Steric and Solvation Effects in the Heterolysis of Carbon–Carbon σ Bonds in Hydrocarbons Giving Stable Carbocations and Carbanions[1]

Atsushi Miyabo, Toshikazu Kitagawa, and Ken'ichi Takeuchi*

Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606-01, Japan

Received November 19, 1992

Twelve ionically dissociative hydrocarbons (**1–2b–m**) and a bromo derivative (**1–2a**) have been synthesized by the carbocation–carbanion combination reaction of tris(7*H*-dibenzo[*c,g*]fluorenylidenemethyl)methide ion ($C_{67}H_{39}^-$, 1^-) and substituted tropylium ions (**2a–m**$^+$). The reaction of 1,3- and 1,4-disubstituted tropylium ions gave a single product, but monosubstituted tropylium ions gave two positional isomers. The bicyclo[2.2.1]heptenotropylium ion **2i**$^+$ gave a single product, whereas the bicyclo[2.2.2]octenotropylium ion **2j**$^+$ gave two positional isomers. MMP2 calculations on model compounds suggested that the difference in the behavior between **2i**$^+$ and **2j**$^+$ may be explained on the basis of the relative steric energies of the covalent products. Spectrophotometric studies for the behavior of **1–2a–j** revealed their reversible ionization in DMSO or 5/95 3-methylsulfolane/sulfolane into the corresponding ionic species. Conductometric studies have also shown the partial ionization of **1–2c,e,f** in DMSO. When the cationic part has a methyl, ethyl, or isopropyl group (**1–2k–m**), the ionization becomes irreversible owing to the polymerization of the tropylium ions via heptafulvene intermediates. The standard free energies of heterolysis (ΔG°_{het}) for **1–2a–j** were lower by ~10 kcal/mol than those predicted from pK_{R^+} and pK_a values by Arnett's master equations, indicating that steric congestion in the covalent compounds plays an important role in enhancing the cleavage. The entropy term ($-T\Delta S_{het}$) of the heterolysis of **1–2c** was found to be ~+5 kcal/mol, which is interpreted as a result of solvation to the tropylium ion. The significance of the steric factor was similarly demonstrated for the heterolysis which leads to phenylmalononitrile anion and tri-*tert*-butylcyclopropenylium ion in acetonitrile.

Carbon–carbon σ bonds generally undergo homolytic fission at high temperatures. Since homolysis is one of the most fundamental reactions of hydrocarbons, systematic studies have been conducted by many workers. Among them, Rüchardt and his co-workers investigated the products and kinetics of thermolysis of a large number of highly branched aliphatic hydrocarbons and phenyl- or cyano-substituted derivatives and have quantitatively shown the influence of strain in the molecules and the stability of the radicals on the homolytic cleavage of carbon–carbon σ bonds.[2]

However, as a rare case, some investigators have reported the heterolytic dissociation of carbon–carbon σ bonds to give a carbocation and a carbanion. The first example of such fission has been reported by Cram in the ring opening of optically active cyclopropanes which on heterolytic cleavage give zwitterionic intermediates stabilized by both electron-donating and electron-withdrawing substituents.[3]

With the progress in the synthesis of stable carbocations and carbanions, the direct observation of heterolysis of carbon–carbon σ bonds became a subject of kinetic, thermodynamic, and mechanistic studies. Arnett and his co-workers found the first example of such molecules, which dissociate into cyclopropenylium ions and arylmalononitrile anions.[4] As one of the results of their systematic studies on the carbon–carbon bond formation through the reaction of cations and anions, they proposed empirical relationships (master equations)[5,6] which correlate the heat of heterolysis (ΔH_{het}) with the thermodynamic stabilities of cations (pK_{R^+}) and anions (pK_a(RH)) over a wide range. However, the influence of the steric effect, one of the most important factors in the cleavage of chemical bonds, has remained uncertain in the heterolytic cleavage of carbon–carbon σ bonds.

We have reported a covalent hydrocarbon, **1–2c**,[7] which partly dissociates into tris(7*H*-dibenzo[*c,g*]fluorenylidenemethyl)methide ion (1^-, pK_a(RH) 5.9)[8] and the tropylium ion **2c**$^+$ in solution. This compound would permit the examination of the importance of electronic and steric effects, since the property of the cationic part can be changed by using a variety of substituents. In addition, **1–2c** has another advantage of being a hydrocarbon, so that it is a good model compound for which theoretical approaches can be applied without suffering from lack of computational parameters.

The present paper describes the synthesis of 11 new ionically dissociative hydrocarbons (**1–2b,d–m**) and a related bromo derivative (**1–2a**) from carbocation–carbanion combination reaction of 1^- with substituted tropylium ions whose pK_{R^+} values range from 3.25 to 7.80. The standard free energies of heterolysis (ΔG°_{het}) of **1–2a–j** in DMSO and 5/95 3-methylsulfolane/sulfolane at 25 °C were spectrophotometrically measured and assessed by Arnett's master equations to evaluate the steric effect and the solvation effect in the ionic cleavage of carbon–carbon σ bonds.

---

[1] A preliminary communication of this work has been published: Miyabo, A.; Kitagawa, T.; Takeuchi, K. *Chem. Lett.* **1992**, 679.

[2] Rüchardt, C.; Beckhaus, H.-D. *Angew. Chem. Int. Ed. Engl.*, 1980, *19*, 429 and references cited therein.

[3] Cram, D. J.; Ratajczak, A. *J. Am. Chem. Soc.* **1968**, *90*, 2198. Yankee, E. W.; Badea, F. D.; Howe, N. E.; Cram, D. J. *J. Am. Chem. Soc.*, 1973, *95*, 4210.

[4] Arnett, E. M.; Troughton, E. B.; McPhail, A. T.; Molter, K. E. *J. Am. Chem. Soc.* **1983**, *105*, 6172.

[5] Arnett, E. M.; Chawla, B.; Amarnath, K.; Whitesell, L. G., Jr. *Energy Fuels* **1987**, *1*, 17.

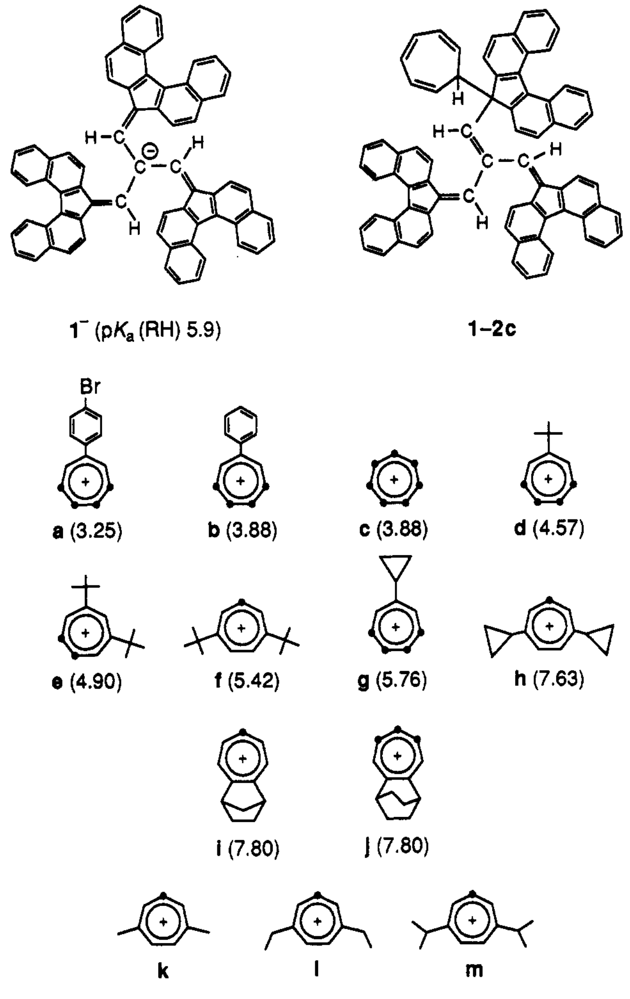
[6] Arnett, E. M.; Amarnath, K.; Harvey, N. G.; Cheng, J.-P. *J. Am. Chem. Soc.* **1990**, *112*, 344.

[7] Okamoto, K.; Kitagawa, T.; Takeuchi, K.; Komatsu, K.; Takahashi, K. *J. Chem. Soc., Chem. Commun.* **1985**, 173.

[8] Kuhn, R.; Rewicki, D. *Angew. Chem.* **1967**, *79*, 648.

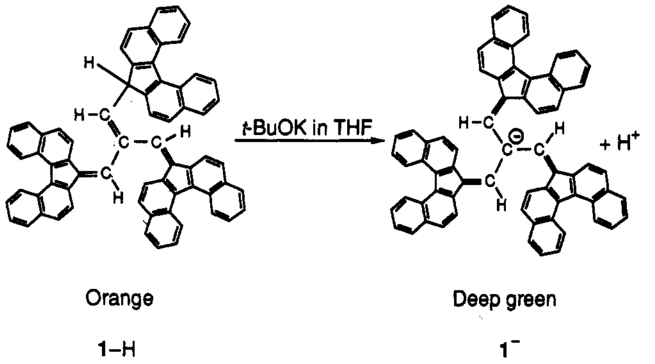
0022-3263/93/1958-2428$04.00/0

Chart I

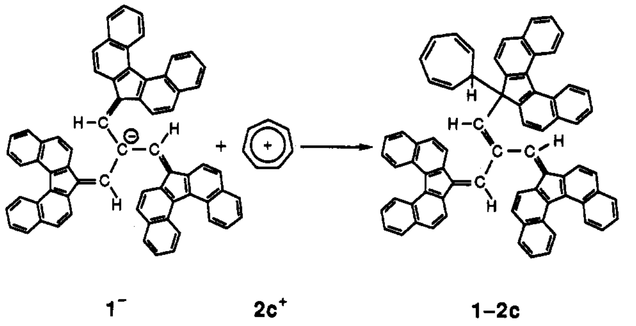


2^+ (pK_{R^+} in 50% aq. MeCN); The position indicated by • denotes the carbon forming the C–C σ bond.

Scheme I



Scheme II



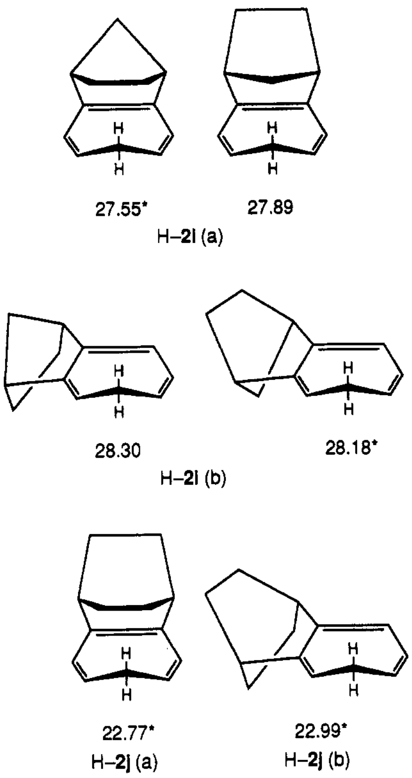


Figure 1. Steric energies (kcal/mol) of H–**2i** and H–**2j** calculated by using MMP2 (the energy difference was calculated from the values marked with an asterisk).

Results and Discussion

Synthesis of Covalent Compounds 1–2a–m. The anion 1^- was handled under argon in the dark since it is sensitive to oxygen and light. A deep green solution of 1^- was prepared by mixing the parent hydrocarbon (1–H, orange powder) and t-BuOK (2–5% excess) in THF (Scheme I). An equimolar amount of a cation salt ($2^+ClO_4^-$ or BF_4^-) in THF–acetonitrile (1/1) was added to the solution of 1^-K^+. The deep green color of 1^- vanished and the solution became orange, indicating the formation of a covalent product. Scheme II shows an example.

The inorganic salt ($KClO_4$ or KBF_4) was removed by evaporation of the solvent and subsequent extraction with chloroform or benzene. Compounds **1–2a–f** were successfully purified further by TLC (SiO_2) and reprecipitation (CH_2Cl_2–pentane) to give the analytically pure hydrocarbons as orange powders. On the other hand, compounds **1–2g–m** were difficult to purify in this way because they decomposed gradually in chloroform and benzene or on a TLC plate. However, the samples obtained by quick extraction with chloroform or benzene followed by evaporation and vacuum-drying at room temperature ($<10^{-4}$ mmHg) or at 50 °C (3 mmHg) were shown to be essentially pure by NMR except that they contained about 5% (wt) of THF. Physical properties of all the isolated covalent compounds are summarized in Table I.

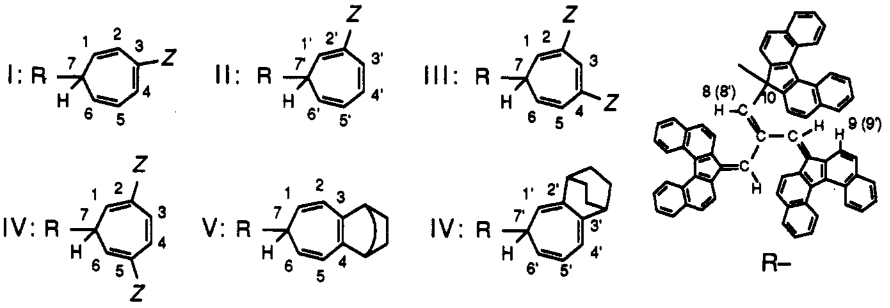
Structure of Covalent Compounds 1–2a–m. Table II presents the selected ^1H NMR data for **1–2a–m**. A finely split triplet or a broad singlet at 6.43–6.56 ppm (H-8) indicates that the cycloheptatriene ring is attached at C-10 in one of the three dibenzofluorene moieties. The presence of a highly shielded aromatic proton signal at 6.52–6.61 ppm, which is not observed for 1–H and can be assigned most probably to H-9, implies that compounds **1–2a–m** have a considerably more strained conformation than that of 1–H. The full assignments of H-8, -8′, -9, and

Table I. Physical Properties of Ionically Dissociative Hydrocarbons and a Bromo Derivative (**1–2a–m**)

compound (mol form.)	crystalline form	yield[a] (%)	mp[b] (°C)	anal. obsd (calcd) C	H	Br
1–2a ($C_{80}H_{49}Br$)	orange powder	59	167.5	88.15 (88.14)	4.52 (4.53)	7.13 (7.33)
1–2b ($C_{80}H_{50}$)	orange powder	47	169.5	94.74 (95.02)	5.07 (4.98)	–
1–2c ($C_{74}H_{46}$)	orange powder	66	198.0	94.76 (95.04)	5.24 (4.96)	–
1–2d ($C_{78}H_{54}$)	orange powder	51	175.5	94.30 (94.51)	5.39 (5.49)	–
1–2e ($C_{82}H_{62}$)	orange powder	85	174.0	93.84 (94.03)	6.00 (5.97)	–
1–2f ($C_{82}H_{62}$)	orange powder	86	173.0	94.03 (94.03)	6.05 (5.97)	–
1–2g–m	orange solid	≈100	*c*	–	–	–

[a] Isolated yield. [b] Decomposition temperature. [c] Not measured.

Table II. Selected ^1H NMR Data for Covalent Compounds **1–2a–m**



compd	structure	solvent	field strength (MHz)	δ, multiplicity (*J*(Hz)) H-7/7′	H-8/8′	H-9/9′
1–2a	I+II	$CDCl_3$	270	2.90, dd (5.7, 6.2)	*a*	*a*
				2.77, dd (5.9, 6.2)	*a*	*a*
1–2b	I+II	$CDCl_3$	270	2.92, dd (5.5, 5.9)	6.53, br s	*a*
				2.80, dd (5.5, 6.2)	6.56, br s	*a*
1–2c	I	$CDCl_3$	300	2.72, t (5.7)	6.52, t (1.4)	6.59, d (8.4)
1–2d	I+II	$CDCl_3$	270	2.73, dd (5.6, 5.6)	*a*	*a*
				2.58, dd (5.9, 5.9)	*a*	*a*
1–2e	III	$CDCl_3$	300	2.62, dd (5.3, 5.9)	6.51, br s	6.52, d (9.3)
1–2f	IV	$CDCl_3$	300	2.34, t (6.1)	6.53, br s	6.52, d (7.8)
1–2g	I+II	$CDCl_3$	270[b]	2.79, dd (5.6, 5.9)	6.52, br s	6.61, d (8.5)
				2.74, dd (5.4, 5.4)	6.43, br s	6.60, d (8.5)
1–2h	IV	$CDCl_3$	270	2.65, t (5.7)	6.53, br s	*a*
1–2i	V	C_6D_6	270	2.95, t (5.5)	*a*	*a*
1–2j	V+VI	C_6D_6	270	3.06, t (5.4)	*a*	*a*
				2.96, dd (5.0, 6.8)	*a*	*a*
1–2k	IV	$CDCl_3$	270	2.85, t (5.8)	6.50, br s	6.59, d (8.8)
1–2l	IV	$CDCl_3$	270	2.71, t (5.5)	6.51, br s	6.56, d (8.8)
1–2m	IV	$CDCl_3$	270	2.54, t (6.0)	*a*	6.55, d (8.3)

[a] Overlapped by aromatic and/or olefinic protons. [b] $CHCl_3$ (7.26 ppm) as an internal standard.

-9′ were not achieved in some cases when their signals overlapped with those of aromatic protons.

The reaction of 1^- with 1,3-disubstituted (**2e**$^+$) and 1,4-disubstituted (**2f,h,k–m**$^+$) tropylium ions gave a single isomer whereas monosubstituted tropylium ions (**2a,b,d,g**$^+$) gave two positional isomers. The major product in the latter case was the covalent compound with the substituent (Z) at the 3-position, which is, as molecular models indicate, less crowded than the 2′-substituted isomer. The fractions of 3-Z/2′-Z for **1–2a,b,d,g**, determined by the integration of H-7 or the *tert*-butyl signals, were 55/45, 60/40, 65/35, and 70/30, respectively.

The reaction between 1^- and bicyclo[2.2.1]heptenotropylium ion **2i**$^+$ gave a single product in which the bicyclic framework is annelated on the C-(3)–C-(4) bond (see Table II). In contrast, bicyclo[2.2.2]octenotropylium ion **2j**$^+$ gave equal amounts of two positional isomers with the bicyclic framework on the C-(3)–C-(4) and C-(2)–C-(3) bonds. The difference in the regioselectivity between **2i**$^+$ and **2j**$^+$ may be explained in terms of the strain energies of the covalent products. The difference in the strain between **1–2i** and **1–2j** was estimated by MMP2 calculations by using bicyclo[2.2.1]hepteno- and bicyclo[2.2.2]octenocycloheptatrienes (**H–2i** and **H–2j**, respectively) as model compounds. Figure 1 presents the steric energies of two positional isomers of **H–2i** and of **H–2j**, together with the steric energies of less stable two conformational isomers of **H–2i**. The slightly larger steric energy difference in **H–2i** (0.63 kcal/mol) than that in **H–2j** (0.22 kcal/mol) is consistent with the experimental results.

$\Delta G°_{het}$ of Covalent Compounds 1–2a–j in DMSO and Sulfolane. The heterolytic dissociation of covalent compounds **1–2a–j** in DMSO and 5/95 3-methylsulfolane/sulfolane was examined at 25 °C by measuring their UV-vis spectra in vacuo. When they were dissolved in DMSO, the deep green color of 1^- (λ_{max} (DMSO or sulfolane) 697 nm, log ε 5.18) appeared immediately. Its intensity became constant in a few minutes except for the case of **1–2a**, which required 20 min to reach a constant intensity. On the other hand, in sulfolane, small amount of radical $1^\bullet$ (0.5 – 11%, λ_{max} (DMSO) 551 nm, log ε 4.90) was also detected even when freshly distilled solvent was used. For calculations of equilibrium constants, the sum of the concentration of $1^\bullet$ and that of 1^- was taken as a corrected concentration of 1^-.

The concentration equilibrium constants for heterolysis

Table III. Thermodynamic Properties for Heterolysis of 1–2a–j in DMSO and 5/95 3-Methylsulfolane/sulfolane at 25 °C Together with the $\Delta G°_{het}$ To Give the Phenylmalononitrile Anion and Tri-*tert*-butylcyclopropenylium Ion in MeCN at 25 °C

compound	solvent	concn ($\times10^{-4}$ M)	obsd [1^-] ($\times10^{-4}$ M)	obsd [$1^•$] ($\times10^{-4}$ M)	K_{het}[a] ($\times10^{-6}$ M)	$\gamma\pm^2$	$K°_{het}$ ($\times10^{-6}$ M)	$\Delta G°_{het}$ (kcal/mol)	predicted ΔH_{het}[b] (kcal/mol)
1–2a[c,d]	DMSO	2.65	0.110	0	0.475	0.982	0.466	8.64	19.8
		2.13	0.095	0	0.441	0.984	0.434	8.68	
1–2b[c,d]	DMSO	2.50	0.188	0	1.52	0.977	1.49	7.95	19.6
		1.02	0.079	0	0.667	0.985	0.657	8.43	
1–2c[c]	DMSO	2.49	0.136	0	0.785	0.980	0.769	8.34	19.6
		1.98	0.132	0	0.940	0.981	0.922	8.23	
1–2d[d]	DMSO	2.00	0.124	0	0.822	0.981	0.806	8.31	19.4
		1.01	0.108	0	1.30	0.982	1.28	8.04	
	sulfolane	6.43	0.062	0.030	0.133	0.981	0.130	9.39	
		5.67	0.032	0.075	0.209	0.979	0.205	9.12	
1–2e	DMSO	2.50	0.158	0	1.07	0.979	1.05	8.16	19.3
		2.00	0.136	0	1.00	0.980	0.980	8.20	
	sulfolane	4.43	0.064	0.040	0.253	0.979	0.248	9.01	
		3.01	0.011	0.053	0.138	0.984	0.136	9.37	
1–2f	DMSO	2.50	0.203	0	1.78	0.976	1.74	7.86	19.1
		2.01	0.216	0	2.62	0.975	2.55	7.63	
	sulfolane	2.97	0.084	0.092	1.10	0.973	1.07	8.14	
		1.91	0.107	0.061	1.63	0.974	1.59	7.91	
1–2g[d]	DMSO	1.35	0.284	0	7.55	0.972	7.34	7.00	19.0
		0.718	0.177	0	5.76	0.978	5.63	7.16	
	sulfolane	1.64	0.100	0.047	1.44	0.975	1.40	7.99	
		1.12	0.093	0.021	1.29	0.978	1.26	8.05	
1–2h	DMSO	1.69	1.172	0	263	0.943	248	4.92	18.4
		1.25	0.915	0	252	0.950	239	4.94	
	sulfolane	1.13	0.262	0.082	15.1	0.962	14.5	6.60	
		0.831	0.145	0.088	9.13	0.969	8.85	6.89	
1–2i	DMSO	1.00	0.625	0	104	0.958	99.6	5.46	18.4
		0.801	0.621	0	214	0.958	205	5.03	
	sulfolane	1.34	0.431	0.092	33.4	0.954	31.9	6.13	
		0.945	0.200	0.071	10.9	0.967	10.6	6.79	
1–2j[d]	DMSO	0.743	0.539	0	143	0.961	137	5.27	18.4
		0.472	0.353	0	104	0.968	101	5.45	
	sulfolane	0.798	0.350	0.059	43.3	0.960	41.6	5.98	
		0.467	0.121	0.042	8.74	0.974	8.51	6.92	
PM + TCP[e]	MeCN	3.40	2.84[f]	–	1449	0.894	1295	3.94	10.2
		5.61	4.46[f]	–	1718	0.869	1493	3.85	

[a] Calculated by using corrected concentration of 1^- (1^-(obsd) + $1^•$(obsd)). [b] Calculated by using master equation for secondary cations presented in ref 5 (eq 7). [c] These covalent compounds do not dissociate in sulfolane at 10^{-4} M. [d] Mixture of two isomers. [e] Phenylmalononitrile anion + tri-*tert*-butylcyclopropenylium ion. [f] Concentration of phenylmalononitrile anion.

(K_{het}) were determined by using eq 1, where c is the concentration and α the degree of dissociation calculated from the absorbance of 1^-. The intensity of the cations' absorption could not be determined owing to interference from intense solvent absorptions. The thermodynamic equilibrium constants of heterolysis ($K°_{het}$) were calculated and converted to the standard free energies of heterolysis ($\Delta G°_{het}$) by using eqs 2 and 3.[9] The mean activity

$$K_{het} = c\alpha^2/(1 - \alpha) \tag{1}$$

$$K°_{het} = K_{het} \times \gamma\pm^2 \tag{2}$$

$$\Delta G°_{het} = -RT\ln K°_{het} \tag{3}$$

coefficients ($\gamma\pm$) were calculated by the Debye-Hückel, limiting law.

Table III summarizes the $\Delta G°_{het}$ values for **1–2a–j**. The $\Delta G°_{het}$ values determined at two different concentrations were in good agreement with each other as well as with the values obtained from electric conductivity measurements (see below). Determination of $\Delta G°_{het}$ in MeCN for (triphenylcyclopropenyl)(*p*-nitrophenyl)malononitrile in this work afforded a value (5.42 ± 0.12 kcal/mol) which is in close agreement with the reported one (5.39 ± 0.03 kcal/mol).[9] As shown in Figure 2, the $\Delta G°_{het}$ values for **1–2a–j** in DMSO at 25 °C are linearly correlated with the pK_{R^+} values of **2a–j**$^+$. The contribution of the entropy term (ΔS_{het}) will be discussed later.

Electric Conductivity of Ionically Dissociative Hydrocarbons in DMSO. The partial dissociation of **1–2c,e,f** in DMSO was also evidenced by electric conductivity measurements. The plot of the equivalent conductances (Λ) against the square root of the concentrations (Onsager's plot) gave curved lines, which are typical of weak electrolytes (Figure 3) and apparently different from straight lines generally observed for strong electrolytes such as the perchlorate salts of **2c,e,f**$^+$ (Figure 4). The equivalent conductances at infinite dilution for substituted tropylium ions (**2c**$^+$, **2e**$^+$, and **2f**$^+$) in DMSO were determined by subtracting Λ_0 for ClO_4^- (24.52 mho·cm^2·mol^{-1})[10] from observed Λ_0's of **2c,e,f**$^+ClO_4^-$. The results are summarized in Table IV.

The Λ_0 values of 1^-[11] and of the cations enabled us to determine the degrees of dissociation (α) and the equilibrium constants (K_{het}) by using eqs 4 and 5, where Λ_c is the conductance at concentration c.

$$\alpha = \Lambda_c/(\Lambda_0(\mathbf{2c,e,f}^+) + \Lambda_0(1^-)) \tag{4}$$

$$K_{het} = c\alpha^2/(1 - \alpha) \tag{5}$$

Figure 5 shows a plot of K_{het} against the concentrations

---

(9) Troughton, E. B.; Molter, K. E.; Arnett, E. M. *J. Am. Chem. Soc.*, **1984**, *106*, 6726.

(10) Gopal, R.; Shanker Jha, J. *J. Phys. Chem.* **1974**, *78*, 2405.

(11) Okamoto, K.; Kitagawa, T.; Takeuchi, K.; Komatsu, K.; Kinoshita, T.; Aonuma, S.; Nagai, M.; Miyabo, A. *J. Org. Chem.* **1990**, *55*, 996.

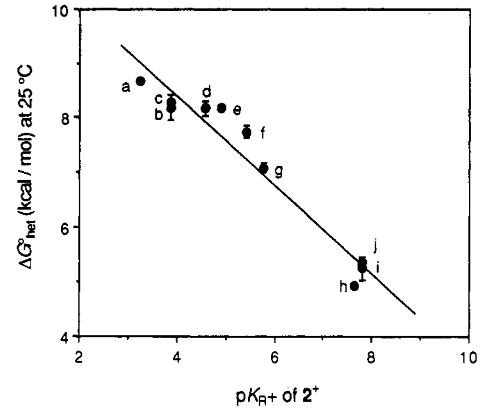


Figure 2. Relation between pK_{R^+} of **2**$^+$ and $\Delta G°_{het}$ of **1–2** in DMSO at 25 °C.

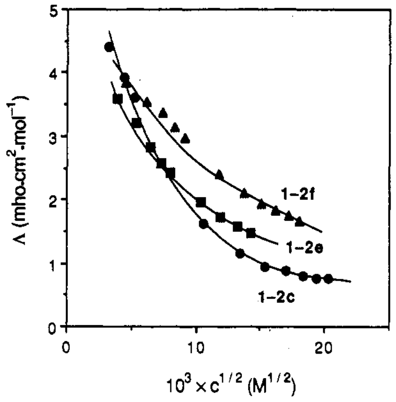


Figure 3. Onsager's plot for **1–2c**, **1–2e**, and **1–2f** in DMSO at 25 °C.

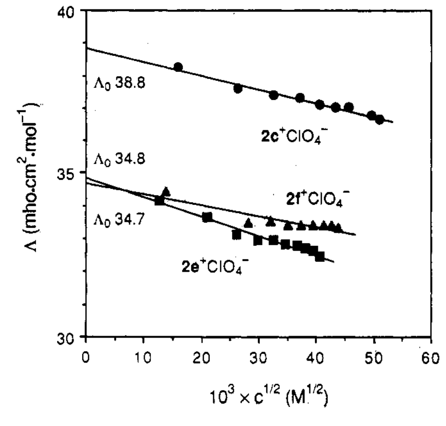


Figure 4. Onsager's plot for **2c**$^+ClO_4^-$, **2e**$^+ClO_4^-$, and **2f**$^+ClO_4^-$ in DMSO at 25 °C.

of solution. Although experimental errors are large owing to the fluctuation of conductance especially at lower concentrations, K_{het} becomes almost constant at >2 × 10^{-4} M. The K_{het} values for **1–2c**, **1–2e**, and **1–2f** are 0.6 × 10^{-6}, 2.3 × 10^{-6}, and 5.9 × 10^{-6} M, respectively; they are roughly in agreement with the spectrophotometrically obtained values (0.86 × 10^{-6}, 1.0 × 10^{-6}, and 2.2 × 10^{-6} M, respectively; see Table III).

Behavior of 1–2k–m in DMSO. Although the pK_{R^+} values of **2k–m**$^+$ are considered to be close to that of **2f**$^+$, the concentrations of **1**$^-$ observed for covalent compounds **1–2k–m** in DMSO were considerably higher than expected (see Table V). This result suggested a possibility that the heterolysis was further advanced owing to the deterioration of the alkyltropylium ions. Accordingly, we examined the behavior of the cation moieties (**2k**$^+$, **2l**$^+$, and **2m**$^+$) in DMSO. When the perchlorate salt of **2m**$^+$ was dissolved in DMSO-d_6 (17 mM) under argon at room temperature, the pale brown solution once formed became turbid in 2 min. Filtration of the insoluble substance by means of a membrane filter (0.5 μm) gave a pale brown filtrate. ^{1}H NMR analysis of the filtrate (Figure 6) showed that the major component was 3-isopropyl-8,8′-dimethylheptafulvene which was formed by the deprotonation of **2m**$^+$. The DMSO-d_6 solutions of the tropylium ions with less bulky substituents, **2k**$^+ClO_4^-$ and **2l**$^+ClO_4^-$, became turbid too, but their filtrates showed essentially no proton signals.

These facts indicate that the irreversible decomposition

Table IV. Equivalent Conductances at Infinite Dilution for Ionic Species of Ionically Dissociative Hydrocarbons in DMSO at 25 °C

ionic species	Λ_0 (mho·cm^2·mol^{-1})
1$^-$	5.3[b]
2c$^+$	14.3
(**2c**$^+ClO_4^-$)	38.8
2e$^+$	10.3
(**2e**$^+ClO_4^-$)	34.8
2f$^+$	10.2
(**2f**$^+ClO_4^-$)	34.7
ClO_4^-	24.52[a]

[a] Reference 10. [b] Reference 11.

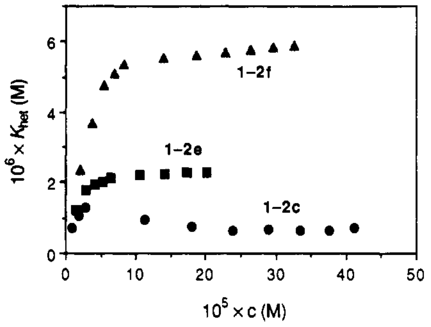


Figure 5. Equilibrium constants (K_{het}) of **1–2c**, **1–2e**, and **1–2f** in DMSO at 25 °C.

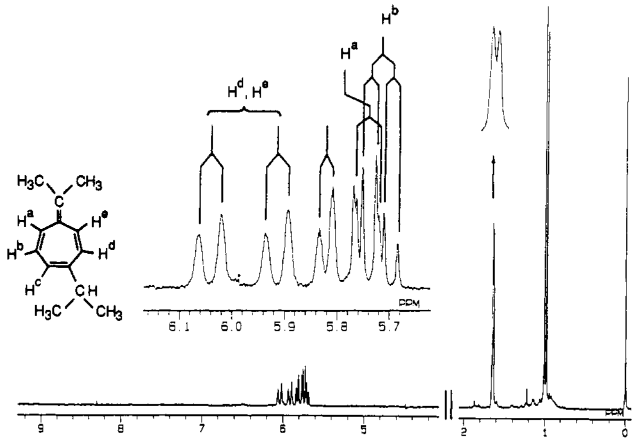


Figure 6. ^{1}H NMR spectrum (270 MHz) of the filtrate of **2m**$^+ClO_4^-$ in DMSO-d_6 (signal for isopropyl methine proton is overlapped by that of DMSO).

Table V. Degree of Dissociation of 1–2k–m in DMSO

compound	initial concn (×10^{-4} M)	obsd [**1**$^-$] (×10^{-4} M)	degree of dissociation (%)
1–2k	0.500	0.340	68
1–2l	0.500	0.405	81
1–2m	0.498	0.359	72

Scheme III

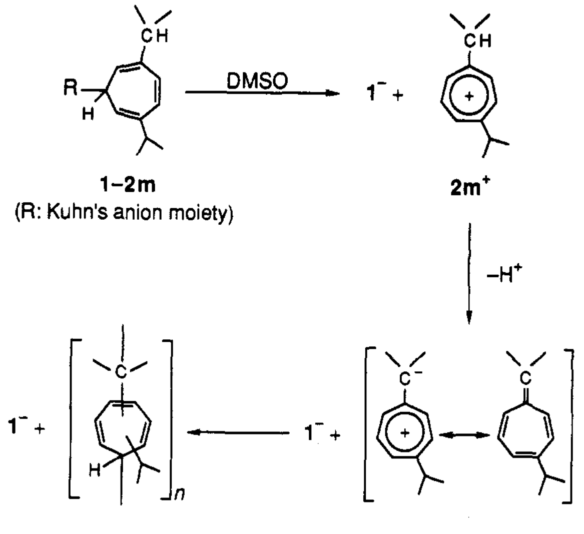


Table VI. Enthalpy of Heterolysis (ΔH_{het}) and Entropy of Heterolysis (ΔS_{het}) for 1-2c in DMSO

run	temp (°C)	concn[a] ($\times10^{-4}$ M)	1^- (%)	K_{het} ($\times10^{-6}$ M)	ΔH_{het}[b] (kcal/mol)	ΔS_{het}[b] (eu)
1	50	1.89	9.46	1.86	3.12	-16.6
	25	1.99	7.59	1.24		
2	50	1.89	9.70	1.97	3.00	-16.8
	40	1.92	9.01	1.72		
	25	1.99	7.85	1.33		

[a] Corrected concentrations (see Experimental Section). [b] Average for run 1 and 2: ΔH_{het} 3.06 ± 0.06 kcal/mol; ΔS_{het} −16.7 ± 0.1 eu.

of **2k–m**$^+$ in DMSO due to polymerization via heptafulvene intermediates (Scheme III) shifts the equilibrium, resulting in the formation of an unexpectedly high concentration of 1^- from **1–2k–m**. Cations **2g,h**$^+$ are stable in DMSO, however, despite the presence of the methine hydrogen in the cyclopropyl group. This is apparently because of the highly strained structure of the expected cyclopropylidenecycloheptatriene.

Entropy Effect in Heterolysis. The entropy effect usually plays an important role in the heterolysis of neutral molecules in solution. Accordingly, the entropy of heterolysis (ΔS_{het}) for **1–2c** as a typical example was determined in DMSO under argon. The measurements were conducted within 30 min after dissolution, because spectrophotometric analysis showed that **2c**$^+$ decomposed less than 1% in the same period. The results are shown in Table VI. Arnett has reported that the $\Delta S°_{het}$ for (triphenylcyclopropen-1-yl)(*p*-nitrophenyl)malononitrile is considerably negative (-21 ± 2 eu) in 1,2-dichloroethane, but close to 0 (0 ± 2 eu) in a more polar solvent, MeCN.[9] Our system gave a much smaller value for $\Delta S°_{het}$ (-16.7 eu) than expected from the large dielectric constant of DMSO. Apparently, the basic coordinating tendency of DMSO leads to strong solvation of the cation, which should be accompanied by a significant loss of entropy. The $\Delta S°_{het}$ in sulfolane is presumed to be close to 0, since this solvent has a dielectric constant (43.3) and a donor number (14.8)[12] similar to those of MeCN (37.5 and 14.1, respectively).[12]

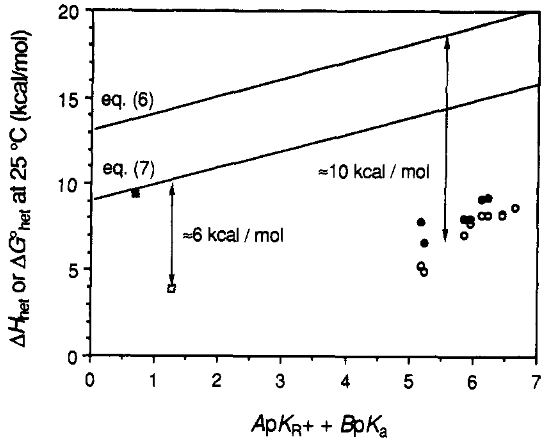


Figure 7. Plot of $\Delta G°_{het}$ on the master equation scale: open circle, **1–2a–j** in DMSO; closed circle, **1–2d–j** in sulfolane; open square, tri-*tert*-butylcyclopropenylium ion + phenylmalononitrile anion (in MeCN); closed square, trimethylcyclopropenylium ion + phenylmalononitrile anion (in MeCN).

Steric Effect in Heterolysis. Arnett's master equation is an empirical relationship for predicting the heat of heterolysis (ΔH_{het}) which leads to resonance-stabilized cations and anions.[6] It is based on the ΔH_{het} values for more than 90 kinds of covalent compounds calorimetrically measured in 5/95 3-methylsulfolane/sulfolane or in acetonitrile at 25 °C. When discussion is limited to the heterolysis of carbon–carbon σ bonds, the relationship can be expressed by one of the two equations (6 and 7),

$$\text{For secondary cations: } \Delta H_{het} = 13.18 - 0.324(pK_{R^+}) + 1.307(pK_a) \quad (6)$$

$$\text{For tertiary cations: } \Delta H_{het} = 8.895 - 0.648(pK_{R^+}) + 1.294(pK_a) \quad (7)$$

depending on the class of the cation.[6] However, it was uncertain if these equations could be extended to the present system, since they were derived from sterically unencumbered ions.

To calculate the ΔH_{het} values for **1–2a–j**, eq 6 should be employed since cations **2a–j**$^+$ are categorized to secondary ones. As shown in Figure 7, the $\Delta G°_{het}$ values for **1–2a–j** both in DMSO and in sulfolane are about 10 kcal/mol lower than ΔH_{het} values predicted from eq 6. Although DMSO and sulfolane have similar dielectric constants (46.5 and 43.3, respectively), the former has a much larger donor number (29.8)[12] than the latter (14.8).[12] Assuming that in sulfolane specific coordination to the cation is negligible and $\Delta S°_{het} \simeq 0$ (vide supra), the deviation of the observed $\Delta G°_{het}$ ($\simeq \Delta H°_{het}$) from the master equation is explained by the steric congestion in **1–2a–j**. On the other hand, the high donating ability of DMSO may contribute to the lowering of ΔH_{het} to some extent. The $\Delta H°_{het}$ for **1–2c** in DMSO (Table VI) indicates that the difference in ΔH_{het} between **1–2a–j** and eq 6 is about 15 kcal/mol in DMSO, if one assumes that the entropy term ($-T\Delta S°_{het}$) is constant at ~5 kcal/mol throughout the present system. Thus, heterolysis of **1–2a–j** is shown to be enhanced by ca. 15 kcal/mol by the steric and solvation effects, which is partly (~5 kcal/mol) cancelled by the contribution of the entropy arising from the solvation by DMSO to the cations.

A similar deviation arising from the steric effect was also observed for the $\Delta G°_{het}$ value obtained from the coordination of the tri-*tert*-butylcyclopropenylium ion (pK_{R^+} 6.5)[13] with phenylmalononitrile anion (pK_a(RH)

---

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

(13) Ciabattoni, J.; Nathan, III, E. C. *J. Am. Chem. Soc.* **1969**, *91*, 4766.

4.24)[9] in MeCN. The $\Delta G°_{\mathrm{het}}$ value, 3.9 kcal/mol, is about 6.3 kcal/mol smaller than the ΔH_{het} value expected from eq 7 (see Table III), whereas the deviation is only 0.15 kcal/mol for (trimethylcyclopropen-1-yl)phenylmalononitrile which dissociates into less hindered trimethylcyclopropenylium ion and phenylmalononitrile anion (observed $\Delta G°_{\mathrm{het}}$:[9] 9.44 kcal/mol; observed $\Delta H°_{\mathrm{het}}$:[9] 8.5 kcal/mol; predicted ΔH_{het} 9.59 kcal/mol).

The large deviation of our system was also demonstrated from Arnett's modified master equation, which was shown to give greater precision and generality (eqs 8[5] and 9[6]).

$$\Delta H_{\mathrm{het}} = 30.74 - 10.23(\Delta M_{\mathrm{i}}) + 1.34(\mathrm{p}K_{\mathrm{a}}) \qquad (8)$$

$$\Delta H_{\mathrm{het}} = -11.893 + 0.925(\Delta H_{\mathrm{CMF}}) + 1.335(\mathrm{p}K_{\mathrm{a}}) \qquad (9)$$

Even when π-delocalization energy (ΔM_{i}) or heat of reaction with 9-(carbomethoxy)fluorenide ion (ΔH_{CMF}) is used instead of $\mathrm{p}K_{\mathrm{R^+}}$ values, the deviations of $\Delta G°_{\mathrm{het}}$ for **1–2c** in DMSO are 9.9 and 10.7 kcal/mol, respectively.

Although the exact conformation of our covalent compounds **1–2** remains uncertain, they are certainly much more congested than **1**–H, as expected from the ^{1}H NMR spectra (see above). We believe that eqs 6 and 7 intrinsically involve steric effects, as reflected by lower ΔH_{het}'s for the systems giving tertiary cations than for the systems giving secondary cations. Arnett has pointed out a similar steric effect in the reaction of alkylamines or pyridines with various carbocations in sulfolane.[14] Our system is somewhat restricted in view of the range of $\mathrm{p}K_{\mathrm{R^+}}$ and the selection of the anion system; however, their behavior in highly polar solvents clearly demonstrates that steric effect of covalent and ionic species and the solvation effect of ionic species are significant in the heterolysis of carbon–carbon σ bonds involving a resonance-stabilized carbocation and carbanion.

Experimental Section

Melting points are uncorrected. ^{1}H NMR spectra were recorded on a Hitachi R-24 (60 MHz), a JEOL GSX-270 (270 MHz), or a Nicolet NP-300NB (300 MHz) spectrometer. ^{13}C NMR spectra were recorded on a JEOL FX-100 (25 MHz) spectrometer. UV-vis spectra were taken on a Hitachi 200-10 spectrophotometer. A Sartorius 4503MP6 microbalance was used for precise weighing. Elemental analyses were performed by Microanalytical Center, Kyoto University, Kyoto.

Tetrahydrofuran was freshly distilled over lithium aluminum hydride under nitrogen atmosphere before use. Acetonitrile was refluxed and distilled over phosphorus pentoxide. Dimethyl sulfoxide (DMSO), sulfolane, and 3-methylsulfolane were kept at least for a week over molecular sieves (4A) and distilled over calcium hydride (DMSO) or NaOH pellets (sulfolane and 3-methylsulfolane). Tri-*tert*-butylcyclopropenylium tetrafluoroborate[13] and phenylmalononitrile[9] were prepared according to the literature. The preparation of Kuhn's hydrocarbon (**1**–H) was described in our previous paper[11].

Substituted Tropylium Ions. Substituted tropylium ions **2a**$^+\mathrm{ClO_4^-}$,[15] **2b**$^+\mathrm{ClO_4^-}$,[15] **2c**$^+\mathrm{BF_4^-}$,[16] **2d**$^+\mathrm{ClO_4^-}$,[17] **2e**$^+\mathrm{ClO_4^-}$,[18] **2f**$^+\mathrm{ClO_4^-}$,[18] **2g**$^+\mathrm{BF_4^-}$,[19] **2h**$^+\mathrm{ClO_4^-}$,[18] **2i**$^+\mathrm{ClO_4^-}$,[20] **2j**$^+\mathrm{ClO_4^-}$,[21] and **2k**$^+\mathrm{ClO_4^-}$[22] were synthesized according to the literature. The dimethyl- and diisopropyltropylium ions **2l**$^+\mathrm{ClO_4^-}$ and **2m**$^+\mathrm{ClO_4^-}$ were synthesized by the ring expansion of 1,4-dialkylbenzenes with diazomethane, followed by hydride abstraction with $\mathrm{Ph_3C^+ClO_4^-}$. The crude cations were purified by reprecipitation (acetonitrile–ether), but analytically pure ones were not obtained owing to hygroscopicity. **2l**$^+\mathrm{ClO_4^-}$: brown oil; ^{1}H NMR ($\mathrm{CF_3COOH}$; 60 MHz) δ 8.9 (s, 5 H, tropylium ring protons), 3.4 (q, 4 H, *J* = 6 Hz, $\mathrm{C}H_2\mathrm{CH_3}$), 1.5 (t, 6 H, *J* = 6 Hz, $\mathrm{CH_2C}H_3$). **2m**$^+\mathrm{ClO_4^-}$: white powder; mp 136.0–137.0 °C; ^{1}H NMR ($\mathrm{CD_3CN}$; 270 MHz) δ 8.93–8.90 (m, 5 H, tropylium ring protons), 3.53 (m, 2 H, *J* = 6.8 Hz, $\mathrm{C}H(\mathrm{CH_3})_2$), 1.44 (d, 12 H, *J* = 6.8 Hz, $\mathrm{CH(C}H_3)_2$); IR (KBr disk) 2968 (m), 1573 (w), 1494 (m), 1466 (w), 1425 (w), 1091 (vs), 937 (w), 882 (w), 828 (w), 628 (m), 592 (m) cm^{-1}. The $\mathrm{p}K_{\mathrm{R^+}}$ values for substituted tropylium ions (except **2k**$^+$, **2l**$^+$, and **2m**$^+$) has already been reported.[20,23]

Generation of Kuhn's Anion (1$^-$). As has been reported by Kuhn and Rewicki[8] and by us,[11] **1**$^-$ was quantitatively generated when the hydrocarbon **1**–H was dissolved in DMSO. The anion **1**$^-$ was also generated from **1**–H and *t*-BuOK in THF under vacuum. Detailed UV-vis absorptions have been reported previously.[11] Precautions were taken to protect the anion solution from visible light, since the radical **1**$^\bullet$ was found to be readily formed by photoinduced electron transfer occurring even by room light.

Isolation of Covalent Compounds 1–2a–m. General procedure is as follows. To a stirred THF solution (3–5 mL) of **1**–H (0.05–0.1 mmol) was added a 5% excess amount of *t*-BuOK (0.1 M THF solution) under argon in the dark at room temperature. After stirring for 5 min, a THF–acetonitrile solution (1/1, 3–5 mL) of **2**$^+\mathrm{ClO_4^-}$ (or $\mathrm{BF_4^-}$) was added dropwise until the deep green color of **1**$^-$ disappeared. In the case of **2h–j**$^+\mathrm{ClO_4^-}$, a minimum amount of solvent (ca. 0.5 mL) was used to prevent dissociation of the covalent compounds by acetonitrile. After evaporation of the solvent, the resulting orange solid was subjected to purification. Details of the purification are described in the text and physical properties are summarized in Table I. **1–2a**: ^{1}H NMR ($\mathrm{CDCl_3}$; 270 MHz) δ 8.94–6.53 (m, aromatic and olefinic including H-3′,4,4′,8,8′,9,9′), 6.21 (d, *J* = 9.5 Hz, H-2), 6.12 (dd, *J* = 6.8, 9.7 Hz, H-5), 6.10–6.02 (m, H-5′), 5.54 (dd, *J* = 5.7, 9.5 Hz, H-1), 5.42 (d, *J* = 6.2 Hz, H-1′), 5.25–5.18 (m, H-6,6′), 2.90 (dd, *J* = 5.7, 6.2 Hz, H-7), 2.77 (dd, *J* = 5.9, 6.2 Hz, H-7′). **1–2b**: ^{1}H NMR ($\mathrm{CDCl_3}$; 270 MHz) δ 8.93–6.53 (m, aromatic and olefinic including H-3′,4,4′,9,9′), 6.56 (br s, H-8′), 6.53 (br s, H-8), 6.29 (d, *J* = 9.9 Hz, H-2), 6.14 (dd, *J* = 6.0, 9.0 Hz, H-5), 6.05 (dd, *J* = 5.5, 9.2 Hz, H-5′), 5.55–5.49 (m, H-1,1′), 5.24–5.19 (m, H-6,6′), 2.92 (dd, *J* = 5.5, 5.9 Hz, H-7), 2.80 (dd, *J* = 5.5, 6.2 Hz, H-7′). **1–2c**: ^{1}H NMR ($\mathrm{CDCl_3}$; 300 MHz) δ 8.84–7.02 (m, 37 H, aromatic and olefinic), 6.592 (d, 2 H, *J* = 3.0 Hz, H-3, 4), 6.591 (d, 1 H, *J* = 8.4 Hz, H-9), 6.52 (t, 1 H, *J* = 1.4 Hz, H-8), 6.06 (dd, 2 H, *J* = 3.0, 9.3 Hz, H-2, 5), 5.21 (dd, 2 H, *J* = 5.7, 9.3 Hz, H-1,6), 2.72 (t, 1 H, *J* = 5.7 Hz, H-7); ^{13}C NMR ($\mathrm{CDCl_3}$; 25 MHz) δ 146.8–117.5 (aromatic and olefinic), 58.2 (s, C-10), 47.8 (d, C-7). **1–2d**: ^{1}H NMR ($\mathrm{CDCl_3}$; 270 MHz) δ 8.84–7.03 (m, aromatic and olefinic) 6.83–6.49 (m, H-3′,4,4′,8,8′,9,9′), 6.13 (d, *J* = 10.2 Hz, H-2), 6.01 (dd, *J* = 6.5, 9.1 Hz, H-5), 5.92 (dd, *J* = 5.4, 8.9 Hz, H-5′), 5.30–5.13 (m, H-1,1′,6,6′), 2.73 (dd, *J* = 5.6, 5.6 Hz, H-7), 2.58 (dd, *J* = 5.9, 5.9 Hz, H-7′), 1.10 and 0.83 (s, $\mathrm{C(C}H_3)_3$). **1–2e**: ^{1}H NMR ($\mathrm{CDCl_3}$; 300 MHz) δ 8.83–6.99 (m, 37 H, aromatic and olefinic), 6.74 (s, 1 H, H-3), 6.52 (d, 1 H, *J* = 9.3 Hz, H-9), 6.51 (br s, 1 H, H-8), 5.93 (d, 1 H, *J* = 9.3 Hz, H-5), 5.31 (d, 1 H, *J* = 5.3 Hz, H-1), 5.13 (dd, 1 H, *J* = 5.9, 9.3 Hz, H-6), 2.62 (dd, 1 H, *J* = 5.3, 5.9 Hz, H-7), 1.10 and 0.88 (s, 9 H each, $\mathrm{C(C}H_3)_3$); ^{13}C NMR ($\mathrm{CDCl_3}$; 25 MHz) δ 151.9–115.1 (aromatic and olefinic),

---

(14) Arnett, E. M.; Venimadhavan, S. *J. Org. Chem.* **1991**, *56*, 2742.

(15) Jutz, C.; Voithenleitner, F. *Chem. Ber.* **1964**, *97*, 29.

(16) Dauben, Jr., H. J.; Gadecki, F. A.; Harmon, K. M.; Pearson, D. L. *J. Am. Chem. Soc.* **1957**, *79*, 4557.

(17) Okamoto, K.; Komatsu, K.; Murai, O.; Sakaguchi, O.; Matsui, Y. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 1785.

(18) Komatsu, K.; Takeuchi, K.; Arima, M.; Waki, Y.; Shirai, S.; Okamoto K., *Bull. Chem. Soc. Jpn.* **1982**, *55*, 3257.

(19) Bauld, N. L.; McDermed, J. D.; Hudson, C. E.; Rim, Y. S.; Zoller, J., Jr.; Gordon, R. D.; Hyde, J. S. *J. Am. Chem. Soc.* **1969**, *91*, 6666.

(20) Okamoto, K.; Takeuchi, K.; Komatsu, K.; Kubota, Y.; Ohara, R.; Arima, M.; Takahashi, K.; Waki, Y.; Shirai, S. *Tetrahedron* **1983**, *39*, 4011.

(21) Nakazawa, T.; Abe, N.; Kubo, K.; Murata, I. *Tetrahedron Lett.* **1979**, *20*, 4995.

(22) Takeuchi, K.; Yokomichi, Y.; Kurosaki, T.; Kimura, Y.; Okamoto, K. *Tetrahedron* **1979**, *35*, 949.

(23) Komatsu, K.; Akamatsu, H.; Okamoto, K. *Tetrahedron Lett.* **1987**, *28*, 5889.

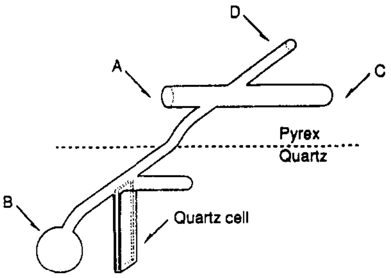


Figure 8. Quartz cell used for the measurements of UV-vis spectra under vacuum: cell path 1 mm.

58.4 (s, C-10), 46.6 (d, C-7), 36.2 and 35.1 (s, $C(CH_3)_3$), 30.6 and 30.2 (q, $C(CH_3)_3$). **1-2f**: ^{1}H NMR ($CDCl_3$; 300 MHz) δ 8.80–7.04 (m, 37 H, aromatic and olefinic), 6.68 (s, 2 H, H-3,4), 6.53 (br s, 1 H, H-8), 6.52 (d, 1 H, J = 7.8 Hz, H-9), 5.05 (d, 2 H, J = 6.1 Hz, H-1,6), 2.34 (t, 1 H, J = 6.1 Hz, H-7), 0.80 (s, 18 H, $C(CH_3)_3$); ^{13}C NMR ($CDCl_3$; 25 MHz) δ 148.1–113.5 (aromatic and olefinic), 58.8 (s, C-10), 45.9 (d, C-7), 34.5 (s, $C(CH_3)_3$), 29.9 (q, $C(CH_3)_3$). **1-2g**: ^{1}H NMR ($CDCl_3$; 270 MHz) δ 8.84–7.04 (m, aromatic and olefinic), 6.61 (d, J = 8.5 Hz, H-9), 6.60 (d, J = 8.5 Hz, H-9′), 6.55–6.49 (m, H-3′,4′), 6.52 (br s, H-8), 6.43 (br s, H-8′), 6.38 (d, J = 6.3 Hz, H-4), 5.97 (dd, J = 6.3, 9.0 Hz, H-5), 5.90 (dd, J = 5.3, 9.0 Hz, H-5′), 5.81 (d, J = 9.89 Hz, H-2), 5.27–5.22 (m, H-1,1′), 5.15–5.10 (m, H-6,6′), 2.79 (dd, J = 5.6, 5.9 Hz, H-7), 2.74 (dd, J = 5.4, 5.4 Hz, H-7′), 1.62–1.60 (m, cyclopropyl methine), 0.78–0.37 (m, cyclopropyl methylene (E and Z)). **1-2h**: ^{1}H NMR ($CDCl_3$; 270 MHz) δ 8.82–6.56 (m, 38 H, aromatic and olefinic including H-9), 6.53 (br s, 1 H, H-8), 6.27 (s, 2 H, H-3,4), 4.93 (d, 2 H, J = 5.7 Hz, H-1,6), 2.65 (t, 1 H, J = 5.7 Hz, H-7), 1.86–1.83 (m, 2 H, cyclopropyl methine), 0.96–0.87 and 0.70–0.61 (m, 4 H, each, cyclopropyl methylene (E and Z)). **1-2i**: ^{1}H NMR (C_6D_6; 270 MHz) δ 9.23–6.72 (m, 39 H, aromatic and olefinic including H-8,9), 6.12 (d, 2 H, J = 9.3 Hz, H-2,5), 5.27 (dd, 2 H, J = 5.5, 9.0 Hz, H-1,6), 2.95 (t, 1 H, J = 5.5 Hz, H-7), 2.91 (s, 2 H, bridgehead), 1.53–0.96 (m, 6 H, bicyclic methylene). **1-2j**: ^{1}H NMR (C_6D_6; 270 MHz) δ 9.40–6.67 (m, aromatic and olefinic including H-8,8′,9,9′), 6.27 (d, J = 5.8 Hz, H-4′), 6.07 (d, J = 9.2 Hz, H-2,5), 5.93 (dd, J = 5.8, 7.5 Hz, H-5′), 5.52 (d, J = 5.0 Hz, H-1′), 5.33 (dd, J = 5.4, 9.2 Hz, H-1,6), 5.11 (dd, J = 6.8, 7.5 Hz, H-6′), 3.06 (t, J = 5.4 Hz, H-7), 2.96 (dd, J = 5.0 and 6.8 Hz, H-7′), 2.49 (s, bridgehead), 2.40 and 2.31 (s, bridgehead), 1.43–1.22 (m, bicyclic methylene). **1-2k**: ^{1}H NMR ($CDCl_3$; 270 MHz) δ 8.83–7.03 (m, 37 H, aromatic and olefinic), 6.59 (d, 1 H, J = 8.8 Hz, H-9), 6.50 (br s, 1 H, H-8), 6.37 (s, 2 H, H-3,4), 5.05 (d, 2 H, J = 5.8 Hz, H-1,6), 2.85 (t, 1 H, J = 5.8 Hz, H-7), 1.67 (s, 6 H, CH_3). **1-2l**: ^{1}H NMR ($CDCl_3$; 270 MHz) δ 8.84–7.04 (m, 37 H, aromatic and olefinic), 6.56 (d, 1 H, J = 8.8 Hz, H-9), 6.51 (br s, 1 H, H-8), 6.43 (s, 2 H, H-3,4), 5.03 (d, 2 H, J = 5.5 Hz, H-1,6), 2.71 (t, 1 H, J = 5.5 Hz, H-7), 1.97 (q, 4 H, CH_2CH_3), 0.70 (t, 6 H, CH_2CH_3). **1-2m**: ^{1}H NMR ($CDCl_3$; 270 MHz) δ 8.86–7.05 (m, 37 H, aromatic and olefinic), 6.55 (d, 1 H, J = 8.3 Hz, H-9), 6.51 (br s, 3 H, H-3,4,8), 5.03 (d, 2 H, J = 6.0 Hz, H-1,6), 2.54 (t, 1 H, J = 6.0 Hz, H-7), 2.22 (m, 2 H, $CH(CH_3)_2$), 0.73 and 0.70 (d, 6 H each, $CH(CH_3)_2$).

UV-vis Spectra. (a) 1-2a–m in DMSO and 5/95 3-Methylsulfolane/Sulfolane. For UV-vis measurements was employed a quartz cell shown in Figure 8. A typical procedure is as follows. The covalent compounds (1-2a–m; 0.200–0.500 mg) were weighed by the use of a microbalance in a tared glass tube and the tube was placed in chamber C from the inlet A. After position A was sealed off, freshly distilled solvent (2–5 mL) was placed in chamber B. After degassing solvent by repeating the freeze-pump-thaw cycle for four times, the tube was sealed under vacuum at position D, and the sample solution was prepared in the dark to be ready for the measurement.

(b) The $\Delta G°_{het}$ Which Leads to Tri-*tert*-butylcyclopropenylium Ion and Phenylmalononitrile Anion in Acetonitrile. To 11.7 mg (0.0823 mmol) of phenylmalononitrile was added 0.0949 M *t*-BuOK in THF (0.875 mL, 0.0830 mmol) under argon with stirring. After 15 min, the solution was evaporated and the resulting potassium salt of phenylmalononitrile anion was dried under vacuum (<10^{-4} mmHg, 1 h). In two tared glass tubes were weighed equimolar amounts (0.00172 mmol) of the cation (BF_4^- salt) and the potassium salt of the anion, respectively; they were placed in a vacuum cell replaced with argon. After degassing the acetonitrile (5.06 mL) and sealing the cell, the solution was subjected to the measurements of UV-vis spectrum at 25.0 ± 0.1 °C. The $\Delta G°_{het}$ was determined by the absorption of phenylmalononitrile ion (λ_{max} 298 nm, log ε 4.32).

Determination of ΔS_{het} for 1-2c in DMSO. The sample solution was prepared in the same way as described above, except that the quartz cell was filled with argon (1 atm) after degassing DMSO and closed by a teflon cock at position D. The cell was placed in a chamber that had been maintained at 50.0 ± 0.5 °C. The spectrum was scanned after the absorbance of 1^- became constant (ca. 5 min). Then the solution temperature was lowered and the spectra were recorded at 40 and 25 °C.

Changes in the concentration due to heat expansion of DMSO were calibrated as follows by using the data on the temperature dependence of the absorbance of 1^- in DMSO: 1-H was dissolved in DMSO ($\simeq 3.7 \times 10^{-5}$ M) in a quartz cell filled with argon in the manner described above. The relative absorbances of 1^- at 697 nm observed at 25, 40, and 50 °C (1.00, 0.966, and 0.948, respectively) were used as the correction factors to obtain the concentration of 1-2c at respective temperatures.

Reaction of 1,4-Diisopropyltropylium Perchlorate ($2m^+$-ClO_4^-) in DMSO. To 1,4-diisopropyltropylium perchlorate (3.8 mg, 0.0138 mmol) was added DMSO-d_6 (0.8 mL) under argon. After 10 min, the resulting suspension was filtered through a membrane filter (0.5 μm), and the filtrate was analyzed by ^{1}H NMR (DMSO-d_6; 270 MHz) δ 6.50 (d, 1 H, J = 11.1 Hz, H^d or H^e), 6.37 (d, 1 H, J = 11.1 Hz, H^d or H^e), 6.28 (d, 1 H, J = 7.1 Hz, H^a), 6.20 (d, 1 H, J = 11.2 Hz, H^c), 6.18 (dd, 1 H, J = 7.1, 11.2 Hz, H^b), 1.65 and 1.64 (s, 3 H each, $=C(CH_3)_2$), 1.01 and 0.98 (d, 6 H, J = 7.0 Hz, $CH(CH_3)_2$). The position of each proton is shown in Figure 6. The isopropyl methine proton is overlapped by the DMSO's peak.

Electric Conductivity Measurements of Ionically Dissociative Hydrocarbons. The conductivity was measured with a Toa Electronics Ltd. Model CM-6A conductivity meter equipped with a conductivity cell CG-2001PL (cell constant 0.0990). The method has been described in our previous paper.[11]

Acknowledgment. This work was supported by Grant-in-aid for Scientific Research on Priority Areas (No. 01648002 and 03214102) from the Ministry of Education, Science and Culture, Japan.

Supplementary Material Available: ^{13}C and/or ^{1}H NMR spectra for substituted tropylium ion ($2m^+ClO_4^-$) and covalent compounds (1-2a–m) (18 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.