coupling product, the percentage yield of dried precipitate is a check on the completeness of reaction. The phenols used were analytical reagent grade. The methylolphenols were prepared in accordance with the references listed in Table I.

The analyses for unreacted methylolphenols in the filtrate were made by the paper chromatographic method using spot weights as a measure of concentration.[5]

Conclusions

Several conclusions may be drawn from the experimental data in Table I.

In all examples studied, a *p*-methylol group is more difficult to replace than a *p*-hydrogen atom. A similar result also was obtained in the case of the *p*-carboxylic acid. Diazonium coupling is known to be of the electrophilic aromatic substitution type.[15a,b] The inductive effect of a *p*-methylol substituent is to withdraw electrons and hence to deactivate the ring to electrophilic substitution. In a competitive reaction, therefore, the unsubstituted parent phenol should be more reactive than a *p*-methylol substituted phenol. Our results agree with this conclusion. A similar effect was reported for the case of formaldehyde adding to the phenolic nucleus.[4]

In agreement with Ziegler and Zigeuner, it was observed that an *o*-methylol group is replaced more easily than an *o*-hydrogen atom. The presence of an *o*-methylol group also enhances the reactivity of the molecule toward diazonium coupling. This effect likewise has a parallel in the formaldehyde addition reaction.[4] The two latter conclusions do not appear to be amenable to the type of explanation accorded the *p*-methylol substituent. The factor which apparently differentiates the *o*-methylol compound from either the *para* or *meta* isomer is the possibility of chelation or hydrogen bonding between the *ortho* substituent and the phenolic hydroxyl group. Such internal hydrogen bonds are known to exist in *ortho* methylolphenols[16] and are believed to account for certain observed anomalies.[17]

[15] (a) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1949, p. 297; (b) H. Zollinger, *Chem. Revs.*, **51**, 347 (1952).

[16] R. E. Richards and H. W. Thompson, *J. Chem. Soc.*, 1260 (1947).

[17] G. Sprengling and C. W. Lewis, This Journal, **75**, 5709 (1953).

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Cleavage of Some Organosilicon Compounds by Formic Acid

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When tri-(2-biphenylyl)-silanol was refluxed for 24 hours with 98–100% formic acid in an attempt to prepare hexa-(2-biphenylyl)-disiloxane, the only pure product isolated so far was biphenyl. The extension of the reflux period to 48 hours resulted in a 76.5% yield of biphenyl based upon the cleavage of all three biphenylyl groups. A quantitative yield of hexaphenyldisiloxane (m.p. 220–222°) has been obtained when triphenylsilanol was refluxed for 16 hours with 98% formic acid.[1]

$$(2\text{-}C_6H_5C_6H_4)_3SiOH + HCOOH \longrightarrow C_6H_5C_6H_5$$
$$(C_6H_5)_3SiOH + HCOOH \longrightarrow (C_6H_5)_3SiOSi(C_6H_5)_3$$

A similar treatment of tris-(*p*-chlorophenyl)-ethoxysilane with formic acid gave hexakis-(*p*-chlorophenyl)-disiloxane.[2]

The above results suggested the possibility that the cleavage reaction is characteristic of sterically hindered aryl silanols, while the condensation to disiloxane is characteristic of non-sterically hindered silanols. The isolation of naphthalene from the tri-(1-naphthyl)-silanol reaction and of hexa-(*p*-tolyl)-disiloxane from the attempt to cleave tri-(*p*-tolyl)-silanol supported the conjecture. The cleavage of 2-biphenylyltriphenylsilane and of tri-(2-biphenylyl)-silane, however, demonstrated that the cleavage reaction was not limited to silanols. The failure of tri-(2-biphenylyl)-chlorosilane to undergo cleavage and the isolation of benzene from the reaction of triphenylsilane and formic acid stress the importance of factors other than steric hindrance. It is also interesting to note that the yield of benzene from triphenylsilane was practically identical with the yield of biphenyl from tri-(2-biphenylyl)-silane.

In the cleavage of triphenylsilanol in glacial acetic acid with hydrogen chloride[3] hexaphenyldisiloxane is probably an intermediate since under milder condition (10% hydrochloric acid in acetic acid) hexaphenyldisiloxane was obtained.[4] The lack of reaction between hexaphenyldisiloxane and formic acid indicates that formic acid is a weaker cleaving agent than the hydrogen chloride–glacial acetic acid combination. This weakness also is substantiated by the failure of formic acid to cleave tetraphenylsilane which has been cleaved by hydrogen chloride.[4]

Experimental[5]

General Procedure.—Into a dry, round-bottomed flask containing the organosilicon compound and some boiling chips was added 10–15 ml. of 98–100% formic acid per gram of the compound to be cleaved. Nitrogen under slight pressure was introduced through the top of the reflux condenser and the flask was heated with a heating mantle. The reaction mixture was refluxed gently for 48 hours, cooled, filtered, then washed with 98–100% formic acid. The product obtained was purified, then identified by a mixed melting point with an authentic sample. The filtrate was distilled and the fraction distilling at the boiling point of the product sought or at the boiling point of its azeotropic mixture with formic acid was neutralized and redistilled. The residue from the first distillation was neutralized and the resulting precipitate was filtered, then purified and identified in the manner previously described.

Tri-(2-biphenylyl)-silanol.[6]—The filtration of the product from the reaction of 4 g. (0.0074 mole) of tri-(2-biphenylyl)-silanol and 50 ml. of formic acid yielded 1.76 g. of biphenyl melting at 70–70.5°. The mixed melting point with an authentic sample of biphenyl was not depressed. The filtrate was diluted with 50 ml. of water, neutralized with sodium carbonate and filtered. The crude product when recrystallized from a mixture of petroleum ether (b.p. 77–115°) and ethanol weighed 0.42 g. and melted at 67.5–69.5°. The crude material recovered from the filtrate was chromatographed on alumina with benzene as the solvent and eluent. The two biphenyl fractions obtained were 0.16 g. (m.p. 69–70°) and 0.27 g. (m.p. 66–68°). The total yield of the biphenyl isolated was 2.61 g. (76.5%).

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[1] H. W. Melvin, unpublished studies.

[2] H. Gilman and L. S. Miller, This Journal, **73**, 968 (1951).

[3] H. Gilman and F. J. Marshall, *ibid.*, **71**, 2066 (1949).

[4] F. S. Kipping and L. L. Lloyd, *J. Chem. Soc.*, **79**, 449 (1901).

[5] All melting points are uncorrected.

[6] H. Gilman and K. Oita, *J. Org. Chem.*, **20**, in press (1955).

Tri-(1-naphthyl)-silanol.[7]—When the reaction mixture from 3 g. (0.0071 mole) of tri-(1-naphthyl)-silanol and 40 ml. of formic acid was filtered, 2.04 g. of a product melting over the range 74–140° was obtained. The mother liquor upon concentrating and cooling yielded 0.31 g. of naphthalene melting at 80–81°. No depression was observed in the mixed melting point determination with an authentic specimen. The product melting over the range 74–140° was vacuum-sublimed to give 0.64 g. of naphthalene melting at 80–81.5°. The identity of this product also was confirmed by the method of mixed melting point. The total yield was 1.12 g. (41.4%).

Tri-(*p*-tolyl)-silanol.[8]—From the reaction of 1.0 g. (0.0031 mole) of tri-(*p*-tolyl)-silanol and 15 ml. of formic acid, 0.75 g. of a white precipitate was obtained upon filtration. Recrystallization of this product from a mixture of petroleum ether (b.p. 77–115°) and benzene yielded 0.18 g. of product melting at 226.5–227.5°. By concentrating the mother liquor, 0.20 g. of a product melting at 225–226.5° was obtained. The mixed melting point of the former product with an authentic sample of hexa-(*p*-tolyl)-disiloxane (m.p. 228.5–229.5°) was 228.5–229°. The total yield of hexa-(*p*-tolyl)-disiloxane was 0.38 g. (39.2%).

2-Biphenylyltriphenylsilane.[6]—A sticky, white product was obtained from the filtration of the reaction mixture from 2 g. (0.0049 mole) of 2-biphenylyltriphenylsilane and 25 ml. of formic acid. The recrystallization of this product from a mixture of petroleum ether (b.p. 77–115°) and benzene gave 0.57 g. (28.5% recovery) of 2-biphenylyltriphenylsilane melting at 133–136°. The mixed melting point with an authentic sample melting at 136.5–137.5° was 135–136°.

The distillate from the distillation of the original filtrate upon neutralization and redistillation did not give any fraction which boiled near the boiling point (69.3°) of the benzene–water azeotrope. The residue from the first distillation when neutralized gave a precipitate which when filtered and dried weighed 0.34 g. (m.p. 68–70.5°). Its identity as biphenyl was established by a mixed melting point determination with an authentic specimen. The yield of biphenyl was 45.5%.

Tri-(2-biphenylyl)-silane.[6]—Filtration of the reaction-mixture from the reaction of 4 g. (0.0082 mole) of tri-(2-biphenylyl)-silane and 50 ml. of formic acid gave 4.07 g. of white product melting over the range 164–167°. By recrystallizing the crude product from a mixture of petroleum ether (b.p. 77–115°) and benzene, 2.33 g. (58.4% recovery) of tri-(2-biphenylyl)-silane melting at 170–171° was obtained. The mixed melting point with an authentic sample of tri-(2-biphenylyl)-silane (m.p. 170–171°) was not depressed.

When the original filtrate was neutralized, cooled and filtered 0.34 g. (8.9%) of biphenyl melting at 70–71° was obtained. The identity was confirmed in the usual manner.

Tri-(2-biphenylyl)-chlorosilane.[6]—When the material from the reaction mixture of 4 g. of tri-(2-biphenylyl)-chlorosilane and 50 ml. of formic acid was filtered and dried, 3.85 g. (96.5% recovery) of the starting material melting at 240–240.5° was obtained. The mixed melting point with an authentic sample melting at 240–240.5° was 240–240.5°.

Triphenylsilane.—The clear solution from the reaction of 5 g. (0.02 mole) of triphenylsilane and 50 ml. of formic acid was fractionally distilled. The first fraction which weighed 4.57 g., boiling range 73.5–98.5°, was neutralized with sodium carbonate, diluted with water and redistilled to give a benzene–water azeotrope weighing 0.44 g., boiling range 65–70°. This azeotrope was approximately 0.40 g. in benzene; therefore, the yield was 8.8% assuming cleavage of all the phenyl groups. The benzene was derivatized as *m*-dinitrobenzene. The crude *m*-dinitrobenzene weighing 0.35 g. (m.p. 75–82°), upon recrystallization from a mixture of water and ethanol gave 0.17 g. of pure product melting at 89–90°.

The residue from the distillation was diluted with about 100 ml. of methanol. The methanol was partially separated from the resulting sticky white product by decantation. When a crystallization attempt was carried out with a mixture of methanol and benzene, an oil resulted. This oil crystallized after cooling in a refrigerator at 0° for a month. The product obtained weighed 0.52 g. and melted over the range 175–217°.

Hexaphenyldisiloxane.—Filtration of the mixture from the attempted cleavage of 5 g. of hexaphenyldisiloxane with 50 ml. of formic acid resulted in a recovery of 4.81 g. (96%) of the starting material, m.p. 228–228.5°. Distillation of the filtrate did not give any evidence of benzene.

Tetraphenylsilane.—From the attempted cleavage of 5 g. of tetraphenylsilane with 50 ml. of formic acid, 4.83 g. (96.5% recovery) of tetraphenylsilane melting at 234.5–236.5° was obtained. A mixed melting point with an authentic sample melting at 236.5–237° was 235–237°.

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Conversion of Thianthrene-5-oxide to Dibenzothiophene by *n*-Butyllithium

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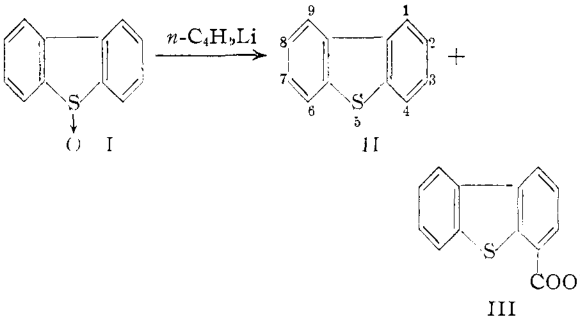
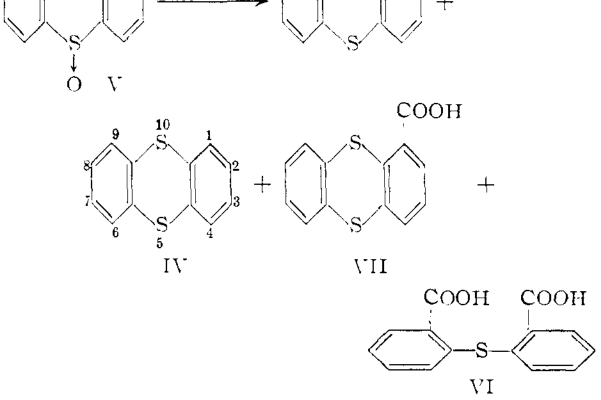
Metalation of dibenzothiophene-5-oxide (I)[1] at −5 to −15° with 3.2 equivalents of *n*-butyllithium gave a 10.8% yield of dibenzothiophene (II) and a 35.7% yield of dibenzothiophene-4-carboxylic acid (III).



When one equivalent of *n*-butyllithium was used in the above reaction the result was a 56% recovery of dibenzothiophene-5-oxide, a 3.5% yield of dibenzothiophene-4-carboxylic acid and a 4.4% yield of dibenzothiophene.

In the course of a general investigation of the metalation of thianthrene (IV) and its derivatives we found that the treatment of thianthrene-5-oxide (V) with *n*-butyllithium resulted in varying yields of dibenzothiophene, thianthrene and small amounts of acidic materials.



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[8] A. R. Steele and F. S. Kipping, *J. Chem. Soc.*, 357 (1929).

[1] H. Gilman and D. L. Esmay, THIS JOURNAL, **74**, 266 (1952).