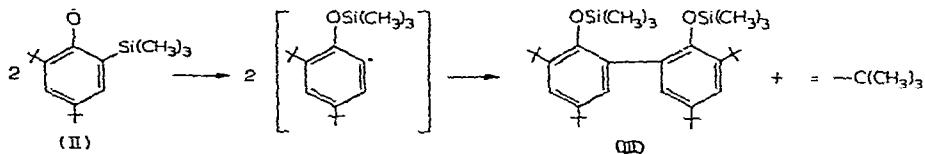
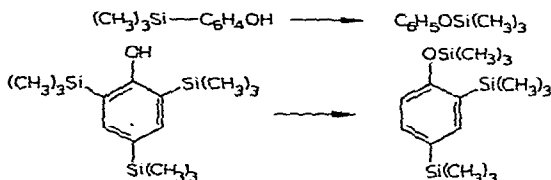


Rearrangement of 2,4-di-tert-butyl-6-trimethylsilylphenoxyl

The radical 2,4-di-tert-butyl-6-trimethylsilylphenoxyl (II) has been obtained in *n*-hexane or benzene solution by the oxidation with lead peroxide or an alkaline solution of $K_3Fe(CN)_6$ of 2,4-di-tert-butyl-6-trimethylsilylphenol (I)¹ previously synthesized by us according to Speer² and Cooper³. Radical II is a structural analogue of the well-known 2,4,6-tri-tert-butylphenoxyl. Solutions of both radicals are dark blue in colour (λ_{max} 620 and 630 $m\mu$, respectively), and the ESR spectra are practically identical triplets (1 : 2 : 1; $\alpha_H \approx 1.7$). Although 2,4,6-tri-tert-butylphenoxyl is stable in *n*-hexane solution in the absence of oxygen, we noticed that under the same conditions the solution colour and the ESR signal of II rapidly disappeared and we did not therefore succeed in obtaining the radical in the solid state. We decided to separate the product of the conversion of free radical II. For this purpose, the oxidation by lead peroxide in *n*-hexane, benzene and diethyl ether, and by an alkaline solution of $K_3Fe(CN)_6$ in *n*-hexane, benzene, diethyl ether and pyridine under an atmosphere of nitrogen, and in vacuum, at room temperature was carried out. After removal of solvent, 2,2'-bis(trimethylsiloxy)-3,5,3',5'-tetra-tert-butylidiphenyl (III) was separated quantitatively. It is a white crystalline substance with m.p. 134–136° sparingly soluble in alcohols but readily soluble in other organic solvents. In the IR spectrum of III there are absorption bands at 760, 847, 1250 and 1290 cm^{-1} characteristic of the trimethylsiloxy group⁴. On hydrolysis of III by sodium methoxide in methanol the corresponding diphenol-2,2'-dihydroxy-3,5,3',5'-tetra-tert-butylidiphenyl⁵ is formed. Compound III is formed as the result of the transition of the trimethylsilyl group from the aromatic ring to the aryloxy oxygen with the subsequent dimerization of the aryl radicals formed, according to the scheme:



Transitions of the trimethylsilyl group from the aromatic ring to the oxygen of the hydroxyl group are described for mono- and polytrimethylsilyl substituted phenols^{2,3} following the scheme:



These rearrangements proceed on prolonged heating at a high temperature (200–250°). Rearrangement in the free radical II, observed by us, occurs at ordinary temperature and is accompanied by dimerisation. Such a type of rearrangement has so far been unknown.

Experimental

2,4-Di-*tert*-butyl-6-trimethylsilylphenol was synthesized according to the procedures of Speer² and Cooper³.

2,4-Di-*tert*-butyl-6-bromophenoxytrimethylsilane, IV. An equimolecular mixture of 0.02 mole of 2,4-di-*tert*-butyl-6-bromophenol, triethylamine and trimethylchlorosilane in 50 ml of toluene was refluxed with stirring for 3 h. After the solution had cooled, petroleum ether (50 ml) was added, the solution was filtered from the precipitate of triethylamine hydrochloride and the solvent removed *in vacuo*. The residue was triturated with methanol and the insoluble residue formed recrystallized from methanol. 5.7 g (0.16 mole, 80%) of IV, white crystals, m.p. 92–94° were obtained. (Found: C, 57.43; H, 8.46; Br, 22.20%; mol.wt. 354, cryoscopic in benzene. C₁₇H₂₉·SiBrO calcd.: C, 57.12; H, 8.18; Br, 22.36%; mol.wt. 357.

2,4-Di-*tert*-butyl-6-trimethylsilylphenoxytrimethylsilane, V. A solution of 0.015 mole of trimethylchlorosilane in 5 ml of toluene was added dropwise to 0.01 mole of IV and 0.02 g-atom of sodium in 10 ml of boiling toluene, with vigorous stirring under an atmosphere of nitrogen. The reaction mixture was heated for 4 h, cooled to room temperature and then 75 ml of petroleum ether was added. After filtration and removal of the solvent *in vacuo* there remained a colourless oil that crystallized on standing. After recrystallization, 2.2 g (0.0062 mole; 62%) of V, m.p. 63–64.5° was obtained from water–methanol. (Found: C, 67.85; H, 10.95%; mol.wt. 345, cryoscopic in benzene. C₂₀H₃₈Si₂O calcd.: C, 68.49; H, 10.92%; mol.wt. 351.

2,4-Di-*tert*-butyl-6-trimethylsilylphenol, I. 0.01 mole of V was dissolved in 50 ml of 2 M sodium methoxide in methanol. After 30 min the mixture was diluted with a large excess of water and extracted with petroleum ether. The extract was dried over MgSO₄. After removal of the solvent *in vacuo* there remained an oil which crystallized on standing. After recrystallization from water–methanol, 2.5 g (0.0088 mole; 88%) of I, m.p. 71–72° (correct.) was obtained. (Found: C, 73.10; H, 10.95%; mol.wt. 284, cryoscopic in benzene. C₁₇H₃₀SiO calcd.: C, 73.31; H, 10.86%; mol.wt. 278.

2,2'-Bis(trimethylsiloxy)-3,5,3',5'-tetra-*tert*-butyl diphenyl, III. (a) 0.5 g of I and 0.5 g of lead peroxide in 15 ml of oxygen-free n-hexane was stirred under an atmosphere of nitrogen until the blue colour of the solution had entirely disappeared. After 4-h stirring, the solution was filtered, the solvent evaporated and the residue washed on the glass filter with cold methanol (10 ml). 0.4 g (80%) of III a white crystalline substance, m.p. 134–136° (from methanol) was obtained. (Found: C, 73.83; H, 10.64%; mol.wt. 550, cryoscopic in benzene. C₃₄H₅₈Si₂O₂ calcd.: C, 73.58; H, 10.53%; mol.wt. 555.) The IR spectrum of III showed trimethylsiloxy-group absorption bands at 760, 847, 1250 and 1290 cm⁻¹. There was also a strong band in the spectrum at 945 cm⁻¹ found by us for a series of substituted phenoxysilanes (939–945 cm⁻¹) that, according to ref. 3, can be referred to the Si–O–Ar bond. (b) Oxygen-free solutions of I (0.4 g) in 10 ml of diethylether and K₃Fe(CN)₆ (0.6 g) in 5 ml of aqueous 2 N KOH were shaken in a sealed evacuated ampoule for 30 min. After this time the blue colour had disappeared. The ampoule was broken, the ethereal layer separated, dried over MgSO₄ and the solvent evaporated. The residue (0.35 g) was washed on the glass filter with methanol. 0.32 g (80%) of a white crystalline substance, m.p. 133–135° (from methanol) was obtained. No depression of melting temperature was shown by a mixed sample with III.

Hydrolysis of 2,2'-bis(trimethylsiloxy)-3,5,3',5'-tetra-tert-butylidiphenyl, III. 0.2 g of III was dissolved in 25 ml of 2 M sodium methoxide in methanol. After standing for 1-h the solution was diluted with a large excess of water, extracted with petroleum ether and the extract dried over MgSO₄. After filtration and evaporation of the solvent, the residue was recrystallized from water-methanol. 0.12 g (80%) 2,2'-dihydroxy-3,5,3',5'-tetra-tert-butylidiphenyl, m.p. 190–192° (literature, m.p. 194.5–195.5°)⁵ were obtained. No depression of melting temperature was shown by a mixed sample with the known substance.

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BOOK REVIEW

Annual Surveys of Organometallic Chemistry, Volume 2 (covering the year 1965), by D. SEYFERTH AND R. B. KING, Elsevier Publishing Company, Amsterdam, 1966, pp. xv + 424, \$20.—, £5.10.0, D.fl.55.—.

When the first volume of this series, covering the year 1964, appeared, Professor J. Chatt, wrote that it was the first new chemistry periodical he had welcomed in twenty years (*J. Organometal. Chem.*, 6 (1966) 444). All the other organometallic chemists whose views are known to your reviewer also received it with enthusiasm, and authors in other fields of chemistry have been quick to follow the precedent. It is reasonably safe to predict that there will be at least ten such annual surveys of specialized branches of chemistry within five years.

There is little which need be said about this second volume except that it is impressively comprehensive, that it is indispensable to anyone working in the field of organometallic chemistry, and that it was produced with considerable speed at an acceptable cost in appearance of the pages of text. Organometallic chemists can only hope that Drs. Seyferth and King will keep up their most valuable work.

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