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BENZOLOGS OF PENTANONA- AND HEPTANONA-FULVALENES[1]

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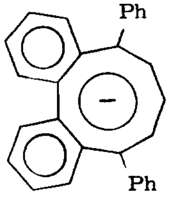
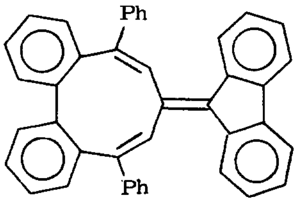
[m,n] Fulvalenes[2] can be divided into two categories: (a) those having an "aromatic potential" i. e. proved to contribute significantly to a dipolar ground state, e. g. [3,5], [5,7] and [5,11][2b] fulvalenes; (b) [3,3],[3] [5,5], [3,7],[3] [7,7] and [5,13][4] fulvalenes, which show no such potential. The first example of a [7,9] fulvalene has been prepared recently[5] and was reported to be nonaromatic. We report the preparation of nonafulvalenes belonging to classes (a) and (b), viz. [7,9] and [5,9] fulvalenes. We hoped that their properties would shed light on the extent of their aromaticity.

Treatment of the anion (I)[6] with fluorenone (ether, 25°, 1.5 hrs) gave the corresponding crude alcohol. Dehydration with TsOH (benzene, reflux, 1.5 hrs) and chromatography yielded 35% of the [5,9] fulvalene,[7,8] 2,7-diphenyl-3,4:5,6:9,10:11,12-tetrabenzopentanonafulvalene (II), yellow-orange plates (EtOH, m.p. 259°), λ_{max}^{EtOH} 248 ($\mathcal{E}$ 41,000), 269^{s} (28,000), 280^{s} (22,000), 307 (13,000), 320^{s} (12,400), 336^{s} (10,400), 412 nm (33,000).[9] Nmr δ ($CDCl_3$) 7.50-7.20 (m, 4H), 7.00-6.50 ppm (m, 24H). Similar treatment of (I) with tetracyclone and reaction with TsOH yielded 5%[7,8] of 2,7,9,10,11,12-hexaphenyl-3,4:5,6-dibenzopentanonafulvalene (III) (orange plates, EtOH, m.p. 215), $\lambda_{max}^{CH_2Cl_2}$ 248 ($\mathcal{E}$ 50,000), 291^{s} (15,000), 300^{s} (8,600), 335^{s} (900), 405 nm (830). Nmr δ ($CDCl_3$) 7.20-6.53 ppm (m, all protons). This route was also successful for the preparation of [7,9] fulvalenes. Anion (I) was combined with dibenzotropone (ether, reflux, 4.5 hrs) to yield the corresponding crude carbinol. Reflux with benzene and TsOH for 1.5 hours yielded after chromatography light-yellow crystals of the [7,9] fulvalene, 2,7-diphenyl-3,4:5,6:9,10:13,14-tetrabenzoheptanona fulvalene (IV), (75%,[7,8] EtOH, m.p. 272°), $\lambda_{max}^{C_6H_{12}}$ 225 ($\mathcal{E}$ 42,000), 252 (29,000), 289 (23,000), 338 (18,000), 343^{s} (17,200), 350^{s} nm (13,400).[9] Nmr δ ($CDCl_3$) 7.44-6.36 (m, 28H); 6.13 ppm (2H, S). Finally the anion (I) was treated with a slight excess of tropylium fluoroborate at -20°C and the violet reaction mixture brought to room temperature. Chromatography yielded



(I)



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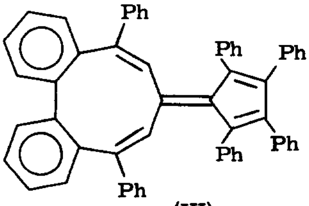
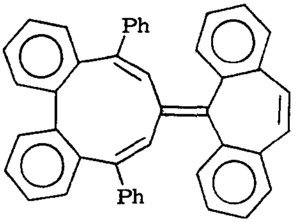


(III)

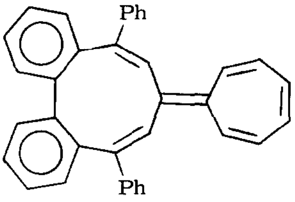
the[7,9]fulvalene (V) (intense yellow crystals 14%, [7,8,10] EtOH). $\lambda_{max}^{C_6H_{12}}$ 245 (ε 21,000), 265^s (17,000), 275^s (14,000), 290^s (8,200), 300^s (4,300), 401 nm (320).[9] Nmr δ ($CDCl_3$) 7.35-7.30 (m, 20H); 7.21-6.83 ppm (m, 8H). An attempt to prepare the [5,9]fulvalene from cyclopentadienyl thallium and the bromide derived from the parent nine-membered ring hydrocarbon or from cyclopentadienyl lithium and the [9]annulenone[11] did not lead to any product.

Since fulvalenes bearing a highly polar central bond have been reduced by $LiAlH_4$,[2a] we treated the fulvalenes (II) and (IV) with $LiAlH_4$ (ether, 3 hrs). After workup the starting materials were recovered, and no reduction product was observed.

The [7,9] and [5,9]fulvalenes are stable compounds, but their physical and chemical properties suggest little, if any, aromatic character. Their long wavelength uv band, typical of fulvenes and fulvalenes, is not sensitive to solvent polarity,[9] and attempts to protonate (IV) and (V) in trifluoroacetic acid failed. The refractoriness to $LiAlH_4$ indicates low polarity of the central double bond, i.e. a relatively small contribution of a dipolar structure. The dipole moments measured[12] were $\mu = 1.13$ Debye for the [5,9]fulvalene (II), and $\mu = 1.37$ Debye for the [7,9]fulvalene (IV). These low dipole moments and especially the small difference of the moments of the two nonafulvalenes which belong to class (a) and (b) respectively, supports the conclusion reached from their uv spectra.



(IV)



(V)

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3. Presently unknown.
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7. In all reactions with anion (I) ca. 50% of the parent hydrocarbon[11] was recovered in chromatography. The yields are based on consumed hydrocarbon.
8. All new compounds gave satisfactory elementary analysis.
9. Practically identical spectra were observed in cyclohexane, methylene chloride, and ethanol.
10. On trituration of the reaction mixture with hot ethanol a white crystalline product m.p. 260° precipitated. It was assumed to be the dihydro[7,9]fulvalene[8] on the basis of its uv, nmr and mass spectra.
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