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THE SYNTHESIS OF HEPTATRIDECAFULVALENE DERIVATIVES[1]

Toyonobu Asao, Noboru Morita

Department of Chemistry, College of General Education, Tohoku University
Kawauchi, Sendai 980 Japan

Jūro Ojima and Masamitsu Fujiyoshi

Department of Chemistry, Faculty of Science, Toyama University
Gofuku, Toyama 930 Japan

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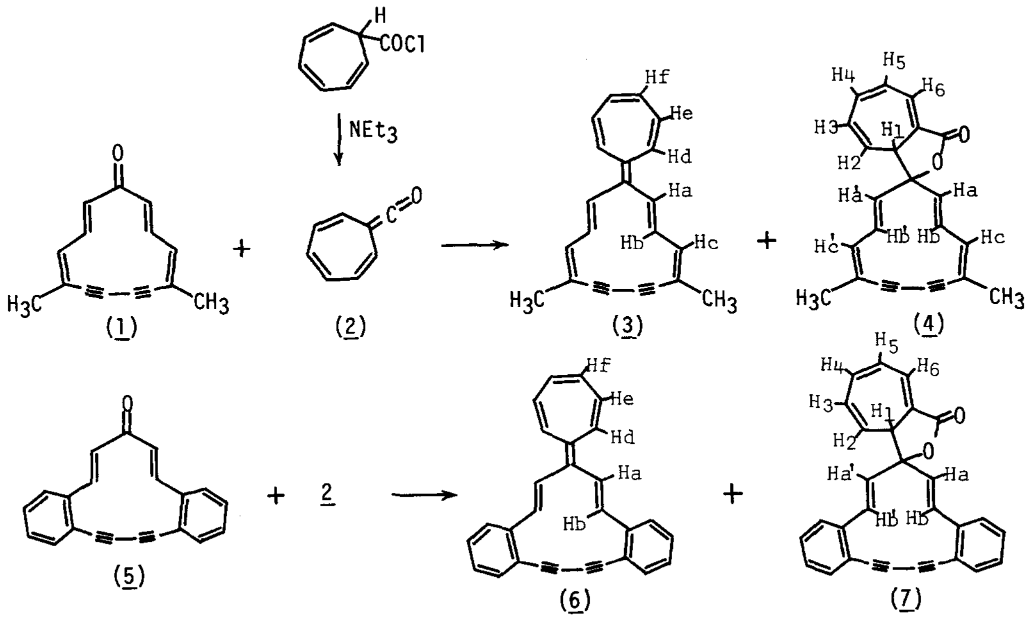
In recent year, theoretical and experimental studies on the bicyclic polyenes containing a cyclic cross-conjugated π-electron system, fulvalene, have been extensively investigated.[2] One group (A) of these compounds, in which one ring is (4n + 1) membered and the other is (4n + 3) membered such as sesquifulvalene, is potentially aromatic since polarization of the central double bond will make both rings (4n + 2) π-electron systems. The other group (B), in which both rings are (4n + 1) or (4n + 3) membered such as pentafulvalene or heptafulvalene, is not potentially aromatic since polarization of the central double bond will make one ring a (4n + 2) system, but the other a (4n) system. The only known macrocyclic compounds of these types are derivatives of pentaundecafulvalene[3] belonging to the group (A) and derivatives of pentatridecafulvalene,[4] pentaphenafulvalene[5] and undecafulvalene[6] belonging to the group (B).

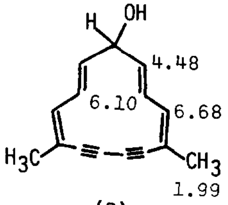
We have investigated the synthesis of fulvalene containing cycloheptatrienylidene moiety by the reaction of 8-oxoheptafulvene with various annulenones.[7] Reaction of 8-oxoheptafulvene with [13]annulenone may give heptatridecafulvalene belonging to the group (A). We wish to report a synthesis and properties of heptatridecafulvalene derivatives.

The reaction of 5,10-dimethyl-6,8-bisdehydro[13]annulenone (1)[8] and 8-oxoheptafulvene (2) formed *in situ* from cycloheptatrienyl-7-carbonyl chloride and triethylamine in anhydrous benzene at 80°C for 0.5 hr afforded unstable reddish needles (3), color changed from around 110°C and decomposed without melting, and pale yellow prisms (4), mp 159~160°C (decomp.), in 3.9% and 41%, respectively, after purification by column chromatography on alumina. Similarly, the reaction of dibenzo[d,j]-6,8-bisdehydro[13]annulenone (5)[9] and 2 afforded moderately stable crystals (6), decomposed from around 150°C without melting, and pale yellow crystals (7), mp 191~194°C,



in 23.8% and 14%, respectively.

Mass spectra of 3 and 6 show their parent ion peaks at 282 and 354, respectively, and IR (KBr) of 3 and 6 display acetylenic bands at 2140 and 2175 cm^{-1}, respectively. In the UV sepctra (Fig. 1) of 3 and 6, the longest maxima occurred at 459 and 422 nm, respectively, demonstrating that 3 must be more highly delocalized system than benzannelated compound (6) as was similarly observed between 1 and 5.[10] Table 1 shows ^{1}H-NMR of 3 and 6, and the differences between the chemical shifts of the corresponding protons of 1,[8] 3, 5,[9] 6, alcohol (8),[11] sesquifulvalene (9)[12] and heptafulvalene (10).[1, 13] Spectral data of 4 and 7 were shown in Table 2.



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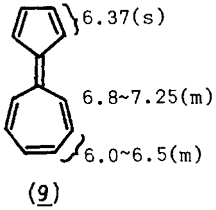

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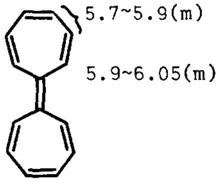

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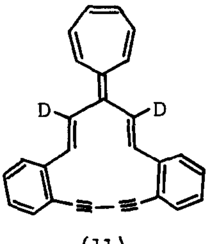

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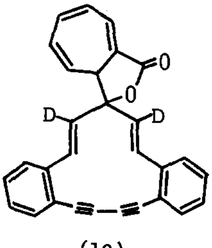

(12)

Chemical shifts assignments of Ha and Hb of 6, and Ha, Ha', Hb and Hb' of 7 were determined by the comparison with the spectra of specifically deuterated compounds (11 and 12)[14] which were synthesized from the corresponding deuterated [13]annulenone.[10]

The compounds 1 and 5 are reported to be weakly paratropic in the order of 1 > 5. However, a polarization of π-electron from 7-membered ring to 13-membered ring of 3 and 5 will make the

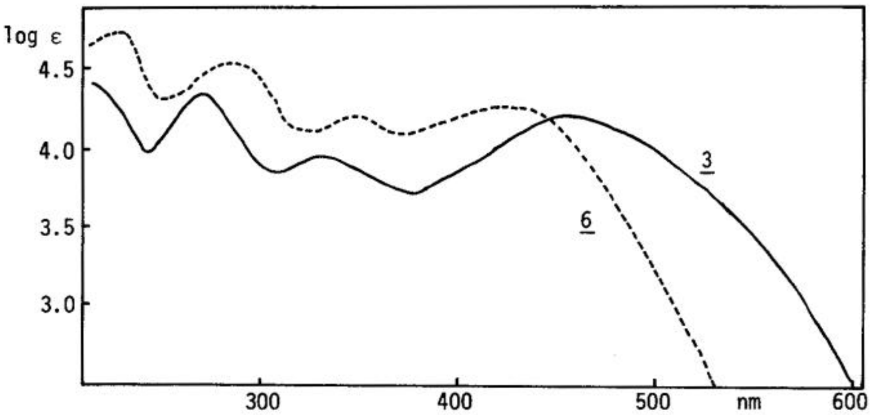

Fig 1. Electronic Spectra of 3 and 6 in EtOH.

Table 1. ^{1}H-NMR Chemical Shifts (δ ppm) of 1, 3, 5 and 6 in $CDCl_3$.*

Compd	Ha	Hb	Hc	Hd	He,f	CH_3	Benzenoid
1	6.10 (d,16.5)	9.39 (d,d,16.5,9.5)	6.29 (d,9.5)			1.74 (s)	
3	6.4~6.9(m)				5.8~6.2(m)	1.91(s)	
Δ(1-3)	-0.3~-0.8	2.5~3.0	-0.1~-0.6			-0.17	
Δ(8-3)			~0			0.08	
Δ(9-3)				*ca.* +0.4	*ca.* +0.3		
Δ(10-3)				*ca.* -0.5	*ca.* -0.2		
5	6.76(d,16)	8.47(d,16)					7.2~7.5(m)
6	6.87(d,17)	7.23(d,17)		6.53(bd,10)	6.1(m)		7.1~7.7(m)
Δ(5-6)	-0.11	1.24					
Δ(9-6)				*ca.* +0.4	*ca.* +0.1		
Δ(10-6)				*ca.* -0.5	*ca.* -0.3		

* Multiplicity and J values (Hz) are shown in parentheses.

Table 2. Spectral Data of 4 and 7.

4	Mass, m/e 326 (M^+); IR (KBr) 2170 cm^{-1}(C≡C), 1745 (C=O); UV λ_{max}^{EtOH} 258 nm (log ε 4.38), 316 (3.90); ^{1}H-NMR ($CDCl_3$) δ 1.93 (d,d, J=1, 1Hz, Me), 1.96 (d,d, 1, 1, Me), 3.14 (m, H_1), 5.17 (d,d, 15.5, 1, Ha), 5.21 (d,d, 15.5, 1, Ha'). 5.41 (d,d, 9.6, 4, H_2), 6.05 (d,d,q, 15.5, 5, 1, Hb or Hb'), 6.05 6.25 (m, H_3), 6.39 (d,d,q, 15.5, 5, 1, Hb' or Hb), 6.51 (d,d,q, 5, 1, 1, Hc or Hc'), 6.63 (d,d,q, 5, 1, 1, Hc' or Hc), 6.75 (m, $H_{4,5}$), 7.14 (m, H_6)
7	Mass, m/e 398 (M^+); IR (KBr) 2190, 1745; UV λ_{max}^{EtOH} 223 (4.81), 259 (4.52), 273 (4.50), 321 (4.18), 341 (4.16); ^{1}H-NMR ($CDCl_3$) δ 3.01 (m, H_1), 5.44 (d,d, 10, 4, H_2), 6.22 (d,m, 10, H_3), 6.39 (d, 16, Ha), 6.46 (d, 16, Ha'), 6.65 (d, 16, Hb or Hb'), 6.78 (m, $H_{4,5}$), 6.91 (d, 16, Hb' or Hb), 7.22 (m, H_6, benzenoid H)

both rings diatropic; the former 6π and the latter 14π systems.

Comparison of the chemical shifts of the various protons of 13-membered rings of the fulvalenes (3 and 6) with those of the annulenones (1 and 5) shows that the inner protons of the fulvalenes resonate higher fields in the value of 1.2~3.0 ppm, and the outer protons and methyl protons resonate slightly lower fields. However, no significant differences between Hc and methyl protons of 3 and olefinic alcohol (8)[11] were observed. Furthermore, comparison of 7-membered ring protons of 3 and 6 with those of sesquifulvalene (9) (group A) and heptafulvalene (10) (group B) shows that those of 3 and 6 resonate at slightly higher fields than 9 and slightly lower fields than 10, which does not show a more extensive charge separation than is found in 9.

These observations indicate that paratropicity of 13-membered ring system disappears in the fulvalenes and 7-membered ring system shows very weak diatropic property, therefore, it can be assumed that the fulvalenes are olefinic rather than aromatic, although further study is needed to conclude their tropicities.

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