Communications

Reversible Carbon−Carbon Bond Heterolysis of a Hydrocarbon Derived from *tert*-Butylfulleride Ion and Tricyclopropylcyclopropenylium Ion

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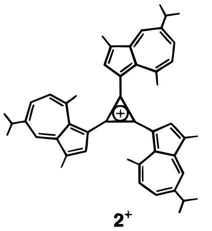
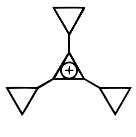
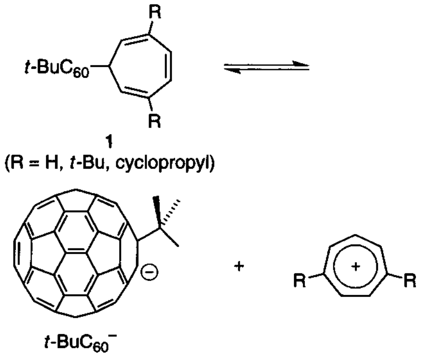
It is generally assumed that carbon−carbon bonds in hydrocarbons are covalent in nature and that the standard mode of the thermal cleavage of these bonds is homolysis. Although heterolysis of a carbon−carbon single bond, an alternative pathway for bond dissociation, under thermal conditions is a rare phenomenon, we recently reported that a series of hydrocarbons **1**, which are derived from *tert*-butylfulleride ion (t-BuC$_{60}^{-}$) and substituted tropylium ions, undergo partial heterolysis into ions in polar media (Scheme 1).[1,2] Furthermore, the combination of t-BuC$_{60}^{-}$ and a highly stabilized cyclopropenylium ion **2**$^{+}$ was isolated as an ionic solid.[3] Our explanation for the existence of hydrocarbon t-BuC$_{60}^{-}$·**2**$^{+}$ in a stable salt form is based on the high thermodynamic stability of the component ions, as well as steric repulsion between the *tert*-butyl group and the guaiazulenyl groups, which prevent covalent bond formation. We now report that the coordination of a less bulky cyclopropenylium ion (**3**$^{+}$) regioselectively reacts with t-BuC$_{60}^{-}$ to give a 1,4-dialkyl adduct. We also found that the adduct reversibly dissociates into the original ions, **3**$^{+}$ and t-BuC$_{60}^{-}$, in polar solvents.


2^{+}

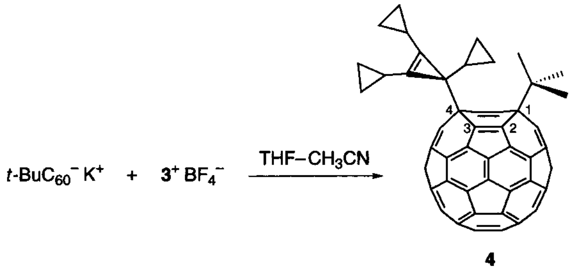

3^{+}

The adduct **4**, a dark brown solid, was synthesized in essentially quantitative yield by the addition of the tetrafluoroborate salt of tricyclopropylcyclopropenylium ion (**3**$^{+}$)[4] to a THF solution of *tert*-butylfulleride ion (t-BuC$_{60}^{-}$)[5,6] in a 1:1 molar ratio (Scheme 2).[7]

Scheme 1



Scheme 2



NMR spectra[8] showed that the product consisted of only one regioisomer. The three cyclopropyl groups are nonequivalent, indicating that the molecule has no element of symmetry. Consistent with this is the observation of 57 aromatic carbon signals in the region of δ 135−161. The product is most likely the 1,4-adduct **4** (Scheme 2), based on the absence of symmetry and the ^{1}H NOE difference spectrum, which clearly indicates that the three methine protons of the cyclopropyl groups are in close contact with the *tert*-butyl group.[9] The heats of formation of all possible isomers of dihydrofullerenes have been calculated by Henderson[10] and Matsuzawa,[11] who concluded that the 1,2-addition is thermodynamically the most favorable, while the 1,4-adduct is the next most stable due to somewhat unfavorable π-conjugation. For the case of the 1,4-dialkyl adduct **4**, the loss of π-conjugation energy appears to be compensated by relief of steric repulsion between the two groups attached to C$_{60}$.[12]

FAB mass spectra (negative ion, *o*-nitrophenyl octyl ether matrix) showed peaks for **4** (M, *m*/*z* 936), as well as

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(1) Kitagawa, T.; Tanaka, T.; Takata, Y.; Takeuchi, K.; Komatsu, K. *J. Org. Chem.* **1995**, *60*, 1490.

(2) Kitagawa, T.; Tanaka, T.; Takata, Y.; Takeuchi, K.; Komatsu, K. *Tetrahedron* **1997**, *53*, 9965.

(3) Tanaka, T.; Kitagawa, T.; Komatsu, K.; Takeuchi, K. *J. Am. Chem. Soc.* **1997**, *119*, 9313.

(4) Komatsu, K.; Tomioka, I.; Okamoto, K. *Tetrahedron Lett.* **1980**, *21*, 947.

(5) Fagan, P. J.; Krusic, P. J.; Evans, D. H.; Lerke, S. A.; Johnston, E. *J. Am. Chem. Soc.* **1992**, *114*, 9697.

(6) t-BuC$_{60}^{-}$ was generated by the deprotonation of t-BuC$_{60}$H with 1 equiv of t-BuOK in THF. t-BuC$_{60}$H was synthesized according to the procedure of Hirsch: (a) Hirsch, A.; Grösser, T.; Skiebe, A.; Soi, A. *Chem. Ber.* **1993**, *126*, 1061. (b) Hirsch, A.; Soi, A.; Karfunkel, H. R. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 766.

(7) The inorganic byproduct, KBF$_4$, was removed by extraction with carbon disulfide followed by filtration through a 0.45 μm Teflon membrane filter. The obtained product **4** was essentially pure and was used without further purification for spectroscopic characterization and related studies.

(8) Spectral data for **4**: ^{1}H NMR (400 MHz, CS$_2$−CDCl$_3$ 2:1) δ 2.13−2.03 (m, 1H), 1.94 (s, 9H), 1.80−1.71 (m, 1H), 1.71−1.62 (m, 1H), 1.04−0.89 (m, 4H), 0.71−0.55 (m, 6H), 0.55−0.48 (m, 1H), 0.43−0.35 (m, 1H); ^{13}C NMR (100.5 MHz, CS$_2$−CDCl$_3$ 2:1), δ 27.9 (CH$_3$), 4.3, 5.1, 9.98, 10.05, 10.5, 10.8 (CH$_2$), 6.5, 6.9, 18.4 (CH), 40.5, 42.4, 67.7, 68.1, 117.2, 117.4 (C). The aromatic carbons of C$_{60}$ showed 57 peaks in the range of δ 160.4−135.7. NMR signal assignments are based on DEPT, COSY, and H−C COSY measurements. UV/vis (cyclohexane) λ_{max} (ϵ) 213 (131 000), 257 (10 100), 327sh (29 900), 446 (5920) with end absorption to 750 nm. Details are given in the Supporting Information.

(9) Irradiation of the *tert*-butyl protons led to significant enhancement (21, 17, and 17%) of the three methine-proton signals.

(10) (a) Henderson, C. C.; Cahill, P. A. *Chem. Phys. Lett.* **1992**, *198*, 570. (b) Henderson, C. C.; Rohlfing, C. M.; Cahill, P. A. *Chem. Phys. Lett.* **1993**, *213*, 383.

(11) Matsuzawa, N.; Dixon, D. A.; Fukunaga, T. *J. Phys. Chem.* **1992**, *96*, 7594.

(12) PM3 calculations indicated that the formation of the 1,4-isomer is thermodynamically more favorable than the 1,2-isomer by 22.1 kcal/mol.

10.1021/jo981503e CCC: $18.00

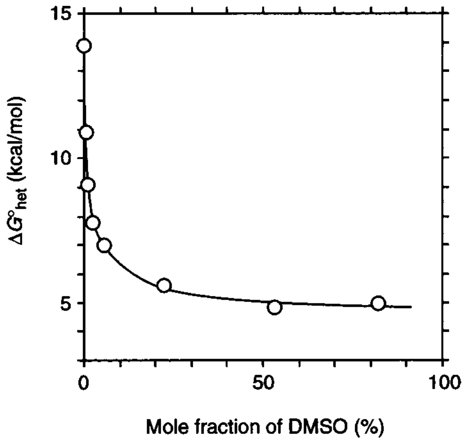

Figure 1. Plot of free energy of heterolysis of **4** at 25 °C in DMSO−THF mixed solvents vs mole fraction of DMSO.

fragments corresponding to M − *t*-Bu (879), *t*-BuC_{60} (777), and C_{60} (720). UV/vis spectra of **4** (in cyclohexane) showed a broad peak at 446 nm, which is typical of 1,4-adducts.[2] In contrast, 1,2-adducts generally exhibit a sharp absorption peak in the vicinity of 430 nm.[13]

When dissolved in mixtures of DMSO−THF or DMSO−CS_2, hydrocarbon **4** dissociated into the original ions, *t*-BuC_{60}^- and $\mathbf{3}^+$, giving a greenish colored solution, which is indicative of the formation of fulleride ions. Ionic dissociation was more directly demonstrated by ^{1}H NMR spectroscopy, which showed the formation of $\mathbf{3}^+$ and *t*-BuC_{60}^- in DMSO-d_6−THF-d_8 (1:1 v/v). In nonpolar solvents such as chloroform and carbon disulfide, no dissociation was observed.

In DMSO−THF binary solvents, the degree of dissociation[14] changed from 0.1 to 80% by increasing the solvent polarity from pure THF to a 4:1 (v/v) mixture of DMSO−THF. A plot of free energy of heterolysis, $\Delta G°_{het}$, against the mole fraction of DMSO showed that $\Delta G°_{het}$ is not related to the composition of the solvent in a straightforward manner (Figure 1). A large decrease in $\Delta G°_{het}$ initially occurred upon the addition of small amounts of DMSO to pure THF, while a gradual decrease was observed at DMSO concentrations higher than 5 mol %. This suggests that the heterolysis is not only controlled by the bulk polarity of the solvent but also by the preferential solvation of ions by DMSO. The large donor number of DMSO (46.5)[15] suggests the importance of Lewis base type coordination of the sulfoxide oxygen to cation $\mathbf{3}^+$.

Surprisingly, an essentially complete conversion (>99%) to the ionized form occurred in DMSO−CS_2 (4:1 v/v), indicating that the free energy of heterolysis is 4 kcal/mol or less in this solvent. The ions are gradually hydrolyzed by traces of water in the solution, as indicated by the appearance of *t*-BuC_{60}H, as evidenced by NMR spectroscopy.

The facile dissociation of the carbon−carbon bond to form *t*-BuC_{60}^- was also demonstrated by cyclic voltammetry.[16] Compound **4** exhibited three reversible reduction waves at −1.28, −1.63, and −2.18 V (vs Fc/Fc^+ in 1,2-dichlorobenzene). These potentials are, respectively, ca. 0.1 V more negative than the first three reduction waves for C_{60}, as is commonly observed for substituted dihydrofullerenes.[2,17] In addition, a reversible wave at −1.99 V and an irreversible oxidation wave at −0.67 V, which exhibited somewhat smaller currents than other reduction waves, were observed. We attribute these additional waves to the anion *t*-BuC_{60}^-, which is formed during the initial reduction process, since the *t*-BuC_{60}^-, generated by deprotonation of *t*-BuC_{60}H, showed reduction and oxidation waves at the same potentials in 1,2-dichlorobenzene.

In summary, we report the synthesis of a new dialkyl-1,4-dihydrofullerene **4** with complete regioselectivity. The high tendency of a carbon−carbon bond in this compound toward heterolysis has been demonstrated by its facile heterolysis into stable ions *t*-BuC_{60}^- and $\mathbf{3}^+$ in polar solvents. The kinetics of the heterolysis and the physical properties of **4** originating in the ion formation, e.g., solution electrical conductivity, are currently under investigation.

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Supporting Information Available: Synthetic procedure, cyclic voltammogram, and spectral data for compound **4**, including ^{1}H and ^{13}C NMR, ^{1}H NOE difference, COSY, H−C COSY, FAB mass, and UV/vis spectra. Spectral evidence for the ionic dissociation of **4** (vis/near-IR spectrum in DMSO−CS_2 4:1 v/v and ^{1}H NMR spectrum in DMSO-d_6−THF-d_8 1:1 v/v) is also given (12 pages).

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(13) For example: (a) Komatsu, K.; Murata, Y.; Sugita, N.; Takeuchi, K.; Wan, T, S, M. *Tetrahedron Lett.* **1993**, *34*, 8473. (b) Komatsu, K.; Kagayama, A.; Murata, Y.; Sugita, N.; Kobayashi, K.; Nagase, S.; Wan, T. S. M. *Chem. Lett.* **1993**, 2163.

(14) The degree of dissociation was determined using vacuum-degassed ~10^{-4} M solutions, based on the absorption of *t*-BuC_{60}^- (λ_{max} 995 nm, ϵ 2400, ref 3).

(15) Gutmann, V. In *The Donor−Acceptor Approach to Molecular Interactions*; Plenum Press: New York, 1978; Chapter 2.

(16) Measured in the presence of $Bu_4N^+PF_6^-$ (0.1 M) as a supporting electrolyte and using ferrocene as an internal standard.

(17) Suzuki, T.; Maruyama, Y.; Akasaka, T.; Ando, W.; Kobayashi, K.; Nagase, S. *J. Am. Chem. Soc.* **1994**, *116*, 1359.