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THE SYNTHESIS OF HEPTATRIDECA-, HEPTAPENTADECA-, AND HEPTAHEPTADECAFULVALENE DERIVATIVES(1)

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Title fulvalenes (6~9) were synthesized in one step by the reaction of the corresponding large membered annulenones (1~4) with 8-oxoheptafulvene, and ^{1}H-nmr spectra were discussed in connection with their tropicity.

We have reported the synthesis of dimethyl and dibenzo derivatives of bisdehydroheptatridecafulvalene by the reaction of the corresponding annulenones with 8-oxoheptafulvene.(2) In this paper, we will report further studies on the synthesis and properties of heptatrideca-, heptapentadeca-, and heptaheptadecafulvalene derivatives which belong to group A, B, and A, respectively.(3)

The synthesis was accomplished by the similar method to our previous report,(2) and we have obtained the objective fulvalenes in moderate yields. Thus, the reaction of 10-methylbenzo[d]-6,8-bisdehydro[13]annulenone (1),(4) 5,10-dimethyl-6,8-bisdehydro[15]annulenone (2),(5) 5,10,15-trimethyl-6,8-bisdehydro[15]annulenone (3),(6) and 7,12-dimethyl-8,10-bisdehydro[17]annulenone (4)(5) with 8-oxoheptafulvene (5) formed *in situ* from cycloheptatriene-7-carbonyl chloride and triethylamine in anhydrous benzene at 80°C afforded the corresponding heptatrideca- (6), heptapentadeca- (7 and 8), and heptaheptadeca- (9) fulvalene derivatives, as moderately stable dark reddish crystals in the yields of 67, 30, 86, and 52%, respectively. In these reactions, no spiro compound by [2 + 8] cycloaddition was formed.(7)

The structures of these fulvalenes were established by their spectroscopic data shown in Table 1.

In the electronic spectrum of 6, the longest maximum was observed at 448 nm, the value of which is between those of 4,9-dimethyl-5,7-bisdehydroheptatrideca-

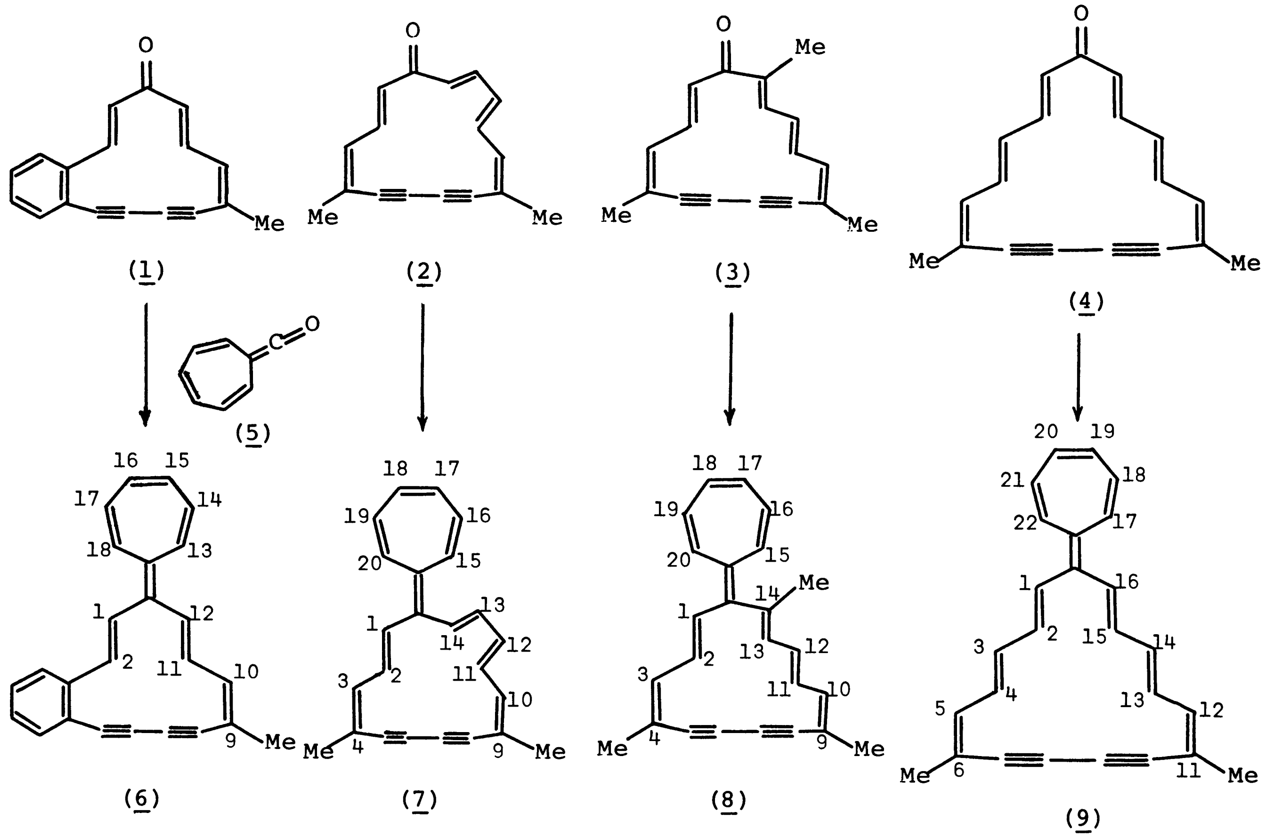

Table 1. Melting Points and Spectral Data of Fulvalenes (6, 7, 8, and 9)

Compd.	Mp(°C)	Mass (%)	Ir (cm^{-1})	Es [λ_{max}^{EtOH} nm (log ε)]	^{1}H-Nmr in $CDCl_3$ (δ ppm, J in Hz)
6	150(d)	318(M$^+$,77) 303(58) 302(100)	2100[a] 2160	274(4.55) 334(4.22) 448(4.33)	1.9 (s, Me), 6.1 (m, H-14,15,16, 17), 6.4~7.2 (m, H-1,2,10,11,12,13, 18), 7.21 (m, benzenoid-3H), 7.56 (dm, J=9, benzenoid-1H)
7	100~101	308(M$^+$,100) 293(38) 278(55)	2160[a]	282(4.48) 366(4.32) 415(4.37)	1.82 (s, Me-4,9), 5.73 (ddd, H-16, J=12,5.5,3.5), 5.75 (ddd, H-19, J=11.5,5,3.5), 5.92 (dd, H-17,18, J=5,3.5), 6.27 (d, H-15, J=12), 6.44 (d, H-20, J=11.5), 6.30~6.57 (m, H-1,3,10,12,13), 7.24 (d, H-14, J=15.5), 7.66 (dd, H-2, J=15,11.5), 7.69 (dd, H-11, J=14.5,11)
8	99~100	322(M$^+$,71) 307(71) 292(83) 291(100) 277(67)	2170[b]	284(4.26)^{sh} 360(4.42) 441(4.20)	1.85 (s, Me), 1.87 (dd, Me, J=1.5,1.5), 1.94 (d, Me-14, J=1.5), 5.63 (ddd, H-16, J=12,5,4.5), 5.75 (ddd, H-19, J=11.7,5.2,3.7), 5.85 (m, H-17,18), 5.90 (d, H-10, J=10), 6.14 (d, H-15, J=12), 6.19 (dd,H-12, J-15.5,5), 6.34 (d, H-20, J=11.5), 6.49 (d, H-13, J=5), 6.51 (d, H-1, J=15), 6.56 (dd, H-3, J=11.5, 1.5), 6.81 (ddd, H-11, J=15.5, 10,1), 6.95 (dd, H-2, J=15,11.5)

9	180~181 (d)	334(M$^+$,100) 319(58)	2165^a	295(4.46) 361(4.38) 487(4.33)	2.00 (s, Me), 5.85 (ddd, H-18, J=11.5,4.5,4), 5.96 (dd, H-19, J=4.5,4), 6.07 (dd, H-2, J=15.5,10), 6.27 (d, H-1, J=15.5), 6.33 (dd, H-4, J=15,11), 6.44 (d, H-17, J=11.5), 6.61 (dd, H-3, J=15,10), 6.78 (dm, H-5, J=11)

a; in KBr disk. b; in CCl_4.

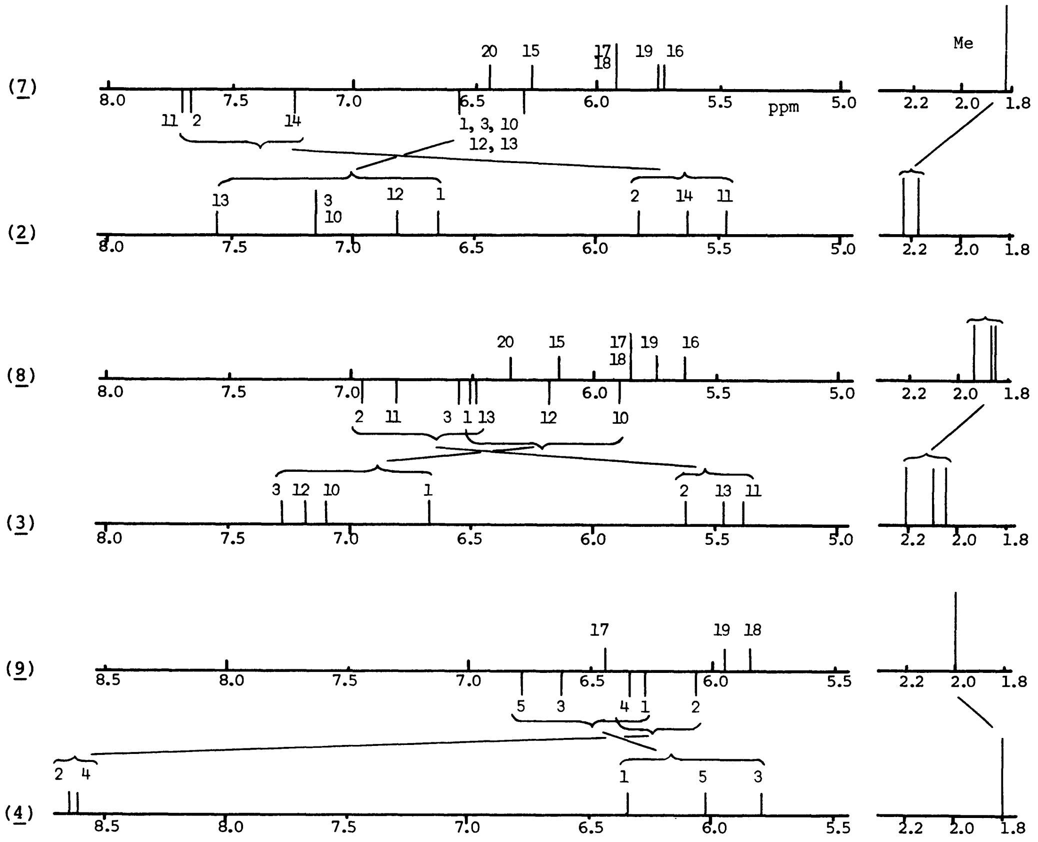

Fig. 1. Chemical Shift Diagram of ^{1}H-nmr of 2~4 and 7~9.

fulvalene (10) (459 nm)2) and dibenzo[d,j]-5,7-bisdehydroheptatridecafulvalene (11) (422 nm).2) The similar order was observed between the corresponding annulenones.4) This indecates that the condensed benzene ring inhibits the delocalization of π-electron, and π-electron delocalization would decrease in the sequence 10 > 6 > 11.

Mass spectra of these fulvalenes show their parent ion peaks, and ir spectra display acetylenic bands around 2160~2170 cm^{-1}. ^{1}H-Nmr of 6 could not be fully assigned, but by passing from the annulenone (1) to the fulvalene (6) a small down field shift of methyl proton resonance (0.08 ppm) does not show a more charge separation in 6 than that is observed in 10.2) However, ^{1}H-nmr of 7, 8, and 9 taken at 200 MHz were assigned by intensive decoupling techniques, and the differences between the chemical shifts of the fulvalenes and the corresponding annulenones can be clearly seen from Fig 1 which shows chemical shift diagram of ^{1}H-nmr of the fulvalenes (7~9) and the annulenones (2~4).

The diagram indicates that outer protons of 7 and 8 appear at higher field of 0.21~1.19 ppm than those of 2 and 3, and inner protons of 7 and 8 resonate at lower field of 1.02~2.22 ppm than those of 2 and 3, although downfield shift of inner protons by anisotropy of acetylenic bonds must be considered. Furthermore, methyl signals of 7 and 8 resonate at slightly higher field than those of 2, 3, and open-chain precursors of the annulenones.[5,6] These changes of the chemical shifts can be explained by considering that 15-membered rings of 7 and 8 are very weakly paratropic. Seven membered rings of 7 and 8 resonate at higher and lower fields than those of sesquifulvalene (pentaheptafulvalene; group A)[2] and heptafulvalene (group B),[2] respectively, which indicates that the seven membered rings of 7 and 8 are slightly diatropic. From these facts, it can be considered that a very little π-electron polarization from 7-membered ring to 15-membered ring occurs in the fulvalenes.

The similar study of ^{1}H-nmr of 4, 9, and pentaheptadecafulvalene derivative [8] shows that both of 7- and 17-membered rings in 9 are diatropic rather than atropic, therefore, a very little π-electron polarization from 7-membered ring to 17-membered ring would occur in the fulvalene (9).

References and Notes

1) Part XI in the series of "8-Oxoheptafulvene," the preceding part X, T. Asao, N. Morita, and K. Kato, Heterocycles, 11, 287 (1978).

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3) See ref. 2); Group A is potentially aromatic fulvalenes in which one ring is (4n + 1) membered and the other is (4n + 3). Group B is not potentially aromatic fulvalenes in which both rings are (4n + 1) or (4n + 3) membered.

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