The One-electron Reduction of Carbonium Ions. Part 12.[1] The Conformational Effect of the *para*-Cyclopropyl Group on the Stability of Phenyltropylium Ions and on their Reducibilities with Chromium(II) Ion

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A series of *p*-cyclopropylphenyltropylium ions with and without flanking methyl groups has been synthesized together with various methyl-substituted phenyltropylium ions as reference compounds. The conformational effect of the *para*-cyclopropyl group upon the cation stability has been studied by means of ^1H n.m.r. spectroscopy, pK_{R^+} measurements, and rate measurements of one-electron reduction with chromium(II) ion. Examination of the ^1H n.m.r. spectra and the pK_{R^+} values of these cations indicates that stabilization due to charge delocalization to the *para*-cyclopropyl group decreases with the introduction of the flanking methyl groups. A linear free-energy relationship is observed when log k_2 for the chromium(II) ion reduction is plotted against the summation of the substituent constants σ^+ for unsubstituted, *m*- and *p*-methyl-, *m,m*-dimethyl-, and *p*-cyclopropyl-phenyltropylium ions, but log k_2 for the *p*-cyclopropyl-substituted cation with one or two flanking methyl groups deviates greatly from the linear correlation line, reflecting the loss of stabilization caused by conformational change of the cyclopropyl group.

It is now generally accepted that the cyclopropyl group can stabilize an electron-deficient sp^2 carbon atom by conjugative electron donation when the ' bisected ' conformation is attained.[2] In a solvolytic study on *p*-cyclopropyl-t-cumyl chloride [1-(*p*-cyclopropylphenyl)-1-methylethyl chloride], the conformational effect of the cyclopropyl group was examined by the use of the elegant method of introducing flanking methyl groups to fix the cyclopropyl conformation.[3] In our previous work, this method was applied to a kinetic study of the one-electron reduction of cyclopropyltropylium ions in order to confirm the importance of the bisected conformation of the cyclopropyl group directly attached to the Hückel aromatic cation, the tropylium ion.[4]

In previous work [5] we examined the rate of one-electron reduction of substituted tropylium [5b,d,e] and cyclopropenium ions.[5c] It was found that log k_2 for chromium(II) ion reduction [5b-d] or log $k_{rel.}$ for zinc reduction [5e] of the stable cations correlates linearly with the transition energy of the charge-transfer band with a given electron donor. Thus, the ' one-electron reducibility ', expressed by log(reduction rate), was shown to be a useful criterion for the electron affinity of stable cations in solution. Recently, Bowie and Feldmann also reported a kinetic study on the chromium(II) ion reduction of a variety of heteroaromatic and tropylium cations; the Marcus theory for outer-sphere electron transfer reactions was successfully applied to interpret the kinetic data.[6] For a series of structurally related cations, a linear correlation was also found to hold between log k_2 for the chromium(II) ion reduction and the cation stability represented by the pK_{R^+} value, the more stable cation being reduced more slowly.[5b-d] A quantitative treatment on this relation was made by Bowie and Feldman.[6]

In this paper we report the results of a kinetic study of the chromium(II) ion reduction of *p*-cyclopropylphenyltropylium ions with and without flanking methyl groups. In this system the aryl and tropylium rings are supposed to be considerably twisted due to the steric repulsion of the *ortho*-hydrogens.[7,8] Thus, it seemed of interest to examine how much of the conjugative stabilizing effect of the *p*-character of the cyclopropyl group is transmitted to the tropylium-ion moiety across the phenyl ring. A conformational change of the *para*-cyclopropyl group is expected to affect the reactivity of the tropylium ring greatly, if the positive charge is delocalized to the *para*-position of the phenyl ring.

RESULTS AND DISCUSSION

Synthesis.—The aryltropylium ions (3a—g) were synthesized by a method similar to that reported by Jutz and Voithenleitner [7] from 7-arylcycloheptatrienes (2a—g), which were obtained by the reaction of the Grignard reagents of the aryl bromides (1a—g) with 7-ethoxycycloheptatriene (Scheme 1).† The bromides (1e and f) were obtained by direct bromination of cyclopropylbenzene and *o*-cyclopropyltoluene, respectively, whereas the bromide (1g) was prepared by the sequence shown in Scheme 2.

^1H *N.m.r. Spectra.*—The ^1H n.m.r. spectral data for the aryltropylium ions (3a—g) are summarized in Table 1 together with those for the 7-(*p*-cyclopropylphenyl)-cyclohepta-1,3,5-trienes (2e—g). A close examination of the chemical shifts of cyclopropyl protons offers information on the conformation and the charge-delocalizing effect of the *para*-cyclopropyl group. First, the signal for the (*Z*)-methylene protons (3'-, 5'-H) in both the cycloheptatrienes (2) and the cations (3) experiences an upfield shift upon the introduction of each flanking methyl group, while that for the (*E*)-methylene protons (2'-, 4'-H) is affected only slightly. This spectral change clearly demonstrates a change of the averaged conformation of the cyclopropyl group from the ' bisected ' arrangement (A) to the ' parallel ' one (B); in the latter conformation the (*Z*)-methylene protons are placed far out of the plane of the aromatic

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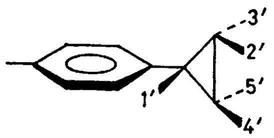
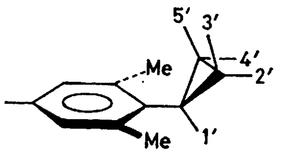
† The cycloheptatriene (2g) was obtained in higher yield by the reaction of 1-cyclopropyl-4-lithio-2,6-dimethylbenzene with tropylium fluoroborate (see Experimental section).

ring, and the molecular model indicates that they are rather located nearly on a boundary of the shielding region of the phenyl ring.



(A)



(B)

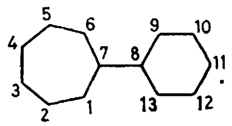
TABLE 1

^{1}H N.m.r. spectral data for the aryltropylium ions (3a—g) in CF_3CO_2H and the 7-arylcyclohepta-1,3,5-trienes (2e—g) in CCl_4

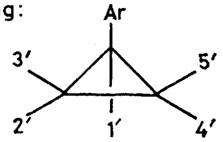
Chemical shift δ

Compound	Seven-membered ring [a]				Phenyl [a]					Methyl [a]			Cyclopropyl [b]		
	3-, 4-H	2-, 5-H	1-, 6-H	7-H	9-H	13-H	10-H	12-H	H-11	10-Me	12-Me	11-Me	1'-H	2'-, 4'-H	3'-, 5'-H
(3a)	9.37—9.07				7.79										
(3b)	9.34—8.99				7.89		7.57					2.53			
(3c)	9.36—9.04				7.78	7.66		7.66		2.52					
(3d)	9.33—9.03				7.55				7.45	2.51					
(3e)	9.22—8.87				7.85		7.40						2.07	1.22	0.92
(3f)	9.23—8.87				7.70	7.67		7.17		2.58			2.07	1.15	0.82
(3g)	9.27—8.93				7.58					2.63			1.89	1.21	0.68
(2e)	6.58	6.10	5.25	2.58	7.03								1.80	0.87	0.65
(2f)	6.60	6.09	5.28	2.63	6.93	6.90		7.02		2.42			1.83	0.86	0.60
(2g)	6.63	6.12	5.27	2.49	6.87					2.37			1.67	0.96	0.51

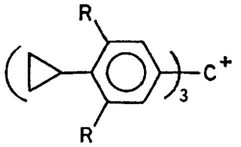
[a] Numbering



[b] Numbering:



Secondly, it is shown that the downfield shift of the methylene proton signals, observed on going from the neutral cycloheptatrienes (2e—g) to the cations (3e—g), increases in the order (3g) < (3f) < (3e); the difference in the averaged chemical shifts of the methylene protons (3'-, 5'-H and 2'-, 4'-H) between (3) and (2) is 0.21 for (3g) and (2g), 0.26 for (3f) and (2f), and 0.31 p.p.m. for (3e) and (2e). The largest downfield shift of the methylene proton signals observed for (3e) serves as evidence for the most effective delocalization of the positive charge to the cyclopropyl group attained in the bisected conformation (A). A similar observation has been made with respect to the ^{1}H n.m.r. spectra of the tris-(*p*-cyclopropylphenyl)methyl cation (4).^{9} In this system the difference in the averaged chemical shifts of the cyclopropyl methylene protons between the cation (4) and the corresponding alcohol is found to be 0.54 p.p.m. for the system without flanking methyls and 0.38 p.p.m. when the flanking methyls are introduced.^{9} The ratio of these values (0.54/0.38 = 1.42) is comparable with that observed in the present system (0.31/0.21 = 1.48), suggesting that the relative effectiveness in charge delocalization of the 'bisected' cyclopropyl group (A) with reference to the 'parallel' one (B) in the present system (3) is quite similar to that in system (4).



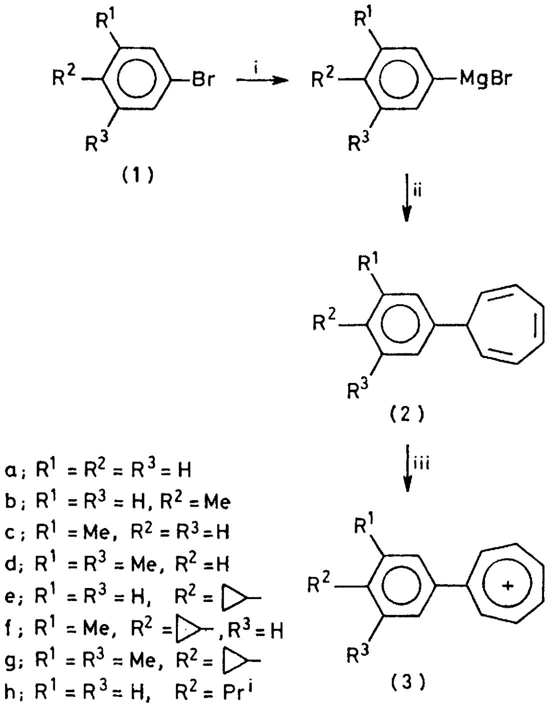
(4)

a; R = H

b; R = Me

pK_{R^+} *Values*.—In order to examine the stability of cations (3) in aqueous solution, the pK_{R^+} values were determined spectrophotometrically in 23% ethanol to give the results shown in Table 2. The effect of the *para*-cyclopropyl group is indicated by subtracting the pK_{R^+} values for the cations without the cyclopropyl group [(3a, c, and d)], from those for the corresponding cyclopropyl-substituted cations [(3e, f, and g)], respectively. In agreement with the prediction from ^{1}H n.m.r. data, the stabilizing effect of the cyclopropyl group is shown to be the greatest for the cation (3e), which favours the bisected cyclopropyl conformation, and decreases in the order, (3e) $\{\Delta pK_{R^+}[(3e) - (3a)] = 0.90\} > (3f)$ $\{\Delta pK_{R^+}[(3f) - (3c)] = 0.26\} > (3g)$ $\{\Delta pK_{R^+}[(3g) - (3d)] = 0.10\}$.

Chromium(II) *Ion Reduction*.—As has been reported for a variety of substituted tropylium ions,^{5b,d} the reaction of the aryltropylium ions (3) with chromium(II) ion in 10% HCl quantitatively affords the dimeric products, *i.e.* aryl-substituted bitropyls (5). These products are most probably formed by coupling of the aryltropyl radicals generated by one-electron reduction of the cations (Scheme 3). In the case of zinc reduction of tropylium ion, the generation of tropyl radical has been verified by the use of a spin-trapping technique.[10] Since the formation of arylcycloheptatrienes was not observed in spite of the reaction taking place in such a strongly acidic medium, the possibility of intervention of a chromium complex, such as that reported for the chromium(II) ion reduction of benzyl halides,[11] is ruled out in the present study.



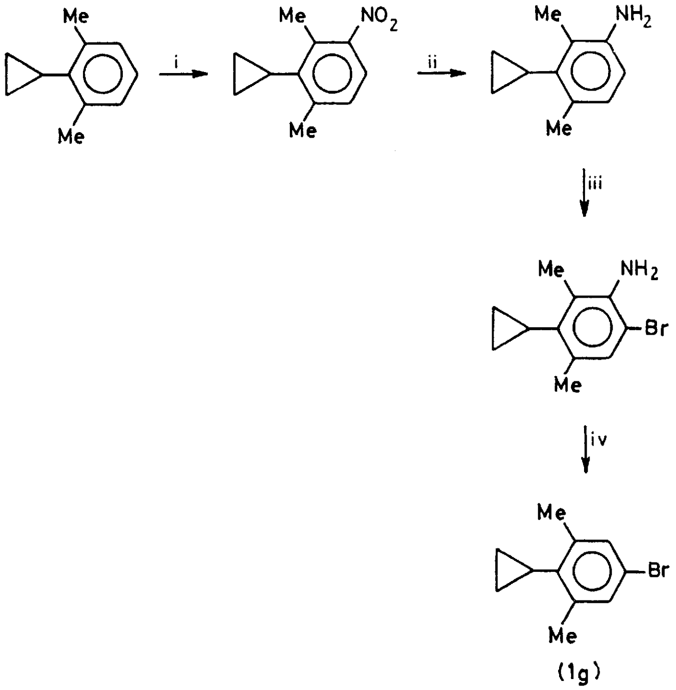
SCHEME 1 Reagents: i, Mg–Et$_2$O; ii, EtOC$_7$H$_7$–Et$_2$O; iii, Ph$_3\overset{+}{C}$–MeCN

TABLE 2

Results of the measurements of reduction-rate (25 °C in 10% HCl) and pK_{R^+} for the aryltropylium ions (3)

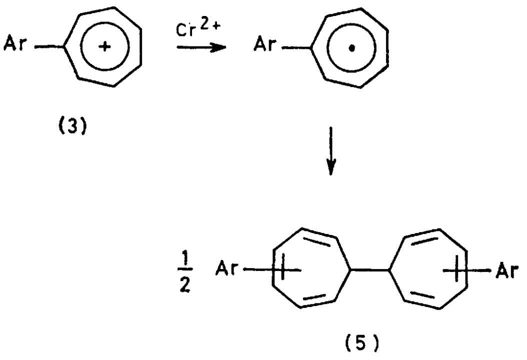
Cation	10^3[(3)]/ M	10^3[Cr^{2+}]/ M	k_2/ l mol^{-1} s^{-1}	$k_{2\,\text{average}}$/ l mol^{-1} s^{-1}	pK_{R^+} [a] in 23% EtOH
(3a) [b]	4.26	8.57	140	144	4.13
	4.62	9.28	147		
(3b) [b]	3.23	9.10	99.0	100	4.61
	4.70	12.7	94.2		
	5.03	12.3	108		
(3c)	1.97	8.75	120.1	124.7	4.51
	2.00	8.75	129.3		
(3d)	3.13	7.85	123.9	123.7	4.54
	2.92	7.37	123.4		
(3e)	2.59	5.53	88.7	86.2	5.03
	2.63	6.92	85.2		
	4.85	13.8	84.9		
(3f)	1.95	9.30	92.7	92.6	4.77
	1.80	8.30	92.4		
(3g)	1.80	8.53	118.8	119.3	4.64
	1.90	8.30	119.8		

[a] Probable error ±0.05. [b] Data taken from ref. 5*d*.



SCHEME 2 Reagents: i, HNO$_3$–Ac$_2$O; ii, Sn–HCl; iii, Br$_2$–AcOH; iv, NaNO$_2$–H$_2$SO$_4$–EtOH

Kinetic measurements for the chromium(II) ion reduction of the cations (3) in 10% HCl * were carried out by the use of a flow method reported previously.[5a] The rate constants were determined under second-order reaction conditions to give the results shown in Table 2. From the results of our previous studies,[5b-d] which indicated a linear correlation between log k_2 for the reduction and the electron affinity of the cations, it has been established that the one-electron transfer step is rate determining in this reaction. Therefore, if we assume, as a first approximation, that the energy levels of a series of the aryltropyl radicals do not differ sig-



SCHEME 3

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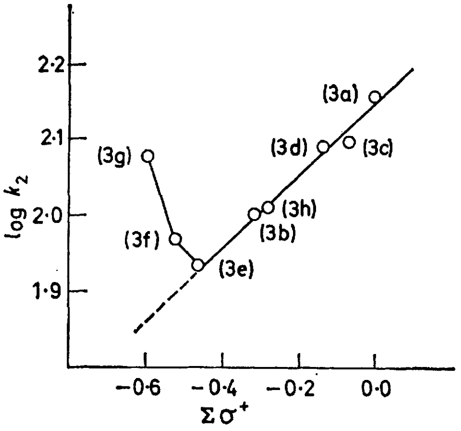
* For the advantage in using such a strongly acidic medium, see refs. 5*a* and *b*.

nificantly from each other * and the levels of the transition state are close to those of the radicals, then the values of log k_2 are expected to correlate with energy levels of the starting aryltropylium ions (3). Since the stability of the cations (3) should also have a correlation with the substituent constant σ^+ † the values of log k_2 were plotted against the summation of σ^+,[12] assuming that the additivity holds for the substituent effect in the present system.

As shown in the Figure, a good linear free energy relationship is observed for the cations (3a—e) and also the isopropyl-substituted cation (3h) ‡ (ρ 0.47). However, the points for cations (3f and g) dramatically deviate upward from the straight line. These deviations are most probably ascribed to a change in the cyclopropyl conformation, and the extent of the upward deviation from the line can be taken as a measure of the decrease in the stabilizing effect of the cyclopropyl group which is prevented from adopting the bisected conformation by the flanking methyl groups.



Plot of log k_2 for the chromium(II) ion reduction of the substituted phenyltropylium ions (3) against summation of σ^+

Thus, the present kinetic results together with the ^{1}H n.m.r. and pK_{R^+} data clearly indicate that the *para*-cyclopropyl group in a bisected conformation exerts the greatest conjugative stabilization on the tropylium ion across the phenyl ring, and that the extent of stabilization is sensitively affected by a change in cyclopropyl conformation. As for the inductive effect of the cyclopropyl group, there have already been accumulated data which show that such an effect is negligible or only slightly electron-withdrawing reflecting its double-bond character. For example, the Taft σ_I value for the cyclopropyl group has been estimated to be +0.017—0.0 depending on the method of estimation.[13] On the other hand, the results of the present work demonstrate that the cyclopropyl group flanked by two methyl groups is still weakly electron donating; the σ^+ value for the cyclopropyl group in (3g) corrected for two flanking methyls is estimated to be −0.034 from the difference in log k_2 between (3g and d) (−0.016) and the ρ value (0.47) of the straight line in the Figure. Therefore, the conjugative effect of the cyclopropyl group is not completely eliminated by the introduction of two flanking methyls but still remains somewhat to stabilize the cation; the steric effect of the two methyl groups is apparently not large enough to constrain the cyclopropyl group rigidly to the parallel conformation. Similarly, in the solvolytic study of the t-cumyl system, the *para*-cyclopropyl group flanked with two methyl groups has been reported to still exert about one-half of its maximum conjugative stabilization of the cationic centre during solvolysis.[3] The difference in the carbon framework in these two systems, the phenyltropylium and t-cumyl cations, is responsible for the change in flanking methyl effect exerted upon the conformation of the cyclopropyl group.

EXPERIMENTAL

M.p.s and b.p.s are uncorrected. Elemental analyses were performed by the Microanalytical Centre, Kyoto University, Kyoto. I.r. and u.v. spectra were recorded with Hitachi 215 and 200-10 spectrometers, respectively. ^{1}H N.m.r. spectra were taken on a Hitachi R-24 spectrometer (60 MHz) or on a Varian HA-100 spectrometer (100 MHz) with tetramethylsilane as internal standard. Mass spectra were taken on a JEOL JMS-01SG spectrometer.

Materials.—Reagents were of reagent grade quality except where otherwise noted. Acetonitrile, b.p. 81.6—81.8 °C, and ethyl acetate, b.p. 77.4—77.5 °C, were refluxed and distilled over phosphorus pentaoxide. 7-Ethoxycycloheptatriene was prepared from tropylium fluoroborate [14] and sodium ethoxide. Trityl perchlorate was prepared by the method of Dauben *et al.*[15] A 1M solution of chromium(II) chloride in 10% HCl was prepared by dissolving chromium metal in 10% HCl under nitrogen. 5-Bromo-1,3-dimethylbenzene (1d) was prepared in 83.1% yield by deamination of 4-amino-5-bromo-1,3-dimethylbenzene, obtained in 71.3% yield by bromination of 2,4-dimethylaniline in acetic acid; (1d) b.p. 75.5—78.5 °C at 5 mmHg (lit.,[16] 83—87 °C at 15 mmHg), $\delta(CCl_4)$ 7.06 (2 H, s), 6.84 (1 H, s), and 2.27 (6 H, s). 4-Bromo-1-cyclopropylbenzene (1e) was prepared by bromination of cyclopropylbenzene [17] in acetic acid–potassium acetate, according to the method of Hahn *et al.*; [18] (1e) b.p. 75—80 °C at 2 mmHg (lit.,[18] 61—63 °C at 1 mmHg).

4-*Bromo*-1-*cyclopropyl*-2-*methylbenzene* (1f).—1-Cyclopropyl-2-methylbenzene was prepared by the use of the Simmons–Smith reaction.[17] The slow addition of 2-methylstyrene [19] was found to minimize polymerization and thus remarkably increase the yield. A representative procedure is as follows. Freshly distilled di-iodomethane (80.4 g,

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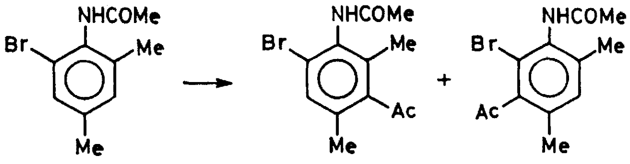
* Although the conjugative interaction of the cyclopropyl group with the π-radical is known (for example, see N. L. Bauld, J. D. McDermed, C. E. Hudson, Y. S. Rim, J. Zoeller, jun., R. D. Gordon, and J. S. Hyde, *J. Amer. Chem. Soc.*, 1969, **91**, 6666), this effect is supposed to be much smaller than the conjugative stabilization effect of the cyclopropyl group in the cations, to affect the energy levels.

† In the previous study on the chromium(II) ion reduction of a series of phenyltropylium ions carrying a variety of alkyl and heteroatom substituents,[5d] we observed a better linear correlation of log k_2 with Hammett σ (correlation coefficient 0.9795) than with σ^+ substituent constants (correlation coefficient 0.9280). However, the exact reason for this phenomenon still remains to be clarified (see ref. 6).

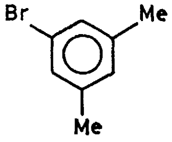
‡ The second-order rate constant k_2 for the chromium(II) ion reduction of *p*-isopropylphenyltropylium ion (3 h) has been determined as 102 l mol^{-1} s^{-1} in 10% HCl at 25 °C (K. Komatsu, R. Ohara, and K. Okamoto, unpublished data).

0.300 mol), zinc powder (19.6 g, 0.300 g atom), and a small amount of iodine were stirred in dry monoglyme (75 ml). To the stirred mixture was added dropwise a solution of 2-methylstyrene (17.7 g, 0.150 mol) in monoglyme (75 ml) over 9 h with heating to reflux. After refluxing for an additional 22 h, the mixture was filtered and washed well with ether. The filtrate was treated with diluted HCl and worked up in the usual way to give 1-cyclopropyl-2-methylbenzene (14.2 g, 71.8%) after vacuum distillation, b.p. 47—53 °C at 2 mmHg (lit.,[20] 193.5 °C at 745 mmHg); δ(CCl_4) 6.94br (4 H, s), 2.37 (3 H, s), 1.80 (1 H, m), and 0.89—0.50 (4 H, m). A solution of 1-cyclopropyl-2-methylbenzene (6.61 g, 50.0 mmol) and bromine (8.00 g, 50.1 mmol) in freshly distilled n-hexane (160 ml) was let stand at −20 °C for 73 h in the dark under oxygen; the reaction conditions were adopted from those employed for the *para*-bromination of cyclopropylbenzene.[21] The mixture was then washed with 10% sodium thiosulphate. The usual work up and vacuum distillation afforded (1f) (6.35 g, 60.2%) as an oil, b.p. 99—100 °C at 4 mmHg; δ(CCl_4) 7.18 (1 H, s), 7.10 (1 H, d), 6.73 (1 H, d), 2.37 (3 H, s), 1.75 (1 H, m), and 0.93—0.50 (4 H, m).

4-*Bromo*-1-*cyclopropyl*-2,6-*dimethylbenzene* (1g).—For the preparation of the bromide (1g), Sharpe and Martin[9] described a method which involved the Friedel–Crafts acetylation of the acetanilide (6) to give (7), followed by removal of the acetylamino group and conversion of the acetyl group into the cyclopropyl group in three steps. However, when we attempted the Friedel–Crafts acetylation of (6), we were always confronted with the formation of an inseparable mixture of (7) and its positional isomer (8) in a *ca.* 1 : 1 ratio. Our result agrees well with the report of Rabideau and his co-workers[22] on the acetylation of 5-bromo-1,3-dimethylbenzene (9), which indicates that C(2) and (4) have equal reactivity. Thus, we adopted the preparative method shown in Scheme 2 (see text) and described below in detail.



(6) (7) (8)



(9)

According to the method of Stock and Young,[23] 1-cyclopropyl-2,6-dimethylbenzene was prepared from 2,6-dimethylstyrene. The Simmons–Smith reaction was further repeated twice on the crude product, giving a 64.9% yield of the cyclopropyl compound in contrast to the reported yield of 20%,[23] b.p. 88—98 °C at 5 mmHg. To an ice-cooled solution of 1-cyclopropyl-2,6-dimethylbenzene (6.19 g, 42.3 mmol) in acetic anhydride (17 ml) there was added concentrated nitric acid (3.50 ml, 46.7 mmol) dropwise with vigorous stirring over 10 min. After stirring for 5 h at room temperature, the mixture was poured into ice–water (100 ml), neutralized with 40% NaOH, and worked up to give the crude product, which was shown to contain 86.0% of 1-cyclopropyl-2,6-dimethyl-3-nitrobenzene (5.90 g, 72.9%) by ^1H n.m.r. analysis. Purification was effected by vacuum distillation, b.p. 119—125 °C at 0.7 mmHg; δ(CCl_4) 7.45 (1 H, d), 6.95 (1 H, d), 2.47 (3 H, s), 2.41 (3 H, s), 1.70 (1 H, m), 1.11 (2 H, m), and 0.51 (2 H, m). To a stirred mixture of 1-cyclopropyl-2,6-dimethyl-3-nitrobenzene (10.99 g, 57.5 mmol) and mossy tin (30.0 g, 0.253 g atom) there was added concentrated HCl (86 ml) dropwise over 4 h with occasional cooling to keep the temperature at 40—50 °C. After removal of excess of tin the mixture was extracted with ether and worked up to give crude 3-amino-1-cyclopropyl-2,6-dimethylbenzene (8.72 g, 94.1%), which was further purified by vacuum distillation, b.p. 100—103 °C at 0.4 mmHg; δ(CCl_4) 6.62 (1 H, d), 6.23 (1 H, d), 3.40br (2 H, s), 2.26 (3 H, s), 2.16 (3 H, s), 1.60 (1 H, m), 0.93 (2 H, m), and 0.44 (2 H, m). A solution of bromine (13.45 g, 84.2 mmol) in acetic acid (13 ml) was added dropwise to an ice-cooled solution of 3-amino-1-cyclopropyl-2,6-dimethylbenzene (12.45 g, 77.2 mmol) in acetic acid (19 ml) for 40 min with vigorous stirring. After stirring at 55 °C for 1.5 h, ice–water (30 ml) was added to the mixture, which was then extracted with chloroform and worked up to give 3-amino-4-bromo-1-cyclopropyl-2,6-dimethylbenzene (15.52 g, 83.6%), b.p. 120—140 °C (bath temperature) at 0.1 mmHg; δ(CCl_4) 6.92 (1 H, s), 3.80br (2 H, s), 2.20 (6 H, s), 1.52 (1 H, m), 0.96 (2 H, m), and 0.43 (2 H, m). A solution of 3-amino-4-bromo-1-cyclopropyl-2,6-dimethylbenzene (15.50 g, 64.6 mmol) in ethanol (20 ml) was added slowly to an ice-cooled solution of concentrated sulphuric acid (11.5 ml) in ethanol (26 ml), followed by the dropwise addition of an aqueous solution (10 ml) of sodium nitrite (9.05 g, 0.131 mmol) over a 1 h period with stirring at 5 °C. Then copper bronze (2.05 g) was added and the mixture was stirred at room temperature for 1 h and at 50 °C for 1.5 h. After addition of water (50 ml) and benzene (50 ml) the mixture was worked up and distilled under reduced pressure to give the bromide (1 g) (7.19 g, 49.5%) as a pale yellow viscous oil, b.p. 81—85 °C at 0.25 mmHg; δ(CCl_4) 6.99 (2 H, s), 2.35 (6 H, s), 1.54 (1 H, m), 0.99 (2 H, m), and 0.50 (2 H, m).

Aryltropylium Perchlorate.—3-*Methylphenyltropylium perchlorate*. To a stirred solution of 3-methylphenylmagnesium bromide, prepared from 1-bromo-3-methylbenzene (10.0 g, 58.5 mmol) and magnesium turnings (1.49 g, 61.3 mg atom) in dry ether (8 ml), there was added 7-ethoxycycloheptatriene (8.78 g, 64.5 mmol) dropwise. After refluxing for 1 h the mixture was worked up and distilled under reduced pressure to give 7-(3-methylphenyl)-cyclohepta-1,3,5-triene (2c) (5.89 g, 55.3%) as an oil, b.p. 86—101 °C at 0.3 mmHg; δ(CCl_4) 7.06 (4 H, m), 6.60 (2 H, t), 6.14 (2 H, dm), 5.28 (2 H, dd), 2.59 (1 H, t), and 2.30 (3 H, s). To a stirred solution of (2c) (3.98 g, 21.8 mmol) in acetonitrile (11 ml), there was added trityl perchlorate (7.63 g, 22.3 mmol) in one portion. After stirring at 60 °C for 10 min and at 80 °C for 5 min, ethyl acetate (15 ml) was added to the resulting dark red solution. The precipitates which separated upon cooling were collected by filtration, washed with dry ether, and dried under vacuum to give the *perchlorate salt* of (3c) (4.38 g, 71.4%) as yellow plates, m.p. 122.0—122.5 °C (decomp.) (from acetonitrile–ethyl acetate) (Found: C, 59.9; H, 4.9. $C_{14}H_{13}ClO_4$ requires

C, 59.9; H, 4.65%). The i.r. and u.v. spectral data for the cations (3) are given in Table 3.

3,5-*Dimethylphenyltropylium perchlorate.* In a similar manner 7-(3,5-dimethylphenyl)cycloheptatriene (2d) was obtained by the reaction of 3,5-dimethylphenylmagnesium bromide with 7-ethoxycycloheptatriene in 52.5% yield, b.p. 85—93 °C at 0.2 mmHg; $\delta(CCl_4)$ 6.90 (2 H, s), 6.83 (1 H, s), 6.65 (2 H, t), 6.15 (2 H, dm), 5.32 (2 H, dd), 2.55 (1 H, t), and 2.26 (6 H, s). Hydride abstraction with trityl perchlorate afforded the *perchlorate salt* of (3d) as yellow needles in 73.4% yield, m.p. 187.0—188.0 °C (decomp.) (Found: C, 61.05; H, 5.2. $C_{15}H_{15}ClO_4$ requires C, 61.1; H, 5.15%).

4-*Cyclopropylphenyltropylium perchlorate.* 7-(4-Cyclopropylphenyl)cycloheptatriene (2e) was similarly prepared from the bromide (1e) in 43.5% yield, b.p. 111—121 °C at 0.1 mmHg. Hydride abstraction afforded the *perchlorate salt* of (3c) as a yellowish orange powder in 74.9% yield, m.p. 119.0—119.5 °C (decomp.) (Found: C, 62.45; H, 4.8. $C_{16}H_{15}ClO_4$ requires C, 62.65; H, 4.95%).

4-*Cyclopropyl*-3-*methylphenyltropylium perchlorate.* 7-(4-Cyclopropyl-3-methylphenyl)cycloheptatriene (2f) was prepared from the bromide (1f) in 43.9% yield, b.p. 110—119 °C at 0.09 mmHg. Hydride abstraction gave the *perchlorate salt* of (3f) as red-orange crystals in 69.6% yield, m.p. 144.1—145.1 °C (decomp.) (Found: C, 63.4; H, 5.45. $C_{17}H_{17}ClO_4$ requires C, 63.65; H, 5.45%).

TABLE 3

I.r. and u.v. spectral data for the aryltropylium ions (3)

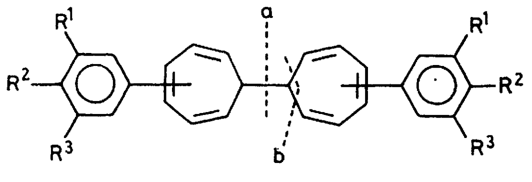
Cation	$\nu_{max.}$(KBr)/cm^{-1}	$\lambda_{max.}$(10% HCl)/nm (log ε)
(3a) [a]	3 020w, 1 600s, 1 520s, 1 480s, 1 430m, 1 380m, 1 320m, 1 275m, 1 240m, 1 200s, 1 100brs, 860m, 830m, 790s, 740s, 735sh	226 (4.58) 271 (4.17) 368 (4.21)
(3b) [a]	3 020w, 1 600s, 1 530sh, 1 510s, 1 480s, 1 430m, 1 380m, 1 275s, 1 200m, 1 100brs, 830m, 760s, 715w	227 (4.51) 275 (4.09) 395 (4.27)
(3c)	3 020w, 1 600s, 1 580w, 1 530s, 1 520m, 1 480s, 1 440m, 1 390m, 1 370m, 1 300m, 1 270s, 1 190m, 1 100brs, 810m, 750s, 700m	225 (4.49) 272 (4.12) 375 (4.14)
(3d)	3 030w, 1 600s, 1 570w, 1 530m, 1 520m, 1 490m, 1 420w, 1 385m, 1 360m, 1 315m, 1 280s, 1 200m, 1 100brs, 860s, 760s, 695s	227 (4.55) 270 (4.29) 381 (4.15)
(3e)	3 020w, 1 600s, 1 530s, 1 515s, 1 485s 1 445m, 1 420m, 1 380m, 1 300m, 1 270s, 1 200m, 1 100brs, 900s, 840m, 810w, 765s, 720s	233 (4.47) 277 (3.95) 415 (4.28)
(3f)	3 020w, 1 600s, 1 510s, 1 480s, 1 440m, 1 370m, 1 260s, 1 100brs, 900s, 880sh, 840w, 830w, 760s	232 (4.44) 276 (3.92) 414 (4.21)
(3g)	3 020w, 1 600s, 1 520s, 1 475s, 1 450m, 1 380m, 1 310s, 1 280s, 1 200m, 1 100brs, 880m, 860w, 820m, 770s	230 (4.48) 277 (3.91) 408 (4.21)

[a] Data taken from ref. 5*d*.

4-*Cyclopropyl*-3,5-*dimethylphenyltropylium perchlorate.* Tropylium fluoroborate (3.20 g, 18.0 mmol) was added, under nitrogen, to a stirred solution of 4-cyclopropyl-3,5-dimethylphenyl-lithium, prepared by the reaction of n-butyl-lithium (14.0 mmol) in n-hexane (10 ml) with the bromide (1g) (2.42 g, 10.7 mmol) in dry tetrahydrofuran (19 ml) at −78 °C. After stirring at −78 °C for 30 min and at room temperature for 5 h, the mixture was hydrolysed and worked up to give the crude product (4.35 g). Preparative t.l.c. over SiO_2 developed with n-hexane afforded 7-(4-cyclopropyl-3,5-dimethylphenyl)cycloheptatriene (2g) (1.84 g, 72.6%). Hydride abstraction by trityl perchlorate gave the *perchlorate salt* of (3g) as orange needles in 85.7% yield, m.p. 194.3—194.5 °C (decomp.) (Found: C, 64.4; H, 5.7. $C_{18}H_{19}ClO_4$ requires C, 64.55; H, 5.7%).

Determination of pK_{R^+}.—The pK_{R^+} values were determined spectrophotometrically in 23% ethanol at 25 °C by the method of Breslow and Chang.[24]

Chromium(II) *Ion Reduction of the Cations* (3).—Procedures for the reduction of the cation (3e) are described below for a representative case. A 10% HCl solution of chromium(II) chloride (1M × 5.0 ml, 5.0 mmol) was added to a stirred solution of the perchlorate salt of (3e) (0.155 g, 0.506 mmol) in 10% HCl (20 ml) by the use of a syringe under nitrogen. After stirring for 10 min at room temperature, the mixture was extracted with hexane and worked up to give an isomeric mixture of *x,x'*-bis-(4-cyclopropylphenyl)bicycloheptatrienyl (5e) (0.105 g, 100.6%) as a solid, $\lambda_{max.}$ ($CHCl_3$) 250 (log ε 4.56) and 290sh nm (4.23); $\delta(CCl_4)$ 7.3—7.0 (8 H, m), 6.9—6.0br (6 H, n), 5.7—5.3br (4 H, m), 2.2 (2 H, m), and 1.2—0.7 (8 H, m). The ^1H n.m.r. spectra of the other diarylbitropyls (5c, d, f, and g) all exhibited quite similar patterns for the seven-membered ring protons together with the multiple signals for the substituents implying the existence of positional isomers. The mass spectrum of (5e) does not exhibit a molecular ion peak but shows the fragment peaks corresponding to both symmetrical cleavage, a, and disproportionation, b; *m/e* 220 ($M^+/2$ +13, 3%), 207 ($M^+/2$, 15), and 194 ($M^+/2$ −13, 100).



(5)

The chromium(II) ion reduction of the other aryltropylium ions were carried out in the same way to give the bitropyls (5) in 90—100% yields: (5c), $\lambda_{max.}$ ($CHCl_3$) 245 (log ε 4.50) and 280sh nm (4.10); *m/e* 194 ($M^+/2$ +13, 12%), 181 ($M^+/2$, 100), and 168 ($M^+/2$ −13, 23); (5d), $\lambda_{max.}$ ($CHCl_3$) 245 (log ε 4.51) and 280sh nm (4.13); *m/e* 208 ($M^+/2$ +13, 12%), 195 ($M^+/2$, 100), and 182 ($M^+/2$ −13, 17); (5f), $\lambda_{max.}$ ($CHCl_3$) 248 (log ε 4.50) and 290sh nm (4.16); *m/e* 234 ($M^+/2$ +13, 7%), 221 ($M^+/2$, 87), and 208 ($M^+/2$ −13, 100); (5g), $\lambda_{max.}$ ($CHCl_3$) 247 (log ε 4.55) and 290sh nm (4.18); *m/e* 248 ($M^+/2$ +13, 3%), 235 ($M^+/2$, 10), and 222 ($M^+/2$ −13, 100).

Kinetic Measurements.—The second-order rate constants for the chromium(II) ion reduction of the cations (5) in 10% HCl at 25 °C were determined by the use of a flow method described previously.[5a] The diarylbitropyls (5), formed at times ranging from 0.1 to 0.7 s, were determined by u.v. spectroscopy using the characteristic absorption bands shown above.

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