Isolation of a Hydrocarbon Salt and Preparation of a Hydrocarbon which Heterolyses to a Carbocation and a Carbanion

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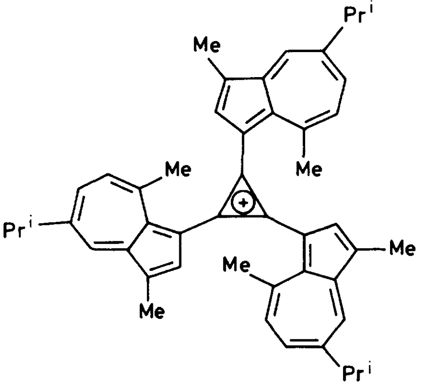
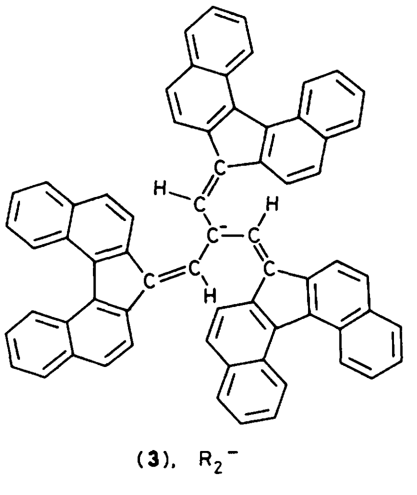
The first example of a hydrocarbon salt (**1**), $C_{48}H_{51}^+C_{67}H_{39}^-$, greenish black, stable crystals, has been isolated by mixing tetrahydrofuran solutions of Agranat's carbocation (**2**) and of Kuhn's carbanion (**3**), followed by recrystallization from dimethyl sulphoxide; the hydrocarbon (**4**), $C_{74}H_{46}$, orange powder, which heterolyses into the tropylium ion and the carbanion (**3**) in acetone or dimethyl sulphoxide, has been prepared by the reaction of the component hydrocarbon ions in tetrahydrofuran–acetonitrile.

Carbocation–carbanion salt formation has been reported between the tropylium ion (or the triphenylcyclopropenylium ion) and the pentakis(methoxycarbonyl)cyclopentadienide ion[1] or the 1,2,4-tris(2,2-dicyanoethenyl)cyclopentadienide ion.[2] However, isolation of a salt which consists solely of carbon and hydrogen has not been reported.

We now report such a hydrocarbon salt (**1**), $C_{48}H_{51}^+$-$C_{67}H_{39}^-$, which is stable for 6 months or more under argon in the dark at 10 °C. Equivalent amounts, in tetrahydrofuran (THF) solution, of the perchlorate salt of the tris-1-(5-isopropyl-3,8-dimethylazulenyl)cyclopropenylium ion (**2**), Agranat's cation R_1^+, $pK_{R+} > 10$,[3] and the potassium salt of the tris(7*H*-dibenzo[*c*,*g*]fluorenylidenemethyl)methide ion (**3**), Kuhn's carbanion R_2^-, pK_a for R_2H *ca.* 6,[4] were mixed under argon.† The black precipitate, a mixture of $KClO_4$ and $R_1^+R_2^-$, separated and was recrystallized from Me_2SO to give greenish black crystals, m.p. 230 °C decomp., in ≥60% yield.



(**2**), R_1^+



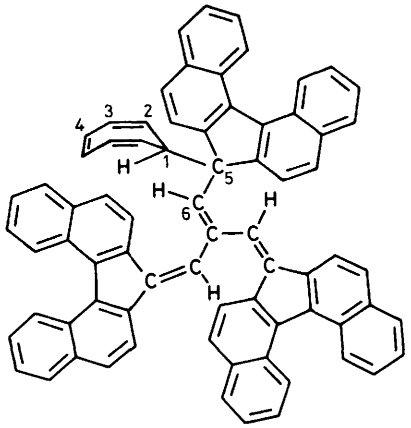
(**3**), R_2^-

(**1**) = $R_1^+ R_2^-$

Proof for the salt structure for $R_1^+R_2^-$ rests on satisfactory elemental analyses for $C_{115}H_{90}$, its i.r. spectrum (KBr disc), and its u.v. -visible spectrum of a solution in Me_2SO *in vacuo*. These spectra consist of those of R_1^+ and R_2^- superimposed.‡

Normally a carbocation and a carbanion react with each other to form a carbon–carbon σ bond and do not form a salt. However, as a rare case the heterolytic cleavage of the σ bond has been proposed for the racemization pathway of optically active cyano-cyclopropanes.[5] Recently, Arnett and his coworkers have reported on the heterolytic dissociation of a cyano-nitro-hydrocarbon into a cyclopropenylium ion and a carbanion, stabilized by the cyano and nitro groups.[6] However, there have been no reports on the heterolytic cleavage of a purely hydrocarbon system.

An orange solution of the novel hydrocarbon (**4**), $C_{74}H_{46}$, orange powder, m.p. 198 °C decomp., was prepared by mixing a THF solution of the potassium salt of (**3**) with an acetonitrile solution of an equivalent amount of tropylium fluoroborate, pK_{R+} 4.7,[7] under argon. The hydrocarbon (**4**) was isolated by evaporation and subsequent extraction with CH_2Cl_2; the crude reddish orange solid was purified by t.l.c. on SiO_2, in 66% yield.



(**4**)

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† The R_2^- ion solution is sensitive to light and oxygen in THF and Me_2SO.

‡ Selected $\lambda_{max.}$ (Me_2SO) 483 (R_1^+) and 697 (R_2^-) nm; selected $\nu_{max.}$ (KBr) 1527vs, 1466s, 1442vs, 1390vs, 1362s, and 1271s cm^{-1} for R_1^+; 1502vs, 1442vs, 1390vs, 1260s, 1238s, 1208s, 1166vs, 1152s, and 1137vs cm^{-1} for R_2^-.

The structure of (**4**) was assigned on the basis of satisfactory elemental analyses, and its ^{1}H and ^{13}C n.m.r. spectra.§

When (**4**) was dissolved in Me_2SO (1.11×10^{-4} M) it dissociated to the extent of *ca.* 17% to give Kuhn's carbanion (**3**) as measured spectrophotometrically, making the solution greenish. In addition, an acetone solution of (**4**) became green, when pyrene was added to the solution, indicating the formation of (**3**). Thus the otherwise negligible dissociation in acetone was assisted by shift of the equilibrium due to charge-transfer complex formation between the tropylium ion and pyrene.[8] Consequently, (**4**) is the first example of an ionically dissociative system among molecules solely consisting of carbon and hydrogen.

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§ ^{1}H N.m.r. ($CDCl_3$) δ 2.68 (t, 1H, H-1, *J* 5.4 Hz), 5.15 (dd, 2H, H-2, *J* 5.4 and 9.2 Hz), 5.98 (d, 2H, H-3, *J* 9.2 Hz), 6.53 (br. s, 2H, H-4), 6.45 (s, 1H, H-6), and 6.58—8.83 (m, 38H); ^{13}C n.m.r. ($CDCl_3$) δ 47.8 (C-1, d), 58.2 (C-5, s) and 117.5—146.8 (aromatic and olefinic C).