

catalyzed bromination presented here to be superior to any of these methods from the point of view of yield, cost, and convenience.<sup>10</sup>

*p*-Ethylbenzonitrile has been prepared from *p*-bromoethylbenzene by Dornow, Kühllcke, and Baxman<sup>11</sup>; but the conditions used were drastic, and the yields were low (25%). We have found a modification of the procedure of Newman<sup>12</sup> for  $\alpha$ -naphthonitrile to be much more satisfactory. *p*-Ethylbenzonitrile is brominated readily in the  $\alpha$ -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<sup>13</sup>

*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.,  $d_{25.5}^{25}$  1.343,  $n_D^{25}$  1.5428 (*p*-bromoethylbenzene  $n_D^{25}$  1.54228, *o*-bromoethylbenzene  $n_D^{25}$  1.54632).<sup>14</sup>

*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.<sup>12</sup> 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.,  $n_D^{25}$  1.5231,  $d_{25.5}^{25}$  0.960 (reported b.p. 103–104°/12 mm.,<sup>11</sup>  $n_D^{25}$  1.5274,<sup>15</sup>  $d_{20}^{20}$  0.9716<sup>15</sup>).

*p*-( $\alpha$ -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.<sup>16</sup> After refluxing for 4 hr., the carbon

(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. Kühllcke, and F. Baxman, *Ber.*, **82**, 254 (1949).

(12) M. S. Newman, *Org. Synthesis*, Coll. Vol. III, 631 (1955).

(13) Boiling points are uncorrected.

(14) R. R. Dreisbach and R. A. Martin, *Ind. Eng. Chem.*, **41**, 2875 (1949).

(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.

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*-( $\alpha$ -bromoethyl)benzonitrile b.p. 109–111/2 mm.,  $d_{25.5}^{25}$  1.375,  $n_D^{25}$  1.57874.

*Styrene-p-carboxylic acid*. *p*-( $\alpha$ -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 30 $\mu$  pressure for 4 hr.; weight 2.62 g. (52.2%). The analytical sample was recrystallized from aqueous ethanol and sublimed at 10 $\mu$  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<sup>2</sup> report 143–144° for material presumably free of ortho isomer.

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## Fluorine-Containing Nitrogen Compounds.

### II. Trimerization of Trifluoroacetonitrile<sup>1</sup>

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2,4,6-Tris(trifluoromethyl)-1,3,5-triazine was first synthesized by McBee, Pierce, and Bolt<sup>3</sup> by trimerization of trichloroacetonitrile in the presence of hydrogen chloride and subsequent fluorination of the trimer. This method was improved somewhat by Norton.<sup>4</sup> More recently Reilly and Brown<sup>5</sup> 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-

(1) This work was performed under the auspices of the U.S. Atomic Energy Commission.

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(3) E. T. McBee, O. R. Pierce, and R. O. Bolt, *Ind. Eng. Chem.*, **39**, 391 (1947).

(4) T. R. Norton, *J. Am. Chem. Soc.*, **72**, 3527 (1950).

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

tures as a catalyst.<sup>6</sup> Table I lists yields of crude trimer obtained at various temperatures with three different ratios of nitrile to hydrogen chloride. It is interesting to note that with a nitrile to hydrogen chloride ratio of 4 or 5 to 1 there is a marked decrease in yield as the temperature of reaction is raised. With lower ratios this effect is less pronounced. We interpret this an indication that the initial step in the trimerization is a rapid, reversible equilibrium between the nitrile and hydrogen chloride, which is shifted toward the two components as the temperature increases.

TABLE I

Millimoles			Temp., °C.	Recovery, Millimoles		% Recovery	% Yield
CF <sub>3</sub> CN <sup>a</sup>	HCl <sup>a</sup>	Ratio		Gas <sup>a</sup>	Liq. <sup>b</sup>		
32.35	8.1	4.0	<sup>c</sup>	11.6	26.9	95.3	83.3
32.41	8.1	4.0	100		15.0		46.3
31.81	7.7	4.1	100	26.5	11.8	97.0	37.0
32.08	6.3	5.1	150	32.5	5.3	98.3	16.4
32.58	6.4	5.1	150	32.9	4.5	96.1	13.9
31.9	15.7	2.0	<sup>c</sup>	16.0	25.6	87.4	80.0
32.4	16.2	2.0	100	22.9	21.9	92.1	67.6
32.1	32.2	1.0	<sup>c</sup>	20.3	30.2	78.7	94.1
32.9	32.2	1.0	100		28.2		85.7
31.7	32.1	1.0	125	36.7	23.8	94.8	75.0
33.0	32.7	1.0	150	37.1	24.7	94.1	74.9
32.7 <sup>d</sup>	32.1	1.0	<sup>c</sup>	33.1	18.8	80.2	57.7

<sup>a</sup> Calculated from P-V-T measurements assuming an ideal gas. <sup>b</sup> Millimoles of nitrile appearing as trimer. <sup>c</sup> Room temperature which varied from about 10 to 30°. <sup>d</sup> This experiment was run in a 100-ml. Parr high-pressure hydrogenation bomb.

## EXPERIMENTAL

Trifluoroacetonitrile was prepared by dehydration of trifluoroacetamide according to the procedure of Gilman and Jones.<sup>7</sup> Hydrogen chloride and boron trifluoride were taken from Matheson Co. cylinders, frozen in liquid nitrogen in a glass trap and outgassed to remove a small amount of non-condensable material.

Trimerizations were effected in a 25-ml. bomb made from a 5½-in. length of 1-in. diameter stainless steel rod with a 5/8-in. hole drilled to a depth of 5 in. The end was threaded to take a No. 55-660 Matheson needle valve. A 1/16-in. thick Teflon gasket was used to ensure a vacuum-tight seal. The outlet of the needle valve was fitted with an 18-mm. brass ball which allowed direct connection to a standard glass vacuum manifold. The reactants were measured as gases in a calibrated bulb with a Wallace and Tiernan model FA 160 absolute pressure gage having a range of 0-400 mm. of Hg. They were condensed in the previously evacuated and outgassed bomb by means of liquid nitrogen. The valve was then closed, the bomb allowed to warm to room temperature and maintained at the specified temperature for 18-20 hr. Temperatures between 100 and 150° were maintained to ±5° by a stirred oil bath. The bomb was then cooled to room temperature, if necessary, and reconnected to the vacuum

(6) R. T. Foster, U.S. Patent 2,375,545 (1945), reports preparation of 2,4,6-tris(trichloromethyl)-1,3,5-triazine together with monomer and tetramer by passing chlorine and acetonitrile over carbon impregnated with halides of zinc, copper, or an alkaline earth metal at 200-400°.

(7) H. Gilman and R. G. Jones, *J. Am. Chem. Soc.*, **65**, 1458 (1943).

manifold. The contents were pumped slowly through two traps in series, the first at -78° and the second at -196°. The amount of material in the -196° trap (listed in Table I as millimoles of recovered gas) was measured gasometrically. Infrared analysis showed it to consist mainly of HCl with varying amounts of unreacted nitrile. In many of the spectra a very weak doublet appeared at 5.5-5.6μ in the C=C or C=N region. This band is, at present, unassigned and could be due to traces of either a by-product or of one of the reaction intermediates. Several attempts at concentration of the species responsible were unproductive. The material from the -78° trap was vacuum distilled into a tared tube and weighed. It consisted primarily of trimer contaminated by a little HCl, which could be removed either by washing with aqueous sodium carbonate or by vacuum distilling the vapors through a small bed of ascarite. The latter proved to be more convenient on a small scale. Linde Molecular Sieve type 5A was less effective. A typical sample of trimer had  $n_D^{25}$  1.32208,  $d_{25.5}$  1.595 (reported  $n_D^{25}$  1.3161,<sup>6</sup> 1.3231<sup>3</sup>;  $d_{25}$  1.593<sup>5</sup>;  $d_{26}$  1.5857<sup>3</sup>).

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### Kojic Acid and $\alpha$ -Chloro- $\alpha$ -deoxykojic Acid in Reactions Catalyzed by Sulfuric Acid and Potassium Acetate

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In several previous communications<sup>2,3</sup> new reactions of 4-pyrones have been revealed by attempting to ascertain to what extent these compounds exhibit an aromatic character. To this end it was decided to determine if nuclear hydroxy-4-pyrones such as kojic acid and  $\alpha$ -chloro- $\alpha$ -deoxykojic acid would participate in the Pechmann<sup>4</sup> reaction.

The reaction of kojic acid with citric, malic, and maleic acids in the presence of concentrated sulfuric acid reveals that the Pechmann reaction does take place to form pyrono-coumarins but the products are highly contaminated compounds which are difficult to isolate and still more difficult to purify. Compound I was the only one produced in anything like satisfactory purity and yields. Infrared data were not sufficient for a decision as to the true nature of such a complicated compound, due to the fact that the pyrone carbonyl, nonnuclear carbonyl, lactone groupings, and esters all absorb frequencies in the near vicinity of each other. However, the formation of coumarins by the reaction of phenols with malic acid and under Pechmann conditions is well known and no further investigation on the nature of the compound is presented due to the fact that the syn-

(1) The person to whom all communications regarding this paper should be directed.

(2) L. L. Woods, *J. Am. Chem. Soc.*, **77**, 3161 (1955).

(3) L. L. Woods, *J. Org. Chem.*, **22**, 341 (1957).

(4) R. Adams, *Org. Reactions*, **7**, 1 (1954).