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ELECTRON TRANSFER REACTIONS OF SOME HINDERED SILICON-CONTAINING PHENOLS WITH PHENYLMERCURIC HYDROXIDE

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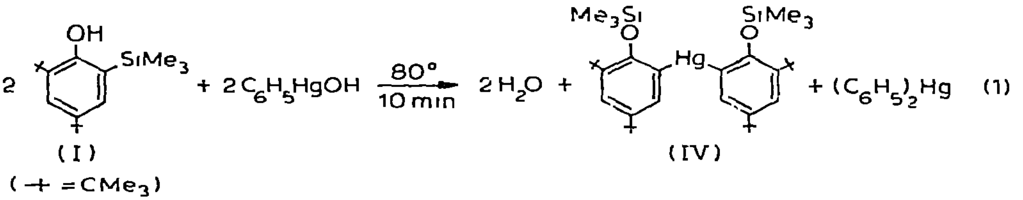
Summary

Reactions between hindered silicon-containing phenols and C_6H_5HgOH have been studied. These reactions, as shown by ESR-spectra, proceed via the intermediate formation of phenoxyls arising from an electron transfer from the phenol to the phenylmercury cation. In the reactions of C_6H_5HgOH with silicon-containing phenols [2,6-bis(trimethylsilyl)-4-tert-butyl-, 2,4-bis(trimethylsilyl)-6-tert-butyl-, and 2-phenyldimethylsilyl-4,6-di-tert-butyl-phenols] which have *ortho*-triorganosilyl group capable of migrating to the phenoxyl oxygen, mercurated products have been formed. In the interaction between C_6H_5HgOH and 2,6-di-tert-butyl-4-trimethylsilylphenol, which has a *para*-trimethylsilyl group which is unable to migrate to the oxygen, no mercurization occurs; phenol oxidation only was observed.

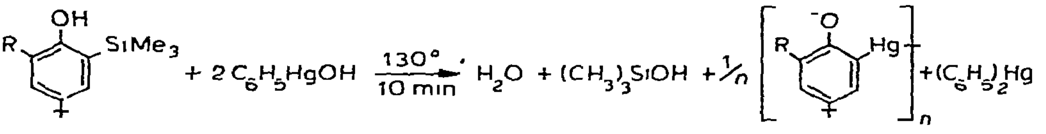
Introduction

Earlier [1] we reported that hindered silicon-containing phenols react with C_6H_5HgOH to form mercurizates; for example, the reaction of 2-trimethylsilyl-4,6-di-tert-butylphenol (I) with C_6H_5HgOH produced bis(2-trimethylsiloxy-3,5-di-tert-butylphenyl)mercury (IV) (eqn. 1).



Reaction 1 proceeds with initial formation of the 2-trimethylsilyl-4,6-di-tert-butylphenoxy radical, the mercuration of which is the second stage of the reaction.

The silicon-containing phenols with less hindered hydroxyl groups, 2-methyl-4-tert-butyl-6-trimethylsilyl- (II) and 2-trimethylsilyl-4-*tert*-butyl- (III) phenols, react with C_6H_5HgOH to give polymeric arylmercuroxides containing no trimethylsilyl groups (eqn. 2).

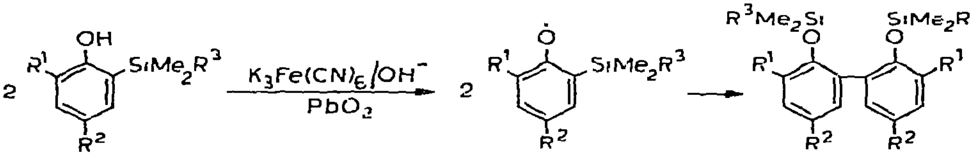


(2)

(II,R = CH₃,
III,R = H)

(V,R = CH₃,
VI,R = H)

Hindered silicon-containing phenols possessing at least one *ortho*-triorganosilyl group undergo one-electron oxidation by $K_3Fe(CN)_6$ in alkali medium or by PbO_2 [2, 3] to form stabilized phenoxyls which react further to give dimeric products, the corresponding disiloxydiphenyls (eqn. 3).



(3)

(VII-XI) (XII-XIV) (XV-XVII)

VII , XII , XV $R^1 = SiMe_3$, $R^2 = CMe_3$, $R^3 = CH_3$
VIII, XIII, XVI . $R^1 = CMe_3$, $R^2 = SiMe_3$, $R^3 = CH_3$
XI , XIV, XVII $R^1 = CMe_3$, $R^2 = CMe_3$, $R^3 = C_6H_5$

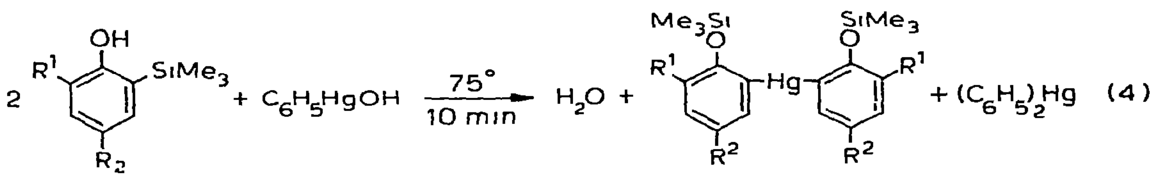
It was of interest for us to study the effect on the reaction with phenylmercury hydroxide of (a) the number of the trimethylsilyl groups in the phenol ring (b) the position of the trimethylsilyl group in the ring and (c) the replacement of a methyl by a phenyl group in a trimethylsilyl substituent.

Results and discussion

2,6-Bis(trimethylsilyl)-4-tert-butylphenol (VII), 2,4-bis(trimethylsilyl)-6-tert-butylphenol (VIII), 2,6-di-tert-butyl-4-trimethylsilylphenol (IX), 2-tert-butyl-4-trimethylsilylphenol (X), and 2-phenyldimethylsilyl-4,6-di-tert-butylphenol (XI) are known compounds, except for X, whose characteristics are given in Table 1.

The reactions of phenols VII-IX and XI with C_6H_5HgOH were carried out either without solvent at 75—130° or in diglyme medium at room temperature. Reaction of the less hindered phenol X was also carried out with $(C_6H_5)_2Hg$.

Phenols VII and VIII each having two trimethylsilyl substituents, react with C_6H_5HgOH at 75° to give the diarylmercuric products XVIII and XIX, respectively, and diphenylmercury and water (eqn. 4).



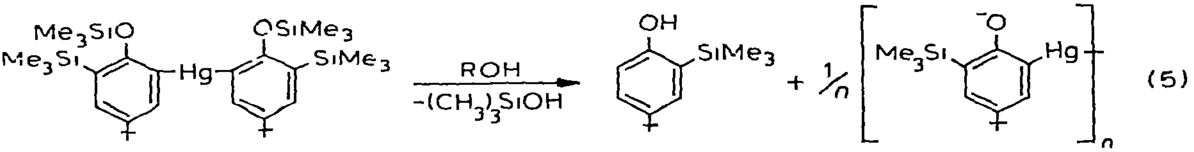
(VII,VIII) (XVIII,XIX) (80-90%) (4)

VII, XVIII: $R^1 = SiMe_3, R^2 = CMe_3$

VIII, XIX: $R^1 = CMe_3, R^2 = SiMe_3$

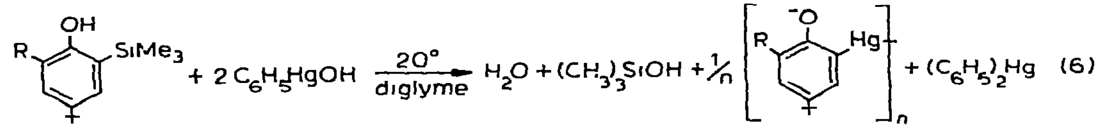
Like reaction 1, reaction 4 proceeds via the corresponding phenoxyls XII and XIII. The ESR-spectrum of the phenoxyl XII consits of a triplet (1/2/1 ratio) ($a_{H,\ meta}$ 1.8 Oe), arising from two *meta* protons of the aromatic ring with additional splitting of each component by the methyl group protons ($a_{H,SiMe_3}$ ~ 0.4 Oe) (Fig. 1). The ESR-spectrum of phenoxyl XIII, due to its non-equivalent *meta*-protons, consist of four bands ($a_{H^1,\ meta}$ 1.7 Oe; $a_{H^2,\ meta}$ 1.2 Oe).

The diarylmercury XVIII on treatment with hydroxylic solvents gives 2-trimethylsilyl-4-tert-butylphenol (III) and XX, a polymeric arylmercuroxide (eqn. 5).



(XVIII) (III) (XX) (5)

In diglyme at room temperature the phenols VII and I react slowly with C_6H_5HgOH (10h) to give arylmercuroxides XX and XXI, respectively (eqn. 6) in better yield than when no solvent is used.



(I, R = CMe_3, (VII, R = $SiMe_3$) (XXI, R = CMe_3, XX, R = $SiMe_3$) (70%) (6)

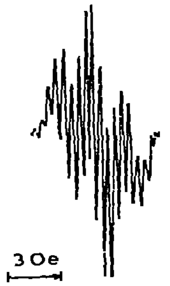
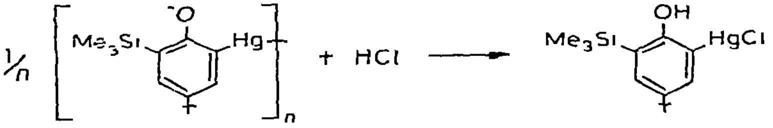


Fig. 1. ESR-spectrum of 2,6-bis(trimethylsilyl)-4-tert-butyl-phenoxyl radical (XII).

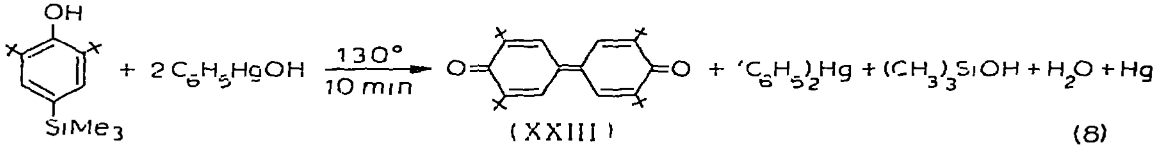
The arylmercuroxide XX on treatment with an equimolar amount of hydrochloric acid is quantitatively converted to 2-trimethylsilyl-4-tert-butyl-6-chloromercurphenol (XXII) (eqn. 7).



(XX) (XXII) (95 %) (7)

The structures of the compounds XVIII-XX, XXII and also of all new compounds, described in this paper, were established by IR spectra, elementary analyses and in some cases by molecular weight determinations.

The reaction between phenol IX and C_6H_5HgOH (1/2 mole ratio) without solvent proceeds under more severe conditions (130°) to give 3,3', 5,5'-tetra-tert-butyl-diphenoquinone-1,4 (XXIII), diphenylmercury, metallic mercury, water and trimethylsilanol (eqn. 8). With a mole ratio of (80%) 1/1 only half the phenol was consumed. Diphenoquinone XXIII is also the product of the one-electron oxidation of phenol IX [3].



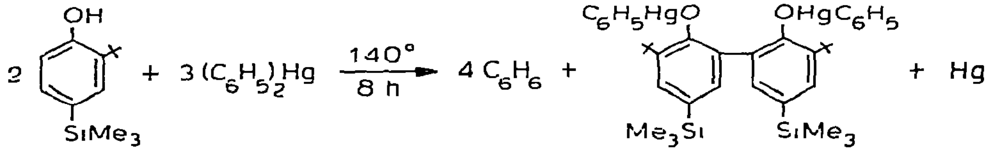
(IX) (XXIII) (80 %) (8)

Reaction 8 like reactions 1 and 4 occurs via the intermediate formation of 2,6-di-tert-butyl-4-trimethylsilylphenoxyl (triplet 1/2/1, $a_{H,\ meta}$ 1.8 Oe).

In diglyme medium at room temperature, phenol IX reacts very slowly with C_6H_5HgOH giving the same products as obtained without solvent.

We conclude that the position of the trimethylsilyl group in the aromatic ring of phenol does affect the reaction with phenylmercury hydroxide. If this group is in the *para*-position of the aromatic ring and unable to migrate to the phenoxyl oxygen [3] and though it is cleaved from the benzene ring, no mercurizate is formed, only phenol oxidation proceeding. Thus, the ability of the trimethylsilyl group to migrate to the phenoxyl oxygen is responsible for the formation of mercurated products.

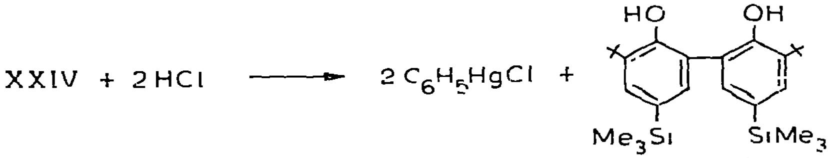
The reaction of phenol X, in which one *ortho*-position of the ring is free, and diphenylmercury at 140° for 8 h produced dimeric phenylmercuriphenolate XXIV, metallic mercury and benzene (eqn. 9).



(X) (XXIV) (65 %) (9)

2,2'-Dihydroxy-3,3'-di-tert-butyl-5,5'-bis(trimethylsilyl)diphenyl (XXV) was also formed - a product of the oxidative dimerization of phenol X. The dimeric phenylmercuriphenolate XXIV resulted from further reaction between dihydroxydiphenyl XXV and $(C_6H_5)_2Hg$. A similar interaction was observed in the reaction of 2,4-di-tert-butylphenol with diphenylmercury [4].

On treatment of XXIV with diluted HCl it is quantitatively converted to phenylmercuric chloride and XXV, a dihydroxydiphenyl (eqn. 10).

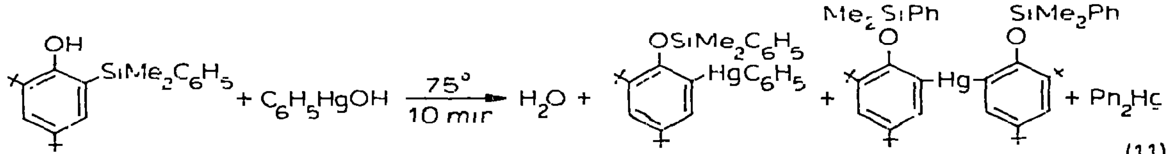


(XXV)

(10)

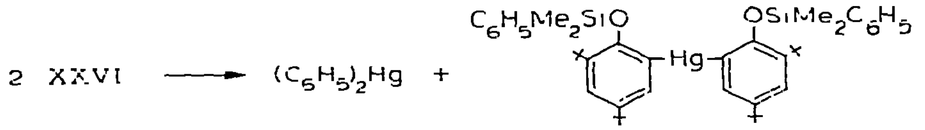
Thus, phenol X in the reaction with diphenylmercury behaves as its carbon analog 2,4-di-tert-butylphenol. Reaction 9 differs greatly from that of the *ortho*-organosilicon isomer of phenol X i.e. phenol III with $(C_6H_5)_2Hg$, which proceeds by migration of the *ortho*-trimethylsilyl group to oxygen and further mercurization of the ring [1].

The reaction products of phenol XI with C_6H_5HgOH at 75° are 2-(phenyldimethylsiloxy)-3,5-di-tert-butylphenylphenylmercury (XXVI), diphenylmercury, bis(2-phenyldimethylsiloxy-3,5-di-tert-butylphenyl)mercury (XXVII), and water (eqn. 11).



(XI) (XXVI) (60%) (XXVII) (20%) (11)

The diarylmercury compound XXVII is formed as a result of partial symmetrization of compound XXVI under the reaction conditions; this was confirmed by the symmetrization of arylphenylmercury XXVI under the same conditions (eqn. 12).



(XXVII)

(12)

While reaction of XI (eqn. 11) led to the nonsymmetric compound XXVI, the analogous reactions of phenols VII and VIII with C_6H_5HgOH gave only symmetric compounds analogous to diarylmercury XXVII. In diglyme at room temperature, phenol XI reacts with phenylmercury hydroxide more slowly (70% after 5 h), to give the same reaction products as found in the reactions without solvent.

The structure of compound XXVI was established by its IR-spectrum, elementary analysis (Table 1) and its reaction with dilute HCl, which gave phenylmercuric chloride and 2,4-di-tert-butylphenol.

Reaction 11, as that between phenols VII—IX and C_6H_5HgOH, proceeds

TABLE 1

CHARACTERISTICS OF NEW COMPOUNDS

No.	Yield (%)	M.p. (°C)	Analysis found (calcd) (%) C	H	Si	Hg	Empirical formula	Mol. weight found (calcd.)	IR spectrum (cm^{-1}) Ar–O–Si	SiMe$_3$	Ar–Si
X	79	73–75	70.50 (70.21)	9.93 (9.97)	12.71 (12.63)		$C_{13}H_{22}OSi$	215 (222)		850 1260	1150
XVIII	90	126–128	48.82 (48.80)	7.18 (7.40)	14.32 (14.29)	25.26 (25.42)	$C_{32}H_{58}O_2Si_4Hg$	–	940	845 1230	1110
XIX	80	121–124	48.00 (48.80)	7.40 (7.40)	14.18 (14.29)	25.18 (25.42)	$C_{32}H_{58}O_2Si_4Hg$	710 (787)	955	850 1255	1120
XX	70	*a*	– –	– –	6.63 (6.67)	47.26 (47.65)	$C_{13}H_{20}OSiHg$	–	–	850 1250	–
XXII[b]	95	195 (decomp.)	34.08 (34.13)	4.86 (4.62)	5.84 (6.14)	43.10 (43.65)	$C_{13}H_{21}OSiHgCl$	–	–	840 1250	–
XXIV	65	217 (decomp.)	45.78 (45.80)	5.16 (5.32)	5.86 (5.99)	40.26 (40.11)	$C_{38}H_{50}O_2Si_2Hg_2$	890 (990)	–	840 1250	1130
XXVI	60	107–110	54.80 (54.50)	5.99 (5.88)	4.44 (4.55)	32.82 (32.50)	$C_{28}H_{36}OSiHg$	–	950	*c*	–
XXVII	20	175–178	59.88 (60.02)	7.19 (7.11)	6.40 (6.38)	22.40 (22.80)	$C_{44}H_{62}O_2Si_2Hg$	850 (879)	950	*d*	–
XXX	70	143–146 (decomp.)	49.62 (49.73)	5.61 (5.45)	– –	42.30 (41.55)	$C_{20}H_{26}OHg$	–	–	–	–
XXXI	70	145–146 (decomp.)	45.03 (45.01)	4.22 (4.25)	– –	46.76 (46.99)	$C_{16}H_{18}OHg$	–	–	–	–

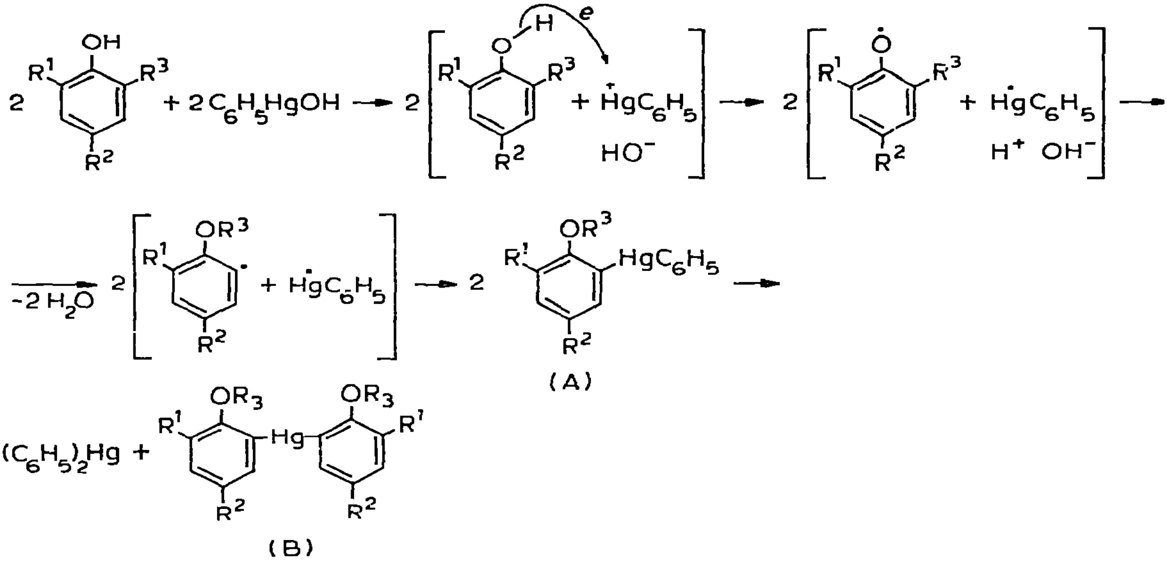
[a] No decomposition on heating up to 275°. [b] Cl, found, 7.51, calcd, 7.74. ν(OH) 3575 cm^{-1}. [c] ν(Me$_2$Si) 835, 1245; ν(SiPh) 1120 cm^{-1}. [d] ν(Me$_2$Si) 840, 1245; ν(SiPh) 1120 cm^{-1}.

via the intermediate formation of the phenoxyl XIV, and this was confirmed by ESR-spectra.

Substitution of phenyldimethylsilyl for the trimethylsilyl substituent in the phenol aromatic ring does not greatly affect the reaction with C_6H_5HgOH; however it does enable an intermediate compound, the non-symmetric aryl-phenylmercuric product XXVI, to be obtained.

The above findings allow us to make certain conclusions on the reaction mechanism of hindered silicon-containing phenols with C_6H_5HgOH. As has already been mentioned, all the reactions proceed via the formation of phenoxyls. We presume the phenoxyls are formed as a result of an electron transfer from phenol to the phenylmercuric cation (phenylmercury hydroxide is a base [5]) as the first step in Scheme 1, with further reaction depending on the phenoxyl.

SCHEME 1

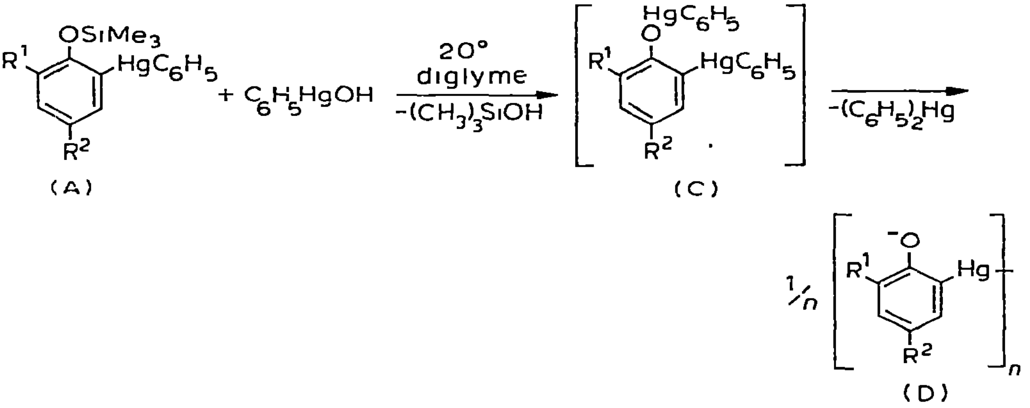


In the case of phenoxyls having an *ortho*-triorganosilyl group able to migrate to the phenoxyl oxygen, migration of this group is observed as well as its replacement in the ring by the phenylmercuric radical; a non-symmetric arylphenylmercuric product is formed (A). In the case where R^3 = $SiMe_2C_6H_5$ and R^1 = R^2 = CMe_3, the compound is stable and can be isolated, but if R^3 = $SiMe_3$ the non-symmetric product (A) is quickly symmetrized under the reaction conditions to give diphenylmercury and diarylmercury (B).

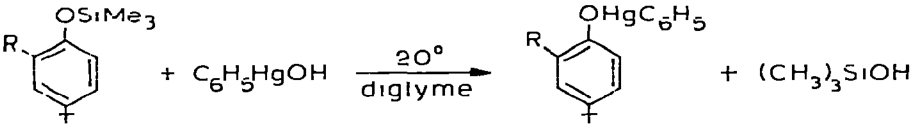
In the reaction of the phenol IX with C_6H_5HgOH the phenoxyl formed contains a *para*-trimethylsilyl group unable to migrate to the phenoxyl oxygen and no mercurizate is formed; the phenylmercuric radical disproportionates to give diphenylmercury and metallic mercury.

In diglyme at 20° the hindered phenols slowly react with C_6H_5HgOH, the non-symmetric product (A) (R^3 = $SiMe_3$) further reacts with another C_6H_5HgOH molecule to give trimethylsilanol and phenylmercurophenolate of the mercury-containing phenol (C), which is unstable and decomposes to diphenylmercury and polymeric arylmercuroxide (D) (Scheme 2).

SCHEME 2



The reaction of phenol trimethylsilyl ethers with C_6H_5HgOH in diglyme leads to phenylmercurophenolates as shown by the reactions of 2,4-di-tert-butylphenoxytrimethylsilane (XXVIII) and 4-tert-butyl-phenoxytrimethylsilane (XXIX) with C_6H_5HgOH (eqn. 13).



(13)

(XXVIII, R = CMe3, XXIX, R = H)

(XXX, R = CMe3, XXXI, R = H) (70%)

So, hindered silicon-containing phenols VII—IX and XI react with phenylmercury hydroxide with one electron-transfer and formation of phenoxyls. The terminal reaction products depend on the properties of phenoxyls formed.

Experimental

Silicon-containing phenols VII—XI were obtained according to a modification [2, 3] of the published technique [6, 7] and purified by recrystallization from aqueous ethanol.

Phenol IX was obtained by hydrolysis of 2,6-di-tert-butyl-4-trimethylsilylphenoxytrimethylsilane, which was formed from 3,5-di-tert-butyl-4-trimethylsiloxyphenylmagnesium bromide and trimethylchlorosilane.

All the reactions between the silicon-containing phenols and C_6H_5HgOH, and phenol X with $(C_6H_5)_2Hg$ without solvent were carried out in evacuated glass ampules by heating in an oil bath. When the reactions were complete the liquid products were collected in a liquid nitrogen cooled trap and then analyzed following the procedure given in ref. 1.

2,6-Bis(trimethylsilyl)-4-tert-butylphenol (VII) and C_6H_5HgOH

1.50 g of phenol VII and 1.50 g of C_6H_5HgOH were heated at 75° for 10 min. The liquid products obtained were 0.10 g of water with traces of trimethylsilanol. With grinding the reaction mass with n-hexane, 0.60 g (70%) of diphenylmercury was formed. After evaporation of the n-hexane, the residue was treated with ethanol. The white solid was separated into its two components on acetone treatment. The soluble part consisted of diarylmercury XVIII (0.80 g, 45%), m.p. 126—128° (from ethanol), the insoluble part was a hydrolysis product of diarylmercury XVIII, i.e. polymeric arylmercuroxide XX, (0.40 g, 44%) which after recrystallization from benzene was not decomposed with heating to 270°. After these procedures 2-trimethylsilyl-4-tert-butylphenol (III) (0.21 g, 44%) was detected in the residue by GLC.

2,4-Bis(trimethylsilyl)-6-tert-butylphenol (VIII) and C_6H_5HgOH

2.00 g of phenol VIII and 2.00 g of C_6H_5HgOH were heated at 75° for 10 min. The reaction mass was foaming. 0.11 g of water with traces of trimethylsilanol were formed. Treatment of the reaction mixture with n-hexane gave 0.80 g (67%) of diphenylmercury. After removing hexane the residue was ground with ethanol. 1.80 g (80%) of diarylmercury XIX was obtained, m.p. 121—124° (from acetone).

Arylmercuroxide XX and HCl

The suspension of 0.28 g arylmercuroxide XX in 5 ml of benzene was shaken for 1 h with 1 ml of 1*M* HCl in 4 ml of ethanol. The organic layer was separated and dried. After removing benzene, 0.28 g (95%) of 2-trimethylsilyl-4-tert-butyl-6-chloromercurophenol (XXII) was obtained, m.p. 195° (with decomp.) (from aqueous ethanol).

2,6-Di-tert-butyl-4-trimethylsilylphenol (IX) and C_6H_5HgOH

1.20 g of phenol IX and 2.80 g of C_6H_5HgOH were heated at 130° for 15 min. After cooling the reaction mixture was red-brown in colour with metallic mercury on the bottom of the ampule. The products obtained were: 0.08 g (90%) of water; 0.25 g (70%) of trimethylsilanol; 0.75 g (85%) of metallic mercury. Diphenoquinone XXIII (80%) was determined using a Tswett-1 chromatograph with a column (10.5 m; d 0.3 cm), packed with Termol-3 on Shimalite-B, the oven temperature being 230° and the gas-carrier (helium) flow 30 ml/min. The internal standard was 2,2'-dioxy-3,3',5,5'-tetra-tert-butyldiphenyl. After the separation of the above products the reaction mixture was treated with dilute HCl, and 1.40 g of C_6H_5HgCl was obtained (equivalent to 1.60 g (88%) of diphenylmercury).

2-tert-butyl-4-trimethylsilylphenol (X) and $(C_6H_5)_2Hg$

2.5 g of X and 3.4 g of $(C_6H_5)_2Hg$ were heated for 8 h at 140°. The reaction mixture after cooling consisted of a deep dark brown liquid with mercury doplets on the bottom of the ampule.

Products obtained were: 0.86 g (92%) of benzene, 0.60 g (98%) of metallic mercury. Dimeric phenylmercurophenolate XXIV was formed by treating the reaction mass with boiling ethanol. Its yield was 1.80 g (65%), m.p. 215—217° (with decomp.) (twice from acetone).

2-phenyldimethylsilyl-4,6-di-tert-butylphenol (XI) and C_6H_5HgOH

1.50 g of XI and 1.29 g of C_6H_5HgOH were heated at 75° for 10 min. The reaction occurred with foaming. The reaction mixture consisted of colourless liquid with no traces of metallic mercury. 0.08 g of water (90%) was isolated.

On grinding the reaction mixture with n-hexane 0.10 g (15%) of diphenylmercury was deposited. After keeping the hexane solution for 24 h at 0°, 1.50 g (60%) of crystalline 2-phenyldimethylsiloxy-3,5-di-tert-butylphenylphenylmercury (XXVI) was obtained, m.p. 107—110° (from acetone). Hexane was then evaporated, and the residue was treated with boiling ethanol. 0.25 g (15%) of the diarylmercury XXVII was obtained, m.p. 175—178° (from acetone).

Reactions in diglyme were also carried out in vacuum ampules. Diglyme was evacuated from peroxides by boiling over KOH. The fraction boiling at 162° was collected. After the reaction was accomplished the liquid products were analyzed as described in ref. 1.

Phenol VII and C_6H_5HgOH in diglyme

A suspension consisting of 1.50 g of VII and 1.50 g of C_6H_5HgOH in 10 ml of diglyme was shaken for 10 h at room temperature. A white deposit of XX, an arylmercuroxide, was formed (0.60 g, 70%). 0.15 g (70%) of trimethylsilanol was determined by GLC. The diglyme was then evacuated at reduced pressure and the residue was treated with n-hexane. 0.51 g (60%) of diphenylmercury was isolated.

Phenol XI and C_6H_5HgOH in diglyme

The suspension of 1.20 g of XI and 1.00 g of C_6H_5HgOH in 10 ml of diglyme were shaken for 5 h. The clear solution was washed with water to remove the diglyme. The reaction mixture was extracted with sulphuric ether, dried and the ether was evacuated under reduced pressure.The residue was treated in the same way as in the reaction without solvent. The products obtained were: 0.20 g (30%) of diphenylmercury; 0.50 g (60%) of arylphenylmercury compound XXVI and 0.15 g (20%) of diarylmercury compound XXVII.

2,4-Di-tert-butylphenoxytrimethylsilane (XXVIII) and C_6H_5HgOH in diglyme

1.40 g of phenoxysilane XXVIII and 1.30 g of C_6H_5HgOH in 10 ml of diglyme were shaken for 10 h. The diglyme was then evacuated under reduced pressure. The residue consisting of tar-like liquid was ground with n-hexane. The products isolated were: 1.51 g (70%) of phenylmercurophenolate XXX, m.p. 143—146° (with decomp.) (from benzene).

References

1 G.A. Razuvaev, N.S. Vasileiskaya and N.N. Vavilina, Zh. Obshch. Chim., 44 (1974) 135.
2 G.A. Razuvaev, N.S. Vasileiskaya and D.V. Muslin, Dokl. Akad. Nauk SSSR, 175 (1967) 620.
3 G.A. Razuvaev, N S. Vasileiskaya, D V. Muslin, N.N Vavilina and S.N. Uspenskaya, Zh. Org. Chim., 6 (1970) 980.
4 N.N. Vavilina, N.S Vasileiskaya and G.A. Razuvaev, Zh. Obshch. Chim . 42 (1972) 548.
5 F. Witmor, Mercury organic compounds ONTI, Chimteor, Leningrad, 1938, p. 140.
6 C.D. Cooper, J. Org. Chem., 26 (1961) 925
7 J.L. Speier, J. Amer. Chem. Soc., 74 (1952) 1003.