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Generation, Characterization, and Reactions of Fulvene Dianions

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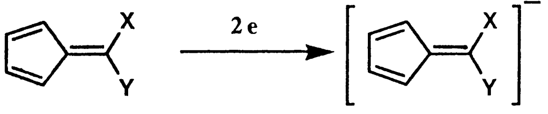
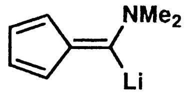
The dianion of 6,6-diphenylfulvene obtained by reduction with lithium metal was first characterized spectroscopically. Reduction of 6-dimethylamino-6-phenylfulvene also generated its dianion whose reactions with electrophiles led to 6-phenylfulvene derivatives, demonstrating synthetic utility of fulvene dianions.

We have recently reported the novel reductive reactions of 6-dimethylaminofulvenes, which turned out to be of synthetic use owing to the leaving ability of dimethylamino group: while 6-dimethylaminofulvene gives, upon treatment with lithium naphthalene in THF, 6,6'-bifulvenyl in high yield through coupling of the intermediate anion radical, 6,6-bis(dimethylamino)fulvene (**1**) produced 6-dimethylamino-6-lithiofulvene (**3**), a 6-fulvenyl anion of potential synthetic utility.[1)] For the latter reaction, we suggested intermediate formation of dianion **2**, ascribing the spontaneous elimination of lithium dimethylamide to electronic repulsion in the dianion.[1b)] Introduction of an anion-stabilizing substituent in place of the dimethylamino group would favor more the formation and allow the characterization of fulvene dianions. Concerning this, Oku and co-workers reported that alkali metal reduction of 6,6-diphenylfulvene (**4**) yielded, after quenching with water, dihydro compounds probably via dianion **5**.[2)] However, neither **2** nor **5** has been yet definitely established. We here report the first NMR observation of fulvene dianion **5** and the generation and reactions of another dianion **7** derived from 6-dimethylamino-6-phenylfulvene (**6**), **7** revealing its synthetic utility.



1 : X=Y= NMe$_2$ 2
4 : X=Y= Ph 5
6 : X= NMe$_2$, Y= Ph 7



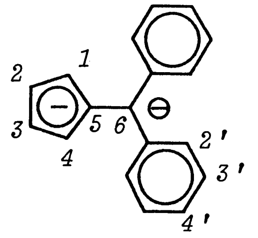
3

Upon electrochemical reduction (cyclic voltammetry), diaminofulvene **1** shows irreversible reduction at E_{pa} = -2.83 V (vs. Ag/Ag(I); DMF, n-Bu_4NClO_4). Replacement of the dimethylamino groups with a phenyl group one by one makes the reduction easier, showing two quasi-reversible one-electron reductions (**6**: $E_{1/2}$ = -1.99, -2.34 V; **4**:

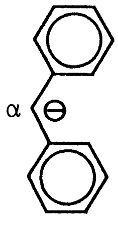
-1.44, -2.01 V). This trend is in agreement with the decrease of theoretical HOMO-LUMO gap of 6-phenylfulvene relative to that of 6-aminofulvene.[3] The reduction potentials of **4** is even less negative than those of benzophenone.[4] We, therefore, expected dianion **5** to be stable enough for spectroscopic measurements, in particular, for NMR measurement.

Treatment of **4** with a small excess of lithium powder in THF-d_8 for 20 min under sonication cleanly afforded a deep purple solution of the expected dianion **5**. This dianion was stable in the solution at room temperature under inert gas atmosphere and regenerated **4** (81%) on exposure to oxygen.[5]

^1H and ^{13}C NMR data of 5 (Table 1) are consistent with the dianion structure. The averaged ^{13}C chemical shift (δ_{av} = 117.9) reasonably agrees with the calculated value (δ = 116.0) according to O'Brien's empirical equation.[6] The most notable feature in the NMR data is that ^1H and ^{13}C chemical shifts of the cyclopentadienyl and diphenylmethyl parts of **5** are similar to those of cyclopentadienyl anion and diphenylmethyl anion (**8**),[7] respectively, except for the appreciably low field appearance of the phenyl ortho protons (H2',6'; δ 7.25) compared with ortho protons of **8** (δ 6.51). Charge densities (Table 1) obtained by the MNDO calculation are consistent with the ^{13}C NMR results.[8] Thus, dianion **5** is best represented by the separated dianion structure **5A**, that is, a cyclopentadienyl anion weakly perturbed by diphenylmethyl anion. The low field shift of C2' protons of **5** may be due to additional anisotropy effect by the aromatic cyclopentadienyl ring.



5A



8

Table 1. ^1H and ^{13}C NMR spectral data[a] and calculated charge densities[b]

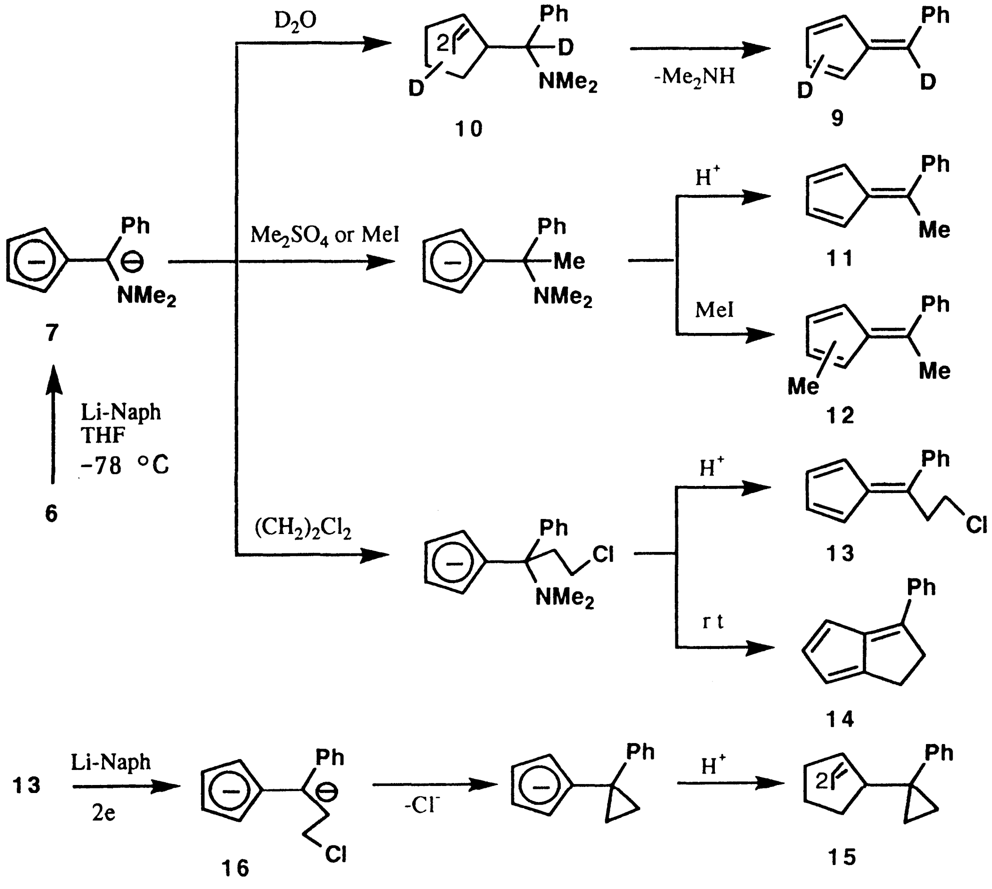
Position	^1H Chemical shifts (δ)		^{13}C Chemical shifts (δ)		Charge densities
	5[c,d]	8[e]	5[f]	8[e]	5
1, 4	5.92		100.60		1.212
2, 3	5.56		99.25		1.233
5			127.94		1.062
6			81.30	78.5 (C-α)	1.301
1'			148.94	147.4	0.906
2', 6'	7.25	6.51	121.18	117.5	1.115
3', 5'	6.39	6.54	127.94	128.1	1.067
4'	5.67	5.65	109.67	107.1	1.221

a) In THF-d_8. b) Calculated by the MNDO method, c) At 400 MHz. d) $J_{1,2}$ = $J_{1,3}$ = 2.6 Hz, $J_{2',3'}$ = 7.9 Hz, $J_{3',4'}$ = 7.0 Hz. e) Ref. 7, f) At 100 MHz.

Although less stable than **5**, dianion **7** derived from **6** is still stable enough to take part in the reactions with electrophiles at low temperatures. Thus, treatment of **6** with 2.5 equivalents of lithium naphthalene in THF at -78 °C (5 min) followed by quenching with D_2O gave dideuterated 6-phenylfulvene (**9**) in 81% yield probably via **10** (degree of deuterium incorporation: 95% at C-6; 90% at C1-C4 by ^1H NMR). This result sharply contrasts with the incorporation of only one deuterium in the similar reaction of **1** under the same condition where 6-fulvenyl anion **3** is rapidly formed as the intermediate.

Interestingly, the cyclopentadienide part and the phenyldimethylaminomethyl part (C-6) of **7** displays different reactivity towards alkylations: the reaction of **7** with dimethylsulfate at -78 °C for 1 h and subsequent quenching with water afforded 6-methyl-6-phenylfulvene (**11**, 90%), whereas the reaction with methyl iodide at -78-0 °C for 2 h did dimethylated fulvene **12** (41%).[9,10] Thus, C-6 is more reactive than the aromatic cyclopentadienide part to offer an advantage for synthetic applications. A typical example is the reaction of **7** with 1,2-dichloroethane: while the reaction at 0 °C for 10 min produced chloroethylfulvene **13**[11] (63%), the reaction at room temperature (2 h) led to cyclization giving dihydropentalene **14**[12] (27%) along with **13** (13%).

Further reductive reaction of **13** with Li-Naph (THF, -78 °C) yielded cyclopropylcyclopentadiene **15**[13] (45%), probably again through dianion **16**.



To conclude, fulvene dianions can be readily generated by alkali metal reductions when anion stabilizing group(s) is present at C6 and be used as synthetic intermediates.

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References

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3) K. N. Houk, J. K. George, and R. E. Duke, Jr., Tetrahedron, **30**, 523 (1974).
4) B. S. Jensen and V. D. Parker, J. Chem. Soc., Chem. Commun., **1974**, 367.
5) No appreciable change in NMR spectra was observed after a week at room temperature, and reaction with iodine also regenerated **4**.
6) D. H. O'Brien, A. J. Hart, and C. R. Russel, J. Am. Chem. Soc., **97**, 4410 (1975). O'Brien's equation was proposed for a series of potassium salts of organic anions. Although ^{13}C chemical shifts of lithium salts like **5** are usually more sensitive to solvent and temperature (ion-pairing effects), the ion-pairing effects rather affect the distribution of charge in the molecule with little change in the averaged chemical shifts.
7) R. Waack, M. A. Doran, E. B. Baker, and G. A. Olah, J. Am. Chem. Soc., **88**, 1272 (1966); K. Takahashi, Y. Kondo, and R. Asami, Org. Magn. Reson., **6**, 580 (1974).
8) Optimized C5-C6 and C6-C1' bond lengths are 149 and 146 pm, respectively, with about 50° of twisting between the cyclopentadienyl and phenyl groups.
9) Compound **12** is a mixture of the positional isomers (at least two) in the five-membered ring; ^{1}H NMR ($CDCl_3$, 100 MHz) δ = 2.02 (1.8H, s), 2.11 (1.2H, s), 2.55 (3H,s), 6.10-6.70 (3H, m), 7.25-7.40 (5H, m).
10) The reaction with methyl iodide at -78 °C for 1 h gave mostly **11** together with a small amount of **12.**
11) Red oil; ^{1}H NMR ($CDCl_3$, 100 MHz) δ= 3.22-3.62 (4H, m), 6.08 (1H, dt, J=5.5, 2.0 Hz), 6.49 (1H, ddd, J=5.5, 2.0, 1.0 Hz), 6.55-6.63 (2H, m), 7.25-7.45 (5H, m).
12) Dark red crystals, mp 62-62.5 °C; ^{1}H NMR ($CDCl_3$, 270 MHz), δ = 2.76-2.84 (2H, m), 3.42-3.51 (2H, m), 5.95 (1H, dd, J=1.98, 1.49 Hz), 6.49 (1H, dd, J=4.95, 0.74 Hz), 6.93 (1H, dd, J=4.95, 1.98 Hz), 7.33-7.47 (3H, m), 7.77-7.84 (2H, m); ^{13}C NMR ($CDCl_3$, 67.5 MHz) δ = 22.95, 41.23, 111.61, 114.10, 128.70, 129.02, 129.80, 135.87, 142.36, 147.97, 152.49, 152.85.
13) About 3:2 mixture of two possible isomers; ^{1}H NMR ($CDCL_3$, 100 MHz) δ = 1.10-1.25 (4H, m), 2.75 (0.6H, m), 2.91 (0.4H, m) 5.73 (0.4H, m), 5.92(0.6H, m), 6.10-6.40 (3H, m), 7.05-7.40 (5H, m).

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