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SILYL ANIONS VII. ELECTRON TRANSFER FROM TRIMETHYLSILYLPOTASSIUM TO BENZOPHENONE AND NAPHTHALENE. GENERATION OF ANION RADICALS IN NONPOLAR SOLVENTS SUCH AS *n*-HEXANE[1)]

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Trimethylsilylpotassium, prepared in a nonpolar solvent by the reaction of hexamethyldisilane with potassium methoxide in the presence of 18-crown-6, is a useful reagent for efficient homogeneous electron transfer. The first esr spectra of anion radicals of benzophenone and naphthalene in *n*-hexane as well as those in THF and benzene were recorded.

In a previous paper from this laboratory,[2)] it has been described that trimethylsilylpotassium can be prepared in nonpolar solvents by the reaction of hexamethyldisilane with potassium methoxide in the presence of 18-crown-6.[3)]

$$Me_3SiSiMe_3 \; + \; KOMe \xrightarrow{\text{18-crown-6/solvent}} Me_3SiK \; + \; Me_3SiOMe$$

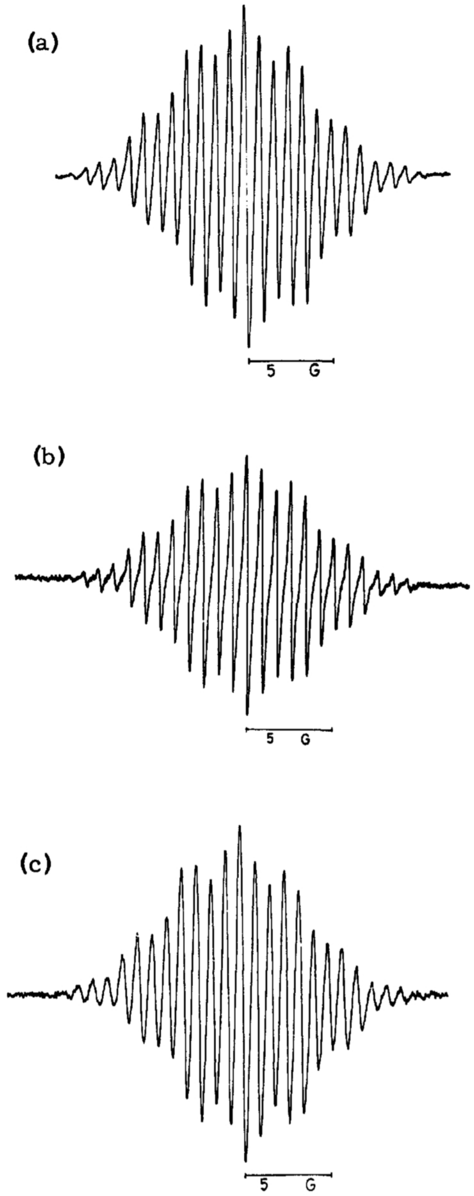
Since trimethylsilylsodium prepared in hexamethylphosphoramide is demonstrated to be an excellent electron transfer reagent for the purpose of producing anion radicals,[4)] we expected that trimethylsilylpotassium could also be used as a homogeneous electron transfer reagent in nonpolar solvents. Anion radical formation in nonpolar solvents using crown ethers and alkali metals is a current interest in esr spectroscopy.[5-7)] We have found that this reagent can actually produce a variety of anion radicals even in n-hexane. To our knowledge, this paper is the first report of the preparation of anion radicals in an aliphatic hydrocarbon.

In a 50 ml two necked flask equipped with a dropping funnel and a three-way tap, potassium methoxide (0.35g, 5mmol)[8)] and 18-crown-6 (1.32g, 5mmol)[9)] were placed. The flask was evacuated and filled with dry argon and then a solvent (4ml) was added to the mixture. Hexamethyldisilane (0.73g, 5mmol) dissolved in the solvent (2ml) was added dropwise at room temperature during the period of 10 min. The mixture became yellow homogeneous solution after stirring for additional 15 min.

A portion of the solution (0.5ml) was added from a hypodermic syringe under argon to ca. 0.1mg of a sample compound in a glass tube constructed with a 8x100mm portion and a 3x120 mm side arm. The tube was then sealed off after three freez-thaw cycles on a vacuum line.

Representatively in this paper, we show anion radicals of benzophenone (Fig. 1) and naphthalene (Fig. 2) in THF, benzene, and *n*-hexane, respectively, among a variety of results.

Figure 1. Esr spectra of the benzophenone ketyl at room temperature: (a) in THF; (b) in benzene; and (c) in n-hexane.



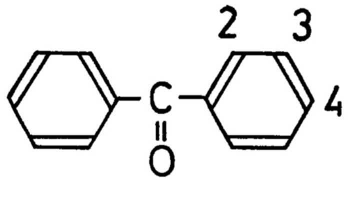
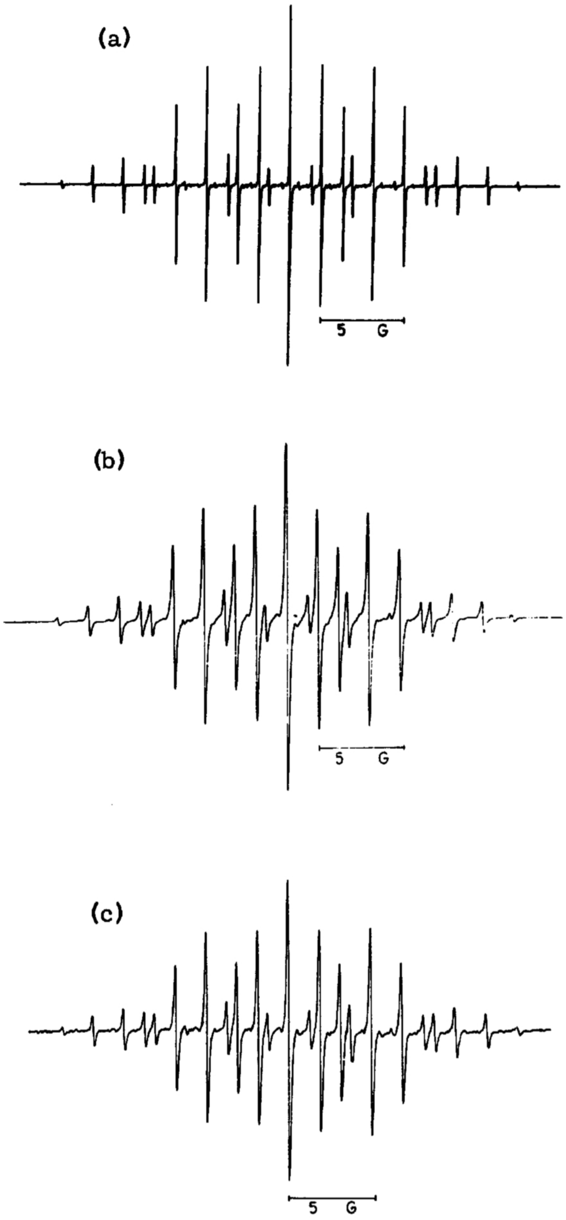


Table 1. Hyperfine coupling constants of the benzophenone ketyl at room temperature

Solvent	THF			Benzene		n-Hexane
Method	Me_3SiK-CE[a]	K-CE	K	Me_3SiK-CE	K-CE	Me_3SiK-CE
a_K/G	----[b]	----	0.24	----	----	----
a_2/G	2.55	2.55	2.58	2.57	2.58	2.60
a_3/G	0.87	0.87	0.86	0.87	0.87	0.87
a_4/G	3.39	3.40	3.44	3.39	3.41	3.50

a. 18-crown-6. b. not observed.

Figure 2. Esr spectra of the naphthalene anion radical at room temperature: (a) in THF; (b) in benzene; and (c) in n-hexane.



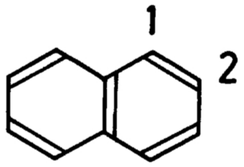


Table 2. Hyperfine coupling constants of the naphthalene anion radical at room temperature

Solvent	THF			Benzene		n-Hexane
Method	Me_3SiK-CE[a]	K-CE	K[b]	Me_3SiK-CE	K-CE	Me_3SiK-CE
a_1/G	4.90	4.90	4.90	4.89	4.91	4.87
a_2/G	1.83	1.82	1.83	1.82	1.83	1.84

a. 18-crown-6.

b. A. Carrington and J. doc Santos-Veiga, Mol. Phys., **5**, 21 (1962).

For the purpose of comparison, the anion radicals were also prepared by the reduction with potassium mirror both in the absence of 18-crown-6 in THF and in the presence of the crown ether in THF and in benzene. These spectra are not recorded in Figures but hyperfine coupling constants are listed in Table 1 and 2.

Being more efficient than other methods of reduction, homogeneous electron transfer from trimethylsilylpotassium always resulted in well-resolved spectra even in benzene. In *n*-hexane, reduction with potassium mirror in the presence of the crown ether gave no esr signal for naphthalene and only very weak signal without hyperfine splitting for benzophenone.

We could not observe hyperfine coupling due to ^{39}K nucleus of the potassium-crown complex cation in the case of both benzophenone and naphthalene. However, judging from the linewidth and the hyperfine coupling constants, there may also be unresolved hyperfine splitting of ^{39}K. The formation of ion pairs between anion radicals and potassium-crown complex cations has been proposed for mesitylene.7) Eastman et al.10, 11) have observed metal couplings for tetracyanoethylene anion radicals with crown ether-complexed potassium and sodium. Therefore, anion radicals prepared in hydrocarbon may be stabilized by the formation of ion pairs. We have analyzed such an ion pair interaction between crown ether-complexed potassium and sodium cations and nitrobenzenes,12) the detail of which will be published in a forthcoming paper.

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REFERENCES

1) Chemistry of Organosilicon Compounds. 105.

2) H. Sakurai and F. Kondo, J. Organometal. Chem., 92, C46 (1975).

3) P. J. Pederson and H. K. Frensdorf, Angew. Chem. Int. Ed., 11, 16 (1972).

4) H. Sakurai, A. Okada, H. Umino, and M. Kira, J. Am. Chem. Soc., 95, 955 (1973).

5) B. Kaempf, S. Raynal, A. Collet, F. Schue, and J. M. Lehn, Angew. Chem. Int. Ed., 13, 611 (1974).

6) M. A. Komarynsky and S. I. Weissman, J. Am. Chem. Soc., 97, 1589 (1975).

7) G. V. Nelson and A. von Zelewsky, J. Am. Chem. Soc., 97, 6279 (1975).

8) A. R. Ranzio and W. B. Cook, Org. Synth. col. vol. 3, 71 (1955).

9) G. W. Gokel, D. J. Cram, C. L. Liotta, H. P. Harris, and F. L. Cook, J. Org. Chem., 39, 2445 (1974).

10) M. T. Watts, M. L. Lu, R. C. Chen, and M. P. Eastman, J. Phys. Chem., 77, 2959 (1973).

11) M. P. Eastman, D. A. Ramirez, C. D. Jaeger, and M. T. Watts, J. Phys. Chem., 80, 182 (1976).

12) H. Umino, M. Kira, F. Kondo, and H. Sakurai, 15th Symposium on ESR, Kumamoto, Oct. 16, 1976; Abstracts, p. 108.

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