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The One-electron Reduction of Carbonium Ions. VIII. The Reducibility of Hetero-substituted Tropylium Ions as Measured by the Competitive Reduction Method with Zinc Powder

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A series of hetero-substituted tropylium salts ($\mathrm{X\text{-}C_7H_6^+\cdot Y^-}$), including three new compounds, have been synthesized. Their relative reactivities in one-electron reductions with zinc powder have been determined by the use of a competitive-reaction method, which gave the following reactivity sequence: $\mathrm{CH_3O\text{-}C_7H_6^+}$ ($k_{\mathrm{rel.}}=0.0295$), t-$\mathrm{C_4H_9\text{-}C_7H_6^+}$ (0.146), $\mathrm{CH_3S\text{-}C_7H_6^+}$ (0.255), $\mathrm{C_7H_7^+}$ (1.00), $\mathrm{C_6H_5\text{-}C_7H_6^+}$ (2.50), $\mathrm{(C_6H_5)_3Si\text{-}C_7H_6^+}$ (7.50), $\mathrm{Cl\text{-}C_7H_6^+}$ (16.8), $\mathrm{CH_3OCO\text{-}C_7H_6^+}$ (35.7), $\mathrm{NC\text{-}C_7H_6^+}$ (163). The values of log $k_{\mathrm{rel.}}$ for the t-$\mathrm{C_4H_9}$-, H-, and $\mathrm{C_6H_5\text{-}C_7H_6^+}$ ions exhibit a good linear relationship with those of log k_2 in the chromous-ion reduction. A linear correlation is also observed between log $k_{\mathrm{rel.}}$ and the transition energy for the charge-transfer band of the respective cations, with pyrene as a donor. A plot of log $k_{\mathrm{rel.}}$ against σ_p (for the ring substituent, X) gives a greater ρ-value (+4.0) than in the case of $\mathrm{X\text{-}C_6H_4\text{-}C_7H_6^+}$ (+1.31), reflecting the influence of the direct substitution on the tropylium ring.

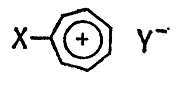
In earlier publications,1) we have demonstrated that the "one-electron" reducibility (log k_2) for some of the substituted tropylium and cyclopropenium ions in the chromous-ion reduction is linearly correlated with the electron affinity, which was estimated from the transition energy for the charge-transfer bands of the respective cations, with pyrene as the donor. Also, with respect to substituted phenyltropylium ions, the existence of the Hammett linear free-energy relationship was demonstrated.1d) We were, therefore, encouraged to extend these studies to the tropylium ions with a variety of hetero-substituents which are directly bonded to the seven-membered ring.

However, the previous method of the chromous-ion reduction is not applicable to the hetero-substituted tropylium ions because of the instability of these cations in "aqueous" media. Furthermore, acetonitrile, in which these cations are stable, is not a good solvent for chromous ion. Hence, we have attempted to estimate the relative reducibility of these substituted tropylium ions by the use of a competitive heterogeneous reduction with zinc powder in "anhydrous" acetonitrile. The use of zinc powder as a one-electron reductant for the carbonium ions has been well documented2) since the first observation of the zinc reduction of the tropylium ion to give bitropyl reported by Doering and Knox.2a) In addition, the formation of the radical species (tropyl radical) in the course of the zinc reduction of the tropylium ion has been proved by the radical-trapping technique.3)

In this paper, the correlation of the reducibility of the hetero-substituted tropylium ions with the electron affinity and the substituent effect on the rates of reduction will be discussed by the use of the relative reduction rates as measured by the competitive-reduction method.

Results and Discussion

Syntheses of the Hetero-substituted Tropylium Ions. Among the perchlorates of the hetero-substituted tropylium ions, I-VIII, those of the chloro-4) (III), methoxy5) (VI), diethylamino-6) (VII), and t-butylamino-6) (VIII) derivatives were prepared according to the literatures. The cyano- (I), carbomethoxy-(II) and methylthiotropylium4) (V) perchlorates were synthesized by hydride abstraction from the corresponding 3-substituted 1,3,5-cycloheptatrienes, which had been obtained from the 7-substituted derivatives7) by thermal isomerization. The triphenylsilyltropylium perchlorate (IV) was synthesized in the same way from 7-triphenylsilyl-1,3,5-cycloheptatriene, which had itself been obtained by the reaction of 7-ethoxy-1,3,5-cycloheptatriene with triphenylsilyllithium.8) Among these salts, I,9) II, and IV are new compounds.



	X	Y
I	-CN	$\mathrm{ClO_4}$
II	$\mathrm{-CO_2CH_3}$	$\mathrm{ClO_4}$
III	-Cl	$\mathrm{ClO_4}$
IV	$\mathrm{-Si(C_6H_5)_3}$	$\mathrm{ClO_4}$
V	$\mathrm{-SCH_3}$	$\mathrm{ClO_4}$
VI	$\mathrm{-OCH_3}$	$\mathrm{ClO_4}$
VII	$\mathrm{-N(C_2H_5)_2}$	$\mathrm{ClO_4}$
VIII	-NH-t-$\mathrm{C_4H_9}$	$\mathrm{ClO_4}$
IX	$\mathrm{-C_6H_5}$	$\mathrm{BF_4}$
IX′	$\mathrm{-C_6D_5}$	$\mathrm{BF_4}$
X	-H	$\mathrm{BF_4}$
XI	-t-$\mathrm{C_4H_9}$	$\mathrm{ClO_4}$

Previously, we have observed a homolytic dissociation of 7-triphenylmethyl-1,3,5-cycloheptatriene into the tropyl (cycloheptatrienyl) and triphenylmethyl radicals by means of ESR measurements at 60—95 °C.10) Larrabee11) has found that 7-triphenylstannic-1,3,5-cycloheptatriene undergoes a similar thermal cleavage at 160 °C and also reported on the fluxional behavior of the triphenylstannic group around the seven-membered ring on the basis of NMR measurements at 0—139 °C. The ease of these homolytic cleavages may be attributed to the considerable resonance-stabilization of the "symmetrical" tropyl radical.12) However, in spite of the close similarity of the structure, 7-triphenylsilyl-1,3,5-cycloheptatriene does not exhibit such behavior. It does not show any evidence of bitropyl formation when heated at 200 °C, indicating the resistance of the C-Si bond to homolytic dissociation.

Competitive Reductions. First, the one-electron reduction of each single cation with an excess (twenty-fold of the theoretical amount) of zinc powder was carried out in acetonitrile for ten minutes. An almost quantitative formation of the x,x'-disubstituted bitropyl was confirmed, except for the aminotropylium ions, VII and VIII, which were not reduced, but were recovered unchanged under these conditions. This indicates the exceptional stability due to electron donation by the amino group. The analytical and spectral data for x,x'-disubstituted bitropyls are tabulated in Table 2 (see Experimental).

Then, the competitive reduction was conducted as follows. Each pair of equal amounts of cations (R_A^+, R_B^+) was subjected to a competitive reduction in acetonitrile at 25 °C with zinc powder 1/4∼1/2 of the theoretical amount required for the complete reduction of a single cation. The mixture of the coupling products of the radicals formed from both cations (R_A–R_A, R_A–R_B, R_B–R_B) was then extracted. The yield of each radical was determined from the weight of the coupling-product mixture and by NMR analysis.[13] In each case, the material balance of the reduction was found to be 90—105% from the UV analysis of the unchanged cation. When we assume the first-order dependence of the reaction rate on the cation concentration, the ratio of rate constants for the competing cations is expressed by the following equation:[14]

$$k_A/k_B = \log([R_A^+]/[R_A^+]_0)/\log([R_B^+]/[R_B^+]_0)$$

where $[R_A^+]_0$ and $[R_B^+]_0$ denote the initial concentrations of the R_A^+ and R_B^+ cations respectively. The application of this equation to the present case was justified by the linearity of the plot of $\log([R_A^+]/[R_A^+]_0)$ against $\log([R_B^+]/[R_B^+]_0)$ through the point of origin, with regard to each cation pair, as is shown in Figs. 1 and 2. From the slope of each straight line, the relative rate constant ($k_{\mathrm{rel.}}$) for the zinc reduction of each cation was determined. The results are listed in Table 1, together with the charge-transfer maxima (*vide infra*) of the respective cations.

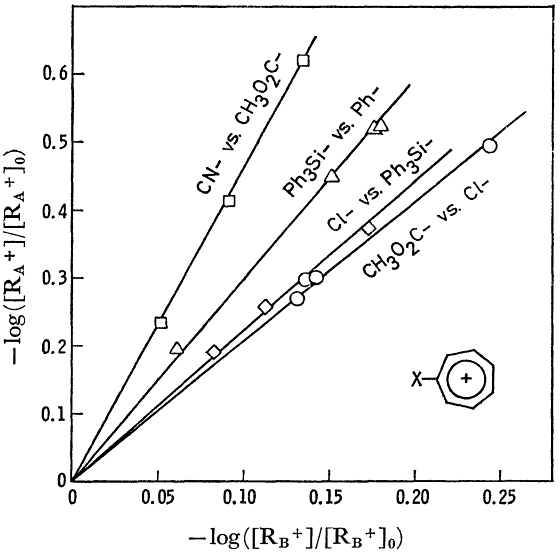


Fig. 1. Plot of $-\log([R_A^+]/[R_A^+]_0)$ *vs.* $-\log([R_B^+]/[R_B^+]_0)$ for the competitive reduction of NC-, CH_3OCO-, Cl-, $(C_6H_5)_3Si$-, and C_6H_5-$C_7H_6^+$ with Zn in CH_3CN at 25 °C.

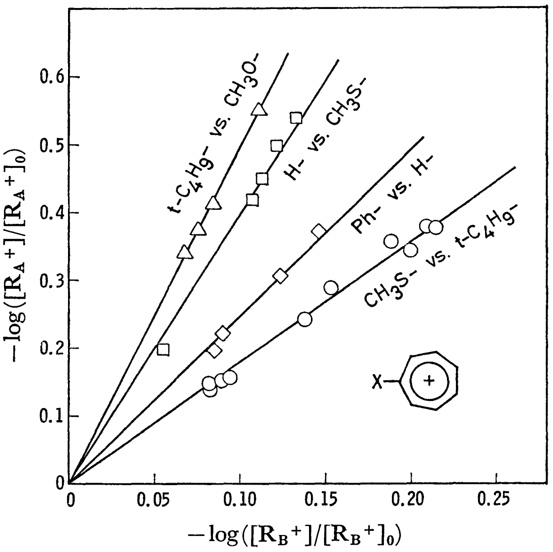


Fig. 2. Plot of $-\log([R_A^+]/[R_A^+]_0)$ *vs.* $-\log([R_B^+]/[R_B^+]_0)$ for the competitive reduction of C_6H_5-, H-, CH_3S-, t-C_4H_9-, and CH_3O-$C_7H_6^+$ with Zn in CH_3CN at 25 °C.

Table 1. Relative rate constants for the zinc reduction of hetero-substituted tropylium ions and absorptions of their charge-transfer spectra

Substituent	$k_{\mathrm{rel.}}$[a]	$\log k_{\mathrm{rel.}}$	C. T. band[b]	
			$\lambda_{\max}$ nm	$\nu_{\max}$ $10^4\,\mathrm{cm}^{-1}$
CH_3O-	0.0295	−1.530	480	2.083
t-C_4H_9-	0.146	−0.836	508	1.969
CH_3S-	0.255	−0.594	510	1.961
H-	1.000	0.000	540	1.852
C_6H_5-	2.50	0.398	543	1.842
$(C_6H_5)_3Si$-	7.50	0.875	555	1.802
Cl-	16.8	1.225	580	1.724
CH_3OCO-	35.7	1.552	610	1.639
NC-	163	2.212	680	1.471

a) Determined by the competitive reduction in acetonitrile at 25 °C. b) Measured in 1,2-dichloroethane with pyrene as a donor.

In order to compare the results obtained by the present method ($k_{\mathrm{rel.}}$) with that determined from the homogeneous chromous-ion reduction (k_2), $\log k_{\mathrm{rel.}}$ was plotted against $\log k_2$. A linear correlation with the slope of 0.98 has been observed, as is shown in Fig. 3. This result clearly indicates that, in spite of the heterogeneous condition, the present method gives reasonably correct relative values for the reducibility inherent in the carbonium ions.

The Correlation of log $k_{\mathrm{rel.}}$ with the Charge-transfer Energy. In order to examine the correlation of the reducibility with the electron affinity, the values of $\log k_{\mathrm{rel.}}$ were plotted against the wave number corresponding to the maximum absorption at the charge-transfer spectrum ($\nu_{\max}$, see Table 1) of each substituted tropylium ion, with pyrene as the standard electron donor. A good linear correlation was obtained, as is shown in Fig. 4. Since, for a given donor molecule,

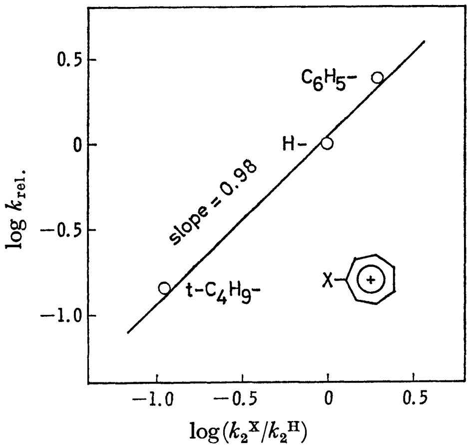


Fig. 3. Plot of $\log k_{\mathrm{rel.}}$ measured by the competitive reduction *vs.* $\log(k_2^{\mathrm{X}}/k_2^{\mathrm{H}})$ determined by the chromous-ion reduction.

the $\nu_{\max}$ for the charge-transfer spectrum of a series of acceptors should correlate with the electron affinity of the acceptors,[15] this correlation (Fig. 4) clearly indicates that the reducibility of these cations is essentially regulated by the electron affinity inherent in the cation itself. Thus, the correlation[1] which holds for the alkyl- and aryl-substituted tropylium and cyclopropenium series has been successfully extended to a series of hetero-substituted tropylium ions.

The Correlation of $\log k_{\mathrm{rel.}}$ *with Hammett's* σ_p. The variation in the reactivity of substituted tropylium ions obviously reflects the influence of the electronic stabilization or destabilization caused by these substituents. In order to compare the substituent effect with that observed in the case of substituted phenyltropylium ions, the values of $\log k_{\mathrm{rel.}}$ were plotted against Hammett's σ_p[16] (Fig. 5). The one-electron reducibility of the substituted tropylium ion thus measured is considered to be an average of the reactivity of the seven individual carbon atoms in the ring toward the reductant. Hence, the use of a single σ_p constant, though it includes both resonance and inductive electronic effects, may not be explicitly called for. This is perhaps one of the causes of the scatters in Fig. 5.[17] Thus, although we can not avoid such a theoretical ambiguity, if we express the sensitivity to the substituent effect with the ρ-value it will amount to about +4.0. The increase in ρ-value, compared with that obtained in the case of a substituted phenyltropylium system (+1.31),[1d] is evidently caused by the direct transmission of the electronic effect of the substituent to the tropylium ring.

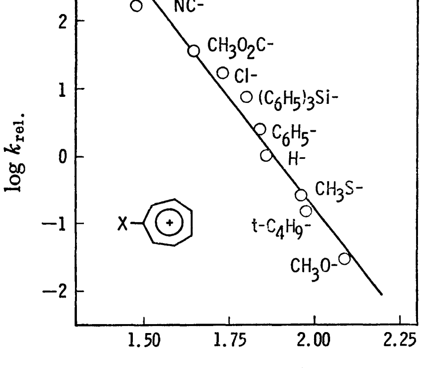


Fig. 4. Plot of $\log k_{\mathrm{rel.}}$ *vs.* $\nu_{\max}$ of the charge-transfer spectra.

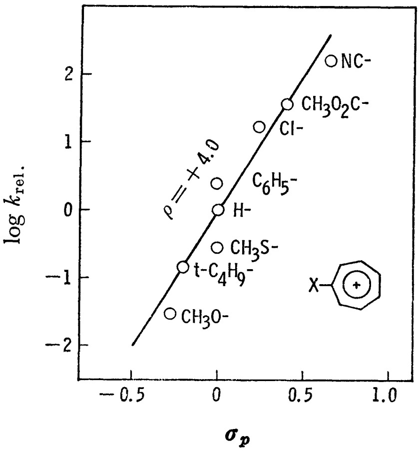


Fig. 5. Plot of $\log k_{\mathrm{rel.}}$ *vs.* Hammett's σ_p.

Experimental[18]

Materials. All the reagents employed were of a reagent-grade quality. The acetonitrile and ethyl acetate were refluxed and distilled over phosphorus pentoxide; acetonitrile, bp 80.5—81.1 °C; ethyl acetate, bp 75.5—76.5 °C. The carbon tetrachloride, chloroform and 1,2-dichloroethane were refluxed and distilled over calcium chloride; carbon tetrachloride, bp 75.0—75.5 °C; chloroform, bp 60.0—60.3 °C; 1,2-dichloroethane, bp 83.0—83.5 °C. The tetrahydrofuran (THF) was distilled over lithium aluminum hydride; bp 66.0—66.4 °C.

The chloro-[4] (III), methoxy-[5] (VI), diethylamino-[6] (VII), and *t*-butylamino-[6] (VIII) tropylium perchlorates were prepared by the methods reported in the literature; III, mp 175.0—176.0 °C (lit, mp 172—173 °C[4]), $\lambda_{\max}^{\mathrm{CH_3CN}}$ 232 nm (ε, 37200), 308 nm (9100) (lit, $\lambda_{\max}^{\mathrm{CH_3CN}}$ 232 nm ($\log \varepsilon$, 4.57), 308 nm (3.96)[4]); VI, mp 107.0—107.5 °C (lit, mp 107 °C[5]), $\lambda_{\max}^{\mathrm{CH_3CN}}$ 232 nm (ε, 34700), 313 nm (11000) (lit, $\lambda_{\max}^{\mathrm{CH_3CN}}$ 232 nm ($\log \varepsilon$, 4.54) 313 nm (4.04)[4]); VII, mp 68.0—72.0 °C (lit, mp 75—76 °C,[6]), $\lambda_{\max}^{\mathrm{CH_3CN}}$ 241 nm (ε, 20000) 335 nm (16300) (lit, $\lambda_{\max}^{\mathrm{CH_3CN}}$ 241 nm ($\log \varepsilon$, 4.30), 335 nm (4.21)[6]); VIII, mp 111.5—112.0 °C (lit, mp 112—113 °C[6]), $\lambda_{\max}^{\mathrm{CH_3CN}}$ 239 nm (ε, 18400), 242.5 nm (18400), 333 nm (13000) (lit, $\lambda_{\max}^{\mathrm{CH_3CN}}$ 237 nm ($\log \varepsilon$, 4.35), 330 nm (4.18)[6]).

The phenyl- (IX) and unsubstituted (X) tropylium fluoroborates and *t*-butyltropylium perchlorate (XI) were prepared by previously-reported methods.[1b]

Synthesis of Cyanotropylium Perchlorate (I). 7-Cyano-1,3,5-cycloheptatriene[2a] was heated in an evacuated ampoule at 175 °C for 1.5 hr and distilled under reduced pressure to give a mixture of 3- and 1-cyano-1,3,5-cycloheptatrienes; bp 86.5—90.0 °C/5 mmHg. To a solution of 3.498 g (29.8 mmol) of an isomeric mixture of cyanocycloheptatrienes in 7.7 ml of acetonitrile, we added 10.231 g (29.8 mmol) of triphenylmethyl (trityl) perchlorate. The mixture was magnetically stirred at 60 °C for 1 hr and then at 80 °C for 5 min; most of the crystals of trityl perchlorate thereby disappeared and the mixture turned dark red. After the addition of 26 ml of ethyl acetate, the mixture was cooled to 0 °C, The pale yellow crystals that separated out were collected by filtration, washed successively with ethyl acetate and ether, and dried *in vacuo* to give 4.885 g (22.7 mmol) of I; 76.2% yield. For the analyses, I was purified by recrystallization from acetonitrile-ethyl acetate; mp 158.0 °C (decomposition with violent explosion); $\lambda_{\max}^{\mathrm{CH_3CN}}$ 293 nm (ε, 6610), 298 nm (6450); $\nu_{\max}^{\mathrm{KBr}}$ 3020, 2220, 1630, 1595, 1525, 1480, 1440, 1380, 1150—1080, 955, 940, 870, 740 cm^{-1}; NMR, $\tau_{\mathrm{CF_3COOH}}$ 0.4 (s, tropylium ring protons).

Found: C, 44.34; H, 2.81%. Calcd for $\mathrm{C_8H_6NClO_4}$: C, 44.57; H, 2.81%.

Synthesis of Carbomethoxytropylium Perchlorate (II). 7-Carbomethoxy-1,3,5-cycloheptatriene[7)] was thermally isomerized at 175 °C for 1.5 hr to give a mixture of 3- and 1-carbomethoxy-1,3,5-cycloheptatrienes; bp 74.0—77.0 °C/3 mmHg. In 6.4 ml of acetonitrile, 3.509 g (23.4 mmol) of a mixture of carbomethoxycycloheptatrienes was allowed to react with 8.012 g (23.3 mmol) of trityl perchlorate with magnetic stirring at 60 °C for 6 min; the trityl salt disappeared almost instantaneously when the mixture was heated, and instead pale yellow crystals separated. After the addition of 24 ml of ethyl acetate, the mixture was cooled to 0 °C and then filtered to give 5.427 g (21.8 mmol) of II as pale yellow crystals; 93.4% yield; mp 143.0—143.3 °C (after recrystallization from acetonitrile-ethyl acetate); $\lambda_{\max}^{\mathrm{CH_3CN}}$ 225.5 nm (ε, 43000), 286 nm (4660); $\nu_{\max}^{\mathrm{KBr}}$ 3015, 2960, 1730, 1615, 1480, 1440, 1370, 1350, 1290, 1270, 1250, 1150—1070, 970, 940, 925, 870, 805, 760, 740, 680 cm^{-1}; NMR, $\tau_{\mathrm{CF_3COOH}}$ 0.0 (m, 2H, tropylium ring protons), 0.5 (m, 4H, tropylium ring protons), 5.7 (s, 3H, methyl protons).

Found: C, 43.21; H, 3.58%. Calcd for $\mathrm{C_9H_9ClO_6}$: C, 43.48; H, 3.65%.

Synthesis of Methylthiotropylium Perchlorate (V). To a magnetically-stirred solution of 10.356 g (58.1 mmol) of tropylium fluoroborate in 110 ml of 0.1 M HCl, we added 9.5 g of a 30% methanolic solution of methanethiol (58.7 mmol); a slightly exothermic reaction then took place, and the solution turned yellow. After stirring for 20 min at room temperature, the turbid solution was extracted with three 100-ml portions of ether, washed with 10% NaCl, and dried over $\mathrm{MgSO_4}$. The ethereal solution, after evaporation and distillation, gave 4.309 g (31.2 mmol) of 7-methylthio-1,3,5-cycloheptatriene as a pale yellow oil; 53.6% yield; bp 74 °C/5 mmHg; NMR, $\tau_{\mathrm{CCl_4}}$ 3.5 (t, 2H, $\mathrm{H^{3,4}}$), 3.9 (m, 2H, $\mathrm{H^{2,5}}$), 4.7 (d of d, 2H, $\mathrm{H^{1,6}}$), 6.9 (t, 1H, $\mathrm{H^7}$), 7.9 (s, 3H, methyl protons).

Found: C, 69.72; H, 7.42%. Calcd for $\mathrm{C_8H_{10}S}$: C, 69.51; H, 7.29%.

A solution of 2.092 g (15.1 mmol) of the isomeric mixture of methylthiocycloheptatrienes (bp, 50.0—61.0 °C/4 mmHg), obtained by the thermal isomerization described above, in 10 ml of acetonitrile was added to a magnetically-stirred suspension of 5.205 g (15.2 mmol) of trityl perchlorate in 10 ml of acetonitrile over a 2-min period at room temperature. During the addition, the reaction temperature rose from 22.5 °C to 30.0 °C and all the trityl salt dissolved to give a dark red solution. After stirring for 15 min at room temperature, 100 ml of ethyl acetate was added and the mixture was cooled to 0 °C. The yellow crystals that thus separated out were collected, washed, and dried as has been described above to give 2.860 g (12.1 mmol) of V: 80.0% yield; mp 114.0—115.0 °C (lit, mp 114—115 °C[4)]); $\lambda_{\max}^{\mathrm{CH_3CN}}$ 219.5 nm (ε, 23300), 260 nm (17000), 380 nm (19800) (lit, $\lambda_{\max}^{\mathrm{CH_3CN}}$ 258 nm (ε, 14800), 378 nm (17400)[4)]); $\nu_{\max}^{\mathrm{KBr}}$ 3010, 2910, 1615, 1600, 1510, 1470, 1430, 1420(sh), 1370, 1325, 1280, 1235, 1225, 1120—1040, 845, 740 cm^{-1}.

Synthesis of 7-Triphenylsilyl-1,3,5-cycloheptatriene. To a stirred solution of 5.791 g (45.9 mmol) of 7-ethoxy-1,3,5-cycloheptatriene in 20 ml of THF, we added 130 ml of a THF solution of triphenylsilyllithium, prepared from 15.0 g (51.0 mmol) of triphenylsilyl chloride and 1.40 g (0.202 g-atom) of lithium according to the method of Gilman *et al.*, [8)] by the use of a hypodermic syringe over a 25-min period at room temperature; the reaction temperature rose from 25.0 °C to 35.0 °C, and the dark reddish brown color of triphenylsilyllithium, which was, at the beginning, instantaneously discharged upon addition to the ethoxycycloheptatriene solution, began to remain during the course of addition. The dark brown mixture with white precipitates was stirred at room temperature for 2.5 hr and then left to stand overnight. Then, 150 ml of 10% HCl was cautiously added and the mixture was worked up in the usual way to give 17.5 g of a partially-solidified yellowish oil, from which, upon recrystallization from benzene, 0.451 g (0.836 mmol) of hexaphenyldisilane was separated as white crystals; mp 355—360 °C (lit, mp 361—362 °C[8)]); the IR spectrum was identical with that of the authentic sample. The mothor liquor was concentrated *in vacuo*, and the residual solid, upon recrystallization from ethanol, gave 3.338 g (9.53 mmol) of 7-triphenylsilyl-1,3,5-cycloheptatriene as white crystals; this compound begins to melt at 152 °C, but at 155 °C another solid, presumably the 3-triphenylsilyl isomer, appears, which eventually melts at 178 °C; NMR, $\tau_{\mathrm{CCl_4}}$ 2.6 (m, 15H, phenyl protons), 3.4 (t, 2H, $\mathrm{H^{3,4}}$), 3.7 (m, 2H, $\mathrm{H^{2,5}}$), 4.8 (d of d, 2H, $\mathrm{H^{1,6}}$), 8.2 (t, 1H, $\mathrm{H^7}$).

Found: C, 85.48; H, 6.07%. Calcd for $\mathrm{C_{25}H_{22}Si}$: C, 85.66; H, 6.33%.

The filtrate of the recrystallization, upon evaporation, gave 12.260 g of a yellowish solid, which was then chromatographed over 310 g of silica gel (Nakarai, No. II-A, 100—200 mesh). From the fractions eluted with *n*-hexane-benzene (9 : 1—6 : 1) we obtained a mixture of 0.163 g (0.898 mmol) of bitropyl and 0.340 g (0.131 mmol) of triphenylsilane; the composition was determined by the NMR analysis. From the fractions eluted with *n*-hexane-benzene(3 : 1) we isolated 4.654 g (13.3 mmol) of 7-triphenylsilyl-1,3,5-cycloheptatriene, whereas the following fractions, when eluted with *n*-hexane-benzene(2 : 1), gave 0.657 g (1.22 mmol) of hexaphenyldisilane after recrystallization from chloroform. In addition, the fractions eluted with benzene-ether (1 : 1) afforded 3.364 g (12.2 mmol) of triphenylsilanol after recrystallization from benzene; mp 152—155 °C (lit, mp 153—155 °C[8)]).

Thus, the yields of each isolated product may be summarized as follows: bitropyl, 3.9%; 7-triphenylsilyl-1,3,5-cycloheptatriene, 47.5%; the tropylium ion, 21.2% (as determined from the UV spectrum of the aqueous layer); hexaphenyldisilane, 4.8% (based on triphenylsilyl chloride); triphenylsilane, 2.6% (*vide supra*); triphenylsilanol, 24.1% (*vide supra*).

7-Triphenylsilyl-1,3,5-cycloheptatriene was sealed in a Pyrex tube under a vacuum and heated at 200 °C for 30 min. The tlc analysis of the recovered sample indicated the presence of an isomeric mixture of triphenylsilylcycloheptatrienes, but no spot corresponding to bitropyl was detected.

Synthesis of Triphenylsilyltropylium Perchlorate (IV). 7-Triphenylsilyl-1,3,5-cycloheptatriene was thermally isomerized at 150 °C for 5 hr to give 3-triphenylsilyl-1,3,5-cycloheptatriene; NMR, $\tau_{\mathrm{CCl_4}}$ 2.6 (m, 15H, phenyl protons), 3.1 (d, 1H, $\mathrm{H^4}$), 3.7 (m, 2H, $\mathrm{H^{2,5}}$), 4.5 (m, 2H, $\mathrm{H^{1,6}}$), 7.7 (t, 2H, $\mathrm{H^7}$). A suspension of 0.638 g (1.82 mmol) of the triphenylsilylcycloheptatriene and 0.634 g (1.85 mmol) of trityl perchlorate in 10 ml of acetonitrile was magnetically stirred at 55 °C for 30 min and then at 80 °C for 5 min to give a dark red solution. After the addition of 100 ml of ethyl acetate, the solution was cooled to 0 °C. The glittering, brownish crystals that separated out were collected in the usual way to give 0.702 g (1.57 mmol) of IV; 86.0% yield. Recrystallization from acetonitrile–ethyl acetate gave a mp of 188.0 °C (decomposition with explosion); $\lambda_{\max}^{CH_3CN}$ 218 nm (ε, 65000), 265 nm (sh) (6960), 271.5 nm (6800), 281 nm (6500); $\lambda_{\max}^{KBr}$ 3080, 3050, 3020, 1590, 1485, 1440(sh), 1430, 1380, 1265, 1240, 1190, 1160, 1120—1070, 1030, 1000, 940, 870, 750, 745(sh), 715, 700, 680 cm^{-1}; NMR, τ_{CH_3COOH} 0.5—0.8 (m, 6H, tropylium ring protons), 2.5 (s, 15H, phenyl protons).

Found: C, 66.80; H, 4.52%. Calcd for $C_{25}H_{21}SiClO_4$: C, 66.88; H, 4.72%.

Synthesis of Phenyl-d$_5$*-tropylium Perchlorate (IX′).* For the purpose of product analysis in the competitive reduction of IV and IX (*vide infra*), the phenyl-d_5 derivative of IX was synthesized from bromobenzene-d_5,[19] following the methods used for the preparation of IX;[1b] mp 152.0—153.0 °C (dec) (lit, mp for IX 151.0—152.0 °C[1b]); $\nu_{\max}^{KBr}$ 3020, 3000, 2950, 2270, 2080, 1630, 1600, 1520, 1480, 1440, 1430, 1380, 1315, 1283, 1273, 1240, 1200, 1130—1000, 880, 860, 845, 830, 800, 790, 740 cm^{-1}; NMR, τ_{CF_3COOH} 0.6—0.9 (m, tropylium ring protons).

One-electron Reduction of the Substituted Tropylium Ions with Zinc Powder. To a magnetically-stirred solution of 0.500 g (2.01 mmol) of II in 20 ml of acetonitrile, we added 1.315 g (20.1 mg-atom) of zinc powder. The mixture was stirred for 10 min at room temperature under an atmosphere of nitrogen. The excessive zinc was then filtered off, and 40 ml of carbon tetrachloride and 40 ml of water were added to the filtrate, which was then worked up in the usual way to give 0.317 g (1.06 mmol) of x,x′-dicarbomethoxybitropyl as a viscous oil; 105.6% yield; NMR, τ_{CCl_4} 2.2—4.7 (m, 10H, olefinic ring protons), 6.1 and 6.2 (s, 6H, methyl), 8.0 (br, 2H, methine).

The Reductions of I, III, IV, V, VI, IX, and XI were carried out in the same way to give the disubstituted bitropyls in yields of 91—108%. The UV spectra and the results of the elemental analyses of all the products are tabulated in Table 2.

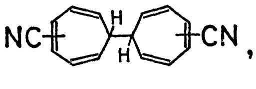
Under the same reaction conditions, 0.0557 g (0.239 mmol) of VII was allowed to react with 0.160 g (2.46 mg-atom) of zinc powder in 2 ml of acetonitrile. After filtration, 20 ml of ether was added to the filtrate and the white precipitates that separated were collected in the usual way to give 0.0503 g (0.216 mmol) of unchanged VII; 90.4% recovery. The ethereal filtrate gave 0.0015 g of an unidentified oily substance. An attempted reduction of VIII, with the same procedures, also resulted in a 106% recovery of VIII.

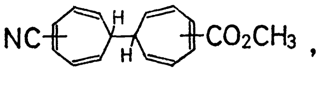
Table 2. Ultraviolet spectral and analytical data for x,x′-disubstituted bitropyls[a]

Substituent	UV		Elemental analysis	
	$\lambda_{\max}^{EtOH}$ nm	(ε)	Found (Calcd) C %	H%
CH_3O-	250.5	(6580)	79.08	7.50
	285	(5270)	(79.31)	(7.49)
CH_3S-	302	(8800)	70.06	6.84
			(70.02)	(6.61)
$(C_6H_5)_3Si$-	255.5	(11800)	85.73	6.10
	261	(11820)	(85.91)	(6.06)
	265(sh)	(11050)		
Cl-	261	(6800)	66.94	4.81
			(66.95)	(4.82)
CH_3O_2C-	223.5	(37100)	71.73	6.01
			(72.47)	(6.08)
NC-	263	(6340)	82.60	5.47
			(82.73)	(5.21)

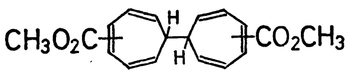
[a] As for the data for diphenyl-, di-*t*-butyl-, and unsubstituted bitropyls, see Ref. 1b.

Competitive Reductions. With respect to the competitive reduction of the I, II, III, IV, IX, and X cations the details of the procedures may be illustrated by the following description of a representative run for the competition of I and II. Into a 25-ml, four-necked flask equipped with a thermometer, a magnetic-stirring bar, and a nitrogen inlet and outlet, which had been immersed in a water bath thermostated at 25.0 °C, there was stirred a solution of 0.108 g (0.502 mmol) of I and 0.125 g (0.503 mmol) of II in 5.0 ml of acetonitrile. To this solution we then added 0.0169 g (0.259 mg-atom) of zinc powder, and the mixture was stirred under a nitrogen atmosphere for 10 min. The reaction appeared to be very fast, completing in less than 1 min, as indicated by the rapid disappearance of the zinc powder. The solution was evaporated under reduced pressure to give an oily solid, which was then extracted in five portions with 25 ml of carbon tetrachloride. The carbon tetrachloride solution was washed with three 35-ml portions of water, dried over $MgSO_4$, and evaporated to give 0.0626 g of a colorless oil, which was then analyzed by means of NMR as follows: regarding the product oil as a mixture of substituted bitropyls such as,



,


,



the molar ratio of the cyano- and carbomethoxytropyl groups was determined to be 3.32 : 1.00 from the relative values of the integrated intensities (average of 5 measurements) for the signals corresponding to the methyl protons and the total olefinic ring protons (H^{2-7}). From this molar ratio and the weight of the product mixture, the radical yield was calculated to be 77.2% for the reduction of I and 23.3% for the reduction of II. On the other hand, the residual solid from the carbon-tetrachloride extraction was dissolved in acetonitrile and subjected to UV analysis. The amounts of the unchanged cations, I and II, were determined to be 0.116 mmol (23.1% recovery) and 0.373 mmol (74.2% recovery) respectively by the use of the absorbance and the molar extinction coefficient of each cation at the wave lengths corresponding to the maximum absorptions of the individual cations, assuming the additivity of the absorbance of the respective cations at each wavelength. The results of the competitive reduction were treated as has been described above. For the competition of IV and IX, the phenyl-d_5 derivative (IX′)[20] was employed instead of IX itself, so that the NMR analysis of the product ratio became more accurate by integrating the signals for phenyl protons which came from IV and the total of the olefinic ring protons.

With respect to the V, VI, X, and XI cations, exactly the same method was adopted except for the following procedures: after the reaction, 20 ml of 10% HCl was added to the reaction mixture, after which the products were extracted with ether, worked up, and analyzed as has been described above, while the unchanged cations were determined by UV analyses of the acidic aqueous layer.

The validity of the analytical methods described above is verified by the fairly good material balance (90—105%) obtained in each case.

Measurements of the Charge-transfer Bands with Pyrene. The charge-transfer spectra were measured in 1,2-dichloroethane as has been reported previously.[1b] The concentrations of the donor (pyrene) and of the acceptor (the substituted tropylium ion) were 0.1 M and 1×10^{-3} M respectively. The previously-described[1d] precautions were taken against the light, and the spectra were measured immediately after the preparation of the sample solution.

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16) The values of σ_p were cited from D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958), except that for -CO_2CH_3, which was cited from H. van Bekkum, P. E. Verkade, and B. M. Wepster, *Rec. Trav. Chim.*, **78**, 815 (1959).

17) When log $k_{\text{rel.}}$ is plotted against Brown's $\sigma_p{}^+$ (H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, **80**, 4979 (1958)), the correlation is worse than that in Fig. 5. This may be a reflection of the fact that the extent of conjugation of the substituent with the seven-membered ring is not changed so much throughout the reaction path from the tropylium ion to the tropyl radical, whereas, from the definition, $\sigma_p{}^+$ is applicable to those reactions in which the conjugative interaction of the carbonium-ion center with the substituent arises and develops during the course from the ground state to the intermediate.

18) The melting points and boiling points are uncorrected. The elemental analyses were performed by the Microanalytical Center, Kyoto University, Kyoto. The infrared and ultraviolet spectra were recorded on a Hitachi model 215 and Shimadzu model UV-50M spectrometers repsectively. The NMR spectra were taken with a Hitachi model R-24 spectrometer with tetramethylsilane as the internal standard.

19) Bromobenzene-d_5 was prepared by bromination of benzene-d_6 (99.6%, CEA, France), according to the method of L. Gatterman and F. H. Wieland, "Die Praxis des organischen Chemikers," Walter de Gruyter & Co., Berlin (1961), p. 95.

20) The reducibility of IX′ was examined also by the use of the chromous-ion reduction method. It was indicated that the reducibility of IX was not affected by deuteration of the phenyl ring.