylic Chlorides. II. Addition of Hypochlorous Acid to Allylic Chlorides[1]

J. REID SHELTON and LIENG-HUANG LEE[2]

The addition of hypochlorous acid to allylic chlorides yielded products which were not always consistent with expected results based on a comparison with the addition of hydrogen halide to the same compounds. The addition products observed were: 2,3,3-trichloropropan-1-ol (98%) and 1,1,3-trichloropropan-2-ol (2%) for 3,3-dichloropropene; 2,3,3,3-tetrachloropropan-1-ol for 3,3,3-trichloropropene; 1,1,3-trichloropropan-2-ol and a small amount of 1,1,2,3-tetrachloropropane for 1,3-dichloropropene; 1,1,3-tetrachloropropan-2-ol and 1,1,1,2,3-pentachloropropane for 1,1,3-trichloropropene. No detectable allylic isomerization was found to accompany the addition of hypochlorous acid to 3,3-dichloropropene and 3,3,3-trichloropropene.

Introduction. The products obtained by addition of hydrogen halides to certain allylic chlorides have

(1) This is an abstract of a part of the doctoral thesis submitted by Lieng-huang Lee.

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been described in Part I[3] of this series on the addition of halogens and halogen compounds to allylic chlorides. This second paper of the series is concerned with the orientation of the addition of hypochlorous acid to these same allylic chlorides.

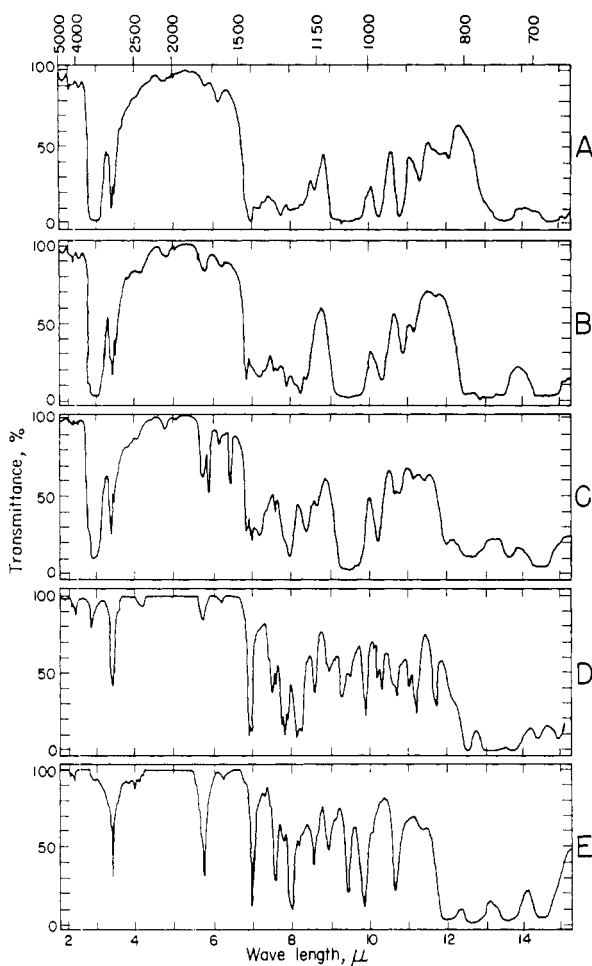(3) Part I, *J. Org. Chem.*, **23**, 1876 (1958).

Fig. 1. Infrared spectra of the hypochlorous acid addition products: A, 2,3-dichloropropan-1-ol from allyl chloride; B, 2,3,3-trichloropropan-1-ol from 3,3-dichloropropene; C, 2,3,3,3-tetrachloropropan-1-ol from 3,3,3-trichloropene; D, 1,1,3-trichloropropan-2-ol and 1,1,2,3-tetrachloropropane from 1,3-dichloropropene; E, 1,1,1,3-tetrachloropropan-2-ol and 1,1,1,2,3-pentachloropropane from 1,1,3-trichloropropene. (Cell thickness: 0.02 mm.)

It is well known[4−6] that the OH group adds at a different position in allyl chloride as compared to propene. Thus the major product with propene is 1-chloropropan-2-ol (90%) while with allyl chloride the isomer formed in largest amount is 2,3-dichloropropan-1-ol (70%). The isomer ratios reported[4−6] were obtained by use of a kinetic analysis based on a marked difference in the rates at which the two isomers obtained in a given reaction react with sodium hydroxide solution.

De la Mare and Pritchard[6] studied the addition of hypochlorous acid to allyl chloride and allyl alcohol. The rate determining electrophilic reagents were found to be Cl^+ and its hydrate, $ClOH_2^+$, which are of ionic nature. By using a radioactive chlorine isotope, they were able to show that a

(4) L. Smith and S. Skyle, *Acta. Chem. Scand.*, 4, 39 (1950).

(5) L. Smith, *Z. physik. Chem.*, 92, 717 (1918).

(6) P. B. D. De la Mare and J. G. Pritchard, *J. Chem. Soc.*, 3910, 3990 (1954).

small amount (12%) of the 2,3-dichloropropan-1-ol came from exchange of the substituent of the compound and the entering group through the intermediate chloronium ion. Another possibility postulated to account for the observed products was migration of the entering group from the point of initial attack to the neighboring carbon due to an electrostatic interaction of the substituents. The tendency for this migration increases as the reagents varied from HCl to HOCl to ICl. However, these effects of exchange and migration did not appear to be sufficient to account for the amount of primary alcohol formed in the addition of HOCl to these allylic compounds.

Discussion. The present study attempts to correlate the effect of substituents upon the orientation of the addition of HOCl to allylic halides. Allyl chloride, 3,3-dichloropropene, 3,3,3-trichloropropene, 1,3-dichloropropene, and 1,1,3-trichloropropene were employed for this purpose. The methods of preparation are given in Part I.[3]

In addition to the kinetic method of analysis used in the case of additions to 3,3-dichloropropene, the structures of the chlorohydrins obtained from the additions of hypochlorous acid to the allylic chlorides were identified with the aid of infrared analysis. Those chlorohydrins with the hydroxyl groups at the terminal carbon resemble other primary alcohols in the infrared spectra with a broad band between 1010 and 1090 cm.$^{-1}$ as shown in Figures 1A, 1B, and 1C. The chlorohydrins with the hydroxyl group at a secondary carbon resemble other secondary alcohols with a band at 1110 to 1115 cm.$^{-1}$ as shown in Figures 1D and 1E. The two types of chlorohydrins are thus readily distinguishable.

The chlorohydrin obtained in largest amount in the case of allyl chloride was thus the isomer in which the alcohol is primary as previously noted.[4−6] While this product has been accounted for in part by migration and exchange reactions,[6] the observed results can be explained independently of these effects on the basis of the inductive effect of the chlorine already present upon the polarization of the double bond. This interpretation is supported by the comparable products obtained with the di- and trichloropropenes which have even stronger inductive effects due to the additional allylic halogen.

The following addition products of hypochlorous acid to allylic chlorides were found: 2,3,3-trichloropropan-1-ol (98%) and 1,3,3-trichloropropan-2-ol (2%) for 3,3-dichloropropene; 2,3,3,3-tetrachloropropan-1-ol for 3,3,3-trichloropropene; 1,1,3-trichloropropan-2-ol for 1,3-dichloropropene; and 1,1,1,3-tetrachloropropan-2-ol for 1,1,3-trichloropropene; and 1,1,1,3-tetrachloropropan-2-ol for 1,1,3-trichloropropene. No allylic isomerization was observed to accompany the addition of hypochlorous acid to 3,3-dichloropropene and 3,3,3-trichloropropene.

The isomeric di- and trichloropropenes containing vinylic halogen thus also gave addition products with hypochlorous acid which were contrary to those predicated by analogy to the products obtained by addition of hydrogen halides. In these cases, the inductive effects of both vinylic and allylic halogens reduce the electron density around the central carbon and thus direct the attack by the positive reagent to the carbon bearing the vinylic halogen so that the Cl^+ becomes attached at that point. The vinylic halogen probably exerts a stronger influence upon the over-all effect than the allylic halogen, since the contribution of the inductive effect of the vinylic halogen is greater, as will be shown in a future paper (Part III) on relative rates of halogen addition.

$$Cl \longleftarrow CH{=}CH{-}CH_2 \longrightarrow Cl$$
$$\delta+$$
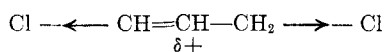
Addition of hypochlorous acid to 1,3-dichloropropene and 1,1,3-trichloropropene was comparatively more difficult than the addition to 3,3-dichloropropene and 3,3,3-trichloropropene. This is presumably due to a combination of steric and inductive effects. During the longer period of contact of these compounds with hypochlorous acid, some decomposition of hypochlorous acid took place to give chlorine which added to the double bond in competition with the hypochlorous acid.

The presence of the small amount of secondary trichlorohydrin in the mixture of the addition products of 3,3-dichloropropene was found by a careful fractional distillation. The first fraction showed the band at 1110 to 1115 cm.$^{-1}$, which corresponds to a secondary alcohol group. The kinetic analysis was used to determine the composition of the mixture as described in the experimental part. It was assumed that the rates of reaction of sodium hydroxide solution with the isomeric trichlorohydrins are also sufficiently different so that the same method could be used as previously established for dichlorohydrins.[6]

The products obtained in this study, together with results reported in the literature for allyl chloride, indicate that the mode of addition of hypochlorous acid to allylic chlorides is primarily determined by the inductive effect of the halogen already present. This is in contrast to the results obtained by addition of hydrogen halides in which case the orientation of the addition appeared to be influenced to a greater extent by electromeric and hyperconjugative effects (Part I).[3]

The relations between the effect of the nature and reactivity of the reagent and the effect of various electronic factors upon the orientation of addition will be discussed in the final paper of this series.

EXPERIMENTAL

A. Addition of hypochlorous acid to allylic chlorides. Materials: 3,3-Dichloropropane (b.p. 81–82°, 742.5 mm.), 3,3,3-trichloropropene (b.p. 45°, 103 mm.), 1,1,3-trichloropropene

(b.p. 132°, 760 mm.), and 1,3-dichloropropene (b.p. 104–112°) were obtained as described in Part I.[3] The hypochlorous acid solution (b.p. 39–40°, 50 mm.) contained 0.05 mole or 0.25% of HOCl.

For the following experiments the allylic chloride (1.2 mole) was gradually added to a flask containing the required amount (1 mole) of hypochlorous acid. Vigorous stirring was required during the time of addition. As the solution lost its bleaching power on litmus paper, the stirring was stopped. The organic layer was separated and washed with water. The aqueous layer and the washings were saturated with sodium chloride and extracted with ether. The extract was dried over anhydrous sodium sulfate. After evaporation of the ether, the remaining portion was combined with the organic layer. The mixture was fractioned and subjected to analysis.

3,3-Dichloropropene. The organic portion (19.5 g.) was fractionated: (a) 30–80°, 10 mm.—2 g.; (b) 83–92°, 10 mm. —13.6 g. Fraction (a) proved to be a mixture of 2,3,3-trichloropropan-1-ol and 1,1,3-trichloropropan-2-ol, although the 1,1,3-trichloropropan-2-ol was not isolated as a pure product. Fraction (b) contained mainly 2,3,3-trichloropropan-1-ol and a small amount of the oxidation product. The residue left in the flask was a high boiling oxidation product. Fraction (b) was redistilled at 3 mm. to give 2,3,3-trichloropropan-1-ol which boiled at 68–69°, 3 mm., n_D^{20} 1.5038, d_4^{20} 1.5094 (lit.: b.p. 95–96°, 14 mm., n_D^{25} 1.5029, d^{15} 1.5059).[7]

Anal. Calcd.: C, 22.0; H, 3.0; Cl, 65.2. Found: C, 22.2; H, 3.1; Cl, 65.2.

3,3,3-Trichloropropene. The organic portion (15.8 g.) was fractionated: (a) b.p. 84.5–85.5°, 5.5 mm.—8.8 g.; (b) b.p. above 85.5°—1.5 g. Fraction (a) was found to contain 2,3,3,3-tetrachloropropan-1-ol and a small amount of 2,3,3,3-tetrachloropropanal. Fraction (b) contained a trace of high boiling ester. Fraction (a) was redistilled to give 2,3,3,3-tetrachloropropan-1-ol (b.p. 66–67°, 2 mm.) which crystallized on standing to needle-like crystals (m.p. 38–40°). The supercooled liquid had a refractive index of n_D^{20} 1.5041 (lit.: m.p. 38–39°, b.p. 47°, 0.1 mm.).[7]

Anal. Calcd.: C, 18.2; H, 2.0; Cl, 70.7. Found: C, 18.2; H, 1.7; Cl, 71.2.

1,3-Dichloropropene. The organic portion was fractionated: (a) b.p. 45°, 8.5 mm.; (b) b.p. 50°, 8.5 mm., n_D^{20} 1.4920. Both fractions contained the same compounds, except that fraction (a) was not as pure as (b). The compounds were mainly 1,1,3-trichloropropan-2-ol and small amounts of 1,1,3-trichloropropan-2-one and 1,1,2,3-tetrachloropropane.

1,1,3-Trichloropropene. The organic portion was fractionated: (a) b.p. 30–42°, 2 mm., n_D^{20} 1.4958; (b) b.p. 42–50°, 2 mm., n_D^{20} 1.5079 and (c) b.p. 50–52°, 2 mm., n_D^{20} 1.5080. Fraction (a) was the unreacted compound; fraction (b) was 1,1,1,3-tetrachloropropan-2-ol (lit.: b.p. 87–90°, 14 mm., n_D^{20} 1.5145)[8] and a small amount of 1,1,3-trichloropropene. Fraction (c) contained a small amount of 1,1,1,3-tetrachloropropan-2-ol and 1,1,1,2,3-pentachloropropane (lit.: b.p. 64–65°, 8 mm., n_D^{20} 1.5105).[9] A trace amount of the ketone, 1,1,1,3-tetrachloropropan-2-one, was found as a result of the oxidation of 1,1,1,3-tetrachloropropan-2-ol.

B. *Kinetic analysis of the addition products of 3,3-dichloropropene. Preparation of sample.* The addition of hypochlorous acid (1 mole, 8 g. in 3280 ml. of H_2O) to 3,3-dichloropropene (1.2 mole, 20 g.) was carried out according to the previously mentioned procedure. Special care was taken to prevent oxidation of the product. A mixture of trichlorohydrins (17.5 g.) was obtained. Infrared analysis indicated that the

(7) H. J. Prins, *Rec. trav. chim.*, **72**, 551, 867 (1953).

(8) H. Meervwin, B. v. Bock, Br. Kirschnick, W. Lenz, and A. Migge, *J. prakt. Chem.*, **147**, 211 (1936).

(9) A. N. Nesmeyanov, R. Kh. Freidlina, and V. I. Firstov, *Izvest. Akad. Nauk S.S.S.R.*, *Otdel. Khim. Nauk* **1951**, 505; *Chem. Abstr.*, **46**, 7034 (1952).

TABLE I

RESULT OF KINETIC ANALYSIS OF TRICHLOROHYDRINS

Time (min.)	7	12	20	30	40	50	60	80	100
Titre (ml.)	1.03	1.15	1.37	1.57	1.70	1.83	1.96	2.10	2.25
$a - x (M)$	0.01770	0.01674	0.01500	0.01340	0.01236	0.01134	0.01030	0.00918	0.00798
$\frac{1}{a - x} (M)^{-1}$	56.5	59.5	66.5	74.5	81.0	88.0	97.0	109.0	125.5

mixture did not contain any other impurity. This mixture was used for the kinetic analysis.

Kinetic determination.[6] A sample bottle containing 0.3253 g. (0.2 ml.) of the mixture of trichlorohydrins was dropped into 50 ml. of alcohol solution. The corrected volume of the final mixture was 50.2 ml. To this mixture, 50 ml. of 0.0398N alkali was added at 25°. At intervals, 5 ml. samples were taken with the aid of a syringe and added to 2.5 ml. of 0.0518N hydrochloric acid. The solution was back-titrated with 0.0398N alkali.

The data are summarized in Table I. The plot of $1/a - x$ against t was used to find the composition of the mixture. A straight line with a slope k_2 gave an intercept at $1/a$ on the $1/a - x$ axis. The percentage of 2,3,3-trichloropropan-1-ol was obtained by comparing the "a" value with the known total concentration of the mixed trichlorohydrins.

The values found were: slope, $k_2 = 0.74$ (liter) (mole)$^{-1}$ (min.)$^{-1}$; intercept, $\frac{1}{a} = 51.4M^{-1}$; a (calcd.) $= 0.01946M$; a' (known total concentration) $= 0.01986M$; 2,3,3-trichloropropan-1-ol (98%); 1,1,3-trichloropropan-2-ol (2%).

[CONTRIBUTION FROM FRICK LABORATORY, PRINCETON UNIVERSITY]

The Solvolysis of 4,4-Dimethylcholesteryl p-Toluenesulfonate

ROBERT M. MORIARTY[1] AND EVERETT S. WALLIS

The solvolysis of 4,4-dimethylcholesteryl p-toluenesulfonate (I) was carried out in 60% aqueous acetone in the presence of potassium acetate. Under these conditions cholesteryl p-toluenesulfonate rearranges to 3,5-cyclocholestan-6β-ol ("*i*-cholesterol"). In the case of 4,4-dimethylcholesteryl p-toluenesulfonate no 3,5-cyclosterol was obtained. Nearly 70% of the product was a mixture of isomeric, conjugated dienes (II). Twenty per cent of the product was an A-ring contracted alcohol for which structure III is proposed and 7% 4,4-dimethylcholesterol (IV) was also obtained. A preliminary study of the rate of solvolysis indicated that the rate of acetolysis is 10 times faster than that of cholesteryl p-toluenesulfonate. The mechanistic implications of these results are discussed.

A general reaction of 3β-hydroxy-Δ⁵-sterols is solvolysis *via* an intermediary homoallylic type carbonium ion to yield a 3,5-cyclosteroid as the kinetically determined product of the reaction.[2] Winstein and Adams have shown this process to be a case of neighboring group participation of the π-electron system at carbon atoms C_5–C_6 in the rate determining ionization step. This postulate accounted for the retention of the β-configuration at C_3 and the solvolytic rate enhancement of this compound compared to the saturated cholestanyl tosylate. These authors chose to represent the intermediate ion by formula (VII).

If the solvolytic reaction medium is buffered with an added salt such as potassium acetate, the product of kinetic control is formed. If no buffer is added the product resulting from thermodynamic control is formed, namely 3β-substituted-Δ⁵-com-

VII

I → III

II   IV
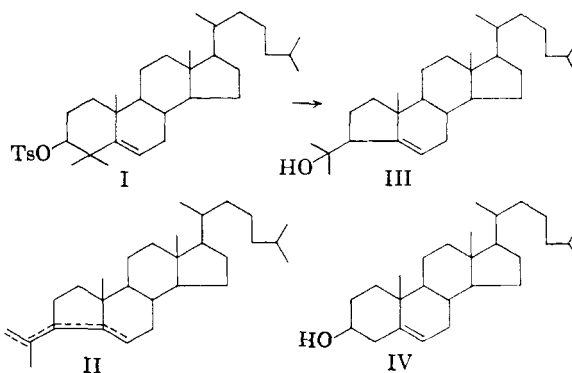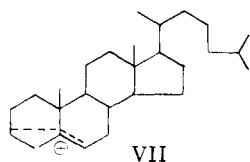
(1) Allied Chemical and Dye Corporation Fellow 1958–59.
(2) (a) E. S. Wallis, E. Fernholz and F. T. Gephart, *J. Am. Chem. Soc.*, **59**, 137 (1937). (b) E. G. Ford and E. S. Wallis, *J. Am. Chem. Soc.*, **59**, 1415 (1937). (c) M. M. Hafez, G. Halsey and E. S. Wallis, *Science*, **110**, 474 (1949). (d) S. Winstein and R. Adams, *J. Am. Chem. Soc.*, **70**, 838 (1948). (e) C. W. Shoppee, *J. Chem. Soc.*, 1147 (1946).