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Ionically Dissociative Hydrocarbons Containing the C_{60} Skeleton[1†]

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Abstract: The coordination of *tert*-butylfulleride ion (t-BuC_{60}^-) with tropylium (**1a**$^+$), 1,4-di-*tert*-butyltropylium (**1b**$^+$), and 1,4-dicyclopropyltropylium (**1c**$^+$) ions yielded 1-*tert*-butyl-4-(3,6-R_2-2,4,6-cycloheptatrien-1-yl)-1,4-dihydrofullerenes (**2a**: R = H, **2b**: R = *t*-Bu, **2c**: R = *cyc*-Pr) in isomerically pure form. The structures of **2a–c** were determined from the ^1H and ^{13}C NMR spectra, which clearly indicate the absence of symmetry in the molecules, and from ^1H NMR NOE experiments. Spectrophotometric studies showed that **2a–c** are unique hydrocarbons that regenerate t-BuC_{60}^- and **1**$^+$ in polar solvents by heterolysis of a carbon–carbon σ bond. Although this facile heterolysis is due principally to the high thermodynamic stabilities of both t-BuC_{60}^- and **1a–c**$^+$, the free energies of heterolysis are considerably lower than predicted from pK_{HA} of t-BuC_{60}^- and pK_{R^+} of **1a–c**$^+$ using Arnett's master equation. The results suggest that steric repulsion between the 1-*tert*-butyl group and the cycloheptatrienyl group on the surface of C_{60} plays an important role in enhancing the heterolysis of **2a–c**. © 1997 Elsevier Science Ltd.

INTRODUCTION

In general, thermal dissociation of carbon–carbon σ bonds in hydrocarbon molecules involves homolytic cleavage. We have reported, on the other hand, the synthesis of a series of hydrocarbons that dissociate to give highly stabilized tris(7*H*-dibenzo[*c,g*]fluorenylidenemethyl)methide ion and a tropylium or a cyclopropenylium ion in aprotic polar solvents such as DMSO and sulfolane.[2] To our knowledge this represents the only example of the heterolytic cleavage of a carbon–carbon bond in genuine hydrocarbon molecules reported to date.

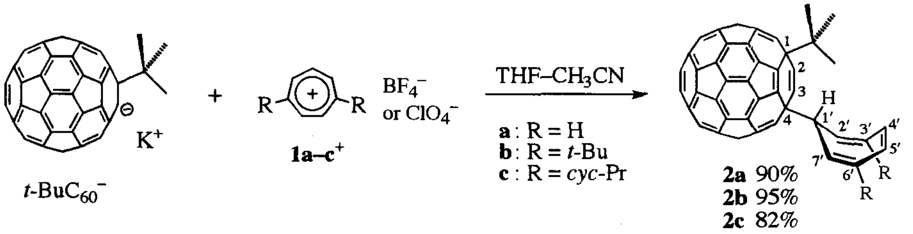
The high electron affinity[3] of fullerene (C_{60}) suggests that this structure also represents a potential framework for highly stabilized carbanions. Recent studies of the controlled addition of organolithium and Grignard reagents to C_{60} clearly demonstrate the formation of monosubstituted fulleride ions (RC_{60}^-) as stable intermediates.[4–8] In particular, *tert*-butyl-[4] and 1-octynyl-[5a] fulleride ions have been successfully prepared in solution or isolated as a solid. Fagan et al.[4] have reported that the *tert*-butyl-1,2-dihydrofullerene (t-$BuC_{60}H$) has a pK_a of 5.7 in DMSO, which ranks its conjugate anion, t-BuC_{60}^-, as one of the most stable hydrocarbon anions. In our laboratory, attention has been focused on the synthesis of a new class of hydrocarbon by combining this anion with resonance-stabilized hydrocarbon cations and investigations of their heterolytic behavior. In this paper we report the syntheses of disubstituted dihydrofullerenes **2a–c** in isomerically pure form via the reaction of t-BuC_{60}^-, generated by deprotonation of t-$BuC_{60}H$, with three substituted tropylium ions (**1a–c**$^+$), and the thermodynamic behavior with respect to their reversible heterolysis to regenerate t-BuC_{60}^- and **1a–c**$^+$ in highly polar solvents.

[†] This work is respectfully dedicated to Prof. William von E. Doering on the occasion of his 80th birthday.

RESULTS AND DISCUSSION

Synthesis

Compounds **2a–c** were synthesized by the carbocation–carbanion coordination reaction of *t*-BuC_{60}^- and tropylium ions. A dark green solution of *t*-$BuC_{60}^-K^+$ was prepared in THF by treatment of the parent hydrocarbon, *t*-$BuC_{60}H$,[4,7] with a 5% excess of *t*-BuOK. The addition of a 1.1 equivalent of the BF_4^- or ClO_4^- salt of a tropylium ion (**1a**$^+BF_4^-$, **1b**$^+ClO_4^-$, or **1c**$^+ClO_4^-$) in a THF–CH_3CN mixed solvent 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 the inorganic components (KBF_4 or $KClO_4$) and unchanged tropylium salts, as well as small amounts of polar byproducts. Evaporation of CS_2 yielded the coordination products (**2a–c**) as dark brown solids in 82–95 % yields. Further purification of these compounds by flash chromatography (SiO_2) was unsuccessful because of partial hydrolysis to *t*-$BuC_{60}H$.



Scheme 1

As discussed below, NMR data showed that products **2a–c** were essentially pure 1,4-adducts. Negative-ion FAB mass spectra (Fig. 1) showed the corresponding molecular ion peaks for the adduct as well as ions corresponding to *t*-BuC_{60} (*m*/*z* 777) and C_{60} (*m*/*z* 720). The clear evidence for the formation of *t*-BuC_{60}^- suggests a facile cleavage of the *t*-BuC_{60}–C bond (vide infra). Although compounds **2a–c** are stable in the solid state and in solution in nonpolar solvents, they decompose rapidly in polar solvents because of facile ionic dissociation to regenerate *t*-BuC_{60}^- followed by hydration or air-oxidation.

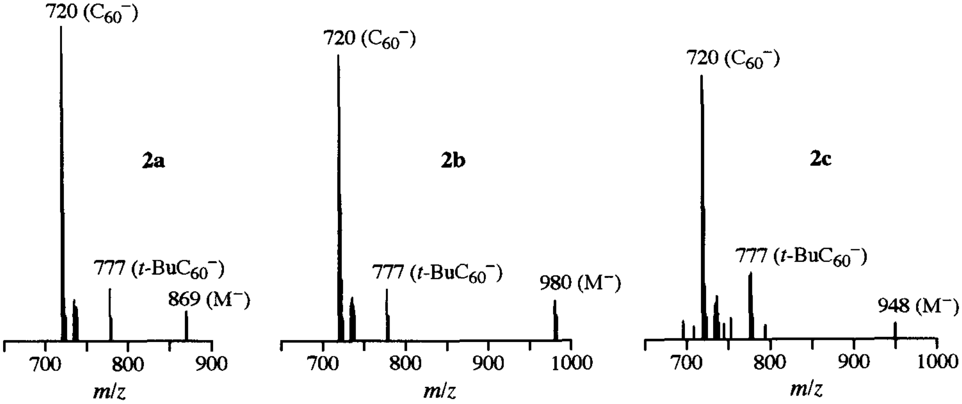


Fig. 1. FAB mass spectra of **2a–c** (negative ion, *o*-nitrophenyl octyl ether matrix).

Reactions between a resonance-stabilized carbocation and a carbanion can involve a single-electron transfer to produce a pair of radicals as an alternative to carbon–carbon covalent bond formation.[9] However, an electron transfer between t-BuC$_{60}^-$ and 1^+ is unlikely, since the reduction potentials for **1a**$^+$, **1b**$^+$, and **1c**$^+$ (–0.59, –0.80, and –0.84 V vs Fc/Fc$^+$, respectively, in 50% aqueous CH_3CN)[10,11] are much more negative than the oxidation potential of t-BuC$_{60}^-$ (–0.33 V vs Fc/Fc$^+$ in DMSO).[4]

Structure determination

^{1}H NMR spectra showed that the obtained products consist of only a single isomer. The cycloheptatriene moiety of **2b** and **2c** showed a triplet at δ 3.18 and 3.39, respectively, and four doublets in the olefinic region (Fig. 2), indicating that the *tert*-butyl and cyclopropyl groups are attached to positions 3 and 6 of the 2,4,6-cycloheptatrien-1-yl ring. The unequal chemical shifts of all the olefinic protons indicate that the molecules **2a–c** have no element of symmetry. For the ^{13}C NMR spectrum, these molecules exhibited 60–64 sp^2 carbon signals (the spectrum for **2a** is shown in Fig. 3). This observation is consistent with the absence of symmetry in the molecules, in which all the carbons are nonequivalent except for the methyl carbons in the *tert*-butyl groups.

Based on PM3 calculations, the negative charge as well as the HOMO of t-BuC$_{60}^-$ is largely distributed in the vicinity of the *tert*-butyl group (i.e., C-2, -4, and -11) with the values for C-2 being the largest (Table 1).[12] This suggests the highest reactivity for C-2, irrespective of the nature of the reaction (orbital or charge controlled), and agrees with the experimental observation that a 1,2-addition to the 6–6 bond is usually observed for the reactions of alkynyl-[5a] and cyano-[13] substituted C_{60} anions with electrophiles such as proton, alkyl halides, benzoyl chloride, and tosyl cyanide. On the other hand, compounds **2a–c** are most likely to be produced as a result of a 1,4-addition across a six-membered ring (Scheme 1) based on the absence of symmetry and ^{1}H NOE difference spectra, which showed that the cycloheptatriene ring is in close proximity to the *tert*-butyl group. As shown in Table 2, irradiation of the 1-*tert*-butyl protons resulted in a significant enhancement of the H-1' signal. Smaller enhancements were also observed for H-4' and H-5',

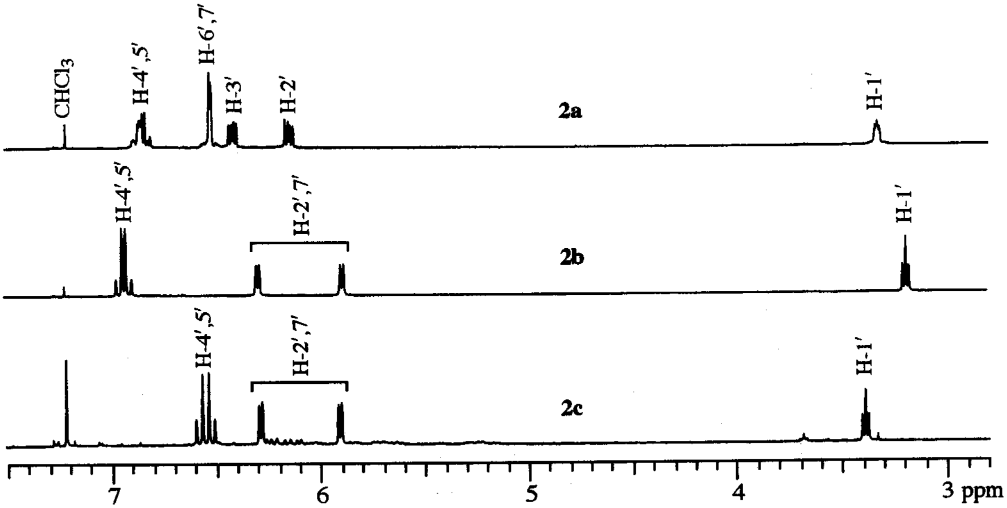


Fig. 2. ^{1}H NMR spectra of **2a–c** (400 MHz, CS_2–$CDCl_3$ 2:1). The assignments of peaks are based on ^{1}H homodecoupling and COSY measurements.

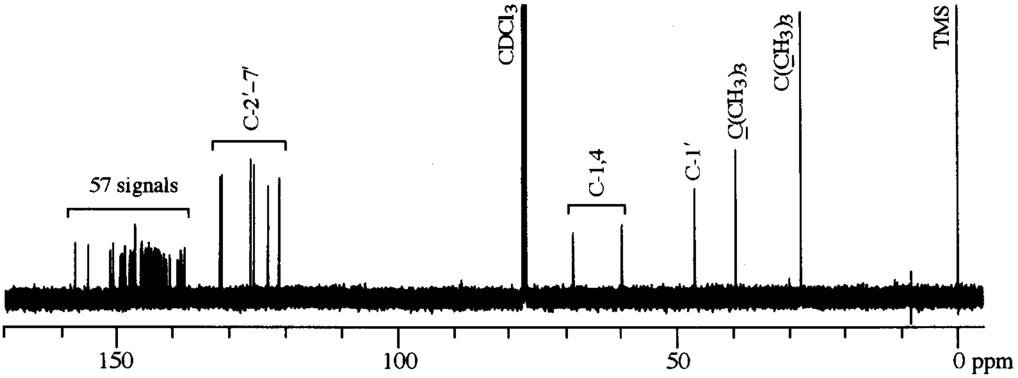
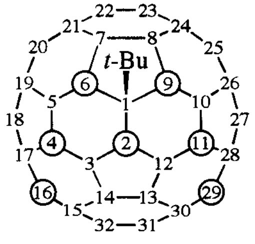


Fig. 3. ^{13}C NMR spectrum of **2a** (100 MHz, CS_2–$CDCl_3$ 2:1).

Table 1. HOMO Coefficients and Charge Densities on Carbon Atoms of *t*-BuC_{60}^- Calculated by PM3.

Position[a]	HOMO coefficient	Charge density
2	0.531	–0.330
4 (11)	0.375	–0.153
16 (29)	0.240	–0.094
6 (9)	0.182	–0.073

a) The numbering of C_{60} carbons is according to ref. 14.



Scheme 2

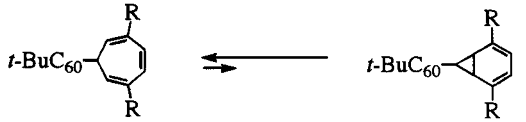
Table 2. Proton Nuclear Overhauser Enhancements Observed by Irradiation of the 1-*tert*-Butyl Protons of **2a–c**.[a]

Compound	Position of irradiation, ppm	NOE %	
		H-1'	H-4',5'[b]
2a	1.71	37	0.5
2b	1.70	36	0.6
2c	1.71	35	0.7

a) Measured using degassed solutions in CS_2–$CDCl_3$ (2:1). *b*) Average of the NOE's observed for H-4' and H-5'.

suggesting the conformation of the seven-membered ring as illustrated in Scheme 1. UV/vis spectra of **2a–c** (in cyclohexane) showed a broad absorption at 440–444 nm, which is typical to the 1,4-adducts[15] and is in contrast to the fact that 1,2-adducts generally exhibit a sharp absorption maximum at 430 nm.[16]

The ^{13}C NMR signals for C-2' and C-7' of the cycloheptatriene ring of **2c** at δ 117.7 and 116.0 were significantly broadened, indicating a rapid interconversion of the cycloheptatriene ring with a norcaradiene form (Scheme 3). We have reported earlier that the introduction of bulky substituents, especially *tert*-butyl groups, shifts the cycloheptatriene–norcaradiene equilibrium in favor of norcaradiene.[17] This tendency is more significant for the case of **2b**, whose spectrum showed no visible signals corresponding to C-2' and C-7'



Scheme 3

because of extreme line-broadening. However, the contribution of the norcaradiene form would be expected to be very small, since the H-2' and the H-7' signals appear in the normal olefinic region.

In contrast to the rapid isomerization of 1-*tert*-butyl-1,4-dihydrofullerene to its 1,2-isomer at 25 °C,[4] **2a–c** did not rearrange in $CDCl_3$, even at 75 °C. PM3 calculations (Table 3) showed that the heats of formation of **2a–c** (1,4-adduct) are 18 kcal/mol lower than those of the corresponding 1,2-isomers, whereas the 1,4-isomers of *t*-$BuC_{60}H$ and $C_{60}H_2$[18] are 3.0 and 3.8 kcal/mol higher in energy, respectively, than the 1,2-adducts.

Table 3. Calculated (PM3) Heats of Formation of Dihydrofullerene Derivatives R^1-C_{60}-R^2.[a]

R^1	R^2	Heat of formation (kcal/mol)			
		1,2-adduct	1,4-adduct	1,16-adduct	1,6-adduct
H	H	776.1[b]	779.9[b]	791.6[b]	794.5[b]
t-Bu	H	760.2	763.2	775.1	777.8
t-Bu	C_7H_7	834.3	816.2	829.3	846.5
t-Bu	3,6-(*t*-Bu)$_2C_7H_5$	789.2	771.4	784.6	801.4
t-Bu	3,6-(cyc-Pr)$_2C_7H_5$	872.5	854.5	867.9	884.7

a) The numbering of C_{60} carbons is shown in Scheme 2. *b*) Ref. 18.

Electrochemical behavior

Fig. 4 shows the cyclic voltammograms of **2a–c** obtained in 1,2-dichlorobenzene. Redox potentials of C_{60}, *t*-$BuC_{60}H$, and **2a–c** vs ferrocene/ferrocenium ion (Fc/Fc$^+$) are summarized in Table 4. Compounds **2a–c** showed three reversible reductions [$E_{red}(1)$, $E_{red}(2)$, and $E_{red}(3)$] under our analytical conditions. In addition, an irreversible oxidation wave (E_{ox}) resulting from the C_{60} skeleton was observed at approximately +1.4 V in each voltammogram. It is known that reduction potentials of 1,2-adducts, e.g. alkyl-substituted 1,2-dihydrofullerenes and methanofullerenes, are shifted to the negative side by 0.1–0.2 V compared with parent C_{60}.[5b,16,19] In addition, Suzuki et al.[19] have reported that the $E_{red}(1)$ and $E_{red}(2)$ of 1,2-cycloadducts of C_{60} correlates with LUMO energy levels in a linear fashion, whereas the $E_{red}(3)$ is better correlated with LUMO+1. The results in Table 4 indicate that the reduction potentials of 1,4-adducts show a similar trend. The reduction potentials of **2a–c** are 0.08–0.17 V more negative than the corresponding potentials of C_{60}, which is in accord with the rise of LUMO and LUMO+1 levels by ca. 0.2 eV. The relatively low sensitivity of the reduction potentials compared to the MO levels can be attributed to ion pairing or solvation of reduced species in solution.

The cyclic voltammogram of **2c** showed an additional reduction wave (Figure 4, marked with an asterisk, −1.99 V) just prior to $E_{red}(3)$. This reduction shows a somewhat smaller current than the other

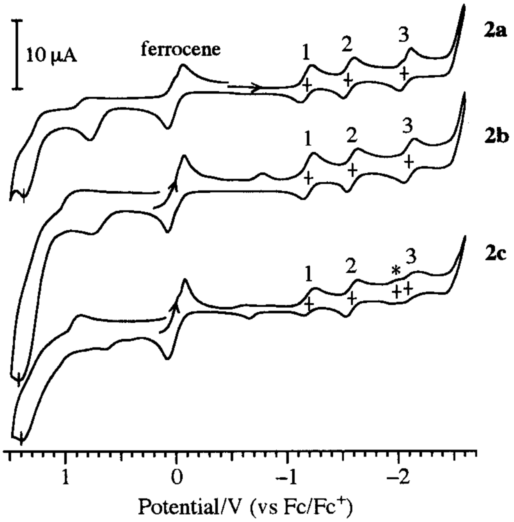


Fig. 4. Cyclic voltammograms of **2a–c** in 1,2-dichlorobenzene at room temperature. The wave marked with an asterisk is attributed to t-BuC_{60}^-.

Table 4. CV Redox Potentials and MO Energy Levels of C_{60}, t-BuC_{60}H, and **2a–c**.[a]

Compound	Redox potential (V vs Fc/Fc$^+$)[b]					MO energy level (eV)[c]	
	E_{ox}[d]	$E_{red}(1)$[e]	$E_{red}(2)$[e]	$E_{red}(3)$[e]	$E_{red}(4)$[e]	LUMO	LUMO+1
C_{60}	1.37	−1.09	−1.48	−1.93	−2.42	−2.89	−2.89
t-BuC_{60}H[f]	1.43	−1.22	−1.59	−2.13		−2.77	−2.66
2a	1.36	−1.18	−1.56	−2.06		−2.74	−2.70
2b	1.41	−1.19	−1.59	−2.09		−2.72	−2.68
2c[f]	1.38	−1.20	−1.58	−2.10		−2.72	−2.68

a) Solvent, 1,2-dichlorobenzene; scan rate, 20 mV/s; supporting electrolyte, 0.1 M of $Bu_4N^+PF_6^-$. *b*) Half-wave potentials. Peak potentials are shown for irreversible waves. *c*) Obtained by PM3 calculations. *d*) Irreversible. *e*) Reversible. *f*) An extra reversible reduction wave was observed at −1.99 V.

reductions. We attribute this reduction wave to t-BuC_{60}^- that is formed during the prior reduction processes, since t-BuC_{60}H, which can give t-BuC_{60}^- by deprotonation, also exhibits an extra reduction wave at the same position. Deprotonation induced by electrochemical reduction has been suggested for C_{60}(CN)H.[13]

Heterolytic cleavage of carbon–carbon σ bond

The most striking feature of hydrocarbons **2a–c** is their ability to ionize into a carbocation and a carbanion in solution. When **2a–c** are dissolved in DMSO or DMSO–CS_2, they undergo partial dissociation to give greenish yellow solutions. The visible/near-IR spectra (Fig. 5 shows an example) showed absorption peaks at 656 and 995 nm, which agreed with the absorption peaks of t-BuC_{60}^- (ε = 3650 and 2400, respectively) generated from t-BuC_{60}H and excess t-BuOK in DMSO. Cations **1a–c**$^+$ show no absorption in

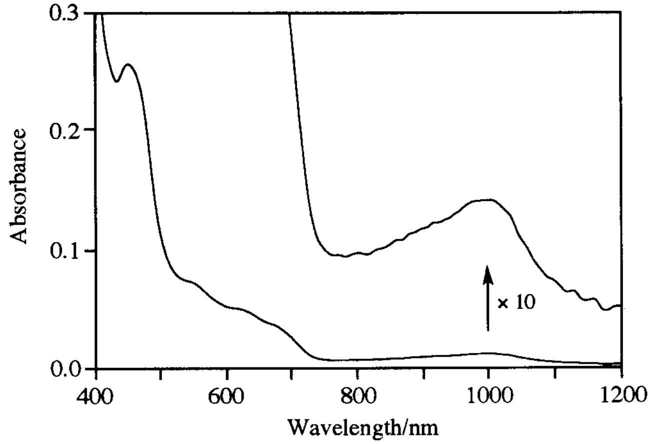


Fig. 5. Visible/near-IR absorption spectrum of **2a** in degassed DMSO–CS_2 (4:1 v/v), 4.97×10^{-5} M, cell length 1 cm.

Table 5. Equilibrium Constant and Free Energy of Heterolysis of **2a–c** in DMSO–CS_2 (4:1 v/v) at 25 °C.

Compound	Initial concentration c (10^{-5} M)	Degree of dissociation α (%)^a	K_{het} (10^{-7} M)	$\Delta G°_{het}$ (kcal/mol)
2a	4.97	5.7	1.69	9.27
	8.30	4.0	1.41	9.34
	12.3	3.2	1.30	9.39
	15.3	2.9	1.31	9.39
2b	1.96	22.4	12.6	8.05
	2.76	18.5	11.7	8.09
	3.57	14.7	9.05	8.24
	4.30	14.3	10.3	8.17
	9.31	9.3	8.81	8.26
2c	1.64	28.9	19.3	7.80
	5.96	17.8	22.9	7.69
	8.76	14.9	22.8	7.70
	18.8	10.2	21.6	7.73

a) Determined from the absorbance at 995 nm.

the visible region. In contrast, **2a–c** showed no absorption attributable to *t*-BuC_{60}^- in nonpolar solvents such as cyclohexane and CS_2.

The degree of dissociation (α) was determined in DMSO–CS_2 (4:1 v/v)[20] at 25 °C by monitoring the absorbance at 995 nm for solutions of different initial concentrations, c (Table 5). The agreement of dissociation constants [$K_{het} = c\alpha^2/(1-\alpha)$] obtained from four or five runs for each compound indicated that the equilibrium **2** $\rightleftarrows$ *t*-BuC_{60}^- + $\mathbf{1}^+$ was established. The free energy of heterolysis ($\Delta G°_{het}$), calculated from

Table 6. Thermodynamic Properties for Heterolysis of **2a–c** in DMSO–CS_2 (4:1 v/v) at 25 °C.

Compound	ΔG°_{het} (kcal/mol)	ΔH°_{het} (kcal/mol)		pK_{R^+} of tropylium ion[c]
		observed[a]	predicted[b]	
2a	9.3	4.3	19.4	3.88
2b	8.2	3.2	18.9	5.42
2c	7.7	2.7	18.2	7.63

a) Calculated from the ΔG°_{het} values with the assumption ΔS°_{het} = –17 cal/K ·mol. *b*) Predicted from Arnett's empirical equation using pK_{HA} = 5.7. c) Ref. 10.

the dissociation constant (Table 6), decreased as the pK_{R^+} of 1^+ increased. We have reported[2b] that the heterolysis of a carbon–carbon σ bond of a hydrocarbon in DMSO to form a resonance-stabilized carbanion and tropylium ion is accompanied by a significant loss (–17 cal/mol · K) of entropy, due to strong solvation of the cation. If the same magnitude of entropy change applies to the present system, the predicted ΔH°_{het} of **2a–c** would be 2.7–4.3 kcal/mol.

On the other hand, Arnett has reported a 'master equation,'

$$-\Delta H^\circ_{het} = 13.18 - 0.324\,(pK_{R^+}) + 1.307\,(pK_{HA})^{21} \qquad (1)$$

for correlating the enthalpy of heterolysis of carbon–carbon bond to give π-conjugated ions based on comprehensive calorimetric studies of the coordination reaction of carbocations and carbanions. This equation allows precise prediction of the enthalpies of heterolysis for many systems from the thermodynamic stability parameters, pK_{HA} and pK_{R^+}, of the generated ions. However, the ΔH°_{het} values predicted for **2a–c** (Table 6) are smaller by as much as 15 kcal/mol than observed. The large deviations of the observed ΔH°_{het} from prediction can be explained by two factors. First, an extremely large steric repulsion between the cycloheptatrienyl group and the 1-*tert*-butyl group in **2a–c** is released on ionization. Second, tropylium ions **1a–c**$^+$ are efficiently stabilized by strong solvation by DMSO. These factors are not significant in the systems used for derivation of equation 1, where the ions are sterically unencumbered and solvents, sulfolane and acetonitrile, have considerably weaker solvating powers than DMSO.

CONCLUSION

The exclusive formation of 1,4-adducts has been achieved by the coordination between *t*-BuC_{60}^- and tropylium ions. This is in contrast to the formation of 1,2-adducts, which have been reported for reactions of substituted fulleride ions with various electrophiles. The present finding suggests that regioselectivity with respect to adduct formation can be controlled by steric effects of the reactant molecules. The obtained 1,4-adducts, as designed, were found to undergo heterolysis of the carbon–carbon bond at room temperature in polar solvents. The heterolysis was reversible, and the absence of concurrent isomerization allowed simple thermodynamic treatment of the data. The facile heterolysis can be attributed principally to the high thermodynamic stabilities of the generated ions, but an analysis, based on Arnett's master equation, suggests that strong steric repulsion between the two substituents on the C_{60} framework is an additional important factor, as is strong solvation of the tropylium ion by DMSO.

EXPERIMENTAL

General

FAB mass spectral analyses were performed with a JEOL JMS-HX110 mass spectrometer. IR spectra were recorded on a Perkin-Elmer model 1600 spectrophotometer. Visible/near-IR spectra were measured with a Shimadzu UV-365 spectrophotometer. PM3 calculations were carried out using the MOPAC package[22] on an IBM RS/6000 computer.

^1H and ^{13}C NMR spectra were obtained with a JEOL EX400 (^1H, 400 MHz; ^{13}C, 100 MHz) instrument. Peak assignments are based on ^1H homodecoupling, DEPT, COSY, and C–H COSY measurements. The ^{13}C NMR data for **2a–c** was obtained using ca. 6 mg samples. Approximately 1.5×10^4 free induction decays were collected using 128 K data points and a pulse interval of 3 s. The accumulated data were processed after zero-filling to 1024 K. No window function was applied. A large number of data points was essential for the observation of the aromatic and olefinic carbons as separated signals. ^1H NOE's were determined by the gated decoupling method using degassed solutions of **2a–c** in CS_2–$CDCl_3$ (2:1). A saturation period of 8 s was taken before each pulse.

Reagents were of reagent-grade quality except where otherwise noted. Anhydrous solvents used for syntheses and visible/near-IR spectrometry were purified using the standard procedures. Tropylium tetrafluoroborate (**1a**$^+BF_4^-$) was prepared by the method described in the literature.[23] The perchlorate salts of 1,4-disubstituted tropylium ions, **1b**$^+ClO_4^-$ and **1c**$^+ClO_4^-$, were synthesized as reported previously by the CuBr-catalyzed ring expansion of 1,4-dialkylbenzene with diazomethane and subsequent hydride abstraction with triphenylmethylium perchlorate.[10]

1-tert-Butyl-1,2-dihydrofullerene[60] (t-BuC$_{60}$H)

This compound was synthesized essentially according to the procedure of Hirsch.[7] In a two-necked flask, equipped with a three-way stopcock and a rubber septum, was placed 100.1 mg of C_{60}. The flask was flushed with argon, and toluene (165 mL), which had been refluxed and distilled over sodium immediately before use, was added. A pentane solution of *tert*-butyllithium (1.6 M) was added dropwise at room temperature using a syringe at a rate of one drop per 3 minutes. During the addition of *tert*-butyllithium, a small aliquot was occasionally withdrawn for TLC analysis. The addition was continued until most of the C_{60} disappeared. Under the conditions employed, 2–5 equivalents of *tert*-butyllithium were required. The mixture was then neutralized by the addition of 0.01 M HCl in MeOH, and the solvent was evaporated under vacuum. The dark brown residue was dissolved in CS_2, and inorganic materials were filtered off. The filtrate was then evaporated to give a dark brown solid, which, on separation by flash chromatography (SiO_2, hexane–benzene 95:5), afforded 30.5 mg (28%) of pure *t*-BuC$_{60}$H.

1-tert-Butyl-4-(2,4,6-cycloheptatrien-1-yl)-1,4-dihydrofullerene[60] (2a)

To a stirred THF solution (10 mL) of *t*-BuC$_{60}$H (7.64 mg, 9.81 μmol) was added a 5% excess of *t*-BuOK in THF (16.4 mM) under argon in the dark at room temperature. After 30 min, a THF–acetonitrile solution (3:1 v/v, 0.4 mL) of **1a**$^+BF_4^-$ (1.92 mg, 10.8 μmol) was added dropwise. The mixture was stirred for 15 min, and the solvent evaporated under vacuum. The dark brown residue was dissolved in CS_2 and quickly filtered through a column of SiO_2 (0.2 g) to remove KBF_4 and unchanged **1a**$^+BF_4^-$. The CS_2 was evaporated to give **2a** as a dark brown solid (7.7 mg, 90%). This solid was found to be essentially pure, and all analyses and heterolysis measurements were carried out without further purification. ^{1}H NMR (400 MHz, CS$_2$–CDCl$_3$ 2:1) δ 6.85 (m, 2H, H-4' and H-5'), 6.53 (m, 2H, H-6' and H-7'), 6.42 (dd, J = 4.9 and 9.3 Hz, 1H, H-3'), 6.15 (dd, J = 5.9 and 9.3 Hz, 1H, H-2'), 3.33 (m, 1H, H-1'), 1.71 (s, 3H, *t*-Bu); ^{13}C NMR (100 MHz, CS$_2$–CDCl$_3$ 2:1) δ 27.8 (CH$_3$); 131.5, 131.1, 126.0, 125.4, 122.9, 120.9, 46.8 (CH$_2$); 157.4, 155.1, 151.1, 150.6, 149.3, 149.0, 148.43, 148.42, 147.6, 147.5, 147.1, 147.0, 146.9, 146.8, 146.68, 146.67(×2), 145.7, 145.5, 145.41, 145.40, 145.0, 144.9, 144.7, 144.64, 144.60, 144.58, 144.20, 144.18, 144.16, 144.04, 144.01, 143.96, 143.9, 143.8, 143.4, 143.34, 143.29, 143.2, 143.1, 143.02, 142.98, 142.9, 142.80, 142.79, 142.58, 142.55, 142.5, 142.3, 142.11, 142.06, 141.5, 141.1, 140.5, 139.0, 138.5, 138.3, 137.8, 68.3 ,59.8, 39.5 (C); IR (KBr) 2961, 1461, 1430, 1393, 1364, 1204, 1189, 735, 700, 523. UV/vis (cyclohexane) λ_{max} (ε) 212 (129000), 257 (99600), 328 (27900), 444 (5820) with end absorption to 720 nm. The FAB mass spectrum and the cyclic voltammogram are shown in Figs. 1 and 4, respectively.

1-tert-Butyl-4-(3,6-di-tert-butyl-2,4,6-cycloheptatrien-1-yl)-1,4-dihydrofullerene[60] ***(2b)***

This compound was synthesized by the method described above using 7.66 mg (9.83 μmol) of *t*-BuC$_{60}$H and 3.38 mg (11.2 μmol) of $\mathbf{1b}^+$ClO$_4^-$. Dark brown solid; yield 95%; ^{1}H NMR (400 MHz, CS$_2$–CDCl$_3$ 2:1) δ 6.95 and 6.90 (AB quartet, J = 11.7 Hz, 1H each, H-4' and H-5'), 6.29 (d, J = 6.4 Hz, 1H, H-2' or H-7'), 5.89 (d, J = 5.9 Hz, 1H, H-7' or H-2'), 3.18 (t, J = 5.9 Hz, 1H, H-1'), 1.70 (s, 3H, *t*-Bu), 1.23 (s, 3H, *t*-Bu), 1.13, (s, 3H, *t*-Bu); ^{13}C NMR (100 MHz, CS$_2$–CDCl$_3$ 2:1) δ 29.9, 29.8, 27.8 (CH$_3$); 130.4, 130.1, 44.4 (CH); 157.4, 155.8, 151.8, 150.5, 149.4, 148.9, 148.38, 148.35, 147.63, 147.59, 147.4, 147.02, 146.96, 146.72, 146.65, 146.63, 146.62, 145.55, 145.4, 145.3, 145.2, 145.1, 145.0, 144.84, 144.80, 144.63, 144.61, 144.58, 144.5, 144.2(×2), 144.1, 144.02, 143.97, 143.95, 143.87, 143.8, 143.5, 143.3, 143.2, 143.1, 142.99, 142.98, 142.9(×2), 142.72, 142.69, 142.6, 142.53, 142.48, 142.3, 142.1, 142.0, 141.6, 141.1, 140.3, 138.8, 138.27, 138.26, 137.8, 68.2, 60.5, 39.5, 34.50, 34.45 (C); IR (KBr) 2960, 1460, 1429, 1364, 1201, 1188, 839, 526. UV/vis (cyclohexane) λ_{max} (ε) 212 (123000), 257 (93400), 328 (26600), 444 (5970) with end absorption to 720 nm. The FAB mass spectrum and the cyclic voltammogram are shown in Figs. 1 and 4, respectively.

1-tert-Butyl-4-(3,6-dicyclopropyl-2,4,6-cycloheptatrien-1-yl)-1,4-dihydrofullerene[60] ***(2c)***

This compound was synthesized by the method described for the synthesis of **2a** using 7.27 mg (9.34 μmol) of *t*-BuC$_{60}$H and 2.67 mg (10.3 μmol) of $\mathbf{1c}^+$ClO$_4^-$. Dark brown solid; yield 82%; ^{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 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); 157.5, 155.5, 151.5, 150.5, 149.3, 149.0, 148.40, 148.39, 147.6, 147.5, 147.3, 147.1, 147.0, 146.74, 146.70, 146.66, 146.65, 145.6, 145.40, 145.383, 145.380, 145.0, 144.9, 144.8, 144.62, 144.60, 144.57, 144.20, 144.19, 144.13, 144.03, 144.02, 143.97, 143.86, 143.83, 143.4, 143.31, 143.26, 143.15, 143.03, 143.01, 142.96, 142.93, 142.8, 142.7, 142.6, 142.54, 142.50, 142.3, 142.13, 142.05, 141.5, 141.1, 140.4, 138.9, 138.43, 138.35, 138.3, 137.9, 137.8, 68.3, 60.2, 39.5 (C); IR (KBr) 2961, 1514, 1460, 1428, 1365, 1205, 1190, 1043, 1017, 526. UV/vis (cyclohexane) λ_{max} (ε) 212 (108000), 256 (81500), 325sh (27100), 440 (6230) with end absorption to 750 nm. The FAB mass spectrum and the cyclic voltammogram are shown in Figs. 1 and 4, respectively.

Cyclic voltammetry

Cyclic voltammetry was carried out with a BAS CV-50W instrument. A three-electrode cell, consisting of a BAS 11-2012 glassy carbon working electrode, a Pt wire counter electrode, and a $Ag/AgNO_3$ (0.01 M in CH_3CN) reference electrode, was employed. The measurements were carried out at a scan rate of 20 mV/s for 1,2-dichlorobenzene solutions containing 1 mM of sample, 1 mM of ferrocene as an internal standard, and 0.1 M of $Bu_4N^+PF_6^-$ as a supporting electrolyte.

Visible/near-IR spectra

For the determination of the molar absorptivities of t-BuC_{60}^-, a DMSO solution of t-$BuC_{60}^-K^+$ was prepared by dissolving 439 μg (0.564 μmol) of t-$BuC_{60}H$ in 10.10 mL of degassed DMSO containing 2.4 equivalents of t-BuOK in a vacuum-sealed, ($<10^{-5}$ Torr) 1-cm quartz cell. Similarly, the degree of heterolytic dissociation of **2a–c** in DMSO–CS_2 (4:1) was determined by measuring the visible/near-IR spectra of 0.2–2 μM solutions of these compounds. Details of the apparatus and procedure have been described previously.[2b]

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REFERENCES AND NOTES

1. A preliminary report of this work has been published: Kitagawa, T.; Tanaka, T.; Takata, Y.; Takeuchi, K.; Komatsu, K. *J. Org. Chem.* **1995**, *60*, 1490-1491.
2. (a) Okamoto, K.; Takeuchi, K.; Kitagawa, T. *Adv. Phys. Org. Chem.* **1995**, *30*, 173-221. (b) Miyabo, A.; Kitagawa, T.; Takeuchi, K. *J. Org. Chem.* **1993**, *58*, 2428-2435. (c) Takeuchi, K.; Kitagawa, T.; Miyabo, A.; Hori, H.; Komatsu, K. *J. Org. Chem.* **1993**, *58*, 5802-5810. (d) Okamoto, K.; Kitagawa, T.; Takeuchi, K.; Komatsu, K.; Kinoshita, T.; Aonuma, S.; Nagai, M.; Miyabo, A. *J. Org. Chem.* **1990**, *55*, 996-1002. (e) Okamoto, K.; Kitagawa, T.; Takeuchi, K.; Komatsu, K.; Miyabo, A. *J. Chem. Soc., Chem. Commun.*, **1988**, 923-924. (f) Okamoto, K.; Kitagawa, T.; Takeuchi, K.; Komatsu, K.; Takahashi, K. *J. Chem. Soc., Chem. Commun.*, **1985**, 173-174.
3. (a) Subramanian, R.; Boulas, P.; Vijayashree, M. N.; D'Souza, F.; Jones, M. T.; Kadish, K. M. *J. Chem. Soc., Chem. Commun.* **1994**, 1847-1848; (b) Stinchcombe, J.; Pénicaud, A.; Bhyrappa, P.; Boyd, P. D. W.; Reed, C. A. *J. Am. Chem. Soc.* **1993**, *115*, 5212-5217; (c) Dubois, D.; Jones, M. T.; Kadish, K. M. *J. Am. Chem. Soc.* **1992**, *114*, 6446-6451; and references cited therein.
4. Fagan, P. J.; Krusic, P. J.; Evans, D. H.; Lerke, S. A.; Johnston, E. *J. Am. Chem. Soc.* **1992**, *114*, 9697-9699.
5. (a) Murata, Y.; Motoyama, K.; Komatsu, K.; Wan, T. S. M. *Tetrahedron* **1996**, *52*, 5077-5090. (b) Komatsu, K.; Murata, Y.; Takimoto, N.; Mori, S.; Sugita, N.; Wan, T. S. M. *J. Org. Chem.* **1994**, *59*, 6101-6102.

6. Timmerman, P.; Anderson, H. L.; Faust, R.; Nierengarten, J. F.; Habicher, T.; Seiler, P.; Diederich, F. *Tetrahedron* **1996**, *52*, 4925-4947.
7. (a) Hirsch, A.; Grösser, T.; Skiebe, A.; Soi, A. *Chem. Ber.* **1993**, *126*, 1061-1067; (b) Hirsch, A.; Soi, A.; Karfunkel, H. R. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 766-768.
8. Nagashima, H.; Terasaki, H.; Kimura, E.; Nakajima, K.; Itoh, K. *J. Org. Chem.* **1994**, *59*, 1246-1248.
9. (a) Komatsu, K.; Aonuma, S.; Takeuchi, K.; Okamoto, K. *J. Org. Chem.* **1989**, *54*, 2038-2039. (b) Arnett, E. M.; Molter, K. E.; Marchot, E. C.; Donovan, W. H.; Smith, P. *J. Am. Chem. Soc.* **1987**, *109*, 3788-3789
10. Komatsu, K.; Takeuchi, K.; Arima, M.; Waki, Y.; Shirai, S.; Okamoto, K. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 3257-3261.
11. Derived from values reported vs Ag/Ag^+ using a conversion factor of –0.083 V. For conversion from Ag/Ag^+ to Fc/Fc^+, see Komatsu, K.; Masumoto, K.; Waki, Y.; Okamoto, K. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2470-2479.
12. Hirsch et al. obtained similar results regarding the charge distribution of t-BuC_{60}^- using the AM1 method (ref. 7b).
13. Keshavarz-K, M.; Knight, B.; Srdanov, G.; Wudl, F. *J. Am. Chem. Soc.* **1995**, *117*, 11371-11372;
14. Taylor, R. *J. Chem Soc., Perkin Trans. 2* **1993**, 813-824.
15. (a) Murata, Y.; Komatsu, K.; Wan, T. S. M. *Tetrahedron Lett.* **1996**, *37*, 7061-7064. (b) González R.; Wudl, F.; Pole, D. L.; Sharma, P. K.; Warkentin, J. *J. Org. Chem.* **1996**, *61*, 5837-5839. (c) Schick, G.; Kampe, K.-D.; Hirsch, A. *J. Chem. Soc., Chem. Commun.* **1995**, 2023-2024.
16. For example, (a) Komatsu, K.; Murata, Y.; Sugita, N.; Takeuchi, K.; Wan, T, S, M. *Tetrahedron Lett.* **1993**, *34*, 8473-8476. (b) Komatsu, K; Kagayama, A.; Murata, Y.; Sugita, N.; Kobayashi, K.; Nagase, S.; Wan, T. S. M. *Chem. Lett.* **1993**, 2163-2166.
17. (a) Takeuchi, K.; Kitagawa, T.; Ueda, A.; Senzaki, Y.; Okamoto, K. *Tetrahedron* **1985**, *23*, 5455-5463. (b) Takeuchi, K.; Kitagawa, T.; Toyama, T.; Okamoto, K. *J. Chem. Soc., Chem. Commun.* **1982**, 313-314. (c) Takeuchi, K.; Arima, M.; Okamoto, K. *Tetrahedron Lett.* **1981**, *22*, 3081-3084.
18. (a) Henderson, C. C.; Rohlfing, C. M.; Cahill, P. A. *Chem. Phys. Lett.* **1993**, *213*, 383-388. (b) Henderson, C. C.; Cahill, P. A. *Chem. Phys. Lett.* **1992**, *198*, 570-576. (c) Matsuzawa, N.; Dixon, D. A.; Fukunaga, T. *J. Phys. Chem.* **1992**, *96*, 7594-7604.
19. Suzuki, T.; Maruyama, Y.; Akasaka, T.; Ando, W.; Kobayashi, K.; Nagase, S. *J. Am. Chem. Soc.* **1994**, *116*, 1359-1363.
20. CS_2 was added to increase the solubility, since **2a–c** are sparingly soluble in DMSO.
21. Equation for tertiary cations: (a) Arnett, E. M.; Chawla, B.; Amarnath, K.; Whitesell, Jr., L. G. *Energy and Fuels*, **1987**, *1*, 17-23. (b) Arnett, E. M.; Amarnath, K.; Harvey, N. G.; Cheng, J.-P. *J. Am. Chem. Soc.* **1990**, *112*, 344-355.
22. MOPAC version 6, Stewart, J. J. P. *QCPE* No. 455; revised as ver. 6.01 by Hirano, T., University of Tokyo, for UNIX machines.
23. Dauben Jr., H. J.; Gadecki, F. A.; Harmon, K. M.; Pearson, D. L. *J. Am. Chem. Soc.* **1957**, *79*, 4557-4558.

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