

acetate, 2.0 g. (0.019 mole) of benzaldehyde and 100 ml. of methanol. The mixture was heated in a water-bath for 1 hr. and then cooled and filtered. After washing with cold water and with methanol, and vacuum-drying, the white powdery product, X, weighed 0.9 g. (0.0038 mole, 19%), m.p. 243–244° dec., undepressed by admixture with X obtained from the isatin-benzylamine reaction.

**Acid Hydrolysis of X.**—Recrystallized X (0.80 g., 3.4 mmoles) from the isatin-benzylamine reaction, was mixed in a Claisen flask with 50 ml. of 2 *N* hydrochloric acid and 0.5 g. of silicone antifoaming agent. The mixture was distilled slowly, fresh water being added to keep the flask level constant. The distillate was caught in a filtered solution of 1.2 g. of 2,4-dinitrophenylhydrazine in 300 ml. of 2 *N* hydrochloric acid. Approximately 1 hr. was needed for the X to dissolve completely, and in 3 hr. the steam distillation was complete. Benzaldehyde 2,4-dinitrophenylhydrazone, m.p. 238–240.5° (0.83 g., 2.9 mmoles, 85%), was obtained by filtration of the distillate. A mixture melting point with authentic benzaldehyde 2,4-dinitrophenylhydrazone was not depressed.

The acid solution in the flask was evaporated under nitrogen to 10 ml., and taken up with a mixture of 50 ml. of isopropyl alcohol and similar volumes of *n*-butyl alcohol and ether. After refrigeration 0.35 g. (1.9 mmoles, 56%) of impure II-HCl separated. When acetylated at room temperature as described above for the preparation of monoacetyl-3-aminoindole, the unrecrystallized acetyl derivative melted at 245–249°. The mixture with pure monoacetyl-3-aminoindole melted at 247–250°.

**3-Methyloxindole.**—The Brunner cyclization<sup>10</sup> of  $\beta$ -propionylphenylhydrazine was employed. It was found that calcium hydride gave a better yield than lime in this reaction, but it also should be mentioned that sodium amide was much inferior in this case. The product was purified by vacuum distillation in a short path system, b.p. 132° (1.5 mm.), with over-all yields varying from 38–50%, m.p.

(10) K. Brunner, *Monatsh.*, **18**, 533 (1897).

121.5–123.5°. After recrystallization from toluene and butanol, with 25% recovery, the product was pure white, m.p. 123.8–124.6°. When crystallized from water the melting point was unchanged, failing to corroborate the reports of earlier workers.<sup>10,11</sup>

*Anal.* Calcd. for C<sub>9</sub>H<sub>9</sub>NO: C, 73.46; H, 6.16; N, 9.52. Found: C, 73.36; H, 6.22; N, 9.80.

Treatment of 3-methyloxindole with nitrous acid in water solution, or with butyl nitrite in methanol, gave sirupy polymeric products which could neither be sublimed nor crystallized. No evidence of nitrosation was found.

**3-Methyl-3-hydroxyoxindole.**—To a solution of 20.0 g. (0.113 mole) of *o*-acetylaminacetophenone in 150 ml. of methanol was added 32 g. (0.28 mole) of ammonium carbonate, 13.0 g. (0.20 mole) of potassium cyanide and 150 ml. of water. After stirring in an open beaker for 1 hr. at 50°, the mixture was slowly boiled down (hood) to a volume of 200 ml. Hydrochloric acid was cautiously added to pH 4, and the mixture was then evaporated to dryness and extracted with hot methanol. Evaporation of the methanol gave 11 g. of crude product. Recrystallization from water gave 9.5 g. (0.058 mole, 51%) of white crystals, m.p. 159.5–160.5° (reported<sup>12</sup> 160°).

*Anal.* Calcd. for C<sub>9</sub>H<sub>9</sub>O<sub>2</sub>N: C, 66.24; H, 5.56; N, 8.59. Found: C, 66.35, 66.35; H, 5.48, 5.54; N, 8.21, 8.43.

Reaction of 3-methyl-3-hydroxyoxindole with either concentrated hydrochloric acid or with thionyl chloride gave non-crystalline polymeric material which could not be purified.

**Acknowledgment.**—The authors hereby thank the National Aniline Division, Allied Chemical and Dye Corporation, for a generous gift of isatin.

(11) P. Trinius, *Ann.*, **227**, 274 (1885).

(12) M. Kohn and A. Ostersetzer, *Monatsh.*, **32**, 911 (1911).

BROOKLYN, NEW YORK

## NOTES

### Preparation of Acenaphthylene from Acenaphthene<sup>1</sup>

By ARTHUR G. ANDERSON, JR., AND ROBERT G. ANDERSON  
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In connection with efforts to introduce further unsaturation into the pyracene molecule the conversion of acenaphthene to acenaphthylene was investigated. Two practical routes were found.<sup>2</sup>

Bromination of acenaphthene with two moles of *N*-bromosuccinimide gave 1,2-dibromoacenaphthene. Debromination of this intermediate with zinc and alcohol or tetrahydrofuran gave acenaphthylene in 80% yield. The over-all yield was ca. 45% when the dibromo compound was isolated and purified (56%) but was raised to 67% when the crude dibromo derivative was used.

The second method involved vapor phase pyrolysis of 1-acenaphthenyl acetate. Conditions were found which gave a 71% yield for this step

(1) Support for a part of this work by contract DA-04-200-ORD-235 with the Office of Ordnance Research is gratefully acknowledged.

(2) After the present work had been completed, the dehydrogenation of acenaphthene with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone was reported by E. A. Braude, A. G. Brook and R. P. Linstead, *J. Chem. Soc.*, 3569 (1954). As the quinone must be prepared separately this method is probably not superior to those described herein.

and a 53% over-all yield from acenaphthene was realized. Subsequently it was discovered that a similar method had been reported in a patent.<sup>3</sup>

#### Experimental<sup>4</sup>

**1,2-Dibromoacenaphthene.**—A mixture of 19.7 g. (0.128 mole) of acenaphthene, 45.6 g. (0.256 mole) of *N*-bromosuccinimide, 250 ml. of dry carbon tetrachloride and a few crystals of benzoyl peroxide was heated under reflux for 30 minutes. The solid succinimide was separated and the solvent removed from the filtrate. The yellow solid remaining could be used in the dehalogenation reaction. Recrystallization from absolute ethanol-benzene and then from absolute ethanol gave 19.9 g. (56%) of product as colorless needles, m.p. 120.5–123°.<sup>5</sup>

**Acenaphthylene. A.** From 1,2-Dibromoacenaphthene.—A solution of 12.3 g. (0.039 mole) of purified 1,2-dibromoacenaphthene in 250 ml. of absolute ethanol<sup>6</sup> was added with stirring over a period of 1 hour to a boiling mixture of 65 g. (1.0 mole) of zinc dust and 300 ml. of absolute ethanol. After an additional reflux period of 1 hour the mixture was allowed to cool, the zinc dust removed by centrifugation and the ethanolic solution poured into 500 ml. of warm 5% hydrochloric acid. Upon standing a yellow solid (5.5 g.,

(3) R. G. Flowers, U. S. Patent 2,390,363, Dec. 4, 1945.

(4) Melting points are uncorrected.

(5) M. Blumenthal, *Ber.*, **7**, 1092 (1874).

(6) Dry tetrahydrofuran may be used as the solvent for the reaction. In this case water is added (after removal of the zinc) until the mixture is cloudy. The product separates and solidifies after several hours.

m.p. 88–92°) precipitated from the cloudy solution. Sublimation gave 4.7 g. (80.1%) of pure material, m.p. 91–92°.<sup>7</sup>

Dehalogenation of the crude dibromoacenaphthene by this same procedure gave an over-all yield of 67% from acenaphthene.

The picrate was obtained as orange crystals, m.p. 201–202°.<sup>8</sup>

Bromination (in ether) gave 1,2-dibromoacenaphthene, m.p. 121–123°.<sup>5</sup>

**B. From 1-Acenaphthenyl Acetate.**—A solution of 1 g. (0.006 mole) of 1-acenaphthenyl acetate<sup>9</sup> in 20 ml. of acetic acid was dropped into a Pyrex column (57 cm. long and 15 mm. in diameter) packed to a depth of 47 cm. with  $\frac{3}{32}$  inch Pyrex helices. The internal temperature of the column was maintained at  $480 \pm 10^\circ$ . The drop rate was such that the addition required 2 hours (ca. 2 drops per min.). Nitrogen was passed through the column throughout the addition at a rate (measured at room temperature) of 11 l. per hour. The pyrolysate (collected in a trap cooled by a Dry Ice-acetone-bath) was poured into 40 ml. of water. The crystalline material (0.67 g.) which formed slowly was separated after 3 hours and sublimed. The yield of pure (m.p. 91–92°)<sup>7</sup> acenaphthylene was 0.65 g. (71%).

(7) A. Behr and W. A. Van Dorp, *Ber.*, **6**, 753 (1873).

(8) A. Behr and W. A. Van Dorp, *Ann.*, **172**, 263 (1874).

(9) J. Cason, "Organic Syntheses," Vol. 21, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 1.

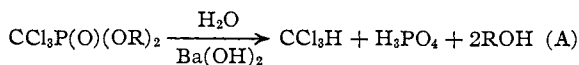
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### An Alkaline Hydrolysis of Trichloromethylphosphonic Esters

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The acidic hydrolysis of dialkyl trichloromethylphosphonates,  $\text{CCl}_3\text{P}(\text{O})(\text{OR})_2$ , proceeds without cleavage of the carbon-phosphorus bond to yield the expected trichloromethylphosphonic acid.<sup>2</sup> The only alkaline hydrolytic study of these esters is reported by Yakubovich and Ginsburg who employed an aqueous solution of 1.4 *N* barium hydroxide at 60–80°<sup>2b,3</sup>; cleavage of the carbon-phosphorus bond was observed and symbolized by the following indefinite equation.



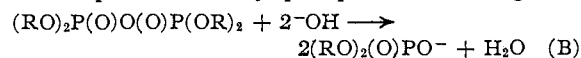
This proposed hydrolytic scheme must proceed *via* the dialkyl phosphate anion after the chloroform is liberated. Helleiner and Butler,<sup>4</sup> however, have recently shown that only a small proportion (0.1–0.4%) of the total phosphorus of phosphate diesters is converted to inorganic phosphate during hydrolysis with barium hydroxide. The observation, therefore, by Yakubovich and Ginsburg<sup>3</sup> that the barium hydroxide hydrolysate gives a yellow precipitate with ammonium molybdate reagent is not a definite proof that phosphoric acid is a major hydrolytic reaction product.

In addition, saponification equivalent data, as

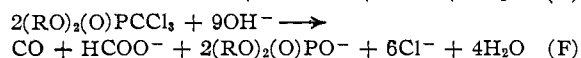
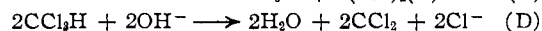
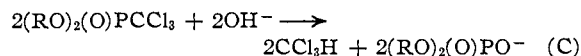
- (1) General Electric Research Laboratory, Schenectady 5, N. Y.
- (2) (a) A. Ya. Yakubovich, V. A. Ginsburg and S. P. Makarov, *Doklady Akad. Nauk S.S.S.R.*, **71**, 303 (1950); (b) A. Ya. Yakubovich and V. A. Ginsburg, *ibid.*, **82**, 273 (1952); (c) P. C. Crofts and G. M. Kosolapoff, *THIS JOURNAL*, **75**, 5738 (1953); (d) A. Ya. Yakubovich and V. A. Ginsburg, *J. Gen. Chem. U.S.S.R.*, **24**, 1465 (1954); (e) I. S. Bengelsdorf and L. B. Barron, *THIS JOURNAL*, **77**, 2869 (1955).
- (3) A. Ya. Yakubovich and V. A. Ginsburg, *J. Gen. Chem. U.S.S.R.*, **24**, 2250 (1954).
- (4) C. W. Helleiner and G. C. Butler, *Can. J. Chem.*, **33**, 705 (1955).

determined in this work by refluxing the esters with 0.5 *N* ethanolic potassium hydroxide solution, revealed that the alkaline hydrolytic scheme in 95% ethanol as the solvent can be more complex than as proposed above. This is due to two factors; (i) chloroform itself is attacked further by alkali,<sup>5</sup> and (ii) the dialkyl phosphate anion,  $(\text{RO})_2(\text{O})\text{PO}^-$ , although hydrolyzable by acids, is resistant toward further alkaline hydrolysis.

Plimmer and Burch have shown that the dialkyl phosphate anion, whether it is derived from a dialkyl phosphoric acid or a trialkyl phosphate, is resistant toward alkaline hydrolysis.<sup>6</sup> In addition, Toy<sup>7</sup> and Dvornikoff and Morill<sup>8</sup> have observed that the alkaline hydrolysis of pyrophosphoric esters stops at the dialkyl phosphate anion stage.



The stoichiometry of the ethanolic alkaline hydrolysis, therefore, strongly suggests that dialkyl trichloromethylphosphonates are hydrolyzed according to the following reaction sequence (Eqn. C-E); the over-all reaction is represented by Eqn. F.



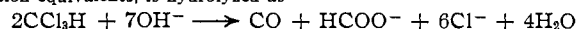
This hydrolytic scheme is verified by the following observations: (1) The observed saponification equivalents of the esters are in close agreement with the expected values, *i.e.*,  $\frac{2}{9}$  of the molecular weight.

(2) At the start of the hydrolysis, the presence of chloroform is indicated by a positive phenyl isonitrile test; at the end of the hydrolysis, this test is negative, *i.e.*, chloroform is absent.<sup>9</sup>

(3) Formate and chloride ions, respectively, are shown to be present in the hydrolysate, by the production of a violet coloration with chromotropic acid, and the precipitation of silver chloride.

(4) Phosphate ion is absent in the alkaline hydrolysate, for no precipitation is observed when it is treated with a nitric acid-ammonium molybdate solution.<sup>10</sup> If the alkaline hydrolysate, however, is further hydrolyzed with acid, then the test for

(5) Chloroform, according to experimentally determined saponification equivalents, is hydrolyzed as



The observed saponification equivalent is equal to  $\frac{2}{9}$  of the molecular weight. The kinetics of this reaction are reviewed and discussed by J. Hine, *THIS JOURNAL*, **72**, 2438 (1950). Excellent evidence that dichlorocarbene,  $\text{CCl}_2$ , is an intermediate in the alkaline hydrolysis of chloroform recently has been advanced by W. von E. Doering and A. K. Hoffmann, *THIS JOURNAL*, **76**, 6162 (1954).

(6) R. H. A. Plimmer and W. J. N. Burch, *J. Chem. Soc.*, 279 (1929).

(7) A. D. F. Toy, *THIS JOURNAL*, **72**, 2065 (1950).

(8) M. N. Dvornikoff and H. L. Morill, *Anal. Chem.*, **20**, 935 (1948).

(9) F. W. Bennett, H. J. Emeleus and R. N. Haszeldine, *J. Chem. Soc.*, 3598 (1954), report that whereas trifluoromethylphosphonic acid,  $\text{CF}_3\text{P}(\text{O})(\text{OH})_2$ , is not cleaved by alkali, trifluoromethylphosphonic acid,  $\text{CF}_2\text{P}(\text{O})(\text{OH})_2$ , gives fluoroform when it is so treated.

(10) This observation is not necessarily contradictory to the findings of Yakubovich and Ginsburg,<sup>3</sup> because Helleiner and Butler<sup>4</sup> have shown that although barium hydroxide liberates little phosphate from phosphate diesters, sodium hydroxide is even less effective in this respect.