

trous acid removed with urea. The diazonium solution was then buffered at a pH of about 6 by the addition of 50 g. of sodium acetate and 15 cc. of glacial acetic acid in 50 cc. of water.<sup>13</sup> The diazonium solution was then added dropwise with stirring at 0° during a 2-hr. period to a solution of 4 g. of  $\beta$ -mercaptopropionic acid and 10 g. of sodium acetate in 50 cc. of water. There was an immediate formation of a yellow-white solid and an evolution of gas during the addition. The best method of working up the product was to collect it and recrystallize it once from aqueous alcohol. The product was then allowed to stand in aqueous acetone with some concd. hydrochloric acid for 3 days at room temperature, following the hydrolysis procedure described above for the ester XI. The solution was extracted with ether, the extracts were washed with sodium carbonate, and the desired acid VI was obtained by acidification of the carbonate solution; it weighed 4.7 g. (36%) and melted at 135–137°. The ether extract yielded an appreciable amount of neutral crystalline material, m.p. 82–82.5°, shown to be 4-methoxybiphenyl by a mixed m.p.

**5-Phenyl-8-methoxythiochromanone (V).**—The only way found for the cyclization of VI to V was the following. The acid VI (1 g.) was treated in a platinum dish with 20–30 g. of anhydrous hydrogen fluoride. The dish was placed in a paraffin-coated desiccator over calcium chloride and allowed to stand overnight. The viscous oil in the dish was dissolved in benzene, with warming on a steam-bath, and was extracted with sodium carbonate; the residue in the dish was also extracted by sodium carbonate; usually about 0.6 g. of the starting acid VI was recovered by acidification of the carbonate extracts. The benzene solution was washed with water, dried, and chromatographed on alumina, using dry benzene as the eluent. The benzene yielded a dark oil, from which was obtained crystalline material, which, after two crystallizations from methanol, weighed 0.2 g. (50%, based on unrecovered starting material) and melted at 124–125°.

(13) The reaction did not take place in an unbuffered solution of low pH; cf. D. S. Tarbell, E. G. Lindstrom, *et al.*, *THIS JOURNAL*, **70**, 1381 (1948).

*Anal.* Calcd. for  $C_{16}H_{14}O_2S$ : C, 71.08; H, 5.22. Found: C, 71.02; H, 5.43.

The dinitrophenylhydrazine melted, after two recrystallizations from chloroform-ethanol, at 253–256°.

*Anal.* Calcd. for  $C_{22}H_{18}N_4O_6S$ : C, 58.65; H, 4.02. Found: C, 58.70; H, 4.39.

**$\beta$ -(2-Naphthyl)-mercaptopropionic Acid.**—This compound was not obtained by the action of diazotized  $\beta$ -naphthylamine on  $\beta$ -mercaptopropionic acid, using either an acetate buffer or an acid solution; tar and naphthalene were the products. It was readily prepared by heating 4 g. of  $\beta$ -thionaphthol with 10 g. of methyl acrylate and a few drops of piperidine for 6 hr. The volatile material was then removed *in vacuo*, the residue was dissolved in acetone, concd. hydrochloric acid was added until a precipitate appeared, and additional acetone was added to clear the solution. After standing for 4 days, the mixture was worked up as described above, and 4.5 g. (77%) of the desired acid was obtained, m.p. 102–103°, after crystallization from benzene.<sup>14</sup>

**5,6-Benzothiochromanone (XII).**<sup>14</sup>—This compound was prepared in 60% yield by the cyclization with anhydrous hydrogen fluoride, by essentially the procedure described above for V. The same yield was obtained by the use of sulfuric acid (as in ref. 14) but the product from the hydrogen fluoride was easier to work up.

**5,6-Benzothiochromanone Sulfone (XIII).**—The thiochromanone (1 g.) was refluxed 1 hr. with 10 g. of 30% hydrogen peroxide in glacial acetic acid, and the excess peroxide was decomposed by addition of manganese dioxide. The solution was filtered, was diluted with water and the resulting precipitate was isolated. After three crystallizations from ethanol, 0.79 g. (69%) of sulfone, m.p. 150–151°, was obtained.

*Anal.* Calcd. for  $C_{13}H_{10}O_3S$ : C, 63.45; H, 4.06. Found: C, 63.57; H, 4.10.

(14) The m.p. reported for the acid (F. Krollpfeiffer and H. Schultze, *Ber.*, **56**, 1819 (1923)) prepared by the action of  $\beta$ -bromopropionic acid on  $\beta$ -thionaphthol, is 104–105°.

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## NOTES

### Preparation of $\beta$ -Hydroxydialkyl Peroxides

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Three  $\beta$ -hydroxydialkyl peroxides were prepared by a reaction of *t*-butylhydroperoxide with epoxides. The compounds synthesized were  $\beta$ -hydroxyethyl-*t*-butyl peroxide,  $\beta$ -hydroxypropyl-*t*-butyl peroxide and  $\beta$ -hydroxyisobutyl-*t*-butyl peroxide. Yields obtained ranged from 33–43%. No effort was made to develop optimum conditions to improve these yields. 3,5-Dinitrobenzoates of two of the hydroxy peroxides were prepared. It seems likely that reactions of this type could be used as a general preparative method for  $\beta$ -hydroxydialkyl peroxides or hydroperoxides.

**$\beta$ -Hydroxyethyl-*t*-butyl Peroxide.**—A 500-ml. round-bottom flask fitted with a mercury-sealed stirrer, dropping funnel, condenser and thermometer, was immersed in an ice-salt-bath. Forty-four grams (1.0 mole) of ethylene oxide and 150 ml. of ethyl ether were introduced. Maintaining the temperature below 3°, 15 ml. of 40% potassium hydroxide was added over a 30-minute period. Forty-seven grams (0.33 mole) of 63% *t*-butyl hydroperoxide obtained from the Union Bay State Company was added drop-

wise over a 1.5-hr. interval, maintaining the temperature below 5°. The mixture was allowed to come to room temperature and stirring continued for four hours. The aqueous layer was discarded. Light ends were removed from the organic phase by distillation at atmospheric pressure followed by vacuum distillation to 30° (20 mm.) head temperature. From the bottoms 14.6 g. (33% yield) of crude product was recovered, b.p. 35° at 35 mm. to 34° at 1.5 mm. Redistillation of this material produced 11.5 g. of product, b.p. 37–38° at 2 mm.,  $n_D^{20}$  1.4249,  $d_4^{20}$  0.9561.

*Anal.*<sup>1</sup> Calcd. for  $C_8H_{14}O_3$ : C, 53.71; H, 10.51. Found: C, 53.79; H, 10.49.

The 3,5-dinitrobenzoate of this compound was prepared by the method of Malone and Reid.<sup>2</sup> The derivative was recrystallized several times from aqueous ethanol and finally from absolute ethanol. It had a melting point of 63–63.6°.

*Anal.* Calcd. for  $C_{15}H_{16}O_5N_2$ : C, 47.56; H, 4.91; N, 8.53. Found: C, 47.32; H, 4.99; N, 8.67.

**$\beta$ -Hydroxypropyl-*t*-butyl Peroxide.**—In similar manner to the above, but in the absence of the ether, 39 g. (0.67 mole) of 1,2-propene oxide, 10 ml. of 40% potassium hydroxide and 24 g. (0.17 mole) of 63% *t*-butyl hydroperoxide were agitated. After the addition of the hydroperoxide was complete, the mixture was allowed to come to room temperature and then was heated to 40° for two hours. The

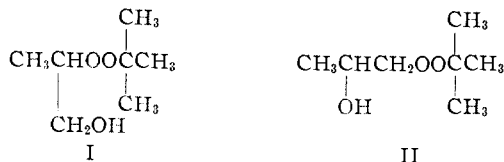
(1) Microanalyses were made by Microchemical Specialties, Berkeley, California.

(2) C. B. Malone and B. B. Reid, *THIS JOURNAL*, **51**, 3424 (1929).

yield of crude product on distillation of the organic layer was 11 g. (44%). Pure material was obtained on redistillation; b.p. 36.6–37.1° at 2.5 mm.,  $n_D^{20}$  1.4184,  $d_4^{20}$  0.9296.

Anal. Calcd. for  $C_7H_{16}O_3$ : C, 56.73; H, 10.88. Found: C, 57.55; H, 10.75.

From the condensation reaction of 1,2-propene oxide with *t*-butyl hydroperoxide, two isomeric  $\beta$ -hydroxy peroxides are possible: a primary alcohol represented below by formula I and a secondary alcohol, formula II.



Stephan<sup>3</sup> showed that primary and secondary alcohols could be separated by boiling in benzene with phthalic anhydride. Under such conditions the primary alcohol rapidly esterifies while the secondary reacts very slowly. Cox, Nelson and Cretcher<sup>4</sup> separated the isomeric *n*-propyl ethers of 1,2-propylene glycol by this method. An indication that the compound isolated from the reaction of *t*-butyl hydroperoxide with 1,2-propene oxide was the secondary alcohol was obtained by this procedure as follows:

To 25 ml. of benzene, 3.7 g. of reaction product and 4.5 g. of phthalic anhydride were added. The mixture was refluxed for one hour, allowed to cool, and filtered. On distillation *in vacuo*, 3.4 g. (89%) of the starting material was recovered.

The 3,5-dinitrobenzoate of the  $\beta$ -hydroxypropyl-*t*-butyl peroxide was prepared in the same way as the dinitrobenzoate of  $\beta$ -hydroxypropyl-*t*-butyl peroxide. The derivative was recrystallized twice from ethyl ether and had a melting point of 88–89°.

Anal. Calcd. for  $C_{14}H_{18}O_8N_2$ : C, 49.12; H, 5.30; N, 8.18. Found: C, 49.44; H, 5.21; N, 8.26.

**$\beta$ -Hydroxyisobutyl-*t*-butyl Peroxide.**—As above, the reaction of 72 g. (1.0 mole) of 1,2-isobutene oxide with 60 g. (0.42 mole) of 63% *t*-butyl hydroperoxide in the presence of 20 ml. of 40% potassium hydroxide was carried out. After the peroxide addition was complete the mixture was permitted to come to room temperature and then was heated with stirring to 55–60° for two hours. Distillation of the organic phase produced 25 g. (37%) of crude product, b.p. 45–48° at 5–6 mm. Pure material was obtained by redistillation, b.p. 37–37.5° at 4 mm.,  $n_D^{20}$  1.4165,  $d_4^{20}$  0.9085.

Anal. Calcd. for  $C_8H_{18}O_3$ : C, 59.23; H, 11.18. Found: C, 59.60; H, 11.25.

(3) K. Stephan, *J. prakt. Chem.*, [2] **60**, 248 (1899).

(4) H. L. Cox, W. L. Nelson and L. H. Cretcher, *THIS JOURNAL*, **49**, 1080 (1927).

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## The Synthesis of 2,4,6-Trinitrostyrene and Some Intermediates

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Preparation of 2,4,6-trinitrostyrene polymer was attempted in the hope that it might combine the explosive properties of 2,4,6-trinitrotoluene with the flexibility in the control of mechanical properties characteristic of polymers. Concurrent investigations of a similar nature have already been described by Wiley and Behr,<sup>1</sup> who reported the successful synthesis of 2,4,6-trinitrostyrene and the failure of the monomer to undergo polymerization. The present report is concerned, therefore, only

(1) R. H. Wiley and L. C. Behr, *THIS JOURNAL*, **72**, 1922 (1950).

with those phases of our study which extend the work of these authors or involve different preparative methods.

Attempted preparation of 2,4,6-trinitrostyrene by dehydration of 2-(2,4,6-trinitrophenyl)-ethyl alcohol was unsuccessful due to the failure of the alcohol to lose water when heated with concentrated sulfuric acid, with a mixture of sirupy phosphoric acid and phosphoric anhydride or with aluminum chloride in benzene. The olefin was obtained conveniently, however, by conversion of the alcohol to the corresponding chloride which, with pyridine, gave 2-(2,4,6-trinitrophenyl)-ethylpyridinium chloride, whose degradation with sodium carbonate proceeded readily. Attempts to prepare the olefin by direct dehydrohalogenation of the chloride with alcoholic potassium hydroxide, pyridine or aqueous carbonate led to the formation of unidentifiable resinous materials. Dehydrohalogenation could be accomplished by mild heating of the chloride but only dark resinous products which could not be adequately characterized were obtained.

Trinitrostyrene was also obtained by the general procedure of Wiley and Behr.<sup>1</sup> The Mannich condensation of dimethylamine with 2,4,6-trinitrotoluene was accomplished by the method of Bruson and Butler.<sup>2</sup> The resulting 2-(2,4,6-trinitrophenyl)-ethyl dimethylamine was isolated as the hydrochloride and then directly converted to the quaternary iodide in good yield. This latter was degraded to trinitrostyrene by heating with dilute aqueous sodium carbonate.

As reported, 2,4,6-trinitrostyrene could not be polymerized by catalysis by peroxides or boron trifluoride. Other Friedel-Crafts catalysts and basic catalysts, such as sodium and sodium amide, also failed to yield polymers. The olefin was unreactive toward bromine in either water or carbon tetrachloride solution, but reacted readily with ammonia in anhydrous ether to form bis-(2,4,6-trinitrophenylethyl)-amine. This behavior is in accord with the strong electrophilic character of 2,4,6-trinitrostyrene. Similar reactions between ammonia and 3-nitro-6-bromo- $\beta$ -nitrostyrene<sup>3</sup> and  $\beta$ -nitrostyrene<sup>4</sup> have been reported.

### Experimental

**Attempted Dehydration of 2-(2,4,6-Trinitrophenyl)-ethyl Alcohol.**—2-(2,4,6-Trinitrophenyl)-ethyl alcohol<sup>5</sup> was heated directly with sirupy phosphoric acid at 150° and recovered unchanged. At 200° considerable charring occurred and neither the residue nor the supernatant liquid decolorized alkaline permanganate. Similar attempts at heating with concd. sulfuric acid or a mixture of phosphoric anhydride and phosphoric acid failed to yield the desired product.

2-(2,4,6-Trinitrophenyl)-ethyl alcohol was suspended in benzene and anhydrous aluminum chloride was added. The bright orange precipitate, which was immediately formed, reacted readily with moisture in the air to give aluminum hydroxide and an unidentified material which did not decolorize alkaline permanganate.

**Dehydrohalogenation of 2-(2,4,6-Trinitrophenyl)-ethyl Chloride.**—2-(2,4,6-Trinitrophenyl)-ethyl chloride<sup>6</sup> was heated with pyridine for various lengths of times to yield py-

(2) H. A. Bruson and G. B. Butler, *ibid.*, **68**, 2348 (1946).

(3) D. E. Worrall and J. Finkel, *ibid.*, **61**, 2969 (1939).

(4) D. E. Worrall, *ibid.*, **49**, 1598 (1927).

(5) V. Vender, *Gazz. chim. ital.*, **45**, II, 97 (1915).

(6) F. Challenger and P. H. Clapham, *J. Chem. Soc.*, 1612 (1948).