

followed by heating to 50° for one-half hour and allowing to come to room temperature. (b) The acid chloride was added to an excess of the amino alcohol in benzene. (c) A 30% excess of the aminoalcohol was added to the acid chloride in benzene. After two hours the reaction mixture was worked up.

M. Perkin reaction using 2,4-dichlorobenzaldehyde.

N. 2,4-Dichlorobenzylisothiourea hydrochloride was prepared from the corresponding chloride and thiourea.<sup>5</sup>

O. 2,4-Dichlorobenzaldehyde was converted to the nitrile by way of the bisulfite addition compound. The nitrile was hydrolyzed by heating with concentrated hydrochloric acid for five hours at 100°.<sup>6</sup>

P. The epoxypropane compound was formed by reaction of the phenol with epichlorohydrin in presence of aqueous sodium hydroxide solution for forty-eight hours at room temperature.<sup>7</sup>

Q. *p*-Chlorobenzyl mercaptan dissolved in aqueous sodium hydroxide was treated with chloroacetic acid.<sup>8</sup>

R. The corresponding mercapto compound dissolved in a mixture of equal volumes of acetic anhydride and glacial acetic acid was oxidized by hydrogen peroxide.

S. The phenol was condensed with chloroacetic acid in presence of aqueous sodium hydroxide.<sup>9</sup>

T. The chlorophenoxyacetic acid was brominated at 80° for six hours with excess bromine in presence of aluminum chloride.

U. The ester was hydrolyzed by refluxing for one and one-half hours with a mixture of concentrated hydrochloric acid and glacial acetic acid.

V. Dry hydrogen chloride was passed into a mixture of ethyl *p*-chlorophenoxyacetate, paraformaldehyde and anhydrous zinc chloride, heated at 60°, for one hour.

W. Ethyl 2-chloromethyl-4-chlorophenoxyacetate in acetone was refluxed for six hours with an aqueous solution of potassium cyanide, using sodium iodide as a catalyst. The cyanomethyl acid was obtained by acidification of the mixture after removal of acetone.

X. The oxime was formed by addition of an excess of hydroxylamine hydrochloride in concentrated aqueous solution to a solution of the ketone in alcohol.<sup>10</sup>

Y. The mercaptan was converted to the disulfide by an excess of hydroxylamine hydrochloride in alcoholic solution.<sup>11</sup>

Z. A solution of the mercaptan in absolute ethanol was refluxed with a 10% excess of sodium methylate for one-half hour.

(a) A slight excess of ethyl bromoacetate was added and the mixture refluxed for one hour. Saponification was accomplished by alcoholic sodium hydroxide solution and the acid isolated in the usual manner.

(b) A slight excess of benzyl chloride was added and the mixture refluxed for one hour.

(5) Urquhart, Gates and Connor, "Organic Syntheses," **21**, 36 (1941).

(6) Gnehm and Schüle, *Ann.*, **299**, 347 (1898).

(7) Marle, *J. Chem. Soc.*, **101**, 305 (1912).

(8) Gabriel, *Ber.*, **12**, 1639 (1879).

(9) Hayes and Branch, *THIS JOURNAL*, **65**, 1555 (1943).

(10) Zincke and Suhl, *Ber.*, **39**, 4148 (1906).

(11) Fasbender, *ibid.*, **21**, 1470 (1888).

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### Derivatives of Fluorene

**Tetrabiphenylene-butane.**—A solution of 4 g. of 1-bromodibiphenylene-ethane<sup>1</sup> in 75 cc. of purified benzene

(1) Grignard and Courtot, *Compt. rend.*, **152**, 1494 (1911); Courtot, *Ann. chim.*, (9) **4**, 165 (1915).

containing freshly prepared copper powder was heated in a carbon tetrachloride bath for ten hours, and since the reaction appeared to be rather sluggish the heating was continued on a steam-bath for an additional eight hours. The reaction mixture was filtered, the filtrate removed by distillation, and the residue consisting of dibiphenylene-ethylene and tetrabiphenylene-butane was crystallized from ethyl acetate; yield of butane derivative, 1.1 g. This was recrystallized from acetic acid yielding glistening needle-like prisms, m. p. 291°.

*Anal.* Calcd. for C<sub>32</sub>H<sub>24</sub>: C, 94.80; H, 5.20. Found: C, 94.90; H, 5.49.

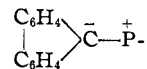
The compound is soluble in benzene, pyridine, ethyl acetate, carbon tetrachloride and ether.

**Fluorenyl-9-ethylcarboxylate-9-dimethyloxyde.**—This compound was prepared by the reaction of 6.5 g. of fluorenyl-9-ethylcarboxylate, 0.75 g. of sodium and 3 cc. of chloromethyl ether in anhydrous ether by the method of Wislicenus and Mocker.<sup>2</sup> The reaction product was extracted with ether and distilled at 262–268° at 1 mm. pressure, yield 5 g., crystallized from ligroin as large prisms, m. p. 64–65°.

*Anal.* Calcd. for C<sub>18</sub>H<sub>18</sub>O<sub>2</sub>: C, 76.56; H, 6.43. Found: C, 76.51; H, 6.35.

Various attempts to hydrolyze or to decarboxylate the ester were unsuccessful. The compound was practically unaltered after fifteen minutes heating at 270° and ten minutes at 360° in a sealed tube. No change was effected after letting it stand in alcoholic ammonium hydroxide for several weeks or by heating an alcoholic solution of the ester in presence of hydrochloric acid. By heating it in an alcoholic solution of sodium hydroxide at 150° for six hours, less than 10% of the ester was converted to 9-methylfluorene,<sup>3</sup> m. p. 45°, which was isolated by two sublimations and recrystallization from methyl alcohol.

*Anal.* Calcd. for C<sub>14</sub>H<sub>12</sub>: C, 93.28; H, 6.72. Found: C, 93.45; H, 6.69.

**Triphenylphosphine Fluorenylidene,** 

(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>.—Staudinger and Meyer,<sup>3</sup> attempted to prepare triphenylphosphine fluorenylidene by pyrolyzing triphenylphosphazene fluorenylidene and obtained a resinous product which could not be purified. We found that this compound could be prepared in the following manner. To a solution of 3 g. of 9-bromofluorene in about 40 cc. of nitromethane was slowly added 3.21 g. of triphenylphosphine. As the last portion was added, fluorenyl-9-triphenylphosphonium bromide began to crystallize. The reaction was exothermic, evidenced by a 10° rise in temperature of the solution. After two hours, 5.75 g. of the bromide was removed, m. p. 303° (dec.). Triphenylphosphine fluorenylidene was obtained by dissolving 3 g. of the salt in 150 cc. of boiling alcohol and making the solution alkaline with about 8 cc. of ammonium hydroxide. Yellow glistening plates crystallized as the solution cooled, weight 2.4 g., m. p. 253°.

*Anal.* Calcd. for C<sub>31</sub>H<sub>25</sub>P: C, 87.28; H, 5.44; P, 7.28. Found: C, 87.15; H, 5.66; P, 7.25, 7.26.

The compound remained unaltered when refluxed with aniline, phenol and hydrazine hydrate in alcohol.

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(2) Wislicenus and Mocker, *Ber.*, **46**, 2772 (1913).

(3) Staudinger and Meyer, *Helv. Chim. Acta.*, **2**, 619 (1919).

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