Nuclear Magnetic Resonance Spectra of Carbanions. I. 1, 1-Diphenylethylene Dimer Dianion

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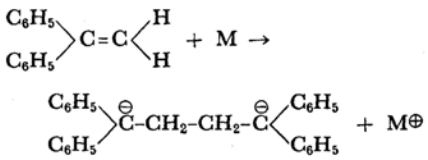
Carbanions are of particular interest from the standpoint of their charge distribution, since the excess charges are substantially larger than in neutral molecules. Only a few NMR studies have been carried out on carbanions, particularly some organolithium compounds[1] and the cyclopentadienyl anion.[2] 1, 1-Diphenylethylene dissolved in

1) V. R. Sandel and H. H. Freedman, *J. Am. Chem. Soc.*, **85**, 2328 (1963); R. Waack, M. A. Doran, E. B. Baker and G. A. Olah, *ibid.*, **88**, 1272 (1966).

2) G. Fraenkel, R. E. Carter, A. McLachlan and J. H. Richards, *ibid.*, **82**, 5846 (1960).

THF gives colored solutions in contact with excess alkali metals at room temperature for about twenty-four hours. These colored solutions served as samples for the NMR measurements. The evolved reaction in THF might be expressed as follows:[3]



Typical spectra are shown in Fig. 1, representing a solution produced from 1, 1-diphenylethylene in contact with potassium sodium alloy in THF.[4] The peaks in the region of aromatic protons are clearly divided into three, appearing as a doublet, a triplet, and a triplet respectively from the lower to the higher field. Since their intensity ratios are 2 : 2 : 1, it seems that they can be assigned to the peaks of ortho-, meta-, and para-protons respectively, similar to those of triphenylmethyllithium in THF as assigned by Sandel and Freedman.[1] The chemical shifts are given in Table 1, in which the solvent peak serves as an internal reference (the higher-field peak of THF is taken to be at 1.79 ppm from TMS). The chemical shifts between the ortho- and para-protons amount to about 1.4 ppm, but they are not sensitive to the kind of alkali metal. The chemical shift values shown in Table 1 exhibit shifts to a higher field as compared with that of benzene, which shows an absorption at 7.32 ppm in THF. Since the shift of about 10 ppm is assumed to be the contribution of one excess electron,[2] more than fifty per cent of the negative charge of the 1, 1-diphenylethylene dimer dianion might be located on the phenyl rings,[1] but this is only a rough estimate because we lack information on carbons with no protons and on methylene groups. In the solutions of these carbanions, a single peak is observed near 2.5 ppm, just between two large solvent peaks. The 1, 1, 4, 4-tetraphenylbutane which was prepared by treating these carbanions with water shows PMR signals at 2.00, 3.88, and 7.14 ppm in a carbon tetrachloride solution; these signals are identified as coming from the methylene, methine, and phenyl protons in this compound respectively. From this knowledge, the peak at 2.5 ppm mentioned above might be assigned as coming from the methylene protons in the carbanion. If this assignment is correct, one interesting point is the shift towards a lower field of the methylene protons of the carbanion as compared to those of the corresponding hydrocarbon; this shift can not be attributed to the charge, but it may be due to the change in the hybridization of the carbon atom from the hydrocarbon to the carbanion.

The carbanions produced from α-methylstyrene and cumyl methyl ether also showed large higher-field shifts in the aromatic regions of the spectra. These will be described later elsewhere.

Fig. 1. The spectrum in the region of aromatic protons of the carbanion produced from 1, 1-diphenylethylene in contact with excess potassium sodium alloy in THF. Applied magnetic field increases from left to right, at 60 Mcps.

Table 1. The chemical shifts of aromatic protons of carbanions produced from 1, 1-diphenylethylene in contact with excess alkali metals in THF, in ppm at 60 Mcps

Metal used	Assignment		
	Ortho	Meta	Para
Potassium	7.01	6.55	5.67
Sodium	7.18	6.61	5.75
Lithium	7.03	6.49	5.66

3) W. Schlenk, J. Appernodt, A. Michael and A. Thal, *Ber.*, **47**, 473 (1914); M. Szwarc, *J. Polymer Sci.*, **C1**, 339 (1963).

4) Only potassium reacts with 1, 1-diphenylethylene.