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The One-Electron Reduction of Carbonium Ions. V. A Kinetic Study on the Reduction of the Substituted Cyclopropenium Ions with Cr(II)[1]

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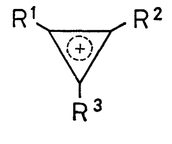
The one-electron reduction of a series of phenyl- and/or *n*-propyl-substituted cyclopropenium ions with Cr(II) has been carried out in a 10% HCl solution. The reduction of triphenylcyclopropenium (Ia), diphenyl-*n*-propylcyclopropenium (Ib), and phenyldi-*n*-propylcyclopropenium (Ic) ions quantitatively gives dimers of the respective cyclopropenyl radicals, *i.e.*, the bis(cyclopropenyl) derivatives, whereas the tri-*n*-propylcyclopropenium ion (Id) is quite unreactive. A kinetic study has shown that the reactivity of these stable carbonium ions toward the one-electron reductant (Cr(II)) is lowered with a decrease in the number of the phenyl substituent: $k_2^{25\,^\circ\mathrm{C}}=3.0\times10^{-4}$ l/g-ion·s for Ia, 2.7×10^{-6} l/g-ion·s for Ib, 2.8×10^{-9} l/g-ion·s for Ic, and $<10^{-11}$ l/g-ion·s for Id. The added NaCl was found to accelerate the reduction rate of Ia, whereas the added HCl showed an initial rate enhancement effect, followed by a slight rate-retarding effect. A plot of log k_2 against the electron affinities of the respective cations, estimated from the transition energies of the charge-transfer bands for Ia,b with pyrene, has been found to fit a linear correlation previously obtained for a series of tropylium ions. The values of log k_2 also exhibit a linear free-energy relationship with the $\mathrm{p}K_{\mathrm{R}^+}$ of these cations.

In previous papers of this series[2] we have reported on the reducibility of various substituted tropylium ions with Cr(II). It was demonstrated that log k_2 for the one-electron reduction of the tropylium ions has a linear free-energy relationship with the electron affinity, the polarographic half-wave potential, and also with the $\mathrm{p}K_{\mathrm{R}^+}$ values; thus, the log k_2 can be regarded as a relative measure for the electron affinity of the carbonium ions in solution. In order to examine the applicability of this method for stable carbonium ions other than the tropylium ions, we have now investigated the chromous-ion reduction of a series of phenyl- and/or *n*-propyl-substituted cyclopropenium ions.

In their systematic studies of the synthesis and stability of substituted cyclopropenium ions,[3] Breslow and his coworkers have reported on the polarographic reduction of some *p*-substituted triphenylcyclopropenium ions[3c] and have interpreted the results on the basis of HMO calculations. They have also reported on the zinc reduction of the triphenylcyclopropenium ion to give its dimer,[3b] but no kinetic study of the one-electron reduction for this series of stable carbonium ions seems to have been carried out. In this paper, the results of the kinetic measurements and their correlation with the electron affinities and $\mathrm{p}K_{\mathrm{R}^+}$'s of the cyclopropenium ions will be discussed in comparison with the results[2] previously obtained for a series of substituted tropylium ions.

Results and Discussion

One-Electron Reduction of the Cyclopropenium Ions (Product Study). A series of cyclopropenium ions substituted with a phenyl and/or *n*-propyl group (Ia-d) was prepared according to the method of Breslow *et al.*,[3d,f] except for Ic, which is a new compound and which was synthesized by analogy with the synthesis of Id.[3f]



I

	R_1	R_2	R_3
Ia	Ph	Ph	Ph
Ib	Ph	Ph	*n*-Pr
Ic	Ph	*n*-Pr	*n*-Pr
Id	*n*-Pr	*n*-Pr	*n*-Pr

The reduction of the cyclopropenium ions, Ia-d, with the chromous ion was carried out in 10% HCl (2.9 M) under an atmosphere of nitrogen at an appropriate temperature (Ia : 25 °C, Ib: 75 °C, Ic,d: 125 °C).[4] Ia, Ib, and Ic were found to be reduced with Cr(II) to give dimers in almost quantitative yields, as in the case of the zinc reduction of Ia.[3b] The reduction products of Ia and Ib were purified by thin-layer chromatography and were identified as bis(1,2,3-triphenyl-2-cyclopropen-1-yl) (II) and bis(1,2-diphenyl-3-*n*-propyl-2-cyclopropen-1-yl) (III) respectively. On the other hand, the reduction of Ic with Cr(II) was too slow to give the reduction product in an amount sufficient for the structural analysis. Therefore, Ic was reduced with zinc powder for the purposes of the product analysis. Preparative thin-layer chromatography showed that the product was the same as in the case of the chromous-ion reduction and that it contained bis(1,2-di-*n*-propyl-3-phenyl-2-cyclopropen-1-yl) (IV) and bis(2,3-di-*n*-propyl-1-phenyl-2-cyclopropen-1-yl) (V) in almost equal amounts. The cation, Id, was quite inert to the chromous-ion reduction and gave a trace of an unidentified oil only, after a reaction time of 48 hr at 125 °C.

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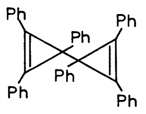
[1] Presented in part at the 22nd Symposium on the Organic Reaction Mechanism, Nagoya, October, 1971.

[2] a) K. Okamoto, K. Komatsu, O. Murai, and O. Sakaguchi, *Tetrahedron Lett.*, **1972**, 4989; b) Part III: K. Okamoto, K. Komatsu, S. Tsukada, and O. Murai, This Bulletin, **46**, 1780 (1973); c) Part IV: K. Okamoto, K. Komatsu, O. Murai, O. Sakaguchi, and Y. Matsui, *ibid.*, **46**, 1785 (1973).

[3] a) R. Breslow and C. Yuan, *J. Amer. Chem. Soc.*, **80**, 5991 (1958); b) R. Breslow and P. Cal, *ibid.*, **81**, 4747 (1959); c) R. Breslow, W. Bahary, and W. Reinmuth, *ibid.*, **83**, 1763 (1961); d) R. Breslow and H. W. Chang, *ibid.*, **83**, 2367 (1961); e) R. Breslow, J. Lockhart, and H. W. Chang, *ibid.*, **83**, 2375 (1961); f) R. Breslow, H. Höver, and H. W. Chang, *ibid.*, **84**, 3168 (1962).

[4] A control experiment showed that either the carbonium ion or the chromous ion was stable enough at the respective temperature.



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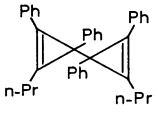

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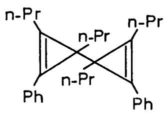

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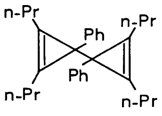

(V)

Kinetic Measurements for the Reduction of the Triphenylcyclopropenium Ion with Cr(II). The Effect of the Added Anion. The reactions of the triphenylcyclopropenium ion (Ia) with a large excess of Cr(II) were conducted in 2.9 M HCl under an atmosphere of nitrogen, and the decrease in the unchanged carbonium ion was followed by ultraviolet spectroscopy; in all cases, good first-order behavior was observed. The first-order rate constants thus obtained were proportional to the initial concentrations of Cr(II), as is shown in Fig. 1 for the reactions at 30 °C, indicating that the overall reaction rate can be expressed by the ordinary second-order rate equation: rate$=k_2$[Ia]$\cdot$[Cr(II)]. The second-order rate constants determined in this way at various temperatures are listed in Table 1. From the Arrhenius plot, the values of an activation energy and an activation entropy were estimated to be 13.9 kcal/mol and −7.1 e.u. at 25 °C.

In a previous mechanistic study,[2b)] the chloride ion added either as HCl or NaCl was shown to accelerate the chromous-ion reduction of the tropylium ion, possibly because of the effectiveness of the chloride ion in forming an electron-transfer bridge between the two

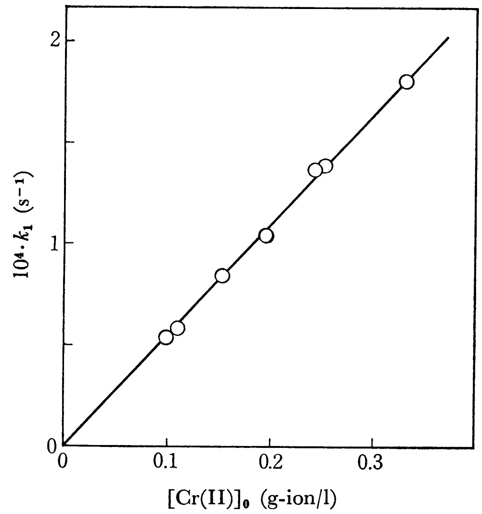

Fig. 1. Dependence of the first-order rate constant (k_1) for the chromous-ion reduction of Ia on the initial concentration of Cr(II).
[Ia]$_0$: 3.0×10^{-3} g-ion/l, Temperature: 30.0 °C, Solvent: 2.9 M HCl

Table 1. Rates of the chromous-ion reduction of the triphenylcyclopropenium ion (Ia) in 2.9 M HCl

Temp. °C	Initial concn [Ia]$_0$ *g*-ion/l	Initial concn [Cr(II)]$_0$ *g*-ion/l	$10^4\cdot k_2$ l/*g*-ion·s	Number of measurements
25.0	6.87×10^{-4}	0.139	3.0±0.2	5
30.0	2.99×10^{-4}	0.198	5.4±0.4	7
35.0	2.75×10^{-4}	0.158	8.0±0.5	4
45.0	2.77×10^{-4}	0.141	15.2±0.7	3
50.0	3.02×10^{-4}	0.130	22.2±1.9	4

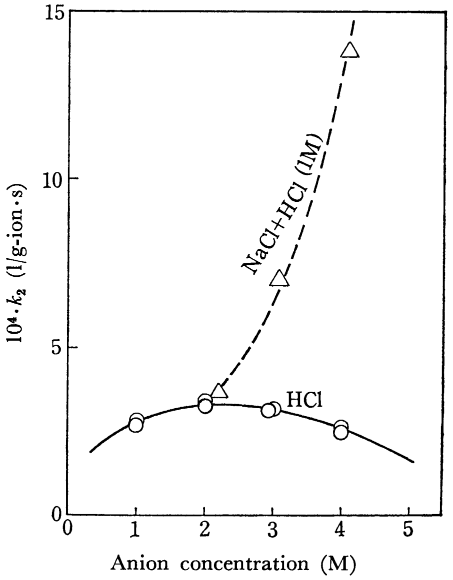

Fig. 2. The effect of an added anion on the reduction rate of Ia with Cr(II) at 25 °C.
○: Effect of HCl concentration. ([Ia]$_0$=1.6×10^{-3} g-ion/l, [Cr(II)]$_0$=0.14 g-ion/l)
△: Effect of the concentration of NaCl added to 1 M HCl. ([Ia]$_0$=7.8×10^{-4} g-ion/l, [Cr(II)]$_0$=0.14 g-ion/l)

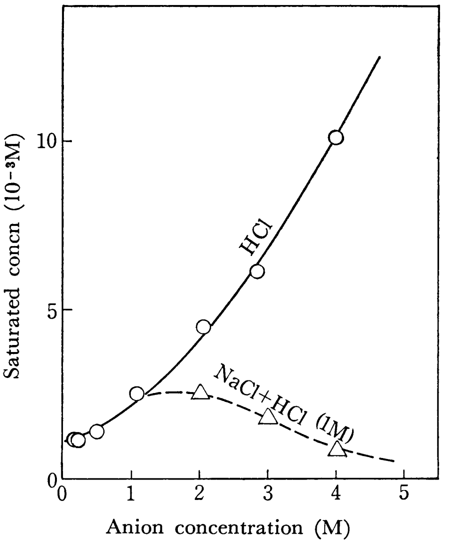

Fig. 3. The effect of an added anion on the saturated concentration of Ia in aqueous HCl solution.
○: Effect of HCl concentration.
△: Effect of the concentration of NaCl added to 1 M HCl.

Table 2. Rates of the chromous-ion reduction of the cyclopropenium ions (Ia-d) in 2.9 M HCl

Cyclopropenium ion	Temp. °C	Initial concn		k_2 l/g-ion·s	ΔE_a kcal/mol
		$10^3[\mathrm{I}]_0$ g-ion/l	$10[\mathrm{Cr(II)}]_0$ g-ion/l		
Ia	25.0	1.51	1.31	3.01×10^{-4}	13.9
Ib	75.0	2.30	2.81	4.85×10^{-4}	—
	50.0	2.30	2.81	4.45×10^{-5}	—
	25.0	—	—	2.72×10^{-6} [a]	21.3
Ic	125.0	2.31	6.50	1.53×10^{-5}	—
	100.0	2.31	6.50	2.75×10^{-6}	—
	25.0	—	—	2.78×10^{-9} [a]	20.2
Id	125.0	3.77	6.68	$<10^{-6}$ [c]	—
	25.0	—	—	$<10^{-11}$ [b]	—

a) Extrapolated from the data at elevated temperatures.
b) Estimated by the assumption that the activation energy is the same as in the case of Ic.
c) An estimated value (see Experimental).

reagents. It was observed that this rate-increasing effect gradually reaches its maximum in the anion concentration range of 3—4 g-ion/l; consequently, the reaction was expected to proceed completely by way of the chloride-ion bridging in this concentration range. Therefore, 10% HCl (2.9 M) was chosen as the standard solvent for the previous study on the reduction of the substituted tropylium ions[2c)] and also for the present study.

However, the effects of the added HCl and NaCl[5)] on the reduction rate of the triphenylcyclopropenium ion characteristically showed different tendencies from each other, as is shown in Fig. 2; addition of NaCl brings about a remarkable rate-enhancement, whereas the increase in the HCl concentration results in an initial rate-enhancement, followed by a slight rate-retarding effect. On the other hand, the effects of the concentration of added HCl and/or NaCl on the solubility (saturation concentration) of the carbonium ion (Fig. 3) exhibit a reversal of the tendency of the reduction rate (Fig. 2). From a comparison of the tendencies shown in Figs. 2 and 3, it may be supposed that undissociated HCl molecules (or $[\mathrm{H{-}Cl{-}H}]^+$ ions), which are predominant at higher HCl concentrations, strongly stabilize or solvate the carbonium ion, thus icreasing the solubility but preventing an attack by Cr(II), whereas the free $\mathrm{Cl^-}$ ions from the added NaCl suppress the solubility but facilitate the chromous-ion reduction by means of a ready formation of a $\mathrm{Cl^-}$ bridge between the two reagents.

Kinetic Measurements for the Reduction of the Cyclopropenium Ions with Cr(II). The second-order rate constants for the chromous-ion reduction of Ia, Ib, Ic, and Id are listed in Table 2. It is apparent that the substitution of *n*-propyl group for the phenyl group brings about a great suppression in the reactivity of the cyclopropenium ions. This is in accord with the increase in the stability of the cyclopropenium ion by the substitution of the *n*-propyl group, as has already been reported;[3f)] this is the same trend as is seen in the reduction of the substituted tropylium ions, although the latter reaction is much more rapid.[2)]

Correlation of the Reducibility with the Electron Affinity and with $\mathrm{p}K_{\mathrm{R}^+}$. Several examples of charge-transfer (C.T.) interactions between carbonium ions and some aromatic hydrocarbons have been reported,[6)] and the relationship between the C. T. transition energy and the electron affinity of the carbonium ion has been discussed.[6c,e,f)] We also observed the C.T. band when the cyclopropenium ions, Ia and Ib, were added to a 1,2-dichloroethane solution of pyrene. The values of the electron affinity were estimated from the C.T. transition energies by a method previously reported by Feldman and Winstein,[6e)] and the correlation of $\log k_2$ with the electron affinity was examined together with

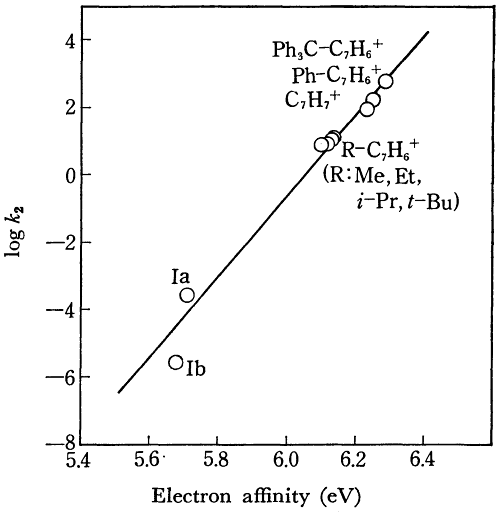

Fig. 4. The correlation of $\log k_2$ with electron affinities of the carbonium ions.

[5)] Because of the poor solubility of the triphenylcyclopropenium ion in a dilute HCl solution (<1M), the effect of HCl in concentrations of less than 1 M was not examined.

[6)] a) M. Feldman and S. Winstein, *J. Amer. Chem. Soc.*, **83**, 3338 (1961); b) M. Nepras and R. Zahradnik, *Collct. Czech. Chem. Commun.*, **29**, 1545 (1964); c) M. Feldman and B. G. Graves, *J. Phys. Chem.*, **70**, 955 (1966); d) S. N. Bhat and C. N. R. Rao, *J. Chem. Phys.*, **47**, 1863 (1967); e) M. Feldman and 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.

TABLE 3. RESULTS OF THE MEASUREMENTS OF REDUCTION RATES, CHARGE-TRANSFER BANDS, AND pK_{R^+}'S OF THE STABLE CARBONIUM IONS

Carbonium ion	$\log k_2$[a]	C. T. band[b]		pK_{R^+}[d]	
		λ_{max}, mμ	$E_{aff.}$[c], eV	Obsd	Lit.[3f]
Cyclopropenium ion					
Ia	−3.51	~420	~5.71	2.6	2.8
Ib	−5.57	~415	~5.68	4.0	3.8
Ic	−8.56	—	—	5.6	—
Id	<-11	—	—	—	7.2[e]
Tropylium ion[f]					
Trityl	2.75	550—560	6.27—6.30	3.6	
Phenyl	2.16	543	6.25	4.1	
Unsubst'd	1.87	540	6.24	4.3	
Methyl	1.05	513	6.13	—	
Ethyl	1.01	512	6.13	—	
Isopropyl	0.91	505	6.10	—	
t-Butyl	0.90	508	6.11	5.0	

a) The logarithmic value of the rate constant for the chromous-ion reduction of the respective carbonium ion. b) Measured in 1,2-dichloroethane with pyrene as a donor. c) Estimated by the method reported by Feldman and Winstein from the relation, $E_{CT}=[I_p]_{Donor}-[E_{Aff}]_{Acceptor}+\text{Const.}$ (Ref. 6e) d) Measured spectrophotometrically in 23% ethanol. e) Determined by potentiometric titration in 50% aq. acetonitrile. f) Data from Ref. 2c.

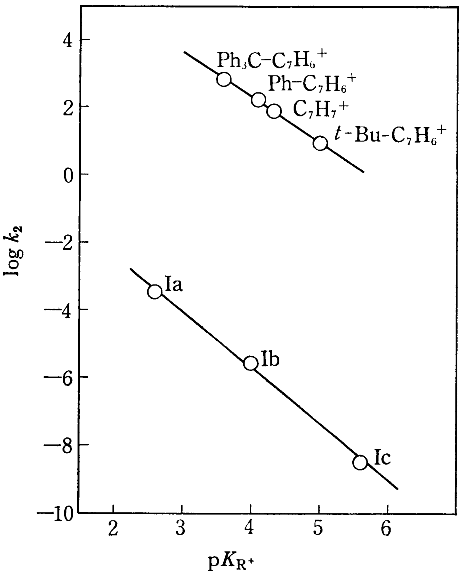

Fig. 5. The correlation of $\log k_2$ with pK_{R^+}.

the cases of substituted tropylium ions. From the results shown in Table 3 and Fig. 4, it may be seen that the linear relationship observed between the chromous-ion reducibility and the electron affinity of the substituted tropylium ion extends also to the cyclopropenium system, suggesting that the reduction of the tropylium and cyclopropenium ions proceeds by a similar mechanism, with the electron-transfer step as the rate-determining one.[7] Thus, it seems that the value of $\log k_2$ for the chromous-ion reduction may be regarded as a chemical criterion for the electron affinity of the stable carbonium ions in solution.

A plot of $\log k_2$ against the pK_{R^+} values measured spectrophotometrically in 23% ethanol[3f] also exhibits a good linear relationship, as is shown in Fig. 5. The straight line thus obtained apparently lies parallel with that obtained in the case of the substituted tropylium ions. From the definition, pK_{R^+} value is represented as the difference between $\log k_b$ and $\log k_f$, where k_f denotes the rate constant for the hydrolysis of the carbonium ion, and k_b, that for the reverse reaction.

$$R^+ + H_2O \underset{k_b}{\overset{k_f}{\rightleftharpoons}} ROH + H^+$$

It may be supposed that $\log k_2$ (a measure for the electron affinity) might linearly correlate with $\log k_f$ (a measure for the electrophilicity of R^+), but not with k_b (a measure for the nucleophilicity of ROH). This may be one of the reasons for the separation of the plot of $\log k_2$ *vs.* pK_{R^+} into two lines (in Fig. 5); further relevant studies remain to be done before we can account for these tendencies.

Experimental[8]

Materials. All the reagents employed were of a reagent-grade quality except when otherwise noted. Acetonitrile and ethyl acetate were refluxed and distilled over phosphorus pentoxide; acetonitrile, bp, 81.0—81.3 °C; ethyl acetate, bp, 77.0—77.5 °C. Ethyl ether was dried over sodium metal.

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[7] In view of the effects of the added HCl and NaCl, the reduction of cyclopropenium ions in 2.9 M HCl may not proceed completely by way of Cl^- bridging, and thus the values of k_2 measured in 2.9 M HCl may be rather smaller than those for the complete Cl^- bridging. However, this uncertainty is assumed to be within one unit in the log k_2 scale; therefore, the $\log k_2$-E_{Aff} plot (Fig. 4) may be regarded as still linear, even if we take this uncertainty into consideration.

[8] 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 taken on Shimadzu models IR-27 and UV-50 M spectrometers respectively. The 60 MHz and 100 MHz NMR spectra were obtained with a JEOL model JNM-3H-60 spectrometer and a Varian model HA-100D spectrometer respectively, with tetramethylsilane as the internal standard.

Triphenylcyclopropenium fluoroborate (Ia$\cdot BF_4^-$) was prepared from triphenylcyclopropenyl methyl ether[3a)] as follows. Into a solution of 0.964 g (3.23 mmol) of triphenylcyclopropenyl methyl ether in 15 ml of methanol, we added 1.0 ml of 42% aqueous fluoroboric acid. The white precipitates which were immediately formed were collected, washed with dry ethyl ether, and dried under reduced pressure to give 0.925 g (2.62 mmol) of Ia–BF_4^- as white crystals; 81.1% yield; mp 308—310 °C (dec); $\lambda_{max}^{2.9M\ HCl}$ 259 nm (ε, 18100), 309 nm (64100), 324 nm (54500).

Diphenyl-*n*-propylcyclopropenium fluoroborate (Ib$\cdot BF_4^-$) was prepared following the method of Breslow *et al.*;[3f)] mp 175—177 °C (dec) (lit,[3f)] mp 179 °C (dec)); $\lambda_{max}^{2.9M\ HCl}$ 246 nm (ε, 15700), 293 nm (33600), 307 nm (34400) (lit,[3f)] $\lambda_{max}^{1M\ HCl-23\%\ EtOH}$ 292 nm (ε, 32000), 305 nm (33000)).

Di-*n*-propylphenylcyclopropenium prechlorate (Ic–ClO_4^-) was prepared from the di-*n*-propylcyclopropenium ion[3f)] as follows. To a suspension of 1.503 g (6.74 mmol)of di-*n*-propylcyclopropenium perchlorate in 10 ml of dry ethyl ether, we slowly added 20 ml of a 1 M ethereal solution of phenyllithium (20 mmol) with vigorous stirring at −78 °C. The stirring was continued for 1 hr at −78° C and then for an additional hour at room temperature. To the reaction mixture we then added 30 ml of 1M HCl, and the aqueous layer was extracted with three 40-ml portions of ethyl ether. The combined ethereal solution was washed with 10% NaCl and dried over $MgSO_4$. The solvent was removed *in vacuo* to give 1.60 g of a brownish oil which was supposed to be crude 1,2-di-*n*-propyl-3-phenyl-1-cyclopropene. To this oil we then added a solution of 0.769 g (2.25 mmol) of triphenylmethyl perchlorate[9)] in 24 ml of acetonitrile, and the whole mixture was left to stand for 30 min at room temperature. The solvent was evaporated under reduced pressure. Then, 10 ml of ethyl acetate and 100 ml of dry ethyl ether were added to the dark-brown residual oil to cause the formation of white precipitates. The precipitates were collected, washed with dry ethyl ether, and dried *in vacuo* to give 0.537 g (1.89 mmol) of Ic$\cdot ClO_4^-$ as white crystals, which can be recrystallized from chloroform-ethyl ether; 80.0% yield, based on triphenylmethyl perchlorate; mp 157.5—158.5 °C (dec); $\lambda_{max}^{2.9M\ HCl}$ 262 nm (ε, 26400); NMR (100 MHz), τ_{CDCl_3} 2.89 (d, 2H, *ortho* protons), 3.10 (t, 1H, *para* proton), 3.25 (t, 2H, *meta* protons), 7.08 (t, 4H, α-methylene protons), 8.23 (sext, 4H, β-methylene protons), 9.07 (t, 6H, methyl protons); ν_{max}^{KBr} 695, 780, 1095, 1440, 1460(sh), 1500, 1600, 2900, 3000 cm^{-1}.

Found: C, 60.26; H, 6.49%. Calcd for $C_{15}H_{19}ClO_4$: C, 60.30; H, 6.41%.

Tri-*n*-propycylopropenium perchlorate (Id$\cdot ClO_4^-$) was prepared according to the method of Breslow *et al.*;[3f)] mp 183.5—185 °C (lit,[3f)] 184—185 °C)

A solution of chromous chloride in 2.9 M HCl was prepared as previously reported.[2c)]

One-Electron Reduction of the Cyclopropenium Ions. Reduction of Ia with Cr(II). In a 200-ml, four-necked flask equipped with a mechanical stirrer, a serum rubber cap, and a nitrogen inlet and outlet, there was charged a solution of 0.105 g (0.295 mmol) of Ia$\cdot BF_4^-$ in 100 ml of 2.9 M HCl. To this solution we then added 20 ml of a 1.17 M solution of chromous chloride in 2.9 M HCl by the use of a hypodermic syringe. The solution was stirred at 25 °C for 21 hr under an atmosphere of nitrogen, and then the organic product was extracted with four 100-ml portions of *n*-hexane, washed with 10% NaCl, and dried over $MgSO_4$. The solvent was subsequently removed *in vacuo* to give 0.0758 g (0.142 mmol) of bis(1,2,3-triphenyl-2-cyclopropen-1-yl) (II) as white crystals; 96.2% yield; mp 223—225 °C (lit.,[3c)] mp 225—226 °C); NMR (60 MHz), τ_{CDCl_3} 2.65 (br.s, phenyl protons).

Reduction of Ib with Cr(II). In the same manner, the reduction of 0.131 g (0.409 mmol) of Ib$\cdot BF_4^-$ with 46 mmol of chromous chloride was carried out in 160 ml of 2.9 M HCl at 75 °C for 22 hr under a nitrogen atmosphere. The reaction mixture was worked up in the same way to give 0.0927 g of a crude product, which was then purified by the use of preparative thin-layer chromatography over silica-gel (Merck, Kieselgel PF_{254}), with *n*-hexane–benzene (3 : 1) as the solvent, to give 0.0781 g (0.168 mmol) of bis(1,2-diphenyl-3-*n*-propyl-2-cyclopropen-1-yl) (III) as white crystals; 82.1% yield; mp 152—159 °C (with rapid resolidification[10)]); λ_{max}^{EtOH} 267 nm (ε, 16300); ν_{max}^{KBr} 690, 700, 760, 800, 1025, 1090, 1265, 1440, 1495, 1600, 1850, 3000 cm^{-1}; NMR (100 MHz), τ_{CCl_4} 2.78, 2.97 (m and s, 20H, phenyl), 7.30 (t, 4H, α-methylene), 8.30 (sext, 4H, β-methylene), 8.99 (t, 6H, methyl).

Reduction of Ic with Zn and with Cr(II). In a similar manner, 2.0 g (30 mg-atom) of zinc powder was added to a solution of 0.201 g (0.670 mmol) of Ic$\cdot ClO_4^-$ in 85 ml of 0.1 M HCl; the mixture was then magnetically stirred at 20 °C for 5 hr under an atmosphere of nitrogen. Then the unchanged zinc was filtered off and washed with four 50-ml portions of ethyl ether. The aqueous solution was extracted with three 70-ml portions of ethyl ether, and the combined ethereal solution was washed with 10% NaCl, dried over $MgSO_4$, and evaporated to give 0.130 g of a partially-solidified yellowish oil, which gave three main spots (R_f, 0.23, 0.4—0.5, and 0.67) on a silica-gel thin-layer plate, with *n*-hexane–benzene (9 : 1) as the solvent. By the use of preparative thin-layer chromatography, a component with R_f 0.67 was isolated as 0.0512 g of a colorless oil and was identified as bis(1,2-di-*n*-propyl-3-phenyl-2-cyclopropen-1-yl) (IV: 0.129 mmol; 38.5% yield; $\nu_{max}^{CCl_4}$ 695, 1380, 1440, 1460, 1490, 1600, 1830, 2900, 2970, 3000 cm^{-1}; NMR (60 MHz),[11)] τ_{CCl_4} 2.70 (s, 10H, phenyl), 7.80 (m, 8H, α-methylene), (m, ∼8H, β-methylene), 9.00 (m, ∼12H, methyl). In the same way, a component with R_f 0.23 was isolated as 0.0527 g of white crystals and was identified as bis(2,3-di-*n*-propyl-1-phenyl-2-cyclopropen-1-yl) (V); 0.133 mmol; 39.7% yield; mp 26.0—28.0 °C; λ_{max}^{EtOH} 240 nm (ε, 9400), 273 nm (sh) (1100), 280 nm (763); $\nu_{max}^{CCl_4}$ 700, 1380, 1440, 1450, 1460, 1490, 1600, 1870, 2900, 2970, 3000 cm^{-1}; NMR (100 MHz),[12)] τ_{CCl_4} 3.00 (s, 10H, phenyl), 7.56 (t, 8H, α-methylene), 8.43 (sext, 8H, β-methylene), 9.04 (t, 12H, methyl). On the other hand, the component with R_f 0.4—0.5 gave 0.0202 g of a pale yellow oil, which exhibited an infrared spectrum quite similar to those of IV and V, though its structure was not fully identified.

For the purpose of comparing the reaction products, a reduction of Ic with Cr(II) was conducted in the following way. To a solution of 0.0164 g (0.0548 mmol) of Ic$\cdot ClO_4^-$ in 8.0 ml of 2.9 M HCl placed in a 20-ml ampoule we added

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9) H. J. Dauben, Jr., L. R. Honnen, and K. M. Harmon, *J. Org. Chem.*, **25**, 1442 (1960).

10) This resolidification may indicate a thermal rearrangement of III to a tetraphenyldi-*n*-propylbenzene derivative, as was observed in the case of II,[3b)] but no further investigation on the rearranged material was attempted.

11) The chemical shift of the phenyl protons shows that the phenyl group is attached to an olefinic carbon; also the complex multiplicity of the signals of propyl groups seems to indicate the presence of two types of propyl groups with different magnetic environments.

12) The phenyl group has been shown to be attached to a saturated carbon, while the propyl group is supposed to be of only one type for reasons previously presented.[11)]

8.0 ml of a 1.3 M solution of chromous chloride in 2.9 M HCl by the use of a hypodermic syringe under a stream of nitrogen. The ampoule was immediately sealed under nitrogen and immersed in an oil bath thermostated at 125 °C. After 20 hr the organic products were extracted with three 20-ml portions of ethyl ether, washed with 10% NaCl, and dried over $MgSO_4$. The evaporation of the ethereal solution under reduced pressure gave 0.0112 g of a partially-solidified, yellowish oil, which was found to contain the same products in the same composition as in the case of the zinc reduction of Ic described above, on the basis of an analysis with thin-layer chromatography.

Attempted Reduction of Id with Cr(II). The reaction of 0.0193 g (0.0730 mmol) of $Id\cdot ClO_4^-$ with the chromous ion (2.64 mg-ion) in 4.0 ml of 2.9 M HCl at 125 °C was attempted in an ampoule in the same way as has been described above. After 48 hr, the solution was worked up in the same way to give 0.0031 g of an unidentified oil. This was shown to contain the same components as in the case of the control experiments in which the cation, Id, alone was kept at 125 °C under the same conditions. The acidic aqueous layer was made alkaline with 10% NaOH, and the turbid solution which resulted was worked up in the usual way to give 0.0093 g of a colorless oil which was tentatively identified as 1,2,3-tri-*n*-propyl-2-propen-1-one on the basis of its infrared spectrum and also by analogy with the alkaline ring opening of Ia giving 1,2,3-triphenyl-2-propen-1-one;[3a] 0.056 mmol; 77% yield; $\nu_{max}^{CCl_4}$ 1380, 1460, 1665, 2900, 2980 cm^{-1}.

Kinetic Measurements. The rates of the reduction of Ia and of Ib were measured in the following way. A solution of a weighed amount of the cyclopropenium salt in 40 ml of 2.9 M HCl was charged in a 100-ml, four-necked flask equipped with a mechanical stirrer, a serum rubber cap, and a nitrogen inlet and outlet. The solution was bubbled with nitrogen for 10 min, while the reaction flask was placed in a thermostated bath. To this solution we then added a known amount (4.0—12.0 ml) of a 1.30 M solution of chromous chloride in 2.9 M HCl by the use of hypodermic syringe, and the solution was stirred under an atmosphere of nitrogen. At appropriate time intervals, 2.00-ml aliquots were sampled out by the use of a hypodermic syringe, extracted with three 5-ml portions of *n*-hexane, and diluted to a 100-fold volume with 2.9 M HCl. The amount of the unchanged cyclopropenium ion was analyzed on the diluted solution by means of ultraviolet spectrophotometry, using 308 nm (ε, 52800) as the characteristic band for Ia and 307 nm (ε, 34400) for Ib. The rate constants were calculated from the first-order rate equation and treated as has been described in text. The initial concentrations of the cyclopropenium ion and of the chromous ion were determined by ultraviolet spectroscopy and by iodometry respectively.

The kinetic measurements of the reduction of Ic were conducted by the use of the sealed-ampoule technique. To 1.0-ml portions of the solution of Ic in 2.9 M HCl placed in ampoules we added 1.0-ml portions of a 1.30 M solution of chromous chloride in 2.9 M HCl under a stream of nitrogen. The ampoules were immediately sealed and immersed in a thermostated bath. At appropriate time intervals the ampoules were opened and the amount of the unchanged cyclopropenium ion was determined spectrophotometrically, using 262 nm (ε, 26400) as the characteristic band; the results were then treated according to the first-order rate equation.

As has been mentioned in the previous section, the cation, Id, was not appreciably reduced with the chromous ion and was recovered in a 77% yield under the given reaction conditions. Even when it is assumed that the unrecovered amount corresponds to the reduction products which might have been decomposed to unidentified materials, a 77% recovery after the reaction time of 48 hr in the presence of 0.66 M of the chromous chloride gives the value of $2.3\times 10^{-6}\ M^{-1}\cdot s^{-1}$ for the upper limit of the apparent second-order rate constant; the real rate constant must be much smaller than this value.

The solubility of $Ia\cdot BF_4^-$ in Aqueous HCl with and without NaCl. In 10-ml test tubes with ground glass stoppers we placed various mixture of 0.010-g portions of $Ia\cdot BF_4^-$ with 2.0-ml portions of either aqueous HCl or aqueous HCl containing NaCl; the mixtures were shaken vigorously for 50 hr at 15—21 °C. Each mixture was then filtered, and amount of Ia dissolved in the filtrate was determined by ultraviolet spectroscopy; the results are shown in Fig. 3.

Measurements of the Charge-Transfer Bands with Pyrene. 1,2-Dichloroethane solutions of the cyclopropenium ion (3×10^{-3} g-ion/l) and of pyrene (2×10^{-3} M) were mixed in the dark[13] to give a slightly orange-colored, yellowish solution, and its visible spectrum was immediately recorded. In the cases of Ia and Ib, a widely-absorbing shoulder, which was not observed in the spectrum of either single component, appeared at the longer wavelength. These new absorptions were supposed to be due to formation of charge-transfer complexes; the values of the wavelength corresponding to the midpoint of the new band are listed in Table 3.

On the other hand, only the end absorption was observed in the region of wavelengths longer than pyrene in the cases of Ic and Id.

Determination of pK_{R^+}'s. The pK_{R^+}'s of Ia, Ib, and Ic were determined in 23% aqueous ethanol at 25 °C, as has been described by Breslow and Chang,[3d] by the use of the spectrophotometric method. Because the characteristic bands of the cations were found to decrease during the measurements for Ib and Ic, the absorbancy, which was extrapolated to the time of the dissolution of the cations, was plotted against pH to give classical titration curves, whose inflection points were taken as pK_{R^+}'s. The pH's were read on a Horiba model H pH meter calibrated with standard buffers before use.

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[13] It was observed that the exposure of the mixed solution to room light caused the appearance of new absorption bands at 430 and at 455 nm which seemed to be due to some photochemical reaction products, but the nature of the reaction was not investigated further.