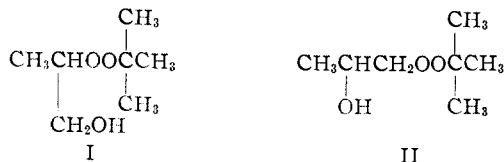


yield of crude product on distillation of the organic layer was 11 g. (44%). Pure material was obtained on redistillation; b.p. 36.6–37.1° at 2.5 mm., n_D^{20} 1.4184, d_4^{20} 0.9296.

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 β -hydroxy peroxides are possible: a primary alcohol represented below by formula I and a secondary alcohol, formula II.



Stephan³ 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 Cretcher⁴ 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 β -hydroxypropyl-*t*-butyl peroxide was prepared in the same way as the dinitrobenzoate of β -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.

β -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,¹ 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.¹ The Mannich condensation of dimethylamine with 2,4,6-trinitrotoluene was accomplished by the method of Bruson and Butler.² 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- β -nitrostyrene³ and β -nitrostyrene⁴ have been reported.

Experimental

Attempted Dehydration of 2-(2,4,6-Trinitrophenyl)-ethyl Alcohol.—2-(2,4,6-Trinitrophenyl)-ethyl alcohol⁵ 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 chloride⁶ 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**, 2069 (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).

ridine hydrochloride and products varying from dark resins to brown, infusible materials, depending on length of heating. One such resin analyzed correctly (17.48%) for nitrogen (theory for trinitrostyrene, 17.58%) but was not otherwise characterized.

Dehydrohalogenation could be accomplished by heating the chloride at 85–90° until the evolution of HCl was completed as evidenced by testing with moist litmus paper. The products were brittle, resinous substances with a softening temperature of 50–60° which did not change on further heating.

2-(2,4,6-Trinitrophenyl)-ethylpyridinium Chloride.—2-(2,4,6-Trinitrophenyl)-ethyl chloride, 27.6 g. (0.1 mole), was added to 23.7 g. (0.3 mole) of pyridine. After the entire mass had solidified (about 20 minutes) the excess pyridine was extracted with low-boiling petroleum ether. Recrystallization of the residue from a methanol-methyl ethyl ketone mixture gave 17.7 g. (50%) of light yellow to colorless 2-(2,4,6-trinitrophenyl)-ethylpyridinium chloride, m.p. 132.0–134.2°.

Anal. Calcd. for $C_{13}H_{11}O_6N_4Cl$: N, 15.80; Cl, 10.00. Found: N, 15.90; Cl, 9.94.

On dilution of the pyridine extract with water, colorless platelets were deposited which on recrystallization from carbon tetrachloride melted at 63–64°. These were shown, by mixed melting point with an authentic sample, to be 2,4,6-trinitrostyrene.

Preparation of 2,4,6-Trinitrostyrene from 2-(2,4,6-Trinitrophenyl)-ethylpyridinium Chloride.—To a mixture of 5 g. (0.014 mole) of 2-(2,4,6-trinitrophenyl)-ethylpyridinium chloride and 100 ml. of water, 0.75 g. (0.007 mole) of sodium carbonate was added with shaking, forming a cherry-red solution, which gradually turned darker. Pyridine was evolved and a brown precipitate settled. After 20 minutes, the solution was neutralized with dilute hydrochloric acid. Extractions of the precipitate with carbon tetrachloride yielded a solution from which was isolated 1.0 g. (29%) of trinitrostyrene, m.p. 63–64°, which failed to add bromine but did decolorize alkaline permanganate.

Anal. Calcd. for $C_8H_5N_3O_6$: C, 40.18; H, 2.11; N, 17.57. Found: C, 40.44; H, 2.22; N, 17.54.

2-(2,4,6-Trinitrophenyl)-ethyltrimethylammonium Iodide.—To a warm solution of 12.8 g. (0.04 mole) of 2-(2,4,6-trinitrophenyl)-ethyltrimethylamine hydrochloride¹ in 80 g. (2.5 moles) of methanol, 9.9 g. (0.07 mole) of methyl iodide and 2.7 g. (0.048 mole) of potassium hydroxide pellets were added with vigorous shaking. The brick-red precipitate which began to form in about 20 minutes was promptly separated by decanting and was recrystallized from methanol to give 12.7 g. (75%) of 2-(2,4,6-trinitrophenyl)-ethyltrimethylammonium iodide, m.p. 139–141°.

Addition of Ammonia to 2,4,6-Trinitrostyrene.—To a solution of 0.69 g. of the olefin in 25 ml. of anhydrous ether, 0.5 ml. of anhydrous ammonia was added. On partial evaporation of the solvent, 0.5 g. (70%) of yellow bis-(2,4,6-trinitrophenylethyl)-amine, m.p. 129.5–130.5° after repeated washing with dry ether, separated.

Anal. Calcd. for $C_{16}H_{13}O_6N_7$: N, 19.80. Found: N, 19.61.

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The Dichlorination of *o*-Xylene¹

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Hinkel and co-workers^{3,4} reported that the low temperature, iron-catalyzed dichlorination of *o*-

(1) Abstracted mainly from a portion of a thesis on "The Dielectric Properties of Solid Nitrodichloro-*o*-xylenes" directed by Dr. Reuben E. Wood and submitted in partial fulfillment of the requirements for the M.S. degree at The George Washington University, May, 1952.

(2) Research and Development Department, Naval Powder Factory, Indian Head, Md.

(3) L. E. Hinkel, E. E. Ayling and L. C. Bevan, *J. Chem. Soc.*, 1874 (1928).

(4) L. E. Hinkel, E. E. Ayling and T. M. Walters, *ibid.*, 1946 (1934).

xylene with chlorine gas yielded only the 4,5- and 3,4-dichloro-isomers. The absence of substantial quantities of 3,5-dichloro-*o*-xylene would, of course, be expected because of the ortho-para directive power of the chlorine atom, but the failure of these workers to obtain 3,6-dichloro-*o*-xylene is puzzling in view of the tendency of catalyzed chlorination to occur predominantly in the position para to chlorine already present.⁵ In addition, White, Biggs and Morgan⁶ reported that 5-nitro-3,4-dichloro-*o*-xylene which was prepared according to the method of Hinkel and co-workers had a melting point higher than the one given by the original authors. White and co-workers attributed the higher melting point to contamination of their product with 3-nitro-4,5-dichloro-*o*-xylene in solid solution.

In the present work a low temperature, iron-catalyzed dichlorination of *o*-xylene was carried out and the products fractionated. 4,5-Dichloro-*o*-xylene was identified by its melting point and the melting point of the mononitro derivative. The distillation fractions in which 3,4-dichloro-*o*-xylene would be expected on the basis of the previous work were found to have melting points substantially higher than that of the pure compound (8–9°^{3,4}). Recrystallization of these fractions yielded a compound which melted at the same temperature as that recorded for 3,6-dichloro-*o*-xylene (29°⁴). The infrared spectrum of the compound shows a strong absorption band at 8.03 cm.^{-1} , a frequency which is characteristic of 1,2,3,4-tetrasubstituted benzenes.⁷ The mononitro derivative prepared from these fractions was found, after purification, to have the melting point recorded for 4-nitro-3,6-dichloro-*o*-xylene (84°⁴) rather than that for 5-nitro-3,4-dichloro-*o*-xylene (78°³). To confirm the conclusion that 3,6-dichloro-*o*-xylene was formed in the chlorination, a dinitro-derivative was prepared from one of these fractions. This compound had a melting point closer to the recorded value for 4,5-dinitro-3,6-dichloro-*o*-xylene (174°⁴) than that for 5,6-dinitro-3,4-dichloro-*o*-xylene (172°^{3,4}).

No attempt was made to isolate 3,4-dichloro-*o*-xylene which was probably present as a minor constituent in the fractions containing 3,6-dichloro-*o*-xylene. These two isomers have the same boiling point (234°^{3,4}). The melting points of the distillation fractions (Table I, below) indicate that the major constituent of fractions 6, 7 and 8 is the 3,6-dichloro-isomer. The decreasing melting points of the later fractions are probably due to the presence of increasing amounts of 4,5-dichloro-*o*-xylene as a contaminant.

Experimental

Five moles of *o*-xylene (City Chemical Corporation, b.p. 143.5–144.5°, n_D^{20} 1.5047) with 5.5 g. of iron filings was chlorinated at –10 to 0° using chlorine dried with concentrated sulfuric acid. A total of 32 hours was required for the reaction mixture to gain the weight corresponding to dichlorination. This weight increase was determined after aspirating the reaction product. The chlorinated product was washed with water, refluxed one hour with 10% sodium

(5) H. J. Lucas, "Organic Chemistry," American Book Company, New York, N. Y., 1935, p. 360.

(6) A. H. White, B. S. Biggs and S. O. Morgan, *THIS JOURNAL*, 62, 16 (1940). 3,4-Dichloro-*o*-xylene is erroneously referred to as 4,5-dichloro-*o*-xylene on p. 17 of this article.

(7) F. J. Launer and D. A. McCaulay, *Anal. Chem.*, 23, 1875 (1951).