leum ether (b.p. 60–68°) there was obtained 60.0 g. (62%) of the acid chloride I, m.p. 72–75°. Concentration of the filtrate yielded 19.0 g. (0.11 mole) of the acid II, m.p. 72–74°.

1,1,2,3,3-Pentamethyltrimethylenephosphinic Acid (II).—Refluxing the acid chloride I with water for 2 hr. gives a quantitative yield of the acid II as its dihydrate; white shiny platelets, m.p. 54–58°; calcd. for $C_8H_{16}PO_2H \cdot 2H_2O$, neut. equiv. 212; found, neut. equiv. 216. Drying in a vacuum desiccator or heating above its melting point converts the hydrate to the anhydrous acid II, m.p. 72–74°.

Methyl Ester of II.—A solution of 98.0 g. (0.50 mole) of the acid chloride I in 150 ml. of methanol was added dropwise with stirring to a solution of sodium methoxide made from 18.2 g. (0.55 g.-atom) of sodium in 500 ml. of methanol. After standing for 20 hr., the methanol was stripped off *in vacuo*. The solid remaining was taken up in water and this solution was extracted several times with methylene chloride. After drying and removal of the solvent, distillation gave 89.1 g. (94%) of ester III, b.p. 66–69°/0.2 mm.

Saponification of the methyl ester with aqueous base followed by acidification regenerates the acid II as its dihydrate. The anhydrous acid is readily converted to the acid chloride by short refluxing with thionyl chloride in benzene.

The analytical data on compounds I, II, and III are summarized in Table II.

5,10-Dihydrosilanthrene Derivatives

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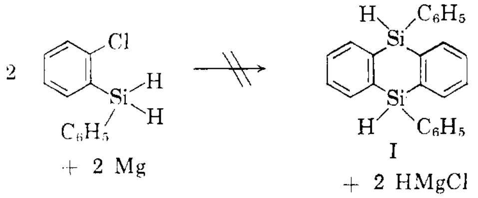
5,10-Dihydrosilanthrene derivatives have been prepared by the intermolecular sodium coupling of *o*-chlorophenyl silicon compounds containing a silicon-hydrogen grouping In the appropriately substituted derivatives, a separation of the *cis-trans* isomers has been accomplished Attempts to treat *o*-chlorophenylsilane with magnesium in tetrahydrofuran were unsuccessful.

The 5,5,10,10-tetraphenyl and 5,5,10,10-tetrabenzyl derivatives of 5,10-dihydrosilanthrene have recently been prepared by treating *o*-phenylenedilithium with dichlorodiphenylsilane and with dibenzyldichlorosilane, respectively.[1] Those derivatives were the first members of a new cyclic organosilicon system, the silicon analog of 9,10-dihydroanthracene. We now wish to report the syntheses of 5,10-dihydrosilanthrene derivatives by new procedures, which involved intermolecular Wurtz-type coupling reactions.

The initial approach in this investigation was concerned with the preparation and possible intermolecular cyclization of *o*-chlorophenylphenylsilane. Two attempts to prepare *o*-chlorophenylphenylsilane by treating phenylsilane[2] with *o*-chlorophenylmagnesium bromide were unsuccessful, but the compound was obtained in fair yield by the interaction of the Grignard reagent and phenylbromosilane. In light of the recent successes in the preparation of Grignard reagents from aryl chlorides[3] and in the reactions of Grignard reagents with silicon hydrides[2] through the use of tetrahydrofuran as the solvent, reactions of *o*-chlorophenylphenylsilane with magnesium in tetrahydrofuran were attempted in an effort to obtain 5,10-diphenyl-5,10-dihydrosilanthrene (I). However, this aryl chloride could not be induced to react with magnesium, probably because of steric reasons.



Attention was subsequently turned to Wurtz-type coupling reactions as a means of preparing 5,10-dihydrosilanthrene compounds. Clarke[4] had shown that *o*-chlorophenyltrimethylsilane and chlorotrimethylsilane could be readily coupled upon treatment with molten sodium in refluxing toluene to give *o*-phenylenebis (trimethylsilane). Also, Benkeser and Foster[5] found that organosilicon compounds such as triphenylsilane were unaffected by molten sodium metal. It therefore seemed desirable to investigate the possible intermolecular cyclization by sodium of certain *o*-chlorophenyl silicon derivatives containing a silicon-hydrogen grouping.

Treatment of *o*-chlorophenylphenylsilane with phenylmagnesium bromide in refluxing tetrahydrofuran gave *o*-chlorophenyldiphenylsilane in good yield. A toluene solution of this *o*-chlorophenyl derivative was then added to a suspension of molten sodium in refluxing toluene to afford 5,5,10,10-tetraphenyl-5,10-dihydrosilanthrene (II), which was shown to be identical with the material obtained by the interaction of *o*-phenylenedilithium and dichlorodiphenylsilane.[1] In addition, lesser amounts

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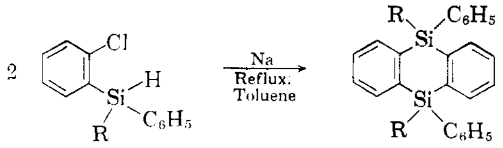
(1) H. Gilman and E. A. Zuech, *Chem. & Ind.*, 120 (1960); *J. Am. Chem. Soc.*, **82**, 3605 (1960).

(2) For the reactions of organometallic compounds with silicon hydrides, see H. Gilman and E. A. Zuech, *ibid.*, **81**, 5925 (1959).

(3) H. E. Ramsden, A. E. Balint, W. R. Whitford, J. J. Walburn, and R. Cserr, *J. Org. Chem.*, **22**, 1202 (1957); H. Normant, *Compt. rend.*, **239**, 1510 (1954), and, particularly, pp. 1–65 in "Advances in Organic Chemistry," Interscience Publishers, New York, 1960.

(4) H. A. Clark, A. F. Gordon, C. W. Young, and M. J. Hunter, *J. Am. Chem. Soc.*, **73**, 3798 (1951).

(5) R. A. Benkeser and D. J. Foster, *ibid.*, **74**, 5314 (1952).



R =
II. C_6H_5—
III. n-$C_{12}H_{25}$—
IV. CH_3—
V. p-$CH_3C_6H_4$—

of tetraphenylsilane and (*o*-diphenylsilylphenyl)-triphenylsilane were also obtained.

Reaction of *o*-chlorophenylphenylsilane with a tetrahydrofuran solution of *n*-dodecylmagnesium bromide gave *o*-chlorophenyl-*n*-dodecylphenylsilane. This material was likewise treated with a refluxing toluene suspension of molten sodium to give 5,10-di-*n*-dodecyl-5,10-diphenyl-5,10-dihydrosilanthrene (III) which, by a difficult process of fractional crystallization and subsequent recrystallizations, was separated into its respective *cis-trans* isomers. In an analogous manner, *o*-chlorophenyl-methylphenylsilane and *o*-chlorophenylphenyl-*p*-tolylsilane were prepared and treated with molten sodium to give the corresponding *cis-trans* isomers of 5,10-dimethyl-5,10-diphenyl-5,10-dihydroilanthrene (IV) and of 5,10-diphenyl-5,10-di-*p*-tolyl-5,10-dihydrosilanthrene (V). From the reactions of *o*-chlorophenyl-*n*-dodecylphenylsilane and *o*-chlorophenylmethylphenylsilane, there were also obtained *n*-dodecyltriphenylsilane and methyltriphenylsilane, respectively.

A few *cis-trans* isomers of this type have been reported in the 9,10-dihydroanthracene series. Rigaudy[6] has shown that the *trans* isomer of 9,10-dibenzoyl-9,10-dihydroanthracene melts at 195°, while the *cis* compound melts at 170–171°. Similarly, Badger[7] has assigned the *trans* structure to the higher melting isomer of 9,10-dimethyl-9,10-dihydroanthracene. Therefore, by analogy, the higher melting isomers of these 5,10-dihydrosilanthrene compounds have been tentatively assigned the *trans* configuration.

Experimental

All reactions were carried out in an atmosphere of dry, oxygen-free nitrogen, and all melting and boiling points are uncorrected. The tetrahydrofuran was dried and purified by successively distilling from sodium wire and then from lithium aluminum hydride immediately before use.

***o*-Chlorophenylphenylsilane.**—An ethereal solution containing 0.047 mole of *o*-chlorophenylmagnesium bromide,[8] prepared from 11 g. (0.057 mole) of *o*-bromochlorobenzene and 1.7 g. (0.07 g.-atom) of magnesium, was added to 11.5 g. (0.05 mole) of phenylbromosilane[9] in 50 ml. of ether. After stirring for 1 hr. at room temperature, Color Test I[10] was negative and hydrolysis was effected with 50 ml. of 5% hydrochloric acid. The aqueous layer was separated, extracted with ether, and discarded. The combined organic solutions were dried, and the ether removed by distillation. The residue was then distilled twice at reduced pressure to give 4.52 g. (44%) of colorless liquid, b.p. 84–85° (0.03 mm.), n^{20}_{D} 1.5927, d^{20}_{20} 1.129.

Anal. Calcd. for $C_{12}H_{11}ClSi$: Si, 12.85; MR_D, 65.82. Found: Si, 12.82, 13.00; MR_D, 65.58.

In another run employing 0.46 mole of *o*-chlorophenylmagnesium bromide and of phenylbromosilane, there was obtained a 65.4% yield of the silane.

Two attempts to prepare *o*-chlorophenylphenylsilane were made by treating *o*-chlorophenylmagnesium bromide with phenylsilane. However, none of the desired compounds could be isolated from either run; only unidentifiable materials were obtained.

Reaction of *o*-Chlorophenylphenylsilane and Magnesium in Tetrahydrofuran (Attempted).—A mixture of 3.5 g. (0.016 mole) of *o*-chlorophenylphenylsilane and 25 ml. of tetrahydrofuran containing 0.73 g. (0.03 g.-atom) of suspended magnesium turnings was refluxed for 60 hr. There was no evidence of a reaction and Color Test I remained negative throughout the heating. After cooling, the mixture was filtered to remove the magnesium and hydrolyzed with 5% hydrochloric acid. The organic layer was worked up in the usual manner and the residue distilled at reduced pressure to give 2.15 g. (61%) of recovered *o*-chlorophenylphenylsilane, b.p. 88–91° (0.1 mm.). The remaining resin-like material could not be crystallized or otherwise purified.

In another run, the reaction mixture was heated at reflux for 4 days and, in addition, several small crystals of iodine were added. As before, no evidence of a reaction was noted, and 92% of the *o*-chlorophenylphenylsilane was recovered.

***o*-Chlorophenyldiphenylsilane.**—A solution of 21.8 g. (0.1 mole) of *o*-chlorophenylphenylsilane in 25 ml. of tetrahydrofuran was treated with a tetrahydrofuran solution containing 0.15 mole of phenylmagnesium bromide. The reaction mixture was heated at gentle reflux for 17 hr., and then hydrolyzed by pouring upon crushed ice containing a small amount of sulfuric acid. Ether was added and the aqueous layer separated and extracted with ether. The combined organic solutions were dried with anhydrous calcium sulfate and the solvent removed by distillation. The resulting material was distilled at reduced pressure to give 27 g. (91.5%) of colorless liquid, b.p. 148–152° (0.03 mm.), which solidified upon standing. A portion was recrystallized from absolute ethanol to give colorless crystals, m.p. 51–52.5°.

Anal. Calcd. for $C_{18}H_{15}ClSi$: Si, 9.53. Found: Si, 9.62, 9.52.

Reaction of *o*-Chlorophenyldiphenylsilane and Sodium.—A solution of 24.9 g. (0.084 mole) of *o*-chlorophenyldiphenylsilane in 50 ml. of dry toluene was added dropwise to 4.15 g. (0.18 g.-atom) of molten sodium suspended in 100 ml. of refluxing toluene. The dark brown reaction mixture was then heated at reflux for 18 hr. After allowing the mixture to cool, 50 ml. of 95% ethanol were carefully added to destroy the excess sodium. Hydrolysis was then effected by pouring upon iced water, and ether was added. The organic layer was worked up in the usual manner and evaporated under an air-jet, with the last traces of toluene being removed with the aid of a water aspirator. The resulting brown oily material was susequently chromatographed over alumina. Elution with petroleum ether (b.p. 60–70°) gave a colorless solid, m.p. 180–210°, which resisted purification by crystallization. Using cyclohexane as the eluant, there was obtained 5.1 g. of colorless solid, m.p. 200–225°. This material was recrystallized four times from ethyl acetate to give 3.15 g. (14.5%) of colorless crystals, m.p. 234–236°, which was identified as 5,5,10,10-tetraphenyl-5,10-dihydrosilanthrene by mixed melting point with an authentic sample and by comparison of the infrared spectra.[1] Further elution with other solvents gave only oils which could not be identified.

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[7] G. M. Badger, M. L. Jones, and R. S. Pearce, *J. Chem. Soc.*, 1700 (1950).

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[9] M. C. Harvey, W. H. Nebergall, and J. S. Peake, *ibid.*, **79**, 1437 (1957).

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The material obtained from the first eluates, which had resisted purification, was then rechromatographed. Careful elution with petroleum ether (b.p. 60–70°) gave a colorless solid. After three recrystallizations from ethyl acetate, there was obtained 0.39 g. of colorless needles, m.p. 231–234°, identified as tetraphenylsilane by mixed melting point and by comparison of the infrared spectra. Further elution with petroleum ether and then with cyclohexane gave a colorless solid, m.p. 195–210°. This material was recrystallized three times from ethyl acetate to give 0.44 g. of colorless solid, m.p. 211–214°. An additional recrystallization from the same solvent raised the melting point to 213–215°. The compound was shown to be (*o*-diphenylsilylphenyl)triphenylsilane by mixed melting point with an authentic sample and by comparison of the infrared spectra.[1]

***o*-Chlorophenyl-*n*-dodecylphenylsilane.**—A tetrahydrofuran solution containing 0.14 mole of *n*-dodecylmagnesium bromide was added to 19.8 g. (0.091 mole) of *o*-chlorophenylphenylsilane in 50 ml. of tetrahydrofuran. After refluxing for 17 hr., the reaction mixture was poured upon crushed ice acidified with sulfuric acid. The aqueous layer was separated, extracted with ether, and discarded. The resulting tetrahydrofuran-ether solution was worked up in the usual manner, and the residue distilled at reduced pressure to give 26.2 g. (74.3%) of colorless liquid, b.p. 190–196° (0.01 mm.), $n^{20}{}_D$ 1.5304, $d^{20}{}_{20}$ 0.984.

Anal. Calcd. for $C_{24}H_{35}ClSi$: Si, 7.26; MR_D, 121.32. Found: Si, 7.29, 7.37; MR_D 121.59.

Reaction of *o*-Chlorophenyl-*n*-dodecylphenylsilane and Sodium.—A solution of 23.5 g. (0.0607 mole) of *o*-chlorophenyl-*n*-dodecylphenylsilane in 50 ml. of toluene was added dropwise to a suspension of 4 g. (0.17 g.-atom) of molten sodium in 100 ml. of refluxing toluene. After refluxing for 4 hr., the reaction was allowed to cool and carefully treated with 50 ml. of 95% ethanol. Hydrolysis was then effected by pouring upon crushed ice containing a small amount of sulfuric acid. Ether was added, and the organic layer worked up in the usual manner. The reaction products were subsequently chromatographed over alumina, but only oils were obtained which could not be caused to crystallize. The oils from the petroleum ether (b.p. 60–70°) and cyclohexane eluates were then collected with the aim of distilling out the more volatile materials at reduced pressure. A portion boiling at 160–180° (0.01 mm.) was caused to crystallize by treatment with methanol. After two recrystallizations from methanol, there was obtained 0.98 g. (3.8%, based on the silicon) of colorless flakes, m.p. 65–67°, identified as *n*-dodecyltriphenylsilane by mixed melting point and by comparison of the infrared spectra.

The distillation residue was taken up in a mixture of absolute ethanol and benzene to give a colorless solid. This material was recrystallized twice from the same solvent mixture to give 2.39 g. of colorless solid, m.p. 74–80°. Fractional crystallization from absolute ethanol, after much effort, gave colorless flakes, m.p. 74–80°, and colorless needles, m.p. 74–80°. The flakes were recrystallized four times from absolute ethanol to give 0.98 g. (4.6%) of colorless flakes, m.p. 86–88°, believed to be *trans*(?)-5,10-di-*n*-dodecyl-5,10-diphenyl-5,10-dihydrosilanthrene.

Anal. Calcd. for $C_{48}H_{68}Si_2$: C, 82.21; H, 9.77; Si, 8.01. Found: C, 82.24, 82.26; H, 9.36, 9.53; Si, 8.04.

The colorless needles were recrystallized five times from absolute ethanol to give 0.81 g. (3.8%) of small colorless needles, m.p. 85–87°, believed to be *cis*(?)-5,10-di-*n*-dodecyl-5,10-diphenyl-5,10-dihydrosilanthrene.

Anal. Calcd. for $C_{48}H_{68}Si_2$: C, 82.21; H, 9.77; Si, 8.01. Found: C, 82.35, 82.30; H, 9.25, 9.32; Si, 8.03, 7.83.

An admixture of the two compounds melted over the range 75–80°. The infrared spectra of the compounds as carbon disulfide solutions were nearly superimposable. Prominent absorption bands were present at 3.3, 3.5, 13.3, and 13.6 μ, which are characteristic of C—H aromatic and aliphatic groups, and aromatic *ortho*-disubstitution and monosubstitution, respectively. A doublet was also present at 9.0–9.1 μ, possibly indicative of the two types of silicon-phenyl linkages. Both compounds volatilized at 455–460° with apparent decomposition.

***o*-Chlorophenylmethylphenylsilane.**—A solution of 31.6 g. (0.145 mole) of *o*-chlorophenylphenylsilane in 250 ml. of tetrahydrofuran was treated with 0.18 mole of an ethereal solution of methylmagnesium iodide. The diethyl ether was removed by distillation and the tetrahydrofuran solution heated at reflux for 18 hr. The reaction mixture was poured upon crushed ice containing sulfuric acid, and ether was added. After the usual work-up, the residue was distilled at reduced pressure to give 30.5 g. (90%) of colorless liquid, b.p. 94–96° (0.01 mm.), $n^{20}{}_D$ 1.5867, $d^{20}{}_{20}$ 1.1185

Anal. Calcd. for $C_{13}H_{13}ClSi$: Si, 12.07; MR_D, 70.39. Found: Si, 11.92, 11.81; MR_D, 69.91.

Reaction of *o*-Chlorophenylmethylphenylsilane and Sodium.—A suspension of 6.9 g. (0.3 g.-atom) of molten sodium in 100 ml. of refluxing toluene was treated with 28.2 g. (0.12 mole) of *o*-chlorophenylmethylphenylsilane in 50 ml. of toluene. The brown reaction mixture was heated at reflux for 4 hr., allowed to cool, and carefully treated with 100 ml. of 95% ethanol. Hydrolysis was then effected by pouring upon crushed ice. Ether was added, and the organic layer separated and dried with anhydrous sodium sulfate. After removing the solvents by distillation, the residue was distilled at reduced pressure. The fraction boiling 100–138° (0.008 mm.) was taken up in methanol to give colorless crystals, m.p. 56–62°. This material was recrystallized twice from methanol to give 1.53 g. (5.1%, based on the silicon) of colorless crystals, m.p. 66–68°, which was shown to be methyltriphenylsilane by mixed melting point and by comparison of the infrared spectra.

From the distillation, there was also obtained 9.65 g. of viscous liquid, b.p. 192–195° (0.008 mm.), which solidified upon standing. Treatment with petroleum ether (b.p. 60–70°) gave a colorless solid, m.p. 112–130°. This material was then fractionally recrystallized from petroleum ether (b.p. 60–70°) to give two substances. The more insoluble material was recrystallized numerous times from petroleum ether and from absolute ethanol to give finally 3.13 g. (13.3%) of colorless needles, m.p. 148–150°, believed to be *trans*(?) - 5,10 - dimethyl-5,10-diphenyl-5,10 - dihydrosilanthrene.

Anal. Calcd. for $C_{26}H_{24}Si_2$: C, 79.53; H, 6.16. Found: C, 79.64, 79.76; H, 6.06, 6.29.

The more soluble material was likewise recrystallized numerous times from both petroleum ether and absolute ethanol to give 1.40 g. (5.9%) of colorless crystals, m.p. 140–141.5°, believed to be *cis*(?)-5,10-dimethyl-5,10-diphenyl-5,10-dihydrosilanthrene.

Anal. Calcd. for $C_{26}H_{24}Si_2$: C, 79.53; H, 6.16. Found: C, 79.62, 79.86; H, 6.31, 6.16.

The melting point of a mixture of the compounds was depressed, melting 115–133°. The infrared spectra of the two compounds, as well as that from the 9.65 g. which had been initially distilled, were nearly identical. Prominent absorption bands indicative of C—H aromatic and aliphatic groups, the silicon-methyl and silicon-phenyl linkages, and aromatic *ortho*-disubstitution and monosubstitution were readily discernible. Both of the isomeric compounds volatilized at 440–445°, with no apparent decomposition.

***o*-Chlorophenylphenyl-*p*-tolylsilane.**—A tetrahydrofuran solution containing 0.15 mole of *p*-tolylmagnesium bromide was added to 21.8 g. (0.1 mole) of *o*-chlorophenylphenylsilane in 50 ml. of tetrahydrofuran. After refluxing for 17 hr., hydrolysis was effected by pouring upon crushed ice acidified with sulfuric acid. Ether was added, and the organic layer separated and worked up in the usual manner. Reduced pressure distillation gave 23.5 g. (76.3%) of colorless liquid, b.p. 160–163° (0.01 mm.), $n^{20}{}_D$ 1.6178, $d^{20}{}_{20}$ 1.1419.

Anal. Calcd. for $C_{19}H_{17}ClSi$: Si, 9.09; MR_D, 94.84. Found: Si, 9.18, 9.05; MR_D, 94.74.

Reaction of *o* - Chlorophenylphenyl - *p* - tolylsilane and Sodium.—A solution of 20.2 g. (0.0654 mole) of *o*-chlorophenylphenyl-*p*-tolylsilane in 50 ml. of toluene was added dropwise to a suspension of 3.5 g. (0.15 g.-atom) of molten sodium in 100 ml. of refluxing toluene. The reaction mixture was heated at reflux for 4 hr. and, after cooling to room temperature, cautiously treated with 100 ml. of 95% ethanol. The reaction mixture was then poured upon crushed ice containing sulfuric acid, and subsequently worked up in the usual manner. Chromatography of the reaction products over alumina with petroleum ether (b.p. 60–70°) gave 3.87 g. of colorless solid, m.p. 190–214°. This material was fractionally recrystallized, with much effort, from a mixture of absolute ethanol and benzene to give two substances. The more insoluble material was recrystallized many times from absolute ethanol-benzene mixtures to give ultimately 0.39 g. (2.2%) of colorless crystals, m.p. 221–222.5°, of *trans*(?)-5,10-diphenyl-5,10-di-*p*-tolyl-5,10-dihydrosilanthrene.

Anal. Calcd. for $C_{38}H_{32}Si_2$: C, 83.8; H, 5.92; Si, 10.30. Found: C, 83.9; H, 5.82; Si, 10.21.

The more soluble material was likewise recrystallized many times from absolute ethanol-benzene mixtures to give 1.02 g. (5.7%) of colorless crystals, m.p. 215–217°, of *cis*(?)-5,10-diphenyl-5,10-di-*p*-tolyl-5,10-dihydrosilanthrene.

Anal. Calcd. for $C_{38}H_{32}Si_2$: C, 83.8; H, 5.92; Si, 10.30. Found: C, 84.2; H, 5.91; Si, 10.13.

An admixture of this compound with the above material melted over the range 214–222°. The infrared spectra of the compounds as carbon disulfide solutions were nearly superimposable. Absorption bands, indicative of C—H aromatic and aliphatic groups, and aromatic *para*-disubstitution, *ortho*-disubstitution, and monosubstitution, were present at 3.3, 3.45, 12.5, 13.3, and 13.7 μ, respectively. A doublet was also present at 8.95–9.05 μ, possibly indicative of the types of silicon-phenyl linkages. Both isomers volatilized at 530–540° with decomposition, turning light brown at 480°.

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Syntheses of Polymethylphenols and Their Derivatives. I

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Simple methods of syntheses of prehentenol and durenol have been studied. Reactions of prehentenol, durenol, hemimelletenol, and isopseudocumenol with formaldehyde have been studied qualitatively in order to isolate various phenol methylols and dihydroxydiphenylmethanes. All the new phenolmethylols isolated have also been prepared by alternate routes, not involving addition of formaldehyde.

In order to study the general nature and kinetics of phenol–formaldehyde reactions and the effect of methyl and methylol substituents on reactions rates, it was convenient to choose phenols with only one reactive position, since the reactions are less complex and are expected to lead to the formation of one monomethylol only. Results with 2,4- and 2,6-xylenols are not useful because of their low reactivities towards formaldehyde. Further, there is no conclusive evidence with regard to reactivities of free *meta* positions in phenols towards formaldehyde. Edell[1] claims to have isolated 2,3′-dihydroxydiphenylmethane from the acid condensation of phenol and formaldehyde which is interesting as a first reported case of *meta* substitution. Megson,[2] Finn and co-workers,[3,4] and Martin[5] have reported evidence for the condensation between formaldehyde and the *meta*-hydrogen of phenol under certain conditions. Nickerson,[6] Lilley,[7] and Imoto[8] also think that reaction in the *meta* position should not be excluded, particularly with phenols with a methyl group in the *para* position which might activate *meta* position. More recently Wegler and Regel[9] reported condensation of formaldehyde with the *meta* positions of phenols substituted in both *ortho* and *para* positions. On the other hand *meta* substitution may be obviated by using 3,5-dimethyl-phenols for rate studies. The use of the latter brings the added advantage of the *ortho-para* directing methyl groups located *meta* to the phenolic hydroxyl group, enhancing the reactivity of the phenol.[10] As examples of such substituted phenols, the monofunctional phenols prehentenol and durenol, and the difunctional phenols, hemimelletenol and isopseudocumenol, have been chosen for our studies. Simple methods of synthesis of these phenols have been evolved starting from 3,5-xylenol, and a qualitative study

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