

PRELIMINARY COMMUNICATION

METALATION REACTIONS

IV. STUDY OF THE ESR SPECTRA AND STABILITY OF 9,9-DIPHENYLFLUORENE AND 5,5-DIPHENYLDIBENZOSILOLE ANION RADICALS

EDWARD G. JANZEN, W.B. HARRISON and JOHN B. PICKETT

Department of Chemistry, The University of Georgia, Athens, Georgia 30601 (U.S.A.)

(Received October 17th, 1968)

Recent work in our laboratory has shown that weak carbon acids are metalated through the intermediacy of initially produced radical anions¹⁻³. The carbanion production is accompanied by the formation of dihydro derivatives probably by a proton transfer mechanism⁴. At lower temperatures the ESR spectra of fluorene⁵, 9-methylfluorene and 9-phenylfluorene radical anions have been obtained^{*}. In this connection it was of interest to make an ESR study of the reduction of 9,9-disubstituted fluorene derivatives. Gilman and Gorsich⁶ have shown that 9,9-diphenylfluorene is cleaved by lithium in tetrahydrofuran to give 9-phenylfluorenyl carbanion as evidenced by the isolation of 9-phenylfluorene upon hydrolysis. These products were also formed in the cleavage of 9-benzyl-9-phenylfluorene with 40% sodium amalgam in ether⁷.

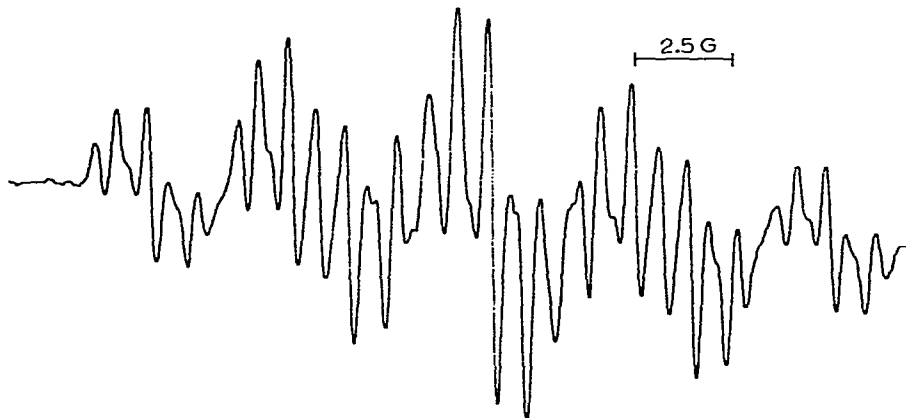


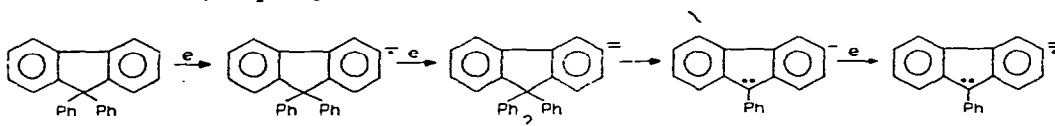
Fig.1. Electron spin resonance spectrum of 9,9-diphenylfluorene obtained as the initial product of the potassium reduction of 9,9-diphenylfluorene in dimethoxyethane. Samples were prepared using vacuum line techniques and studied with a Varian 4502 EPR spectrometer.

^{*}Unpublished work of John L. Gerlock in our laboratories. The reported analyses of fluorene radical anion are in error⁵. Using lithium in tetrahydrofuran the coupling constants are: $a_{1,3,6,8}^H = 0.83, 1.14$; $a_{2,7}^H = 4.82$; $a_{4,5}^H = 3.99$, $a_9^H = 3.64$ gauss.

9,9-Diphenylfluorene^{6,8} was reduced with potassium in 1,2-dimethoxyethane (DME) to give a green solution and a strong ESR signal. The hyperfine spectrum is consistent with the 9,9-diphenylfluorene radical anion structure (Fig.1). The hyperfine coupling constants and assignments are: $a_{1,3,6,8}^H = 0.56, 0.74$; $a_{4,5}^H = 3.6$; $a_{2,8}^H = 5.0$ gauss. These values are in



good agreement with splittings obtained from a similar reduction of 9,9-dimethylfluorene ($a_{1,3,6,8}^H = 0.8$; $a_{4,5}^H = 3.9$; $a_{2,8}^H = 5.0$ gauss), fluorene, 9-methylfluorene or 9-phenylfluorene radical anions^{*}. 9,9-Diphenylfluorene radical anion appears reasonably stable at room temperature although the signal decays upon further reduction. The color of the solution changes from dark green to orange after continued reduction and a strong ESR signal due to 9-phenylfluorenyl dianion radical^{1,2} is obtained. These observations show that the alkali metal cleavage of the phenyl group proceeds through the intermediacy of the radical anion and possibly the dianion. Since the dilithium adduct of biphenyl has been made⁴ the formation of a 9,9-diphenylfluorene dianion, however short-lived, is reasonable.



It was of interest to compare the behavior of 5,5-diphenyldibenzosilole, the silicon analog of 9,9-diphenylfluorene, with the above observations. The reduction of the silicon derivative with potassium in DME gives a dark blue solution and an ESR spectrum of seven evenly-spaced fairly broad lines. The splitting and assignments are: $a_{3,7}^H = 3.1$; $a_{1,9}^H = 1.56$; $a_{2,4,6,8}^H < 0.3$ gauss. These values are consistent with the structure of 5,5-diphenyldibenzosilole radical anion but are somewhat different from those obtained from the 5,5-dimethyl^{9**} ($a_{3,7}^H = 4.0$; $a_{1,9}^H = 1.0$; $a_{4,6}^H = 0.8$; $a_{2,8}^H = 0.2$; $a_{Me}^H = 0.2$ gauss) and the 5,5-tetramethylene¹⁰ derivative $a_{3,7}^H = 4.10$; $a_{1,4,6,9}^H = 1.04$; $a^H = 0.55$ (4 protons) gauss. Apparently the phenyl groups influence the spin distribution in the biphenylene ring differently than do the methyl groups. The same spectrum is obtained when sodium is used.

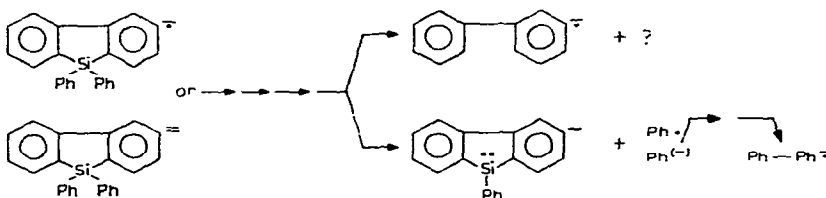
The radical anion of 5,5-diphenyldibenzosilole is more stable than the radical anion of 9,9-diphenylfluorene. Whereas 9-phenylfluorenyl carbanion is produced within minutes during potassium reduction of 9,9-diphenylfluorene and its radical anion, the spectrum due to the silicon derivative persists during many hours of reduction. A second difference is that whereas 9-phenylfluorenyl carbanion is produced as a product of the reduction of 9,9-diphenylfluorene, a strong signal due to biphenyl radical anion appears during the later stages of the reduction of the silicon derivative and increases in intensity until it dominates the spectrum observed. Biphenyl radical anion is frequently observed in the alkali metal reduction of phenylated compounds *e.g.* tetraphenylmethane¹¹, diphenyl-, diphenyldimethyl- and phenyltriethylsilane¹², triphenylamine¹³, triphenylboron¹⁴, triphenylphosphine oxide¹⁵. The mechanism of this reaction has not been established. The appearance of biphenyl radical anion in the reduction of 5,5-diphenyldibenzosilole is thus

*See footnote previous page.

** 5,5-Dimethyldibenzosilole radical anion appears to be stable.

not as unusual as the absence of this product in the reduction of 9,9-diphenylfluorene. The difference in the ease of cleavage of the radical anions or dianions formed in the reduction of 9,9-diphenylfluorene and the silicon analog may be attributed to the greater "aromatic" stabilization of the electron pair in the fluorenyl carbanion than in the silicon analog and to stabilization of the carbon-silicon bonds in the organosilane radical anion from delocalization of charge into available *d*-orbitals.

Two sources of biphenyl exist in the reduction of 5,5-diphenylbenzosilole:



Reduction of substituted dibenzosiloles could provide a choice between these two routes.

ACKNOWLEDGEMENTS

This research is supported by a grant from the Dow Corning Corporation. Grateful acknowledgement is hereby made. We are also grateful to Dr. W.H. Atwell for providing us with a sample of 5,5-diphenyl- and 5,5-dimethylbenzosilole and for helpful discussions.

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