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LINEAR FREE-ENERGY RELATIONSHIPS BETWEEN STABILITY PARAMETERS OF SUBSTITUTED TROPYLIUM AND CYCLOPROPENYLIUM IONS AS MEASURED BY REDUCTION RATE WITH CHROMIUM(II), REDUCTION POTENTIAL, CHARGE-TRANSFER ENERGY, AND pK_{R^+} VALUES†

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Abstract—Nine tropylium ions have been synthesized and the empirical stability parameters (i)–(iv) have been measured along with the parameters of known tropylium and cyclopropenylium ions: (i) the Cr(II)-ion reduction rate constant (k_2) in 10% aqueous hydrochloric acid at 25.0°; (ii) the charge-transfer frequency ($\nu_{CT\,max}$) with pyrene in 1,2-dichloroethane; (iii) the reduction peak potential (E_{red}) in dichloromethane or in acetonitrile; and (iv) the pK_{R^+} values in 23% aqueous ethanol, in 50% aqueous ethanol, and in 50% aqueous acetonitrile. When the linear free-energy relationships (LFER) of these and previously reported results were examined (a) between the charge-transfer energy {E_{CT}, $119.5 \times \nu_{CT\,max}$ (cm^{-1}), kJ mol^{-1}} and the E_{red} {$96.36 \times E_{red}$ (V), kJ mol^{-1}}; (b) between the log k_2 {$5.70 \times \log k_2$ (l mol^{-1} s^{-1}), kJ mol^{-1}} and the E_{red}; and (c) between the log k_2 and the E_{CT}, satisfactory interrelations were found.

On the basis of these LFER's the electron affinity scales (log k_2, E_{CT}, and E_{red}) are interchangeable for each other as the stability parameters for the cyclopropenylium and tropylium ions. When the pK_{R^+} values ($5.70 \times pK_{R^+}$, kJ mol^{-1}) of 15 cyclopropenylium and 21 tropylium ions were compared with the E_{red} values (kJ mol^{-1}), not one but eight correlation lines were shown within the range of slopes −0.25 to −1.05 for each of (1) 12 cyclopropenylium ions in 50% aqueous acetonitrile, (2) nine cyclopropenylium ions in 23% aqueous ethanol, (3) five cyclopropyl-substituted tropylium ions in 50% aqueous acetonitrile, (4) four t-butyl-substituted tropylium ions in 50% aqueous acetonitrile, (5) 10 tropylium ions in 23% aqueous ethanol, (6) nine polymethyl tropylium ions and others in 50% aqueous acetonitrile (7) six 1-aryl-8-tropylionaphthalenes in 50% aqueous ethanol, and (8) five bicycloalkanes fused with the tropylium ion in 50% aqueous ethanol. Thus, the pK_{R^+} scale, i.e. the water-affinity scale of the cations, is *not* generally interchangeable with the E_{red}, i.e. an electron-affinity scale of the cations, even though the pK_{R^+} values in a *single* solvent were compared with the E_{red} values (see categories (1), (3), (4) and (6)). The implications of such divergence of the pK_{R^+}–E_{red} correlation are discussed.

In the previous papers,[1–18] which described the syntheses and properties of the substituted cyclopropenylium and tropylium ions, we selected four empirical stability parameters: (i) the Cr(II)-ion reduction rate constant in 10% aqueous hydrochloric acid at 25° (as log k_2),[2–7,9–12] (ii) the charge-transfer energy (E_{CT}) with pyrene in 1,2-dichloro-ethane, calculated from the charge-transfer frequency ($\nu_{CT\,max}$),[2,3,5,7,8,12,17,18] (iii) the reduction potential (E_{red}) in dichloromethane or in acetonitrile by cyclic voltammetry (CV),[1,2,10,14,15,17] or by polarography,[3,5] and (4) the pK_{R^+} value in 23% aqueous ethanol, 50% aqueous ethanol, or 50% aqueous acetonitrile;[1,3,5–7,10,11,13–18] we showed several linear free-energy relationships (LFER)[2,3,5–9,11,12,14,18] among these parameters.

Bowie and Feldman similarly showed the existence of a LFER between the Cr(II)-ion reduction rate constant (as log k_2) and the reduction peak potential, by CV, for a series of stable heterocyclic cations; they included the tropylium ion (**1a**) as a carbocation.[19] Subsequently, Feldman and Flythe showed LFER's of the pK_{R^+} values with reduction potentials for a series of p-substituted triphenylmethyl cations and a series of stable heterocyclic cations; they also included **1a** and the dibenzotropylium ion.[20]

Recently, additional tropylium and cyclopropenylium ions have been synthesized in our laboratory, and considerable data of the relative stabilities has been accumulated. Hence, we have extended the examination of the correlations to include those carbocations with wider structural change, 80 tropylium and 18 cyclopropenylium ions. This paper describes the results, and the discussion concentrates in particular on examining the consistency of the slope value of the LFER's with theory of the correlation among these stability parameters.[19–22]

RESULTS AND DISCUSSION

Correlation of charge-transfer energies of substituted tropylium ions with the reduction peak potentials

The first synthesis of the tropylium bromide was reported by Doering and Knox in 1954.[23] Two years later, the charge-transfer complex formation of the tropylium ion (**1a**) with the iodide ion was suggested by Doering[24] and Kosower.[25] Subsequently, in 1968 two major contributions were made to the theoretical understanding of the charge-transfer complex formation of the tropylium ion system. First, Feldman and Winstein found a linear correlation of the charge-transfer energies (E_{CT}, eV) of **1a** with ionization potentials (I_p, eV) of several donors,

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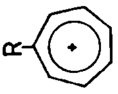
†Dedicated to Prof. William von E. Doering, Harvard University, on the occasion of his 65th birthday; presented in part at the International Symposium on Organic Reaction Mechanisms, Kyushu University, Fukuoka, August 1982.



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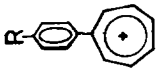

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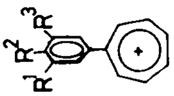

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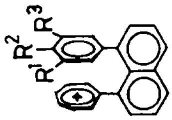

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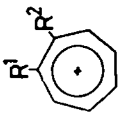

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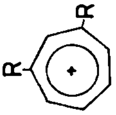

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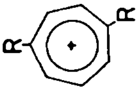

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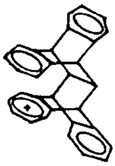

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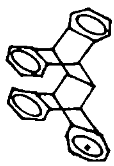

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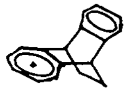

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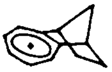

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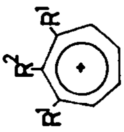

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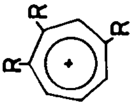

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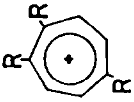

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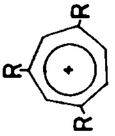

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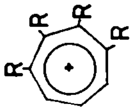

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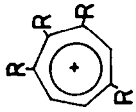

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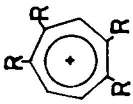

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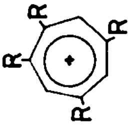

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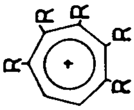

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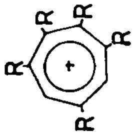

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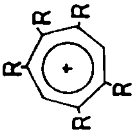

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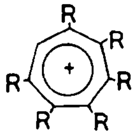
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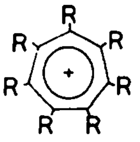
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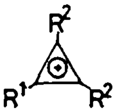
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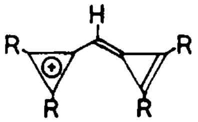
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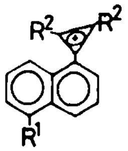
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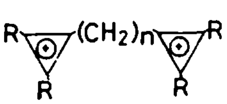

(29)

a; R = H.
b; R = Me.
c; R = Et.
d; R = Pr.
e; R = *iso*-Pr.
f; R = Bu.
g; R = *tert*-Bu.
h; R = Pentyl.
i; R = Hexyl.
j; R = *cyclo*-Pr.
k; R = 1-Norbornyl.
l; R = exo-2-Norbornyl.
m; R = *endo*-2-Norbornyl.
n; R = Ph$_3$C.
o; R = Ph.
p; R = 1-Naphthyl.
q; R = CN.
r; R = CO$_2$Me.
s; R = OH.
t; R = MeO.
u; R = Ph3Si.
v; R = MeS.
w; R = Cl.
x; R = Br.

a'; R^1= R^2= MeO.
b'; R^1= R^2= Et.
c'; R^1= R^2= Pr.
d'; R^1= R^2= *iso*-Pr.
e'; R^1= R^2= *tert*-Bu.
f'; R^1= R^2= *cyclo*-Pr.
g'; R^1= R^2= Ph.
h'; R^1= R^2= *p*-(*iso*-Pr)$_2$NC$_6$H$_4$.
i'; R^1= R^2= 2-Thienyl.
j'; R^1= H, R^2= Ph.
k'; R^1= Me, R^2= *iso*-Pr.
l'; R^1= Me, R^2= *cyclo*-Pr.
m'; R^1= Me, R^2= Ph.
n'; R^1= Pr, R^2= Ph.
o'; R^1= Ph, R^2= Pr.
p'; R^1= Ph, R^2= p-(*iso*-Pr)2NC$_6$H$_4$.
q'; R^1= PhC≡C, R^2= Ph.
r'; R^1= *p*-(*iso*-Pr)2NC$_6$H$_4$, R^2= Ph.
s'; R = Ph, n = 3.
t'; R = Ph, n = 4.
u'; R = Ph, n = 5.
v'; R = Ph, n = 6.

a"; R^1= R^2= R^3= H.
b"; R^1= R^3= H, R^2= Me.
c"; R^1= R^3= H, R^2= CF$_3$.
d"; R^1= R^3= H, R^2= MeO.
e"; R^1= H, R^2= *cyclo*-Pr, R^3= Me.
f"; R^1= Me, R^2= R^3= H.
g"; R^1= R^3= Me, R^2= H.
h"; R^1= R^3= Me, R^2= *cyclo*-Pr.
i"; R^1= MeO, R^2= R^3= H.
j"; R^1= R^3= CF$_3$, R^2= H.

such as toluene, xylene, naphthalene, and durene.[21] Since the slope of the regression line was 1.0, they interpreted the result as substantiation of the Mulliken's equation (eqn 1), which indicates a linear correlation of E_{CT} with I_p.[21]

$$E_{CT} = I_p - E_a + \text{constant}. \qquad (1)$$

Secondly, Dauben and Wilson showed a linear correlation of the E_{CT} values with the electron affinity (E_a in eqn (1)) of mono-substituted tropylium ions: **1a**, **1g**, **1q**, **1s**, **1t**, **1w**, and **1x**. They selected pyrene as the reference electron donor, and compared the $\nu_{CT\,max}$ values with polarographic half-wave potentials as the E_a values. As expected from eqn (1), the slope of the regression line had a negative value but not a value of − 1.0. The value was − 1.45 when calculated by us in kJ mol^{-1} for both E_{CT} and E_a.

We recently measured the $\nu_{CT\,max}$ (cm^{-1}) with pyrene for all members of polymethyltropylium ions: **1b**, **5a'**, **6b**, **7b**, **13a'**, **14b** – **24b**, and **25b**; this examination showed a satisfactory correlation with slope of − 0.90 (correlation coefficient r – 0.984), close to − 1.0 as expected from eqn (1), when the E_{CT} and E_a values were plotted by the use of the unit of kJ mol^{-1}, i.e. 119.5 × $\nu_{CT\,max}$ for E_{CT} and 96.36 × E_{red} (V vs sce) for E_a.

Thus we extended our examination to 43 tropylium ions, which have wider structural variation in the substituents (see Table 1). When the E_{CT} (kJ mol^{-1}) in 1,2-dichloroethane are plotted against the E_{red} (kJ mol^{-1}) in dichloromethane, a satisfactory regression line (r – 0.9527) was found for 41 tropylium ions, including 16 polymethyltropylium ions (Fig. 1). The slope of the regression line was − 0.877, a value fairly consistent with theoretical prediction from eqn (1).

Methoxytropylium ion (**1t**) and heptamethyltropylium ion (**25b**) significantly deviate from the regression line, and are excluded from the calculation. When no E_{red} values vs sce were obtainable, the values vs Ag/AgNO$_3$ in acetonitrile were calibrated for the values vs sce in dichoromethane by addition of 0.38 V, which value was derived from the difference of redox potential of ferrocene, determined under these two conditions. The difference for **1a** was actually found to be 0.39 V (see Table 1).

The deviation of **25b** is attributed to the steric congestion of the methyl groups in the ground state,[2] and the deviation of **1t** to the uncertainty of the E_{red} value, caused by instability of **1t**.[22] The causes are not clear with regard to significant dispersion, which is observed in some of the other less stable tropylium ions: **1g**, **2j**, **3e"**, and **3h"**. It exceeds the range of the experimental errors, 2 kJ mol^{-1} for the E_{red} and 6–10 kJ mol^{-1} for the E_{CT}.

Despite such dispersion Mulliken's theoretical prediction can be verified on the tropylium-ion system with a wide range of structural variation. Thus, the E_{CT} parameter (a stability scale to a reference π-electron donor) is, despite its lack of precision, able to interchange with the E_{red} parameter (a stability scale to an electron on the cathode), as long as the comparison is made in wide structural change.

Correlation of Cr(II) ion reduction rates of substituted cyclopropenylium and tropylium ions with the reduction peak potentials

Doering and Knox revealed a facile and quantitative

Table 1. Summary of some chemical and physical properties of substituted tropylium ions[a]

Cation	log k_2[b]	$E_{red.}$[c]	$10^{-4}\nu_{CT\ max.}$[d]	pK_{R^+}[e]
1a	1.87	-0.120[f] -0.510[f] -0.126[i] -0.21[j]	1.85[g] 1.97[g]	4.30[h] 4.74[h] 4.76[k] 3.10[l] 3.88[l] 4.01[l,m] 4.2[l,n]
1b	1.05	-0.233[i] -0.187[i]	1.88	
1c	1.01	-0.195[i]	1.88	
1d	1.06		1.89	
1e	0.915	-0.235[i]	1.89	
1f	0.986		1.96	
1g	0.902	-0.61[f] -0.215[i]	1.97[g] 1.99[g]	5.0[l] 4.57[l]
1h	1.01		1.89	
1i	0.961		1.98	
1j	0.665	-0.290[f] -0.640[f]	1.90	5.76[l]
1k		-0.249[f] -0.611[f]	1.90	4.96[l]
1l		-0.236[f] -0.605[f]	1.89	4.90[l]
1m		-0.249[f] -0.610[f]	1.86	5.4[l,n]
1n	2.75	-0.069[i]	1.81	3.6
1o	2.16	-0.119[i] -0.090[i]	1.79	4.13[k] 2.59[k] 3.88[l]
1p	2.48	-0.113		3.72[k] 2.25[k]
1q	4.08[o]		1.47[g] 1.48[g]	
1r	3.42[o]		1.67	
1t	0.34[o]	-0.27[j]	2.08[g] 2.08[g]	
1u	2.75[o]		1.72	
1v	1.28[o]		1.96	
1w	3.07[o]	0.04[j]	1.72[g] 1.65[g]	
1x		0.01[j]	1.71[g]	
2b	2.00	-0.171	1.78	4.61[l] 4.17[l]
2c	1.92		1.85	4.73
2e	2.01		1.86	4.80
2g	2.09		1.85	4.50
2j	1.94	-0.168	1.75	5.03
2o	2.24		1.74	3.76
2q	3.18		1.79	2.51
2s	1.81		1.88	5.32[l] 4.96[l]
2t	1.79		1.75	5.17[l] 4.59[l]
2w	2.37		1.80	3.99[l] 3.30[l]
2x	2.40		1.74	3.65[l] 3.25[l]
3e"	1.97	-0.173	1.72	4.77
3f"	2.10	-0.135	1.77	4.51
3g"	2.09	-0.153	1.77	4.54
3h"	2.08	-0.160	1.75	4.64
3i"	2.39		1.72	4.16[l] 3.51[l]
4a"		-0.295		4.35[k]
4b"		-0.300		4.40[k]
4c"		-0.217		3.06[k]
4d"		-0.289		4.42[k]
4g"		-0.317		4.51[k]
4j"		-0.178		2.11[k]
5a'	-0.042	-0.348	1.98	4.5[l,n]
5k'	0.0043		1.99	
5l'	-0.032		1.96	
5m'	1.35		1.89	
6b	0.134	-0.298	1.94	
6c		-0.336	1.93	
6e		-0.353[f] -0.690[f]	1.95	
6g		-0.377[f] -0.695[f]	1.99	4.90[l]
6j		-0.760[f]	1.98	7.56[l]

Table 1. (*Contd*)

Cation	log k_2[b]	$E_{red.}$[c]	$10^{-4}\nu_{CT\ max.}$[d]	pK_{R^+}[e]
7b	-0.063	-0.312	1.94	
7g		-0.720[f]	2.00	5.42[l]
7j		-0.760[f]	2.00	7.63[l]
8		-0.405		7.93[k]
				8.67[l]
9		-0.280		5.65[k]
				6.35[l]
10		-0.310		6.23[k]
11		-0.375		7.08[k]
		-0.455[i]		8.82[p,q]
12		-0.387		7.50[k]
13a'	-0.830	-0.428	2.01	4.7 [l,n]
13k'	-0.418		2.00	
13l'	-0.475		1.99	
13m'	-0.386		1.99	
14b	-0.772	-0.438	2.01	
15b	-0.943	-0.420	1.99	
16b	-0.971	-0.395	1.99	
16g		-0.840[f]	2.04	6.26[l]
16j		-0.856[f]	2.04	8.72[l]
17b	-1.68	-0.500	2.07	6.01[l]
18b	-1.59	-0.517	2.07	6.15[l]
19b	-1.79	-0.521	2.08	
20b	-1.56	-0.495	2.04	
20j		-0.938[f]	2.07	9.10[l]
21b	-2.16	-0.548	2.13	6.40[l]
22b	-2.36	-0.549	2.11	
23b	-2.58	-0.604	2.13	
24b	-2.66	-0.594	2.17	6.60[l]
25b	-2.03	-0.588	2.35	4.86[l]

[a] References for the data are cited in text, except those in footnotes g, h, m, and p.

[b] k_2 ($l\ mol^{-1}\ s^{-1}$): rate constant of Cr(II)-ion reduction in 10% aqueous hydrochloric acid at 25°.

[c] CV peak potential (V) vs. sce in dichloromethane with tetrabutylammonium perchlorate as supporting electrolyte at 0.1 V s^{-1}.

[d] Charge-transfer $\nu_{max.}$ (cm^{-1}) with pyrene in 1,2-dichloroethane.

[e] In aqueous 23% ethanol. [f] CV peak potential vs. Ag/$AgNO_3$ in acetonitrile with tetrabutylammonium perchlorate as supporting electrolyte at 0.1 V s^{-1}.

[g] Ref. 22. [h] In water; refs. 23 and 47, respectively.

[i] Polarographic half-wave potential vs. Ag/AgCl in acetonitrile with tetraethylammonium perchlorate as supporting electrolyte.

[j] Polarographic half-wave potential vs. sce in acetonitrile.

[k] In 50% aqueous ethanol. [l] In 50% aqueous acetonitrile.

[m] Ref. 33. [n] Accuracy: ± 0.3 pK_{R^+} unit.

[o] Calculated value (see text). [p] Ref. 46.

[q] In 20% aqueous acetonitrile.

Zn-dust reduction of the tropylium ions (**1a**) to give bitropyl in their first report on the synthesis of **1a**.[23] Thereafter, a similar facile reduction of **1a** with Cr(II)-ion[26,27] and with the other low-valent metals and metallic ions[27] has been reported.

Following these studies, we reported the rate constant (k_2) of Cr(II)-ion reduction of **1a**, along with those of several phenyl- and alkyl-substituted tropylium ions: **1b**, **1c**, **1g**, **1n**, and **1o**;[3] the correlation of the reduction rates (as log k_2) with charge-transfer frequencies ($\nu_{CT\,max}$) or with the polarographic half-wave potentials ($E_{1/2}$) was satisfactory. Subsequently, Bowie and Feldman showed a LFER of the Cr(II)-ion reduction rates (as log k_2) of five heterocyclic cations (R^+ in eqn 2) with the equilibrium constant (K) in the electron-transfer reaction of a heterocyclic cation with N-methylacridyl radical.[19] They calculated the $\Delta \log K$ from the reduction potentials (ΔE_{red}) of these cations.

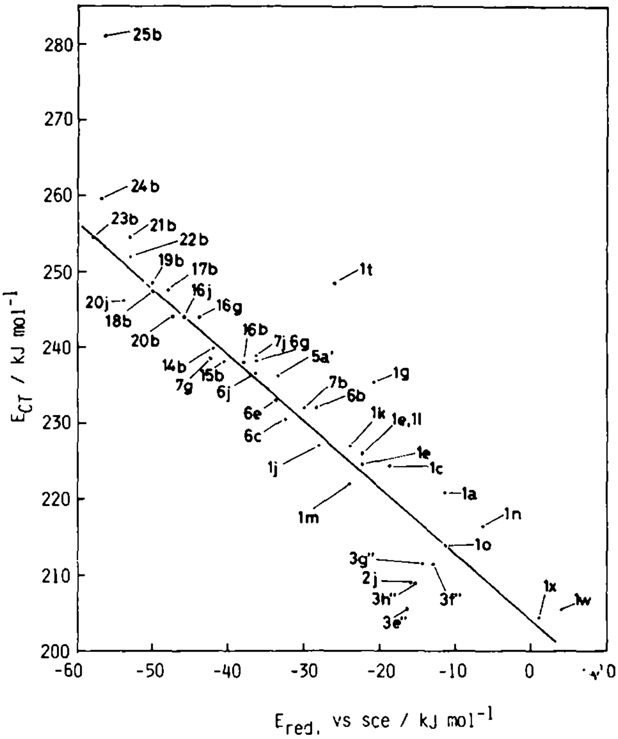


Fig. 1. Correlation of charge-transfer energies with reduction peak potentials for substituted tropylium ions.

$$R^+ + \text{N-Methylacridyl radical} \overset{K}{\rightleftharpoons} R\cdot + \text{N-Methylacridinium ion} \quad (2)$$

The ion **1a** was included in the correlation; the slope of the regression line 0.52, was in satisfactory agreement with the theoretical value of 0.5 in eqn (3), which they derived from the Marcus theory for the outer-sphere mechanism of single-electron transfer reaction.[19]

$$\log k_2 = 0.5 \times \log K + \text{constant}. \quad (3)$$

Since eqn (3) can be rewritten as a linear correlation of $\log k_2$ with E_{red} (eqn 4), we compared in a previous paper the $\log k_2$ in 10% aqueous hydrochloric acid with the E_{red} in dichloromethane (in kJ mol^{-1}) for 17 polymethyltropylium ions.[2] The slope of the regression line was 0.54, consistent with the prediction from eqn (4).

$$5.70 \times \log k_2 = 0.5 \times 96.36 \times E_{red}(V) + \text{constant}. \quad (4)$$

When we extended such examination to the 33 tropylium and four cyclopropenylium ions (see Tables 1 and 2), an excellent correlation (r 0.992) was shown and the slope was 0.575, in fair agreement with theory (Fig. 2).

The point for phenyldipropylcyclopropenylium ion (**26o'**) in Fig. 2 was excluded because of considerable deviation. The value of the reduction potentials in Fig. 2 are calibrated for sce in dichloromethane when the data was available only with Ag/AgNO$_3$ reference electrode in acetonitrile. The $\log k_2$ values are usually associated with an error of 0.3 kJ mol^{-1} or less, except for **26o'**, for which the k_2 value was extrapolated from the data at higher temperatures.[6]

Thus, the $\log k_2$ value can be employed as the stability parameter toward a single-electron donor, similarly to but more precisely than the E_{red}. The latter is usually associated with an error of 2 kJ mol^{-1}.

Because of its higher precision, the $\log k_2$ parameter can also be used for the dissection of steric and electronic factors in the LFER among single-electron reduction rates of these cations. The examples of such LFER examination have been reported for the Cr(II)-ion reduction of polymethyltropylium ions[2] and for cyclopropyl- and isopropylsubstituted tropylium ions.[9,11,12]

Correlation of Cr(II) -ion reduction rates of substituted tropylium ions with charge-transfer energies

The satisfactory correlation of the reduction rates (as $\log k_2$) with the charge-transfer energies (as $\nu_{CT\,max}$) have been reported for some groups of carbocations, such as alkyl- and phenyl-tropylium ions,[3,5,7] heteroatom-substituted tropylium ions,[8] and cyclopropyl-substituted tropylium ions.[12] Moreover, as described in the previous sections, the charge transfer energies (E_{CT}) linearly correlate with the reduction potentials (E_{red}) with the slope of -1.0, and the Cr(II)-ion reduction rates (as $\log k_2$) exhibit a correlation with E_{red} values with the slope of 0.5. Consequently, we can anticipate the linear dependence of $\log k_2$ on E_{CT} with the theoretical slope of -0.5.

When we examined this correlation for 55 tropylium ions, the slope of the regression line was -0.494, almost equal to the theoretical value (Fig. 3). However, when compared with Fig. 2, the dispersion is much wider (r $-$ 0.9211). Although we are not in a position to discuss the details of the dispersion, one of the obvious reasons we can point out is the lower precision of E_{CT} measurement.

Table 2. Summary of some chemical and physical properties of substituted cyclopropenylium ions[a]

Cation	log k_2[b]	$E_{red.}$[c]	pK_{R^+}[d]
26c'		∿-1.7	7.2[e]
26f'		-2.20	10.0[e] 9.4[e,f]
26g'	-3.52	-1.11 -0.94[g,h]	2.6 2.80[i] 2.33[e] 3.18[i,j]
26h'		-1.80[g]	9.75
26i'	-4.00	-0.70[g]	4.33 3.80[e]
26j'		-0.59	-0.67 0.32[i,j]
26n'	-5.57	-1.31	4.0 3.8[i] 3.52[e]
26o'	-8.56	-1.49	5.6 5.22[e]
26p'		-1.54[g]	7.85
26r'		-1.28[g]	6.60
27o		-1.48	7.23 8.9[e]
28j'		-1.07	1.62[e]
28q'		-1.04	1.16[e]
29s'		-0.95	2.06[e] 4.50[e,k]
29t'		-1.16	3.38[e] 4.75[e,k]
29u'		-1.26	3.35[e] 4.80[e,k]
29v'		-1.28	3.35[e] 4.67[e,k]

[a] References for the data are cited in text, except those in footnotes f, h, and i.

[b] k_2 ($l\ mol^{-1}\ s^{-1}$): rate constant of Cr(II)-ion reduction in 2.9 N hydrochloric acid at 25°.

[c] CV peak potential (V) vs. $Ag/AgNO_3$ in acetonitrile with tetrabutylammonium perchlorate as supporting electrolyte at 0.1 $V\ s^{-1}$.

[d] In 23% aqueous ethanol. [e] In 50% aqueous acetonitrile.

[f] Ref. 41. [g] CV peak potential (V) vs. sce in dichloromethane with tetrabutylammonium perchlorate as supporting electrolyte at 0.1 $V\ s^{-1}$.

[h] Ref. 43. [i] Ref. 45. [j] In water.

[k] For the second cyclopropenylium ion equilibrium.

Thus, in practice, the E_{CT} parameter is less suitable for the stability parameter due to its low precision, although in the polymethyltropylium-ion system it showed a satisfactory linear correlation with the calculated LUMO energy levels.[2]

Correlation of the pK_{R^+} values of substituted cyclopropenylium and tropylium ions with the reduction potentials

We showed previously that the rate constants for Cr(II) reduction (as log k_2) linearly correlate with the pK_{R^+} values for alkyl-substituted tropylium ions: **1a**, **1g**, **1n**, and **1o**,[3,5] and p-substituted-phenyl-tropylium ions **2a**, **2q**, **2s**, **2t**, **2w**, **2x** and **3i''**.[7] Moreover, Fig. 2 clearly shows the correlation of log k_2 with the E_{red} value. Consequently we can anticipate a linear relation between the pK_{R^+} values and the E_{red} value.

Bowie and Feldman also discussed the correlation of the log k_2 and the pK_{R^+} for a series of organic cations (N-methyl-acridinium, 2,4,6-triphenylpyrylium, sesquixanthylium, tropylium, flavylium, 9-phenylxanthylium, and 9-phenylthioxanthylium ions).[19] In their subsequent papers Feldman and Flythe have reported on linear correlations between the pK_{R^+} values and the reduction potentials for a series of p-substituted triarylmethyl cations,[20,28] and for a group of benzopyrylium, benzothiopyrylium, and benzotropylium ions.[20]

Thus, when we plotted the pK_{R^+} values (in free-energy unit, $5.70 \times pK_{R^+}$, kJ mol^{-1}) of the carbocation **1**–**29** (Tables 1 and 2) against the E_{red} (vs sce, kJ mol^{-1}), eight linear correlation lines with slopes ranging from − 0.248 to 1.05 were found. The pK_{R^+} values have been measured in three solvents, i.e. 50% aqueous acetonitrile, 50% aqueous ethanol, and 23% aqueous ethanol, and are not corrected for the solvent effect. We can divide the results into two groups: (a) the correlation with the slope of

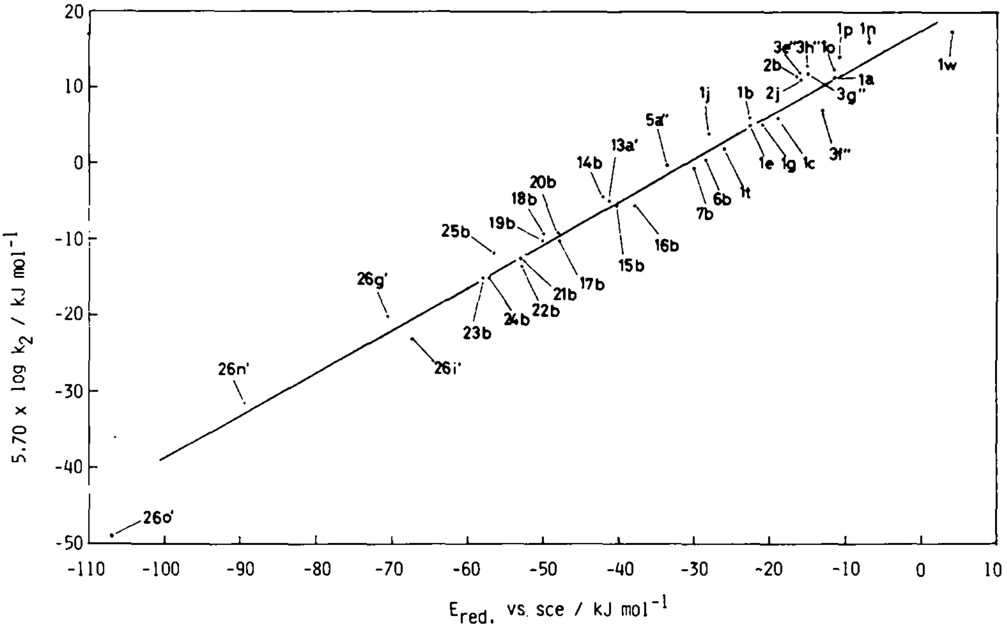


Fig. 2. Correlation of rates for Cr(II)-ion reduction (in free-energy unit) with reduction peak potentials for the substituted cyclopropenylium and tropylium ions.

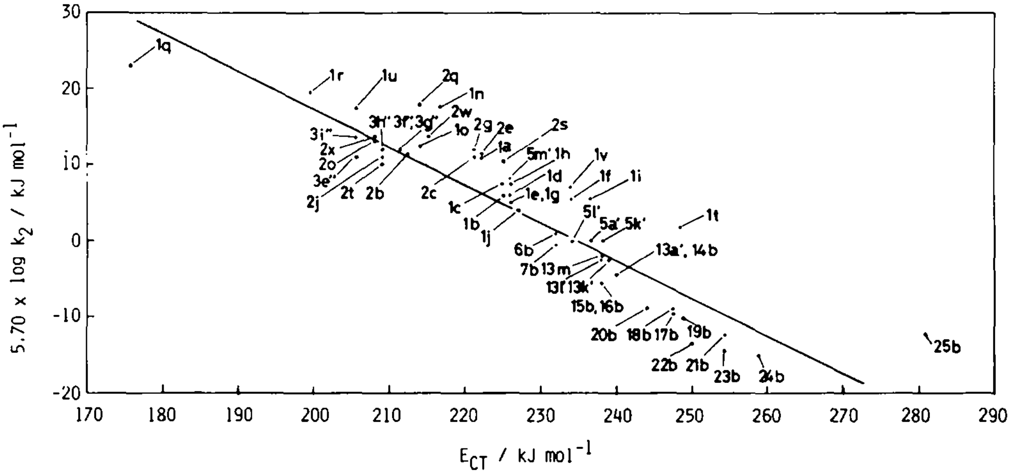


Fig. 3. Correlation of rates for Cr(II)-ion reduction (in free-energy unit) with charge-transfer energies for substituted tropylium ions.

-1.0, and (b) the correlations with the range of the slopes, $0 > \rho > -1.0$.

Correlations with the slope -1.0. Figure 4 shows the correlations with the slope of -1.0. A group of 1,4-bridged tetrahydrobenzotropylium ions (A): **8–12**, and a series of 1-aryl-8-tropylionaphthalenes (B): **4a''–4d''**, **4g''**, and **4j''**, give excellent correlations with slopes of -0.979 ($r-0.998$) and -1.05 ($r-0.989$), respectively.

These results parallel the observation made by Feldman and Flythe for the other stable carbocation systems (*vide supra*),[20] and indicate that within each group of cations the substituent effect on the pK_{R^+} value is obviously controlled by the E_{red} value.

To explain such linear correlation Feldman and Flythe divided the ΔpK_{R^+} into two factors by considering the following equilibria on the ionization of a carbinol ROH.[20]

$$ROH + R_0^+ \rightleftharpoons R^+ + R_0OH \quad (\Delta G_i) \tag{5}$$

$$ROH + R_0\cdot \rightleftharpoons R\cdot + R_0OH \quad (\Delta G_d) \tag{6}$$

$$R\cdot + R_0^+ \rightleftharpoons R^+ + R_0\cdot \quad (\Delta G_{et}) \tag{7}$$

First, they derived the free-energy difference of ionization of ROH and R_0OH (ΔG_i in eqn 5) from the difference of the pK_{R^+} value ($-\Delta pK_{R^+}$) and also derived the free-energy difference of the electron-transfer reaction between R· and R_0^+ (ΔG_{et} in eqn 7) from the difference of the reduction potentials of R^+ and R_0^+ (ΔE_{red}). Then they correlated the free-energy difference of radical dissociation of ROH and R_0OH (ΔG_d in eqn 6),

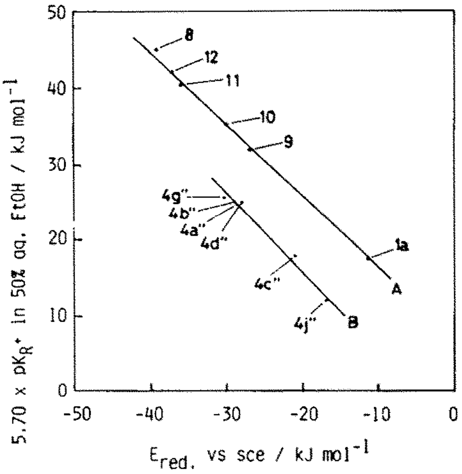


Fig 4. Correlation of pK_{R^+} values in 50% aqueous ethanol with reduction peak potentials for (A) (1,2-tropylio)-bicycloalkanes and (B) 1-aryl-8-tropylionaphthalenes.

which is not observable for these systems, with ΔG_i and ΔG_{et}, using eqn (8).

$$\Delta G_i = \Delta G_d + \Delta G_{et}. \tag{8}$$

Since Fig. 4 shows the slopes of -1.0 for group A cations, it is concluded from eqn (8) that ΔG_d for these cations are virtually zero, if one selects **1a** as the reference cation (R_0^+). In other words, the radical dissociation energies of the carbinols, corresponding to the cations of group A, are virtually not affected by the structural change in the substituents. Thus, it is conceivable for the cations **8**,[15] **9**,[15] and **10**[37] in group A (Fig. 4) that the stabilization due to th intramolecular charge-transfer may virtually vanish in the corresponding radicals and the difference of the radical dissociation (ΔG_d) of ROH's hence becomes relatively small, as compared with the ΔG_i and ΔG_{et}. In addition, if one assumes for the cations **11**[37] and **12** in group A that the ΔG_i is attributed to the stabilization by ring strain, such stabilization would show much less contribution in the respective radicals. This stabilization by ring strain obviously needs further verification with regards to the other structurally related tropylium ions fused with a strained ring system.

For the linear relation of group B cations an elucidation could be offered similar to that made to the cations in group A, if only group B cations are compared. However, the gap between the two correlation lines A and B is open to discussion. The shielding of the tropylium ring by the aryl-ring in group B cations can suppress the forward reaction in the equilibrium with water by half, as compared with the usual open tropylium ions. By the same token, the reduction potentials could become more negative, when compared with the open tropylium ions. Such statistical factors will lower the pK_{R^+} and E_{red} values respectively by 1.72 kJ mol^{-1} in free-energy units. However, this does not explain the whole of the gap, about 10 kJ mol^{-1} in the ordinate in Fig. 4. Thus, when we select **1a** as the reference cation for group B cations, the ΔG_d in eqn (8) does not become zero but a constant. Moreover, the ΔG_d term would consist of such statistical factors, but mainly of the difference between radical dissociation energies of tropyl alcohol and of the carbinols corresponding to B group cations. Since the ΔG_d is not variable for B group cations, the radical dissociation energies of the corresponding carbinols will not be much affected by the structural change of limited range.

Correlations with the slopes $0 > \rho > -1.0$. Figures 5 and 6 show some of the second group of pK_{R^+}–E_{red} correlations with the slopes $0 > \rho > -1.0$. The pK_{R^+} values were measured in 50% aqueous acetonitrile for

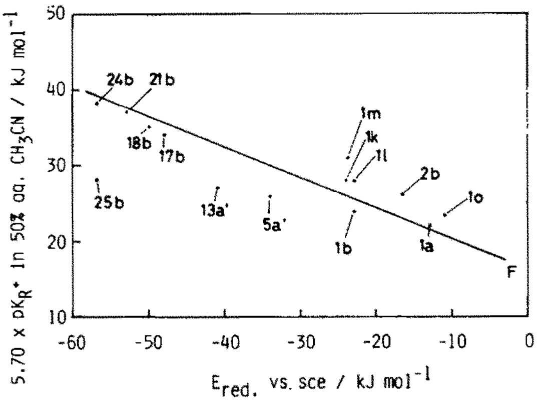


Fig. 6. Correlation of pK_{R^+} values in 50% aqueous acetonitrile with reduction peak potentials for polymethyltropylium ions, norbornyltropylium ions, and phenyltropylium ions.

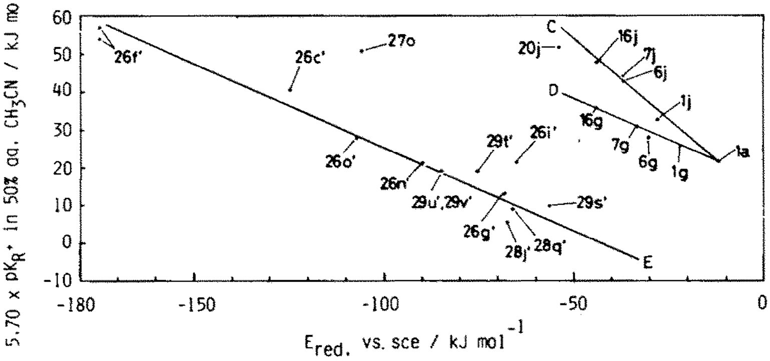
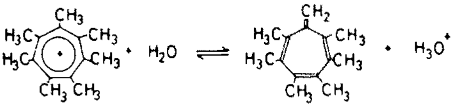


Fig 5. Correlation of pK_{R^+} values in 50% aqueous acetonitrile with reduction peak potentials for (C) cyclopropyltropylium ions, (D) *tert*-butyltropylium ions, and (E) substituted cyclopropenylium ions.

five cyclopropyl-substituted tropylium ions (C): **1j**, **6j**, **7j**, **16j**, and **20j**; four *tert*-butyl-substituted tropylium ions (D): **1g**, **6g**, **7g**, and **16g**; and 13 substituted cyclopropenylium ions (E): **26c′**, **26f′**, **26g′**, **26i′**, **26n′**, **26o′**, **27o**, **28j′**, **28q′**, **29s′**-**29u′**, and **29v′**. The correlations are satisfactory for each group of carbocations, including **1a** (Fig. 5).

The slopes of the regression lines, C, D, and E in Fig. 5, were −0.863, −0.425, and −0.390, and the correlation coefficients were −0.991, −0.987, and −0.974, respectively. The cation **20j** in group C and **27o** in group E were excluded from the calculation because of considerable deviation. The deviation of **20j** may have arisen from the non-additivity in accumulated substituent effect of cyclopropyl groups upon the cation stability,[18] whereas the deviation of **27o** can be attributed to the unique π electronic structure, with a triafulvenyl system resulting in a considerable ΔG_d difference compared with the other simple cyclopropenylium systems.

Figure 6 shows another correlation with the slope $0 > \rho > -1.0$ (line F, ρ − 0.248, r − 0.783). The pK_{R^+} values were measured in 50% aqueous acetonitrile for the polymethyl-tropylium ions: **1b**, **2b**, **17b**, **18b**, **21b**, **24b**, **5a′**, **13a′**, and **25b**; the norbornyltropylium ions: **1k**, **1l**, and **1m**; and the phenyltropylium ions: **1o** and **2b**. The dispersion may be attributed to the inaccuracy of the pK_{R^+} measurement. Besides the normal hydrolysis of the cations, a small but appreciable degree of irreversible decomposition due to deprotonations, as illustrated in eqn (9) in the case of the cation **25b**, was observed during the measurements for some of the methyltropylium ions: **1b**, **5a′**, **13a′**, and **25b**; and the norbornyltropylium ions: **1l** and **1m**.



We have also found satisfactory linear correlations (the slopes $0 > \rho > -1.0$) with the pK_{R^+} data determined in 23% aqueous ethanol, for each of the groups of nine cyclopropenylium ions: **26g′**-**26j′**, **26n′**-**26p′**, **26r′**, and **27o**, and of 11 tropylium ions: **1a**, **1g**, **1n**-**1p**, **2b**, **2j**, **3e″**-**3g″**, and **3h″**. The slopes of the correlation lines were −0.370 (r − 0.929) and −0.596 (r − 0.897), respectively.

Thus we have six pK_{R^+}–E_{red} correlations, which exhibit the range of the slopes $0 > \rho > -1.0$. From these relations we can derive eqn (10), which shows a linear correlation between ΔG_i ($-\Delta pK_{R^+}$) and ΔG_{et} (ΔE_{red}), when we select a reference cation, e.g. **1a** for the lines C and D.

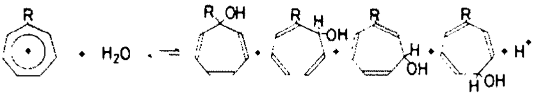
$$\Delta G_i = \alpha\,\Delta G_{et} \quad (1.0 > \alpha > 0). \tag{10}$$

Hence, from eqns (8) and (10), the ΔG_d for each of groups C–E linearly correlates with the ΔG_{et} with a negative slope of the regression line (eqn 11).

$$\Delta G_d = (\alpha - 1)\Delta G_{et} \quad (1.0 > \alpha > 0). \tag{11}$$

Therefore, we can suggest from eqn (11) that within each group of cations the more stable cation gives the less stable radical in single-electron reduction.

Finally, it is worth mentioning that for the pK_{R^+} value of substituted troylium and cyclopropenylium ions, the reverse reaction of the equilibrium with water is composed of the dissociations of, in principle, several isomeric carbinols, and consequently the observed pK_{R^+} value corresponds not to a single equilibrium but to a composite one. This is illustrated in eqn (12) for monosubstituted tropylium ions. The same is true for the substituted cyclopropenylium ions.



Due to this composite feature of the equilibrium and also to two contributing factors, ΔG_d and ΔG_{et} in eqn (8), the dispersion in the pK_{R^+}–E_{red} correlation (as seen in Fig. 6) may not be unexpected, although the elaborated explanation of the origins of the dispersion must await future studies.

EXPERIMENTAL

M.p. and b.p. values are uncorrected. Elemental analyses were performed by the Microanalytical Center, Kyoto University. IR spectra were taken on a Hitachi 215 spectrometer. UV spectra were taken on a Hitachi 200–10 spectrometer or with a Shimadzu UV-50M spectrometer. ^{1}H NMR spectra were recorded with a Hitachi R-24 (60 MHz) spectrometer or on a Varian HA-100 (100 MHz) spectrometer with tetramethylsilane as internal standard. ^{13}C NMR spectra were obtained on JEOL FX-100 spectrometer operated in the pulse Fourier transform mode.

Materials. Reagents were of reagent grade quality except where otherwise noted. Acetonitrile and ethyl acetate were refluxed and distilled over phosphorus pentoxide. Trityl salts were prepared following the method of Dauben *et al.*[29] 7-Ethoxytropilidene was prepared from tropylium fluoroborate and sodium ethoxide in ethanol. 1,4-Methano-1,2,3,4-tetrahydronaphthalene was prepared following the method reported by Wittig and Knauss.[30]

The details of the syntheses of the following tropylium ions have been reported: unsubstituted tropylium (**1a**),[29] methyl (**1b**),[29,31] ethyl (**1c**),[5] propyl (**1d**),[7] isopropyl (**1e**),[5] butyl (**1f**),[7] *tert*-butyl (**1g**),[5] pentyl (**1h**),[7] hexyl (**1i**),[7] cyclopropyl (**1j**)[32] triphenylmethyl (**1n**),[5] phenyl (**1o**),[33] 1-naphthyl (**1p**),[14] cyano (**1q**),[8] carbomethoxy (**1r**),[8] methoxy (**1t**),[29] triphenylsilyl (**1u**),[8] methylthio (**1v**),[8] chloro (**1w**),[29,34] bromo (**1x**),[29] 4-methylphenyl (**2b**),[33] 4-cyclopropylphenyl (**2j**),[11] 4-phenylphenyl (**2o**),[33] 4-cyanophenyl (**2q**),[7] 4-hydroxyphenyl (**2s**),[33] 4-methoxyphenyl (**2t**),[33] 4-chlorophenyl (**2w**),[33] 4-bromophenyl (**2x**),[33] 4-cyclopropyl-3-methylphenyl (**3e″**),[11] 3-methyl-phenyl (**3f″**),[11] 3,5-dimethylphenyl (**3g″**),[11] 4-cyclopropyl-3,5-dimethylphenyl (**3h″**),[11] 3-methoxyphenyl (**3i″**),[33] 8-phenylnaphth-1-yl (**4a″**),[14] 8-(4-methylphenyl-naphth-1-yl (**4b″**),[14] 8-(4-trifluoromethylphenyl)naphth-1-yl (**4c″**),[14] 8-(4-methoxyphenyl)naphth-1-yl (**4d″**),[14] 8-(3,5-dimethylphenyl)naphth-1-yl (**4g″**),[14] 8-(3,5-bistrifluoromethylphenyl)naphth-1-yl (**4j″**),[14] 1,2-dimethyl (**5a′**),[35] 1-isopropyl-2-methyl (**5k′**),[12] 1-cyclopropyl-2-methyl (**5l′**),[12] 1-methyl-2-phenyl (**5m′**),[12] 1,3-dimethyl (**6b**),[12] 1,3-di-*tert*-butyl (**6g**),[illegible] 1,3-dicyclopropyl (**6j**),[18] 1,4-dimethyl (**7b**),[36] 1,4-di-*tert*-butyl (**7g**),[18] 1,4-dicyclopropyl (**7j**),[18] 5,5a,6,11,11a,12-hexahydro-5,12-(*o*-benzeno)-*endo*-6,11-(1,2-tropylio)naphthacene (**8**),[15] 5,5a,6,11,11a,1a-hexahydro-5,12-(*o*-benzeno)-*exo*-6,11-(1,2-tropylio)naphthacene (**9**),[15] 1,2,3,4-tetrahydro-1,4-(1,2-tropylio)naphthalene (**10**),[37] 1,4-ethano-1,2,3,4-tetrahydrobenzo (**11**),[37] 1,2,3-trimethyl (**13a′**),[12] 2-isopropyl-1,3-dimethyl (**13k′**),[12] 2-cyclopropyl-1,3-dimethyl (**13l′**),[12] 1,3-dimethyl-2-phenyl (**13m′**),[12] 1,2,4-trimethyl (**14b**),[36] 1,2,5-trimethyl (**15b**),[36] 1,3,5-trimethyl (**16b**).[36] 1,3,5-tri-*tert*-butyl (**16g**),[18] 1,3,5-tricyclopropyl (**16j**),[18] 1,2,3,4-tetramethyl (**17b**),[36] 1,2,3,5-tetramethyl (**18b**),[36] 1,2,4,5-tetramethyl (**19b**),[36] 1,2,4,6-tetramethyl (**20b**),[36] 1,2,4,6-tetracyclopropyl (**20j**),[18] 1,2,3,4,5-pentamethyl (**21b**),[36] 1,2,3,4,6-pentamethyl (**22b**),[36] 1,2,3,5,6-pentamethyl (**23b**),[36] hexamethyl (**24b**),[36] heptamethyl (**25b**).[39]

The syntheses of the following cyclopropenylium ions have been reported in our previous papers and the others': tripropyl (**26c'**),[40] tricyclopropyl (**26f'**),[16,41] triphenyl (**26g'**),[42] tris(4-N,N-diisopropylaminophenyl) (**26h'**),[43] tri-2-thienyl (**26i'**),[10,44] diphenyl (**26j'**),[45] 1,2-diphenyl-3-propyl (**26n'**),[40] 1-phenyl-2,3-dipropyl (**26o'**),[6] 1,2-bis-(4-N,N-iisopropylaminophenyl)-3-phenyl (**26p'**),[43] 1-(4-N,N-diisopropylaminophenyl)-2,3-diphenyl (**26r'**),[43] 1,2-diphenyl-3-(2,3-diphenylcycloprop-2-enylidenemethyl) (**27o**),[13] 1-(1-naphthyl)-2,3-diphenyl (**28j'**),[1] 1,2-diphenyl-3-(5-phenylethynyl)naphth-1-yl (**28q'**);[1] and the following bis-2,3-di-phenylcyclopropenylium ions: trimethylene (**29s'**),[17] tetra-methylene (**29t'**),[17] pentamethylene (**29u'**),[17] and hexamethylene (**29v'**).[17]

The following tropylium ions: 1-norbonyl (**1k**), *exo*-2-norbornyl (**1l**), *endo*-2-norbornyl (**1m**), 4-ethylphenyl (**2c**), 4-isopropylphenyl (**2e**), 4-t-butylphenyl (**2g**), 1,3-di-ethyl (**6c**), 1,3-diisopropyl (**6e**), and 1,4-methano-1,2,3,4-tetrahydrobenzo (**12**), were prepared as the perchlorates or tetrafluoroborates by abstraction of the hydride ion from the respective substituted tropilidenes with triphenylmethyl salts.[29]

(1-*Norbornyl*)*tropylium perchlorate* (**1k** · ClO$_4^-$). To 1-phenylnorbornane (42.6 g, 247 mmol), which was prepared following the literature method,[48] was added 0.29 M diazomethane (32 mmol, 110 ml) in heptane in the presence of CuBr (1.7 g, 12 mmol) with stirring over 2.5 hr at 107–116°. During the addition, another 1.7 g portion of CuBr (12 mmol) was added. After removal of the heptane at a reduced pressure, the residual liquid contained 1-phenylnorbornane (98.7%) and (1-norbornyl)tropilidene (1.3%) as determined by GLC (PEG 20M Golay 45 m column). Treatment of the above mixture (40.8 g) with trityl perchlorate (1.14 g, 3.32 mmol) in acetonitrile (23 ml) at 55° for 15 min followed by addition of anhydrous ether (250 ml) afforded brown crystals. Reprecipitation from acetonitrile with ethyl acetate gave **1k** · ClO$_4^-$ (0.645 g, 2.26 mmol) as pale yellow needles in 68% yield, m.p. 140° (decomp); ^{1}H NMR (CF$_3$CO$_2$H) δ 9.1 (6H, m), 2.4–2.8 (1H, m), 1.6–2.3 (10H, m); ^{13}C-NMR (CD$_3$CN) δ 181.4 (s), 154.3 (d), 153.9 (d), 153.8 (d), 59.3 (s), 43.9 (t), 39.0 (t), 38.9 (d), 31.6 (t); IR (KBr) 2970 s, 1600 s, 1525 s, 1487 s, 1450 m, 1379 m, 1305 m, 1252 m, 1080 br vs, 760 s cm^{-1}; UV (10% HCl) λ_{max} 221 (log ϵ 4.55), 309 (3.94) nm. Found: C, 58.82; H, 6.11. Calc for C$_{14}$H$_{17}$ClO$_4$: C, 59.06; H, 6.02%.

(*exo-2-Norbornyl*)*tropylium perchlorate* (**1l** · ClO$_4$). *exo*-2-Phenylnorbornane (49.2 g, 286 mmol), which was prepared by the alkylation of benzene with norbornene,[49] was treated with diazomethane (17 mmol) in heptane as described above. A GLC analysis showed the formation of (*exo*-2-norbornyl)tropilidenes in 2.5% yield. Treatment of the mixture (10.5 g) of *exo*-2-norbonyl)tropilidenes (2.5%; 1.34 mmol) and *exo*-2-phenylnorbornane (97.5%) with trityl perchlorate (0.461 g, 1.34 mmol) in acetonitrile (10 ml) at 50° for 5 min followed by addition of anhydrous ether (130 ml) afforded crude **1l** · ClO$_4^-$ (0.290 g, 1.02 mmol) as brown crystals. Two similar reactions were conducted, and the combined crude products (0.977 g) were reprecipitated from acetonitrile with ethyl acetate to give **1l** · ClO$_4$ (0.645 g; 32.0% based on trityl perchlorate) as colorless powdery crystals, m.p. 97.5–98.5°; ^{1}H NMR (CF$_3$CO$_2$H) δ 9.07 (6H, s), 3.60 (1H, dd, J = 9.0, 7.0 Hz), 1.4–2.9 (10H, m); ^{13}CNMR (CD$_3$CN) δ 181.4 (s), 154.7 (d), 154.0 (d), 153.5 (d), 54.1 (d), 43.6 (d), 41.8 (t), 38.7 (d), 37.2 (t), 31.1 (t), 29.0 (t); IR (KBr) 2960 s, 2880 m, 1605 m, 1530 m, 1489 s, 1443 m, 1090 br vs, 750 m cm^{-1}; UV (10% HCl) λ_{max} 228.5 (log ϵ 4.45), 307 (3.82) nm. Found: C, 59.16; H, 6.06. Calc for C$_{14}$H$_{17}$HIO$_4$: C, 59.06; H, 6.02%.

(*endo-2-Norbornyl*)*tropylium perchlorate* (**1m** · ClO$_4$). The direct ring-expansion of *endo*-2-pehnylnorbornane by the use of diazomethane could not be achieved. Consequently, 3-(*endo*-2-norbornyl) tropilidene was prepared by the thermal isomerization of 7-(*endo*-2-norbornyl)tropilidene, which was obtained by the acetolysis of 4-*endo*-2-norbornyl)-2,5-cyclohexadien-1-ylmethyl *p*-toluenesulfonate following the method of Nelson *et al.*[50] The *p*-toluenesulfonate was derived from 4-(*endo*-2-norbornyl)acetophenone *via* four steps, as follows. 4-(endo-2-norbornyl)benzoic acid was prepared by the oxidation of 4-*endo*-2-norbornyl)acetophenone[49] with iodine in pyridine in 59% yield following the literature method,[51] m.p. 162.7–164.3°; ^{1}H NMR (CDCl$_3$) δ 8.00 (2H, d, J = 8.0 Hz), 7.30 (2H, d, J = 8.0 Hz), 3.20 (1H, m), 1.0–2.8 (10H, br m); IR (KBr) 3200–2200 br s, 1671 vs, 1601 s, 1420 m, 1310 m, 1288 s, 1181 m, 851 m, 765 m, 720 m cm^{-1}. Found: C, 77.73; H, 7.53. Calc for C$_{14}$H$_{16}$O$_2$: C, 77.75; H, 7.46. 4-(*endo-2-Norbornyl*)-*2,5-cyclohexadiene*-1-*carboxylic acid* was prepared by the Birch reduction of the corresponding benzoic acid following the literature method.[52] In a 500-ml four-necked flask equipped with a mechanical stirrer, a dry-ice condenser, and thermometer were placed 4-(*endo*-2-norbornyl) benzoic acid (7.7 g, 36 mmol) and dry THF (58 ml). The flask was chilled in a dry-ice bath, and the NH$_3$ gas was introduced until the total volume reached *ca* 160 ml. With stirring, small pieces of Li wire (0.92 g, 133 mmol) were added at −68 to −75° over 5 min, and stirring continued for 12 min. To the resulting deep blue solution was added with stirring anhydrous ethanol (8.7 ml) over 5 min, and the mixture was stirred for 100 s until the blue color faded. Solid NH$_4$Cl (7.1 g, 133 mmol) was added over 100 s and then NH$_3$ was allowed to evaporate at room temperature. To the yellowish solid residue was added 6M HCl (80 ml) with cooling and then the mixture diluted with water (80 ml). The liberated acid was extracted with ether and recrystallized from hexane to give white crystals (2.2 g, 28%), m.p. 124.2–124.9°; ^{1}H NMR (CCl$_4$) δ 11.0 (1H, br s), 5.83 (4H, s), 3.70 (1H, br d, J = 7 Hz), 2.6–0.6 (12H, br); IR (KBr) 3300–2200 br s, 1690 s, 1415 m, 1305 m, 1280 m, 1230 m, 900 m, 770 m, 690 m cm^{-1}. Found: C, 76.77; H, 8.42. Calc. for C$_{14}$H$_{18}$O$_2$: C, 77.03; H, 8.31%.

4-(*endo-2-Norbornyl*)-*2,5-cyclohexadien*-1-*ylmethyl p-toluenesulfonate.* 4-(*endo*-2-Norbornyl)-2,5-cyclohexadiene-1-carboxylic acid (4.64 g, 21.4 mmol) was reduced with LiAlH$_4$ (1.7 g, 45 mmol) in ether and worked up in the usual manner to give 4-(*endo*-2-norbornyl)-2,5-cyclohexadien-1-ylmethanol (3.8 g, 19 mmol) in 87% yield, b.p. 118–120° at 0.3 mmHg; ^{1}H NMR (CCl$_4$) δ 5.60 (4H, s), 3.40 (1H, s, plus 2H d), 3.0–0.6 (13H, m); IR (neat) 3300 br s, 3000 w, 2910 s, 2850 s, 1620 w, 1441 m, 1300 w, 1020 s, 920 w, 880 m, 835 m, 762 m, 701 s cm^{-1}. The crude alcohol (3.3 g, 16 mmol) was treated with *p*-toluenesulfonyl chloride (3.0 g, 16 mmol) in pyridine (46 ml) at 0° for 40 hr. The usual work-up afforded the crude *p*-toluenesulfonate (3.8 g, 11 mmol) in 65% yield, which was then recrystallized from hexane, m.p. 92.8–94.3°; ^{1}H NMR (CCl$_4$) δ 7.70 (2H, d J = 8.0 Hz), 7.30 (2H, d J = 8.0 Hz), 5.60 (4H, br), 3.80 (2H, d J = 6.4 Hz), 2.41 (3H, s), 3.3–0.6 (13H, br); IR (Kbr) 3030 w, 2950 s, 2860 s, 1595 m, 1355 s, 1190 s, 1095 m, 960 s, 815 s, 785 s, 715 s, 660 s cm^{-1}. Found: C, 70.25; H, 7.27. Calc for C$_{21}$H$_{26}$O$_3$S: C, 70.36; H, 7.31%.

7-(*endo-2-Norbornyl*)*tropilidene.* A solution of the crude *p*-toluenesulfonate (3.28 g, 9.15 mmol) and KH$_2$PO$_4$ (2.88 g, 21.2 mmol) was stirred at 90–99° for 41.5 hr. The reaction mixture was worked up in the usual manner to give the crude tropilidene (1.93 g). Distillation at 0.01 mm Hg afforded a fraction (0.947 g) boiling at 66–91°; ^{1}H NMR (CCl$_4$) δ 6.53 (2H, t, J = 3.0 Hz), 6.10 (2H, br d, J = 8 Hz), 5.10 (2H, m), 2.5–0.6 (12H, br m).

(*endo-2-Norbornyl*)*tropylium perchlorate* (**1m** · ClO$_4^-$). The direct hydride abstraction of 7-(*endo*-2-norbornyl)tropilidene with trityl perchlorate failed. Therefore, this tropilidene was isomerized to 3-(*endo*-2-norbornyl)tropilidene by heating at 175° for 1.5 hr in a sealed tube. The crude product (0.712 g) was treated with trityl perchlorate (1.26 g, 3.67 mmol) in acetonitrile (7.5 ml) at 65° for 10 min. Addition of ethyl acetate and ether gave the crude salt. Reprecipitation from acetonitrile with ether afforded **1m** · ClO$_4^-$ (0.467 g, 1.64 mmol) in 43% yield as brown powdery crystals, m.p. 105.5° (decomp.); ^{1}H NMR (CF$_3$CO$_2$H) δ 9.07 (6H, s), 4.00 (1H, m), 3.0–2.0 (3H, m), 2.0–0.9 (7H, m); ^{13}C NMR (CD$_3$CN) δ 179.4 (s), 155.6 (d), 153.7 (d), 153.2 (d), 53.8 (d), 45.2 (d), 42.0 (t), 38.9 (d), 36.4 (t), 30.2 (t), 23.6 (t); IR (KBr) 3030 w, 2960 s, 2880 s, 1608 m, 1530 m, 1495 s, 1445 s, 1090 br vs, 761 m, 690 m cm^{-1}; UV (10% HCl) λ_{max} 221 nm (log ϵ 4.37). Found: C, 57.93; H, 6.08. Calc for C$_{14}$H$_{17}$ClO$_4$: C, 59.06; H, 6.02%.

(4-*Ethylphenyl*)*tropylium fluoroborate* (**2c** · BF$_4^-$). Following the method of Jutz and Voithenleitner for the preparation of substituted phenyltropylium ions,[35] 7-(4-ethylphenyl)tropilidene was prepared from 4-ethylphenylmagnesium bromide and 7-ethoxytropilidene in 58% yield as a pale yellow oil, b.p. 89.5–95.5° at 0.2 mmHg; ^{1}H NMR (CCl$_4$) δ 7.11 (4H, s), 6.60 (2H, t, J = 3.2 Hz), 6.15 (2H, dm), 5.27 (2H, dd, J = 8.8, 5.4 Hz), 2.60 (3H, q(J = 7.8 Hz) + t(J = 5.4 Hz)), 1.22 (3H, t, J = 7.8 Hz). Hydride abstraction with trityl fluoroborate in acetonitrile at 60° followed by recrystallization from acetonitrile–ethyl acetate (1 : 1) afforded **2c** · BF_4^- in 60% yield as yellow needles, m.p. 117.0–118.5° (decomp.); ^{1}H NMR (CF_3CO_2H) δ 9.46–9.01 (6H, m), 7.96 (2H, d, J = 8.2 Hz), 7.65 (2H, d, J = 8.2 Hz), 2.90 (2H, q, 7.8 Hz), 1.38 (3H, t, J = 7.8 Hz); IR (KBr) 3030 w, 2970 m, 1601 s, 1530 s, 1518 sh, 1481 s, 1417 w, 1375 w, 1265 s, 1194 m, 1060 br vs, 848 m, 760 m cm^{-1}; UV (10% HCl) λ_{max} 276.5 (log ε 4.01), 396 (4.24) nm. Found: C, 63.77; H, 5.23. Calc for $C_{15}H_{15}BF_4$: C, 63.86; H, 5.36%.

(4-*Isopropylphenyl)tropylium fluoroborate* (**2e** · BF_4^-). Similarly, 7-(4-isopropylphenyl)tropilidene was prepared as a pale yellow oil, b.p. 112–118° at 0.3 mmHg; ^{1}H NMR (CCl_4) δ 7.06 (4H, s), 6.58 (2H, t, J = 3.3 Hz), 6.10 (2H, dm), 5.23 (2H, dd, J = 8.8, 5.6 Hz), 2.85 (1H, sept, J = 7.2 Hz), 2.67 (1H, t, J = 5.6 Hz), 1.22 (6H, d, J = 7.2 Hz). Subsequent hydride abstraction and recrystallization yielded **2e** · BF_4^- in 73% yield, m.p. 147.0–148.7° (decomp.); ^{1}H NMR (CF_3CO_2H) δ 9.50–8.96 (6H, m), 7.91 (2H, d, J = 8.6 Hz), 7.57 (2H, d, J = 8.6 Hz), 3.12 (1H, sept, J = 7.3 Hz), 1.37 (6H, d, J = 7.3 Hz); IR (KBr) 3035 w, 2960 m, 1602 s, 1530 s, 1515 sh, 1481 s, 1372 m, 1264 m, 1200 w, 1055 br vs, 860 m, 845 m, 770 s, 740 m cm^{-1}; UV (10% HCl) λ_{max} 275.5 (log ε 4.06), 394 (4.26) nm. Found: C, 64.92; H, 5.73. Calc for $C_{16}H_{17}BF_4$: C, 64.89; H, 5.79%.

(4-*t*-Butylphenyl)tropylium fluoroborate (**2g** · BF_4^-). In the same way as has been reported,[33] 7-(4-t-butyl-phenyl)tropilidene was prepared in 45% yield as a pale yellow oil, b.p. 165–170° at 0.7 mmHg; ^{1}H NMR (CCl_4) δ 7.20 (4H, s), 6.60 (2H, t, J = 3.0 Hz), 6.15 (2H, dm), 5.28 (2H, dd, J = 8.8, 5.4 Hz), 1.32 (9H, s). Hydride abstraction and recrystallization afforded **2g** · BF_4^- in 64% yield as yellow crystals, m.p. 117.8–119.2° (decomp.); ^{1}H NMR (CF_3CO_2H) δ 9.50–8.95 (6H, m), 7.90 (4H, s), 1.46 (9H, s); IR (KBr) 3030 w, 2960 s, 1600 s, 1527 sh, 1515 s, 1481 s, 1371 m, 1262 s, 1055 br vs, 845 m, 767 m, 723 m cm^{-1}; UV (10% HCl) λ_{max} 275.5 (log ε 4.13), 3.94 (4.33) nm (lit. λ_{max} (acetonitrile) 273.5 (4.12), 392.5 (4.32)).[33] Found: C, 65.55; H, 6.00. Calc for $C_{17}H_{19}BF_4$: C, 65.85; H, 6.17%.

1,3-*Diethyltropylium perchlorate* (**6c** · ClO_4^-). About 0.4 M solution (160 ml) of diazomethane (64 mmol) in heptane was added dropwise to a stirred solution of 1,3-diethylbenzene (23.6 g, 176 mmol) in the presence of CuBr (2.0 g, 14 mmol) at 80–100° over 1 hr. During the addition, another 1.5-g portion of CuBr (10.5 mmol) was added. The mixture was filtered and most of the heptane distilled off at a reduced pressure. A GLC analysis (Apiezon L Golay 45 m column) showed that the residual oil contained 4.4% of diethyltropilidene and 95.6% of diethylbenzene. The treatment of the mixture with trityl perchlorate (3.55 g, 10.4 mmol) in acetonitrile followed by addition of anhydrous ether gave the crude salt of **6c** · ClO_4^-. Recrystallization from acetonitrile-ethyl acetate gave **6c** · ClO_4^- (1.3 g, 51% based on trityl perchlorate) as colorless needles, m.p. 113.5–114.0°; ^{1}H NMR (CF_3CO_2H) δ 8.90 (5H, s), 3.36 (4H, q, J = 7.2 Hz), 1.55 (6H, t, J = 7.2 Hz); ^{13}C NMR (CD_3CN) δ 176.4 (s), 155.8 (d), 154.1 (d), 152.0 (d), 36.6 (t), 16.3 (q); IR (KBr) 3040 w, 2990 m, 1615 m, 1535 s, 1475 s, 1439 m, 1380 m, 1260 m, 1090 br vs, 822 s cm^{-1}; λ_{max} (10% HCl) 237 (log ε 4.57), 289 (3.75) nm. Found: C, 53.44; H, 6.30. Calc for $C_{11}H_{15}ClO_4$: C, 53.56; H, 6.13%.

1,3-*Diisopropyltropylium perchlorate* (**6e** · ClO_4^-). In a similar manner to that described for **6c** · ClO_4^-, 1,3-diisopropyltropylium perchlorate (2.47 g) was obtained from 1,3-diisopropylbenzene (42.2 g) as colorless needles, m.p. 149.0–150.0°; ^{1}H NMR (CF_3CO_2H) δ 8.95 (5H, s), 3.66 (2H, sept, J = 7.0 Hz) 1.58 (12H, d, J = 7.0 Hz); ^{13}C NMR (CD_3CN) δ 180.5 (s), 153.8 (d), 152.5 (d), 41.7 (d), 24.0 (q); IR (KBr) 3020 w, 2970 m, 1605 m, 1561 m, 1525 s, 1465 s, 1388 m, 1281 w, 1250 w, 1090 br vs, 880 m, 815 s cm^{-1}; UV (10% HCl) λ_{max} 273 (log ε 4.56), 289.5 (3.81) nm. Found: C, 56.66; H, 7.13, Calc for $C_{13}H_{19}ClO_4$: C, 56.83; H, 6.97%.

1,4-*Methano*-1,2,3,4-*tetrahydrobenzotropylium fluoroborate* (**12** · BF_4^-). About 0.4 M soln (23 ml) of diazomethane (9.2 mmol) was added dropwise to a stirred soln of 1,4-methano-1,2,3,4-tetrahydronaphthalene (1.51 g, 10.5 mmol) in heptane (3 ml) in the presence of CuBr (1.0 g, 6.9 mmol) at 100° over 50 min. The mixture was then filtered and the filtrate evaporated to give a pale brown oil (1.40 g), which was shown to contain the starting material (79%) and the olefinic compound (21%) by ^{1}H NMR. To a stirred solution of this mixture in dichloromethane (3 ml) was added trityl perchlorate (0.500 g, 1.46 mmol). After stirring at room temperature for 30 min, anhydrous ether (30 ml) was added to give the crude salt of **12** · BF_4^- (0.366 g), which was recrystallized from acetonitrile-ethyl acetate to give **12** · BF_4^- (0.21 g, 7.8% based on the tetrahydronaphthalene) as off-white plates, m.p. 156.0–157.5° (decomp.); ^{1}H NMR (CD_3CN) δ 8.92 (5H, s), 4.05 (2H, br s), 2.47–1.93 (4H, m), 1.45–1.11 (2H, m); ^{13}C NMR (CD_3CN) δ 179.1 (s), 153.6 (d), 149.5 (d), 147.3 (d), 51.2 (d), 50.0 (t), 24.5 (t); IR (KBr) 3070 w, 3010 w, 2960 w, 2890 w, 1562 w, 1485 w, 1460 w, 1454 s, 1295 m, 1289 m, 1090 br vs, 981 m, 954 s, 925 m, 888 w, 871 w, 825 w, 819 w, 809 w, 766 s, 760 s cm^{-1}; UV (acetonitrile) λ_{max} 237 (log ε 4.50), 280 (3.53), 298.5 (3.59) nm. Found: C, 56.08; H, 5.08. Calc for $C_{12}H_{13}ClO_4$: C, 56.15; H, 5.10%.

Reduction rates with Cr(II). The rate constants for the following tropylium ions have been reported in our previous papers: **1a**,[3,4] **1b**,[3,5] **1c**,[3,5] **1d**,[7] **1e**,[3,5] **1f**,[7] **1g**,[3,5] **1h**,[7] **1i**,[7] **1j**,[9,12] **1n**,[3,5] **1o**,[5] **2b**,[7] **2j**,[11] **2q**,[7] **2s**,[7] **2t**,[7] **2w**,[7] **2x**,[7] **3e″–3h″**,[11] **3i″**,[7] **5a′**,[9,12] **5k′**,[12] **5l′**,[9,12] **5m′**,[12] **6b**,[9,12] **7b**,[2] **13a′**,[9,12] **13k′**,[12] **13l′**,[9,12] **13m′**,[12] **14b–24b**,[2] and **25b**.[12] The rate constants in 10% aqueous hydrochloric acid for the cyclopropenylium ions: **26g′**,[6] **26l′**,[10] **26n′**,[6] and **26o′**,[6] have been reported in our previous papers. The Cr(II)-ion reduction rates for the tropylium ions: **1q**, **1r**, **1t-1v**, and **1w**, were calculated by the use of the LFER between the relative Zn-reduction rates and the Cr(II)-ion reduction rates for **1a**, **1g**, and **1o**.[8] The second-order rate constants for the Cr(II)-ion reduction of the substituted tropylium ions: **1p**, **2c**, **2e**, **2g**, and **2o**, were determined in 10% aqueous hydrochloric acid at 25.0° by measuring the amounts of the bitropyls formed by the coupling of the tropyl radicals at various reaction-time intervals from 0.2 to 0.9 seconds, according to the flow method previously described.[4] The second-order rate constants are summarized in Table 3. The logarithms of the Cr(II)-ion reduction rate constants, in 10% aqueous hydrochloric acid at 25.0°, for the 57 tropylium and the four cyclopropenylium ions are tabulated in Tables 1 and 2, respectively.

Charge-transfer spectra. The values of $\nu_{CT\,max}$ for the following tropylium ions have been reported in our previous papers and that of Dauben and Wilson:[22] **1a**,[2,4,25] **1b**[2,4] **1c**,[3,5] **1d**,[7] **1e**,[3,5] **1f**,[7] **1g**,[3,5,25] **1h**,[7] **1i**,[7] **1j**,[12] **1n**,[3,5] **1o**,[3,5] **1q**,[8,22] **1r**,[8] **1t**[8,22] **1u**,[8] **1v**,[8] **1w**,[8,22] **1x**,[22] **2q**,[7] **2s**,[7] **2t**,[7] **2w**,[7] **2x**,[7] **3i″**,[7] **5a′**,[12] **5k′-5m′**,[12] **6b**,[12] **6g**,[18] **6j**,[18] **7b**,[2] **7g**,[18] **7j**,[18] **13a′**,[12] **13k′–13m′**,[12] **14b–16b**,[2] **16g**,[18] **16j**,[18] **17b**,[2] **20b**,[2] **20j**,[18] **21b–24b**,[2] and **25b**.[2] The charge-transfer frequencies of the following tropylium ions were determined with pyrene in 1,2-dichloroethane by the method previously described:[12,36] **1k–1m**, **2b**, **2c**, **2e**, **2g**, **2j**, **2o**, **3e″–3h″**, **6c**, and **6e**. The concentrations of the donor (pyrene) and of the acceptor (the substituted tropylium ions) were 0.1 M and *ca* 1×10^{-3} M, respectively. The charge-transfer frequencies for the 69 tropylium ions are summarized in Table 1.

Reduction potentials. The values of CV peak potentials, vs sce, in dichloromethane for the following tropylium ions have been reported in our previous papers: **1a**,[2] **1b**,[2] **4a″–4d″**,[14] **4g″**,[14] **4j″**,[14] **5a′**,[2] **6b**,[2] **6g**,[18] **6j**,[18] **7b**,[2] **7g**,[18] **7j**,[18] **8**,[15] **9**,[15] **13a′**,[2] **14b–16b**[2] **16g**.[18] **16j**,[18] **17b–20b**,[2] **20j**,[18] **21b–25b**. The values for the cyclopropenylium ions: **26g′**,[43] **26h′**,[43] **26i**,[10] **26p′**,[43] **26r′**,[43] **29s′–29u′**,[17] and **29v′**[17]; have been reported in the previous papers. The polarographic half-wave potentials, vs Ag/AgCl, in acetonitrile for the tropylium ions: **1a–1c**,[3,5] **1e**,[3,5] **1g**,[3,5] **1n**,[3,5] and **1o**;[3,5] and those potentials, vs sce, in acetonitrile for the tropylium ions: **1a**,[22] **1t**,[22] **1w**,[22] **1x**,[22] and **11**;[46] have been reported in the previous papers. The reduction potentials for the tropylium ions: **1a**, **1g**, **1j–1m**, **6e**, and **16b**; and the cyclopropenylium ions: **26c′**, **26f′**, **26g′**, **26j′**, **26n′**, **26o′**, **27o**, **28j′**, and **28q′**; were measured in acetonitrile by the use of cyclic voltammetry as has been previously reported.[2,14,17] The concentrations of the supporting electrolyte (tetrabutylammonium perchlorate) and the cation were 0.1 M and 1×10^{-3} M, respectively, and the reference electrode was Ag/0.01 M $AgNO_3$ with 0.1 M tetrabutylammonium perchlorate in acetonitrile. The value of the cathodic peak potential was determined from the voltammogram obtained at the scan rate of 0.1 V s^{-1}. Similarly, the CV peak potentials (V), vs sce, were measured in dichloromethane for the tropylium ions:

Table 3. Rates of Cr(II)-ion reduction of various substituted tropylium ions in 10% hydrochloric acid

Cation[a]	$10^3[R^+]$ M	$10^3[Cr(II)]$ M	k_2/ l mol^{-1} s^{-1}	k_2 average/ l mol^{-1} s^{-1}
1p	3.00	8.10	306	301 ± 7
	2.00	7.20	308	
	2.00	7.00	290	
2c	2.68	8.73	80.6	83 ± 2
	2.72	7.85	83.4	
	3.04	6.50	85.9	
2e	2.18	5.72	106.8	102 ± 5
	2.69	6.49	95.6	
	2.49	6.10	109.3	
	2.32	7.80	96.9	
2g	2.24	5.91	127.4	124 ± 3
	2.18	7.11	125.3	
	2.14	5.70	120.2	
2o	0.503	2.55	175	(175)

[a] Perchlorate.

1j–**1m**, **1o**, **1p**, **2b**, **2j**, **3e''**–**3h''**, **6c**, **6e**, **6g**, **10**, **11**, and **12**; and for the cyclopropenylium ion **26i'**. These reduction potentials are summarized in Tables 1 and 2 for the 57 tropylium and 17 cyclopropenylium ions, respectively.

p-K_{R^+} values. The pK_{R^+} values in 23% aqueous ethanol for the following cations have been reported in the previous papers: **1a**,[3,5] **1g**,[3,5] **1n**,[3,5] **1o**,[3,5] **2b**,[7] **2j**,[11] **2q**,[7] **2s**,[7] **2t**,[7] **2w**,[7] **3e''**–**3h''**,[11] **3i''**,[7] **26g'**,[6,45] **26j'**,[45] **26h'**,[43] **26l'**,[10] **26n'**,[6,40] **26o'**,[6] **26p'**,[43] **26r'**,[43] and **27o**.[13] The pK_{R^+} values in 50% aqueous acetonitrile for the following cations have been reported in the previous papers: **1o**,[33] **2b**,[33] **2s**,[33] **2t**,[33] **2w**,[33] **2x**,[33] **3i''**,[33] **6g**,[18] **6j**,[18] **7g**,[18] **7j**,[18] **8**,[15] **9**,[15] **16g**,[18] **16j**,[18] **20j**,[18] **26c'**,[42] **26f'**,[16,41] **26i'**,[44] **29s'**–**29u'**,[17] and **29v'**.[17] The pK_{R^+} values in 50% aqueous ethanol for the following tropylium ions have been reported in the previous papers: **1a**,[14] **1p**,[14] **4a''**–**4d''**,[14] **4g''**,[14] **4j''**,[14] **8**,[15] and **9**[15] The pK_{R^+} values in water for **1a**[23,47] and for the cyclopropenylium ions: **26g'**[45] and **26j'**,[45] have been reported in the previous papers. The pK_{R^+} values for the following cations were determined at 25.0°, according to the spectrophotometrical method originally reported by Breslow and Chang,[47,17] and the pH values were read on a Horiba H pH meter calibrated with standard buffers before use: (in 23% aqueous ethanol) **1p**, **2c**, **2e**, **2g**, and **2o**; (in 50% aqueous acetonitrile) **1a**, **1b**, **1g**, **1j**–**1m**, **5a'**, **13a'**, **17b**, **18b**, **21b**, **24b**, **25b**, **26g'**, **26n'**, **26o'**, **27o**, **28j'**, and **28q'**; (in 50% aqueous ethanol) **1o**, **10**, **11**, and **12**. These pK_{R^+} values are tabulated in Tables 1 and 2 for the 61 tropylium and 17 cyclopropenylium ions, respectively.

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