melted at 184–185° with the evolution of gas and the formation of a yellow liquid.

Anal. Calcd. for $C_{10}H_4Cl_4O_2$: C, 40.2; H, 1.34. Found: C, 40.0; H, 1.34.

On refluxing in xylene, the dione decomposed with the evolution of hydrogen chloride. The xylene was removed by distillation and the residual tan solid was crystallized from ligroin (b.p. 90–100°) to give a colorless micro-crystalline compound, m.p. 262–264°.

The same compound was obtained by heating the dione at its melting point until the evolution of gas ceased.

Anal. Calcd. for $C_{18}H_7Cl_7O_2$: C, 42.9; H, 1.38; mol. wt., 503. Found: C, 43.0, 43.3; H, 1.30, 1.25; mol. wt. (Rast), 520.

5-Bromo-2,3,4-trichloro-2-cyclopentenone.—A solution of 30 g. (0.19 mole) of bromine in 50 ml. of carbon tetrachloride was added dropwise to a refluxing solution of 35 g. (0.19 mole) of 2,3,4-trichloro-2-cyclopentenone in 50 ml. of carbon tetrachloride. Hydrogen bromide was evolved during the addition which required 2.5 hours. The reaction mixture was dried over Drierite and distilled to remove the solvent. Vacuum distillation of the residue yielded 42 g. (91%) of bromoketone boiling at 93–100° (3 mm.). On redistillation of the product from a Vigreux column, almost the entire amount distilled at 89–91° (2 mm.), $n^{20}D$ 1.5848.

Anal. Calcd. for $C_5H_2BrCl_3O$: C, 22.7; H, 0.75. Found: C, 22.8; H, 0.76.

Dehydrochlorination of 5-Bromo-2,3,4-trichloro-2-cyclopentenone.—A mixture of 10 g. (0.041 mole) of 5-bromo-2,3,4-trichloro-7-cyclopentenone, 7.5 g. of sodium acetate and 10 ml. of glacial acetic acid was shaken at room temperature. Heat was evolved and the mixture turned green. After one hour, the mixture was diluted with an equal volume of water and filtered with suction. The colorless solid was crystallized from petroleum ether (b.p. 90–100°) giving 2.1 g. (21%) of diketone, m.p. 170–171° dec.

Anal. Calcd. for $C_{10}H_2Br_2Cl_4O_2$: C, 26.3; H, 0.44. Found: C, 25.8, 26.0; H, 0.54, 0.59.

Bromotetrachloro-1-indone.—A mixture of 1.2 g. of the preceding compound (m.p. 170–171°) and 5 ml. of xylene was refluxed for 2 hours. Hydrogen bromide was evolved, first rapidly, then more slowly until the reaction was complete. The xylene was removed and the residue was crystallized three times from petroleum ether–benzene to give 0.3 g. of yellow needles, m.p. 156–157°.

Anal. Calcd. for C_9HBrCl_4O: C, 31.2; H, 0.29; mol. wt., 347. Found: C, 31.0, 31.1; H, 0.29, 0.32; mol. wt., 356.

Dibromo-2,3,4-trichloro-2-cyclopentenone.—A solution of 50 g. (0.31 mole) of bromine in 50 ml. of carbon tetrachloride was added dropwise to a refluxing solution of 25 g. (0.13 mole) of 2,3,4-trichloro-2-cyclopentenone in 50 ml. of carbon tetrachloride. The reaction proceeded first rapidly with evolution of hydrogen bromide, then more slowly. Part of the carbon tetrachloride was therefore removed by distillation and replaced with 50 ml. of glacial acetic acid. The remainder of the bromine solution was added and the mixture was heated on a steam-bath overnight. Unreacted bromine and carbon tetrachloride were removed and the remaining acetic acid solution was diluted with water. The mixture was extracted with chloroform and the chloroform solution was dried over sodium sulfate. The solvent was removed and the residue was distilled under reduced pressure to give 32 g. (70%) of dibromoketone boiling at 109–113° (2 mm.). Redistillation from a Vigreux column gave an analytical sample, b.p. 112–113° (2 mm.), $n^{20}D$ 1.6227.

Anal. Calcd. for $C_5HBr_2Cl_3O$: C, 17.5; H, 0.29. Found: C, 17.3; H, 0.28.

Acknowledgment.—The authors wish to thank the Hooker Electrochemical Company for financial assistance in this investigation and H. E. Ungnade and D. L. Crain for assistance in the preparation of the manuscript.

W. LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE ROHM AND HAAS COMPANY, REDSTONE ARSENAL RESEARCH DIVISION]

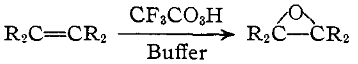
Peroxytrifluoroacetic Acid. IV. The Epoxidation of Olefins[1]

BY WILLIAM D. EMMONS AND ANGELO S. PAGANO

RECEIVED JULY 21, 1954

Satisfactory procedures have been developed for the epoxidation of olefins and negatively substituted olefins with peroxytrifluoroacetic acid. These procedures are dependent on the presence of a buffer such as dibasic sodium phosphate, sodium carbonate, or sodium bicarbonate in the reaction medium. The epoxidation of olefins with peroxytrifluoroacetic acid has substantial advantages over previously described methods of epoxidation.

Peroxytrifluoroacetic acid has been found to be a remarkably efficient reagent for olefin epoxidation and indeed offers a number of advantages over previously known methods. The effectiveness of peroxytrifluoroacetic acid as a hydroxylation reagent for the preparation of α-glycols from olefins[2]



$$R_2C{=}CR_2 \xrightarrow[\text{Buffer}]{CF_3CO_3H} R_2\overset{O}{C{-}C}R_2$$

prompted an investigation of methods which could be employed for isolation of the epoxide intermediates. Peracetic and particularly perbenzoic acid have been widely used for expoxidation of olefins[3]; however, both of these reagents have inherent limitations to their use which peroxytrifluoroacetic acid does not have.

The utilization of peroxytrifluoroacetic acid as an olefin epoxidation reagent is dependent on the fact that the peracid is apparently a much weaker acid than trifluoroacetic acid itself. Efforts to obtain quantitative information regarding this point have been unsuccessful since peroxytrifluoroacetic acid reacts very rapidly with water to form hydrogen peroxide. While this reaction is reversible, qualitative evidence indicates that the equilibrium lies well to the right. However, the dissociation con-

$$CF_3CO_3H + H_2O \rightleftarrows CF_3CO_2H + H_2O_2$$

stants of both performic and peracetic acids have been measured, and the *pK* values are 7.1 and 8.2, respectively.[4] The values for formic and acetic acids are 3.7 and 4.8 so in each case there is a difference of 3.4 in the *pK* values for the acid and the corresponding peracid. On this basis then it is reasonable to assume that peroxytrifluoroacetic acid is a much weaker acid than trifluoroacetic acid

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(1) This research was carried out under Army Ordnance Contract W-01-021-ORD-334.

(2) W. D. Emmons, A. S. Pagano and J. P. Freeman, THIS JOURNAL, **76**, 3472 (1954).

(3) D. Swern, "Organic Reactions," Vol. VII, John Wiley and Sons, Inc., New York, N. Y., 1953, p. 378.

(4) A. J. Everett and G. S. Minkoff, *Trans. Faraday Soc.*, **49**, 410 (1953).

($pK = 0.3$[5]) and can therefore be tolerated in an epoxidation medium. Accordingly, methods for rapid removal of trifluoroacetic acid from the reaction system without affecting the peroxyacid were studied.

The first buffer system chosen for examination was heterogeneous and employed sodium acetate in methylene chloride suspension. This system could indeed be utilized for epoxidation of some olefins, but it was subsequently found that the actual oxidizing agent was peracetic acid which was formed by an exchange reaction. While reaction 2 is undoubtedly reversible, the trifluoroacetic acid formed

$$CF_3CO_2H + CH_3CO_2Na \longrightarrow CF_3CO_2Na + CH_3CO_2H \quad (1)$$

$$CH_3CO_2H + CF_3CO_3H \rightleftarrows CF_3CO_2H + CH_3CO_3H \quad (2)$$

is immediately removed by the sodium acetate so all the active oxygen eventually is converted to peracetic acid.

Sodium carbonate in methylene chloride was the next buffer investigated, and it was found that although this base destroys peroxytrifluoroacetic acid, it can under the proper circumstances be successfully utilized for epoxidation of simple olefins with peroxytrifluoroacetic acid. If an anhydrous solution of peroxytrifluoroacetic acid is added dropwise to a well-stirred heterogeneous mixture of sodium carbonate, the olefin and methylene chloride at reflux, practically quantitative yields of epoxides are obtained. This procedure is dependent on the fact that peroxytrifluoroacetic acid reacts much more rapidly with olefins than it does with sodium carbonate. A novel feature of this system is that after the epoxidation is complete, the sodium carbonate destroys any excess peroxytrifluoroacetic acid. Consequently, the only product left in solution is the epoxide, and indeed after the reaction is over the solution is neither acid to litmus nor does it give a positive starch–iodide test. Removal of the insoluble inorganic salts may be carried out by centrifugation, filtration or by washing with water. We have observed that centrifugation is the most satisfactory procedure particularly in the preparation of volatile epoxides. Removal of the solvent then gives the epoxide in practically quantitative yields. The results of a number of typical epoxidations are summarized in Table I. It is particularly noteworthy that the terminal olefins such as octene-1 and dodecene-1, which as a class are relatively unreactive, could easily be epoxidized in excellent yields. In contrast the epoxidation of these olefins with peracetic acid gave rather low yields (35–50%) and required long reaction times.[6] Furthermore, in the presence of sodium carbonate essentially no hydroxytrifluoroacetate derived from ring opening of the epoxide is formed. In this respect, the reagent appears to be as good as perbenzoic acid and in addition is certainly easier to prepare and use.

TABLE I

EPOXIDATION OF OLEFINS WITH PEROXYTRIFLUOROACETIC ACID[a]

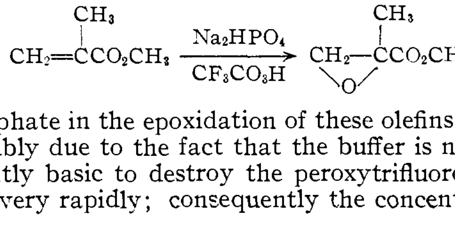
Olefin	Yield of epoxide, %	Base employed	Physical constants of epoxides[b] B.p. °C.	Mm.	$n^{20}D$
Pentene-1	81	Na_2CO_3	89–90	750	1.3963
Pentene-2	81[c]	Na_2CO_3	79–83	750	1.3905
Hexene-1	91[d]	Na_2CO_3	117–119	750	1.4060
Octene-1	87[e]	Na_2CO_3	71–73	27	1.4198
Dodecene-1	90	Na_2CO_3	106–109	6	1.4356
Dodecene-1	82[f]	$NaHCO_3$	.....	..	....
Cyclopentene	83	Na_2CO_3	98–100	750	1.4341
Cyclohexene	74	Na_2CO_3	70–71	110	1.4515
Methyl methacrylate	84[g]	Na_2HPO_4	62–65	32	1.4174
Ethyl methacrylate	81	Na_2HPO_4	80–82	38	1.4164
Ethyl crotonate	73	Na_2HPO_4	88–92	50	1.4191
Ethyl acrylate	54[h]	Na_2HPO_4	88–92	60	1.4180
Hexadiene-1,5	70[i]	Na_2CO_3	77–80	22	1.4390

[a] Unless otherwise indicated the epoxidations were run in methylene chloride at the reflux temperature of the solvent. [b] With the exceptions of 1,2-epoxypentane and 1,2-epoxyhexane all of the epoxides have been previously described in the literature. [c] No effort was made to separate *cis-* and *trans-* epoxides. [d] A 40% yield was obtained with Na_2HPO_4 at 0–5°. [e] A 74% yield was observed in diethyl ether at 0–5° with Na_2HPO_4. [f] Yields of 62 and 82% in diethyl ether were obtained with Na_2HPO_4 at reflux and at 0–5°, respectively. [g] Yields of 43 and 13% were observed with $NaHCO_3$ and Na_2CO_3, respectively. [h] In ethylene dichloride at reflux. [i] Yield of 1,2,5,6-diepoxyhexane.

The epoxidation of negatively substituted olefins in the presence of sodium carbonate was not a satisfactory reaction, however. Under these conditions the reaction of the olefin with the peracid is much slower and consequently the greater part of the peroxytrifluoroacetic acid is destroyed by the sodium carbonate before much epoxidation takes place. Thus only a 13% yield of methyl α-methylglycidate was obtained by oxidation of methyl methacrylate. Sodium bicarbonate proved to be a more satisfactory buffer for this reaction and a 45% yield of methyl α-methylglycidate was obtained. However, sodium bicarbonate reacts with trifluoroacetic acid to form water as one of the products. This is obviously disadvantageous particularly in a sluggish epoxidation, since the water will convert a part of the peroxytrifluoroacetic acid to hydrogen peroxide. This reaction is essentially irreversible in the presence of a base such as sodium bicarbonate, and hence a large portion of the active oxygen will be converted to hydrogen peroxide.

$$CF_3CO_3H + H_2O \longrightarrow CF_3CO_2H + H_2O_2$$

The most suitable buffer for epoxidation of negatively substituted olefins has been found to be disodium hydrogen phosphate and with this base it was possible to epoxidize methyl methacrylate in 84% yield. In similar fashion ethyl crotonate and ethyl acrylate were epoxidized in yields of 73 and 54%, respectively.



$$CH_2{=}\overset{\overset{\displaystyle CH_3}{|}}{C}CO_2CH_3 \xrightarrow[CF_3CO_3H]{Na_2HPO_4} CH_2{-}\overset{\overset{\displaystyle CH_3}{|}}{C}CO_2CH_3$$

The excellence of sodium phosphate in the epoxidation of these olefins is presumably due to the fact that the buffer is not sufficiently basic to destroy the peroxytrifluoroacetic acid very rapidly; consequently the concentration

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(5) A. L. Henne and C. J. Fox, THIS JOURNAL, **73**, 2323 (1951).

(6) D. Swern, G. N. Billen and J. T. Scanlan, *ibid.*, **68**, 1504 (1946).

of the peracid in the reaction medium becomes sufficiently great so that the epoxidation of these relatively unreactive olefins proceeds at a practical rate. Dibasic sodium phosphate is also not as effective at removing trifluoroacetic acid from solution as are sodium carbonate and sodium bicarbonate; however, the acid-catalyzed ring opening of glycidates and substituted glycidates is much slower than it is in the case of simple epoxides, and the epoxidation medium can therefore tolerate greater concentrations of trifluoroacetic acid. Peroxytrifluoroacetic acid thus appears to be the only known peracid which is an effective epoxidation reagent for negatively substituted olefins of the type illustrated here. Certainly the reagent has considerable preparative value for synthesis of glycidates and substituted glycidates.

The epoxidation of simple olefins with dibasic sodium phosphate as the buffer was not a satisfactory reaction. Hexene-1 with sodium phosphate in cold methylene chloride yielded only 40% of epoxide, and the remainder of the product was accounted for as hydroxytrifluoroacetate. It was, however, possible to epoxidize simple olefins with peroxytrifluoroacetic acid and disodium hydrogen phosphate in cold ethyl ether and to obtain fairly good yields of epoxides. This procedure is presumably dependent on the greater basicity of ethyl ether as compared with methylene chloride. It should be noted, however, that the use of ethyl ether and dibasic sodium phosphate with peroxytrifluoroacetic acid is not nearly as satisfactory as the sodium carbonate procedure for epoxidation of simple olefins. The experiments utilizing sodium phosphate are also summarized in Table I.

Experimental[7]

Materials.—Trifluoroacetic anhydride was purchased from Minnesota Mining and Manufacturing Corporation and 90% hydrogen peroxide from the Buffalo Electrochemical Company. Anhydrous sodium carbonate, sodium bicarbonate and disodium hydrogen phosphate were obtained from the General Chemical Division, Allied Chemical and Dye Corporation. The carbonate and bicarbonate were sufficiently fine powders so that it was not necessary to grind them. The sodium phosphate, however, was ground to a fine powder in a hammer mill. All of the salts were dried in a vacuum oven at 50° for 20 hours before use. The methylene chloride was a C.P. grade obtained from Fisher Scientific Company and used without further purification.

1,2-Epoxypentane.—To a suspension of 8.2 ml. (0.3 mole) of 90% hydrogen peroxide in 50 ml. of methylene chloride cooled in an ice-bath was added over a ten-minute period 50.8 ml. (0.36 mole) of trifluoroacetic anhydride. The solution of peroxytrifluoroacetic acid so obtained was stirred in the cold 15 minutes and was transferred to a dropping funnel equipped with a pressure-equalizer tube. It was then added over a 30-minute period with good stirring to a mixture containing 95 g. (0.9 mole) of sodium carbonate, 14.0 g. (0.2 mole) of pentene-1 and 200 ml. of methylene chloride. During the addition the solvent boiled vigorously and it was necessary to use a condenser cooled with ice-water to prevent escape of the pentene-1. After the addition was complete, the mixture was heated under reflux 30 minutes. The insoluble salts were then removed by centrifugation at 3000 r.p.m. for 15 minutes. The salt cake was triturated with 300 ml. of methylene chloride and the resulting mixture centrifuged again. The combined methylene chloride solutions were fractionated through a Todd column 90 × 1.2 cm. packed with 4-mm. glass helices and equipped with a variable reflux ratio head. After most of the solvent had distilled, the residual liquid was fractionated through a Holzman column.[8] There was obtained 14.0 g. (81%) of 1,2-epoxypentane, b.p. 89–90°. Practically no residue was left in the still pot after the fractionation was complete.

Anal. Calcd. for $C_5H_{10}O$: C, 69.72; H, 11.70; oxirane oxygen, 18.57. Found: C, 68.95; H, 11.39; oxirane oxygen, 17.96.

1,2-Epoxyhexane.—Hexene-1 was epoxidized by the same procedure described above. After fractionation of a 0.2-mole run there was obtained 18.3 g. (91%) of 1,2-epoxyhexane, b.p. 117–119°.

Anal. Calcd. for $C_6H_{12}O$: C, 71.95; H, 12.08; oxirane oxygen, 15.97. Found: C, 72.10; H, 12.09; oxirane oxygen, 15.35.

1,2-Epoxydodecane.—A solution of peroxytrifluoroacetic acid was prepared from 7.0 ml. (0.25 mole) of 90% hydrogen peroxide, 42.3 ml. (0.3 mole) of trifluoroacetic anhydride and 50 ml. of methylene chloride. The addition of this solution to a vigorously stirred mixture of 33.6 g. (0.2 mole) of dodecene-1, 200 ml. of methylene chloride and 76 g. (0.9 mole) of dry sodium bicarbonate was carried out over a 35-minute period. After the exothermic reaction was over, the mixture was heated under reflux 30 minutes and then was stirred with 500 ml. of water to dissolve the inorganic salts. The aqueous layer was separated and washed with 50 ml. of methylene chloride. The combined organic extracts were dried over magnesium sulfate and most of the volatile solvent was then evaporated at reduced pressure. The residual liquid, still containing a small amount of solvent, was fractionated through the Holzman column and 30.3 g. (82%) of 1,2-epoxydodecane,[6] b.p. 106–109° (6.0 mm.), was obtained. A residue of 4.0 g. remained in the still pot and infrared analysis indicated that this was largely the hydroxytrifluoroacetate derived from ring opening of the epoxide. When sodium carbonate (0.9 mole) was used as the base and the inorganic salts were separated by centrifugation, a 90% yield of the epoxide was obtained.

Methyl α-Methylglycidate.—A solution of peroxytrifluoroacetic acid was prepared from 7.0 ml. (0.25 mole) of 90% hydrogen peroxide, 42.3 ml. (0.3 mole) of trifluoroacetic anhydride, and 50 ml. of methylene chloride. This reagent was added over a 20-minute period to a well stirred, boiling mixture of 20.0 g. (0.2 mole) of methyl methacrylate, 200 ml. of methylene chloride and 113 g. (0.8 mole) of disodium hydrogen phosphate. After the exothermic reaction had subsided, the solution was heated under reflux for 30 minutes. The resulting mixture was stirred with 500 ml. of water until all the inorganic salts had dissolved. The organic layer was separated and the aqueous layer was extracted with 50 ml. of methylene chloride. The combined methylene chloride extracts were washed with 100 ml. of 10% sodium bicarbonate solution and dried over magnesium sulfate. Most of the solvent was evaporated at reduced pressure, and the residual liquid was fractionated through the Holzman column to yield 19.4 g. (84%) of methyl α-methylglycidate,[9] b.p. 62–65° (32 mm.). There was essentially no residue in the still pot after distillation.

Ethyl β-Methyl Glycidate.—From 22.8 g. (0.2 mole) of freshly distilled ethyl crotonate there was obtained by following the procedure described above 19.0 g. (73%) of ethyl β-methylglycidate,[10] b.p. 88–92° (50 mm.). In addition, 2.5 g. (11%) of ethyl crotonate was recovered.

Ethyl Glycidate.—A solution of peroxytrifluoroacetic acid was prepared from 12.3 ml. (0.45 mole) of 90% hydrogen peroxide, 76.2 ml. (0.54 mole) of trifluoroacetic anhydride, and 50 ml. of ethylene dichloride. This solution was then added dropwise over a 30-minute period with efficient stirring to a boiling mixture of 204 g. (1.44 moles) of disodium hydrogen phosphate, 250 ml. of ethylene dichloride and 20.0 g. (0.2 mole) of ethyl acrylate. The mixture was then heated under reflux for 30 minutes. Water, 600 ml., was added, and the solution was stirred until the salts had dissolved. The organic layer was separated and the aqueous layer extracted with 100 ml. of methylene chloride. The combined organic extracts were washed with 10% sodium bicarbonate solution and dried over magnesium sul-

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[7] All boiling points are uncorrected.

[8] C. W. Gould, G. Holzman and C. Niemann, *Anal. Chem.*, **20**, 361 (1948).

[9] F. Arndt, M. Ozansoy and H. Ustunyar, *Rev. faculte sci. univ. Istanbul* [*N.S.*], **4**, No. 1–2, 83 (1939).

[10] P. Melikoff and N. Zelinsky, *Ber.*, **21**, 2052 (1888).

fate. Approximately 80% of the solvent was evaporated at reduced pressure, and the residual liquid was then fractionated through the Holzman column to yield 12.4 g. (54%) of ethyl glycidate,[10] b.p. 88–90° (60 mm.).

1,2,5,6-Diepoxyhexane.—To 8.2 g. (0.1 mole) of hexadiene-1,5 in 275 ml. of methylene chloride slurried with 95 g. (0.9 mole) of sodium carbonate was added a solution of peroxytrifluoroacetic acid prepared from 8.2 ml. (0.3 mole) of 90% hydrogen peroxide, 50.8 ml. (0.36 mole) of trifluoroacetic anhydride and 50 ml. of methylene chloride. The addition required 25 minutes and the mixture was then heated under reflux for 30 minutes. The inorganic salts were removed by centrifugation. Most of the solvent was distilled off at atmospheric pressure and the residual liquid was fractionated through the Holzman column to yield 8.0 g. (70%) of 1,2,5,6-diepoxyhexane,[11] b.p. 77–80° (22 mm.).

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[11] S. L. Everett and G. A. R. Kon, *J. Chem. Soc.*, 3131 (1950).

HUNTSVILLE, ALABAMA

[CONTRIBUTION FROM THE CHEMISTRY DIVISION OF OAK RIDGE NATIONAL LABORATORY]

Molecular Rearrangements. III. The Mechanism of the Wagner–Meerwein Rearrangement in the 1,2,2-Triphenylethyl System[1]

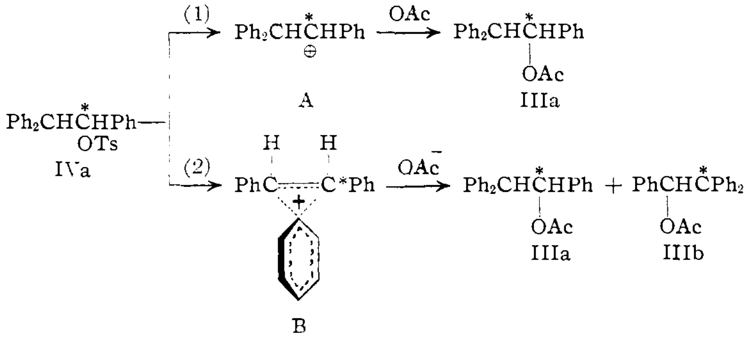
BY CLAIR J. COLLINS AND WILLIAM A. BONNER

RECEIVED APRIL 26, 1954

Several reactions of phenyl-labeled 1,2,2-triphenylethanol (IIc), its acetate (IIIc) and its tosylate (IVc) have been carried out under identical reaction conditions used for the chain-labeled analogs, and the radiochemical consequences of these reactions in both systems of labeling have been compared. It has been shown by this novel double-labeling technique that the reactions studied fall into two categories: (1) those in which a statistical redistribution of radioactivity has been achieved and (2) those in which a statistical redistribution has been approached, but not achieved. A simple kinetic relationship has been derived for the latter class of reactions, which allows a calculation of the radiochemical redistributions for various reactions in one series, knowing the results of the other. These calculated values agree with the observed values within experimental error, allowing the data to be rationalized quantitatively in terms of a mechanism involving open carbonium ion intermediates in which the cations undergo partial or complete radiochemical equilibration, depending upon their lifetimes. There is no evidence for bridged ionic intermediates in the reactions studied.

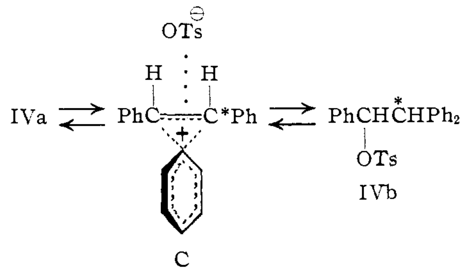
Introduction

The radiochemical results of the solvolytic reactions of 1,2,2-triphenylethyl-1-C^{14} p-toluenesulfonate (IVa) in acetone–water, acetic and formic acids have been described previously.[2] The rearrangements attending these solvolyses were tentatively rationalized in terms of two competing processes, one, 1- (step 1), involving an open carbonium ion A, the other, 1- (step 2), involving a symmetrical phenonium ion B, of the type proposed by Cram.[3a] This mechanism seemed likely in view of the results of Cram,[3b,3c] who claims that both open and bridged ions co-exist as intermediates during solvolytic reactions of closely related systems. These processes are illustrated for the acetolysis of tosylate IVa in glacial acetic acid containing sufficient sodium acetate to react with the p-toluenesulfonic acid formed

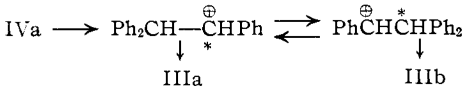


(1)

Under these conditions, the acetolysis product was shown[2] by oxidative degradation and subsequent radioactivity assay of the degradation products to consist of approximately 60% of acetate IIIa, and 40% of acetate IIIb. Neither these results, nor the results of the other solvolytic reactions described could be used as supporting evidence for this interpretation, however, since it was not possible by a study of tosylate IVa to distinguish process 1- (step 2) from one involving internal return,[4] in which the ion B and a tosylate anion are thought to exist as an ion pair (C), which may collapse[4b,5] to a mixture of the tosylates IVa and IVb prior to acetolysis (eq. 2). Similarly, neither of the above interpretations could be distinguished from a mechanism (eq. 3) which may be written most simply as an equilibration of two open carbonium ions



(2)



$$\text{IVa} \longrightarrow \underset{\displaystyle \text{IIIa}}{Ph_2CH\text{—}\overset{\oplus}{\underset{*}{C}}HPh} \rightleftarrows \underset{\displaystyle \text{IIIb}}{Ph\overset{\oplus}{C}H\overset{*}{C}HPh_2} \qquad (3)$$

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[1] This paper is based upon work performed under Contract Number W-7405-eng-26 for the Atomic Energy Commission at Oak Ridge National Laboratory.

[2] W. A. Bonner and C. J. Collins, THIS JOURNAL, **75**, 5372 (1953).

[3] (a) D. J. Cram, *ibid.*, **71**, 3863, 3875 (1949); (b) F. A. Abd Elhafez and D. J. Cram, *ibid.*, **75**, 339 (1953); (c) D. J. Cram and J. D. Knight, *ibid.*, **74**, 5839 (1952).

[4] (a) S. Winstein and D. Trifan, *ibid.*, **74**, 1154 (1952); (b) S. Winstein and K. C. Schreiber, *ibid.*, **74**, 2165, 2171 (1952); (c) S. Winstein and R. Heck, *ibid.*, **74**, 5584 (1952).

[5] D. J. Cram, *ibid.*, **74**, 2129, 2137, 2195 (1952).