and 1360 cm^{-1} (*gem*-dimethyl), 725 cm^{-1} (>C=C<); nmr (CCl_4–TMS) δ 6.36–6.13 (m, 2 H), 4.65 (d, 1 H, J = 5 Hz), 4.29 (s, 1 H), 2.81 (d of *q*, 1 H, J = 7, 5 Hz), 0.89 (s, 3 H), 0.88 (d, 3 H, J = 7 Hz), 1.26 (s, 3 H); mass spectrum (75 eV) *m/e* (rel intensity) 166 (M$^+$, 37), 151 (15), 123 (6), 110 (12), 96 (81), 95 (67), 81 (100), 70 (31), 68 (13), 67 (22), 55 (23), 53 (17), 42 (28), 41 (65), 39 (64).

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.29; H, 8.43. Found: C, 72.10; H, 8.67.

From nmr, **5** appears to be a single isomer; however, of the four possible isomers, we do not know which isomer we have isolated.

1,1,2,6,6-Pentamethyl-5-oxo-4-oxaspiro[2.3]hexane (6).—To a 10% solution of dimethylketene (*ca.* 30 mmol) in CH_2Cl_2 was added a CH_2Cl_2 solution of **4**[18] (*ca.* 20 mmol). The solution was allowed to stand for 6 days at −78°. The resulting solution was concentrated and analyzed by vpc (6 ft × 1/4 in., 22% Carbowax 20M, Chromosorb P, 200°, 120 cc of He/min). The major product was collected and identified as adduct **6** by the following spectral properties: ir $\nu_{max}^{CCl_4}$ 1830 (C=O), 1385 and 1365 cm^{-1} (*gem*-dimethyl); nmr (CCl_4–TMS) δ 1.39 (s, 3 H), 1.29 (s, 3 H), 1.13 (s, 3 H), 1.09 (s, 3 H), 1.06 (d, 3 H, J = 7 Hz), 0.82 (q, 1 H, J = 7 Hz); mass spectrum (75 eV) *m/e* (relative intensity) 168 (3, M$^+$), 153 (2), 124 (1) 123 (2), 108 (7), 70 (100), 55 (25), 42 (41).

5,5-Dimethyl-4-isopropylidene-2-trichloromethyl-1,3-dioxolane (8).—A dilute (<1%) CH_2Cl_2–*n*-pentane solution (10 ml) of tetramethylcyclopropanone was mixed with chloral (1 ml, 10.3 mmol) and left at room temperature overnight. Removal of the solvent on a "Roto-Vap" followed by preparative vpc (6 ft × 3/8 in., 20% SE-30, Chromosorb P, 200 ml of He/min, 210 and 175°) then resulted in the isolation of **8**: ir $\nu_{max}^{CCl_4}$ 1710 cm^{-1}; nmr (CCl_4–TMS) δ 1.46 (s, 3 H), 1.63 (s, 6 H), 1.67 (s, 3 H), 5.39 (s, 1 H); mass spectrum (75 eV) *m/e* (rel intensity) 258 (M$^+$, 8), 153 (2), 141 (33), 131 (5), 112 (7), 97 (10), 95 (100), 84 (51), 69 (50), 67 (16), 55 (15), 44 (39), 43 (34), 41 (32), 40 (31), 39 (12).

Registry No.—**2,** 24165-15-9; **3,** 24165-11-5; **5,** 24165-12-6; **6,** 24165-13-7; **8,** 24165-14-8.

[18] N. J. Turro and R. B. Gagosian, *J. Amer. Chem. Soc.*, in press.

Glycidyltrimethylammonium Chloride and Related Compounds

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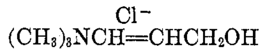
In 1904, Schmidt and Hartmann reported[1] obtaining glycidyltrimethylammonium chloride (I) as a noncrystallizable syrup of unspecified epoxide content by reacting epichlorohydrin with excess trimethylamine in ethanolic solution. The yield was low and the main product was the bis salt, 2-hydroxypropane-1,3-bis(trimethylammonium chloride). Two decades earlier, Reboul had claimed[2] that the viscous syrup which was isolated when equal volumes of epichlorohydrin and triethylamine were heated to 100° was the homologous glycidyltriethylammonium chloride.

More recently a patent has issued to Paschall of the Corn Products Co. which claims the use of the product[3] from the interaction of epichlorohydrin with trimethylamine for the etherification of starch. According to Paschall, I was obtained[3] as a viscous syrupy distillation residue by treating epichlorohydrin with trimethylamine in aqueous solution at 25°. We have found that the syrup obtained by Paschall's procedure has only 40–60% of the theoretical epoxy oxygen value. On standing for 24 hr at 25°, the epoxide content declined to about half of its original value and, after 1 week at 25°, no significant (<5%) amount of epoxide remained. In a recent publication,[4] Burness has observed that reaction of epichlorohydrin with trimethylamine in acetonitrile at 25° affords N-(3-hydroxy-1-propenyl)trimethylammonium chloride (II, 87% yield) rather than I. We now report the preparation of



$$\overset{Cl^-}{(CH_3)_3NCH{=}CHCH_2OH}$$

II

pure, crystalline, stable glycidyltrimethylammonium chloride (I) for the first time.

Results

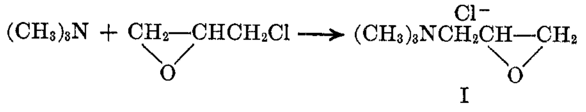
Glycidyltrimethylammonium Chloride.—The reaction of epichlorohydrin and trimethylamine to form I is best carried out in an aprotic solvent in which **I** is essentially insoluble. With excess epichlorohydrin as solvent (4.5:1 mole ratio), the reaction takes place very readily at 25° and I is formed in nearly quantitative yield and conversion. The product, a hygroscopic sharp-melting white crystalline material, is of 98% or better purity on the basis of epoxide content. When the reaction is conducted in other dry aprotic oxygenated solvents such as ethers, ketones, and esters, product of 95–97% epoxide content is isolated in nearly quantitative yield but only 50–75% conversion. The results of several experiments in which 0.25 mol of each reactant was stirred at 25–30° in 100–125 ml of the stipulated solvent for the specified period of time are summarized in Table I. The rate of the reaction is considerably greater in acetone (ε 21) than in other oxygenated aprotic solvents of lower dielectric constant (ε 4–7). In hexane (ε 1.9) the reaction proceeds at such a slow rate as to be impractical although product of good quality is obtained. In contrast, when the

TABLE I

REACTION OF EPICHLOROHYDRIN WITH TRIMETHYLAMINE

(0.25 mol of each reactant in 100–125 ml of solvent at 25–30°)

Solvent	Reaction time, hr	% conversion of epichlorohydrin	% yield of I	% purity (epoxide)
Acetone	35	74	97	96
Tetrahydrofuran	60	60	95	96
Dimethoxyethane	60	56	97	97
Ether	60	40	97	97
Ethyl Acetate	35	40		95
Hexane	60	15	98	96
Ethanol	16	95		20



I

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[1] E. A. Schmidt and H. Hartmann, *Ann.*, **337**, 116 (1904).

[2] E. Reboul, *Compt. Rend.*, **93**, 423 (1881).

[3] E. F. Paschall, U. S. Patent 2,876,217 (1959).

[4] D. M. Burness, *J. Org. Chem.*, **29**, 1862 (1964).

reaction is carried out in a protic solvent such as ethanol in which I is soluble, the viscous syrup which is obtained has less than 20% of the theoretical epoxide content. Reaction in *t*-butyl alcohol solvent at 25° affords[4] II (80% yield) rather than I.

In aprotic solvents, epoxide of optimum purity (97-98%) is obtained when the reaction temperature is maintained below 30°. In dimethoxyethane, the epoxide content falls to 85-90% of theory at 50° and to less than 70% at 65°. Small amounts of water in the reaction medium have a deleterious effect upon oxirane ring content of I. Thus, in 99% dimethoxyethane-1% water, product of 78% epoxide content is obtained, whereas material of 97% purity is isolated from the anhydrous medium.

When isolated in a pure crystalline form, I is surprisingly stable under ordinary conditions. After 1 week at 25°, the epoxide value remained 97%. Only after 1 month at 25° did noticeable decomposition occur with the epoxide content falling to 92%. Epoxide loss is entirely arrested by storage at 0° even after a 1-year period of time.

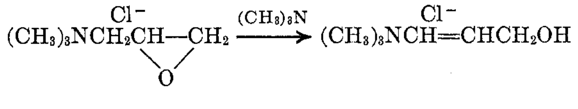
Glycidyltriethylammonium Chloride.—The reaction of epichlorohydrin with triethylamine to form glycidyltriethylammonium chloride (III) is best carried out using equal weights of the reactants and no solvent at 25°. Using this procedure, crystalline III of 98% purity is obtained in good yield. However, this sterically hindered amine reacts so slowly that, even after 90 hr, the conversion is only 20%. When the reaction is carried out either in excess epichlorohydrin or at 50 instead of 25°, material of low (50-70%) epoxide content is obtained. Indeed, at 80° with equal weights of reactants, the product contains no significant epoxide. On this basis, it is believed that the material prepared by Reboul[2] was not III but probably a crude homolog of II.

Glycidyltrimethylammonium Bromide.—Glycidyltrimethylammonium bromide is obtained in 92% yield as a sharp melting crystalline material by reaction of epibromohydrin with trimethylamine in dimethoxyethane solvent at 20°. The compound which has an epoxide value that is 98% of theory appears to be quite stable when stored at 0°.

Discussion

The most important factor in determining the course of the reaction between epichlorohydrin and trimethylamine is the solubility of the initially formed glycidyltrimethylammonium chloride (I) in the reaction medium. In excess epichlorohydrin, the solubility is so low (0.02 g/100 g) as to preclude further reaction of I with itself, solvent, or amine. The excellent results observed in other aprotic oxygenated solvents are also attributed to the low solubility of I in these media.[5] However, in an ethanolic medium the solubility is so great (40 g/100 g) that I is available for further reaction with itself or with solvent or with amine. The result is that a complex mixture of products (I, chlorohydrin[3] of I, etherification product, II, and other unidentified material) is obtained. A similarly complex mixture of products is obtained when the reaction is carried out in aqueous solution. The solubility of I in water is greater than 100 g/100 g of solvent.

In *t*-butyl alcohol, I is also quite soluble (about 15 g/100 g) but in this case the reaction is fairly selective (80% yield) to give II since the alcohol, itself, is relatively unreactive. The intermediacy of I in the formation of II has been confirmed by the ease with which I rearranges to II in *t*-butyl alcohol solvent at 25° in the presence of trimethylamine. Even in the absence of added amine, I is converted into II in *t*-butyl alcohol at 80°. The presence of small amounts of amine formed by decomposition of I is detectable after one hour at 80°. Thus, even trace amounts of the amine can apparently catalyze the rearrangement of I to II at 80°. Burness has also established[4] the intermediacy of the epoxide in the formation of II in his experiments carried out in acetonitrile solution using a sample of I supplied by us. His results confirm the importance of the solubility factor in product determination as the solubility of I in acetonitrile at 25° is greater than 3 g/100 g of solvent.



It should be emphasized that the solubility of I in the reaction medium is not the only factor which appears to be important in the determination of product composition. Thus, the yield of I observed in aqueous solution[3] is five times that observed in acetonitrile[4] despite the fact that the solubility of I in water is 30 times that in the nitrile. Increased basicity of trimethylamine in acetonitrile over that in water may increase the rate of the base-catalyzed isomerization of I to II in nitrile solvent. The water has a "leveling effect" on the basic strength of the amine. Solvation of I by water may also be important in slowing down the rate of conversion of I to II in aqueous solution.

Experimental Section

Glycidyltrimethylammonium Chloride.—The reaction vessel was a 1-l. flask equipped with stirrer, gas addition tube, and a condenser cooled to −20°. Trimethylamine (95 g, 1.61 mol) was added slowly over a 1-hr period to 600 g (7 mol) of epichlorohydrin maintained at −10 to 0° by external cooling. Stirring was continued at 20-25° for 5 hr. The crystals which separated were collected by filtration in a drybox and washed several times with ether. After drying *in vacuo* at 35° for 1 hr, the product weighed 239 g (98%) and melted at 139-141°. The product had an epoxide value[6] of 0.645 equiv/100 g (98% of theory).

Anal. Calcd for $C_9H_{14}ONCl$: C, 47.5; H, 9.2; Cl, 23.4; N, 9.2. Found: C, 47.2; H, 9.4; Cl, 23.6; N, 9.1.

Glycidyltriethylammonium Chloride.—A mixture of 30 g (0.33 mol) of triethylamine and 30 g (0.32 mol) of epichlorohydrin was stirred at 25° for 90 hr. The oil which separated (lower layer) was washed three times with ether in a drybox. The product which crystallized on cooling, mp 32-35°, weighed 9 g (95% yield based on converted epichlorohydrin) after drying *in vacuo* at 35° and had an epoxide value of 0.51 equiv/100 g (98% of theory). Analysis of the upper layer by gas-liquid chromatography showed that 24 g (20% conversion) of epichlorohydrin was recovered.

Anal. Calcd for $C_7H_{16}ONCl$: C, 50.6; H, 9.9. Found: C, 50.4, H, 9.8.

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[5] The solubility of I in oxygenated organic media apparently increases with increasing temperature and the presence of increasing amounts of water. Hence, the poor product purity observed at 65° or in the presence of 1% water is easily rationalized.

[6] O. F. Lubatti, *Chem. Ind.* (London), **51**, 1361T (1932).

Glycidyltrimethylammonium Bromide.—A solution of 15 g (0.25 mol) of trimethylamine and 29 g (0.21 mol) of epibromohydrin in 70 ml of dimethoxyethane was stirred at 0-20° for 18 hr. External cooling was necessary to maintain the temperature. The white crystals were collected by filtration and washed with ether in a drybox. After drying *in vacuo* at 35°, the halide weighed 38 g (92% yield), melted at 151-153°, and had an epoxide value of 0.50 equiv/100 g (98% of theory).

Registry No.—I, 3033-77-0; glycidyltriethylammonium chloride, 15876-88-7; glycidyltrimethylammonium bromide, 13895-77-7.

The Nature of the Activated Complex in the Permanganate Oxidation of Phenylmethanenitronate Anions[1,2]

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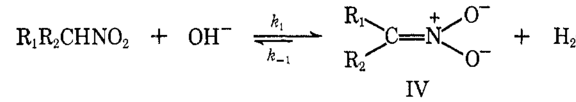
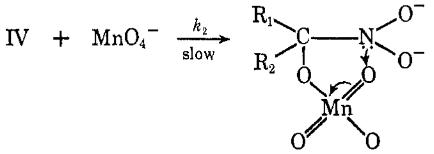
The neutral or alkaline permanganate oxidation of nitronate anions has been shown to give excellent yields of aldehydes and ketones.[3,4] Kinetic studies in our laboratories of phenylmethanenitronate anion (I),[5] cyclohexanenitronate anion (II), and cyclopentanenitronate anion (III)[6] have shown in strongly alkaline media[7] that the reaction is zero order in hydroxide ion, first order in permanganate ion, and first order in nitronate anion. The $\Delta H^{\neq}$ for the oxidation of I is 7.5 kcal/mol and $\Delta S^{\neq}$ is -20 eu.[5] The entropy of activation for the oxidation of II and III are -20 and -27.8 eu, respectively.[6] It was proposed that the rate-determining step involves an attack of permanganate at the carbon of the carbon–nitrogen double bond of the nitronate anion[11] to give V, which rearranges to the observed products according to eq 4.[5,6]

$$3R_1R_2C{=}NO_2K + 2KMnO_4 + H_2O \longrightarrow 3R_1R_2C{=}O + 2MnO_2 + 3KNO_2 + 2KOH \quad (1)$$



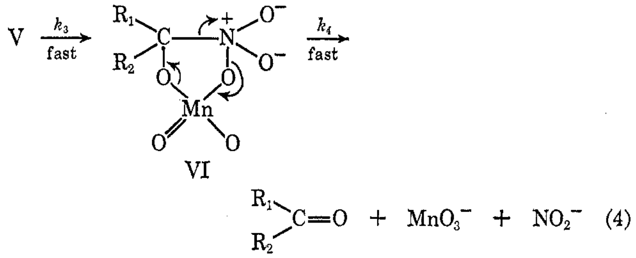
$$R_1R_2CHNO_2 + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R_1R_2C{=}\overset{+}{N}(O^-)O^- + H_2O \quad (2)$$

IV



(3)

V



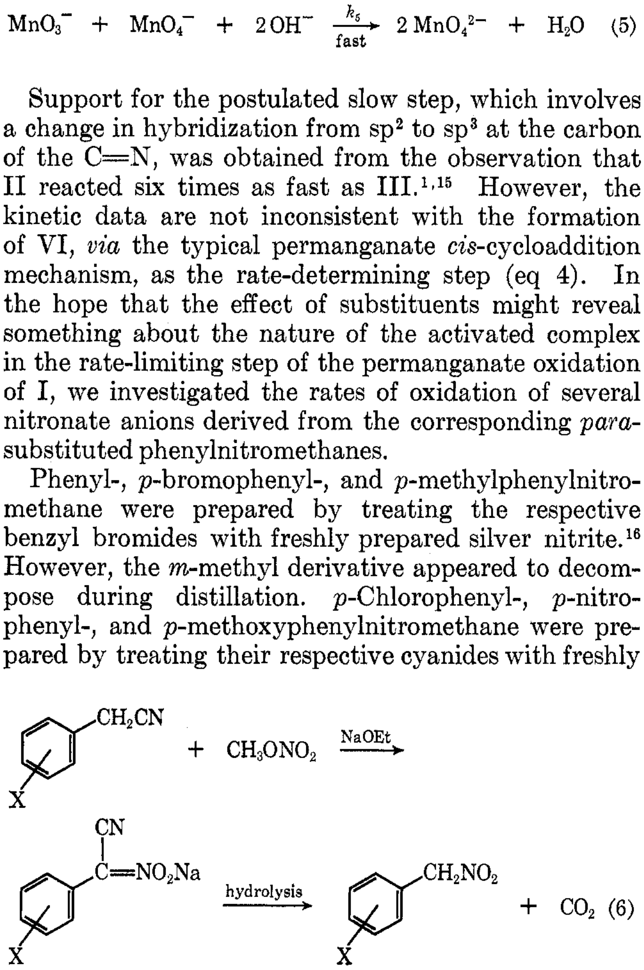
VI

(4)

$$MnO_3^- + MnO_4^- + 2OH^- \xrightarrow[fast]{k_5} 2MnO_4^{2-} + H_2O \quad (5)$$

Support for the postulated slow step, which involves a change in hybridization from sp^2 to sp^3 at the carbon of the C=N, was obtained from the observation that II reacted six times as fast as III.[1,15] However, the kinetic data are not inconsistent with the formation of VI, *via* the typical permanganate *cis*-cycloaddition mechanism, as the rate-determining step (eq 4). In the hope that the effect of substituents might reveal something about the nature of the activated complex in the rate-limiting step of the permanganate oxidation of I, we investigated the rates of oxidation of several nitronate anions derived from the corresponding *para*-substituted phenylnitromethanes.

Phenyl-, *p*-bromophenyl-, and *p*-methylphenylnitromethane were prepared by treating the respective benzyl bromides with freshly prepared silver nitrite.[16] However, the *m*-methyl derivative appeared to decompose during distillation. *p*-Chlorophenyl-, *p*-nitrophenyl-, and *p*-methoxyphenylnitromethane were prepared by treating their respective cyanides with freshly prepared methyl nitrate.[17] An attempt to prepare the *m*-chloro derivative by this method was unsuccessful.



(6)

The rates were followed spectrophotometrically by observing the disappearance of permanganate (522 mμ) in a stopped-flow reactor.[6] Table I summarizes the rate data.

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[1] Previous paper in series: F. Freeman, J. B. Brant, N. B. Hester, A. A. Kamego, M. L. Kasner, T. G. McLaughlin, and E. W. Paull, *J. Org. Chem.*, in press.

[2] Abstracted in part from the M.S. thesis of A. Yeramyan, California State College, Long Beach, Calif., 1969.

[3] H. Shecter and F. T. Williams, Jr., *J. Org. Chem.*, **27**, 3699 (1962).

[4] S. S. Nametkin and O. Madaeff-ssitscheff, *Chem. Ber.*, **59**, 370 (1926).

[5] F. Freeman and A. Yeramyan, *Tetrahedron Lett.*, 4783 (1968).

[6] F. Freeman, A. Yeramyan, and F. Young, *J. Org. Chem.*, **34**, 2438 (1969).

[7] Kinetic studies were performed between pH 12.5 and 13.6. At the higher pH values, phenylnitromethane[8,9] and the nitrocycloalkanes[9,10] are essentially completely converted into the nitronate anions.

[8] W. Kemula and W. Turnowska-Rubaszewska, *Rocz. Chem.*, **37**, 1597 (1963).

[9] F. Freeman and A. Yeramyan, unpublished data, 1969.

[10] P. W. K. Flanagan, H. W. Amburn, H. W. Stone, J. G. Trayham, and H. Shechter, *J. Amer. Chem. Soc.*, **91**, 2797 (1969).

[11] Self-consistent molecular orbital calculations[12,13] and spectroscopic studies[14] have suggested that nitronate anions have essentially a carbon–nitrogen double bond and two equivalent nitrogen–oxygen bonds with low double-bond character.

[12] N. Jonathan, *J. Mol. Spectrosc.*, **7**, 105 (1961).

[13] F. T. Williams, Jr., P. W. K. Flanagan, W. J. Taylor, and H. Shechter, *J. Org. Chem.*, **30**, 2674 (1965).

[14] M. J. Brookes and N. Jonathan, *Spectrochim. Acta*, **25A**, 187 (1969).

[15] III presumably reacts at a slower rate as a result of the increase of I strain (bond opposition forces, compression of van der Waals radii, and distortion of bond angles) in going from IV to V: H. C. Brown and M. Bordowski, *J. Amer. Chem. Soc.*, **74**, 1894 (1952).

[16] N. Kornblum, R. A. Smiley, R. K. Blackwood, and D. C. Iffland, *ibid.*, **77**, 6269 (1955).

[17] A. P. Black and F. H. Babers in "Organic Syntheses," Coll. Vol. II, A. H. Blatt, Ed., John Wiley & Sons, Inc., New York, N. Y., 1943, pp 412, 512.