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Regiospecific Coordination of *tert*-Butylfulleride Ion and 1,4-Dicyclopropyltropylium Ion. Synthesis of a Dialkyldihydrofullerene Having a Heterolytically Dissociative Carbon−Carbon σ Bond

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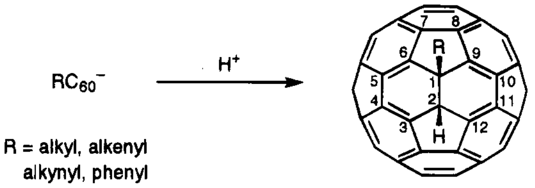
The high electron affinity[1] of fullerene (C_{60}) suggests that this important structure is a framework of highly stabilized carbanions. Recent studies of the controlled addition of organolithium and Grignard reagents to C_{60} demonstrated the formation of monosubstituted fulleride ions (RC_{60}^-) in high yields.[2−5] Their regiospecific protonation to form 1-R-1,2-dihydrofullerenes (Scheme 1)[6] as thermodynamically-controlled products[2−5] has suggested that stepwise introduction of two different alkyl groups into distinct positions of the C_{60} framework can be achieved by using RC_{60}^- as a nucleophile. The reported high stability of *t*-BuC_{60}^- (**1**$^-$) toward electrophiles[2] prompted us to synthesize new ionically-dissociative hydrocarbons by the carbocation−carbanion coordination of **1**$^-$ and highly stabilized hydrocarbon cations. Here we report the synthesis of a disubstituted dihydrofullerene **3** in isomerically pure form by the reaction of *tert*-butylfulleride ion (**1**$^-$), generated by deprotonation of *t*-BuC_{60}H, with 1,4-dicyclopropyltropylium ion (**2**$^+$)[7] and its reversible heterolysis to regenerate **1**$^-$ and **2**$^+$ in highly polar solvents.

A dark green solution of K^+**1**$^-$ was prepared by treating a THF solution (6 mL) of *t*-BuC_{60}H (6.93 mg) with *t*-BuOK (5% excess) under argon. Addition of 1.1 equiv of **2**$^+BF_4^-$ in THF-CH_3CN (3:1, 0.4 mL) gave a brown solution, which after removal of the solvent under vacuum left a dark brown residue. The residue was dissolved in CS_2 and quickly passed through a short SiO_2 column to remove KBF_4 and unchanged reactants as well as small amounts of polar byproducts. Evaporation of CS_2 yielded the coordination product as a dark brown solid (7.0 mg, 83%).

Further purification of this solid by MPLC (SiO_2) was unsuccessful owing to partial decomposition to *t*-BuC_{60}H. The mass spectrum (FAB, negative ion, *o*-nitrophenyl octyl ether matrix) showed signals at *m/z* 777 (*t*-BuC_{60}) and 720 (C_{60}), but the molecular ion signal for the 1:1 coordination product (*m/z* 948) was not clearly observed owing to facile cleavage of the *t*-BuC_{60}−C bond (vide infra).[8]

Scheme 1



In principle, formation of a carbon−carbon covalent bond between **1**$^-$ and **2**$^+$ can produce $3 \times 4 + (56 \times 7)/2 = 208$ isomeric hydrocarbons if the positive and negative charges of the precursor ions are fully delocalized over the conjugated π-systems of the tropylium ring and the C_{60} framework, respectively. The NMR spectroscopic data, however, reveal that the product consists of essentially a single isomer. In the ^{1}H NMR spectrum,[9] the cycloheptatriene moiety shows a triplet at δ 3.39 and four doublets in the olefinic region, indicating that the cyclopropyl groups are attached to positions 3 and 6 of the 2,4,6-cycloheptatrien-1-yl ring. The unequal chemical shifts of H-2 and H-7 and those of H-4 and H-5 indicate that the molecule has no symmetry plane. The ^{13}C NMR spectrum,[9,10] in which all the 77 carbons other than the three methyl carbons in the *tert*-butyl group exhibit different chemical shifts, is also consistent with this conclusion.

AM1 calculations by Hirsch et al.[3b] showed that the negative charge of **1**$^-$ is distributed mostly on C-2, -4, and -11. We propose structure **3** (Scheme 2), i.e., a 1,4-adduct across a six-membered ring, for our coordination product on the basis of the absence of symmetry. This structure is supported by the ^{1}H NMR NOE difference spectrum, which shows that the cycloheptatriene ring is in close proximity to the *tert*-butyl group. Irradiation of the *tert*-butyl protons causes a significant enhancement (35%) of the H-1 signal together with small enhancements (~0.7%) of the H-4 and H-5 signals, suggesting the conformation shown in Scheme 2.

In contrast to the rapid isomerization of 1-*tert*-butyl-1,4-dihydrofullerene to its 1,2-isomer at 25 °C,[2] **3** does not rearrange in $CDCl_3$ even at 75 °C. PM3 calculations (Table 1) show that the heat of formation of **3** (1,4-adduct) is 18 kcal/mol lower than that of the corresponding 1,2-isomer, whereas the heats of formation of the 1,4-isomers

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(8) Neither the signal at *m/z* 948 nor 777 was clearly seen in positive ion FAB mass spectra.

(9) **3**: ^{1}H NMR (400 MHz, CS_2−$CDCl_3$ 2:1) δ 6.59 and 6.53 (AB quartet, *J* = 11.5 Hz, 1H each, H-4 and H-5), 6.29 (d, *J* = 5.9 Hz, 1H, H-2 or H-7), 5.92 (d, *J* = 5.9 Hz, 1H, H-7 or H-2), 3.39 (t, *J* = 5.9 Hz, 1H, H-1), 1.71 (s, 3H, *t*-Bu), 1.7−1.5 (m, 2H, cyclopropyl CH), 0.85−0.3 (m, 8H, cyclopropyl CH_2); ^{13}C NMR (100.5 MHz, CS_2−$CDCl_3$ 2:1), δ 27.8 (CH_3), 8.1, 8.0, 5.8, 5.6 (CH_2), 131.2, 130.7, 117.7, 116.0, 44.9, 16.00, 15.99 (CH), 68.3, 60.2, 39.5 (C), quaternary carbons of C_{60} and cycloheptatriene ring showed 60 peaks at δ 157.5−137.8 Details are given in supplementary material.

(10) The signals of C-2 and C-7 of the cycloheptatriene ring at δ 117.7 and 116.0 were significantly broadened, indicating the contribution of a norcaradiene structure. We have reported that introduction of bulky substituents shifts the cycloheptatriene−norcaradiene equilibrium to the norcaradiene side: (a) Takeuchi, K.; Kitagawa, T.; Ueda, A.; Senzaki, Y.; Okamoto, K. *Tetrahedron* **1985**, *23*, 5455. (b) Takeuchi, K.; Kitagawa, T.; Toyama, T.; Okamoto, K. *J. Chem. Soc., Chem. Commun.* **1982**, 313. (c) Takeuchi, K.; Arima, M.; Okamoto, K. *Tetrahedron Lett.* **1981**, *22*, 3081.

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Scheme 2

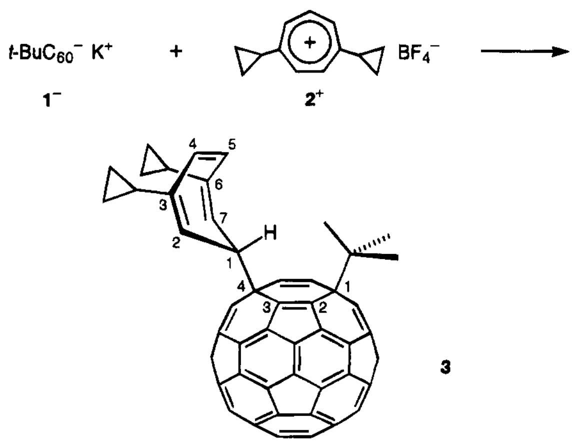

Table 1. Calculated (PM3) Heats of Formation of t-BuC$_{60}$H and t-Bu(C$_{13}$H$_{15}$)C$_{60}$ (C$_{13}$H$_{15}$ = 3,6-Dicyclopropyl-2,4,6-cycloheptatrien-1-yl)

position of substituents	heat of formation, kcal/mol	
	t-BuC$_{60}$H	t-Bu(C$_{13}$H$_{15}$)C$_{60}$
1,2	760.2	872.5
1,4	763.2	854.5
1,6	777.8	884.7

of t-BuC$_{60}$H (Table 1) and $C_{60}H_2$[11] are 3.0 and 3.8 kcal/mol higher than those of the 1,2-adducts, respectively. The difference in the lower-energy isomer structure is ascribed to severe steric repulsion between the eclipsing *tert*-butyl group and the cycloheptatriene ring in the 1,2-isomer of **3**. This finding suggests the possibility of controlling the formation of 1,2- and 1,4-adducts in the reaction of RC_{60}^- and R'^+ by the sizes of R and R'.[12]

An unusual feature of hydrocarbon **3** is its ionization into a carbocation and a carbanion in solution. In general, thermal dissociation of carbon–carbon σ bonds in hydrocarbon molecules takes place homolytically. To our knowledge, the only exceptions are our reports of the heterolysis of a series of hydrocarbons that dissociate at 25 °C in highly polar solvents into tris(7*H*-dibenzo[*c*,*g*]fluorenylidenemethyl)methide ion (Kuhn's carbanion) and a substituted tropylium or cyclopropenylium ion.[13,14] The high thermodynamic stabilities of **1**$^-$ and **2**$^+$, demonstrated by their respective pK_{HA} (5.7[2]) and pK_{R^+} (7.63[7]) values, suggest the possibility that **3** heterolyzes into **1**$^-$ and **2**$^+$ in highly polar media. The master equation, proposed by Arnett,[15] predicts a value of 18.2 kcal/mol for the heat of heterolysis (ΔH_{het}) of **3**.

When **3** is dissolved in DMSO or DMSO–CS_2 (4:1 v/v), it dissociates partially to give a greenish yellow solution. The visible/near IR region spectra exhibit absorption peaks at 656 and 995 nm, which agree with the absorption of **1**$^-$ generated from t-BuC$_{60}$H and excess t-BuOK. By contrast, **3** shows no absorption attributable to **1**$^-$ in nonpolar solvents such as hexane and CS_2.

The degree of dissociation (α) was determined in DMSO–CS_2 (4:1 v/v)[16] at 25 °C by monitoring the absorbance at 995 nm (ϵ 2350) for solutions of different initial concentrations c. The agreement of dissociation constants [$K_{het} = c\alpha^2/(1 - \alpha) = 2.3 \pm 0.2 \times 10^{-6}$ M] calculated from four determinations (α = 0.30, 0.18, 0.15, and 0.10 at c = 1.6, 6.0, 8.8, and 19 × 10^{-5} M, respectively) indicates that the equilibrium $\mathbf{3} \rightleftarrows \mathbf{1}^- + \mathbf{2}^+$ is established.

The free energy of heterolysis (ΔG_{het}) calculated from the dissociation constants is 7.7 kcal/mol. We have shown[13b,c] that heterolysis of a carbon–carbon σ bond of a hydrocarbon in DMSO to form a resonance-stabilized carbocation and carbanion is accompanied by significant loss of entropy due to strong solvation of the cation. This solvation by DMSO makes ΔH_{het} lower by ~5 kcal/mol[13b] than ΔG_{het}, allowing us to expect the ΔH_{het} of **3** to be approximately 3 kcal/mol. This value is ca. 15 kcal/mol smaller than predicted by Arnett's master equation, indicating that the heterolysis of **3** is markedly facilitated by the steric congestion around the dissociating bond.

In summary, the facile heterolysis of the carbon–carbon σ bond of **3** is attributed to the high thermodynamic stabilities of **1**$^-$ and **2**$^+$ and the large steric repulsion between the two substituents on the C_{60} framework. Other ionically dissociative dialkyldihydrofullerenes are being prepared, and the effect of structural change on the heterolysis energy will be reported in due course.

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Supplementary Material Available: ^{1}H and ^{13}C NMR and visible/near IR region spectra of compound **3** (7 pages).

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(12) One should also consider the possibility of single-electron transfer from RC_{60}^- to R'^+ to produce a pair of radicals. In the present case, however, this process is endothermic since the oxidation potential of **1**$^-$ (−0.33 V vs ferrocene/ferrocenium in DMSO, ref 2) is much higher than the reduction potential of **2**$^+$ (−0.76 V vs Ag/Ag$^+$ in CH_3CN (ref 7); this potential corresponds to −0.84 V vs ferrocene/ferrocenium. For conversion from Ag/Ag$^+$ to ferrocene/ferrocenium, see: Komatsu, K.; Masumoto, K.; Waki, Y.; Okamoto, K. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2470).

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(16) CS_2 was added to increase the solubility since **3** is sparingly soluble in DMSO.