Nuclear Magnetic Resonance Spectra of Carbanions. Part 10.[1,2] Dibenzyl-barium, -strontium, and -calcium

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^{1}H and ^{13}C n.m.r. spectra of three benzyl alkaline earth metal compounds were measured and compared with those of other benzyl compounds. Their aromatic proton resonances are substantially upfield from that of benzene. This higher shielding shift is characteristic of benzyl carbanions. Chemical shift considerations indicate that the carbon–metal bonds of the benzyl carbanions in tetrahydrofuran increase in ionic nature as the counterion varies in the order of magnesium, calcium, strontium, lithium, barium, and potassium.

We have observed that dibenzylbarium (2) is formed by the reaction of dibenzylmercury (7) with metallic barium in tetrahydrofuran (THF). This paper presents an outline of the preparative procedure for (2) and its ^{1}H and ^{13}C n.m.r. spectral data. The same procedure has been applied to the calcium and strontium derivatives. Dibenzyl-strontium (4) and -calcium (5) have been prepared, and their n.m.r. data are also included. After we obtained our results, we found that the same compounds had already been reported.[3,4] The ^{1}H n.m.r. and visible data for the compounds are mostly consistent with ours, but the yields of dibenzyl alkaline earth metal compounds are much different. This difference is presumably due to the difference in experimental circumstances, especially temperature.

We have found an interesting tendency for the methylene and aromatic proton chemical shifts of a series of

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[1] Part 9, K. Takahashi, K. Konishi, M. Ushio, M. Takaki, and R. Asami, *J. Organometallic Chem.*, 1973, 50, 1.

[2] K. Takahashi, Y. Kondo, and R. Asami, Preprint presented at the 27th Annual Meeting of the Chemical Society of Japan, Nagoya, 1972, vol. 1, p. 146.

[3] P. West and M. C. Woodville, Preprints, 162nd Amer. Chem. Soc. Meeting, Washington, 1971, INOR 57.

[4] Jap. P. 47-1976/1972.

benzyl compounds. The chemical shifts of (2), (4), and (5) are given in Table 1 with the values for other benzyl compounds. The aromatic protons of (2) in THF showed a spectral pattern similar to those of benzyllithium [5] (3) and -potassium [6] (1). The chemical shifts are intermediate between those of (1) and (3). Therefore, the ionic nature of (2) in THF is probably intermediate between the two, as discussed previously from the viewpoint of the aromatic proton chemical shifts.[6] Unfortunately, we could not find the methylene proton peak of (2) in THF and dimethoxyethene (DME). However, in [$^2H_8$]THF, a broad peak was found at δ 2.09 which was attributable to the methylene protons of (2). By observing the ^1H n.m.r. spectra of (2) in DME at 31.5 °C, it was found that 20% of (2) decomposed within 1 h. Compound (4) was so unstable in DME at room temperature that its ^1H n.m.r. spectrum could not be measured.

TABLE 1

60 MHz ^1H Chemical shifts (δ) of benzyl compounds $C_6H_5CH_2X$ or $(C_6H_5CH_2)_2X$

No.	X	Solvent	Chemical shift *ortho*	*meta*	*para*	CH_2	Ref.
(1)	K	THF [a]	5.59	6.12	4.79	2.24	6
(2)	Ba	THF	5.78	6.43	5.38	2.09 [b]	
			5.76	6.41	5.36		4
		DME [c]	5.70	6.43	5.33		
(3)	Li	THF	6.09	6.30	5.50	1.62	5, 8
(4)	Sr	THF	6.20	6.52	5.64	1.70 [b]	
			6.23	6.51	5.68		4
(5)	Ca	THF	6.36	6.54	5.78	1.58	
			6.35	6.45	5.75	1.50	4
(6)	Mg	THF	6.7 [d]	6.7 [d]	6.3 [d]	1.36	
		C_6D_6 [e]	6.9 [d]	6.9 [d]	6.5 [d]	1.64	
(7)	Hg	THF	7.0 [d]	7.0 [d]	7.0 [d]	2.37	
		C_6D_6	6.8 [d]	6.8 [d]	6.8 [d]	1.80_5 [f]	
(8)	H	THF	7.15_5	7.15_5	7.15_5	2.32	6

[a] The higher field methylene peak of THF, δ 1.79, was used as an internal reference. [b] Measured in [$^2H_8$]THF. [c] The methyl peak of DME, δ 3.28, was used as an internal reference. [d] Approximate value because of complex multiplet structure. [e] Me_4Si in a capillary tube was used as an external reference. [f] J_{CH_2-Hg} 135.0 Hz for isotopic mercury.

For comparison's sake, ^1H n.m.r. data of dibenzylmagnesium (6) and -mercury (7) in THF are also included in Table 1. The shifts of the methylene protons show different behaviour in THF and C_6D_6 for these two compounds. The shift of (6) is more shielded in THF than in C_6D_6 and *vice versa* for (7). The aromatic proton shifts of the two compounds are also different in THF and C_6D_6. This is explained by the nature of the benzyl carbanions because their ionic nature increases in polar solvents. Thus the ionic nature of the metal–carbon bond in (7) is quite small but appreciable in (6).

It should be noted that the net shift of the methylene proton cannot be used as a direct measure of the localized charge on the methylene carbon. We have pointed out before that the methylene proton shift is partly affected by the hybridization change.[6,7] A similar discussion was presented earlier by Waack *et al.* in the case of ^{13}C n.m.r.[8] The effects of charge and hybridization cannot be separated experimentally. Therefore the methylene and aromatic proton shifts must be compared with each other at the same time. Aromatic proton shifts, however, show more exactly the localized charge on bonded carbon atoms than do methylene proton shifts, because the hybridization change is presumably smaller for an aromatic than for a methylene carbon. Among the aromatic proton shifts of the benzyl compounds, the *para*-proton shifts are most characteristic. Data given in Table 1 are arranged in the order of magnitude of the *para*-proton shifts which are a measure of the extra negative charge localized at the *para*-carbons and, consequently, of the ionic nature of the metal–carbon bonds in the benzyl carbanions. Chemical shift considerations indicate that the metal–carbon bonds of the benzyl carbanions in THF increase in ionic nature as the counterion varies in the order magnesium, calcium, strontium, lithium, barium, and potassium. Except for (7) and (8) the order of magnitude of *para*-proton shifts is almost the reverse of that of the methylene proton shifts. It was concluded that the larger the extra charge localized at the *para*-carbon, the larger are the hybridization changes of the methylene carbons. Compounds (7) and (8) show the methylene proton shifts at δ *ca.* 2.3. These values are ascribed to methylene protons undergoing neither charge nor hybridization effects. Another factor, which contributes to the methylene proton chemical shifts, is the extent of aggregation of the benzyl carbanion. We suppose at present that this factor is important for the carbanion in nonpolar but not in polar solvents, because it is monomeric in THF.[9]

TABLE 2

^{13}C Chemical shifts [δ (p.p.m.)] of benzyl compounds $C_6H_5CH_2X$ or $(C_6H_5CH_2)_2X$

No.	X	Solvent	Chemical shift [a] *ipso*	*ortho*	*meta*	*para*	CH_2	Ref.
(1)	K	THF	153.2	111.0	130.8	95.6	52.8	10
(2)	Ba	THF	155.4	114.6	131.6	103.6	57.3	
(3)	Li	THF	161.5	117.0	128.6	104.7	36.9	10
		C_6D_6 [b]	157.8	120.7	130.8	113.6	30.1	10
(4)	Sr	THF	158.8	117.4	129.7	107.0	47.2	10
(4)	Ca	THF	161.0	119.8	128.6	109.4	42.1	10
(6)	Mg	THF	157.8	123.9	128.4	116.0	22.9	
		C_6D_6 [b]	157.9	125.0	129.0	117.1	24.2	
(7)	Hg	THF	145.8	128.7 [c]	128.5 [c]	123.5	46.0	
(8)	H	THF	138.5	129.7 [d]	129.0 [d]	126.1	21.5	10

[a] Referred to the more shielded peak of THF, δ 26.4 p.p.m. with respect to Me_4Si. Errors are within ±0.3 p.p.m. [b] The solution contains an equimolar amount, or more, of THF (C_6D_6 was introduced into the system after THF was pumped out from the carbanionic solution). [c] Assignments may be reversed. [d] The previous values for *ortho-carbon* in ref. 10 should be exchanged with those for *meta*-carbon for $C_6H_5CH_3$, $(C_6H_5)_2CH_2$, and $(C_6H_5)_3CH$.

The ^{13}C chemical shifts of the benzyl compounds studied are given in Table 2. Both ^1H and ^{13}C chemical

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[6] K. Takahashi, M. Takaki, and R. Asami, *Org. Magnetic Resonance*, 1971, **3**, 539.

[7] K. Takahashi and R. Asami, *Bull. Chem. Soc. Japan*, 1968, **41**, 231.

[8] R. Waack, M. A. Doran, E. B. Baker, and G. A. Olah, *J. Amer. Chem. Soc.*, 1966, **88**, 1272.

[9] P. West and R. Waack, *J. Amer. Chem. Soc.*, 1967, **89**, 4395.

shifts for the *para*-positions are plotted in Figure 1. There is a linear relationship between the two. Therefore both the *para* ^{1}H and ^{13}C shifts are a well defined index of electron delocalization. However, ^{1}H and ^{13}C chemical shifts of the methylene groups are not linearly correlated. The order of the magnitude of *para*-carbon chemical shifts is almost the reverse of that of the methylene carbon chemical shifts except for (7). This means that electron delocalization into the phenyl ring in the benzyl carbanion (shown by the *para*-carbon chemical shift) occurs through sp^2 configuration at the methylene carbon (shown by the methylene carbon chemical shift). The hybridization effect for the methylene carbon chemical shift was discussed previously,[10] and it has the opposite effect on the charge. ^{13}C Chemical shifts are often correlated with charge densities as reviewed by Martin.[11] Five different carbon chemical shifts of (1) (a typical delocalized benzyl anion) are correlated with π-electron densities calculated by a semi-empirical SCF MO method (Figure 2) and fall almost on a straight line with a slope of -164 p.p.m. electron^{-1}. π-Electron densities were 0.903, 1.153, 1.023, 1.232, and 1.513 for *ipso-*, *ortho-*, *meta-*, *para-*, and α-carbons, respectively, calculated using Kikuchi's program,[12] and assuming 1.39 Å for all carbon–carbon distances. The values are slightly different from those originally given by Pople,[13] especially for the *meta*-carbon.

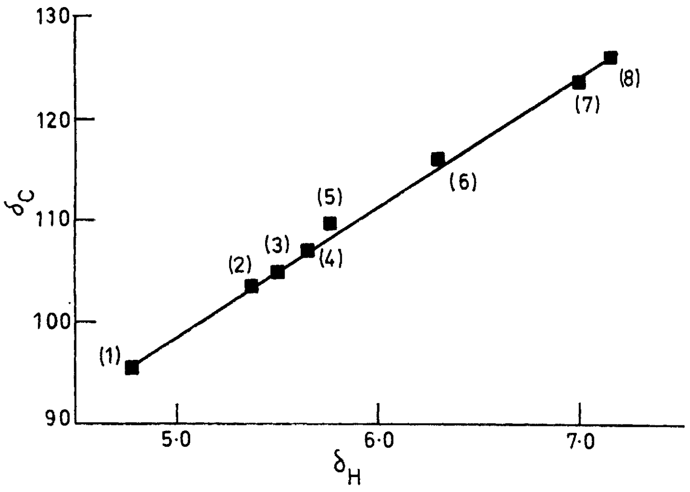

FIGURE 1 Correlation between chemical shifts of *para*-carbon and -hydrogen for benzyl compounds

Visible spectral data for the three benzyl alkaline earth metal compounds are given in Table 3. For benzyl alkali metal compounds, the absorption maximum shifts to longer wavelength as the metal becomes larger in the order Li, Na, and Cs. But for the alkaline earth metal compounds, no such tendency was observed.

Compounds (2) and (4)—(6) are effective as initiators of anionic polymerization but (7) is not.[4,14-16] These results are consistent with the properties of the benzyl carbanions inferred from the ^{1}H and ^{13}C n.m.r. data.

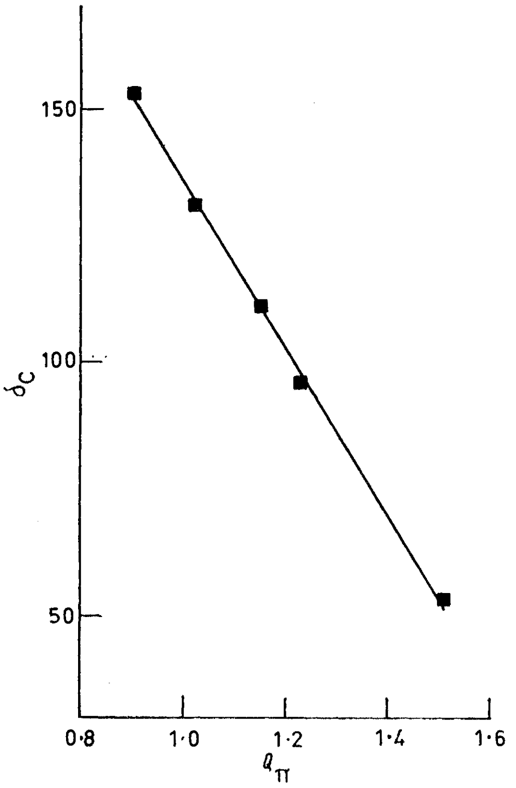

FIGURE 2 Correlation between ^{13}C chemical shifts and π-electron densities calculated by an SCF MO method for the benzyl anion

TABLE 3

The main absorption maximum of the benzyl anion in THF

Counter-ion	$\lambda_{max.}$/nm	ε	Ref.
Li	330	9.6×10^3	*a*
Na	335	1.2×10^4	*b*
	350	3.5×10^3	*c*
Cs	356		*c*
Ba	345	1.9×10^4	This study
Sr	322	1.2×10^4	This study
	323		4
Ca	332	7.2×10^3	This study
	333		4

[a] R. Waack and M. A. Doran, *J. Amer. Chem. Soc.*, 1963, **85**, 1651. [b] R. Asami, M. Levy, and M. Szwarc, *J. Chem. Soc.*, 1962, 361. [c] F. J. Hopton and N. S. Hush, *Mol. Phys.*, 1963, **6**, 209.

EXPERIMENTAL

^{1}H and ^{13}C n.m.r. measurements were carried out on a Hitachi R-20B spectrometer at 60 MHz and on a Hitachi

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[11] G. J. Martin, M. L. Martin, and S. Odiot, *Org. Magnetic Resonance*, 1975, **7**, 2.

[12] O. Kikuchi, ' Bunshi Kidoho ', Kodansha, Tokyo, 1971.

[13] A. Brickstock and J. A. Pople, *Trans. Faraday Soc.*, 1954, **50**, 901.

[14] R. Asami and Y. Kondo, Preprints, 21st Symposium on Macromolecules, Osaka, 1972, vol. 1, p. 255.

[15] R. Asami and Y. Kondo, Preprints, 21st Annual Meeting of the Society of Polymer Science in Japan, Tokyo, 1972, vol. 2, p. 314.

[16] R. Asami and Y. Kondo, ref. 2, p. 65.

R-42-FT spectrometer at 22.6 MHz, respectively. Visible spectral data were obtained for THF solutions using a Hitachi model 124 spectrophotometer.

Dibenzylbarium (2).—A solution of (7) (0.05M) in THF was placed in contact with metallic barium at room temperature in a vacuum. Several minutes after contact, the solution showed the characteristic red colour of the carbanion. After standing for two days at room temperature, the coloured solution was freed from unchanged metal by filtration. An EDTA titration of barium showed that the yield of (2) was *ca.* 27% based of the starting material (7). The solution absorbed at 345 nm. The ^{1}H n.m.r. spectrum of a concentrated solution showed aromatic proton peaks characteristic of the benzyl anion.[5,6] In the aromatic proton region, the intensity of the benzyl anion peaks totalled *ca.* 25%, and the rest is ascribed to impurities. The impurity signals are largely due to 1,2-diphenylethane at δ 2.91 and 7.17 (lit.,[17] 2.92 and 7.21), a small amount of toluene at δ 2.32 and 7.14 (lit.,[6] 2.32 and 7.15_5), and a trace of benzene at δ 7.29 (lit., 7.28,[5] 7.32 [7]), respectively. This result shows that the main product is 1,2-diphenylethane, and (2) is formed as a by-product whose ^{1}H n.m.r. intensity is in accord with the EDTA titration result. Compound (2) can be obtained free from impurities by washing with hexane. Atomic absorption analysis showed that metallic barium used was essentially free from potassium and sodium. A dilute solution of (7) in THF was preferable for preparation of (2), a more concentrated solution giving a lower yield. The reaction of bulk (7) with metallic barium in a sealed tube gave 1,2-diphenylethane only at temperatures higher than the m.p. of (7).

Dibenzylstrontium (4).—Compound (7) (0.504 mmol, 0.05M) in THF was added to strontium (0.3 g) and stirred for 24 h at room temperature. An EDTA titration showed that the yield of (4) was 55%. The recovery of mercury was 79%. An experiment using a 0.57M solution of (7) resulted in 35% yield and 49% conversion.

Dibenzylcalcium (5).—Compound (7) (1.05 mmol, 0.04M) in THF was added to metallic calcium (0.2 g) in vacuum and stirred for 29 h at room temperature. During the reaction, the colour of the solution changed from yellow to red. The solution was filtered and stored in several ampoules with a break-seal. After the residue was treated with water, the recovered mercury was *ca.* 60% based on (7). An EDTA titration of calcium showed that the yield of (5) was 34%.

[7/1467 *Received, 12th August,* 1977]

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