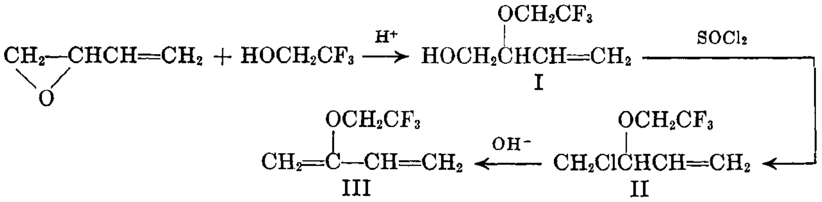
It has been found that trifluoroethanol also reacts with 3,4-epoxy-1-butene to give a 2-alkoxy-1-ol which can be converted in several steps to the diene as shown.



The alcohol showed the absorption peaks at 9.60 μ which is characteristic of primary alcohols. The dehydration of (2-(fluoroalkoxy)ethanol is not a practical route to vinyl ethers[2] and I was consequently converted to the chloro derivative by treatment with thionyl chloride. Dehydrochlorination was carried out by potassium hydroxide in methanol.

The diene polymerized to a rubber-like material during distillation of the first sample; however, polymerization was inhibited by hydroquinone during subsequent preparations.

EXPERIMENTAL[3]

Preparation of 2-(2,2,2-trifluoroethoxy)-3-buten-1-ol. A solution of 0.5 g. of sulfuric acid in 530 g. (5.30 moles) of trifluoroethanol was heated to reflux and 50 g. (0.71 mole) of 3,4-epoxybutene-1 added dropwise with stirring over a 1-hr. period. Stirring at reflux was continued for 2 hr., followed by the addition of 10 g. of potassium carbonate. The solution was stirred overnight at room temperature, the unchanged material stripped and the remainder fractionated to give 46 g. (38% conversion) of 2-(2,2,2-trifluoroethoxy)-3-buten-1-ol. An analytical fraction had the following properties: b.p. 86°/55 mm., n_D^{23} 1.3797, d^{23} 1.198.

Anal. Calcd. for $C_6H_9F_3O_2$: MR$_D$, 32.61; C, 42.35; H, 5.33. Found: MR$_D$, 32.92; C, 42.37: H, 5.46.

Preparation of 3-(2,2,2-trifluoroethoxy)-4-chloro-1-butene. A solution of 47.5 g. (0.6 mole) of pyridine and 102 g. (0.6 mole) of 2-(2,2,2-trifluoroethoxy)-3-buten-1-ol was cooled to 0° and 116 g. (0.98 mole) of thionyl chloride added dropwise with stirring. The mixture was then heated with stirring at 75° for 2 hr., washed with dilute hydrochloric acid, and extracted with ethyl ether, dried and fractionated to give 68 g. (60% conversion) of 3-(2′,2,2-trifluoroethoxy)-4-chloro-1-butene. An analytical sample had the following properties: b.p. 66°/55 mm., n_D^{20} 1.3852, d^{20} 1.209.

Anal. Calcd. for $C_6H_4ClF_3O$: MR$_D$, 35.95; C, 38.21; H, 5.28; Cl, 18.80. Found: MR$_D$, 36.60; C, 38.13; H, 4.31; Cl, 18.69.

Preparation of 2-(2,2,2-trifluoroethoxy)-1,3-butadiene. A solution of 40 g. (0.64 mole) of potassium hydroxide in 220 ml. of methanol was heated to reflux and 65 g. (0.345 mole) of 3-(2,2,2-trifluoroethoxy)-4-chloro-1-butene added and stirred for 1.5 hr. The salt was removed by filtration and the solution washed with water to give an insoluble organic layer which was separated, dried, and fractionated to give 20 g. (38% conversion) of 2-(2,2,2-trifluoroethoxy)-1,3-butadiene. Hydroquinone (0.1 g.) was added to the material before distillation to prevent polymerization. A chromatographically pure sample had the following properties: b.p. 35°/95 mm. and 93°/760 mm., n_D^{21} 1.3778, d^{21} 1.116.

Anal. Calcd. for $C_6H_7F_3O$: MR$_D$, 30.62; C, 47.37; H, 4.64. Found: MR$_D$, 31.41; C, 47.62; H, 4.79.

Optical exaltation may account for the high value observed for the molar refractivity.

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[2] M. L. Brey and Paul Tarrant, *J. Am. Chem. Soc.*, **79**, 6533 (1957).

[3] Analyses by Galbraith Laboratories, Knoxville, Tenn.

Reactions of 1-(*p*-Nitrophenyl)ethyl Nitrate

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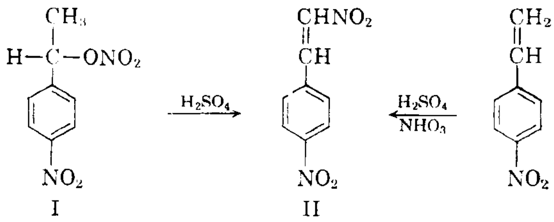
The recent report[1] of the solvolytic conversion of *tert*-butyl nitrate into nitro-*tert*-butyl acetate or trifluoroacetate brought to mind a similar reaction which was encountered in this laboratory some years ago during a brief study of the reactions of 1-(*p*-nitrophenyl)ethyl nitrate (I). This compound has been shown by Troutman[2] to be easily prepared by the nitration of methylphenylcarbinol and to be efficiently and rapidly converted to *p*-nitroacetophenone upon treatment with bases. Upon treatment with strong sulfuric acid at temperatures below 50° the nitronitrate formed *p*,β-dinitrostyrene (II) in high yields.



Boschan and Whitnack[1] quite reasonably speculated that the *tert*-butyl nitrate reaction proceeds by the intermediate formation of isobutylene and the addition of acetyl or trifluoroacetyl nitrate to

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[1] R. Boschan and G. C. Whitnack, *J. Org. Chem.*, **25**, 1253 (1960).

[2] H. D. Troutman, U. S. Patent 2,794,836.

the resulting double bond. In the case of the nitrophenylethyl nitrate, elimination of the elements of nitric acid to form the olefin followed by nitronium ion nitration appears to be a likely possibility since it was found that *p*-nitrostyrene was readily attacked by mixed acid at low temperatures to give *p*,β-dinitrostyrene.

In the reaction of 1-(*p*-nitrophenyl)ethyl nitrate with sulfuric acid care must be taken to keep the temperature below 50° since higher temperatures bring about further reaction of the product dinitrostyrene with the acid. Thus, Friedlander[3] has reported that, after heating the dinitrostyrene with sulfuric acid to 110°, a *p*-nitrobenzaldoxime was isolated from the reaction mixture. Under these conditions we were also able to recover small amounts of Friedlander's product (presumably the *syn*-oxime, m.p. 128°[4]); however, we found *p*-nitrobenzamide also present. Further, by simply diluting the reaction mixture and steam distilling, *p*-nitrobenzaldehyde of high purity crystallized from the distillate in yields of 40–49% and *p*-nitrobenzoic acid crystallized from the cooled kettle residue in yields of 25–35%. Higher temperatures (130–135°) or the use of sulfuric acid fortified with oleum tended to increase the yield of *p*-nitrobenzoic acid at the expense of *p*-nitrobenzaldehyde. This entire sequence of rather interesting consecutive and concurrent reactions can be carried out in one kettle by carefully dissolving 1-(*p*-nitrophenyl)ethyl nitrate in concentrated sulfuric acid at about room temperature, slowly heating to about 110°, and allowing the exothermic reaction with the evolution of carbon monoxide to subside, diluting with ice, and steam distilling. The reactions involved can be rationalized as follows: upon dissolving in sulfuric acid, 1-(*p*-nitrophenyl)ethyl nitrate is converted to *p*,β-nitrostyrene; upon heating, the dinitrostyrene is hydrolyzed and undergoes a reverse aldol forming *p*-nitrobenzaldehyde and nitromethane; the nitromethane, in hot concentrated sulfuric acid, gives hydroxylamine sulfate and formic acid; the formic acid is dehydrated to carbon monoxide; the hydroxylamine and *p*-nitrobenzaldehyde condense to form *syn*- and *anti*-*p*-nitrobenzaldoxime; the *anti*-oxime either undergoes Beckmann rearrangement to give *p*-nitrobenzamide or dehydrates to *p*-nitrobenzonitrile which, in turn, hydrates in the concentrated acid. Upon diluting and steam distilling, the *syn*-oxime is hydrolyzed to *p*-nitrobenzaldehyde, which appears in the distillate, and *p*-nitrobenzamide is hydrolyzed to *p*-nitrobenzoic acid, which remains in the kettle.

EXPERIMENTAL[5]

Preparation of p,β-dinitrostyrene. To 1000 g. of concd. sulfuric acid, maintained at 40° by means of an ice-water bath, there was slowly added, with stirring, 100 g. of 1-(*p*-nitrophenyl)ethyl nitrate,[3] m.p. 48°. (The nitrate should be added in small portions, waiting for each portion to dissolve before subsequent addition, since the reaction can become uncontrollable.) After the addition was completed, the solution was stirred at 40° for a few minutes, poured onto ice, and neutralized with ammonium hydroxide. Filtration gave 88 g. (96%) of crude *p*,β-dinitrostyrene, m.p. 185–190°. One crystallization from dioxane gave pure material, m.p. 201°. An authentic sample, m.p. 200°, was prepared by the condensation of *p*-nitrobenzaldehyde with nitromethane and a mixed melting point determination showed no depression.

Nitration of p-nitrostyrene. To an ice-cold solution of 4 g. of 98% nitric acid in 75 g. of concd. sulfuric acid there was added dropwise 7.5 g. of *p*-nitrostyrene. The resulting solution was poured onto ice and filtered to give 6 g. of product, m.p. 200° after crystallization from dioxane. This compound was shown to be *p*,β-dinitrostyrene by mixed melting point determination with the authentic sample.

Reaction of p,β-dinitrostyrene with sulfuric acid. A solution of 10 g. of *p*,β-dinitrostyrene in 100 ml. of concd. sulfuric acid was slowly heated to 110°. After a few minutes gas evolution ceased and the solution was cooled, diluted with water, and filtered. Crystallization of the filter cake from water gave 0.5 g. of colorless, silvery plates of *syn-p*-nitrobenzaldoxime m.p. 128°. Similar results were obtained by using a solution of the dinitrostyrene in sulfuric acid prepared by dissolving 1-(*p*-nitrophenyl)ethyl nitrate in concentrated sulfuric acid.

In a subsequent run from 50 g. of 1-(*p*-nitrophenyl)ethyl nitrate and 500 g. of sulfuric acid, after gas evolution had ceased at 110° the solution was cooled and poured over ice. The resulting precipitate was slurried with saturated sodium bicarbonated solution, recovered by filtration, dried, and crystallized from ethyl alchol to give 5 g. of almost colorless material, m.p. 196–197°. A mixed melting point (197–200°) with an authentic sample showed this product to be *p*-nitrobenzamide.

Preparation of p-nitrobenzaldehyde and p-nitrobenzoic acid. To 500 g. of concd. sulfuric acid at 40° there was slowly added 50 g. of 1-(*p*-nitrophenyl)ethyl nitrate. After solution was complete, the temperature was slowly raised to 110° at which time an exothermic reaction took place, the reaction temperature rising to 120°. After the reaction subsided, the solution was held at 110° for 15 min. and then poured onto 1000 g. of ice. The resulting solution was distilled at atmospheric pressure and the distillate was filtered to give 17 g. (40% yield) of *p*-nitrobenzaldehyde, m.p. 104°. The residue in the kettle was cooled and filtered to give 10 g. (25% yield) of *p*-nitrobenzoic acid, m.p. 237–240°. Assuming equal probability for the intermediate formation of *cis*- and *trans-p*-nitrobenzaldoxime, the theoretical yields would, of course, be 50% for the aldehyde and 50% for the acid. In a subsequent run, after reaction at 110–117°, the solution was cooled and added continuously to a 2-l. flask which contained boiling water and into which steam was continously introduced. Isolation as before gave a 41% yield of aldehyde and a 35% yield of acid. From a run at 130–135° to yields of aldehyde and acid were, repectively, 28% and 58% while a run using an 80:20 mixture of concd. sulfuric acid and oleum (20% sulfur trioxide) at 110–120° gave only 11% *p*-nitrobenzaldehyde and 68% *p*-nitrobenzoic acid.

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(3) P. Friedlander and J. Mahly, *Ann.*, **229**, 210 (1885).

(4) O. L. Brady and F. P. Dunn, *J. Chem. Soc.*, **103**, 1619 (1913), report m.p. 129° for the *anti*-oxime; however, under modern convention, this is the *syn*-oxime since a stable acetate can be prepared.

(5) Melting points were taken on a Fisher-Johns block.