

Synthesis of 8-Cyano-8-(2,3-diphenylcyclopropenyl)heptafulvenylium Fluoroborate

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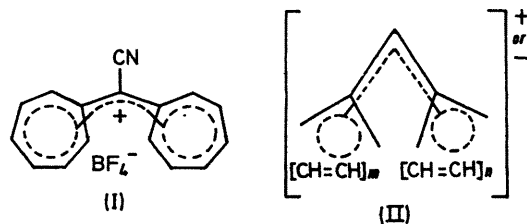
Summary 8-Cyano-8-(2,3-diphenylcyclopropenyl)heptafulvenylium fluoroborate (VII), a stable salt of a new carbonium ion, has been synthesized.

We have recently reported the synthesis of 8-cyano-8-cycloheptatrienylheptafulvenylium fluoroborate (I)¹ as a stable salt of a new carbonium ion, which is an $m=3$, $n=3$ derivative of a class of ionic species (II). We now report the formation of an $m=1$, $n=3$ analogue of (II), 8-cyano-8-(2,3-diphenylcyclopropenyl)heptafulvenylium fluoroborate (VII).

Addition of diphenylcyclopropenylium perchlorate (III)² to a solution of 8-cyanoheptafulvene (IV)³ and a small excess of triethylamine in methylene chloride at room temperature gave the substituted product, 8-cyano-8-(1,2-diphenylcyclopropenyl)heptafulvene (V)[†] as red needles, m.p. 157—157.5°, (72%); ν_{\max} (KBr) 3020w, 2210m, 1816w, 1638w, 1553s, 758s, and 688s cm^{-1} ; λ_{\max} (EtOH) 221sh

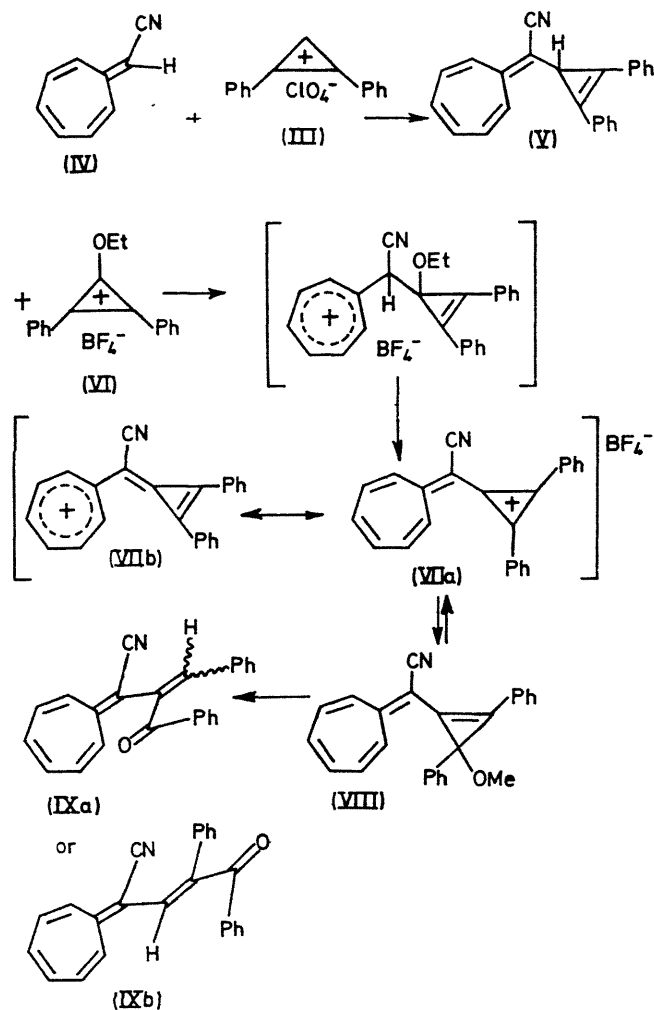
(log ϵ 4.49), 227(4.51), 236(4.47), 296sh(4.46), 314(4.54), 330(4.53), 354sh(4.40), 460sh(2.85), and 540sh nm(2.52); τ (CDCl_3 , Me_4Si) 2.19—2.67 (m, 10H), 2.87—3.40 (m, 2H), 3.67—3.97 (m, 4H), and 7.14 (s, 1H). Hydrogen abstraction of (V) with triphenylmethyl fluoroborate was unsuccessful.

However we could obtain (VII) by the reaction of (IV)



[†] Satisfactory elemental analyses have been obtained for all the new compounds obtained.

with 3-ethoxy-1,2-diphenylcyclopropenylium fluoroborate (VI); stirring a mixture of (IV) and (VI) (0.8 equiv.) in methylene chloride at room temperature gradually caused



(VII) to separate as orange-red crystals, m.p. 226—228°, (19.6% after recrystallization four times from dry acetonitrile-ether). Compound (VII) is stable in air at room temperature, soluble in acetonitrile, and 0.1N-HCl, and insoluble in ether. The spectral data of (VII) are: ν_{max} 2210m, 1833m, 1620m, 1594m, 1483s, 1400vs, 1359vs, 1250vs, 1060vs, 772s, and 691s cm^{-1} ; λ_{max} (0.1N-HCl) 227

(log ϵ 4.43), 257sh(4.41), 272(4.52), 346(3.98), and 461 nm (4.63); τ (MeCN, CH_2Cl_2 as a secondary standard) 1.67—2.11(m), and 2.14—2.53(m) in a ratio of 5 : 3 of integrated area, τ ($\text{CF}_3\text{CO}_2\text{H}$, CH_2Cl_2 as standard) 1.14—1.87(m), 1.86—2.20(m) in the same ratio. In the n.m.r. spectrum of (III) (MeCN), the *ortho*-protons and *meta*- and *para*-protons are clearly separated; the former are at τ 1.43—1.70 and the latter at 1.97—2.43. Therefore, the lower signals of (VII) can be assigned to the four *ortho*-protons of the phenyl groups and the six protons of the seven-membered ring, and the higher to the six *meta*- and *para*-protons. The chemical shifts of the phenyl protons lie between those of (III) and those of diphenylcyclopropenone [τ (MeCN) 2.00—2.30 and 2.34—2.64], suggesting that the three-membered ring has an appreciable positive character.

The observed pK_{R^+} value for (VII) in 23% aqueous EtOH, 3.41 ± 0.05 ,[†] is almost the same as that of (I) (3.44 ± 0.05),¹ confirming its moderate stability.

On treatment with triethylamine in acetonitrile-methanol, (VII) gave the methyl ether, 8-cyano-8-(3-methoxy-2,3-diphenylcyclopropenyl)heptafulvene (VIII) as permanganate-coloured prisms, m.p. 165—166°, (91%); ν_{max} (KBr) 2215m, 1763w, 1630m, 1600w, 1537s, 1416s, 1270s, 1075s, 824s, 765s, 720m, and 700s cm^{-1} ; λ_{max} (EtOH) 220sh (log ϵ 4.44), 289(4.19), and 429 nm (4.55); τ (CDCl_3 , Me_4Si) 2.14(m, 2H), 2.66(m, 8H), *ca.* 3.0(m, 2H), 3.62(br, 4H), and 6.74(s, 3H). The spectral data indicate that (VIII) has an heptafulvene structure rather than triafulvene structure. This result is consistent with the n.m.r. spectrum; although there is an appreciable delocalization of the positive charge throughout the molecule, the contribution of structure (VIIa) may be larger than that of (VIIb) to its resonance hybrids. The n.m.r. spectrum of (VIII) in trifluoroacetic acid is identical with that of (VII) in the same solvent, indicating a reversible interchange.

When compound (VIII) was passed through a basic alumina column, it changed completely into a ketonic compound (IX), red needles, m.p. 171—172°. Compound (IX) has spectral data; ν_{max} 2210m, 1654s, 1633w, 1536vs, 1225s, 754m, 738m, and 700s cm^{-1} ; λ_{max} 233 (log ϵ 4.35), 249(4.37), 280sh (4.27), and 414 nm (4.45); τ (CDCl_3 , Me_4Si) 1.94(m, 2H), 2.50(m, 8H), *ca.* 3.1(m, 2H), 3.20(s, 1H), 3.53(m, 4H). These data together with elemental analysis indicate the presence of a heptafulvene structure and a highly conjugated carbonyl group (1654 cm^{-1}) and the absence of a cyclopropene ring and a methoxy-group, suggesting that the structure is (IXa) or (IXb). These can be formed by ring opening in the three-membered ring. Although we have not yet been able to identify the structure exactly, the structure appears to be the cross conjugated (IXa) from u.v. data; the absorption at 414 nm is almost the same as that of 8-cyano-8-formylheptafulvene (413 nm).⁴

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[†] Measured spectroscopically.

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⁴ M. Oda and Y. Kitahara, *Bull. Chem. Soc. Japan*, 1971, **44**, 296.