crease in rate of production of phenoxy radical over the first hour or so can be completely accounted for by the decrease in peroxide concentration, again implying that the above reaction is not important in our work. The fact that most of the radical has disappeared after 24 hr. at 80°, however, does suggest that this reaction, or a similar one, becomes of some importance in later stages of the reaction since disproportionation of tri-*t*-butylphenoxy is rather slow in dilute solution. Unfortunately, the reaction mixture was an intractable, oily mixture which we were unable to resolve into any pure components other than benzoic acid. It should be pointed out that since the rates are extrapolated to zero time, the incursion of the above reaction, (and also disproportionation of the phenoxy radical) should not introduce any appreciable error with the kinetic analysis.

EXPERIMENTAL

Kinetic runs. The rate of production of phenoxy radicals was followed by use of the reaction vessel shown in Fig. 2. An appropriate amount of 2,4,6-tri-*t*-butyl phenol[11] was placed in one bulb and a solution of benzoyl peroxide in benzene introduced into the other. The vessel was then attached to a manifold by means of the ball joint and the benzene solution degassed by alternate freezing and thawing under vacuum. The vessel was sealed off at the constriction and placed in a constant temperature bath. During these operations, extreme care was taken to prevent mixing of the materials in the two bulbs. Approximately 20 min. were allowed for equilibration. The phenol was then mixed with the benzoyl peroxide solution by vigorous shaking and the apparatus placed in a Beckman DK-1 spectrometer equipped with a thermostated cabinet mounted over the cell housing. Simultaneously, the chart drive was started. The absorbancy was followed at 625 mμ for 15 to 60 min. and the initial slope, as determined with a straight-edge, was taken as $[d(\text{phenoxy})/dt]_i$. The volume was measured by means of the calibrated tube and the concentration of benzoyl peroxide at the time of mixing was calculated from this value and the time of immersion in the bath using Bartlett's equation.[5] It will be noted from Table I that these corrections were not very large.

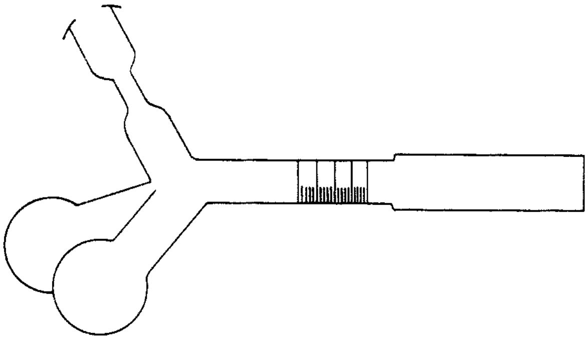

Fig. 2. Reaction vessel for kinetic studies

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Styrene-*p*-carboxylic Acid[1]

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Styrene-*p*-carboxylic acid was first prepared by Marvel and Overberger in 1945.[2] Their method involved the dehydration of *p*-(α-hydroxyethyl) benzonitrile followed by base hydrolysis of the nitrile. The carbinol was prepared from *p*-bromoacetophenone, a relatively expensive starting material.[3] The over-all yield for the four-step synthesis was 13%. A second synthesis, starting from *p*-ethylacetophenone, was reported later by Emerson *et al.*[4] It involves five steps and results in 19% over-all yields. The low yield step in each case was a potassium bisulfate dehydration.[5]

We wish to report a four-step synthesis of styrene-*p*-carboxylic acid from readily available ethylbenzene, which affords over-all yields of 24%. *p*-Bromoethylbenzene was prepared in 87% yield by the iodine-catalyzed bromination of ethylbenzene at 0° in the absence of a solvent. Treatment of this material with cuprous cyanide in pyridine afforded a 63% yield of *p*-ethylbenzonitrile, which was again brominated, this time in the α position. Treatment of the *p*-(α-bromoethyl)benzonitrile thus obtained with alcoholic potassium hydroxide resulted in simultaneous hydrolysis and dehydrobromination to yield styrene-*p*-carboxylic acid. The yields on the last two steps were 84 and 52%, respectively.

p-Bromoethylbenzene has been prepared previously by several methods.[6-9] We believe the iodine

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[1] This work was performed under the auspices of the U. S. Atomic Energy Commission.

[2] C. S. Marvel and C. G. Overberger, *J. Am. Chem. Soc.*, 67, 2250 (1945).

[3] An alternate synthesis from *p*-dibromobenzene resulted in much lower yields.

[4] W. S. Emerson, J. W. Heyd, V. E. Lucas, E. C. Chapin, G. R. Owens, and R. W. Shortridge, *J. Am. Chem. Soc.*, 68, 674 (1946); British Patent 636,196.

[5] An alternate to dehydration, pyrolysis of *p*-cyano-α-methyl-benzylacetate, was reported by C. G. Overberger and R. E. Allen, *J. Am. Chem. Soc.*, 68, 722 (1946). This route affords a five-step synthesis from *p*-bromoacetophenone with over-all yields of 29%.

[6] R. Fittig and J. Konig, *Ann.*, 144, 277 (1867).

[7] P. Karrer, E. Schlitter, K. Pfaehler, and F. Benz, *Helv. Chim. Acta*, 17, 1516 (1934).

[8] J. W. Copenhaver, M. F. Roy, and C. S. Marvel, *J. Am. Chem. Soc.*, 57, 1311 (1935).

[9] P. S. Varma, V. Sahay, and B. R. Subramonium, *J. Indian Chem. Soc.*, 14, 157 (1937).

catalyzed bromination presented here to be superior to any of these methods from the point of view of yield, cost, and convenience.[10]

p-Ethylbenzonitrile has been prepared from *p*-bromoethylbenzene by Dornow, Kühlcke, and Baxman[11]; but the conditions used were drastic, and the yields were low (25%). We have found a modification of the procedure of Newman[12] for α-naphthonitrile to be much more satisfactory. *p*-Ethylbenzonitrile is brominated readily in the α-position in refluxing carbon tetrachloride solution under the influence of sunlight or artificially produced ultraviolet light. The bromo compound is a colorless, viscous liquid of low volatility. It is a vesicant, causing a burning sensation on the skin, and a lacrimator. It can be distilled, but if heating is prolonged, it tends to lose hydrogen bromide and form polymers.

EXPERIMENTAL[13]

p-Bromoethylbenzene. To a stirred solution of 20 g. (0.08 mole) of iodine in 204.0 g. (1.92 mole) of ethylbenzene at 0° was added 320.0 g. (2.00 mole) of bromine. When all the bromine had been added and hydrogen bromide liberation had nearly ceased, stirring was stopped, and the reaction mixture allowed to warm to room temperature and stored overnight. After washing with 200 ml. of 10% aqueous potassium hydroxide, 100 ml. of 10% aqueous sodium bisulfite, 100 ml. of 10% potassium hydroxide and twice with 100 ml. portions of water, the reaction mixture was dried over anhydrous sodium sulfate, filtered and distilled to yield, after a small forerun, 308.0 g. (87%) of colorless bromo compound. A small amount of *p*-bromoacetophenone was removed by refraction on a 90-cm. spinning-band column at a reflux ratio of 30 to 1; b.p. 76–78°/13 mm., $d_{24.5}$ 1.343, n_D^{25} 1.5428 (*p*-bromoethylbenzene n_D^{25} 1.54228, *o*-bromoethylbenzene n_D^{25} 1.54632).[14]

p-Ethylbenzonitrile. A mixture of 59.2 g. (0.32 mole) of *p*-bromoethylbenzene, 35.0 g. (0.39 mole) of cuprous cyanide and 30 ml. of barium oxide-dried pyridine was heated under reflux for 24 hr. The resulting dark brown solution was worked up according to the *Organic Synthesis* procedure.[12] Distillation at 8 mm. gave a forerun of 1.1 ml. boiling at 74–83°/8 mm. and 26.3 g (63%) of *p*-ethylbenzonitrile b.p. 83–86°/8 mm., $n_D^{25.3}$ 1.5231, $d_{23.5}$ 0.960 (reported b.p. 103–104°/12 mm.,[11] n_D^{20} 1.5274,[15] d_{20} 0.9716[15]).

p-(α-Bromoethyl)benzonitrile. To a refluxing solution of 19.3 g. (0.15 mole) of p-ethylbenzonitrile in 100 ml. of carbon tetrachloride was added over a period of 75 min. a solution of 23.6 g. (0.15 mole) of bromine in 50 ml. of carbon tetrachloride. The reaction mixture was stirred during the addition and was irradiated with a 360-watt Uviarc fitted with an aluminum reflector.[16] After refluxing for 4 hr., the carbon tetrachloride was removed by distillation at atmospheric pressure, and the residue was distilled under reduced pressure to yield 25.8 g. (83.5%) of p-(α-bromoethyl)benzonitrile b.p. 109–111/2 mm., $d_{23.5}$ 1.375, $n_D^{25.2}$ 1.57874.

Styrene-p-carboxylic acid. p-(α-bromoethyl)benzonitrile (7.13 g., 0.034 mole) was added to a refluxing solution of 8.0 g. (0.14 mole) of potassium hydroxide and 50 mg. of hydroquinone in 35 ml. of ethanol. The mixture was heated under reflux for 48 hr., cooled to 0°, and filtered. The solid residue was dissolved in 50 ml. of water. After filtering to remove any amide or polymer, the solution was acidified with concentrated hydrochloric acid. The acid which crystallized on cooling was removed by centrifugation, washed with water, dissolved in a small amount of dilute aqueous ammonia, and reprecipitated by addition of concentrated hydrochloric acid. The precipitated acid was removed, washed with water, and dried at room temperature and 30μ pressure for 4 hr.; weight 2.62 g. (52.2%). The analytical sample was recrystallized from aqueous ethanol and sublimed at 10μ pressure and about 100°.

Anal. Calcd.: C, 72.96; H, 5.44. Found: C, 72.63; H, 5.26.

The melting point of 123–128° was not improved by further recrystallization. Marvel and Overberger[2] report 143–144° for material presumably free of ortho isomer.

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[10] Judging from index-of-refraction measurements, about 12.5% orthoisomer is produced. A small amount of *p*-bromoacetophenone (2–5%), which can be removed without difficulty by distillation, is also formed.

[11] A. Dornow, I. Kühlcke, and F. Baxman, *Ber.*, **82**, 254 (1949).

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[15] S. F. Birch, R. A. Dean, F. A. Fidler, and R. A. Lowry, *J. Am. Chem. Soc.*, **71**, 1362 (1949).

[16] George W. Gates and Co., Franklin Square, Long Island, N. Y.

Fluorine-Containing Nitrogen Compounds. II. Trimerization of Trifluoroacetonitrile[1]

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2,4,6-Tris(trifluoromethyl)-1,3,5-triazine was first synthesized by McBee, Pierce, and Bolt[3] by trimerization of trichloroacetonitrile in the presence of hydrogen chloride and subsequent fluorination of the trimer. This method was improved somewhat by Norton.[4] More recently Reilly and Brown[5] have described the high-pressure, high-temperature trimerization of trifluoroacetonitrile in the absence of catalysts. The yield of triazine based on unrecovered nitrile was 45–60% but the conversion was only about 30%.

Although these workers have shown that no catalyst is necessary to effect trimerization of perfluoroalkyl nitriles, we have found that the use of hydrogen chloride as a catalyst produces much more satisfactory results. Yields in excess of 90%, based on nitrile charged, have been achieved at modest pressures and temperatures. Boron trifluoride was found to be ineffective at low tempera-

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[1] This work was performed under the auspices of the U.S. Atomic Energy Commission.

[2] Present address: Department of Chemistry, University of California, Los Angeles, Calif.

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[5] W. L. Reilly and H. C. Brown, *J. Org. Chem.*, **22**, 698 (1957).