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A TRIS(DIALKYLAMINO)SULFONIUM PHENOXIDE[1]

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Summary: The title phenoxide has been prepared from phenyl trimethylsilyl ether and tris(diethylamino)sulfonium difluorotrimethylsiliconate. The conductivity measurement and NMR analysis indicate that this phenoxide dissociates into the ions in THF solution.

Phenoxide and enolates are an important class of anionic species. The structures and reactivities are known to be profoundly affected by the nature of the counter cations and the solvents.[2] As a part of our study on superanions which possess negligible bonding interaction with their counter cations,[1,3,4] we have synthesized a tris(dialkylamino)sulfonium phenoxide as is disclosed herein.

Phenyl trimethylsilyl ether (I) in THF exhibits an ^{1}H NMR signal at δ 0.26 due to the Si—CH$_3$ protons, and tris(diethylamino)sulfonium (TAS) difluorotrimethylsiliconate (II)[5] gives the corresponding signal as singlet at δ -0.18. However, when these two substances were mixed in 1:1 mol ratio in THF, the ^{1}H NMR spectrum showed only a single Si—CH$_3$ signal at δ 0.19, suggesting the occurrence of dynamic equilibria depicted in eq 1 and 2.[6,7] Fluoride ion, generated from II, attacks the silicon atom of I in an S$_N$2 manner or by forming a short-lived pentacoordinate anionic silicon intermediate to produce TAS phenoxide (V) and fluorotrimethylsilane (IV). Indeed, when this mixture was evacuated to 0.01 mmHg at room temperature, 95% of the theoretical amount of IV was obtained as THF solution in a cold trap (-78 °C). In the reaction vessel, there remained the phenoxide V. Washing of the crude product with a small amount of dry ether gave brownish, air-sensitive crystals.

$$\underset{\text{II}}{[(C_2H_5)_2N]_3\overset{+}{S}(CH_3)_3SiF_2^-} \rightleftharpoons \underset{\text{III}}{[(C_2H_5)_2N]_3\overset{+}{S}F^-} + \underset{\text{IV}}{(CH_3)_3SiF} \qquad (1)$$

$$\underset{\text{I}}{(CH_3)_3SiOC_6H_5} + \text{III} \rightleftharpoons \underset{\text{V}}{[(C_2H_5)_2N]_3\overset{+}{S}C_6H_5O^-} + \text{IV} \qquad (2)$$

Conductivity measurements provided direct evidence for the ionic structure for V; a 1.3×10^{-4} M solution of V in THF exhibited a molar conductance of 12 cm^{2}mol^{-1}ohm^{-1} at 25 °C. Thus a possible sulfurane structure was excluded rigorously.

Since the NMR chemical shift is profoundly related to the electron distribution,[8,9] the spectra should provide indication about the type and degree of the ion-pairing. The ^1H NMR spectrum taken in THF of the TAS moiety of V gave the signals at δ 1.17 and 3.34 due to the CH_3 and CH_2 protons. The ^{13}C spectrum (THF) afforded the signals at δ 13.0 (CH_3) and 42.1 (CH_2). Apparently the occurrence of the methylene signals at such low fields is ascribed to the ionic nature of V; the chemical shift values are well compared with those of ionic TAS bromide,[10] δ 3.51 for ^1H and δ 42.5 for ^{13}C.[11] The ^1H data for the phenoxides and the related compounds are summarized in Table I. In THF, TAS phenoxide gives the signals at substantially higher field compared with the alkali metal phenoxides.[12] The chemical shift values are very close to those of the metal phenoxides in hexamethylphosphoric triamide, which are conceived to exist as the free ions.[2e] The ^{13}C NMR data are given in Figure 1. When the spectrum of TAS phenoxide is compared with those of phenol or the silyl ether, the signals due to the ortho, meta, and para carbons move upfield but the ipso signal shifts downfield to a considerable extent. Figure 2 shows the electron distribution of

Table I. ^1H NMR Data for the Aromatic Ring[a]

compound	Chemical shift, δ in ppm[b] ortho	meta	para
phenol[c]	6.73	7.10	6.81
phenyl trimethylsilyl ether	6.88	7.18	6.83
Na phenoxide[d]	6.40 (6.23)	6.88 (6.63)	6.18 (5.78)
K phenoxide[d]	6.31 (6.16)	6.85 (6.61)	6.06 (5.74)
TAS phenoxide[e]	6.15	6.68	5.79

[a] Taken as 0.1 M THF solution at 35 °C. The value in hexamethylphosphoric triamide is given in parenthesis. [b] Tetramethylsilane as internal standard. [c] Taken in CCl_4. [d] Reported by Hudrlik (ref. 12). [e] Taken in THF-d_8 (1 M, 29 °C).

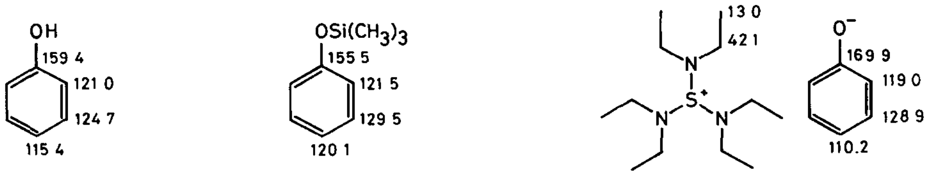

Figure 1. ^{13}C NMR data for phenol, phenyl trimethylsilyl ether (II), and TAS phenoxide (V), δ in ppm (THF-d_8, 23 °C, tetramethylsilane as internal standard).

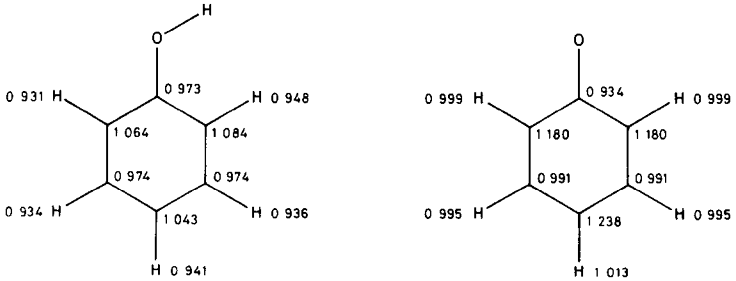

Figure 2. Calculated electron distribution in phenol and phenoxide (1s for hydrogen and $2p_z$ for carbon).

phenol and phenoxide obtained by the ab initio MO calculations with STO-3G minimal basis set.[13] In going from neutral phenol to its anion, electron densities of all of the aromatic hydrogens and the ortho, meta, and para carbons increase, whereas the ipso carbon attached to the oxygen atom becomes more electron deficient. Thus the direction of the shift of the ^{1}H and ^{13}C NMR signals are consistent with the change in electron distribution. The ^{1}H chemical shift is better correlated with electron density of the hydrogen rather than the density at that carbon of the ring. The plot of the ^{13}C chemical shift against the excess electron density (total electron density - 6) gives rise to a straight line with a slope of 216 ppm/electron for the ipso, meta, and para positions.[14] The ortho position deviates slightly from this relationship.

In summary, the phenoxide moiety in V has proved to be little interacted with the TAS counter cation in THF.

When the naked phenoxide thus prepared was reacted with 1.2 equiv of benzyl bromide in THF at -78 °C for 7 h, benzyl phenyl ether was obtained as a sole product in 83% isolated yield. The reaction of V generated in situ from the silyl ether I and the fluoride ion source II gave the same result. Thus when a mixture of I, II, and a reactive alkyl halide, RX, was allowed to stand in THF at low temperature, the corresponding O-alkylated product, VI, was obtained (eq 3). Some examples are given in Table II.

$$\underset{\text{I}}{(CH_3)_3SiOC_6H_5} + \underset{\text{II}}{[(C_2H_5)_2N]_3S^{+}(CH_3)_3SiF_2^{-}} + RX \longrightarrow$$

$$\underset{\text{VI}}{ROC_6H_5} + \underset{\text{IV}}{2\,(CH_3)_3SiF} + [(C_2H_5)_2N]_3S^{+}X^{-} \qquad (3)$$

Table II. Fluoride Ion Promoted Alkylation of the Phenyl Silyl Ether I[a]

alkylating agent	temp, °C (time, min)	% yield of ROC_6H_5[b] (recovered I, %)
benzyl bromide	-78 (120)	67 (18)
chloromethyl methyl ether	-78 (100)	63 (13)
methyl iodide	-78 (30)	55 (18)

[a] The reaction was carried out in THF by using 1.2 equiv of the alkylating agent. The reaction conditions were not optimized. [b] Determined by ^1H NMR analysis of the reaction mixture by using tetrachloroethane as an internal standard.

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