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SYNTHESIS OF HEPTAFULVALENE AND SESQUIFULVALENE DERIVATIVES CONDENSED WITH A FURAN RING[**]

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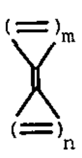
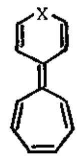
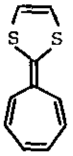
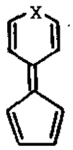
Heptafulvalenes (4 and 5) and sesquifulvalenes (8 and 9) condensed with a furan ring have been synthesized by the reaction of cyclic ketenes with furotropones. Physical properties of the fulvalenes were found to be considerably similar to those of the corresponding carbocyclic fulvalenes.

Carbocyclic fulvalenes (A) have been intensively studied from the standpoint of synthetic and theoretical interests.[1] However,


(A)


(B)
X = O, S


(C)


(D)
X = O, S, NR

[**] Dedicated to Professor Tetsuo Nozoe on the occasion of his 77th birthday.

few heterofulvalenes (e.g. B, C, and D)[2] and no fulvalenes condensed with heteroaromatics have been known.

In the present paper, the synthesis of heptafulvalenes and dibenzosesquifulvalenes condensed with a furan ring by the reaction of cyclic ketenes with furotropones, and the physical properties of the fulvalenes will be reported.

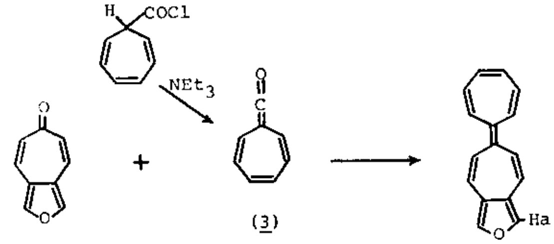
The reactions of [4,5-c] and [3,2-b]-furotropones (1[3] and 2[4]) with 8-oxoheptafulvene (3),[5] formed *in situ* by the reaction of cycloheptatriene-7-carboxylic acid chloride and triethylamine, in anhydrous benzene at 80 °C for 30 min afforded the corresponding fulvalenes (4; 35%, dark brown crystals, mp 150 °C (decomp.)) and (5; 60%, a dark brown oil), respectively, in one step.

The reaction of (1) with cyclopentadienide or tetrachlorocyclopentadienide gave neither sesquifulvalene derivatives (6) nor any other clear products.

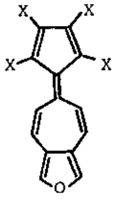
The reactions of (1 and 2) with diphenyleneketene (7),[6] formed from 9-chlorofluorene-9-carboxylic acid chloride and mercury, in anhydrous benzene at room temperature for 2 days afforded (8; 76%, orange needles, mp 104-105 °C) and (9; 20%, a brown oil), respectively.

The compounds (4 and 8) are moderately stable and the compounds (5 and 9) are somewhat unstable.

The [8 + 2]cycloadducts have been obtained as major products from the monocyclic annulenones,[6, 7] but no [8 + 2]cycloadducts such as (10) was isolated in the present case. This must be attributable to instability of quinonoid furan ring in [8 + 2] adducts as in the case of benzotropones.[6, 8]

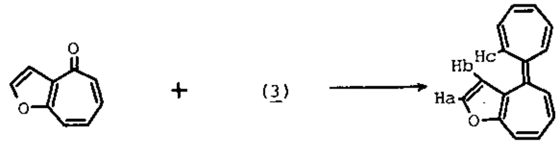


(1) (3) (4)

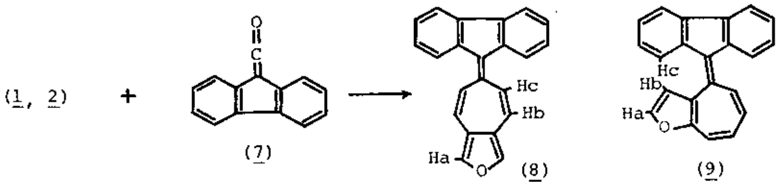


(6)

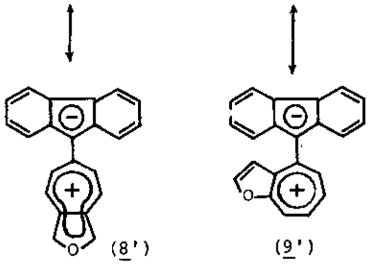
X = H, Cl



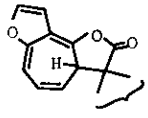
(2) (5)



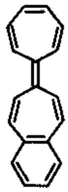
(7) (8) (9)



(8') (9')



(10)



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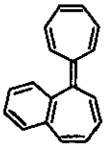

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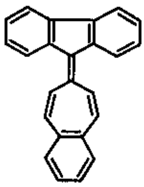

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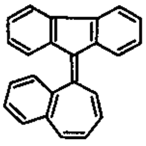

(14)

Table 1. Spectroscopic Data of Furofulvalenes (4, 5, 8, and 9).

Compds.	UV λ_{max}(log ε)^a	IR cm^{-1} ^{b}	NMR (δ, J in Hz)$^{c, d}$	M^+
4	248 (4.43)sh 250 (4.45) 368 (4.48)	1620, 1540 1120, 1040 880, 800 720	6.16-6.33 (m, 10H) 7.20 (s, 2H, Ha) Δ +0.86	220
5	241 (4.29) 294 (3.77) 355 (4.22) 450 (3.15)sh	1560, 1492 1458, 1075 790, 716	5.6-6.1 (m, 9H) 6.5 (m, Hc) 6.49 (d, J=2, Hb) Δ +0.65 7.31 (d, J=2, Ha) Δ +0.39	220
8	230 (4.54)sh 249 (4.68) 274 (4.27)sh 390 (4.36) 425 (4.29)sh	1620, 1498 1446, 1047 896, 878 827, 775 730	6.50 (d, J=12, Hc) 7.12 (d, J=12, Hb) 7.11-7.22 (m, 4H) 7.34 (s, Ha) Δ +0.72 7.59-7.69 (m, 2H) 7.83-7.91 (m, 2H)	294
9	238 (4.74) 290 (3.94)sh 382 (4.10) 460 (3.69)sh	1570, 1500 1442, 1068 908, 714	6.2-6.5 (m, 2H) 6.45 (d, J=2, Hb) Δ +0.69 6.7-7.3 (m, 9H) 7.20 (d, J=2, Ha) Δ +0.5 7.95 (m, Hc)	294

a; 4 and 5 in EtOH, 8 and 9 in MeOH.
b; 4 and 8 in KBr disk, 5 and 9 in neat.
c; 4, 8, and 9 in CDCl$_3$, 5 in CCl$_4$.
d; Δ; differences in chemical shift of furan ring protons from those of the corresponding furotropones (1 and 2).

Spectroscopic data of these furofulvalenes were shown in Table 1.

Electronic spectra of furofulvanenes (4, 5, 8 and 9) show similar patterns to those of the corresponding benzo-annelated derivatives (11, 12, 13, and 14),[6, 8] respectively, except that (9) shows considerable bathochromic shift (ca. 40 nm) of longer wave maximum compared with that ot (14).

Patterns of ^{1}H-NMR of the furofulvalenes are also similar to those of the corresponding benzofulvalenes, respectively.

The chemical shifts of furan ring protons of the furofulvalenes shifted to higher fields (0.4-0.86 ppm) compared with those of (1 and 2).

The fulvalenes (4 and 5) are conceivable as iso-π-electronic oxa-analogs of heptaundecafulvalene and are not potentially aromatic. On the other hand, the fulvalenes (8 and 9) are conceivable as iso-π-electronic analogs of pentaundecafulvalene and are potentially aromatic if they are largely contributed from dipolar structures (8' and 9') having (4n + 2) π-electron system in both rings. Their NMR data, however, suggested little contribution of (8' and 9').

Attempted protonation of (8 and 9) with CF_3COOD or conc D_2SO_4 resulted in the decomposition of the compounds.

References

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6 This method which we have devised for the synthesis of dibenzosesquifulvalenes by the reaction of (7) with annulenones was applied to furotropones; M. Yagihara, Dissertation, Tohoku University (1974).

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