The One-electron Reduction of Carbonium Ions. Part 13.[1] The Conformational Effects of Cyclopropyl, Isopropyl, and Phenyl Substituents Flanked with Methyl Groups on the Reduction Rate of the Tropylium Ion with the Chromous Ion

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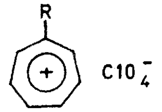
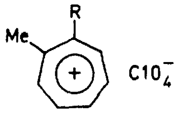
Methyl-, phenyl-, cyclopropyl-, and isopropyl-tropylium ions and the respective tropylium ions with flanking methyl groups have been synthesized, and the second-order rate constants, k_2, for the reduction of the tropylium ions with chromous ion have been determined in 10% hydrochloric acid at 25.0 °C. A linear free-energy relationship is observed when log k_2 values for phenyl-, H-, and methyl-tropylium ions flanked with one [(2e), (1b), and (2b)] and also two methyl groups [(3e), (3a), and (3b)] are plotted against those for the corresponding ions without flanking methyls [(1e), (1a), and (1b)]. However, the log k_2 values for cyclopropyl- or isopropyl-tropylium ions with flanking methyls [(2c), (3c), and (3d)] significantly deviate upward from the linear correlation lines, reflecting the loss of stabilization caused by restriction on the conformation of the isopropyl and cyclopropyl groups. A linear correlation has also been found between the log k_2 values and the charge-transfer energies with pyrene for all the tropylium ions [(1a)—(3e)], indicating that the reducibility of the tropylium ions reflects the electron affinity inherent to the respective ions, irrespective of the presence or absence of the flanking methyl groups.

It is generally accepted that the most favourable conformation of the phenyl group for stabilization of the adjacent carbenium ion is the coplanar arrangement[2] whilst it is the bisected arrangement for the cyclopropyl group.[3] In a study of the solvolysis of substituted t-cumyl chlorides, Brown and Cleveland examined such conformational effects of these substituents by introducing the methyl groups flanking the substituent.[4]

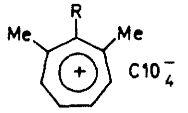
Previously we applied this method to a kinetic study of the one-electron reduction of cyclopropyltropylium ions [(1c), (2c), and (3c)] with chromous ion,[5] and demonstrated the importance of the bisected conformation in stabilizing the tropylium ion, in which the cyclopropyl group is directly attached to an sp^2 carbon. Here, we report both a full account of the above study and also the results of an extension of the same method to test the conformational effects of phenyl and isopropyl substituents on the stability of the tropylium ions as measured by the rates of the one-electron reduction of (1e), (2e), (3e), (1d), (2d), and (3d) with the chromous ion.



(1a),* (1b), (1c),* (1d), (1e)*



(2a)[=(1b)], (2b), (2c), (2d), (2e)



(3a), (3b), (3c), (3d), (3e)

a; R = H b; R = Me c; R = cyclo-Pr d; R = Pr^i e; R = Ph

* Fluoroborate

In our previous work[6] we have examined the rates of the one-electron reduction of various representative substituted tropylium ions with chromous ion[6b,c] or zinc[6d] and have established that there exist linear free-energy relations between the rates of the one-electron reduction and various properties of these ions, such as pK_{R^+} values, polarographic half-wave potentials, and the transition energies of the charge-transfer band with pyrene as a standard electron donor. The results have been interpreted to indicate that the reduction rate depends mainly upon the stability of the cation and is not much affected by the stability of the produced radical. Thus the one-electron reducibility has been shown to be a useful measure for the electron affinity of stable cations in solution.[6,7]

RESULTS AND DISCUSSION

Synthesis.—The substituted tropylium ions were prepared by abstracting the hydride ion from the corresponding substituted tropilidenes with trityl perchlorate.[8] Cyclopropylcyclohepta-1,3,5-triene[9] and di- and trimethylcyclohepta-1,3,5-trienes[10] were prepared by the known methods. Phenyl-, cyclopropyl-, and isopropylcyclohepta-1,3,5-trienes containing one or two flanking methyl groups were prepared by the dehydration of corresponding cyclohepta-2,6-dienols.[11,12] The electronic spectral data and charge-transfer $\nu_{max.}$ values (with pyrene) for the perchlorates or fluoroborates are given in Table 1.

Rate Measurements.—The rates of the Cr^{II} reduction of the tropylium ions were determined in 10% hydrochloric acid at 25.0 °C by measuring the amount of substituted bitropyls, which are formed by the dimerization of the substituted tropyl radicals, following the method previously described.[6a] The second-order rate constants are summarized in Table 2.

Evaluation of the Effect of Flanking Methyl Groups on the Conformation of Substituents.—The substituent effects on the Cr^{II} reduction rates for the series (1a—e) are considered to be the standard effects of the substituents in the absence of excessive conformational restrictions.

TABLE 1

Electronic spectral data and charge-transfer $\nu_{\text{max.}}$ values (with pyrene) of substituted tropylium perchlorates or fluoroborates

Cation [a]	U.v. $\lambda_{\text{max.}}$ (10% HCl)/nm (ε)	10^{-4} × C.T.-$\nu_{\text{max.}}$/cm^{-1} [c]
(1a) [b]	218.0 (50 100), 274.0 (4 070), 281 (sh)	1.81
(1b)	227.0 (50 600), 287.0 (4 760), 300 (sh)	1.88
(1c) [b]	248.0 (26 000), 330.0 (12 800)	1.90
(1d)	228.0 (33 100), 294.0 (5 030), 302 (sh)	1.89
(1e) [b]	226.0 (37 700), 270.5 (14 800), 368 (16 200)	1.79
(2b)	232.0 (46 100), 296.5 (5 160),	1.98
(2c)	252.0 (26 600), 333.0 (7 960)	1.96
(2d)	234.5 (37 900), 282 (sh), 300.0 (5 350), 310 (sh)	1.99
(2e)	229.5 (43 300), 280.0 (8 700), 354 (5 050)	1.89
(3a)	233.5 (48 300), 288.5 (6 150), 295 (sh)	1.94
(3b)	240.0 (54 100), 292.5 (5 660), 300 (sh)	2.01
(3c)	243.0 (40 700), 298.0 (4 400),	1.99
(3d)	245.0 (37 900), 297.0 (4 840)	2.00
(3e)	238.5 (56 700), 288.5 (6 200), 328 (1 250)	1.99

[a] Perchlorate. [b] Fluoroborate. [c] Pyrene was used as an electron donor in 1,2-dichloroethane. Determined by drawing a smooth curve: accurate to ±0.02 × 10^4 cm^{-1}.

TABLE 2

Rates of Cr$^{\text{II}}$ reduction of various substituted tropylium ions in 10% hydrochloric acid at 25.0 °C

	Initial concentration			
Cation [a]	10^2[R$^+$]/ M	10^2[Cr$^{\text{II}}$]/ M	k_2/ l mol^{-1} s^{-1}	$k_{2\,\text{average}}$/ l mol^{-1} s^{-1}
(1a) [b]	2.05	3.75	73.8	74.0 [c]
	1.80	3.05	74.1	
(1b)	1.99	4.13	11.1	11.1 [c]
	2.60	5.39	11.0	
	2.61	5.20	11.3	
(1c) [b]	1.18	3.09	4.63	4.62
	1.19	2.95	4.54	
	1.31	2.99	4.70	
(1d)	2.23	5.26	8.18	8.22 [c]
	2.46	5.31	8.26	
(1e) [b]	0.426	0.857	140	144 [c]
	0.462	0.928	147	
(2b)	0.294	1.10	0.897	0.908
	0.282	1.16	0.917	
(2c)	0.280	0.851	1.02	0.929
	0.275	0.850	0.852	
	0.276	0.915	0.914	
(2d)	0.374	1.46	1.02	1.01
	0.380	1.59	1.00	
(2e)	0.486	1.64	20.7	22.6
	0.503	1.77	24.4	
(3a)	0.334	1.22	1.34	1.36 [d]
	0.354	0.915	1.38	
(3b)	0.271	0.866	0.150	0.148
	0.305	0.995	0.146	
(3c)	0.267	0.829	0.339	0.335
	0.253	0.829	0.335	
	0.259	1.10	0.332	
(3d)	0.321	0.836	0.355	0.382
	0.321	0.785	0.408	
(3e)	0.303	1.09	2.46	2.43
	0.305	0.833	2.50	
	0.277	1.12	2.32	

[a] Perchlorate. [b] Fluoroborate. [c] Data taken from ref. 6*b*. [d] Previous value was too large due to an error in u.v. measurement; see ref. 5.

Meanwhile it appears reasonable to assume that unless the conformation of the substituent is perturbed by the flanking methyl groups in the systems (2) or (3), the linear free-energy relationship would hold for (1)—(3). Furthermore, it is possible to assume that the electron-donating ability of a methyl substituent would not be sterically perturbed by the flanking methyl groups because of its small steric requirement.* With these assumptions, if we find a deviation from the straight lines which pass through the points for R = H and R = Me in the plot of log k_2 values for the system (2) or (3) against those for (1), the deviation would be ascribed to the change in the stabilizing ability of the substituent toward the tropylium ion, most probably caused by the change in the conformation.† Such plots (Figure 1) for the phenyl substituent give straight lines for both systems (2) and (3), whereas those for the cyclopropyl and isopropyl substituents deviate upward. Such upward deviations are likely to be ascribed to the destabilization of the tropylium ions caused by the conformational change of the substituents.

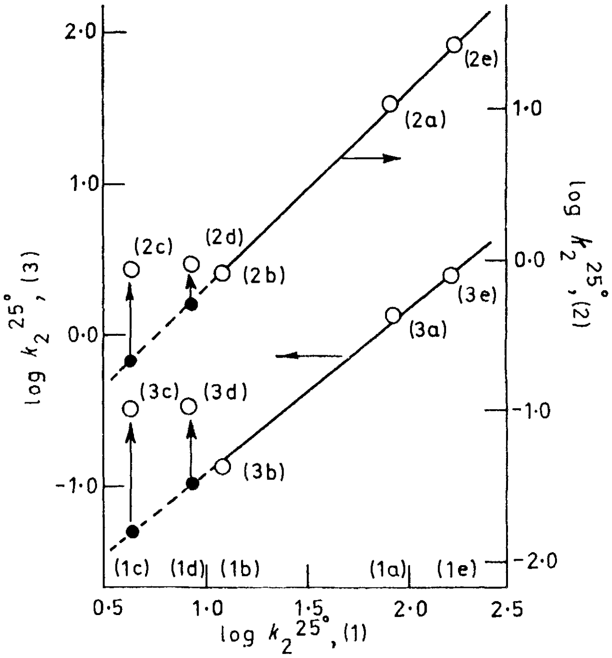


FIGURE 1 Correlation of log k_2 values for (2) or (3) with those for (1) for the Cr$^{\text{II}}$ reduction in 10% HCl at 25.0 °C

In the above interpretation it was assumed that for R = H, Me, or Ph the introduction of flanking methyl groups would not alter the conformational situation and

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* The first-order rate constant for the solvolysis of 3,4,5-trimethyl-t-cumyl chloride [1-methyl-1-(3,4,5-trimethylphenyl)-ethyl chloride] in 90% acetone at 25.0 °C is 1 230 × 10^{-5} s^{-1}, which is in good agreement with the value (1 270 × 10^{-5} s^{-1}) predicted from the $\rho^+\sigma^+$-relation.[13] In contrast, the methyl substituent effect on the rates of the C$^{\text{II}}$-reduction of (1b), (2b), and (3b) is not exactly additive; however, this cannot be ascribed to steric perturbation.

† The Hammett-type plot by using σ or σ^+ is not appropriate because the point for the phenyl substituent cannot be accommodated even in system (1).

that the straight-line correlations might be drawn for these substituents.

Alternatively the data can be assessed by evaluating the variation in the reactivity caused by successive introduction of methyl groups to (1a—e). This can be done by calculating the ratios $k_2^{(1)}k/_2^{(0)}$ and $k_2^{(2)}/k_2^{(0)}$ for each substituent, including the case of R = H, where $k_2^{(0)}$, $k_2^{(1)}$, and $k_2^{(2)}$ stand for the rate constants of the ions containing no, one, and two flanking methyls, respectively.* The ratios are summarized in Table 3.

TABLE 3

The $k_2^{(1)}/k_2^{(0)}$ and $k_2^{(2)}/k_2^{(0)}$ values

	R				
	H	Me	cyclo-Pr	Pr^i	Ph
$k_2^{(1)}/k_2^{(0)}$	0.15	0.082	0.20	0.12	0.16
$k_2^{(2)}/k_2^{(0)}$	0.018	0.013	0.073	0.046	0.017

A relatively large ratio in the series of $k_2^{(1)}/k_2^{(0)}$ or $k_2^{(2)}/k_2^{(0)}$ values means an enhanced rate due to the decreased stabilizing ability of the substituent, R, toward the tropylium ion. The $k_2^{(2)}/k_2^{(0)}$ values for R = H, Me, and Ph are essentially the same, whereas the values for R = cyclo-Pr and Pr^i are significantly larger than the above values. The result indicates the enhanced rates in the latter cases, in accord with the conclusion which was obtained by the use of the plot in Figure 1.

On the other hand, in the $k_2^{(1)}/k_2^{(0)}$ series it appears difficult to point out definitely the effect of the introduction of one flanking methyl. Since the $k_2^{(1)}/k_2^{(0)}$ values for R = H, Pr^i, and Ph may be regarded as almost identical, the relatively high $k_2^{(1)}/k_2^{(0)}$ value for R = cyclo-Pr (0.20) is likely to be interpreted in terms of the enhanced rate of (2c). However, the $k_2^{(1)}/k_2^{(0)}$ value for R = Pr^i (0.12) is smaller than those for R = H or Ph, no indication of the rate enhancement being detected, although a slight rate enhancement was suggested for (2d) in the plot in Figure 1. Thus the combination of the two methods of data assessment leads to the conclusion that the rate is unambiguously enhanced in (2c), (3c), and (3d).

The $k_2^{(1)}/k_2^{(0)}$ value for (2b) is anomalously small in comparison with the other $k_2^{(1)}/k_2^{(0)}$ values. Moreover, the rate of (2b) is considerably smaller than that of (3a). This suggests the possibility that the vicinal methyl groups of (2b) interact with each other in such a manner either to stabilize the ion (2b) or to destabilize the transition state, although it is difficult to conclude at the present stage as to which factor is more important.

It might be argued that the crowding of the substituents might destabilize the tropylium ion owing to possible deformation of the planar structure. However, the phenyl substituent effects in (2e) and (3e) are unaltered by the crowding as evidenced by the linear relations in Figure 1 (*vide infra*). Therefore, it appears most plausible that the deviations of the cyclopropyl and isopropyl substituents are caused by their conformational changes.

Conformational Effect of the Cyclopropyl Substituent.—Abundant data have been accumulated to indicate that the conjugative electron supply from the cyclopropyl group to an adjacent electron-deficient centre decreases as it is made more difficult for the cyclopropyl group to attain the bisected conformation.[3] That the cyclopropyl group attached to the benzene ring and flanked by methyl groups cannot take the bisected conformation has been demonstrated in the solvolysis of the t-cumyl system[4] and, more directly, in the ^1H n.m.r. of the substituted trityl cation (4).[14]

In the Cr^{II} reduction the rate ratio for the series (1a), (1b), and (1c) is 1 : 1/6.7 : 1/16, (1c) being the slowest. This is in accord with the stronger electron-donating ability of the cyclopropyl group compared with the methyl group.[15] When the cyclopropyl substituent is flanked by one methyl group as in (2c), the rate ratio for (2a), (2b), and (2c) becomes 1 : 1/12 : 1/12, (2b) and (2c) being of similar reactivity. The introduction of the two methyl groups yields the ratio 1 : 1/9.2 : 1/4.1 for (3a), (3b), and (3c), (3c) being more reactive than (3b). The decreased electron-donating ability of the cyclopropyl substituent in (2c) and (3c) as reflected in their one-electron reducibilities is qualitatively consistent with the results obtained in the solvolysis of the t-cumyl system,[4] where the *p*-cyclopropyl substituent was flanked by one or two methyl groups. The present results are most reasonably understood in terms of the conformational change of the cyclopropyl substituent from the bisected to the parallel arrangement by the introduction of the flanking methyl groups.

Conformational Effect of the Isopropyl Substituent.—The conformation of the isopropyl group directly attached to a benzene ring has been shown to be controlled by the introduction of methyl groups in the positions *ortho* to the isopropyl group. Mannschreck and Ernst concluded, on the basis of nonequivalence of the 2- and 6-methyl signals in the ^1H n.m.r. at −60 °C,[16] that the preferred isopropyl conformation in 2,4,6-trimethylisopropylbenzene is the one with the tertiary C–H bond lying in the plane of the phenyl ring. The conformational effect of the isopropyl group in stabilizing the electron deficient centre has been tested in the solvolysis of *p*-isopropyl-t-cumyl chlorides † with no, one, and two methyl groups flanking the *para*-substituent.[4] It has been found then that the stabilizing influence of the isopropyl substituent toward the positive charge delocalized to the *para*-position progressively decreases as the number of the flanking methyl group is increased from zero to one to two. The increasing steric interactions were supposed to place the isopropyl group in a conformation in which the carbon–hydrogen hyperconjugation would be less likely.[4]

These results led the present authors to the anticipation that the conformation of the isopropyl group attached to the tropylium ring in (3d) would also be affected by the flanking methyl groups in a manner similar to what

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* We thank the referees for the suggestion of the alternative treatment of the data.

† 1-(4-Isopropylphenyl)-1-methylethyl chloride.

had been observed in the benzene derivatives. Thus, the rates of Cr^{II} reduction of (2d) and (3d) were determined and then logarithmically plotted against that of (1d) in Figure 1. Both the points deviate from the straight lines, and the deviation of (3d) is greater than that of (2d). Although it is difficult to assess the amount of the acceleration for (2d) for the reasons previously mentioned in this paper, the acceleration for (3d) is obvious and the factor of the acceleration is calculated to be 3.7 from Figure 1. The results are qualitatively similar to the effects of flanking methyl groups in the solvolysis of the *p*-isopropyl-t-cumyl chloride,[4] suggesting that the decrease in the electron donating ability of the isopropyl group in the two systems, tropylium and t-cumyl, stems from the same origin.*

Conformational Effect of the Phenyl Substituent.—A phenyl group exhibits its maximum electronic contribution when it attains a coplanar arrangement with the electron-deficient centre.[2,17,18] Previously we reported that the phenyltropylium ion is reduced by Cr^{II} ion 1.9 times as fast as the unsubstituted tropylium ion,[6b] a result which was interpreted to show that the phenyl substituent attached to the tropylium ring acts as an electron-withdrawing group, since the steric repulsive interaction of the two *ortho* hydrogens of the phenyl ring with the 2- and 6-hydrogens of the tropylium ring prevent the two rings from assuming a coplanar arrangement.[6c] The electron-withdrawing character of the phenyl group attached to the tropylium ring was also recognized in the increased electrophilic character of polyphenyltropylium ions.[19,20] Although the phenyl group attached to a tropylium ring is actually electron-withdrawing, if there remained some conjugative interaction between the two rings in (1c), the introduction of the flanking methyl group was thought to decrease the conjugative electron supply from the phenyl substituent to the tropylium ring. Thus, the perchlorates (2e) and (3e) were subjected to Cr^{II} reduction. The relative rates (1e)/(1a), (2e)/(2a), and (3e)/(3a) are, however, 1.9, 2.0, and 1.9, respectively, and are essentially constant. The logarithmic plot of the rate constants for the systems (2) and (3) against those for the system (1) affords a good linear correlation for R = Me, H, or Ph, indicating that the electronic contribution of the phenyl substituent is not altered by the introduction of the flanking methyl groups. The results are most reasonably explained by assuming that the conjugative interaction is little between the two rings even when the methyl groups are absent.

Schuster, Vedrilla, and Polansky carried out extended HMO calculation on the phenyltropylium cation and concluded that the delocalization of the positive charge to the phenyl ring when the interplanar angle is 0, 45, or 90° is 6.9, 4.0, or 1.8%, respectively.[21] Presumably such a small amount of delocalization of the positive charge to the phenyl ring in (1e), where the interplanar angle is estimated to be *ca.* 45°,[18,21] is overcome by the inductive electron-withdrawing character of the phenyl ring, the phenyl substituent being a net electron-withdrawing group. Although the interplanar angle is believed to change from *ca.* 45° in (1e) to nearly 90° in (3e), the difference in the amount of charge delocalization to the phenyl ring between (1e) and (3e) appears to be too small to be reflected in the one-electron reducibility.

The present results are in contrast with the effect of the *p*-phenyl substituent in the solvolysis of t-cumyl chlorides, in which it works as an electron-donating group, the conjugation between the two benzene rings being effectively weakened by the introduction of flanking methyl groups.

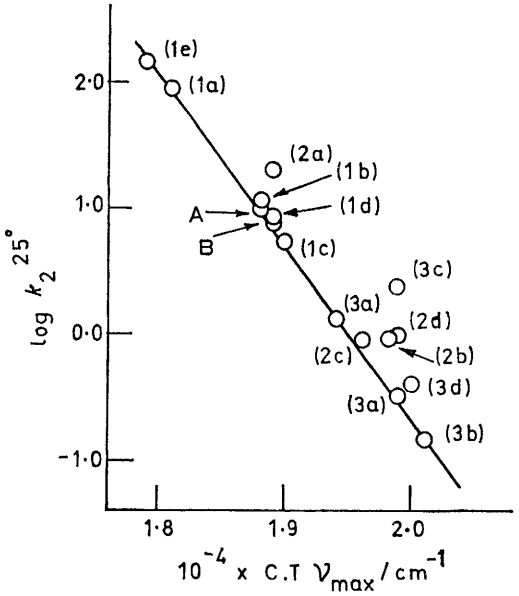

FIGURE 2 Correlation of log k_2 values with charge-transfer energy (C.T.-$\nu_{max.}$) with pyrene; A Et·$C_7H_6^+$; B Bu^t·$C_7H_6^+$

Correlation of the One-electron Reducibility with Charge-transfer Band Energy.—The one-electron reducibilities of substituted tropylium ions with Cr^{II} or zinc have been found to correlate with the charge-transfer band energies of the tropylium ions with pyrene as the donor.[6b–d] Since the charge-transfer band energy is linearly correlated with the electron affinity of the acceptor, the one-electron reducibility is the linear function of the electron affinity of the tropylium ion. The plot of log k_2 values against charge-transfer $\nu_{max.}$ values both in the present and previous works gives a linear correlation, but phenyl- and isopropyl-tropylium ions possessing one or two flanking methyl groups show slight upward deviations (Figure 2). The reason for the deviations does not appear to be straightforward; however, it is plausible that the steric crowding of the substituents enlarge the distance between the donor and the acceptor of the

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* The splitting of the 2- and 7-methyl signals in the ^{1}H n.m.r. of (3d) was not accomplished in CD_2Cl_2 at −75 °C, only broadening of the signal being observed Therefore, we cannot exclude the possibility that other factors are responsible for the rate acceleration. However, an examination of molecular models provides supporting evidence for the view that the more stable conformation of (3d) is the one with the tertiary C–H bond lying in the plane of the tropylium ring.

charge-transfer complex, thus resulting in the increase in the charge-transfer energy shown in Figure 2.

EXPERIMENTAL

M.p.s and b.p.s are uncorrected. Elemental analyses were performed by the Microanalytical Center, Kyoto University, Kyoto. U.v. and n.m.r. spectra were taken on Hitachi model 200-10 and Hitachi R-24 (60 MHz) spectrometers, respectively.

Materials.—2-Methylcyclohepta-2,6-dienone was prepared following the method of Hine and Childs by the acid-catalysed isomerization of 2-methylcyclohepta-3,5-dienone.[22] 2,7-Dimethylcyclohepta-2,6-dienone was prepared following the method reported previously.[11] 1,2-Dimethyltropylium perchlorate (2b) was prepared following the procedure of Müller *et al.*, m.p. 106.0—107.5 °C (lit.,[10] 97—99 °C). Acetonitrile and ethyl acetate were refluxed over phosphorus pentaoxide and distilled. Cyclopropyltropylium fluoroborate (1c) was prepared following the procedure of Bauld *et al.*,[9] m.p. 58.2—60.0 °C. Trityl perchlorate was prepared following the method of Dauben.[8]

1,3-*Dimethyltropylium Perchlorate* (3a).—*m*-Xylene was subjected to a ring-expansion reaction with diazomethane following the procedure of Müller.[10] A mixture of the dimethylcyclohepta-1,3,5-trienes (b.p. 60.0—72.0 °C at 20 mmHg; 1.30 g, 10.8 mmol), whose principal component was 2,4-dimethylcyclohepta-1,3,5-triene, was treated with trityl perchlorate (4.09 g, 11.9 mmol) in acetonitrile to give 0.83 g of 1,3-dimethyltropylium perchlorate (3a) as pale yellow crystals, m.p. 78.0—80.0 °C; δ(CF_3CO_2H) 3.1 (6 H, s) and 8.9 (5 H, m) (Found: C, 49.4; H, 5.3. $C_9H_{11}ClO_4$ requires C, 49.43; H, 5.07%).

1,2,3-*Trimethyltropylium Perchlorate* (3b).—1,2,3-Trimethylbenzene was subjected to a ring-expansion reaction with diazomethane in a manner similar to that described by Müller.[10] A mixture of the trimethylcyclohepta-1,3,5-trienes (b.p. 51.3—53.5 °C at 3.2 mmHg; 1.34 g, 10.0 mmol), whose principal component was 2,3,4-trimethylcyclohepta-1,3,5-triene, was treated with trityl perchlorate (4.11 g, 12.0 mmol) in acetonitrile to give 1.59 g of 1,2,3-trimethyltropylium perchlorate (3b), m.p. 167.5—168.3 °C; δ(CF_3CO_2H) 2.9 (3 H, s), 3.1 (6 H, s), and 8.8 (4 H, m) (Found: C, 51.7; H, 5.6. $C_{10}H_{13}ClO_4$ requires C, 51.62; H, 5.63%).

1-*Cyclopropyl*-2-*methyltropylium Perchlorate* (2c).—A mixture of 2-methylcyclohepta-2,6-dienone, 2-methylcyclohepta-2,4-dienone, and 7-methylcyclohepta-2,4-dienone (5 : 4 : 1) was prepared following the procedure of Hine.[22] The mixture of the dienones (3.05 g, 25 mmol) was treated with cyclopropyl-lithium in diethyl ether to give a mixture consisting of 1-cyclopropyl-2-methylcyclohepta-2,6-dienol, 1-cyclopropyl-2-methylcyclohepta-2,4-dienol, and 1-cyclopropyl-7-methylcyclohepta-2,4-dienol (4.03 g, 98%). The mixture of the dienols (4.03 g, 24.5 mmol) was heated with boric acid (1.52 g, 24.5 mmol) at 200 °C and 95 mmHg to give a distillate,[11,12] which on extraction afforded a mixture of 3-cyclopropyl-2-methylcyclohepta-1,3,5-triene and its isomers (2.80 g, 78.4%). The mixture of the di-substituted cyclohepta-1,3,5-trienes (2.80 g, 19.2 mmol) was treated with trityl perchlorate (6.58 g, 19.2 mmol) to give 1-cyclopropyl-2-methyltropylium perchlorate (2c) (3.86 g, 82%), m.p. 90.6—91.6 °C; δ(CF_3CO_2H) 1.4 (2 H, m), 1.8 (2 H, m), 2.6 (1 H, m), 3.2 (3 H, s), and 8.8 (5 H, m) (Found: C, 53.8; H, 5.3. $C_{11}H_{13}ClO_4$ requires C, 54.00; H, 5.35%).

2-*Cyclopropyl*-1,3-*dimethyltropylium Perchlorate* (3c).—3-Cyclopropyl-2,4-dimethylcyclohepta-1,3,5-triene (3.20 g, 20.0 mmol), which was prepared in the manner described previously,[11] was treated with trityl perchlorate (7.19 g, 21.0 mmol) in acetonitrile to give 2-cyclopropyl-1,3-dimethyltropylium perchlorate (3c) (4.09 g, 79%), m.p. 146.0—146.4 °C; δ(CF_3CO_2H) 0.7 (2 H, m), 1.7 (2 H, m), 2.5 (1 H, m), 3.2 (6 H, s), and 8.7 (4 H, m) (Found: C, 55.9; H, 5.9. $C_{12}H_{15}ClO_4$ requires C, 55.71; H, 5.84%).

1-*Isopropyl*-2-*methyltropylium Perchlorate* (2d).—2-Methylcyclohepta-2,4-dienone (4.4 g, 36 mmol) was dissolved in pentane (25 ml) and cooled to −20 °C. To this during 32 min was added, at the same temperature and with stirring under nitrogen a pentane solution of isopropyl-lithium (39 mmol); the mixture was then refluxed for 100 min. Work-up of the reaction mixture afforded 1-isopropyl-2-methyl-2,4-cycloheptadienol (4.8 g, 29 mmol) as a pale yellow oil in 80% yield. The crude dienol was mixed with 1.79 g of boric acid and heated at 30 mmHg to 150 °C in an oil-bath. The temperature of the oil-bath was gradually raised to 195 °C during 30 min. The distillate obtained in this manner afforded 3-isopropyl-4-methylcyclohepta-1,3,5-triene (0.939 g, 7.0 mmol) in 24.2% yield on distillation with a spinning band column, b.p. 72.0—80.0 °C at 10 mmHg; δ(CCl_4) 1.1 (6 H, d, *J* 7.0), 1.8—3.3 (6 H, m's), and 5.0—6.5 (4 H, m). The cycloheptatriene (0.939 g, 7.0 mmol) was treated with trityl perchlorate (2.33 g, 6.8 mmol) in acetonitrile to give (2d) (0.930 g, 3.77 mmol) as colourless crystals in 53.8% yield, m.p. 75.0—76.0 °C; δ(CF_3CO_2H) 1.6 (6 H, d, *J* 7.0), 3.1 (3 H, s), 3.9 (1 H, m), and 9.0 (5 H, m) (Found: C, 53.7; H, 6.2. $C_{12}H_{15}ClO_4$ requires C, 53.55; H, 6.13%).

2-*Isopropyl*-1,3-*dimethyltropylium Perchlorate* (3d).—2,7-Dimethylcyclohepta-2,6-dienone (2.71 g, 19.8 mmol) was dissolved in pentane (50 ml) and the solution was cooled to −78 °C. To this was added a solution of isopropyl-lithium (24.3 mmol) in pentane during 20 min the temperature being kept below −70 °C. The reaction mixture was refluxed for 80 min and worked up in the usual manner. Evaporation of the solvent afforded a yellow oil (3.19 g), which contained 1-isopropyl-2,7-dimethylcyclohepta-2,6-dienol (61%) and 6-isopropyl-2,7-dimethylcyclohept-2-enone (39%) on ^{1}H n.m.r. analysis. The alcohol mixture was treated with boric acid (0.70 g, 11 mmol) at 170—200 °C and 30 mmHg to give a distillate, which afforded crude 3-isopropyl-2,4-dimethyltropilidene (1.40 g) as a pale yellow oil on redistillation, b.p. 100—118° at 35 mmHg. G.l.c. analysis showed that the distillate contained 56% of the cycloheptatriene and 44% of the 1,4-addition product. The oil was converted into (3d) with trityl perchlorate without further purification. The perchlorate was obtained as colourless crystals in 21% yield, m.p. 120.0—121.0 °C; δ(CF_3CO_2H) 1.7 (6 H, d, *J* 8.0), 3.2 (6 H, s), 4.0 (1 H, m, *J* 8.0), and 8.8 (4 H, m) (Found: C, 54.0; H, 6.6. $C_{12}H_{17}ClO_4$ requires C, 55.28; H, 6.57%).

1-*Methyl*-2-*phenyltropylium Perchlorate* (2e).—To a diethyl ether solution of phenyl-lithium prepared from 6.24 g (39.7 mmol) of bromobenzene and 0.612 g (88.2 mmol) of lithium was added 2-methylcyclohepta-2,4-dienone during 25 min at 0 °C. The reaction mixture was worked up in the usual manner to give 2-methyl-1-phenylcyclohepta-2,4-dienol (5.92 g) as a brown liquid; δ(CCl_4) 1.6 (3 H, s), 2.0br (4 H, s), 5.7br (3 H, s), and 7.3 (5 H, m). The alcohol (5.33 g, 26.6 mmol) was dehydrated with boric acid (2.11 g, 34.1 mmol) at 150 °C and 2 mmHg. Redistillation of the distillate gave a mixture containing 3-methyl-2-phenylcyclohepta-1,3,5-triene (A) and 2-methyl-1-phenylcyclohepta-1,3,5-triene (B) in a ratio of 69 : 31 as determined by ^{1}H n.m.r., in 34% yield, b.p. 102.5—117 °C at 6 mmHg; δ(CCl_4) 1.8 [0.9 H, s, methyl of (B)], 1.9 [2.1 H, s, methyl of (A)], 2.25 [0.69 H, t, *J* 6.3, methylene of (A)], 2.5 [0.31 H, d, *J* 6.8, methylene of (B)], 5.1—6.6 (4 H, m), and 7.0—7.2 (5 H, s). The hydride abstraction of the cycloheptatriene mixture with trityl perchlorate in acetonitrile afforded (2e) in 67% yield, m.p. 102.0—103.0 °C (lit.,[21] 94—106 °C); δ(CF_3CO_2H) 2.9 (3 H, s), 6.6 (5 H, m), and 9.1 (5 H, m) (Found: C, 60.0; H, 4.9. $C_{14}H_{13}ClO_4$ requires C, 59.90; H, 4.67%).

1,3-*Dimethyl-2-phenyltropylium Perchlorate* (3e).—To a solution of phenyl-lithium in diethyl ether prepared from bromobenzene (3.67 g, 23.4 mmol) and lithium (0.36 g, 52 g-atom) was added 2,7-dimethylcyclohepta-2,6-dienone (2.45 g, 18 mmol) in diethyl ether at 0 °C during 20 min. The reaction mixture was refluxed for 30 min and then worked up in the usual manner to give crude 2,7-dimethyl-1-phenylcyclohepta-2,6-dienol (3.57 g, 16.7 mmol); δ(CCl_4) 1.67 (6 H, s), 2.12 (4 H, m), 5.6br (2 H, m), and 7.1—7.6 (5 H, m). The alcohol (1.15 g, 5.35 mmol), when heated with boric acid (0.40 g, 6.4 mmol) at 200 °C and 7 mmHg [11,12] gave a distillate. Extraction with pentane afforded crude 2,4-dimethyl-3-phenylcyclohepta-1,3,5-triene (0.74 g), which was essentially pure on ^{1}H n.m.r. analysis; δ(CCl_4) 1.48 (3 H, s, 2-Me), 1.76 (3 H, s, 4-Me), 2.20 (2 H, t, *J* 6.2, 7-H), 5.23 (1 H, t, *J* 6.2, 1-H), 5.48 (1 H, dt, *J* 9.0, 6.2, 6-H), 5.90 (1 H, d, *J* 9.0, 5-H), and 6.8—7.4 (5 H, m). The hydride abstraction of the cycloheptatriene with trityl perchlorate in acetonitrile afforded (3e) as pale yellow crystals in 66% yield, m.p. 187.0—189.0 °C; δ(CF_3CO_2H) 2.73 (6 H, s), 7.0—7.8 (5 H, m), and 8.63—9.13 (4 H, m).

Synthesis of Substituted Bitropyls.—All the substituted tropylium perchlorates afforded mixtures of the corresponding substituted bitropyls in approximately quantitative yields. A typical example is as follows. 1,2,3-Trimethyltropylium perchlorate (61.0 mg, 0.262 mmol) was dissolved in 10% HCl (15 ml). To this was added 1M Cr^{II}–10% HCl (4 ml) with stirring under a nitrogen atmosphere; the mixture was stirred at room temperature for 40 min. The dimers were extracted with hexane, washed with 10% NaCl, and dried ($MgSO_4$). Evaporation of the solvent under a reduced pressure afforded a mixture of the dimers (34.8 mg, 100%); δ(CCl_4) 1.1—2.3 (20 H, m) and 4.6—6.4 (6 H, m). Extraction of the dimers from (2d), (2e), (3a), (3d), and (3e) was carried out with chloroform because of the low solubility of the dimers in hexane.

Rate Measurement.—The second-order rate constants for the Cr^{II}-reduction of the substituted tropylium ions were determined in 10% HCl at 25.0 °C by measuring the amounts of the bitropyls which were formed by the coupling of the substituted tropyl radicals. The rates of (1c) and (2e) were determined by the flow method previously described.[6a] The rates of (2b), (2c), (2d), (3a), (3b), (3c), (3d), and (3e) were determined by a batchwise method; a typical example follows. Eight test tubes (24 × 200 mm) were attached to a manifold and the air replaced with nitrogen by repeating evacuation and filling nitrogen; 10.00 ml of 0.024 4M-Cr^{II} in 10% HCl solution was placed in each test tube and kept at 25.0 °C in a thermostat. To each Cr^{II} solution was added 10.00 ml of 0.006 68M-(3a) in 10% HCl was added and shaken vigorously. After appropriate intervals (10—60 s), the solution was quenched with 1.0M-cupric sulphate in 10% HCl. The dimer formed was extracted with three 25-ml portions of chloroform. The combined extracts were washed with three 50-ml portions of 10% NaCl and dried ($MgSO_4$). After removal of the $MgSO_4$ by filtration through a glass filter the chloroform solution was diluted to 100.0 ml with chloroform and subjected to u.v. measurement at 260 nm. The ε values of dimers at 260 nm in chloroform are 8 410 (2d), 7 390 (3a), 7 830 (3d), and 17 400 (3e). For the dimers from other perchlorates hexane was used as an extraction solvent and the amount of dimers was determined utilizing the following ε values for $\lambda_{\max.}$ in ethanol; 8 150 [(1c), 259 nm], 7 960 [(2b), 252 nm], 7 700 [(2c), 255 nm], 41 100 [(2e), 234 nm], 7 900 [(3b), 246 nm], and 9 190 [(3c), 247 nm]. The second-order rate constant was calculated from the second-order plot.

Charge-transfer Spectra.—To each perchlorate (5 mg) was added 0.1M-pyrene in 1,2-dichloroethane (5 ml) in the dark and thoroughly shaken. The solution was transferred to a 10-mm quartz cell and the spectrum was measured. In most of the perchlorates the longest wavelength absorption appeared as a shoulder peak. Therefore the wavenumber for the maximum absorption was determined by drawing a smooth curve and by analysing the shoulder peak. The wavenumber determined in this manner was accurate to ±0.02 × 10^4 cm^{-1}.

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