The One-Electron Reduction of Carbonium Ions. Part 14.[1] Effect of Successive Introduction of Methyl Substituents on the Reducibility of Tropylium Ion in Chromium(II) Ion and Cathodic Reductions

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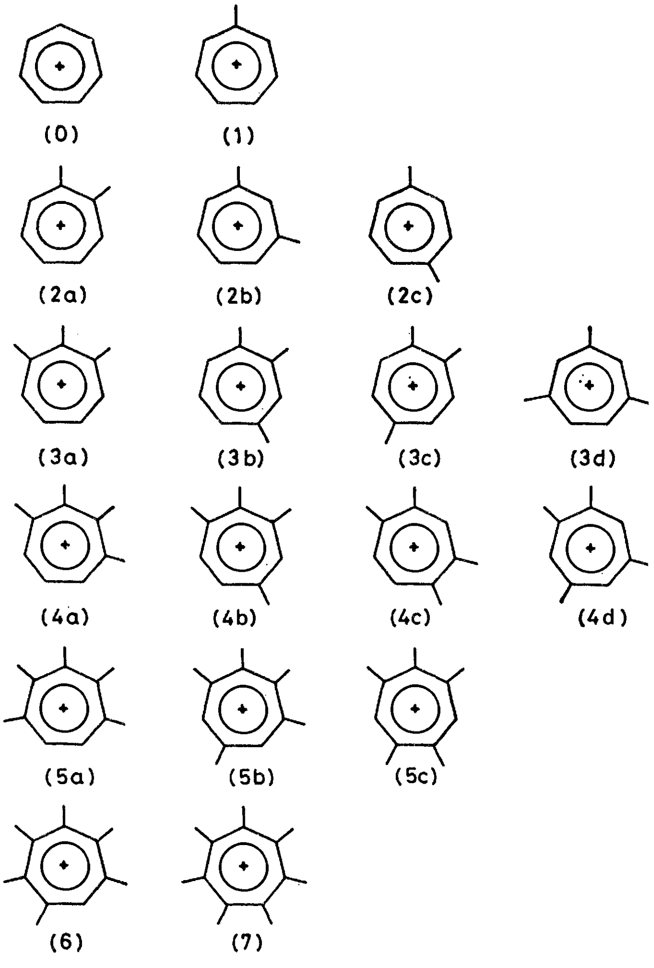
The second-order rate constants (k_2) of one-electron reduction with Cr^{II} ion of methylated tropylium ions [$C_7H_{7-n}(CH_3)_n^+ClO_4^-$, n = 0—7] were determined in 10% hydrochloric acid at 25.0 °C. Reduction peak potentials determined by means of triangular wave cyclic voltammetry and charge transfer energies with pyrene were compared with the rates of Cr^{II} ion reduction in terms of the effect of methyl substituents. The log k_2 values decrease linearly with an increase in the number of methyl groups up to n = 4. However, the decelerating effect per extra methyl substituent becomes smaller when n is 5 or 6, and the seventh methyl substituent accelerates the reduction. The methyl substituent effect on the reduction peak potentials of the carbocations is similar to that found for the Cr^{II} ion reduction, giving rise to a linear correlation. A Marcus treatment suggests that Cr^{II} ion reduction proceeds through an outer-sphere mechanism. The charge transfer energies with pyrene are linearly correlated with reduction potentials for ions with n = 0—6, but considerable deviation is noted when n is 7. The charge transfer energies are linearly correlated with the LUMO energy levels of the methylated tropylium ions, suggesting that the unexpectedly pronounced reducibilities of hexa- and hepta-methyltropylium ions are attributable to steric factors. The deviation from linearity in the Cr^{II} ion reduction and the reduction potential are reasonably explained by assuming that non-bonded repulsive interactions among congested methyl substituents in the carbocations are relieved upon reduction to their corresponding radicals. This explanation is consistent with our previous conclusion from a ^{13}C n.m.r. study that the methyl substituents of 1,2,3,4,5-penta-, hexa-, and hepta-methyltropylium ions are highly congested and distorted out of plane.

THE stability–reactivity relationship for carbocations has long been an interesting problem in physical organic chemistry. In previous papers, we demonstrated the existence of linear free energy relations between the rates of one-electron reduction of various substituted cyclopropenium and tropylium ions with Cr^{II} ion or zinc and properties such as pK_R^+, reduction potential, and charge transfer energy with pyrene.[2] Thus it has been shown that the one-electron reducibility is a good measure of the stability of carbocations.

Feldman and Bowie have found that the log k_2 values for Cr^{II} ion reduction of several organic cations of various structural types including the tropylium ion are linearly correlated with their cathodic reduction potentials with a slope of 0.5.[3] The result was nicely explained by the Marcus theory which indicates that one-electron reduction by Cr^{II} ion proceeds through an outer-sphere mechanism.[4]

With such background, we were interested in examining various correlations over a wide range of stability of various tropylium ions. For this objective, the methylated tropylium system appeared to be suitable since (a) the methyl substituent is not so bulky as to exert a steric effect on the reactivity, (b) the methyl substituent effect has been shown to be nearly additive for monomethyl-, 1,2- and 1,3-dimethyl-, and 1,2,3-trimethyl-tropylium ions,[1] and (c) all the methyltropylium ions were available (Scheme 1).[5]

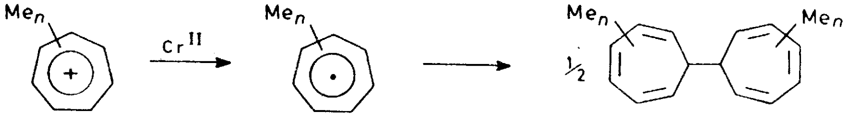
This paper describes the one-electron reducibilities of all the methyltropylium ions with Cr^{II} ion, and their correlations with reduction potentials and charge transfer energies with pyrene. The correlation of the charge transfer energies with LUMO energy levels calculated by the extended HMO method was also examined.



SCHEME 1

RESULTS AND DISCUSSION

Products and Rates of Cr^{II} *Ion Reduction*.—As previously described,[2a] the Cr^{II} ion reduction of the tropylium ions was conducted in 10% hydrochloric acid at 25.0 °C and the reaction was followed by measuring the amount of reduction products by u.v. analysis. With the successive introduction of methyl groups, the reaction became very slow, exhibiting rates not allowing convenient measurements. Therefore, the rates for penta-, hexa-, and hepta-methyltropylium ions were determined under pseudo-first-order conditions by the use of a large excess of Cr^{II} ion. However, in the reactions of (5a—c), (6), and (7), considerable amounts of ' apparently-two-electron ' reduction products (monomers) were formed in addition to the expected bitropyls (dimers) (Scheme 2).



SCHEME 2

Although quantitative analysis of the dimer : monomer ratios has not been conducted in each case, the product from (6) was shown by ^{13}C n.m.r. analysis to be composed of the monomer and the dimer in a mole ratio of *ca.* 2 : 1. From the product mixture from (6) the dimer was isolated in crystalline form, m.p. 204.0—205.0 °C, in 20% yield. Compound (7), in particular, afforded the monomer as the main product.* The formation of two-electron reduction products *via* carbanions has been reported in the potassium reduction of heptaphenyltropylium ion[7] and the Cr^{II} ion reduction of benzyl chloride.[8] Alternatively, the heptamethyltropyl radical, for example, might produce heptamethyltropylidene and hexamethylheptafulvene *via* disproportionation, the latter being protonated to regenerate (7).† We are not in a position to clarify the mechanism for the monomer formation at present.

The second-order rate constants for Cr^{II} ion reduction of the methyltropylium ions were calculated and are listed in the Table. Since the above mentioned observations for (6) and (7) are ambiguous as to the significance of their rate data, the data should be taken as approximate measures for their rates of the Cr^{II} ion reduction.

Rates of Cr^{II} ion reduction at 25.0 °C, reduction peak potentials and charge transfer $\nu_{max.}$ values with pyrene for methyltropylium ions R$^+$

Cation	Initial concentration [a]		k_2/l mol^{-1} s^{-1} [b]	Reduction potential *vs.* s.c.e./V [e]	$10^{-4}\,\nu_{max.}$/cm^{-1}
	10^2[R$^+$]/M	10^2[Cr^{II}]/M			
(0)	1.80	3.05	74.0 ± 0.2 [c]	−0.120	1.81
(1)	1.99	4.13	11.1 ± 0.2 [c]	−0.233	1.88
(2a)	0.294	1.10	0.908 ± 0.01 [d]	−0.348	1.98
(2b)	0.334	1.22	1.36 ± 0.02 [d]	−0.298	1.94
(2c)	0.313	1.23	0.865 ± 0.026	−0.312	1.94
(3a)	0.271	0.866	0.148 ± 0.002 [d]	−0.428	2.00
(3b)	0.300	0.938	0.169 ± 0.005	−0.438	2.01
(3c)	0.302	1.03	0.114 ± 0.001	−0.420	1.99
(3d)	0.300	0.517	0.107 ± 0.004	−0.395	1.99
(4a)	0.742	2.25	$(2.07 \pm 0.01) \times 10^{-2}$	−0.500	2.07
(4b)	0.602	3.18	$(2.55 \pm 0.06) \times 10^{-2}$	−0.517	2.07
(4c)	0.299	1.55	$(1.61 \pm 0.11) \times 10^{-2}$	−0.521	2.08
(4d)	0.544	16.0	$(2.28 \pm 0.01) \times 10^{-2}$	−0.495	2.04
(5a)	0.655	12.4	$(6.89 \pm 0.30) \times 10^{-2}$	−0.548	2.13
(5b)	0.364	6.90	4.32×10^{-3}	−0.549	2.11
(5c)	0.363	12.3	$(2.65 \pm 0.02) \times 10^{-3}$	−0.604	2.13
(6)	0.167	17.9	$(2.17 \pm 0.29) \times 10^{-3}$	−0.594	2.17
(7)	0.0697	16.4	$(7 \pm 2) \times 10^{-3}$	−0.588	2.35

[a] Data for representative measurements. [b] Average for two data. [c] Data taken from ref. 2*b*. [d] Data taken from ref. 1. [e] Solvent, CH_2Cl_2; supporting electrolyte, 0.1M-$Bu^n{}_4NClO_4$; sweep rate, 0.1 V s^{-1}. [f] With pyrene in $Cl(CH_2)_2Cl$: data taken from ref. 5.

In order to examine the additivity of the methyl substituent effect on the rate of Cr^{II} ion reduction, the logarithms of the rate constants were plotted against the number of the methyl substituents (Figure 1). There are four characteristic features in the plot. First, the successive introduction of methyl groups decelerates the reduction except in the case of (7). Secondly, the isomers of di-, tri-, and tetra-methyltropylium ions show similar reactivities in each case. Therefore, when the number of the methyl substituent is less than five, the methyl substituent effect is nearly additive, and the more methylated the tropylium ion, the less reactive are

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* The combination process of the tropyl radical is known to be fast ($t_{1/2} < 10^{-3}$ s) compared with the first one-electron reduction process.[6] In contrast, the highly methylated tropyl radicals are expected to combine at slower rates for steric reasons, giving rise to the two-electron reduction products. In the reaction of (7) the shape of the u.v. spectra of the product changed with time, suggesting the intervention of homolytic cleavage of the dimer once it is formed.

† We thank a referee for the suggestion of the possibility of disproportionation.

the ions due to increased stabilization. Thirdly, discrepancies among the rates of (5a—c) are evident, (5a) being the most reactive, and (6) reacts six times as fast as the rate predicted from the straight line in the plot. Fourthly, the most unexpected feature is that the introduction of the seventh methyl group accelerates the reduction. The faster rate of (7) than (6) was also ascertained from their competitive reduction with zinc powder in acetonitrile (see Experimental section).

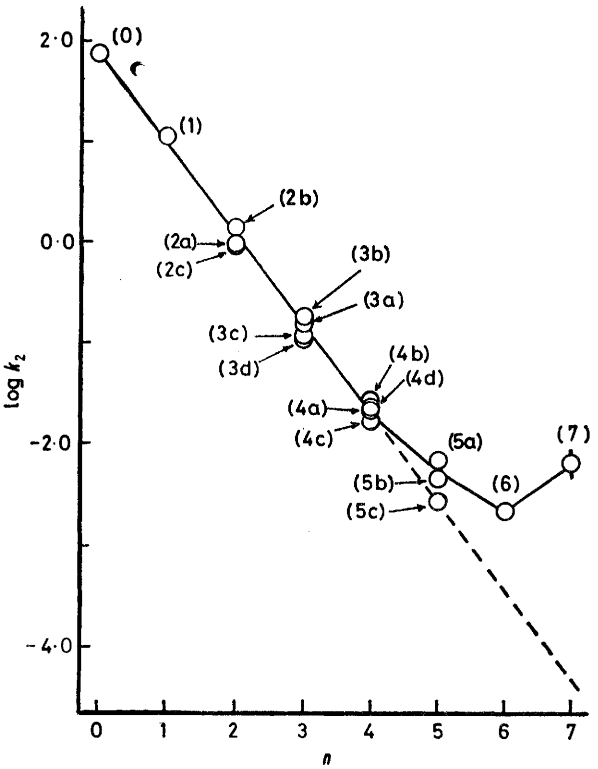

FIGURE 1 Plot of log k_2 for Cr^{II} ion reduction of methyltropylium ions in 10% HCl at 25.0 °C against the number of the methyl substituents

The lack of correlation for (5a) and (6) might be partly ascribed to the possible levelling of the electron-releasing ability of the methyl groups. However, such an effect as a sole factor cannot explain the abrupt change in the behaviour of (7). The most probable rationalization is ascribed to steric reasons.

Previously, we proposed, on the basis of statistical analysis of ^{13}C n.m.r. chemical shifts of the methyl and ring carbons of methyltropylium ions, that the methyl substituents of (5a), (6), and (7) are distorted out of plane, whereas the seven-membered ring is planar.[9] Koenig and Chang proposed on the basis of helium(I) photoelectron spectroscopy that the tropyl radical has deformed C_{2v} symmetry.[10] They suggested that some C–C bonds in the tropyl radical are longer than those in the tropylium ion. Consequently, the pronounced reducibility of (7) may be rationalized by assuming that the non-bonded repulsive interactions among methyl substituents in (7) are relieved by its being converted into the corresponding radical.

Cathodic Reduction.—The Cr^{II} ion reduction of the methyltropylium ions vividly showed the effect of the successive introduction of methyl groups on the reducibility of the tropylium ion. However, as stated above, there remained some ambiguity in the accuracy of the observed rates since some tropylium ions afforded two-electron reduction products. Consequently, with a view to examining whether the characteristic methyl substituent effect observed in the Cr^{II} ion reduction of (6) and (7) is general in the one-electron reduction of methylated tropylium ions, the reduction peak potentials were measured in dichloromethane by triangular wave cyclic voltammetry under irreversible conditions. The results are in the Table.

The reduction potential decreases by *ca.* 0.1 V for each methyl introduction over the range from unsubstituted tropylium (0) to tetramethyltropylium ions (4a—d). However, this regular decrease does not hold for (5a—c), and a reversed trend takes place for (6) and (7), coinciding with the trend of the rates of Cr^{II} ion reduction. This behaviour of hexa- and hepta-methyltropylium ions which is common to both the Cr^{II} ion reduction and the cathodic reduction may be ascribed to the same origin, most probably to the relief of non-bonded repulsive interactions between the methyl substituents on conversion of the carbocations into their corresponding radicals.

The relative rates of Cr^{II} ion reduction designated by $RT\ln(k_2/k_2^{(0)})$ [$= 5.69 \log(k_2/k_2^{(0)})/\text{kJ mol}^{-1}$] can be linearly correlated with the reduction potentials over the whole range ($n = 0$—7) (Figure 2).† The slope of the correlation line, 0.54 (r 0.988), is close to the theoretical value, 0.5, which is deduced from the Marcus theory, suggesting that Cr^{II} ion reduction of methyltropylium ions in 10% hydrochloric acid proceeds through an outer-sphere mechanism.[4] This sort of correlation had been observed by Feldman and Bowie in the Cr^{II} ion

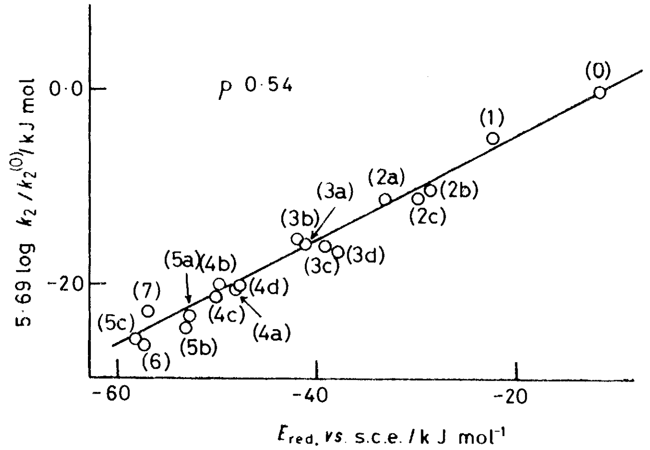

FIGURE 2 Correlation of relative rates for Cr^{II} ion reduction [5.69 log $(k_2/k_2^{(0)})$] with reduction peak potentials for methyltropylium ions

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† We have previously demonstrated linear correlations between the log k_2 values for Cr^{II} ion reduction and the polarographic half-wave potentials for various substituted tropylium ions.[2]

reduction of several organic cations in 75% ethanol in the presence of 2N-perchloric acid.[3]

Correlation of Reduction Peak Potentials with Charge Transfer Energies.—According to Mulliken the charge transfer energy (E_{CT}) is a linear function of the electron affinity ($E_{aff.}$) of an electron acceptor and the ionization potential (I_p) of an electron donor [equation (1)].[11,12] Therefore, the E_{CT} values determined for methyltropylium ions by the use of pyrene as an electron donor [5] (Table) are expected to be linearly correlated with $E_{aff.}$ with a slope of -1.0. In the present case we can use the

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

reduction peak potential (E_{red}) in place of $E_{aff.}$. When the E_{CT} values are plotted as a function of E_{red} a linear correlation is found to hold for the methylated tropylium ions over the range $n = 0$—6 with a slope of -0.90 (r 0.984) in good agreement with prediction (Figure 3). In this correlation also, the point for (6) deviates slightly upward, and that for (7) deviates significantly from the regression line.

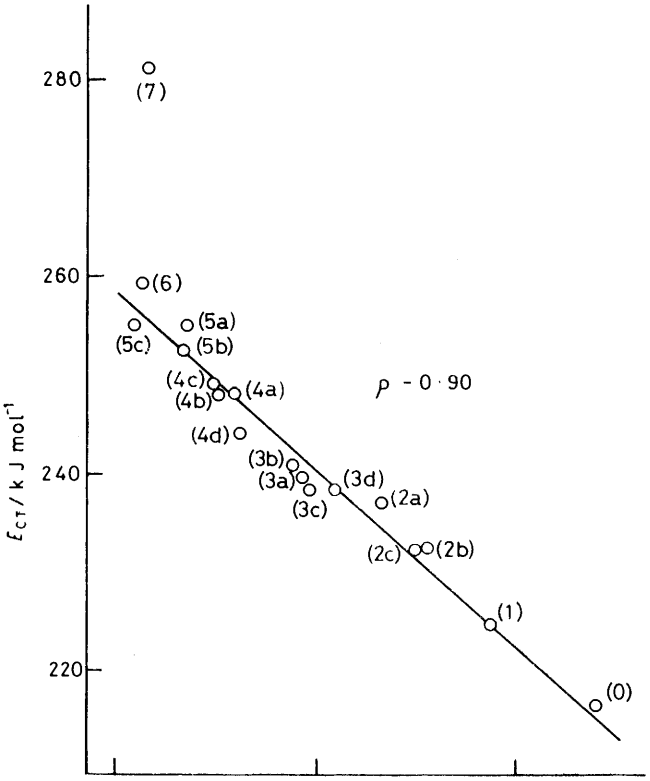

FIGURE 3 Correlation of charge transfer energies with pyrene with reduction peak potentials for methyltropylium ions

As mentioned before, the deviation of one-electron reducibility for these methylated tropylium ions has been ascribed to steric reasons. Meanwhile, the charge transfer energy (E_{CT}) is determined by the LUMO energy level of an electron acceptor.[13] A plot of the LUMO levels calculated by the extended HMO method * against the E_{CT} values affords a fairly good linear correlation with slope 1.01 (r 0.929) (Figure 4). It should be noted

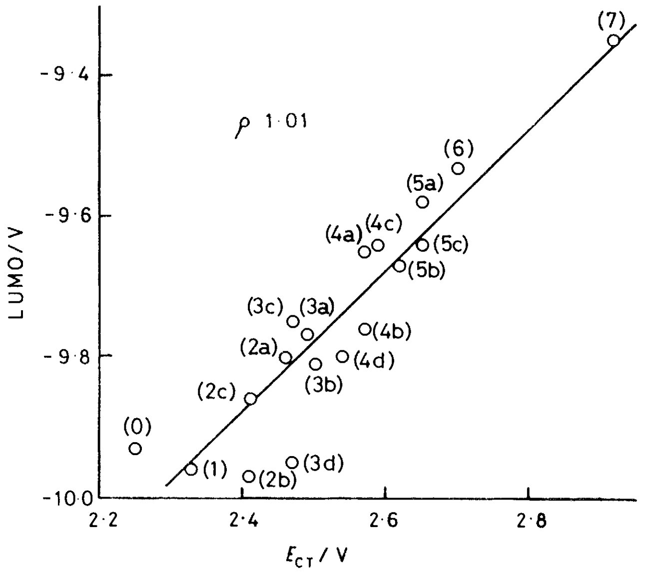

FIGURE 4 Correlation of LUMO energy levels with charge transfer energies with pyrene for methyltropylium ions

that the points for hexa- and hepta-methyltropylium ions do not exhibit exceptional deviation. These results support the aforementioned interpretation that the unexpectedly high reducibilities of (6) and (7) can be attributed to steric reasons. The relief of the repulsive interactions among methyl substituents upon one-electron reduction to form the corresponding radicals provides a reasonable explanation.

EXPERIMENTAL

U.v. spectra were measured with a Hitachi 200-10 spectrophotometer. ^1H N.m.r. spectra were recorded on a Hitachi R-24 (60 MHz) instrument. ^{13}C N.m.r. spectra were recorded on a JEOL FX100 (25.00 MHz) instrument operating in the Fourier transform mode. Cyclic voltammetry was conducted with a Hokuto Denko potentiogalvanostat HA-104 and function generator HB-107A.

Materials.—All the methyltropylium perchlorates were reported previously.[5] All reagents were of reagent grade quality except when otherwise noted.

Product of Cr^{II} *Ion Reduction.*—The isolation of the products from Cr^{II} ion reduction of the methyltropylium ions was conducted under conditions similar to those utilized in kinetic studies. Extraction of the hydrocarbon products with chloroform followed by evaporation of the solvent afforded the reduction products in 95—100% yields. The

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* The C–C bond length for the ring was estimated from the formula, $1.405 + n(1.4113 - 1.4050)$ Å, where 1.4050 Å is the bond length in the tropylium ion, 1.4113 Å is the average C–C bond length in the methyltropylium ring,[14] and n is the number of methyl groups. A regular heptagon was assumed and the bond lengths utilized for C_{ring}–H, C_{ring}–CH_3, and C–H of methyl are 1.108,[14] 1.501,[14] and 1.095 Å,[15] respectively. The appropriate conformation of methyl substituents was assumed by adopting Grant's assumptions on methylated benzenes.[16] Other necessary data were taken from Hoffmann's paper.[17]

crude products were shown to retain the tropylidene moiety by ^{1}H n.m.r. analysis. Although the products from (4a—d) were methylated bitropyls (dimers), those from (5a—c) contained 10—20% of two-electron reduction products (monomers), which were separated by preparative t.l.c. (SiO_2–hexane) and identified by ^{1}H n.m.r. However, the dimers from (5a—c) were unstable and decomposed during separation by t.l.c., exhibiting broad ^{1}H n.m.r. signals at δ 0.9—2.0. The crude product from (6) was shown by ^{13}C n.m.r. ($CDCl_3$) to be composed of 1,2,3,4,5,6-hexamethyltropylidene as the main monomer and dodecamethylbitropyl in a mole ratio of *ca.* 2 : 1; monomer, δ_C ($CDCl_3$) 16.1 (q), 17.7 (q), 20.5 (q), 42.2 (t), 127.0 (s), 129.0 (s), and 135.0 p.p.m. (s); dimer, δ_C ($CDCl_3$) 17.9 (q), 18.2 (q), 24.2 (q), 46.1 (d), 126.7 (s), 133.2 (s), and 133.4 p.p.m. (s); δ_H ($CDCl_3$) 1.53 (12 H, s), 1.68 (12 H, s), 1.90 (12 H, s), and 2.87 p.p.m. (2 H, s). On addition of methanol to the product mixture the dimer was obtained as crystals, m.p. 204.0—205.0 °C. The product from (7) showed a ^{13}C n.m.r. ($CDCl_3$) spectrum identical with that of heptamethyltropylidene, δ_C 14.1 (q), 16.2 (q), 17.7 (q), 39.5 (d), 126.5 (s), 131.6 (s), and 135.1 p.p.m. (s).

Kinetic Studies.—The second-order rate constants were determined by the batchwise method which was essentially similar to that described previously.[1] The percentage reaction of carbocations were determined by measuring the u.v. absorbances of the reduction products at 260 or 265 nm in chloroform. For (4a—d) the absorbance at 10 half-lives were used for that at 100% reaction. The ions (5a—c), (6), and (7) reacted too slowly at the Cr^{II} ion concentrations used in kinetic studies to permit the u.v. absorbance at 100% reaction to be measured; therefore, Cr^{II} ion concentrations of 0.5—1.0M were used and the absorbance at 1—2 h was used for that at 100% reaction. It was ascertained that the absorbances adopted as those for 100% reaction were constant at doubled reaction times.

Competitive Reduction of (6) *and* (7) *with Zinc in Acetonitrile.*—A solution of (6) (5.7 mg, 0.021 mmol) and (7) (4.4 mg, 0.015 mmol) in acetonitrile (10 ml) was magnetically stirred with zinc powder (167 mg, 2.55 mmol) at 15.5 °C under nitrogen. After 30 min 0.50 ml of the solution was withdrawn, diluted with 10% HCl to 5.00 ml, and washed with chloroform to remove hydrocarbon products. The u.v. spectrum of the aqueous phase was essentially superimposable on that of pure (6). Analysis of the absorptions at 311 [ε 5 750 for (6); 2 050 for (7)] and 350 nm [ε 535 for (6); 5 850 for (7)] revealed that (6) and (7) reacted to the extent of 25 and 94%, respectively, indicating that (7) is *ca.* 10 times as reactive as (6) in the zinc reduction under these conditions.

Cyclic Voltammetry.—The reduction peak potentials were measured for 0.001M-cation in 0.1M-$Bu^n{}_4NClO_4$ in CH_2Cl_2 using a three-electrode cell with platinum wire and auxiliary electrodes and a saturated calomel reference electrode. Scanning was conducted from +0.5 to −1.5 V at a rate of 0.1 V s^{-1} under irreversible conditions.

[0/1452 *Received, 22nd September*, 1980]

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