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A ^{13}C NMR Study of 1,4-Diphenyl- and 1,1,4,4-Tetraphenyl-1,3-butadiene Dianions

Yukihiro YOKOYAMA and Kensuke TAKAHASHI*
Department of Applied Chemistry, Nagoya Institute of Technology,
Gokiso-cho, Showa-ku, Nagoya 466

Lithium, sodium, and potassium salts of the title dianions were investigated by means of ^{13}C NMR spectroscopy in THF or DME at room temperature. The structures of the butadiene carbon skeleton and especially the behaviors of the α- and β-carbons caused by the conversion of the precursors into the dianions were reported together with the counter-cation effects.

A number of carbanions have been investigated extensively by the NMR techniques, as reviewed by O'Brien.$^{1)}$ The examples of the acyclic carbanions given in his review are limited to those with odd carbon skeletons, such as allyl, pentadienyl or heptatrienyl carbanions. General formula of the acyclic conjugated carbanions will be written as $[X\text{-}(CH)_n\text{-}Y]^{-m}$; where X or Y is a kind of stabilizing group such as a phenyl group. If n is odd, m=1. If n is even, m=2. Little work has been reported on the NMR parameters of the carbanions with even carbon skeletons. A reason seems to be due to the difficulty of preparing the carbanions. In the odd-carbon carbanions there is at least a nonbonding MO in the simple HMO theory, which can be occupied by an excess electron. However, the even-carbon carbanions must have at least a filled antibonding orbital. In this sense the even-carbon carbanions seem to be more difficult in preparation than the odd-carbon ones. A ^{1}H NMR study of 1,1,4,4-tetraphenylbutadiene dianion (1) was reported in our previous paper,$^{2)}$ and we described in the report that an attempt to observe the spectra of the carbanion (2) produced from 1,4-diphenylbutadiene had failed due to formation of radical species. However, we have recently succeeded in the NMR observation of the spectra of **2**, so we wish to report the structures and the behaviors of these dianions evaluated from their ^{13}C NMR data.

The carbanions were prepared as follows. The starting hydrocarbon (**1a** or **2a**) dissolved in dried and degassed solvent (THF or DME) was placed in contact with alkali metal in a vacuum at room temperature. Immediately after the contact, the solution showed a deep purple color. After standing for two days at room temperature, the colored solution was filtered and sealed in an NMR tube. The solutions appear to be stable for a long period of time even at room temperature. The ^{13}C NMR data of the dianions are given in Table 1 together with the data of their precursors. Assignments of the signals were carried out on the basis of their intensities and proton-coupled splitting patterns.

First, the large upfield shifts of the carbon signals caused by conversion of hydrocarbons into dianions are transpired from the data given in Table 1. Such shifts can be used as an empirical guide to the distributions of electron densities within the carbanions. The excess charges on carbons in the carbanions are obtained from comparison of the chemical shifts between the carbanion and its neutral precursor. The differences of the chemical shifts are extremely large, for example 58-64 ppm at α-carbon, 17-36 ppm at β-carbon

Table 1. ^{13}C Chemical Shifts of the Carbanions and Their Precursors

Compd/Metal	Assignment					
/Solvent	C_i	C_o	C_m	C_p	C_α	C_β
1/Na/THF	145.12	121.94(152)	128.67(151)	112.33(158)	87.31	109.21(139)
2/Li/THF	146.65	118.53(149) 110.60(149)	128.45(149)	104.86(157)	65.74(146)	97.42(146)
2/Na/THF	146.03	118.32(153) 109.69(149)	129.56(146) 128.00(148)	103.01(157)	67.73(b))	98.06(146)
2/K/DME	144.50	118.23(b)) 108.60(b))	130.05(b)) 128.07(b))	103.10(b))	b)	100.59(b))
1a/THF	143.40 140.91	129.74(160$^{b)}$) 128.36(158$^{b)}$)	131.47(159$^{b)}$) 128.93(160$^{b)}$)	128.4$^{b)}$ (158$^{b)}$) 128.17(160$^{b)}$)	145.13	126.61(154)
2a/THF	138.51	127.18(158$^{b)}$)	129.35(159$^{b)}$)	128.21(160)	130.22(158$^{b)}$)	133.66(156)
2a/DME	138.43	127.15(b))	129.36(160)	128.23(161)	130.12(b))	133.66(156)

a) The values in parentheses are the $^{1}J_{CH}$ in Hz. b) With large error or not available because of overlapping or low intensity of the signal.

Table 2. Comparison of Charge Distributions of **1** and **2** in Unit of the Absolute Value of the Charge of an Electron

Anion/Metal /Solvent	q_i	q_o	q_m	q_p	q_{ring}	q_α	q_β
1/Na/THF	-0.019	0.044	0.010	0.100	0.189	0.361	0.109
2/Li/THF	-0.051	0.079a)	0.006	0.146	0.265	0.403	0.227
2/Na/THF	-0.047	0.082a)	0.004a)	0.158	0.283	0.391	0.223
2/K/DME	-0.037	0.086a)	0.002a)	0.157	0.296	b)	0.207

a) Average values of two positions. b) Not available.

and 30-47 ppm at the total sum of the phenyl carbons as shown in Table 1. The estimation of the charges on the carbon atoms is made by using an empirical equation proposed by Fraenkel et al.3) and a factor (160 ppm/electron) presented by Spiesecke and Schneider.4) The experimentally evaluated values are presented in Table 2. As for the carbanion of **2**, in comparison of total excess charges on a phenyl ring, the value of the lithium salt (0.265) is smaller than the values of the sodium and potassium salts (0.283 and 0.296 respectively). On the other hand, the excess charges on the α- and β-carbon atoms increase from potassium to lithium salts. While, the excess charge of **1** is estimated to be 0.189 per a phenyl ring. This value is smaller than that of **2** (0.283). Furthermore, excess charges on the β-carbons are estimated to be 0.207-0.227 for **2**, but for **1** it is almost a half of **2**. The facts can be explained on the basis of the following: relative decrease of the charge on the α- or β-carbon atom is consistent with large delocalization of the charge into phenyl rings. Total excess charges on the carbon atoms of the carbanions, **1** and **2**, are evaluated to be about 1.7-1.8e from Table 2.

Second, the chemical shifts of two ortho or meta carbons of a phenyl ring of **1** are equivalent, but those of **2** are nonequivalent. Additionally, coalescence of meta-carbon lines and broadening of ortho-carbon resonances were observed for the lithium salt of **2**. Appearance of nonequivalency was attributed to higher rotation barrier about the C_α and C_i bond in the sodium and potassium salts. The nonequivalency was caused by a conjugative interaction between these carbons. This fact is consistent with the nonequivalency occurred in α-methylbenzyl anion and α-methylstyrene dimer dianion.5,6) That is, both a phenyl ring and a butadiene skeleton prefer to take their position on a plane because of resonance stabilization. However, in the neutral molecule

(**2a**) there is a free rotation around the bond between the phenyl ring and its adjacent carbon, but in the case of **2** the rotation is restricted in an NMR time scale, whereas, as for the lithium salt of **2**, it seems that a hindered rotation has begun. This is reflected in the fact that a coalescence of the C_m signals and the broadening of the C_o resonances appeared in the spectra of the lithium salt at room temperature. The fact can be interpreted on the basis of the effect of the counter cations.[7)]

On the other hand, the two phenyl rings connected to the α-carbon of **1** cannot be coplanar due to their steric hindrance as well as those of the neutral molecule (**1a**).[6a)] However, the ^{13}C spectra of **1** showed an equivalency of the four ortho- or meta-carbons of the two geminal phenyl rings, while there are two C_i, C_o, C_m, and C_p signals in **1a**. These facts suggest that there is a free rotation about the C_i and C_α bond in **1** and **1a**, while the rotation around the bond between the C_α and C_β atoms are forbidden in **1a** but not in **1** at room temperature.

Finally, the values of $^1J_{CH}$ observed for the carbanions, **1** and **2**, are somewhat smaller than those of the precursors, **1a** and **2a**, as pointed out in other systems by Waack et al.[8)] It seems that the decrease of $^1J_{CH}$ obtained for these dianions is corresponding to the decrease of s character in hybridization of the respective carbon atom. Especially $^1J_{CH}$ of the β-carbon of **1** is smaller than that of **1a** by ca. 15 Hz.

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