peroxide in 100 ml. of methylene chloride was added at room temperature 20.2 ml. (0.144 mole) of trifluoroacetic anhydride in one portion. After an induction period of one or two minutes an exothermic reaction took place causing the solution to reflux. The homogeneous mixture was then stirred a few minutes and a slurry of 9.3 g. (0.03 mole) of 2,4,6-tribromoaniline in 20 ml. of methylene chloride was added over a ten-minute period. The solution was then heated under reflux 30 minutes. It was cooled and washed with 100 ml. of water. The turbid brown methylene chloride extract was separated and the volatile solvent was removed under reduced pressure. There was obtained as a residue 10.2 g. (100%) of yellow 2,4,6-tribromonitrobenzene, m.p. 113–115°. This was recrystallized once from ethanol and melted at 124–125° (lit. m.p. 125°[7]).

Oxidation of *p*-Bromoaniline to *p*-Bromonitrobenzene.—A solution of peroxytrifluoroacetic acid was prepared by addition of 5.4 ml. (0.2 mole) of 90% hydrogen peroxide to 50 ml. of trifluoroacetic acid. To this solution was added 6.9 g. (0.04 mole) of *p*-bromoaniline in one portion. The solution was then warmed to 55° where an exothermic reaction was observed. The temperature of the solution was allowed to increase to 85° and was maintained at 75–85° by intermittent cooling with an ice-bath. After 15 minutes, evolution of heat had ceased, and the mixture was allowed to cool to room temperature. The solution was then poured into 200 ml. of a crushed ice–water mixture and the light tan solid which separated was collected on a filter. There was obtained 6.9 g. (85%) of *p*-bromonitrobenzene, m.p. 122–124°. After recrystallization from ethanol the sample melted at 125–126°.

(7) K. J. P. Orton, *J. Chem. Soc.*, **83**, 797 (1903).

Oxidation of *p*-Phenylenediamine to *p*-Dinitrobenzene.—To 40 ml. of trifluoroacetic acid was added at room temperature 2.2 g. (0.02 mole) of *p*-phenylenediamine in one portion. To this solution was added with stirring 5.4 ml. (0.2 mole) of 90% hydrogen peroxide. No evolution of heat was observed until the mixture was heated to 50°. At this point an exothermic reaction was noted, and the temperature was kept between 60–70° for 45 minutes by intermittent cooling with an ice-bath. After the reaction was over the solution was heated at 60° for 15 minutes. The mixture was then quenched in 200 ml. of a crushed ice–water mixture. The solid *p*-dinitrobenzene so obtained was collected on a filter and dried; yield 3.0 g. (89%), m.p. 160–164°. The sample was recrystallized from ethanol once and melted at 169–171°.

Oxidation of *p*-Chloroaniline to *p*-Chloronitrobenzene with 30% Hydrogen Peroxide.—A solution of 6.4 g. of *p*-chloroaniline (0.05 mole) in 50 ml. of trifluoroacetic acid was heated to reflux. To this refluxing solution was added 28.3 g. (0.25 mole) of 30% hydrogen peroxide over a 30-minute period. The solution was then heated under reflux for 30 minutes and cooled. It was poured into 150 ml. of crushed ice–water mixture, and the light brown precipitate of *p*-chloronitrobenzene was collected on a filter and dried; yield 6.0 g. (71%), m.p. 73–75°. A sample of this material was purified by vacuum sublimation, m.p. 76–78°. Attempts to raise the melting point to the literature value of 83°[8] by further purification were unsuccessful.

(8) I. Heilbron, "Dictionary of Organic Compounds," Oxford University Press, New York, N. Y., 1946, p. 503.

HUNTSVILLE, ALABAMA

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

Peroxytrifluoroacetic Acid. III. The Hydroxylation of Olefins[1]

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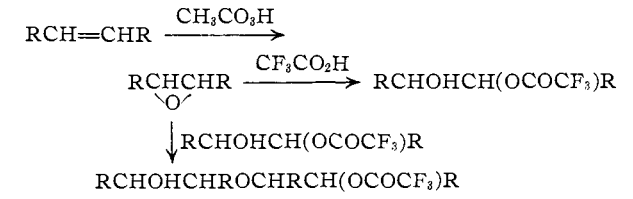
RECEIVED MARCH 8, 1954

Peroxytrifluoroacetic acid has been found to be a superior reagent for olefin hydroxylation. The reagent is particularly useful for preparation of water-soluble α-glycols and for hydroxylation of negatively substituted olefins.

Peroxytrifluoroacetic acid has been found to be extremely reactive in the hydroxylation of olefins and excellent yields of the corresponding α-glycols have been obtained. Most organic peroxyacids have at one time or another been employed for olefin hydroxylation,[2] and performic acid is particularly effective in this reaction. Peroxytrifluoroacetic acid is, however, far more reactive than this reagent and in addition offers some practical advantages in synthesis of water-soluble α-glycols.

Peroxytrifluoroacetic acid, prepared from trifluoroacetic anhydride and 90% hydrogen peroxide in methylene chloride, reacted almost instantaneously even at ice-bath temperatures with all the simple olefins investigated. The products obtained were hydroxytrifluoroacetates derived from the ring opening of the intermediate epoxide with trifluoroacetic acid. These esters could, however, readily be converted to the α-glycols by methanolysis.[3] Initially it was found that the glycols were contaminated by high-boiling products of the cellosolve type. These were undoubtedly derived from condensation of the epoxide, initially formed in the reaction, with the hydroxytrifluoroacetate which accumulates as the reaction proceeds. Formation of these high boiling ethers was prevented, however, by increasing the effective concentration of trifluoroacetate ions present in the reaction medium; this was conveniently accomplished by addition of triethylammonium trifluoroacetate to the solvent in which the oxidation was carried out, and under these conditions pure α-glycols were obtained. In this connection it was observed that the salts of tertiary aliphatic amines and trifluoroacetic acid are extremely soluble in those chlorinated solvents which are capable of hydrogen bonding. A summary of the experimental investigations may be found in Table I.



In general the oxidations were carried out by addition of a methylene chloride solution of peroxytrifluoroacetic acid to the olefin and triethylammo-

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

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

(3) E. J. Bourne, C. E. M. Tatlow and J. C. Tedder, *J. Chem. Soc.*, 1367 (1950).

TABLE I

HYDROXYLATION OF OLEFINS

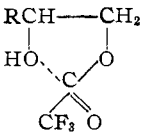
Olefin	Glycol	Yield, %
Allyl chloride	3-Chloro-1,2-propanediol	70
Allyl ethyl ether	3-Ethoxy-1,2-propanediol	60
Pentene-1	1,2-Pentanediol	77
Pentene-2	2,3-Pentanediol	74
Hexene-1	1,2-Hexanediol	80
Cyclohexene	*trans*-1,2-Cyclohexanediol	82
Octene-1	1,2-Octanediol	80
Dodecene-1	1,2-Dodecanediol	95
Tetradecene-1	1,2-Tetradecanediol	92
Oleic acid	9,10-Dihydroxystearic acid	92
Methyl acrylate	Methyl glycerate	77
Ethyl acrylate	Ethyl glycerate	71
Methyl methacrylate	Methyl 1,2-dihydroxyisobutyrate	73
Ethyl methacrylate	Ethyl 1,2-dihydroxyisobutyrate	76

nium trifluoroacetate. A somewhat better grade of product was obtained if the reaction was run in this sequence rather than in the inverse order. Normally a 10% excess of the peroxyacid was employed, and considerable care was necessary in handling this very volatile reagent since it evaporates rapidly from solution. The reaction times employed with peroxytrifluoroacetic acid can be made extremely short if sufficient cooling for the reaction mixture is supplied. Even the higher molecular weight alkenes with terminal unsaturation reacted almost instantaneously with peroxytrifluoroacetic acid whereas these olefins required 8 to 24 hours for hydroxylation with performic acid at 40°.[4] It also has been possible to hydroxylate negatively substituted olefins such as acrylates and methacrylates in good yield with peroxytrifluoroacetic acid. Indeed this reagent offers a convenient laboratory

$$CH_2{=}CHCO_2R \xrightarrow[CH_3OH,\ H^{\oplus}]{CF_3CO_3H} CH_2OHCHOHCO_2R$$

synthesis of glycerates and 1,2-dihydroxyisobutyrates. The hydroxylation of some α,β-unsaturated acids with performic acid has been reported but the yields were low and a very large excess of peracid was required.[5]

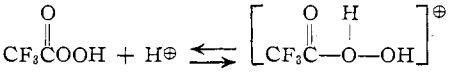
In most of the experiments the isolation of the intermediate hydroxytrifluoroacetate by distillation was necessary in order to separate this product from triethylammonium trifluoroacetate. The ester also contained some ditrifluoroacetate and possibly some of the α-glycol itself since trifluoroacetates undergo transesterification very readily. Consequently, the wide range of boiling points observed for these intermediates is not surprising. The hydroxytrifluoroacetates were in most cases converted to glycols by methanolysis.[3] It was found, however, that methanolic hydrogen chloride was a much more satisfactory reagent for this reaction than methanol itself; indeed, the uncatalyzed methanolysis reaction usually required several days at reflux before it was complete. This may possibly be due to the formation of an intramolecular complex of the type indicated below. The fact that the uncatalyzed methanolysis of the trifluoro-



acetate of *trans*-1,2-cyclohexanediol was fairly rapid, whereas that of the other glycols was relatively slow, offers some support for this hypothesis; in the latter case the formation of such an intramolecular complex is, of course, sterically impossible.

It is interesting to note that methanolysis of the trifluoroacetate esters of methyl glycerate and methyl 1,2-dihydroxyisobutyrate with methanolic hydrogen chloride was relatively unsatisfactory due to the fact that transesterification involving the carboxyl and hydroxyl groups of the glyceric ester took place. This yielded appreciable amounts of low molecular weight polymer. This difficulty was solved, however, by using as a catalyst a sulfonic acid ion exchange resin, Amberlite IR-120, which when stirred with a refluxing solution of the trifluoroacetate in methanol yielded the glycerate without any polymer being formed. Under these conditions the resin acts as a true catalyst and can be reused any number of times. The substitution of methanolysis for alkaline hydrolysis of the hydroxyesters is certainly advantageous in glycol synthesis since it simplifies the preparation of the very water-soluble, low molecular weight glycols enormously. It also should be mentioned that the products obtained by methanolysis were generally of excellent purity and boiled over a very narrow range. The yields listed in Table I for the low molecular weight glycols are undoubtedly on the low side since they reflect the mechanical losses of two distillations in most cases. It is our opinion that the hydroxylation reaction itself is quantitative. The conversion of cyclohexene into *trans*-1,2-cyclohexanediol also indicates that hydroxylation with peroxytrifluoroacetic acid is stereospecific and yields *trans* glycols as do other peracids.

The mechanism of olefin hydroxylation with peroxytrifluoroacetic acid may well be similar to that proposed for other organic peroxyacids.[2] In this system the active reagent would be regarded as the conjugate acid of peroxytrifluoroacetic acid. It is equally probable, however, that peroxytrifluoroacetic acid itself, rather than its protonated complex, is the active species which attacks the olefin. In-



deed, this hypothesis has some support in that the oxidation of olefins in the presence of trifluoroacetate ions proceeds, in a gross sense, as rapidly as when no trifluoroacetate is present; addition of trifluoroacetate ion would, of course, substantially decrease the concentration of the protonated peroxyacid complex. In any case, however, peroxytrifluoroacetic acid has a much weaker oxygen–oxygen bond than that of the known organic peracids and the reactivity of this reagent toward any

(4) D. Swern, G. N. Billen and J. T. Scanlan, THIS JOURNAL, **68**, 1504 (1946).

(5) J. English and J. D. Gregory, *ibid.*, **69**, 2120 (1947).

nucleophilic species such as an olefin is much greater than is observed with other peroxyacids.

Experimental

Triethylammonium Trifluoroacetate.—To 114 g. (1.0 mole) of trifluoroacetic acid in 100 ml. of dry ether cooled in an ice-bath was added dropwise with stirring 101 g. (1.0 mole) of triethylamine. After addition was complete, the ether was evaporated under reduced pressure to yield triethylammonium trifluoroacetate as a colorless, viscous liquid, yield 212 g. (99%).

Anal. Calcd. for $C_8H_{16}O_2NF_3$: neut. equiv., 215. Found: neut. equiv., 217 (perchloric acid in acetic acid).

2,3-Pentanediol.—To a stirred suspension of 6.0 ml. (0.22 mole) of 90% hydrogen peroxide in 50 ml. of methylene chloride cooled in an ice-bath was added 37.2 ml. (0.264 mole) of trifluoroacetic anhydride. The resulting solution was stirred ten minutes in the cold. It was then transferred while cold to a dropping funnel equipped with a pressure equalizer tube and added dropwise over a 30-minute period to a solution of 14.0 g. (0.2 mole) of pentene-2 and 21.4 g. (0.1 mole) of triethylammonium trifluoroacetate in 50 ml. of methylene chloride. Throughout the addition, the exothermic reaction caused the solvent to boil vigorously. After addition was complete the solution was stirred 15 minutes at room temperature. The volatile solvents were then removed at reduced pressure. The residual colorless liquid was distilled to yield 50.5 g. of hydroxytrifluoroacetate, b.p. 38–60° (2.0 mm.). The triethylammonium trifluoroacetate remained in the distillation pot as residual liquid. The trifluoroacetic ester was then heated two hours under reflux with 300 ml. of 3% methanolic hydrogen chloride. The solvent was removed *in vacuo*, and the product was distilled to yield 15.1 g. (74%) of colorless 2,3-pentanediol,[5] b.p. 58–59° (0.5 mm.), $n^{20}D$ 1.4412.

1,2-Pentanediol.—This diol was prepared by essentially the procedure described above. There was obtained 49.6 g. of hydroxytrifluoroacetate, b.p. 38–68° (3.0 mm.), which yielded after methanolysis 16.0 g. (77%) of colorless 1,2-pentanediol,[7] b.p. 78–80°(0.3 mm.), $n^{20}D$ 1.4400.

1,2-Hexanediol.—The procedure for this glycol was again similar to that described above. The intermediate trifluoroacetate ester boiled from 48–100° (1.0 mm.), yield 59.6 g., and some decomposition of the triethylammonium trifluoroacetate was observed at the end of the distillation. Methanolysis of this ester yielded 18.9 g. (80%) of 1,2-hexanediol,[8] b.p. 96–98° (1.0 mm.), $n^{20}D$ 1.4428.

1,2-Octanediol.—1,2-Octanediol was prepared in the usual manner. There was obtained 64.9 g. of the intermediate ester, b.p. 42–80° (2.0 mm.), which yielded after methanolysis 23.3 g. (80%) of α-glycol, b.p. 103–105° (0.5 mm.). After standing three days at room temperature, this product crystallized to yield a colorless, crystalline solid, m.p. 29–30° (lit. m.p. 30.5°[4]).

***trans*-1,2-Cyclohexanediol.**—A cold solution of peroxytrifluoroacetic acid was prepared in the usual manner from 50 ml. of methylene chloride, 37.2 ml. (0.264 mole) of trifluoroacetic anhydride and 6.0 ml. (0.22 mole) of 90% hydrogen peroxide. This solution was added dropwise over a 20-minute period to a solution of 16.4 g. (0.2 mole) of cyclohexene and 21.4 g. (0.1 mole) of triethylammonium trifluoroacetate in 50 ml. of methylene chloride. The exothermic reaction caused the solvent to boil vigorously throughout the addition. The solution was then stirred at room temperature for 15 minutes and the volatile solvents were removed *in vacuo*. The residual liquid was distilled to yield 46.7 g. of intermediate ester, b.p. 48–108° (0.6–3.0 mm.). The distillate was colorless at first but became yellow toward the end of the distillation. Some decomposition of the triethylammonium trifluoroacetate was also observed at the end of the distillation. The distillate was then heated under reflux with 300 ml. of methanol for 20 hours. Evaporation of this solvent yielded 19.0 g. (82%) of colorless, crystalline *trans*-1,2-cyclohexanediol. After one recrystallization from acetone, it melted at 103–104° (lit. m.p. 102–103°[9]).

1,2-Dodecanediol.—To 25 ml. of methylene chloride cooled in an ice-bath was added 3.0 ml. (0.11 mole) of 90% hydrogen peroxide. Trifluoroacetic anhydride, 18.6 ml. (0.13 mole), was added to the resulting mixture in one portion, and the solution so obtained was stirred five minutes in the ice-bath. The resulting solution of peroxytrifluoroacetic acid in methylene chloride was then added dropwise over a 20-minute period to a stirred solution of 16.8 g. (0.1 mole) of dodecene-1 and 10.7 g. (0.05 mole) of triethylammonium trifluoroacetate in 25 ml. of methylene chloride. After addition was complete, the solution was allowed to stand at room temperature 15 minutes, and the volatile solvent was then removed under reduced pressure. To the residual liquid was added 150 ml. of 6% methanolic hydrogen chloride, and the resulting solution was heated under reflux two hours. The methanol was evaporated at reduced pressure and the product poured into 200 ml. of hot water. An oil separated which crystallized after standing overnight at room temperature. This solid was collected on a funnel and dried in a vacuum oven at 50°. There was obtained 19.2 g. (95%) of fairly pure, colorless, crystalline 1,2-dodecanediol which melted at 56–58° (lit. m.p. 60.5°[4]).

Methyl Glycerate.—A solution of peroxytrifluoroacetic acid was prepared in the usual manner from 50.8 ml. (0.36 mole) of trifluoroacetic anhydride, 8.2 ml. (0.3 mole) of 90% hydrogen peroxide and 50 ml. of ethylene dichloride. To this cold solution was added 10.7 g. (0.05 mole) of triethylammonium trifluoroacetate and 17.2 g. (0.2 mole) of methyl acrylate. The resulting solution was heated rapidly to boiling where some evolution of heat was observed. The solution was heated under reflux for two hours. It was then cooled and the volatile solvents removed under reduced pressure. The residual liquid was distilled to yield 43.0 g. of hydroxytrifluoroacetate, b.p. 45–60° (0.5 mm.). This product was dissolved in 300 ml. of methanol and stirred vigorously under reflux with 50 g. of Amberlite IR-120 ion exchange resin for seven hours. The resin was then removed by filtration and evaporation of the methanol filtrate yielded the product. After distillation there was obtained 18.5 g. (77%) of colorless methyl glycerate,[10] b.p. 74–78° (0.5 mm.), $n^{20}D$ 1.4502. When 3% methanolic hydrogen chloride was used for methanolysis, the yield of methyl glycerate was only 36%.

Methyl 1,2-Dihydroxyisobutyrate.—To 8.2 ml. (0.3 mole) of 90% hydrogen peroxide suspended in 100 ml. of methylene chloride cooled in an ice-bath was added dropwise over a ten-minute period 50.8 ml. (0.36 mole) of trifluoroacetic anhydride. To the resulting solution was added 21.4 g. (0.1 mole) of triethylammonium trifluoroacetate. The peroxytrifluoroacetic acid so prepared was added to a boiling solution of 20.0 g. (0.2 mole) of methyl methacrylate in 50 ml. of methylene chloride over a 30-minute period. After addition was complete, the mixture was heated under reflux for one hour. It was then worked up in the usual manner and there was obtained 53.0 g. of hydroxytrifluoroacetate, b.p. 45–60° (0.4 mm.). This product was then heated under reflux for two hours with 300 ml. of 3% methanolic hydrogen chloride. After evaporation of the solvent, the product was distilled to yield 18.9 g. (71%) of methyl 1,2-dihydroxyisobutyrate, b.p. 60–64° (0.1 mm.), $n^{25}D$ 1.4438 (lit. $n^{25}D$ 1.4438[11]). When Amberlite IR-120 was used for methanolysis, it was necessary to heat the solvent-resin mixture for 24 hours and a 73% yield of methyl 1,2-dihydroxyisobutyrate was obtained.

Acknowledgment.—We are indebted to Dr. R. M. Ross for several helpful suggestions and for his encouragement throughout the course of these investigations.

HUNTSVILLE, ALABAMA

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