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Small Difference in Cation Stability in Controlling the Formation of Hydrocarbon Salt or Covalent Hydrocarbon

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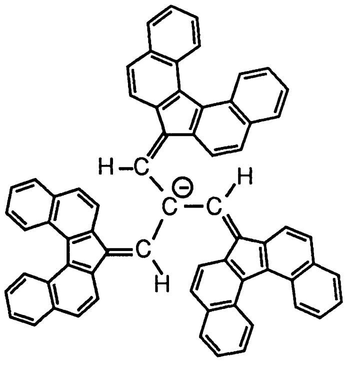
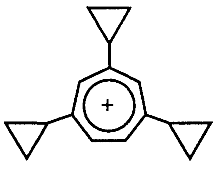
The reaction of sterically comparable cations, 3-(*p*-methylphenyl)- and 3-phenyl-1,2-dicyclopropylcyclopropenylium ions with highly stable Kuhn's anion ($C_{67}H_{39}^{-}$) gives a hydrocarbon salt and a covalent hydrocarbon, respectively, suggesting that a slight difference in cation stability differentiates the formation of either product.

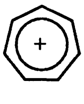
The reaction between a carbocation and a carbanion is certainly one of the most fundamental organic reactions. However, the reaction is not always straightforward. There are three possible pathways. The product may be a covalent compound, an ionic aggregate (salt), or radicals arising from single electron transfer between the carbanion and the carbocation. In fact, the occurrence of these three pathways has been observed,1) and various salts2) and covalent products3) have been isolated. It appears highly essential to clarify the structural characteristics which the carbocation and the carbanion should possess to determine the outcomes of the reaction.



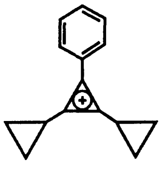
$\mathbf{R_1}^-$



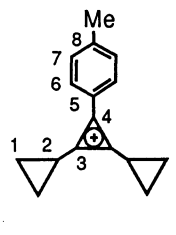
$\mathbf{R_{2a}}^+$



$\mathbf{R_{2b}}^+$



$\mathbf{R_{2c}}^+$



$\mathbf{R_{2d}}^+$

Previously, we reported the first isolation of several carbocation-carbanion salts consisting of solely carbon and hydrogen atoms.4) The increased stabilities of both the carbocation and the carbanion have been anticipated to favor the formation of a salt.4a, d) However, it has not necessarily been clarified how delicately the formation of a salt and a covalent compound would be differentiated. In addition to the intrinsic stabilities of the ions, steric factors are also expected to influence the reaction outcomes. For example, the combination of 1,3,5-tricyclopropyltropylium ion ($\mathbf{R_{2a}}^+$; pK_{R+} 8.7)5) or tropylium ion ($\mathbf{R_{2b}}^+$; pK_{R+} 3.9)6) with highly stable Kuhn's anion $\mathbf{R_I}^-$ ($C_{67}H_{39}^-$; pK_a(RH) 5.9)[7] gave a hydrocarbon salt[4c, d] and a covalent hydrocarbon,[4a] respectively. Although the pK_{R+} difference between the two carbocations is 4.8, the greater steric requirement of $\mathbf{R_{2a}}^+$ was also anticipated to have played a role to give a hydrocarbon salt. Consequently, we decided to work on a system whose stability can be delicately controlled, the steric requirement being kept essentially constant. As a candidate system, we selected 1,2-dicyclopropyl-3-arylcyclopropenylium ions. We now report that 1,2-dicyclopropyl-3-phenylcyclopropenylium ion ($\mathbf{R_{2c}}^+$) gives a covalent hydrocarbon with $\mathbf{R_I}^-$, whereas a sterically comparable 3-(*p*-methylphenyl) homologue ($\mathbf{R_{2d}}^+$) yields a hydrocarbon salt. The results show that a pK_{R+} difference as small as approximately 0.2 determines the salt or covalent product formation.

The fluoroborate salt of $\mathbf{R_{2c}}^+$ was prepared following the reported method.[8] The perchlorate salt of the cation $\mathbf{R_{2d}}^+$ was synthesized in a manner similar to that described for $\mathbf{R_{2c}}^+BF_4^-$. Photolysis (high pressure mercury lamp, quartz vessel) of 3-bromo-3-(*p*-methylphenyl)diazirine[9] (9.0 mmol) in dicyclopropylacetylene[10] (6.0 mmol) for six hours at 5 °C gave pale brown precipitates, which were dissolved in water and treated with an excess amount of perchloric acid. 1,2-Dicyclopropyl-3-(*p*-methylphenyl)cyclopropenylium perchlorate ($\mathbf{R_{2d}}^+ClO_4^-$) was extracted with dichloromethane and chromatographed (SiO_2, CH_2Cl_2-CH_3CN; 5:1 v/v). The major fraction was dissolved in CH_2Cl_2-AcOEt (5:2 v/v) and recrystallized by slow evaporation of CH_2Cl_2 to give $\mathbf{R_{2d}}^+ClO_4^-$ (0.41 mmol) as pale yellow crystals, mp 184.5 – 185.5 °C. The structure was assigned on the basis of satisfactory elemental analyses and ^1H and ^{13}C NMR spectra.[11]

Slightly greater stability of $\mathbf{R_{2d}}^+$ than $\mathbf{R_{2c}}^+$ was demonstrated by determining the equilibrium constant at 25 °C in the methoxy group exchange between 1,2,3-tri-*t*-butyl-3-methoxycyclopropene[12] and $\mathbf{R_{2d}}^+ClO_4^-$ or $\mathbf{R_{2c}}^+BF_4^-$ in CD_3CN in a tube sealed under vacuum by ^1H NMR. Stabilities of $\mathbf{R_{2c}}^+$ and $\mathbf{R_{2d}}^+$ relative to tri-*t*-butylcyclopropenylium ion were calculated from the equilibrium constants to be 2.5 ± 0.4 and 3.6 ± 0.5 kJ / mol, respectively. These results indicate that $\mathbf{R_{2d}}^+$ has a greater pK_{R+} value than that of $\mathbf{R_{2c}}^+$ by about 0.2 ± 0.2 pK_{R+} unit; this value is close to the difference in pK_{R+} for phenyltropylium (3.88) and *p*-methylphenyltropylium (4.17) ion.[13] The very close stabilities were also supported by the close reduction peak potentials ($\mathbf{R_{2c}}^+$ −1.50 V; $\mathbf{R_{2d}}^+$ −1.58 V (vs. Ag/Ag^+) in CH_3CN) in cyclic voltammetry.[14]

When a deep green solution of $\mathbf{R_I}^-K^+$, generated from the parent hydrocarbon $\mathbf{R_I}$H (orange powder) and *t*-BuOK/THF,[4d, 7] was mixed with a THF-CH_3CN (1:1 v/v) solution of an equimolar amount of $\mathbf{R_{2c}}^+BF_4^-$ under argon in the dark, the solution turned deep orange, indicating the formation of a covalent product. After the addition of benzene, KBF_4 was removed with a membrane filter (0.5 µm) and the solvent evaporated to give an orange solid quantitatively. Evidence for the covalent structure $\mathbf{R_I}$–$\mathbf{R_{2c}}$ (Chart 1) for the solid was obtained from its ^1H and ^{13}C NMR spectra measured in $CDCl_3$. Although the compound was not stable enough to tolerate recrystallization or thin layer chromatography over silica gel, the NMR spectra showed that the solid was essentially pure having the structure $\mathbf{R_I}$–$\mathbf{R_{2c}}$, no other isomers being detected within experimental errors.[15] The covalent structure in the solid state was also confirmed by the IR (KBr) spectrum,[15] which showed the

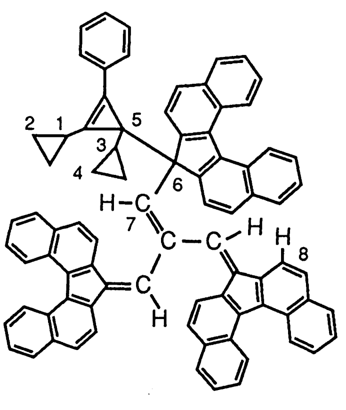


Chart 1. Covalent compound $\mathbf{R_I}$–$\mathbf{R_{2c}}$.

absence of $\mathbf{R_1}^-$ and $\mathbf{R_{2c}}^+$ ions. This covalent hydrocarbon $\mathbf{R_1}$–$\mathbf{R_{2c}}$ partially dissociates into $\mathbf{R_1}^-$ and $\mathbf{R_{2c}}^+$ in DMSO as determined by UV-visible spectroscopy.[16)]

On the contrary, when 1,2-dicyclopropyl-3-(*p*-methylphenyl)cyclopropenylium ion ($\mathbf{R_{2d}}^+$) was used in the reaction with $\mathbf{R_1}^-$, the deep green color of $\mathbf{R_1}^-$ persisted. Removal of the solvent gave a dark green solid, from which organic products were extracted with $CHCl_3$. Evaporation of the solvent again afforded a dark green solid. The solid was dissolved in THF and reprecipitated by addition of five volumes of CH_3CN to give a hydrocarbon salt $\mathbf{R_1}^-\mathbf{R_{2d}}^+$ as a dark green powder in 62% yield. The salt structure of $\mathbf{R_1}^-\mathbf{R_{2d}}^+$ was proved by its IR (KBr) spectrum which consisted of absorptions of $\mathbf{R_1}^-$ and $\mathbf{R_{2d}}^+$, superimposed.[17)]

When the salt $\mathbf{R_1}^-\mathbf{R_{2d}}^+$ was dissolved in $CDCl_3$, it underwent immediate coordination to give a reddish brown solution of the covalent compound $\mathbf{R_1}$–$\mathbf{R_{2d}}$.[18)] In contrast, spectrophotometric studies showed that $\mathbf{R_1}^-$, $\mathbf{R_{2d}}^+$, and $\mathbf{R_1}$–$\mathbf{R_{2d}}$ are in equilibrium in DMSO.[19)] This behavior is identical with what was observed for the salt consisting of tricyclopropylcyclopropenylium ion and $\mathbf{R_1}^-$.[4b)] Considering that the difference of ΔG_{het} for $\mathbf{R_1}$–$\mathbf{R_{2c}}$ and $\mathbf{R_1}$–$\mathbf{R_{2d}}$ in DMSO is only 4 kJ / mol,[16,19)] it is surprising that such a small energy controls the form of the solid, i.e., the salt or the covalent compound. At present, the origin of such facile bond-switching is not wholly clear. Presumably, the balance between the energy of heterolysis of the C–C σ bond and the lattice energy in the salt form determines which of the salt or the covalent compound is obtained. We are now conducting the combination of $\mathbf{R_1}^-$ and $\mathbf{R_{2c}}^+$ with various substituents on the phenyl ring to investigate the nature of the reaction in more precisely controlled systems.

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11) $\mathbf{R_{2d}}^+ClO_4^-$: Anal. Found: C, 62.07; H, 5.44; Cl, 11.75%. Calcd for $C_{16}H_{17}O_4Cl$: C, 62.24; H, 5.55; Cl, 11.48%. ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.77 (d, 2 H, *J* = 8.0 Hz, H–6 or 7), 7.49 (d, 2 H, *J* = 8.0 Hz, H–6 or 7), 2.84 – 2.75 (m, 2 H, H–2), 2.52 (s, 3 H, $-CH_3$), 1.99 – 1.91 (m, 4 H, H–1 (*E*)), 1.79 – 1.73 (m, 4 H, H–1 (*Z*)). ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 167.4 (s, C–3), 155.2 (s, C–4), 149.6 (s, C–8), 134.6 (d, C–6), 131.1 (d, C–7), 116.1 (s, C–5), 22.3 (q, $-CH_3$), 16.3 (t, C–1), 9.3 (d, C–2).

12) Prepared from tri-*t*-butylcyclopropenylium perchlorate and sodium methoxide in methanol. ^{1}H NMR (CD_3CN, 270 MHz) δ 2.83 (s, 3 H, $-CH_3$), 1.23 (s, 18 H, *t*-Bu), 0.95 (s, 9 H, *t*-Bu).

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14) The peak potentials were determined by using 0.1 M tetrabutylammonium perchlorate as a supporting electrolyte and a scan rate of 0.1 V/s.

15) $\mathbf{R_1}$–$\mathbf{R_{2c}}$: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 8.65 – 6.94 (m, 42 H, aromatic and olefinic protons), 6.47 (d, 1 H, *J* = 8.3 Hz, H–8), 6.43 (br.s, 1 H, H–7), 1.91 – 1.83 (m, 1 H, H–1), 1.00 – 0.71 (m, 5 H, H–2 (*E*,*Z*), 3), –0.19 – –0.22 (m, 2 H, H–4 (*Z*)), –0.36 – –0.39 (m, 2 H, H–4 (*E*)). ^{13}C NMR ($CDCl_3$, 67.5 MHz) δ 149.8 – 113.9 (aromatic and olefinic carbons), 65.1 (C–6), 41.2 (C–5), 13.7 (C–3), 10.1, 9.0 (C–2), 8.2 (C–1), 4.1, 3.6 (C–4). IR (KBr disk) 3048 (m), 1512 (m), 1479 (w), 1444 (w), 1344 (m), 1218 (w), 1125 (w), 1029 (m), 858 (w), 814 (vs), 745 (vs), 677 (vs), 626 (w) cm^{-1}.

16) ΔG_{het} in DMSO: 22.9 ± 0.2 kJ / mol (at ≈1 × 10^{-4} M).

17) $\mathbf{R_1}^-\mathbf{R_{2d}}^+$: IR (KBr disk) 3050 (w), 1605 (w), 1505 (vs), 1450 (m), 1435 (m), 1390 (s), 1260 (m), 1240 (m), 1210 (m), 1170 (vs), 1160 (vs), 1140 (vs), 1060 (w), 920 (w), 880 (m), 855 (s), 820 (s), 800 (m), 750 (s) cm^{-1}.

18) $\mathbf{R_1}$–$\mathbf{R_{2d}}$: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 8.63 – 6.95 (m, 41 H, aromatic and olefinic protons), 6.47 (d, 1 H, *J* = 8.4 Hz, H–8), 6.42 (br.s, 1 H, H–7), 2.41 (s, 3 H, $-CH_3$), 1.90 – 1.82 (m, 1 H, H–1), 1.00 – 0.73 (m, 5 H, H–2 (*E*,*Z*), 3), –0.21 – –0.26 (m, 2 H, H–4 (*Z*)), –0.39 – –0.43 (m, 2 H, H–4 (*E*)). ^{13}C NMR ($CDCl_3$, 67.5 MHz) δ 149.9 – 113.8 (aromatic and olefinic carbons), 65.1 (C–6), 41.0 (C–5), 30.3 ($-CH_3$), 13.7 (C–3), 10.0, 8.8 (C–2), 8.2 (C–1), 4.1, 3.5 (C–4).

19) ΔG_{het} in DMSO: 19.0 kJ / mol (at ≈8 × 10^{-5} M).

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