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ELECTROPHILIC SUBSTITUTION REACTION OF MESO-IONIC SESQUIFULVALENE

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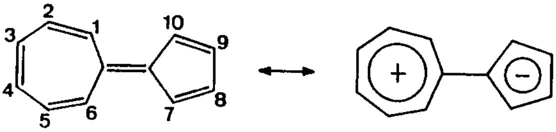
Summary: The aromatic character of the meso-ionic sesquifulvalene (2) is demonstrated by six electrophilic substitution reactions on the cyclopentadienide ring.

Sesquifulvalene (1) is a cross-conjugated π-electron system of theoretical interest because of the potential contribution of the polarized structure to its ground state.1) Experimental studies,2) however, demonstrated that 1 is polyolefinic rather than aromatic. On the other hand, recently synthesized meso-ionic sesquifulvalene (2), which is an isoelectronic π-system with 1, has been shown to be best expressed by the dipolar tetrazolium-cyclopentadienide structure.3) It is of considerable interest to investigate the chemical behavior of 2, especially to determine whether 2 reacts as an aromatic system or not. We now examined the reactions of 2 toward dienophiles and electrophiles, and found that 2 has an aromatic character.



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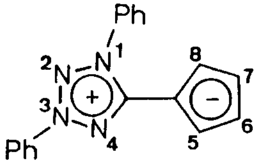


2

Sesquifulvalene derivatives such as 7,9-di-t-butylsesquifulvalene4) and 1,2-dimethoxycarbonyl-8,9-diphenylsesquifulvalene5) are known to undergo [12π + 2π] cycloaddition with tetracyanoethylene (TCNE). In order to examine the olefinic character of the meso-ionic sesquifulvalene (2), we first investigated the reaction of 2 with TCNE. When TCNE was added to a dichloromethane solution of 2, the wine-red color of 2 immediately turned to violet probably due to the formation of a charge-transfer complex of 2 with TCNE. Attempts to isolate the CT-complex were failed. However, when the reaction mixture was chromatographed on alumina, orange-red crystals of the tricyanovinyl compound (3) (mp 276°C) were obtained in 8.2% yield.6) The ^{1}H-nmr (d_6-DMSO, 110°C) of 3 shows that the tricyanovinyl group is attached to the 6-position.7) The three cyclopentadienide protons of 3 appeared at δ 6.91(t,1H,J=2.1 Hz), 6.75(dd,1H, J=4.8, 2.1 Hz), and 6.33(dd,1H,J=4.8, 2.1 Hz). The triplet at the lowest magnetic field (δ 6.91) was assigned to H^5, which is most deshielded due to the two adjacent electron-withdrawing substituents (tricyanovinyl and tetrazolium) and has a smaller coupling constant ($J_{57}=J_{58}=2.1$ Hz). The proton appeared at δ 6.33 was assigned to H^8 because of its comparable chemical shift to that of the parent fulvalene (2) (δ 6.20).[3] The signal at δ 6.75 was assigned to H^7 which is somewhat more deshielded than H^8 due to the tricyanovinyl group. The product (3) is considered to be formed via Michael addition reaction followed by elimination of hydrogen cyanide. The rest of the reaction mixture was a black intractable tar, from which any characterized substance was not isolated. The above result indicates that, in contrast with sesquifulvalene, the meso-ionic fulvalene (2) does not exhibit an olefinic character.

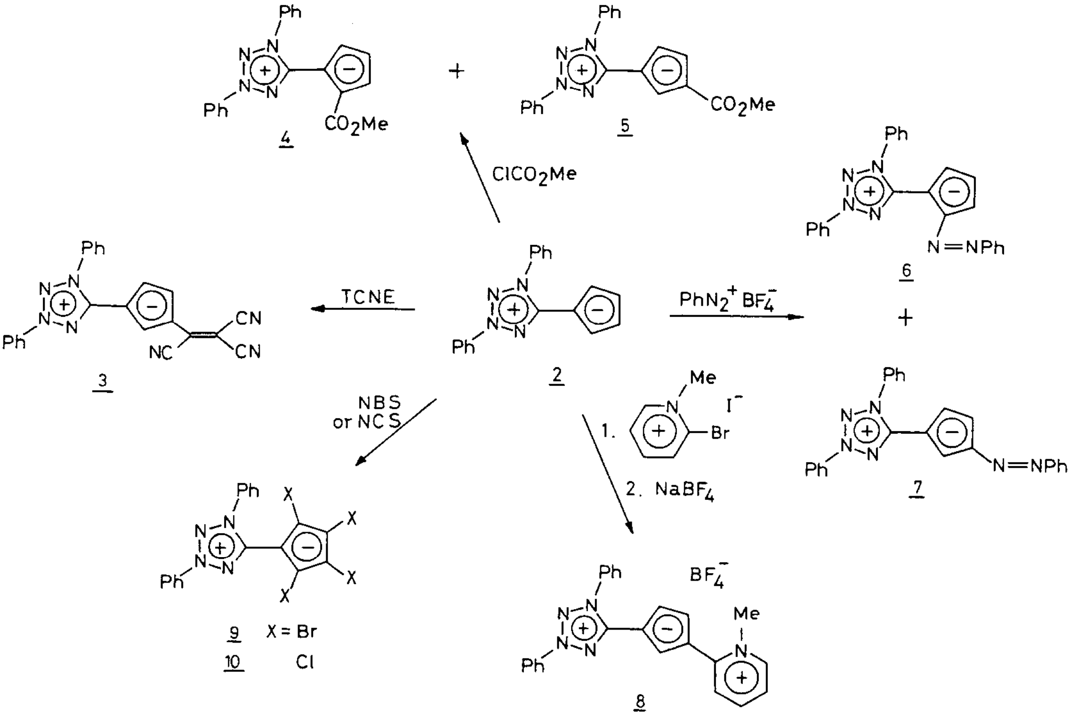
As a next step, the reactions of 2 with several electrophiles were carried out in order to elucidate the aromatic character. Treatment of 2 with methyl chloroformate in the presence of anhydrous pottasium carbonate afforded a 3:1 mixture of the 5- and 6-methoxycarbonylated fulvalenes (4 and 5) in 41% combined yield. The separation of 4 and 5 was achieved by fractional recrystallization from acetone-hexane. The major isomer, deep red solid (mp 85°C), was assigned as the 5-methoxycarbonyl derivative (4) on the basis of the following ^{1}H-nmr spectral data in $CDCl_3$: δ 8.20(m,2H,Ph), 7.8-7.4(m,8H,Ph), 6.87(dd,1H,H^6,J=3.4, 2.2 Hz), 6.45(dd,1H,H^8,J=3.7, 2.2 Hz), 6.10 (bt,1H,H^7,J=3.7, 3.4 Hz), and 3.40(s,3H,CO_2CH_3). The minor isomer (5), deep red needles (mp 206°C), exhibited ^{1}H-nmr signals at δ 8.20(m,2H,Ph), 7.65(m,8H,Ph), 6.92(bt,1H,H^5,J=2.4, 2.0 Hz), 6.49(dd,1H,H^7,J=4.4, 2.0 Hz), 6.03(dd,1H,H^8,J=4.4, 2.4 Hz), and 3.69(s,3H,CO_2CH_3).

When 2 was treated with phenyldiazonium tetrafluoroborate in methanol, diazonium coupling occurred. The 5- and 6-phenylazo derivatives (6 and 7) were isolated from the reaction mixture by fractional recrystallization from ethanol in 3% and 35% yields, respectively. The black powder (dark red in solution) of 6 (mp 190°C (dec)) showed signals in its ^{1}H-nmr ($CDCl_3$) at δ 6.83(dd,1H,H^6,J=3.6, 2.1 Hz), 6.31(dd,1H,H^8,J=3.8, 2.1 Hz), and 6.20(bt,1H, H^7,J=3.8, 3.6 Hz) together with phenyl multiplets at δ 7.1-7.9(13H) and 8.1-8.4(2H). This indicates that 6 is the 5-substituted product. The ^{1}H-nmr (CD_3OD) of 7 (red plates, mp 220°C (dec)) showed doublets of doublet at δ 6.72(J=5.2, 3.1 Hz) due to the H^8 proton. The H^5 and H^7 signals were obscured by the complex multiplet of the phenylazo group at δ 6.9-7.4. It is interesting to note that the present diazonium coupling occurred preferentially at the 6-position of 2. This result contrasts to the facts that the similar dipolar mesomeric systems such as diazocyclopentadiene,[8] and phosphonium,[9] sulphonium,[10] and arsonium cyclopentadienylides[11] all undergo diazonium coupling at the 5-position of the cyclopentadienide ring.

The reaction of 2 with N-methyl-2-bromopyridinium iodide in DMF gave, after the treatment with aqueous sodium tetrafluoroborate, the tripolar mesomeric compound (8) as the tetrafluoroborate salt (orange crystals, mp 206°C) in 70% yield: ^{1}H-nmr (d$_6$-DMSO) δ 8.28(m,3H), 7.87(m,10H), 7.22(m,1H), 6.68(bt,1H,H^5,J=2.3, 2.0 Hz), 6.51(dd,1H,H^7,J=4.6, 2.3 Hz), and 6.10(dd,1H,H^8,J=4.6, 2.0 Hz). The corresponding 5-substituted product was not found in the reaction mixture. HMO calculation suggests that the 5(8)-position of 2 is more reactive than the 6(7)-position.12) Therefore, the observed preferential attack of the diazonium and the pyridinium ions to the 6-position should be attributable to the steric repulsion between the electrophiles and the phenyl group attached to N^1 of the tetrazolium ring in the transition state for the 5-position attack.

Reaction of 2 with four equiv. of N-bromosuccinimide in acetonitrile gave orange crystals of the tetrabromo derivative (9) (mp 175°C (dec)) in 71% yield. Similar reaction with N-chlorosuccinimide afforded unstable brick-red powder of the tetrachloro derivative (10) (mp 197°C (dec)) in 88% yield. The halogenation of 2 with even a small quantity of N-halosuccinimide also gave the tetrahalo derivatives.

In conclusion, the reaction behavior of 2 summarized in Scheme supports the aromatic character of the cyclopentadienide ring of 2.13)



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6) All new compounds synthesized in this paper were fully characterized by their spectra (^{1}H-nmr, ir, and Mass). Also, their satisfactory elemental analyses were obtained except for the unstable **10**.
7) The numbering system of **2** is that adopted for sesquifulvalene.
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12) The superdelocalizabilities (S_E) and the free valences (F_r) calculated by HMO are as follows: 5(8)-position, S_E 1.498 and F_r 0.469; 6(7)-position, S_E 1.438 and F_r 0.431.
13) Nitration ($Cu(NO_3)_2 \cdot 3H_2O$-Ac_2O, $NO_2^{+}BF_4^{-}$), acetylation (Ac_2O-$SnCl_4$), and formylation ($POCl_3$-DMF) of **2** were also investigated but no characterized products were obtained.

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