The One-electron Reduction of Carbonium Ions. VII. A Kinetic Study of the Reduction of the Aryl- and *n*-Alkyl-substituted Tropylium Ions with Cr(II)

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A series of substituted phenyltropylium (I) and *n*-alkyltropylium ions (II) has been synthesized, and the kinetic measurements for the one-electron reduction of these ions have been carried out with Cr(II) in 10% HCl at 25 °C. A linear correlation is observed between the log k_2 values, for I (X-C_6H_4-$C_7H_6^+$, X=*p*-OH, *p*-OCH_3, *p*-CH_3, H, *p*-Cl, *p*-Br, *p*-CN, *m*-OCH_3) and for II (C_nH_{2n+1}-$C_7H_6^+$, n=0, 1—6), and the transition energy of the charge-transfer band of these ions, with pyrene as a donor. In addition, the values of log k_2 for I exhibit a good linear free-energy relationship with pK_{R^+} and also with the σ-value ($\rho=+1.31$), but not with σ^+. The *n*-alkyl group is shown to diminish the reducibility of the tropylium ion, and a slight alternation effect of the length of the *n*-alkyl chain on the k_2's is observed.

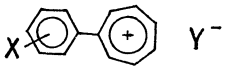
In previous papers of this series, we have reported on the chromous-ion reduction of some substituted tropylium[1a,b] and cyclopropenium ions.[1c] It was demonstrated that the reducibility of these carbonium ions depends mainly on the electron affinity of the respective cations and that it is also linearly correlated with their pK_{R^+} values.

In the present study, first, we have investigated the effect of substituents on the reducibility of the phenyltropylium ion. The problem with regard to the nature and extent of the electronic effect exerted by phenyl substituents upon the electronic state of a tropylium ring has aroused much interest[2,3] especially when it has been assumed that the plane of the phenyl ring makes a considerable dihedral angle with the seven-membered ring in the phenyltropylium system. Thus, Jutz and Voithenleitner[2] have synthesized a series of aryltropylium ions and discussed their pK_{R^+}'s and electronic spectra; Schuster and his coworkers[3] have carried out the HMO calculation of the various aryltropylium ions and compared the results with their electronic and NMR spectra. However, no systematic study of the chemical reactivity of aryltropylium ions seems yet to have been reported.

Secondly, we have also synthesized a series of *n*-alkyltropylium ions and examined the effect of the alkyl-chain length upon the properties and reducibility of these ions.

Results and Discussion

The salts of the aryltropylium ions (Ia—f, h·Y^-) were prepared according to the method of Jutz and Voithenleitner.[2] *p*-Cyanophenyltropylium perchlorate (Ig·ClO_4^-) is a new compound; it was synthesized by hydride abstraction from 7-(*p*-cyanophenyl)-1,3,5-cycloheptatriene, which in turn has been prepared from 7-(*p*-aminophenyl)-1,3,5-cycloheptatriene by the use of the Sandmeyer reaction.



	X	Y
Ia	*p*-OH	BF_4
Ib	*p*-OCH_3	BF_4
Ic	*p*-CH_3	BF_4
Id	H	BF_4
Ie	*p*-Cl	ClO_4
If	*p*-Br	ClO_4
Ig	*p*-CN	ClO_4
Ih	*m*-OCH_3	ClO_4

The perchlorates of the *n*-alkyltropylium ions (II: C_nH_{2n+1}-$C_7H_6^+$·ClO_4^-; n=1—6, 8, 12) were prepared, in part (n=3,4,5,6,8) for the first time, in a similar manner from 7-alkyl-1,3,5-cycloheptatrienes, which had themselves been synthesized by the reaction of alkylmagnesium bromides with 7-ethoxy-1,3,5-cycloheptatriene. The spectral and analytical data for II are listed in Table 1. It is of interest to note that the change in the mp's of these salts with the increase in the alkyl-chain length exhibits a tendency similar to that of *n*-alkylbenzenes, as is shown in Fig. 1.

The I and II ions are all readily soluble and quite stable in such polar solvents as acetonitrile and aqueous HCl except for II (n=8,12), which is hardly soluble in aqueous HCl (10%), though it dissolves rather more readily in a non-polar solvent, benzene.[4] Thus, the one-electron reduction was carried out for I and II (n=1—6) with Cr(II) in 10% HCl and for II (n=8,12) with zinc powder in acetonitrile. The respec-

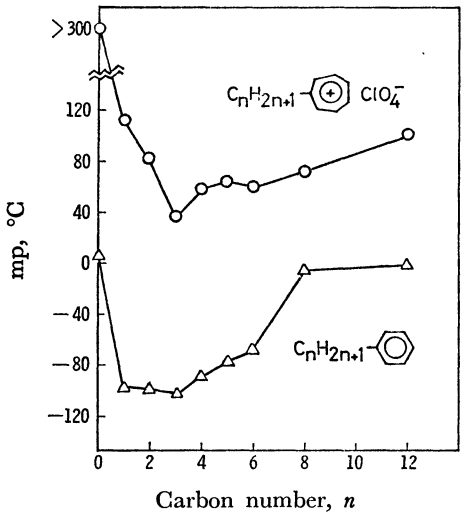


Fig. 1. The effect of the alkyl-chain length on mp's of alkyltropylium perchlorates and of alkylbenzenes. (Δ: mp's of alkylbenzenes, cited from G. Egloff, "Physical Constants of Hydrocarbons," Vol. III, Reinhold Publishing Co., N. Y. (1946))

Table 1. Physical properties and analytical data of *n*-alkyltropylium perchlorates

Substituent	mp °C	UV $\lambda_{max}^{10\%\ HCl}$ nm	UV (log ε)	Elemental analysis Found (Calcd) C%	H%
H-[a]	>300	273.5	(3.64)	—	—
CH_3-[b]	110.0—111.5	287	(3.68)	—	—
C_2H_5-[b]	84.0—84.3	292	(3.69)	—	—
C_3H_7-	36.0—41.1	296	(3.69)	51.59 (51.62)	5.58 (5.63)
C_4H_9-	65.0—66.3	297.5	(3.78)	53.44 (53.55)	6.10 (6.13)
C_5H_{11}-	72.5—73.9	297.5	(3.77)	55.54 (55.28)	6.58 (6.57)
C_6H_{13}-	64.3—65.2	298.5	(3.75)	56.69 (56.82)	6.85 (6.97)
C_8H_{17}-	77.9—79.5	297.5	(3.76)	59.21 (59.49)	7.64 (7.65)
$C_{12}H_{25}$-	99.0—100.0	298	(3.75)	63.43 (63.58)	8.75 (8.71)

a) H. J. Dauben, Jr., F. A. Gadecki, K. M. Harmon, and D. L. Pearson, *J. Amer. Chem. Soc.*, **79**, 4557 (1957). b) Ref. 1b.

tive tropylium ions gave the dimers of each substituted tropyl radical, *i.e.*, x,x'-disubstituted bitropyl, in almost quantitative yields without the formation of any by-product. The NMR spectra of the products indicated a typical pattern for a cycloheptatrienyl system, together with the signals corresponding to each substituents, in a manner similar to one that has previously been reported.[1b] The analytical and ultraviolet spectral data are shown in Table 4 (see Experimental).

A previous mechanistic study[5] indicated that the chromous ion (0.01—0.02 g-ion/l) in 10% HCl (2.9 M) is co-ordinated with the chloride ion and that, therefore, the one-electron reduction of the carbonium ion in this solvent would proceed effectively by way of the chloride-ion bridging between the two reagents. Thus, the kinetic measurements for the chromous-ion reduction of I and II (n=3—6) were carried out in 10% HCl, by the use of the flow method described previously,[5] to give the results listed in Table 2.

It has already been shown that the transition energy for the charge-transfer band observed between carbonium ions and a given electron donor (*e.g.*, pyrene) is correlated with the relative electron affinity of those cations[6] and also with the log k_2 for the chromous-ion reduction.[1] The I and II ions were also found to exhibit a charge-transfer band ($\nu_{C.T.max}$) with pyrene as the standard electron donor (Table 3); the correlation between log k_2 and the values of $\nu_{C.T.max}$ is reasonably good (Fig. 2) and seems to support the previous assumption[1] that the reducibility of these ions with Cr(II) can be regarded as a relative criterion of the electron affinity of the carbonium ion in solution.

With respect to the aryltropylium ions, I, the reducibility (log k_2) is also linearly related to the pK_{R^+} values, measured spectrophotometrically in 23% ethanol (Table 3), as is shown in Fig. 3. The electron-with-

Table 2. Second-order rate constants for the reaction of the aryl- and *n*-alkyltropylium ions with Cr(II) in 10% HCl at 25 °C

Substituent	Initial concn. R^+ 10^{-2} M	Initial concn. Cr(II) 10^{-2} M	k_2 $M^{-1}\cdot s^{-1}$	k_2 average $M^{-1}\cdot s^{-1}$
p-HO-C_6H_4-	0.470	1.10	63.3	64.3
	0.497	1.06	65.2	
	0.533	0.825	64.5	
p-CH_3O-C_6H_4-	0.458	1.09	60.3	62.1
	0.490	0.957	64.5	
	0.510	0.947	58.7	
	0.528	0.877	64.9	
p-CH_3-C_6H_4-	0.323	0.910	99.0	100
	0.470	1.27	94.2	
	0.503	1.23	108	
C_6H_5-[a]	0.426	0.857	140	144
	0.462	0.928	147	
p-Cl-C_6H_4-	0.248	0.549	230	237
	0.254	0.506	260	
	0.273	0.406	220	
p-Br-C_6H_4-	0.203	0.495	249	252
	0.204	0.438	283	
	0.208	0.536	256	
	0.223	0.484	221	
m-CH_3O-C_6H_4-	0.227	0.525	246	243
	0.211	0.502	240	
p-NC-C_6H_4-	0.0440	0.200	1470	1527
	0.0450	0.142	1580	
	0.0481	0.148	1530	
H-[a]	1.80	3.05	74.1	74.0
	2.05	3.75	73.8	
CH_3-[a]	1.99	4.12	11.1	11.1
	2.60	5.39	11.0	
	2.61	5.20	11.3	
C_2H_5-[a]	2.48	4.87	9.90	10.3
	2.50	5.22	9.80	
	2.60	5.22	11.1	
C_3H_7-	0.590	1.40	11.4	11.4
	0.590	1.44	11.4	
C_4H_9-	0.440	1.53	9.52	9.69
	0.511	1.36	9.86	
	0.950	2.43	9.70	
C_5H_{11}-	0.504	1.36	10.1	10.2
	0.514	1.53	10.6	
	0.574	1.22	9.79	
C_6H_{13}-	0.401	1.26	9.90	9.14
	0.520	1.33	9.12	
	0.635	1.20	8.39	

a) Ref. 1b.

drawing substituents accelerate the reaction rate, whereas the electron-donating groups decelerate it. Thus, the Hammett plot, shown in Fig. 4, gave a positive ρ-value (+1.31). The application of the σ-value[7] gave a better linear correlation (correlation coefficient, 0.980) than that of the σ^+-value[8] (correlation coefficient 0.815) as the substituent constant. This would imply that the *para*-substituent on the phenyl group does not

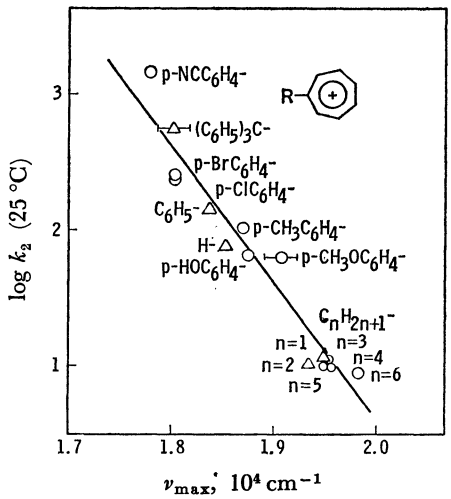


Fig. 2. The correlation of $\log k_2$ with C. T. transition energy (ν_{max}). (Δ: data from Ref. 1a)

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

Substituent	$\log k_2$[a] (25 °C)	C. T. band[b] λ_{max} nm	C. T. band[b] ν_{max} 10^4 cm^{-1}	pK_{R^+} Obsd.[c]	pK_{R^+} Lit.[d]
p-HO-C_6H_4-	1.808	533	1.876	5.32	4.96
p-CH_3O-C_6H_4-	1.793	520—530	1.923—1.887	5.17	4.59
p-CH_3-C_6H_4-	2.002	535	1.869	4.61	4.17
C_6H_5-[e]	2.158	544	1.838	4.13	3.88
p-Cl-C_6H_4-	2.375	555	1.802	3.99	3.30
p-Br-C_6H_4-	2.402	555	1.802	3.65	3.25
m-CH_3O-C_6H_4-	2.386	560—570(sh)[f]		4.16	3.51
p-NC-C_6H_4-	3.184	560	1.786	2.51	—
H-[e]	1.869	540	1.852	4.30	4.7[g]
CH_3-[e]	1.046	513	1.949	[h]	
C_2H_5-[e]	1.013	512	1.953		
C_3H_7-	1.057	512	1.953		
C_4H_9-	0.986	511	1.957		
C_5H_{11}-	1.009	513	1.949		
C_6H_{13}-	0.961	504	1.984		

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 an electron donor. c) Determined in 23% aqueous ethanol. d) Measured in 50% aqueous acetonitrile (Ref. 2). e) Data from Ref. 1b. f) A clear maximum was not observed. g) Determined by potentiometric titration in water (W. von E. Doering and L. H. Knox, *J. Amer. Chem. Soc.*, **76**, 3203 (1954). h) Not determined owing to the decomposition in aqueous media of pH>1.

exert a strong conjugative effect across the phenyl group upon the tropylium ring in either the ground or transition state, in accord with the assumption that the phenyltropylium ion can not be coplanar, but the planes of phenyl and tropylium rings are twisted more than 45°.[2,3,9]

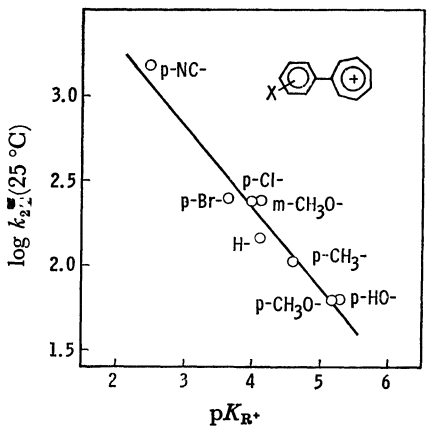


Fig. 3. The correlation of $\log k_2$ with pK_{R^+}.

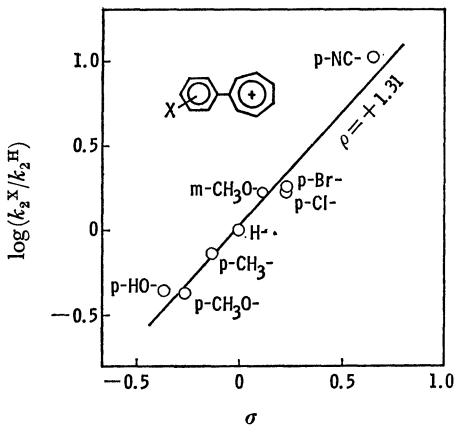


Fig. 4. The correlation of $\log k_2$ with Hammett σ.

The results of the reduction of *n*-alkyltropylium ions, II, indicated that the introduction of the alkyl group into the tropylium ring brings about a decrease in the reducibility of the cation. The chain length of the *n*-alkyl substituent was found to have no remarkable effect upon the reducibility, but a slight alternation of $\log k_2$ is observed with the increase in the carbon number of the *n*-alkyl chain. A similar alternating effect is sometimes observed in the case of S_N2 reactions of *n*-alkyl halides.[10]

Experimental[11]

Materials. All the reagents employed were of a reagent-grade quality except when otherwise noted. The acetonitrile and ethyl acetate were refluxed and distilled over phosphorus pentoxide; acetonitrile, bp 81.5—81.7 °C; ethyl acetate, bp 77.0—77.4 °C. The 1,2-dichloroethane for the measurement of the charge-transfer band was dried and distilled over calcium chloride: bp 83.0—83.5 °C.

Aryltropylium ions, Ia-f, h, were prepared according to the method of Jutz and Voithenleitner.[2]

7-(p-Cyanophenyl)-1,3,5-cycloheptatriene was synthesized from 7-(*p*-aminophenyl)-1,3,5-cycloheptatriene[2] by reference to the preparation of *p*-tolunitrile reported by Clarke and Read[12] as follows. Into 25 ml of 20% HCl we dissolved 10.0 g (54.6 mmol) of 7-(*p*-aminophenyl)-1,3,5-cycloheptatriene by vigorous stirring at 60 °C for 10 min. To this turbid solution there was then slowly added, with ice-cooling,

a solution of 3.9 g (57 mmol) of sodium nitrite in 20 ml of water over a 5-min period with magnetic stirring. The mixture was subsequently stirred at 0 °C for 1.5 hr to give a dark brown solution, which was then neutralized with *ca.* 7 g of sodium carbonate. On the other hand, 60 ml of an aqueous solution of cuprous cyanide was prepared by the reaction of 8.8 g (180 mmol) of sodium cyanide with the aqueous solution of cuprous chloride which had been obtained from 1.72 g (68.9 mmol) of $CuSO_4 \cdot 5H_2O$ and 4.5 g (77 mmol) of NaCl upon the action of 3.6 g (35 mmol) of $NaHSO_3$ and 2.4 g (60 mmol) of NaOH in an aqueous medium. Into a stirred mixture of 50 ml of benzene-ether (4 : 1) and 60 ml of an aqueous solution of cuprous cyanide, a dark brown solution of the diazonium salt was added over a 30-min period with ice-cooling. The mixture was stirred at 0 °C for 40 min, at room temperature for 4 hr, and finally at 60 °C for 30 min. The mixture was then extracted with benzene and worked up in the usual way to give 6.1 g of a viscous, dark red oil, which was chromatographed over 130 g of silica gel (Nakarai, No. II-A, 100—200 mesh). From the fractions eluted with benzene we isolated, by the use of preparative tlc over silica gel (Merck, Kieselgel PF_{254}) with the same eluent, 1.070 g (5.54 mmol) of crude 7-(*p*-cyanophenyl)-1,3,5-cycloheptatriene, which was then further purified by vacuum distillation to give white crystals; 10.1% yield; bp 135 °C (bath tempreature)/0.05 mmHg; mp 68.5—73.8 °C; NMR, τ_{CCl_4} 2.5 (m, 4H, phenyl protons), 3.4 (t, 2H, $H^{3,4}$), 3.8 (m, 2H, $H^{2,5}$), 4.8 (d of d, 2H, $H^{1,6}$)), 7.2 (t, 1H, H^7).

Found: C, 87.13; H, 5.50%. Calcd for $C_{14}H_{11}N$: C, 87.01; H, 5.74%.

p-*Cyanophenyltropylium perchlorate* (*Ig*·ClO_4^-) was synthesized by the following procedures. To a solution of 0.735 g (3.85 mmol) of 7-(*p*-cyanophenyl)-1,3,5-cycloheptatriene in 2.4 ml of acetonitrile, we added 1.30 g (3.79 mmol) of triphenylmethyl perchlorate. The mixture was stirred at 60 °C for 15 min and at 80 °C for 3 min to give a dark red solution. Then, 25 ml of ethyl acetate was added and the solution was cooled to 0 °C. The glittering crystals which separated out were collected, washed successively with ethyl acetate and dry ether, and dried under reduced pressure to afford 1.021 g (3.50 mmol) of Ig·ClO_4^- as yellowish brown crystals; 92.4% yield. The crystals were then further recrystallized from acetonitrile-ethyl acetate; mp 212.5—212.8 °C (dec); ν_{max}^{KBr} 1090 (ClO_4^-), 1480 ($-C_7H_6^+$), 2240 cm^{-1} (-CN); $\lambda_{max}^{10\% HCl}$ 228.5 (ε, 33900), 270.5 (18200), 349 nm (17400); NMR, τ_{CF_3COOH} 0.6 (m, 6H, tropylium ring protons), 1.9 (s, 4H, phenyl protons).

Found: C, 57.66; H, 3.27%. Calcd for $C_{14}H_{10}NClO_4$: C, 57.64; H, 3.46%.

The 7-n-alkyl-1,3,5-cycloheptatrienes were prepared by the reaction of 7-ethoxy-1,3,5-cycloheptatriene with *n*-alkylmagnesium bromides following the procedures reported previously.[1b]

The Alkyltropylium perchlorates (*II*, *n*=3—6, 8, 12) were synthesized by hydride abstraction from the corresponding alkylcycloheptatrienes, following a previously-reported[1b] method. The melting points and ultraviolet-spectral and analytical data are given in Table 1.

One-electron Reduction of the Substituted Tropylium Ions. The Chromous-ion Reduction of Ia-h and II (n=3—6). Details of the procedures will be described below for the reduction of the *p*-chlorophenyltropylium ion (Ie) as a representative case. To a magnetically-stirred solution of 0.209 g (0.692 mmol) of Ie·ClO_4^- in 70 ml of 10% HCl, we added 3.5 ml (3.5 mmol) of a 1M solution of chromous chloride in 10% HCl by the use of a hypodermic syringe under an atmosphere of nitrogen. The solution was stirred for 5 min at room temperature, and then extracted with *n*-hexane and worked up in the usual way to give 0.140 g (0.347 mmol) of x,x'-di(*p*-chlorophenyl)bitropyl (x,x'-di(*p*-chlorophenyl)biscyclohepta-2,4,6-trien-1-yl) as a partially-solidified viscous oil; 100.3% yield; NMR, τ_{CDCl_3} 2.6 (m, 4H, phenyl protons), 3.1—3.5 (m, 3H, H^{3-6}), 4.4 (m, 2H, $H^{2,7}$), 7.8 (m, 1H, H^1). The chromous-ion reductions of Ia—d, If—h, and II (*n*=3—6) were carried out in the same way to give the dimers in yields of 100—106%.

The Zinc Reduction of II (n=8, 12). To a magnetically-stirred solution of 0.0374 g (0.104 mmol) of *n*-dodecyltropylium perchlorate, II·ClO_4^- (*n*=12), in 2.1 ml of acetonitrile, there was added 0.0713 g (1.09 mg-atom) of zinc powder in a stream of nitrogen, after which the mixture was stirred for 10 min at room temperature. After the filtration of the reaction mixture, a 5-ml portion of water was added to the filtrate, which was then extracted with *n*-hexane and worked up in the usual way to give 0.0303 g (0.0582 mmol) of x,x'-di-*n*-dodecylbitropyl as a viscous oil; 106% yield; NMR, τ_{CCl_4} 3.4—4.1 (m, 3H, H^{3-6}), 4.9 (m, 2H, $H^{2,7}$), 7.9 (br, 3H, H^1 and $\rangle C-CH_2-$), 8.8 (s, 20H, $-(CH_2)_{10}-$), 9.2 (t, 3H, $-CH_3$). The zinc reduction of II (*n*=8) was conducted in the same

Table 4. Spectral and analytical data for x,x'-disubstituted bitropyls

Substituent	UV λ_{max}^{EtOH} nm	UV (log ε)	Element analysis Found (Calcd) C %	H %
p-HO-C_6H_4-	243.5	(4.31)	a)	
	288	(4.16)		
p-CH_3O-C_6H_4-	250	(4.42) b)		
	280	(4.22) b)		
p-CH_3-C_6H_4-	242	(4.54)	92.78	7.47
	280 (sh)	(4.12)	(92.77)	(7.23)
C_6H_5- c)	239	(4.57)	93.27	6.64
	280 (sh)	(4.10)	(93.37)	(6.63)
p-Cl-C_6H_4-	248	(4.58) b)	77.43	4.70
	280 (sh)	(4.21) b)	(77.42)	(5.00)
p-Br-C_6H_4-	250	(4.64) b)	63.60	4.11
			(63.44)	(4.10)
p-NC-C_6H_4-	259	(4.45)	86.39 d)	5.30
	280 (sh)	(4.37)	(87.47)	(5.24)
m-CH_3O-C_6H_4-	286	(4.16) b)	84.80	6.66
			(85.24)	(6.64)
C_3H_7-	254	(3.84)	90.01	9.78
			(90.16)	(9.84)
C_4H_9-	254.5	(3.88)	89.68	10.54
			(89.73)	(10.27)
C_5H_{11}-	255	(3.88)	89.48	10.37
			(89.37)	(10.63)
C_6H_{13}-	255	(3.87)	88.83	10.68
			(89.07)	(10.93)
C_8H_{17}-	255	(3.92)	88.50	11.60
			(88.60)	(11.40)
$C_{12}H_{25}$-	255	(3.79)	87.34	12.24
			(87.95)	(12.05)

a) Analyzed as the biscycloheptyl derivatives obtained by catalytic hydrogenation (see Experimental). b) Measured in chloroform as the solvent. c) Data from Ref. 1b. d) Satisfactory analytical data were not obtained owing to the instability of this compound.

way to give the dimer in a 95.0% yield.

The Analysis of the Di-substituted Bitropyls. The elemental analysis and ultraviolet spectroscopy were performed in the reduction products of Ic—h and II (n=3—6, 8, 12), which had been purified by preparative tlc over silica gel (Merck, Kieselgel PF_{254}). The results are listed in Table 4. In the cases of Ia and Ib, the reduction products were not stable enough for purification by tlc. Therefore, they were transformed to x,x'-di(p-methoxyphenyl)biscycloheptyl as follows and then analyzed. First, 0.548 g (1.49 mmol) of crude x,x'-di(p-hydroxyphenyl)bitropyl was catalytically hydrogenated over 1.0 g of palladium carbon (Nakarai, 5%) in 30 ml of dry methanol to give 0.320 g (0.845 mmol) of x,x'-di(p-hydroxyphenyl)biscycloheptyl; 56.7% yield. Then, 0.180 g (0.476 mmol) of the biscycloheptyl was methylated with 0.20 g (1.6 mmol) of dimethyl sulfate in alkaline aqueous ethanol, by reference to the method reported by Vyas and Shah.[13] The subsequent purification of the crude product by the use of preparative tlc afforded 0.102 g (0.251 mmol) of x,x'-di(p-methoxyphenyl)biscycloheptyl as a colorless oil; 52.7% yield; NMR, τ_{CCl_4} 3.2 (q, 8H, phenyl protons), 6.3 (s, 6H, methoxy), 7.5 (br, 4H, methine), 8.3 (br, 20H, methylene).

Found: C, 82.69; H, 9.37%. Calcd for $C_{28}H_{38}O_2$: C, 82.71; H, 9.42%.

The reduction product of Ib was also hydrogenated in the same way to give x,x'-di(p-methoxyphenyl)biscycloheptyl, which showed an infrared spectrum identical with that of the authentic sample described above.

Kinetic Measurements. The reaction rate of the chromous-ion reduction was measured in 10% HCl at 25.0± 0.2 °C by the use of a flow method reported previously.[5] The products were determined by ultraviolet spectroscopy, using the characteristic bands listed in Table 4.

Measurements of the Charge-transfer Bands with Pyrene. The charge-transfer spectrum was measured in 1,2-dichloroethane as has been reported previously.[1b] The concentrations of pyrene and of the tropylium salts were 0.2 M and 2×10^{-3} M respectively. Precautions were taken so that the sample solution was shielded from the room light, and the spectrum was measured immediately after the preparation of the sample.

Determination of pK_{R^+}*'s.* The previously-described spectrophotometric method[1b] was followed for the determination of pK_{R^+}'s for I in 23% ethanol. As for the cations, II, the pK_{R^+} values could not be measured because of the decomposition of II in an aqueous solution with pH$>$1.

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