BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 2559—2560(1971)

Nuclear Magnetic Resonance Spectra of Carbanions. VII.[1] 1,1,4,4-Tetraphenylbutadiene Dianion[2]

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(Received March 29, 1971)

The carbanions produced from α-methylstyrene and 1,1-diphenylethylene were studied in our previous reports.[3,4] The studies have now been extended to the carbanion produced from 1,1,4,4-tetraphenylbutadiene (TPB). Furthermore, we have tried, but failed, to observe the spectra of the carbanion produced from 1,4-diphenylbutadiene (DPB).

Experimental

The procedures used in this study are similar to those described in the previous reports.[3,4] Commercially-available TPB and DPB were used as sources of carbanions after two or three recrystallizations from acetone and methanol respectively. The pmr spectra were observed at about 60 MHz with a frequency-swept Hitachi R-20B spectrometer. The chemical shifts of the carbanions were evaluated from the higher-shielding methylene peak of the solvent, THF, used as an internal reference. This peak of THF was taken to be 1.79 ppm from TMS. All the chemical shifts were calibrated by means of a frequency counter (Takeda Riken TR-3824X).

Results and Discussion

The signals appearing in the aromatic-proton region of the carbanion produced from TPB with sodium as counterion are divided into three groups. They show the structures of a doublet, a triplet, and a triplet from lower to higher shielding, with an intensity ratio of about 2:2:1. They can, therefore, easily be identified as the signals of the ortho-, meta-, and para-protons respectively. The chemical shifts of the carbanions are given in Table 1, along with other previously-reported values for the sake of comparison. On treatment with H_2O, the carbanion forms a mixture of 1,1,4,4-tetraphenylbutene-1 and -2, whose pmr peak positions are 2.82 (2H, triplet, $J=7._5$ Hz), 4.00 (1H, triplet, $J=7._5$ Hz), 5.90 (1H, triplet, $J=7._5$ Hz), 7.00 (weak), and 7.06 (strong) for the former, and 4.72_5 (2H, double doublet, apparently, $J=4$ and $1._5$ Hz), 5.85_5 (2H, double doublet, apparently $J=4$ and $1._5$ Hz), and 7.10_5 ppm for the latter in a CCl_4 solution. The charge localized in the phenyl rings of the carbanion is then estimated to be given in Table 2, taking the reference for the neutral phenyl proton as 7.20 ppm. This charge estimation is not self-consistent because the charge on a carbon with no proton can not be estimated on the proton spectra. However, a series of the data may be compared with each other and may give some information as to the charge distribution of the carbanions. Furthermore, the magnetic anisotropy of the adjacent phenyl ring may contribute to the aromatic proton shifts, especially to the ortho-proton shifts in the carbanion. If we assume the twist angle of the phenyl ring to be 30°, the anisotropy effects will compensate for each other for two far and near ortho-protons, as has been described before.[4] Table 2 shows that the charge localization on the phenyl rings is about 40% for the TPB dianion. The lower charge localization in the phenyl rings of the TPB dianion as compared with that of the 1,1-diphenylethylene dimer dianion is ascribable to the structural difference between I and II, that is, to the presence of a pi-system in the middle part of II:

TABLE 1. THE PROTON CHEMICAL SHIFTS OF CARBANIONS IN ppm

Carbanion	Counterion	Assignment		
		Ortho	Meta	Para
1,1,4,4-Tetraphenyl-butadiene dianion	Na	7.22	6.71	6.00
1,1-Diphenylethylene dimer dianion[a]	Na	7.18	6.61	5.75
Cumyl anion[b]	K	5.16	6.11_5	4.39

a) Ref. 3; b) Ref. 4.

We have tried, but failed, to observe the spectra of

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[1] Part VI in this series, K. Takahashi, M. Takaki, and R. Asami, Preprint presented at the 9th Symposium on NMR Spectroscopy of the Chemical Society of Japan, Kanazawa, October 1970, p. 124.

[2] M. Ushio, K. Takahashi, and R. Asami, Preprint presented shortly at the Tokai District Meeting of the Chemical Society of Japan, Nagoya, October 1970, p. 107.

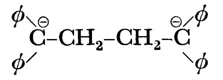
[3] K. Takahashi and R. Asami, This Bulletin, **41**, 231 (1968).

[4] K. Takahashi, M. Takaki, and R. Asami, *J. Phys. Chem.*, **75**, 1062 (1971).

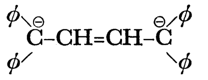
Table 2. The charge distribution in the carbanions in units of the absolute value of the charge of an electron

Carbanion	Counterion	Position Ortho	 Meta	 Para	Sum for a phenyl ring
1,1,4,4-Tetraphenylbutadiene dianion	Na	0.00	−0.05	−0.12	−0.22
1,1-Diphenylethylene dimer dianion[a]	Na	0.00	−0.06	-0.14_5	-0.26_5
Cumyl anion[a]	K	-0.20_5	-0.10_5	−0.28	−0.90

a) Ref. 4.


$\phi_2\overset{\ominus}{C}-CH_2-CH_2-\overset{\ominus}{C}\phi_2$

I


$\phi_2\overset{\ominus}{C}-CH{=}CH-\overset{\ominus}{C}\phi_2$

II

the carbanion produced from 1,4-diphenylbutadiene, using potassium, sodium, and lithium as counterions. Our failure is ascribable to the contamination of the radical anion formed, because the samples used for the NMR measurements gave strong ESR signals. The pmr spectra of the TPB dianion was observed only with sodium counterions. Even in this case, the NMR sample gave weak ESR signals and the PMR spectra are broader than usual spectra. The TPB dianion with potassium as counterions did not give any resolved spectrum in spite of several trials. No information on the *cis-trans* isomerization of the TPB dianion and 1,1,4,4-tetraphenylbutene-2 can be obtained at present. Further studies along this line are in progress.