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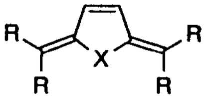
3,5-Dimethylenecyclopentenyl Ions.
Synthesis and Properties of Tetraphenyl Derivatives

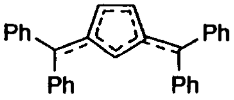
Takeshi Kawase, Seiji Muro, and Masaji Oda*
Department of Chemistry, Faculty of Science, Osaka University,
Toyonaka, Osaka 560, Japan

Abstract: While 3,5-bis(diphenylmethylene)cyclopentenyl anion is substantially stable, the corresponding cation is unstable probably due to its favorable structure for an intramolecular cyclization.

Recently a number of derivatives of 4-hetero-3,5-dimethylenecyclopentene **1** (X = O, S, Se) have been synthesized mainly in relation to the creation of new redox systems.[1,2] However, neither hydrocarbon 3,5-dimethylenecyclopentene **2** nor the fully conjugated ions and radical from it has been reported at all. According to the simple Hückel MO calculation, 3,5-dimethylenecyclopentenyl radical **3** has a non-bonding molecular orbital (NBMO) without atomic orbitals at the C-1, 2, 3 and 5 positions (Fig. 1). The NBMO is thus similar to that of pentadienyl radical, although other molecular orbitals are dissimilar. In this context, the ionic species of **3** would be also interesting molecules. We report here the synthesis and properties of 3,5-bis(diphenylmethylene)cyclopentenyl anion **4** and cation **5**.



1: X = O, S, or Se
2: X = CH_2, R = H



4: anion
5: cation

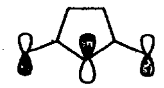
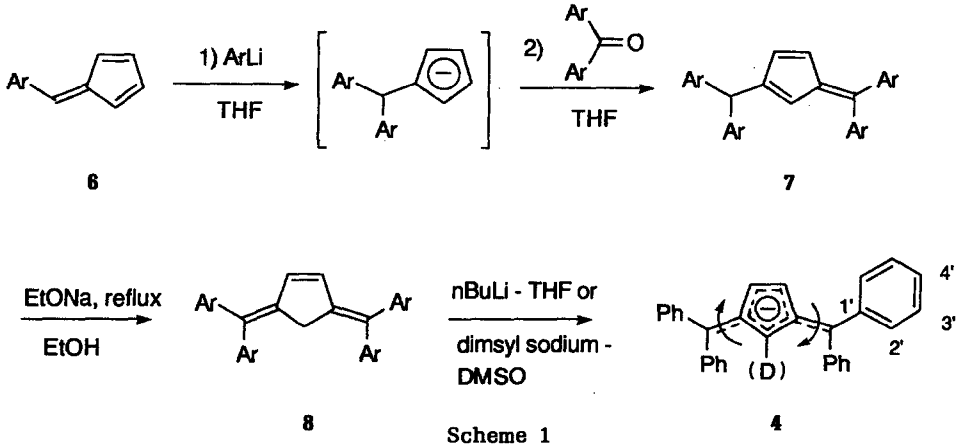


Fig. 1 NBMO of **3**

The successive reaction of 6-phenylfulvene **6**[3] with phenyllithium and then benzophenone in one-pot procedure selectively afforded 2-diphenylmethyl-6,6-diphenylfulvene **7**[4] in 53% yield. The 1-diphenylmethyl isomer of **7** was not formed at all probably owing to the severe steric hindrance by the existing diphenylmethylene group. Treatment of **7** with sodium ethoxide in ethanol effected double bond migration to give 3,5-bis(diphenylmethylene)cyclopentene **8**[4] in 95% yield (Scheme 1). In a similar way, the corresponding tetra-p-tolyl compound was obtained in total yield of 24%.

The base-induced clean isomerization of **7** to **8** suggests fairly ready formation of anion **4** and its regioselective reactions with electrophiles at the C-4 position. Indeed, treatment of **7** or **8** with either n-BuLi in THF at 0 °C or dimsyl sodium in DMSO at room temperature under nitrogen cleanly furnished anion **4** in deep greenish solutions. Anion **4** is thermally appreciably stable in the solutions under inert gas atmosphere; for example, heating of the DMSO solution at 100 °C for 1 h caused little decomposition as judged from the ^{1}H NMR spectra.



Scheme 1

Figure 2 shows ^{1}H NMR spectra of **4** in DMSO-d_6 at 30 and 110 °C. The two triplet signals at 6.71 and 6.84 at 30 °C, which are assigned to the phenyl para protons, coalesced at 75 ± 2 °C and are on the way to single sharp triplet at 110 °C. This NMR change is explained in terms of the rotation of the exomethylene double bonds. The substantially small free energy of activation, $\Delta G^{\ddagger}$ (348 K) = 17.5 ± 0.2 kcal/mol, indicates a considerable delocalization of the negative charge throughout the tetraphenylpentadienyl part. The variable temperature ^{1}H NMR measurements also revealed gradual exchange of the proton at C-4 position (δ 5.64) with deuterium from the solvent. This slow regioselective proton-deuterium exchange in DMSO at the elevated temperatures points to appreciably greater acidity of the precursor hydrocarbons **7** and **8** than DMSO (pKa = 35[5]).

^{13}C NMR spectrum of **4** is more informative on its electronic structure (Table 1); while the carbons at 4, 6 and 7 positions appear at appreciably high field (δ 90.36 and 110.19) in agreement with the expected increase of electron density, the carbons at 1 and 2 positions shift inversely to lower field (δ 145.44) compared to the corresponding carbons of **8**. Thus, anion **4** can be regarded as a conformationally fixed pentadienyl anion only weakly perturbed by a double bond fused at its 2 and 4 positions. This conclusion may also hold for the parent anion.

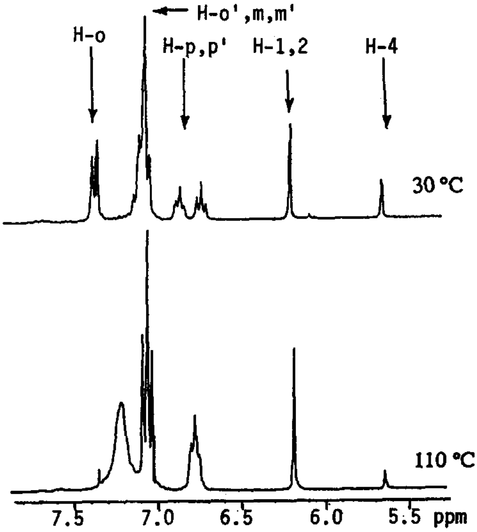
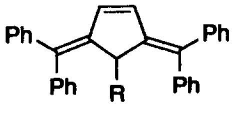


Fig. 2 ^{1}H NMR spectra of **4** at 270 MHz in DMSO-d_6

Table 1. ^1H and ^{13}C NMR spectral data of **4** and **8** (δ ppm, 30 °C)[a]

Compd	Position / Chemical shift	1,2	3,5	4	6,7	1'	2',6'	3',5'	4'
8[b,c]	^1H	6.70	—	3.59	—	—	7.18 ~ 7.33		
	^{13}C	138.19	132.49[d]	36.90	143.02[d]	142.51[d]	129.41	127.99	126.59
						142.61[d]	130.31	128.13	126.71
4[e]	^1H	6.18	—	5.64	—	—	ca.7.05	7.05	6.71
							7.34		6.84
	^{13}C	145.33	129.42	90.36	110.15	145.58	127.09	129.25	120.67
						145.94	127.27	130.38	121.60

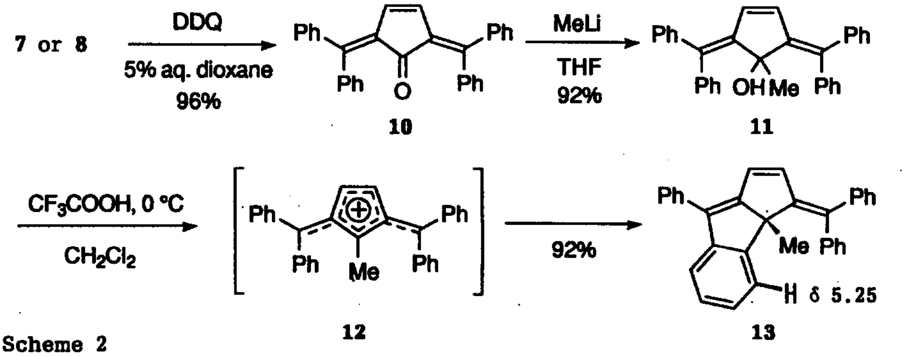
[a] At 270 or 67.5 MHz. [b] In $CDCl_3$. [c] $J_{1,4} = J_{2,4} = 1.5$ Hz, $J_{2',3'} = 7.0$ Hz, $J_{3',4'} = 7.2$ Hz. [d] Tentative assignment for these quarternary carbons. [e] In DMSO-d_6



9a: R = CH_3
9b: R = $Si(CH_3)_3$

Upon reaction with methyl iodide or chlorotrimethylsilane, **4** furnished 4-methyl (95% yield) or 4-trimethylsilyl compound (85%), **9a** or **9b**[6], regioselectively in accordance with the charge distribution based on the ^{13}C chemical shifts as well as the result of base-induced isomerization. With benzophenone as a weak electrophile, however, **4** almost remained unreacted at room temperature.

Both triene **7** and **8** were readily oxidized with dichlorodicyano-p-benzoquinone (DDQ) in 5% aqueous dioxane at room temperature to give ketone **10**[6] in 96% yield (Scheme 2). This smooth oxidation of the trienes with DDQ suggests some stabilization of cation **5** that is to be formed as an intermediate by hydride abstraction from the trienes.[7]



Scheme 2

Cyclic voltammetry of **10** (DMF, -50 °C) showed a quasi-reversible voltammogram with some amphoteric properties (E_1^{red} = -1.43 V, E_2^{red} (peak) = -2.05 V; E_1^{ox} (peak) = 1.38 V vs. Ag/AgCl). The first reduction potential is lower than that of benzophenone (-1.73 V) and almost the same with 6,6-diphenylfulvene (-1.44 V).[8] On dissolution in trifluoroacetic acid, **10** turned from light yellow to deep red (λ_{max} = 475 and 556 sh nm), to suggest the formation of the protonated cation.[9]

Accordingly, the generation of cations **12** and **5** were attempted. Treatment of alcohol **11**,[6] obtained by reaction of **10** with methyllithium, with trifluoroacetic acid in dichloromethane at 0 °C, however, formed **12** only as a reactive intermediate leading to tricyclic hydrocarbon **13**[6] (92% yield) in which one of the benzo protons is highly shielded (δ 5.25) by the nearby phenyl group (Scheme 2). Attempts to observe **12** by NMR spectroscopy at low temperatures down to -30 °C have been unsuccessful. Similar results were obtained for the generation of **5**. Thus, cations **5** and **12** are not stable enough for spectral characterization. Since these cations should not share any strong electronic destabilization, similar to pentadienyl cation, their facile cyclization might be ascribed to the kinetically favorable structures for the intramolecular cyclization.

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References and Notes

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2. K. Takahashi, T. Suzuki, K. Akiyama, Y. Ikegami, and Y. Fukazawa, *J. Am. Chem. Soc.*, **113**, 4576 (1991).
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4. Selected physical data; **7**: mp 136.5-137.5 °C, ^{1}H NMR (270 MHz, $CDCl_3$) δ 5.22 (1H, s), 5.89 (1H, dd, J = 2.0, 1.6 Hz), 6.27 (1H, dd, J = 5.3, 2.0 Hz), 6.42 (1H, dd, J = 5.3, 1.6 Hz), 7.18-7.36 (20H, m); **8**: mp 178-179 °C, UV λ_{max}(EtOH) 253 (log ε 4.23), 360 nm (4.54).
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6. Selected physical data; **9a**: mp 173.5-175.0°C, ^{1}H NMR ($CDCl_3$, 270 MHz) δ 0.64 (3H, d, J = 6.9 Hz), 4.23 (1H, q, J = 6.9 Hz), 6.67 (2H, s), 7.10-7.30 (20H, m); **9b**: mp 176.5-177.0 °C, ^{1}H NMR ($CDCl_3$) δ -0.40 (9H, s), 4.61 (1H, s), 6.73 (2H, s), 7.18-7.31 (20H, m); **10**: mp 221.5-223 °C. ^{1}H NMR ($CDCl_3$) δ 6.84 (2H, s), 7.20-7.37 (20H, m), IR (KBr disc) ν 1703 cm^{-1}(C=O), UV λ_{max} (hexane) 249 (log ε 4.37), 314 (4.45), 354 nm (4.35); **11**: mp 173.5-175.0 °C, ^{1}H NMR ($CDCl_3$) δ 1.23 (3H, s), 1.87 (1H, s), 6.50 (2H, s), 7.17-7.36 (20H, m); **13**: mp 63.5-65.0 °C, ^{1}H NMR ($CDCl_3$) δ 1.70 (3H, s), 5.25 (1H, d, J = 7.6 Hz), 6.66 (1H, t, J = 7.6 Hz), 6.73 (1H, d, J = 5.6 Hz), 6.80 (1H, d, J = 5.6 Hz), 7.04 (1H, t, J = 7.6 Hz), 7.11-7.42 (14H, m), 7.57 (2H, d, J = 7.6 Hz), ^{13}C NMR ($CDCl_3$) δ 33.2, 64.7, and 24 signals for the sp^2 carbons.
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8. T. Kawase, S.Fujino, and M. Oda, *Chem. Letters*, **1990**, 1683.
9. Reasonable NMR spectra of this solution has not been obtained because of poor solubility of **10** in trifluoroacetic acid.

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