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One-Electron Reduction of Carbonium Ions. IV. A Kinetic Study on the Reduction of the Substituted Tropylium Ions with Cr(II)*

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The one-electron reduction of the unsubstituted, methyl-, ethyl-, isopropyl-, *t*-butyl-, triphenylmethyl-, and phenyltropylium ions with Cr(II) in a 10% HCl solution gives, quantitatively, the dimer of the corresponding substituted tropyl radical. The measurements of the reaction rate at 25 °C exhibit this order of reactivity: *t*-butyltropylium (k_2=7.98 l/g·ion·sec), isopropyltropylium (8.22), ethyltropylium (10.3), methyltropylium (11.1), tropylium (74.0), phenyltropylium (144), and triphenylmethyltropylium (567) ions. The values of log k_2 have a linear correlation with the transition energies of the charge-transfer bands observed for these carbonium ions with pyrene, and also with the polarographic half-wave potentials of the respective cations. These correlations indicate that the reactivity of the carbonium ion in the reduction with Cr(II) is determined mainly by the electron affinity inherent in the respective cations. The values of log k_2 also have a good linear correlation with the pK_{R^+} values, implying a parallelism between the electron affinity and the electrophilicity of these stable carbonium ions.

Although the one-electron reduction of carbonium ions in the gas phase has raised much theoretical interest in the ionization of organic radicals to carbonium ions, the reducibility of stable carbonium ions in solutions has received rather little attention; quantitative studies of it have been restricted to electrochemical one, such as polarography[1] and emf measurements of the cells made of equilibrated solutions of the carbonium ions and the corresponding radicals.[2] We demonstrated in previous papers[3,4] that the reducibility of the stable carbonium ion can be estimated from the reactivity

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1) a) M. E. Vol'pin, S. I. Zhdanov, and D. N. Kursanov, *Dokl. Akad. Nauk SSSR*, **112**, 264 (1957); *Chem. Abstr.* **51**, 12057e (1957); b) P. Zuman, J. Chodkowski, H. Potesilova, and F. Santavy, *Nature*, **182**, 1535 (1958); c) M. I. James and P. H. Plesch, *Chem. Commun.*, **1967**, 508; d) R. Breslow, W. Bahary, and W. Reinmuth, *J. Amer. Chem. Soc.*, **83**, 1763 (1961).

2) E. D. Jenson and R. W. Taft, *ibid.*, **86**, 116 (1964).

3) K. Okamoto, K. Komatsu, and H. Shingu, This Bulletin, **42**, 3249 (1969).

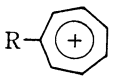
4) K. Okamoto, K. Komatsu, S. Tsukada, and O. Murai, *ibid.*, **46**, 1780 (1973).

toward various metals and low-valent metallic ions, and that among these reductants Cr(II) is a suitable reagent for the kinetic study designed to estimate quantitatively the reducibility of stable carbonium ions in a solution.

Thus, the kinetics of the chromous-ion reduction of the substituted tropylium ions were studied with the idea that the change in the electron affinity of these ions caused by the introduction of various substituents will be reflected in the rate constants. The relative electron affinities of carbonium ions have been estimated from the transition energies of the charge-transfer bands, and also from the polarographic half-wave potentials. We will discuss the correlation of the reducibility of these carbonium ions with the relative electron affinities obtained, and also with the pK_{R^+} values measured for the respective cations, and will show the applicability of this method to the evaluation of the reducibility of stable carbonium ions of the tropylium system in a solution.

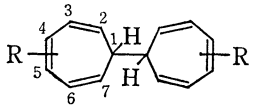
Results and Discussion

Reduction of the Substituted Tropylium Ions with Cr(II). It has been reported that the tropylium ion was readily reduced with Cr(II) to give a quantitative yield of the dimer, bitropyl.[3,5] We have ourselves examined the reduction of the substituted tropylium salts (Ia—f) with Cr(II) in 10% HCl (2.9 M);[6]



I

I a : R=CH_3, X=ClO_4 b : R=C_2H_5, X=ClO_4
c : R=i-C_3H_7, X=ClO_4 d : R=t-C_4H_9, X=ClO_4
e : R=C_6H_5, X=BF_4 f : R=$C(C_6H_5)_3$, X=BF_4



II

We ascertained that, in each case, the dimer (II) was obtained in a yield of more than 95% without the formation of any by-product. The elemental analysis of the respective reaction products gave satisfactory values for the dimers. The NMR spectra (60 MHz) of the dimers showed three groups of multiplets, centered at about τ 3.5, 3.9, and 4.8, along with a broad singlet at about 8.0, typical of a cycloheptatrienyl system, and also the signals corresponding to each substituent. The complex patterns of these multiplets and the multiplicity of the signals of the substituents suggest that the product is a mixture of isomers of x,x'-disubstituted bitropyl (II). The signals centered at τ *ca.* 3.5 ($H^{4,5}$) and at *ca.* 3.9 ($H^{3,6}$) were not fully separated; therefore, integration was made for these four protons (H^{3-6}) as one group. It was found that, although the average of from three to five integrations constantly gave the relative ratio of nearly 1 : 5 for $H^1 : H^{2-7}$, the averaged ratio for $H^{2,7} : H^{3-6}$ varied with the substituents, as is shown in Table 1. Though each integration includes the probable error of *ca.* 5%, there is still a clear tendency for the integrated value of H^{3-6} to decrease with the increase in the bulkiness of the substituent. This seems to reflect the steric hindrance exerted upon the coupling of the substituted tropyl radicals formed by one-electron transfer.[4] Each product mixture seemingly gave one or hardly separating two spots on a silica-gel thin-layer plate (*n*-hexane–benzene, 9 : 1, as the solvent), but all attempts to isolate the single isomer were unsuccessful.

Table 1. Ratio of the integrations for ring protons of x,x'-disubstituted bitropyl

Substituent	H^1	$H^{2,7}$	H^{3-6}
None	2.0	4.0	8.0
Methyl	~2[a]	2.94	7.06
Ethyl	~2[a]	3.36	6.64
Isopropyl	1.90	3.48	6.52
t-Butyl	1.80	3.76	6.24
Phenyl	1.88	4.10	5.90
Trityl	2.00	3.74	6.26

a) Not determined separately because of the substituent signals which appear at the same position.

Kinetic Measurements of the Reduction of the Substituted Tropylium Ions. In order to examine the influence of substituents on the reducibility, the rate of the chromous-ion reduction of various substituted tropylium salts (Ia—f) was measured by the use of the flow method previously described;[4] the reaction was carried out at 25 °C under a nitrogen atmosphere in 10% HCl for 0.2—1.5 sec; the conversion was determined by the ultraviolet spectroscopy of the dimers. The reaction was found to follow good second-order kinetics with respect to each substituted tropylium ion and Cr (II). The results shown in Table 2 demonstrate that, whereas the reactivity of the tropylium ion is markedly increased by the introduction of phenyl and triphenylmethyl substituents, it is suppressed by the introduction of the alkyl groups, among which the effect gradually increases in this order; methyl, ethyl, isopropyl, and *t*-butyl groups.

In a previous mechanistic study[4] it was indicated that the reduction of the tropylium ion with Cr(II) in 10% HCl proceeds through a transition state, in which the chloride ion acts as an electron-transfer bridge between the two reactants, rather than by direct interaction between them. Therefore, it was expected that the influence of the steric effect exerted by each substituent would be minimized and that the reactivity would mainly reflect the intrinsic reducibility of the

5) W. T. Bowie and M. Feldman, *J. Phys. Chem.*, **71**, 3696 (1967).

6) Throughout this work, 10% HCl was used as the standard solvent in order to ensure the enough stability of the respective tropylium ions in the aqueous solution; in the solutions with lower acidities (pH>1), slow decomposition was observed for the methyl-, ethyl-, and isopropyltropylium ions.

Table 2. Second-order rate constants for the reaction of substituted tropylium ions with Cr(II) in 10% HCl at 25 °C

Substituent	Initial concn R-$C_7H_6^+$ 10^{-2} g-ion/l	Initial concn Cr(II) 10^{-2} g-ion/l	k_2 l/g-ion·sec	k_2 average l/g-ion·sec
None	2.05	3.75	73.8	74.0
	1.80	3.05	74.1	
Methyl	1.99	4.12	11.1	11.1
	2.60	5.39	11.0	
	2.61	5.20	11.3	
Ethyl	2.48	4.87	9.90	10.3
	2.50	5.22	9.80	
	2.60	5.22	11.1	
Isopropyl	2.23	5.26	8.18	8.22
	2.46	5.31	8.26	
t-Butyl	2.07	4.83	8.16	7.98
	2.47	5.06	7.74	
	2.51	5.78	8.05	
Phenyl	0.426	0.857	140	144
	0.462	0.928	147	
Trityl	0.096	0.453	610	567
	0.099	0.288	511	
	0.103	0.312	615	
	0.113	0.226	510	
	0.114	0.253	590	

respective carbonium ions. This supposition seems to be verified by the fact that the reduction of the tropylium ion with the bulkiest substituent, the triphenylmethyl group, still proceeds most rapidly. Thus, the results of the kinetic measurements should be interpreted in terms of the difference in the intrinsic reducibility of the respective cations. From the observed results, it also appears that the inductive effect of the substituents controls the reducibility sequence (*t*-Bu<*i*-Pr<Et<Me<H<Ph<Ph_3C) and that the π-conjugative stabilization exerts very little effect in the tropylium system.

Correlation of the Reducibility with the Relative Electron Affinity of the Carbonium Ions. It seems that it would be of interest to compare the observed reducibility of each substituted tropylium ion with the electron affinity determined by the other methods. As one of such methods we made use of the measurement of the charge-transfer bands observed between carbonium ions and an aromatic hydrocarbon.[7] From the interpretation according to the donor-acceptor theory of Mulliken,[8] it can be expected that the frequency of the charge-transfer band, ν_{max}, for a series of similar stable carbonium ions with a given donor molecule would correlate with the electron affinities of these carbonium ions. Actually, Feldman and Winstein[7e] estimated the electron affinities of various organic cations, applying the principle mentioned above. In the present study, it was observed that the dissolution of each substituted tropylium salt in a 1,2-dichloroethane solution of a condensed aromatic hydrocarbon, pyrene, immediately gave a red-colored solution. It exhibits a band in the visible region which is not found in the spectrum of either component and which can be regarded as a charge-transfer band. The results are shown in Table 3, along with the values of log k_2 for the chromous-ion reduction. A plot of log k_2 against ν_{max} exhibits a linear correlation between them, as is shown in Fig. 1.

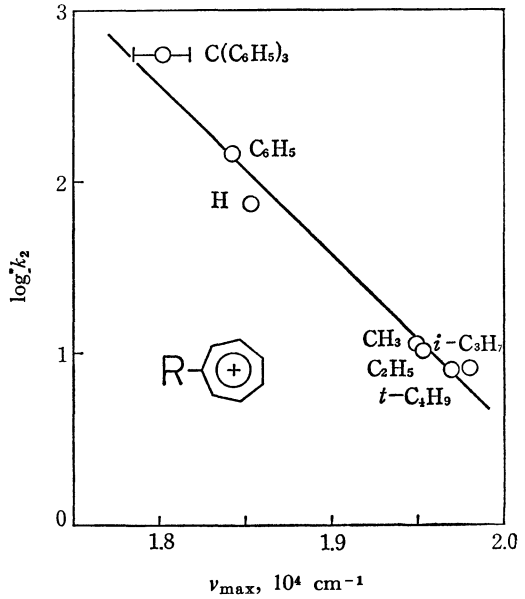


Fig. 1. The correlation of log k_2 with CT transition energies (ν_{max}).

As another measure of the electron affinity of the carbonium ions, electrochemical reduction potentials were determined by polarography with the dropping mercury electrode. The polarography of the tropylium ion was reported to include an irreversible reduction step.[1a-c] While some effects (solvation energy, *etc.*) other than electron affinity are regarded as being reflected in the half-wave potentials for such an irreversible step, for a series of similar cations the relative potentials will serve as a measure of readiness to accept an electron. The half-wave potentials measured in acetonitrile are listed in Table 3, while the correlation with log k_2 is shown in Fig. 2. The linear correlation observed in Figs. 1 and 2 clearly demonstrates that the reactivity of carbonium ions toward Cr(II) can be used satisfactorily as a measure of the electron affinity.

Correlation of the Reducibility with pK_R^+. In order to examine the correlation between the reducibility and the stability of carbonium ions, the pK_R^+ values of some representative substituted tropylium ions[9] were determined in 23% aqueous ethanol by

7) a) M. Feldman and S. Winstein, *J. Amer. Chem. Soc.*, **83**, 3338 (1961); b) M. Nepraš and R. Zahradník, *Collect. Czech. Chem. Commun.*, **29**, 1545 (1964); c) S. N. Bhat and C. N. R. Rao, *J. Chem. Phys.*, **47**, 1863 (1967); d) M. Feldman and B. G. Graves, *J. Phys. Chem.*, **70**, 955 (1966); e) M. Feldman and S. S. Winstein, *Theor. Chim. Acta*, **10**, 86 (1968); f) H. J. Dauben, Jr., and J. D. Wilson, *Chem. Commun.*, **1968**, 1629; g) T. G. Beaumont and K. M. C. Davis, *J. Chem. Soc., B*, **1968**, 1010.

8) R. S. Mulliken, *J. Chem. Phys.*, **19**, 514 (1951).

9) The pK_{R^+} values for the tropylium ions with a hydrogen atom at the α-position of the alkyl substituents could not be measured because of the decomposition of the cations in the low-acidity region; see Refs. 6 and 14.

Table 3. Results of the measurements of charge-transfer bands, polarographic half-wave potentials and pK_{R^+}'s of substituted tropylium ions

Substituent	$\log k_2$[a]	CT Band[b] λ_{max} mμ	CT Band[b] ν_{max} $10^4\,cm^{-1}$	$E_{1/2}$[c] V *vs.* SCE	pK_{R^+}[d]
None	1.87	540[e]	1.852	−0.126±0.002	4.3[f]
Methyl	1.05	513	1.949	−0.187±0.001	
Ethyl	1.01	512	1.953	−0.195±0.004	
Isopropyl	0.91	505	1.980	−0.235±0.002	
t-Butyl	0.90	508[g]	1.969	−0.215±0.002	5.0
Phenyl	2.16	543	1.842	−0.090±0.002	4.1
Trityl	2.75	550	1.818	−0.069±0.001	3.6
		~560	~1.786		

a) The logarithmic value of the averaged rate constant for the chromous-ion reduction of the respective tropylium ions.
b) Measured in 1,2-dichloroethane with pyrene as a donor.
c) Corrected from the values measured in acetonitrile *vs.* Ag/AgCl, whose potential was found to be −0.162 V *vs.* SCE.
d) Measured spectrophotometrically in 23% aqueous ethanol.
e) Lit., λ_{max} 535 mμ (Ref. 7d, e).
f) Lit., pK_{R^+} 4.7 (measured by potentiometric titration in water; Ref. 15).
g) Lit., λ_{max} 503 mμ (Ref. 7e).

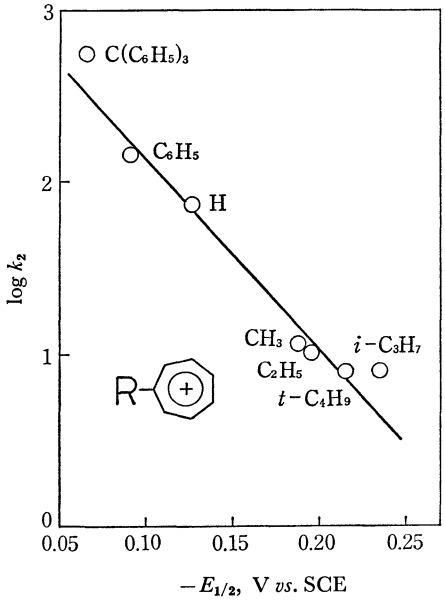


Fig. 2. The correlation of $\log k_2$ with polarographic half-wave potentials ($-E_{1/2}$).

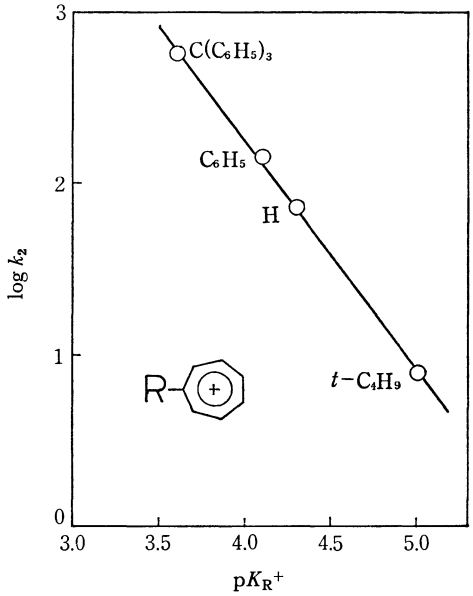


Fig. 3. The correlation of $\log k_2$ with pK_{R^+}.

the spectrophotometric method described by Breslow and Chang.[10] From the results shown in Table 3, it can be seen that, whereas the alkyl substituent increases the stability, the phenyl group rather destabilizes the cation by means of its electron-withdrawing inductive effect, as is shown by the least stability of the triphenylmethyltropylium ion. The greater contribution to the stabilization of the cation by the alkyl group than by the phenyl group has been also observed in a cyclopropenyl system.[11]

A plot of $\log k_2$ against pK_{R^+}, again, gave a good linear correlation, as is shown in Fig. 3. Since the equation for pK_{R^+} is written as Eq. (2), with the rate constants for the forward and backward reactions (k_f and k_b respectively), and since it can be assumed that the backward reaction is not greatly affected by the structural change, this correlation may be generalized to imply that the readiness of the carbonium ion to accept one electron is parallel with the reactivity of the ion toward the electron pair of the nucleophile.

$$R^+ + H_2O \underset{k_b}{\overset{k_f}{\rightleftharpoons}} ROH + H^+ \quad (1)$$

$$pK_{R^+} = \log k_b - \log k_f \quad (2)$$

Experimental[12]

Materials. All the reagents employed were of a reagent-grade quality except when otherwise noted. Aceto-

10) R. Breslow and H. W. Chang, *J. Amer. Chem. Soc.*, **83**, 2367 (1961).
11) R. Breslow, H. Hover, and H. W. Chang, *ibid.*, **84**, 3168 (1962).

12) The melting points and boiling points are uncorrected. The microanalyses were performed by the Microanalytical Center, Kyoto University, Kyoto. The infrared and ultraviolet spectra were recorded with Shimadzu spectrometers, models IR-27 and UV-50M respectively. The NMR spectra were obtained by the use of a JEOL model JNM-3H-60 spectrometer with tetramethylsilane as the internal standard. The polarograms were obtained with a Yanagimoto polarograph, model P8-DP.

nitrile and ethyl acetate were refluxed over phosphorus pentoxide and then distilled; acetonitrile, bp 81.0—81.5 °C; ethyl acetate, bp 77.0—77.4 °C.

Tropylium fluoroborate was prepared from tropilidene according to the method of Conrow.[13]

7-Methyl-, 7-ethyl-, 7-isopropyl-, and 7-*t*-butylcycloheptatrienes were obtained by the reaction of 7-ethoxycycloheptatriene with the corresponding alkyl magnesium halides, as has been reported by Nozoe and his co-workers;[14] 7-methylcycloheptatriene, bp 53 °C/63 mmHg (lit, bp 63 °C/80 mmHg[14]); 7-ethylcycloheptatriene, bp 84 °C/35 mmHg; 7-isopropylcycloheptatriene, bp 88 °C/36 mmHg (lit, bp 74 °C/33 mmHg[14]); 7-*t*-butylcycloheptatriene, 90 °C/24 mmHg (lit, bp 95—98 °C/45 mmHg.[14])

7-Phenylcycloheptatriene was prepared by the reaction of tropylium fluoroborate with phenyllithium according to the method of Doering and Knox;[15] bp 76 °C/0.4 mmHg.

7-Triphenylmethylcycloheptatriene was synthesized by reference to the thesis of Rifi.[16] In a 100-ml four-necked flask equipped with a mechanical stirrer, a thermometer, and a nitrogen inlet and outlet, there was stirred a suspension of 1.467 g (8.74 mmol) of tropylium fluoroborate in 40 ml of dry ethyl ether. To this mixture was slowly added 63 ml of a 0.14 M ethereal solution of triphenylmethylsodium (8.8 mmol), prepared from triphenylmethyl chloride and 1% sodium amalgam according to the method of Renfrow and Hauser,[17] over a 10-min period by the use of a hypodermic syringe. The dark red color of the solution of triphenylmethylsodium was instantaneously discharged when it was added to the ethereal suspension of tropylium fluoroborate. The yellowish gray mixture was stirred for a further 2 hr at 24—26 °C under nitrogen. After the addition of 100 ml of distilled water, the organic layer was separated and worked up in the usual way to give 2.928 g of a yellowish white solid, which was then chromatographed over 100 g of silica gel (Nakarai, No. II-A, 100—200 mesh). Elution with *n*-hexane–benzene (4 : 1) gave 1.263 g (3.78 mmol) of 7-triphenylmethylcycloheptatriene as white crystals; the same infrared spectrum as the authentic sample; 43.3% yield; mp 166.6—170.7 °C (dec) (lit, mps 167—170 °C (dec)[18] and 156 °C[16]).

The isomerization of 7-substituted cycloheptatrienes to the mixtures of 1-, 2-, and 3-substituted cycloheptatrienes was effected thermally by successive sigmatropic 1—5 hydrogen shifts,[19] so that the steric hindrance at the step of hydride abstraction by the triphenylmethyl cation (*vide infra*) might be diminished. 7-Methyl-, 7-ethyl-, 7-isopropyl-, 7-*t*-butyl, and 7-phenylcycloheptatrienes were sealed in Pyrex ampoules under a vacuum ($<10^{-3}$ mmHg), heated in an oil bath at 175 °C for 1.5 hr,[14] and distilled under reduced pressure; methylcycloheptatrienes, bp 65—67 °C/72 mmHg; ethylcycloheptatrienes, bp 95—98 °C/41 mmHg; isopropylcycloheptatrienes, bp 90—94 °C/35 mmHg; *t*-butylcycloheptatrienes, bp 79—80 °C/24 mmHg; phenylcycloheptatrienes, bp 77—79 °C/0.4 mmHg. 7-Triphenylmethylcycloheptatriene was dissolved in *m*-xylene and similarly sealed in a Pyrex ampoule under a vacuum. After heating at 145 °C for 5 hr, the isomer mixtures were recovered as white crystals by chromatography over silica gel (Nakarai, No. II-A, 100—200 mesh), with *n*-hexane–benzene (4 : 1) as the eluent.

Methyltropylium perchlorate (Ia) was synthesized following the method of Conrow.[20] Into a suspension of 7.00 g (0.0204 mol) of triphenylmethyl perchlorate in 40 ml of acetonitrile, we added 2.079 g (0.0195 mol) of thermally-isomerized methylcycloheptatrienes with magnetical stirring at room temperature. In 1 min, the precipitates of triphenylmethyl salt all dissolved. After 10 min, the solvent was evaporated under reduced pressure, a 50-ml portion of ethyl acetate was added, and the yellow solid mass was pulverized. Then the mixture was evaporated again, followed by the addition of another 100 ml of ether acetate and by the trituration of the solid. This time the precipitates were collected under a stream of nitrogen, washed with ten 10-ml portions of ethyl acetate, and dried in a vacuum desiccator to give 3.879 g (0.0190 mol) of crude Ia; 97.4% yield. Recrystallization from acetonitrile–ethyl ether under nitrogen gave white crystals, which rapidly decompose on exposure to air; mp 110.0—111.5 °C (lit, mp 111—112 °C[20], mp 109 °C[21]); $\lambda_{max}^{0.1\,M\,HCl}$ 287 mμ (ε, 4760) (lit, $\lambda_{max}^{conc\,H_2SO_4}$ 288 mμ (ε, 3500)[21]).

Ethyltropylium perchlorate (Ib) was obtained by the same method as white crystals with a pink tinge from the isomerized ethylcycloheptatrienes; 90.5% yield; mp 84.0—84.3 °C; $\lambda_{max}^{0.1\,M\,HCl}$ 292 mμ (ε, 4880).

Isopropyltropylium perchlorate (Ic) was similarly prepared as brownish-white crystals from the isomerized isopropylcycloheptatrienes, except that dry ethyl ether was employed instead of ethyl acetate for the washing of the product; 76.7% yield; mp 35.8—39.8 °C; $\lambda_{max}^{0.1\,M\,HCl}$ 294 mμ (ε, 5030).

t-Butyltropylium perchlorate (Id) was obtained as white crystals by the same procedure as was used in the preparation of Ia except that the reaction time was prolonged to 2 hr; 64.0% yield; mp 179.0—180.0 °C (dec); $\lambda_{max}^{0.1\,M\,HCl}$ 293 mμ (ε, 4880).

Phenyltropylium fluoroborate (Ie) was prepared as yellow crystals by the same method, except that triphenylmethyl fluoroborate was used instead of perchlorate salt; 74.9% yield; mp 151.0—152.0 °C (lit, mp 153—154 °C[22]); $\lambda_{max}^{0.1\,M\,HCl}$ 226 mμ (ε, 37700), 270.5 mμ (14800), 368 mμ (16200).

Triphenylmethyltropylium fluoroborate (If) was synthesized by an essentially similar method. In a 100-ml two necked flask equipped with a thermometer and a reflux condenser connected to soda lime tube, we charged a solution of 0.330 g (1.00 mmol) of triphenylmethyl fluoroborate in 15 ml of acetonitrile. To this solution was then added 0.336 g (1.04 mmol) of thermally-isomerized triphenylmethylcycloheptatrienes, and the whole mixture refluxed for 6.5 hr. The reaction mixture was then evaporated *in vacuo*, pulverized in 7 ml of freshly-added ethyl acetate, and evaporated again. Then an 18-ml portion of ethyl acetate was added;

13) K. Conrow, "Organic Syntheses," Vol. 43, p. 101 (1963).
14) T. Nozoe, K. Takahashi, and H. Yamamoto, This Bulletin, **42**, 3277 (1969).
15) W. von E. Doering and L. H. Knox, *J. Amer. Chem. Soc.*, **76**, 3203 (1954).
16) M. R. Rifi, Ph. D. Thesis, the University of Washington (1963), p. 105.
17) W. B. Renfrow, Jr., and C. R. Hauser, "Organic Syntheses," Coll. Vol. 2, 607 (1943).
18) K. Okamoto, K. Komatsu, T. Kinoshita, and H. Shingu, This Bulletin, **43**, 1901 (1970).
19) a) A. P. ter Borg. H. Kloosterziel, and N. van Meurs, *Rec. Trav. Chim. Pays-Bas*, **82**, 717 (1963); b) A. P. ter Borg and H. Kloosterziel, *ibid.*, **82**, 741 (1963); c) K. W. Egger, *J. Amer. Chem. Soc.*, **89**, 3688 (1967); d) T. Nozoe and K. Takahashi, This Bulletin, **38**, 665 (1965).
20) K. Conrow, *J. Amer. Chem. Soc.*, **83**, 2343 (1961).
21) H. J. Dauben, Jr., F. A. Gadecki, K. M. Harmon, and D. L. Pearson, *ibid.*, **79**, 4557 (1957).
22) J. W. Wilt and D. Piszkiewiez, *Chem. Ind.* (London), **1963**, 1761.

Table 4. Ultraviolet spectral and elementary analytical data for x,x'-disubstituted bitropyl

Substituent	λ_{max}^{EtOH} mμ (ε)	Formula	Elementary analysis Found C%	Found H%	Calcd C%	Calcd H%
Methyl	254 (7400)	$C_{16}H_{18}$	91.51	8.75	91.37	8.63
Ethyl	254 (7140)	$C_{18}H_{22}$	90.81	9.53	90.69	9.31
Isopropyl	254 (7780)	$C_{20}H_{26}$	90.45	9.83	90.16	9.84
t-Butyl	251 (7810)	$C_{22}H_{30}$	89.60	10.24	89.73	10.27
Phenyl	239 (37400) [a]	$C_{26}H_{22}$	93.27	6.64	93.37	6.63
Trityl	261 (10100)	$C_{52}H_{42}$	93.37	6.35	93.65	6.35

a) With a shoulder at 275 mμ (13700).

the yellowish precipitates were then collected, washed with three 5-ml portions of ethyl ether, and dried under reduced pressure. Recrystallization of the crude product from acetonitrile-ethyl ether yielded 0.204 g (0.485 mmol) of If as white crystals with a silvery tinge; 46.6% yield; mp 243.0—243.5 °C (dec); $\lambda_{max}^{2.9\,M\,HCl}$ 226.5 mμ (ε, 46600), 260 mμ(sh) (10500), 309 mμ (5850); NMR, τ_{CH_3CN}, 0.44 (m, 6H, tropylium ring protons), 2.34 (s, 15H, phenyl protons).

Found: C, 74.25; H, 4.77%. Calcd for $C_{26}H_{21}BF_4$: C, 74.30; H, 5.04%.

The solution of chromous chloride in 10% HCl was prepared as has previously been reported.[3]

One-Electron Reduction of the Substituted Tropylium Ions with Cr(II). In a 100-ml, four-necked flask equipped with a magnetic stirring bar, a serum rubber cap, and a nitrogen inlet and outlet, there was charged a solution of 0.258 g (1.05 mmol) of Id in 40 ml of 10% HCl. To this solution was then added 5 ml of 1 M solution of chromous chloride in 10% HCl (5 mmol) by the use of a hypodermic syringe under an atmosphere of nitrogen. The reaction mixture immediately became cloudy with an organic substance dispersed in the solution. The mixture was stirred for 10 min and worked up in the usual way to give 0.157 g (0.534 mmol) of x,x'-di-*t*-butylbitropyl as a viscous oil; 100.1% yield; NMR, τ_{CCl_4} 3.3—4.1 (m, 6.2H, H^{3-6}), 4.7—5.1 (m, 3.8H, $H^{2,7}$), 8.2 (s, 2H, H^1), 8.8, 8.9 (two s, 18H, *t*-butyl). Reductions of Ia, b, c, e, and f were carried out in the same way. The ultraviolet spectra and the results of the elementary analyses of all the products are tabulated in Table 4.

Kinetic Measurements. The reaction rate was measured in 10% HCl at 25.0±0.2 °C by a method reported previously.[3] The products were determined by ultraviolet spectroscopy using the characteristic bands listed in Table 4.

Measurements of the Charge-Transfer Bands with Pyrene. In 5 ml of the solution of pyrene in 1,2-dichloroethane (0.2 M) was dissolved 2—4 mg of the purified sample of the substituted tropylium ion salt, so that the concentration of the cation became 2×10^{-3} g-ion/l. A red color immediately developed; the visible spectrum was then recorded to give the results shown in Table 3.

Determination of pK_{R^+}*'s.* The determination of the pK_{R^+} in 23% aqueous ethanol was carried out spectrophotometrically following the method of Breslow and Chang.[10] The ultraviolet spectrum was recorded on each cation in nine or ten solutions of buffer spaced through a pH range of about two units on each side of the pK_{R^+}. The buffer solutions were made up from various mixtures of 0.1 M citric acid and 0.2 M Na_2HPO_4 according to the procedure of Gomori.[23] The absorbancy at a wavelength characteristic of the cation, described above, was plotted against the pH to give a classical titration curve, whose mid-point was taken as the pK_{R^+}. The pH's were read on a Horiba model H pH meter calibrated with standard buffers before use.

Polarography. The polarograms were obtained on the solutions of the respective cations in acetonitrile (1.0×10^{-3} g-ion/l) containing $Et_4N^+ClO_4^-$ (0.5 M) as the supporting electrolyte at 25 °C. As the reference electrode, we used the Ag/AgCl electrode described by Popov and Geske,[24] whose potential was found to be −0.162 V *vs.* SCE.

23) G. Gomori in S. P. Colowick and N. O. Kaplan, "Methods in Enzymology," Vol. I, Academic Press, New York, N. Y. (1955), p. 138.

24) A. I. Popov and D. H. Geske, *J. Amer. Chem. Soc.*, **79**, 2074 (1957).