Anal. Calcd. for $C_5H_8O_4$: carbonyl value, 0.76 equiv./100 g.; mol. wt., 132. Found: carbonyl value,[13] 0.75 equiv./100 g.; mol. wt. (ebull., benzene-water azeo.), 134.

On standing for 3 weeks, the distilled product had crystallized to the solid dimer, m.p. 115–116°; after recrystallization from acetone, m.p. 131–132° (lit.[15] m.p. 118.5°). The infrared spectrum of this product (Nujol mull) showed strong absorption for hydroxyl (2.90 μ) and either ester or aldehyde carbonyl (5.78 μ); ether-oxygen absorption was not clearly distinguishable.

Anal. Calcd. for $C_{10}H_{16}O_8$: C, 45.45; H, 6.1; carbonyl (combined) value, 0.76 equiv./100 g.; mol. wt., 268. Found: C, 45.4; H, 6.0; carbonyl[13] value (at 60° for 2 hours), 0.78 equiv./100 g.; mol. wt. (ebull., dioxane), 235.

Glycerol α-Acetate.—β-Acetoxylactaldehyde (monomeric liquid) (6.5 g.) in 200 ml. of ethanol was hydrogenated at 50 p.s.i.g. and 25° with Pd-on-carbon catalyst. After the one equivalent of hydrogen had been absorbed, the catalyst was removed by filtration and the solvent distilled under reduced pressure. Claisen-distillation of the residue gave 5.8 g. (89%) of glycerol α-acetate, b.p. 134–135° (4 mm.), $n^{20}D$ 1.4490 (lit.[16] b.p. 129–131° (3 mm.), $n^{20}D$ 1.4500).

Anal. Calcd. for $C_5H_{10}O_4$: C, 44.8; H, 7.5; sapon. equiv., 134; α-glycol value, 0.75 equiv./100 g. Found: C, 44.6; H, 7.6; sapon. equiv., 135; α-glycol value,[14] 0.73 equiv./100 g.

Reaction with Methanol.—A solution of 36 g. (0.50 mole) of glycidaldehyde in 100 ml. (2.5 moles) of methanol was added to a solution of 5 ml. of sulfuric acid in 1400 ml. of methanol. The mixture warmed by itself to 40° and was then allowed to cool to room temperature overnight. After adding barium carbonate to neutralize the acid, the mixture was filtered through filter aid and concentrated to low volume on the steam-bath. Claisen-distillation of the residue afforded 57.6 g. (77%) of product, b.p. 60–62° (2 mm.), $n^{20}D$ 1.4253, whose analysis was in agreement for **β-methoxylactaldehyde dimethyl acetal.**

Anal. Calcd. for $C_6H_{14}O_4$: C, 48.0; H, 9.4; hydroxyl value, 0.67 equiv./100 g. Found: C, 47.9; H, 9.4; hydroxyl value ($LiAlH_4$), 0.67 equiv./100 g.

The unneutralized product from a similar preparation with 9.0 g. (0.125 mole) of glycidaldehyde was freed of unreacted methanol and diluted with water to a volume of 100 ml. The solution was brought to 0.26 *N* acidity by the addition of 0.50 ml. of sulfuric acid, and allowed to stand at room temperature. Hydrolysis of the acetal was followed by a modified α-glycol procedure[17] which quantitatively determines α-hydroxyaldehydes. A constant value of 0.113 equiv./100 ml. of α-hydroxyaldehyde was reached after 9 days, indicating that the hydrolyzed product was at least 90% β-methoxylactaldehyde. On this basis, the distilled β-methoxylactaldehyde dimethylacetal obtained in the preceding experiment may have contained some of the isomer, α-methoxyhydracrylaldehyde.

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[15] H. O. L. Fischer and E. Baer, *Ber.*, **65**, 341 (1932).

[16] H. A. Schuette and J. T. Hale, THIS JOURNAL, **52**, 1978 (1930).

[17] The periodic acid method for α-glycols (ref. 14) was modified by using sodium periodate in buffered neutral solution. With this reagent, the theoretical values were obtained with glyceraldehyde and other α-hydroxy aldehydes.

[CONTRIBUTION FROM THE NATIONAL RESEARCH COUNCIL, OTTAWA 2, CANADA]

Co-catalysis in Friedel–Crafts Reactions. III. Reaction between 2-Butene and Anhydrous Perchloric Acid

BY STEPHEN J. TAUBER* AND A. M. EASTHAM

RECEIVED FEBRUARY 16, 1960

The preparation and handling of anhydrous perchloric acid in a vacuum system are described. Reaction of the acid with *cis*-2-butene in ethylene dichloride solution leads to very rapid absorption of two or three moles of olefin per mole of acid, but the rate of isomerization of the olefin is very slow. The spectrum of the reaction mixture shows three absorption bands in the visible region, each apparently corresponding to a different compound or complex, but no structures have been assigned to the chromophores.

The concept of co-catalysis in Friedel-Crafts reaction was put forward by Polanyi, Evans and coworkers[1] to explain the results of their studies of isobutylene polymerization. They considered that the coördination compound of the catalyst and cocatalyst was a very strong acid which initiated polymerization by protonation of the olefin, *i.e.*

$$BF_3 + H_2O \rightleftarrows BF_3{\cdot}OH_2 \xrightarrow{>C=C<} >CH{-}C^{+}< \;.....\; BF_3^{-}OH$$

It has become increasingly apparent in recent years that this simple scheme is inadequate because the reaction rates of a number of processes are dependent upon higher powers of the catalyst concentration than would be expected from the above equation. In previous papers we have reported some attempts to study the catalyst systems by measuring the rates of isomerization of *cis*- and *trans*-2-butenes brought about by boron fluoride and water.[2] The results of those experiments suggested that the rate of isomerization was given by the expression

$$dI/dt = k(BF_3)(BF_3{\cdot}H_2O)(\text{butene})$$

but subsequent experiments indicate that the order in butene may be less than one.

Concurrently with these studies we have been attempting a more direct test of the Polanyi hypothesis by employing perchloric acid as the catalyst. Because of the experimental difficulties, progress has been very slow, but the preliminary results now seem worth reporting. Perchloric acid is probably the only very strong, non-nucleophilic acid suitable for this purpose because its preparation and properties permit it to be handled entirely within a vacuum system while its solubility in numerous organic solvents should permit a study of its reactions. Unfortunately, the acid reacts readily, even in the anhydrous state, with mercury and with stopcock grease so must be handled when possible in a completely closed system using break seals for transferring materials.

Experimental

The apparatus devised for preparing and manipulating the acid is shown in Fig. 1. The method of preparation

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* N.R.L. Postdoctorate Fellow, 1957–1959.

(1) A. G. Evans and J. Polanyi, *J. Chem. Soc.*, 252 (1947).

(2) A. M. Eastham, THIS JOURNAL, **78**, 6040 (1956); J. M. Clayton and A. M. Eastham, *ibid.*, **79**, 5368 (1957).

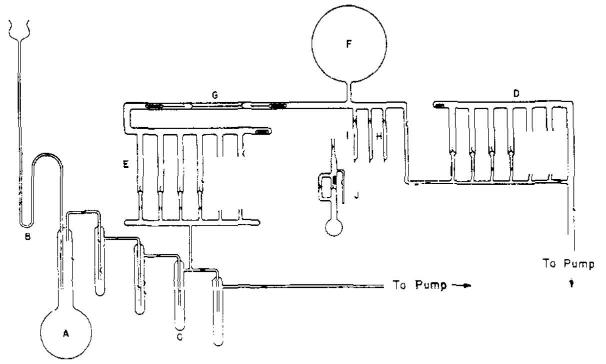

Fig. 1.—Apparatus for the preparation of anhydrous perchloric acid.

was essentially that of Smith.[3] Commercial 70% perchloric acid was run into flask A and was followed by fuming sulfuric acid. The inlet tube was then sealed by freezing a little of the sulfuric acid in bend B, the reaction mixture was frozen down and the apparatus thoroughly pumped out. The perchloric acid was distilled into the first trap and then, after freezing down, the reaction flask was cut off the system. The acid was distilled through the remaining traps so as to leave a middle fraction attached to the system in trap C. The acid is a clear, water-white, mobile liquid which can be kept for at least a week without discoloring, if cooled to a low temperature after use. It gives a negative test for sulfate with barium ions and probably contains very little water both because of the method of preparation and because the monohydrate is a solid of low vapor pressure.

When removing samples of acid from the reservoir C the apparatus was first pumped down to a high vacuum through one of the break seals at D and then sealed off again. A constant temperature bath, usually at 0°, was placed around the reservoir and acid allowed to evaporate through a break seal at E into a system F of known volume. After allowing time for equilibration, flow through the capillary tube G was restricted by inserting the two close-fitting needles (in later experiments glass valves were used) and the two sides of the apparatus were rapidly frozen down with liquid nitrogen at C and H. In preliminary experiments the small vials at H were designed with tips which could be broken under the surface of water so the acid could be titrated. For studying reactions, the vials were replaced by vessels of the type shown at J. Butene and solvent (ethylene dichloride), prepared as previously described,[2] were distilled into the reactor bulb on a separate vacuum system and the by-pass sealed. The reactor was then sealed to the perchloric acid system, the acid was condensed into the side arm and the whole then cut off the system. Mixing of the reactants was obtained by breaking the seal when desired and shaking. For spectrographic studies the reactor bulb was replaced with a cell (1 cm. × 1 cm.) made from precision-bore square Pyrex tubing.

The samples of acid obtained in this way were quite reproducible (about ±1 to 2%). By weighing the vials before and after the titrations, the weight of perchloric acid was obtained and the equivalent weight found to be about 102 (theoretical 100.5), but it seemed desirable to determine the molecular weight as well to make certain that the product was not chlorine heptoxide. To this end a manometer was introduced into the system and, though the mercury became dirty rather quickly, appeared to give satisfactory pressure readings for this purpose. The ratio, molecular weight/equivalent weight, was found to have a value of 0.9 indicating that the acid was in fact perchloric, a conclusion confirmed by calculating the vapor pressure of the acid (from the titrations and the known volume of the system) and comparing it with the vapor pressure of chlorine heptoxide as reported by Goodeve and Powney[4] (Fig. 2).

In measuring the uptake of butene by solutions of perchloric acid, the use of stopcocks and manometers could not be avoided so the experiments were conducted in such a way that these parts were first filled with butene vapor. The amount of perchloric acid reaching the mercury by diffusion through this vapor appeared to be insignificant.

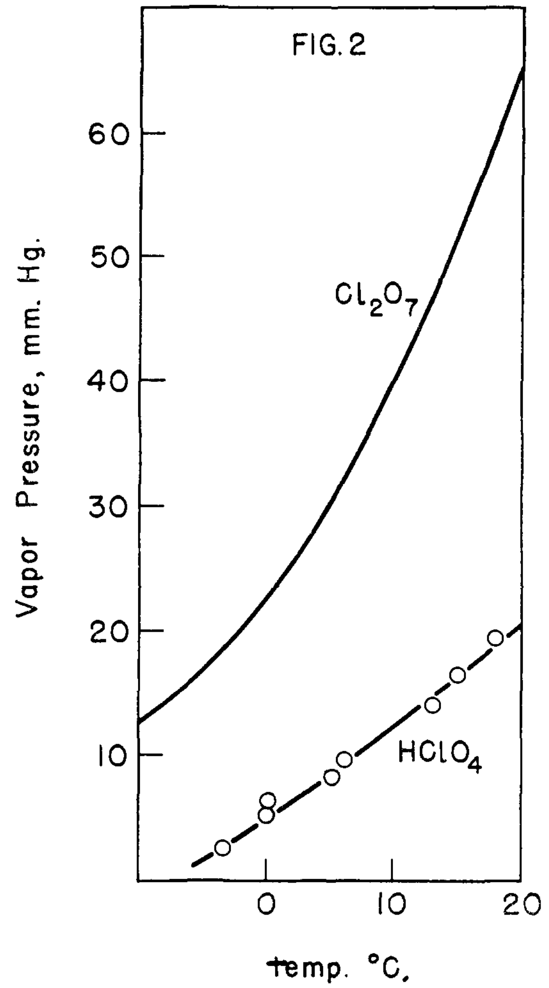

Fig. 2.

Results

When excess *cis*- or *trans*-2-butene reacts with perchloric acid the solution immediately becomes bright yellow in color. The color is rapidly and completely discharged by water if added within a few hours, but on prolonged standing a more permanent color develops. If one attempts to titrate the acid in the system after adding water, it is found that even with very vigorous stirring the neutralization is not rapid but appears to be governed by hydrolysis of an unstable compound or complex in the non-aqueous phase. In a little time, however, quantitative reaction of the acid is obtained and analysis of the aqueous phase for perchlorate ion, by precipitation of the potassium salt from ethanol, accounts for about 95% of the acid added to the original reaction mixture. X-Ray analysis of the recovered salt shows it to be pure potassium perchlorate, so it is clear that by far the greater part of the perchlorate ion passes through these transformations unchanged. The results suggest that an initial butene–perchloric acid colored complex is converted by water to some sort of alkyl perchlorate or else that a colored alkyl perchlorate is colorless on hydration.

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[3] G. F. Smith, THIS JOURNAL, **75**, 184 (1953).

[4] C. F. Goodeve and J. Powney, *J. Chem. Soc.*, 2078 (1932).

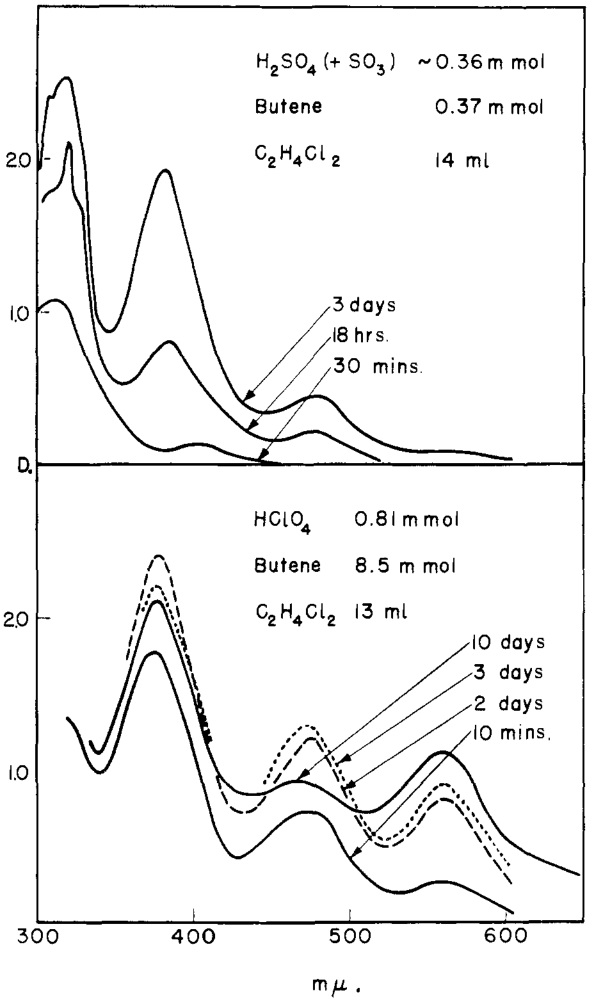


Fig. 3.—Spectra of butene-acid mixtures in ethylene dichloride.

When perchloric acid (0.1–1.0 *m*) in ethylene dichloride reacts with a 3–5-fold molar excess of *cis*-butene at 20° under conditions where the butene pressure can be observed, an immediate absorption of between 2 and 3 mols of butene per mol of acid is observed. This initial reaction is substantially complete in about a minute and is followed by a very slow but seemingly significant pressure *rise* in the system. Quenching these reactions after 1, 17 and 90 hours with dry ammonia leads to the recovery of 75, 80 and 65%, respectively, of the added acid as ammonium perchlorate. The rate of conversion of *cis*- to *trans*-2-butene was followed by sampling the gas above the reaction mixture and analyzing it by gas chromatography on a silver nitrate–glycerol column. In a 0.8 molar solution of acid the isomerization is about half complete in four days which, assuming direct dependence of the rate upon acid concentration, is slower than the isomerization by BF_3–H_2O, by a factor of $10^{-4} - 10^{-5}$. It seems not unlikely that the slow rate of isomerization will prove to be related to the slow change in the absorption spectrum while the slow increase in pressure over the reaction mixture may be due simply to the higher vapor pressure of the *trans* isomer.

A fairly typical absorption spectrum of the colored solution produced from perchloric acid and butene in ethylene dichloride is shown in Fig. 3. The strong peak at 380 mμ grows steadily for two or three days and then declines. A second peak at 475 mμ shows similar though not identical development, while a third at 560 mμ increases steadily over the 10-day period of the experiment and a fourth at 670 mμ is barely detectable. The intensity of the absorption increases with increasing concentration of acid and with an increasing value of the butene/$HClO_4$ mole ratio. The curves shown are for a ratio of about ten at a perchloric acid concentration of about 0.06 *m*. If the ratio is increased to twenty at the same acid concentration, the optical densities are sharply increased to at least double those shown, but the intensities of the three peaks do not change equally. When the butene/acid ratio is reduced to five or lower, the peak at 380 mμ is not markedly altered in ultimate intensity, but the remaining peaks do not develop to nearly the same extent; at ratios of one or lower the 380 mμ peak is very slow to develop. The three peaks clearly correspond to three different compounds or complexes, at least one of which may be in equilibrium with free butene. When the ratio is reduced still further, to 0.25, the peak at 380 mμ disappears and a new one appears at 345 mμ.

A suspension of sulfuric acid (containing a trace of SO_3) in ethylene dichloride reacts with butene to give a bright yellow organic layer with a spectrum remarkably like that obtained from perchloric acid (Fig. 3). The colored solutions obtained from sulfuric acid and olefins are often attributed to oxidation products but this explanation seems inadequate here. No visible colors were obtained from butene with trichloroacetic, trifluoroacetic or toluenesulfonic acid.

Attempts to isolate reaction products after quenching the butene–perchloric acid reactions with water have so far proved unsuccessful. There seems to be a small amount of non-volatile residue (possibly polymer), a trace of a compound resembling dibutyl ether in the gas chromatogram and almost certainly some 2-butanol, although no solid derivatives of this alcohol have been obtained. A 3,5-dinitrobenzoate obtained from one reaction mixture had an almost identical infrared spectrum to that expected from the derivative of 2-butanol but after repeated recrystallization had a melting point of only 67° instead of the required 74°, and analysis gave low values for both carbon and hydrogen. In mixed melting points with the corresponding derivative of 1-butanol it showed a large depression. This work has been hindered so far by our reluctance to use more than a few milligrams of perchloric acid in each experiment, but as no violent reactions have yet been observed an attempt will be made to deal with larger quantities of materials.[4a]

(4a) In very recent experiments a few violent explosions have occurred in these reactions. Except in the design of the break seals the experiments seem identical to those conducted without incident over the past two or three years so we are unable to account for the change in behavior. The explosions occur at the moment of mixing even when the perchloric acid is kept frozen and the butene-solvent mixture is added at the melting point of the mixture.

Discussion

The results of these experiments, limited though they are, lead to one or two interesting conclusions. The very low rate of isomerization of the olefin indicates that if the rapid initial absorption of olefin occurs through a carbonium ion intermediate, then the carbonium ion formation is not reversible. This conclusion, though seemingly contrary to the usual concepts of organic chemistry, was also forced upon Price and Berti[5] by their studies of the BF_3–D_2O catalysis of stilbene polymerization and upon Purlee and Taft[6] by their observations of the hydration of olefins in sulfuric acid solutions. It is a particularly difficult conclusion in the present case because 2-butene does not polymerize rapidly and it is difficult to conceive of other reactions which could remove the carbonium ion as rapidly as it forms. However, as two or three molecules of butene seem to be taken up very rapidly, stabilization of a carbonium ion is not impossible. Taft, *et al.*,[7] suggested as a solution to this problem that the initial reaction product is a π-complex which then slowly isomerizes, in a rate-controlling step, to a carbonium ion which undergoes further rapid reaction. However, this view is directly opposite to that of Evans and co-workers (see below) who believe that an initially formed carbonium ion isomerizes to a π-complex.

The other interesting feature of the perchloric acid–butene reaction is, of course, the strong absorption spectrum. Evans and co-workers[8] have observed rather similar spectra in the dimerization of a number of diphenylethylenes in the presence of a series of strong acids and have presented strong evidence for their belief that the initially formed chromophore is a classical carbonium ion. This ion, they suggest, then isomerizes to a colored π-complex. It is possible that the butene spectra are of a similar type and, if so, their weaker intensity may be attributed to the lower basicity of the butene with a resulting less favorable equilibrium even with the very strong acids required to produce color. This argument, however, is a dangerous one because we have, as yet, no evidence directly relating the colored compounds to a reaction process. Furthermore, the visible color of carbonium ions is always attributed to resonance in the aromatic system and it is by no means certain that aliphatic carbonium ions would show it; certainly, the displacement toward shorter wave lengths in the present case seems small for the replacement of two aryl groups by alkyls. We have recently noted[9] in the reaction of alkyl vinyl ethers with boron fluoride the formation of intense colors which undergo an astonishing series of changes and which may be related to the present case, but we have no explanation for them either. It is possible, perhaps, that all of these spectra are of the charge-transfer type.

[5] C. C. Price and G. Berti, THIS JOURNAL, **76**, 1219 (1954).

[6] E. L. Purlee and R. W. Taft, *ibid.*, **78**, 5807 (1956).

[7] R. W. Taft, E. L. Purlee, P. Riesz and C. A. DeFazio, *ibid.*, **77**, 1584 (1955).

[8] A. G. Evans, N. Jones and J. H. Thomas, *J. Chem. Soc.*, 1824 (1953); A. G. Evans, N. Jones, P. M. S. Jones and J. H. Thomas, *ibid.*, 2757 (1956).

[9] G. L. Latremouille, G. T. Merrall and A. M. Eastham, THIS JOURNAL, **82**, 120 (1960).

[CONTRIBUTION NO. 1600 FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY, NEW HAVEN, CONN.]

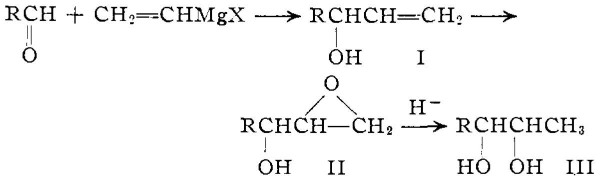
The Epoxidation of Some Allylic Alcohols[1,2]

BY MARTIN L. SASSIVER AND JAMES ENGLISH

RECEIVED MARCH 2, 1960

The composition of the mixtures of stereoisomers produced on epoxidation of a series of allylic alcohols ($RCHOHCH{=}CH_2$) has been determined.

During the course of some other research we became interested in the steric course of the epoxidation by peracids of substituted allylic alcohols of the type I.



$$RCH{=}O + CH_2{=}CHMgX \longrightarrow RCH(OH)CH{=}CH_2\ (\mathrm{I}) \longrightarrow RCH(OH)\overset{O}{CH{-}CH_2}\ (\mathrm{II}) \xrightarrow{H^-} RCH(OH)CH(OH)CH_3\ (\mathrm{III})$$

Henbest and Wilson[3] have observed a marked effect of the free OH group on the stereochemistry and rate of epoxidation of some cyclic analogs of I. Epoxidations also are known in the sterol and carbohydrate fields in which the stereochemistry of cyclic allylic alcohol groups has been elucidated.[4]

Since there seems to have been no recorded study of simple aliphatic allylic alcohols from this point of view, a series of models (I) were prepared in which R was methyl, ethyl, isopropyl and *t*-butyl. All of the carbinols (I) were known compounds and were synthesized by the reaction of the appropriate aldehyde with vinylmagnesium chloride or bromide. The alkylvinylcarbinols were epoxidized with an excess of monoperphthalic acid in ether for about 48 hours, during which time an equivalent of peracid was consumed. The reaction mixtures were quenched in cold alkali and extracted with ether to give about 50% yields of

[1] Taken from the dissertation presented by Martin L. Sassiver to the Graduate School of Yale University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] This work was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command under Contract No. AF 49(638)37.

[3] H. B. Henbest and R. A. Wilson, *J. Chem. Soc.*, 1958 (1957).

[4] P. A. Plattner, H. Heusser and A. B. Kulkarni, *Helv. Chim. Acta*, **32**, 265 (1949); R. Albrecht and C. Tamm, *ibid.*, **40**, 2216 (1957); T. Posternak and H. Friedli, *ibid.*, **36**, 251 (1953); B. Helferich, *Adv. in Carbohydrate Chem.*, **7**, 219 (1952).