obtained. The liquid had the following constants: $n^{25}\text{D}$ 1.5351, d^{25}_{4} 1.0460.

Anal. Calcd. for $C_{18}H_{20}ON_2Si_2$: N, 8.33. Found: N, 8.07.

1,3-Bis-(*p*-carboxyphenyl)-tetramethyldisiloxane (II) A. **From Tetramethyl-1,3-bis-(*p*-tolyl)-disiloxane.**—Eleven grams (0.035 mole) of tetramethyl-1,3-bis-(*p*-tolyl)-disiloxane was dissolved in a mixture of 114 ml. of glacial acetic acid and 114 ml. of acetic anhydride. After cooling to −5° (ice-salt-bath) 17 ml. of concentrated sulfuric acid was added dropwise with stirring. The temperature was not permitted to exceed 5°. Then 20 g. (0.20 mole) of finely ground chromium trioxide was added with vigorous stirring. After stirring for 1 hour at 12°, the solution was poured onto excess chopped ice. A white precipitate separated. The latter was filtered off and washed several times with distilled water. The crude product weighed 10.5 g. (63%) and melted at 236–240°. After charcoal treatment and several crystallizations from dry acetone, the compound melted at 241–242°. The neutral equivalent was 193.

Anal. Calcd. for $C_{18}H_{22}O_5Si_2$: C, 57.80; H, 5.89; Si, 14.98. Found: C, 57.75; H, 5.83; Si, 15.22.

B. **From 1,3-Bis-(*p*-cyanophenyl)-tetramethyldisiloxane.**—A mixture of 2 g. of 1,3-bis-(*p*-cyanophenyl)-tetramethyldisiloxane and 25 ml. of 2% sodium hydroxide was refluxed for 2 hours. On cooling and acidifying the solution, a white solid precipitated. The latter was repeatedly extracted with hot water to remove benzoic acid. The remaining solid was crystallized twice from acetone and melted at 239–241°.

A mixed melting point determination involving this material and the compound described under A showed no depression.

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A Possible Explanation of the Anomalous Substitution Behavior of Iodine Monobromide

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From a theoretical viewpoint, iodine monobromide ($\overrightarrow{\mathrm{IBr}}$) should be an iodinating agent in organic nuclear substitution. Militzer[1] has found that it is actually a brominating agent for phenol, naphthalene and 1-naphthol. This apparent anomaly is now incorporated in recent text-books on mechanisms of organic reactions.[2,3] Bennett and Sharpe[4] believe that iodine monobromide dissociates to iodine and bromine and that iodine-catalyzed bromination is the fastest of the reactions possible. Lambourne and Robertson[5] believe that the reaction is an iodine monobromide-catalyzed bromination.

An interesting observation has been made in this Laboratory which provides an alternate and possibly more attractive explanation. It has been found that hydrogen bromide exchanges with *p*-iodophenol at a rate comparable to the substitution reactions of Militzer[1]

$$2p\text{-IC}_6\text{H}_4\text{OH} + \text{HBr} \longrightarrow p\text{-BrC}_6\text{H}_4\text{OH} + \text{C}_6\text{H}_5\text{OH} + \text{I}_2$$

The above over-all equation may proceed *via* two different routes

$$p\text{-IC}_6\text{H}_4\text{OH} + \text{HI} \longrightarrow \text{C}_6\text{H}_5\text{OH} + \text{I}_2$$

or

$$p\text{-BrC}_6\text{H}_4\text{OH} + 2\,\text{HI} \longrightarrow \text{C}_6\text{H}_5\text{OH} + \text{I}_2 + \text{HBr}$$

Though the first route seems more likely, both lead to the products of the over-all equation.

This observation of the halogen interchange suggests that iodine monobromide may be an iodinating agent, as it should be, but that stability relationships of the theoretical products, *p*-iodophenol and hydrogen bromide (or intermediates leading to these products), favor the formation of *p*-bromophenol.

It was also found that hydrogen chloride did not react appreciably with *p*-iodophenol under similar conditions.

Experimental[6]

p-Iodophenol[7] (8 g., 0.036 mole, m.p. 92–94°) was dissolved in 100 ml. of alcohol-free chloroform contained in a 200-ml. flask, equipped with gas-inlet tube, condenser and drying tubes. Hydrogen bromide (Matheson Co.) was passed through a U-tube containing phenol (to remove elemental bromine) and through a calcium chloride tube, and was then led directly into the chloroform solution, maintained at 45 ± 2°. The rate of flow was approximately one bubble per 15–30 sec., probably sufficient to maintain saturation (calculated as less than 0.05 mole HBr per 100 ml. of chloroform).[8] After 85 minutes, the time of maximum color development, the solution was cooled, washed with 25 ml. of water containing 4 g. of sodium bisulfite, with 20 ml. of water saturated with sodium bicarbonate, and was then dried with anhydrous sodium sulfate. After removing the chloroform, the mixed phenols were distilled at reduced pressure in a 15-ml. flask with a 2-in. Vigreux column. The yield of phenol was 1.52 g., 44% (b.p. 43–45° at 2 mm.; fern-like crystals; phenoxyacetic acid derivative, m.p. 96–99°). The yield of *p*-bromophenol was 2.53 g., 40% (b.p. 77–78° at 2 mm.; m.p. 61–65°; small prisms; after sublimation at room temperature and 2 mm. pressure, m.p. 65–66°; mixed m.p. with *p*-bromophenol 64–66°). No iodophenol could be detected.

Further runs and comments: Chloroform was used rather than carbon tetrachloride because of the poor solubility of *p*-iodophenol in the latter solvent. The reaction also proceeded at room temperature but did not reach its maximum color development until after 8–10 hours exposure to hydrogen bromide. In a second run which was maintained at 45° for 5 hours, the yield of phenol was 47% and of *p*-bromophenol was 32%. In a third run which was maintained at 45° for 10 minutes, the yield of phenol was 36%, of a mixture of *p*-bromo- and *p*-iodophenol (b.p. 75–80° at 2 mm., m.p. 62.5–67.5°) was approximately 35% and of a different composition mixture (b.p. 80–90° at 2 mm., m.p. 69–73°) was 3%. This reaction was therefore incomplete, and it was difficult to separate *p*-bromo- and *p*-iodophenol. In a control experiment in which an equimolecular mixture of phenol and *p*-bromophenol was subjected to the general purification and isolation procedure, the yield of phenol (b.p. 47–48° at 2 mm.) was 48% and *p*-bromophenol (b.p. 81–82° at 2 mm.) was 47%. In a final run, hydrogen chloride was used in place of hydrogen bromide. After 2 hours at 45° and the usual isolation procedure, the yield of unreacted *p*-iodophenol (b.p. 99° at 2 mm., m.p. 92–94°) was essentially quantitative except for a small fraction (0.06 g., b.p. 47–50° at 2 mm.) having the properties of phenol. A light wine color (from iodine liberation) developed in the original hydrogen chloride reaction mixture as contrasted to the dark, iodine colors of the mixtures exposed to hydrogen bromide.

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[2] E. R. Alexander, "Ionic Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 249.

[3] A. E. Remick, "Electronic Interpretations of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 354.

[4] F. W. Bennett and A. G. Sharpe, *J. Chem. Soc.*, 1383 (1950).

[5] L. J. Lambourne and P. W. Robertson, *ibid.*, 1167 (1947).

[6] All melting points are corrected; A.S.T.M. specification, partial immersion thermometer.

[7] "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 355.

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