Synthesis of 8-Cyanoheptafulvene

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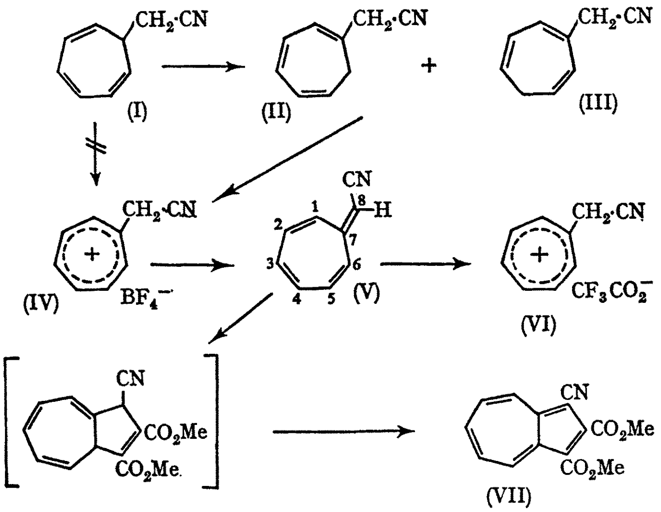
THE only simple 8-monosubstituted heptafulvene previously reported, 8-vinylheptafulvene,[1] is unstable. 8-Cyanoheptafulvene was expected to be more stable, and suitable for theoretical and chemical investigation of heptafulvenes.

Attempts to abstract hydride from 7-cyanomethylcycloheptatriene (I)[2] with triphenylmethyl fluoroborate were unsuccessful, possibly because the cyanomethyl group hinders attack by triphenylcarbonium ion at C-7. Therefore compound (I) was converted into a mixture of 1-cyanomethylcycloheptatriene (II) and 3-cyanomethylcycloheptatriene (III) (*ca* 1 : 4 from n.m.r. spectrum) by heating at 140—150°. The mixture smoothly afforded, as expected, cyanomethyltropylium fluoroborate (IV) (85%) with triphenylmethyl fluoroborate ($CHCl_3$, room temperature).



The fluoroborate (IV) was moderately stable [nonhygroscopic colourless crystals, m.p. 108—109° (decomp.), ν_{max} (KBr), 3025, 2200, 1548, 1490, 1449, 1060, 728, 710, and 694 cm^{-1}; n.m.r. (CF_3CO_2H) τ 0·78 (s, 6H) and 5·28 (s, 2H)]. The n.m.r. values are in good agreement with those for the methylene and the seven-membered-ring protons of both the azulenium[3] and the heptalenium ion.[4]

8-Cyanoheptafulvene (V) (80%) was easily obtained from the fluoroborate (IV) (Et_3N, CH_2Cl_2) as a red liquid [u.v. (iso-octane): λ_{max} 562sh (log ϵ 1·67), 518sh (2·30), 478sh (2·43), 444sh (2·67), 412sh (2·71), 353sh (4·01), 337 (4·31), 326 (4·30), 264sh (3·67), 253sh (3·96) and 237nm (4·00); i.r. (film): ν_{max} 3050w, 3030m, 2205s, 1640m, 1555s, 1520m, 1470m, 1273m, 1250m, 863m, 828m, 763s, and 749m $cm.^{-1}$; n.m.r. (CCl_4): τ 3·42 br (d, *J* 12·5 Hz H-1), 3·97 (m, H-2–H-6), and 5·52 (s, H-8)].

The data are consistent with the structure shown. The ring protons (τ 3·97) were shifted *ca.* τ 0·4 to lower field compared with those of (I),[1] indicating a greater contribution of the dipolar resonance structure than in (I). The n.m.r. spectrum of (V) in trifluoroacetic acid exhibited signals at τ 0·76br (s, 6H) and 5·37br (s, 2H), indicating the protonated structure (VI).

With dimethyl acetylenedicarboxylate (refluxing xylene, higher temperature than the case of parent hydrocarbon heptafulvene)[5] (V) gave dimethyl 1-cyanoazulene-2,3-dicarboxylate (VII) [red-purple needles, m.p. 175–176°, ν_{max} (KBr), 3020, 2220, 1740, 1708, 1455, 786, and 745 $cm.^{-1}$ λ_{max} (EtOH), 233 (log ϵ 4·51), 266 (4·29), 292 (4·59), 302 (4·71), 337 (3·81), and 528nm. (2·90)].

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