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Controlled Substituent Exchange in Cyclopropenium Ions. Role of Counterion in Friedel–Crafts Reactions of the Trichlorocyclopropenium Ion

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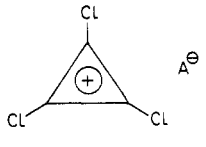
Friedel–Crafts reactions of the trichlorocyclopropenium cation ($C_3Cl_3^+$) with unsaturated substrates are very sensitive to the nature of its counterion. The triflate salt is ideal in Friedel–Crafts reactions with *nonactivated* aromatic substrates and permits facile synthesis of the corresponding triarylcyclopropenium systems. $SbCl_6^-$ is the counterion of choice in reactions of $C_3Cl_3^+$ with *olefinic and acetylenic bonds*. Thus usage of $C_3Cl_3^+SbCl_6^-$ opens up a synthetic pathway to representatives of the hitherto unknown di- and trivinylcyclopropenium salts. A mechanistic model is offered which accounts for the observed anion effects.

Owing to their multifunctional character and high internal energy[1] cyclopropenium ions (and derived cyclopropenes) should possess considerable potential as synthons. With this final aim in mind it is of interest to attach diverse structural units to the cyclopropenium system as a template and thus create molecular frameworks which are both synthetically useful and theoretically interesting.

Trichlorocyclopropenium salts 1 offer a good starting point for such an exercise because they are highly reactive and easily



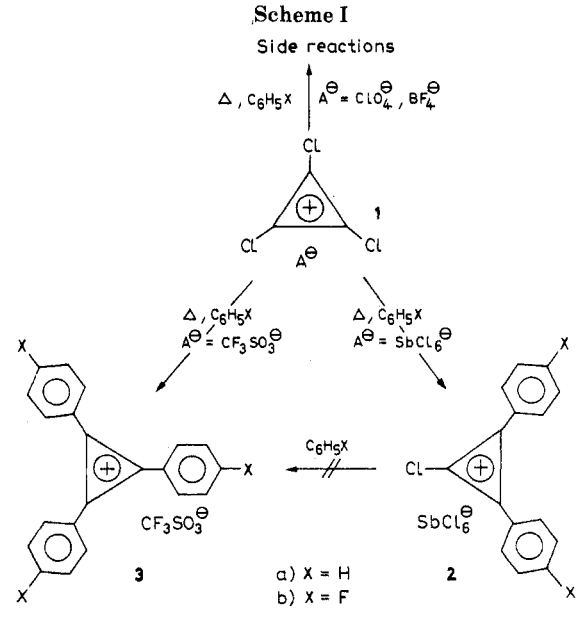
1

accessible on the basis of cheap starting materials.[2] Consequently, since the pioneering work of West[3] considerable efforts have been spent on replacing the chlorine atoms in 1 by various other substituents.[4] As a rule it was not generally possible to control the extent of substituent exchange and, in a number of cases, to avoid destruction of the highly strained cyclopropenium system. We now report that the course of such reactions can be controlled by two important independent factors: (a) selection of an appropriate counterion A^- in 1 and (b) choice of a selective exchange reagent. In this paper we focus on a, looking at Friedel–Crafts reactions of 1, while in subsequent papers[5] we shall deal with b.

Results and Discussion

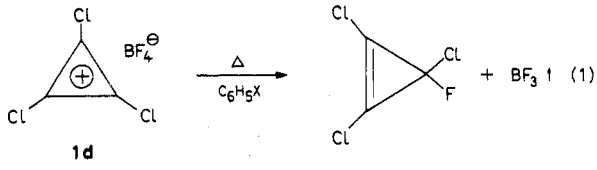
A. Reactions with Aromatic Substrates. Friedel–Crafts reactions of 1 with aromatic substrates were among the first things studied when this highly reactive species became known. Selective temperature-controlled mono- and disubstitutions of Cl atoms in 1 by phenyl and its weakly activated (*p*-alkyl-substituted) or deactivated (*p*-halo-substituted) derivatives were reported by West.[2,6] However, attempts to synthesize *triaryl*cyclopropenium systems via this route met with failure unless strongly activated substrates like phenols were used.[7] In this section we discuss reasons for this restriction and show how it can be relieved. It had occurred to us that in the earlier work one potentially important structural parameter had been neglected, namely the nature of counterion A^- in 1. For it is highly unlikely that the trichlorocyclopropenium ion and its partially arylated successor ions will exist in "free" form in the essentially nonpolar media (benzene and its derivatives) used.[2,6] Rather, these cations will be more or less tightly bound to their counterions A^-. Consequently, we tested the substitution behavior of various trichlorocyclopropenium salts in benzene and fluorobenzene as solvent and substrate, respectively, and indeed found a very pronounced counterion dependence of product distributions. Results are summarized in Scheme I.

Scheme I



First, in order to reduce the danger of counterion association via, e.g., halide bridging, we replaced $AlCl_4^-$ in 1 (West's compound,[6,7] **1a**) by the coordinatively much more stable $SbCl_6^-$ (**1b**). This, however, proved to be of no advantage as

the exchange reaction stopped after disubstitution to give **2** just as with **1a**. When **1c** (**1**, $A^- = ClO_4^-$) and **1d** (**1**, $A^- = BF_4^-$) generated in situ from tetrachlorocyclopropene and the corresponding silver salts were used, no arylcyclopropenium salts were formed. Instead, side reactions set in which resulted in irreversible consumption of the anions (no ir bands attributable to ClO_4^- or BF_4^- could be observed in the ether-soluble product mixture which remained after removal of benzene or fluorobenzene). In **1d** a Schiemann-type reaction (1) probably accounts for the disappearance of BF_4^-:

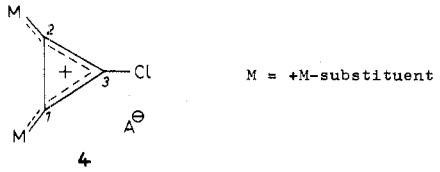


1d

As for the fate of **1c** the appearance of intense C=O vibrations at 1700 cm^{-1} in the ir spectrum of the product mixture points to an oxidizing effect of ClO_4^-, most likely involving a covalent cyclopropenyl perchlorate. Although of interest in themselves neither reaction was investigated in detail.

Finally the triflate **1e** (**1**, $A^- = CF_3SO_3^-$) was generated in situ from C_3Cl_4 and $AgCF_3SO_3$. Using the same reaction conditions as before (several days reflux in benzene or fluorobenzene) *we were thus for the first time able to reach the trisubstitution stage of* **1** *with nonactivated aromatic substrates.* After appropriate workup (cf. Experimental Section) cyclopropenium salts **3** (cf. Scheme I) could be isolated in yields >70%. **3a** was identical with an independently synthesized sample. The structure of hitherto unknown **3b** follows from elemental analysis and spectroscopic data (see Experimental Section). Both **3a** and **3b** show intense broad ir bands in the 1400-cm^{-1} region which are diagnostic of aryl-substituted cyclopropenium ions. *p*-Fluorine substitution in **3b** is evidenced by a symmetrical A_2X_2 pattern for the aromatic protons in NMR.[8]

Viewing our results together with those of West we thus arrive at the conclusion that at the disubstitution stage the role of the counterion may become critical (depending on the nature of the nucleophilic substrate). The following arguments may serve to explain this situation: from application of elementary perturbation theory it can easily be derived that replacement of two Cl atoms in the trichlorocyclopropenium system by stronger +M substituents must lead to a first-order bond fixation.[9] This bond fixation tends to distort the cyclopropenium system toward a trimethine cyanine system of type **4**.



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The stronger the electron-donating character of M the more pronounced this distortion and concomitant delocalization of positive charge onto substituents M. As a consequence counterion A^- gets less and less tightly bound to the three-membered ring, and, with strong donors M, the unperturbed cation is open to attack by the substrate MH (SN1 limit). Whether or not trisubstitution occurs should then only depend on the electronic properties of MH and the di-M-substituted cyclopropenium system and could be theoretically decided upon by looking at one of the various reactivity parameters of aromatic substitution.

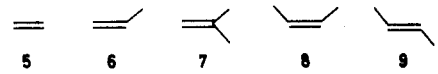
This situation is probably met with MH = anisole or phenol which according to West[7] give trisubstitution of **1** under mild conditions. The situation may change, however, if the donor capacity of M and, as a directly related phenomenon, the nucleophilicity of MH is diminished, e.g., in going over to **4** with M = C_6H_5. This manipulation leads to an increased concentration of positive charge on ring positions 1,2 and in particular 3, which still carries the least stabilizing substituent. As a consequence A^- should become more tightly bound to the cyclopropenium core in general and somewhat asymmetrically to position 3 in particular. The experimental facts that (a) **4** (M = C_6H_5) undergoes further Friedel–Crafts substitution with anisole[7] but not with less nucleophilic benzene for $A^- = AlCl_4^-$, $SbCl_6^-$ while (b) benzene can be brought to reaction with **4** (M = C_6H_5) if $A^- = CF_3SO_3^-$ (the best leaving group known) clearly show that the reaction has now largely adopted SN2 character with its characteristic dependence upon both entering and leaving group.

As a practical consequence of these considerations it can be safely predicted that a large number of new tris aryl-substituted cyclopropenium salts will become accessible via Friedel–Crafts reactions of **1e**.

B. Reactions with Olefins and Acetylenes. The classical synthetic approach toward the cyclopropenium system involves as the key step a carbene addition to an acetylene. This step is bound to meet with considerable difficulties if the substrate contains additional olefinic moieties.[10] It is, therefore, not surprising that to date no simple alkenylcyclopropenium salts have been reported in the literature.

There have been two attempts to bypass this synthetic route by allowing **1a** to react with olefins in a Friedel–Crafts sense.[11,12] However, success in these reactions was restricted to highly chlorinated ethylenes which are not prone to polymerize. Several chloro-substituted divinylcyclopropenones became thus accessible in modest yields (intermediate chlorodivinylcyclopropenium salts were not isolated).[11,12]

We have investigated the behavior of the following simple monoolefins in attempted Friedel–Crafts reactions with **1**:

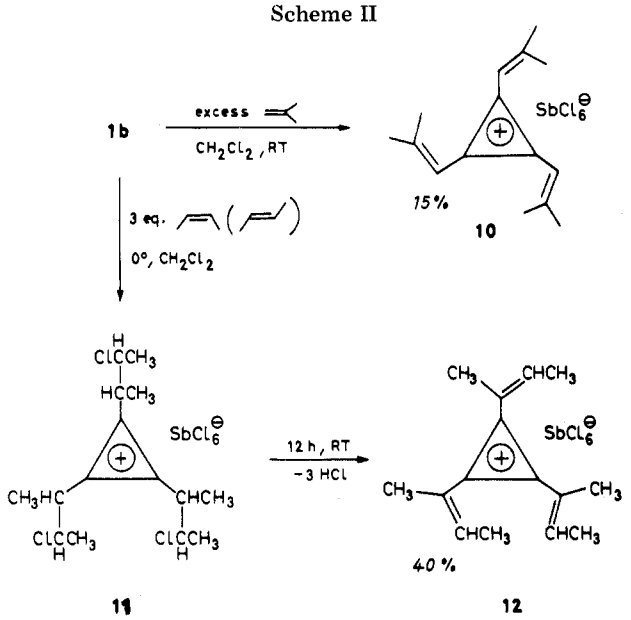


5 **6** **7** **8** **9**

Although all of these nucleophilic substrates readily reacted with **1a** (as a suspension in CH_2Cl_2) at room temperature we were unable to isolate vinylcyclopropenium salts (or, after aqueous workup, vinylcyclopropenones) from the resulting dark solutions. If **1e** was used in reactions with **5–9** the picture was similar. However, when we tested **1b** we were again confronted with a striking counterion influence upon the reactivity of the trichlorocyclopropenium system. While **5** and **6** were too unreactive toward **1b** under the reaction conditions used (0–20 °C, CH_2Cl_2 suspension of **1b**) the more nucleophilic olefins **7–9** gave the desired reaction which proceeded directly to trisubstitution according to Scheme II. Thus the first trivinylcyclopropenium salts **10** and **12** could be isolated in moderate to fair yield after addition of ether to the reaction mixture. These salts are perfectly stable compounds and were fully characterized (cf. Experimental Section). In particular both compounds exhibit a characteristic broad ir band at approximately 1400 cm^{-1}, just as does the corresponding triphenyl species.

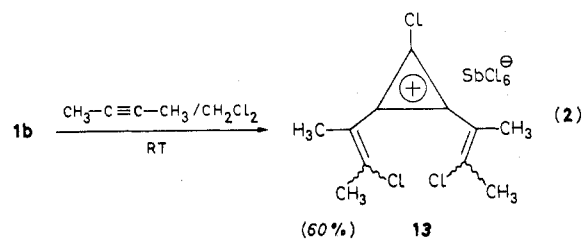
Important conclusions concerning the mechanism of these new reactions can be drawn from our observation that after addition of 3 equiv of *cis-* (or *trans-*) 2-butene to a CH_2Cl_2 suspension of **1b** a primary product can be precipitated as an oil from the dark green reaction mixture. The NMR spectrum of this impure intermediate is consistent with structure **11**; during standing at room temperature in $CDCl_3$ solution the primary NMR signals gradually disappear in favor of the signals of the end product **12** (cf. Experimental Section). This process is accompanied by HCl evolution. These observations

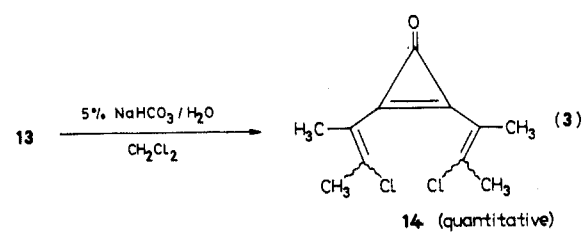
Scheme II



strongly suggest that **12** is formed in an addition–elimination sequence (cf. discussion below). The same should hold for the formation of **10** where no search for intermediates was undertaken. Remarkably, *both cis-* and *trans*-2-butene react with **1b** to give **12**. Presently, we do not know in which reaction step stereospecificity is lost, nor do we know the stereochemical configuration of the end product.

Finally we tested simple alkynes as substrates. Just as with monoolefins (same reaction conditions) **1a** and **1c** gave a complex product mixture with 2-butyne from which no substituted cyclopropenium salts could be isolated. However, again a dramatic effect was observed when the hexachloroantimonate **1b** was allowed to react with the same substrate. Under these conditions a very clean and efficient reaction was observed which proceeded according to eq 2.



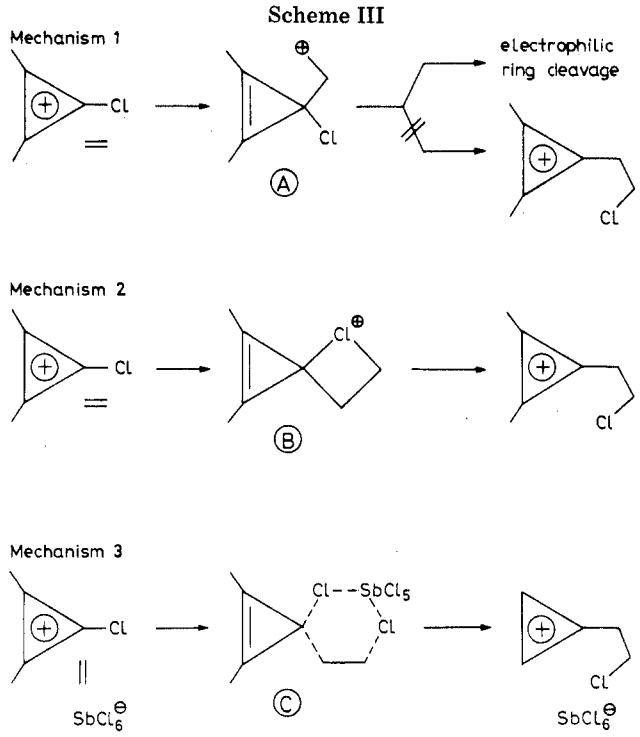


Reaction 2 was almost instantaneously complete with analytically pure **13** precipitating directly from the CH_2Cl_2 solution. Structural identification of **13** rests on its elemental analysis, its characteristic ring vibration at 1420 cm^{-1} in the infrared, and its facile and quantitative conversion into the divinylcyclopropenone **14** according to eq 3. The reaction sequence leading to **14** represents the most convenient and efficient synthesis of a divinylcyclopropenone so far available. Excess of 2-butyne does not lead to formation of the corresponding trivinylcyclopropenium system. It thus seems that the situation is similar as with aromatic substrates. No attempt was made to stop the reaction before the disubstitution stage, however.

The net result of eq 2 is the unprecedented *insertion* of an acetylene into C–Cl bonds of an aromatic halocarbenium ion. The stereochemistry of this process is unknown at present (the NMR spectrum of **13** suggests that one is dealing with a 4:1 mixture of two isomers). The question of cis vs. trans addition could in principle be easily resolved by NMR analysis of the corresponding *acetylene* adduct. Unfortunately the latter could not be obtained as acetylene was not attacked by **1b**. *Mono*alkylacetylenes have not been tested so far.

The specific success of the hexachloroantimonate **1b** and the complete failure of the corresponding triflate in Friedel–Crafts reactions with olefins and acetylenes is in marked contrast to the performance of these salts with aromatic substrates. To account for this situation it is useful to realize that the highly strained cyclopropene system will have very little chance of survival in any process which creates a free carbonium ion in its neighborhood. *Stepwise* addition of the aromatic halocarbenium moiety to an unsaturated substrate (Scheme III, mechanism 1) has to go through such an inter-

Scheme III



mediate A. At this point electrophilic attack at the cyclopropene σ or δ bonds with concomitant release of ring strain should be thermodynamically strongly favored over attack at the Cl atom and formation of the addition product.[13] In principle a concerted four-center process (Scheme III, mechanism 2) would remove the danger of irreversible ring destruction but would be energetically very costly both because of orbital symmetry restrictions and involvement of a highly strained intermediate (or transition state) B.

These difficulties can be avoided by counterion participation as shown in mechanism 3 (cf. Scheme III). In this case empty 5d orbitals on antimony would allow the intimate ion pair to react synchronously with a double (triple) bond via a *six-center* transition state C. This pathway lacks all of the negative features of mechanisms 1 and 2 and should be theoretically open to the corresponding tetrachloroaluminate **1a** as well, *not*, however, to the triflate **1e**, where A hardly can be avoided.

The failure of the latter salt to give vinylcyclopropenium salts with olefins and acetylenes can thus be satisfactorily accounted for. Although the negative role of **1a** in these reactions is not so readily understandable it is clear that one

contributing factor is the polymerizing effect of free $AlCl_3$ generated in the equilibrium of $AlCl_4^-$ with $C_3Cl_3^+$. This may explain why only highly chlorinated olefinic substrates could be induced to react with **1a**.[11,12]

In summary it can be said that Friedel–Crafts reactions of the trichlorocyclopropenium cation with unsaturated substrates are very sensitive to the nature of the counterion. The triflate ion has emerged as an ideal counterion for Friedel–Crafts reactions with aromatics (electrophilic substitution) while $SbCl_6^-$ acts as a specific catalyst in such reactions with double and triple bonds (addition, or addition–elimination).

Work is in process to further extend the scope of the reactions described in this paper with particular emphasis on synthesis and reactions of alkenylpropenium ions.

Experimental Section

General. Melting points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 125 and are reported in units of cm^{-1}. Nuclear magnetic resonance spectra were determined using Models A-60 and EM-360 of Varian Associates, using tetramethylsilane as an internal standard. Chemical shifts are reported in the τ scale. Uv spectra were run on Zeiss Models RPQ 20 and DMR 10. Mass spectra were determined using an AEI MS 902 instrument of Associated Electrical Industries with an ionizing voltage of 70 eV.

Triphenylcyclopropenium Trifluoromethanesulfonate (3a). To a solution of 1.76 g (10.0 mmol) of tetrachlorocyclopropene in 30 ml of dry benzene was added 1 equiv of $AgCF_3SO_3$ (2.57 g). The reaction mixture was refluxed until HCl development ceased (~4 days). After this period the mixture had become dark and a voluminous precipitate of AgCl and **3a** had formed. This precipitate was filtered off and **3a** was extracted with CH_3CN and precipitated with ether as colorless crystals, yield 3.1 g (75%), mp 250 °C dec. Uv, NMR, and ir spectra (apart from absorptions due to the triflate ion at 1140 and 1270 cm^{-1}) were identical with the corresponding spectra of authentic triphenylcyclopropenium bromide.[14] As further structural proof **3a** was reductively dimerized to hexaphenylbicyclopropenyl-3,3′ according to a published procedure.[15]

Anal. Calcd for $C_{22}F_3H_{15}O_3S$: C, 63.46; H, 3.63. Found: C, 63.50; H, 3.55.

Tri-*p*-fluorophenylcyclopropenium Trifluoromethanesulfonate (3b) was prepared analoguously to the procedure described above. Starting from 1.76 g (10.0 mmol) of tetrachlorocyclopropene 3.53 g (75%) of **3b** was obtained as colorless crystals: mp 210 °C dec; ir (KBr) 1600 (m), 1410 (s, broad), 1260 (s, broad) 1150 (m), 1030 (m), 840 cm^{-1} (w); uv (CH_3CN) 322 nm (ϵ 4000), 307 (45 200), 255 (13 800); NMR (CD_3CN) τ 1.47 (center of m, 6 H), 1.73 (center of m, 6 H); mass spectrum *m/e* (rel intensity) 642 (75), 321 (100).

Anal. Calcd for $C_{22}F_6H_{12}O_3S$: C, 56.18; H, 2.57. Found: C, 56.86; H, 2.50.

Tri[(2-methyl)-1-propenyl]cyclopropenium Hexachloroantimonate (10). Isobutylene was bubbled through a suspension of 2.40 g (5.07 mmol) of **1b** in 25 ml of dry CH_2Cl_2 until the reaction mixture became homogeneous (~20 min). Subsequently 100 ml of dry ether was added. After 1 week standing in the refrigerator 0.41 g (15%) of salt **11** had crystallized. Reprecipitation from CH_2Cl_2/ether yielded **10** as yellowish needles: mp 141 °C dec; ir (KBr) 1580 (s), 1420 (s, broad), 1330 (s), 1220 (w), 1070 (w), 940 (w), 830 cm^{-1} (m); uv (CH_2Cl_2) 315 nm (ϵ 36 000), 306 (36 500), 248 (18 200); NMR ($CDCl_3$) τ 3.31 (s, broad, 3 H), 7.52 (s, 9 H), 7.64 (s, 9 H).

Anal. Calcd for $C_{15}Cl_6H_{21}Sb$: C, 33.61; H, 3.94. Found: C, 33.90; H, 3.95.

Tri[(1-methyl)-1-propenyl]cyclopropenium Hexachloroantimonate (12). **1b** (9.60 g, 20.3 mmol) was suspended in 50 ml of dry CH_2Cl_2 and the suspension cooled down to 5 °C. Within 30 min 15 ml of *cis*-2-butene (cooled down to 0 °C) was added dropwise under vigorous stirring. While **1b** gradually dissolved the reaction mixture took on a dark green color. Dry ether (1 l.) was added. Crystallization of **12** started after several hours standing at 0 °C and went to completion after several days standing at −30 °C. Thus was obtained 4.35 g (40%) of slightly greenish needles. After reprecipitation from CH_2Cl_2/Et_2O the compound was colorless: mp 149 °C dec; ir (KBr) 1840 (w), 1630 (s), 1430 (s, broad), 1380 (m), 1330 (m), 1170 (w), 1100 (w), 1070 (w), 1010 (w), 825 (m), 720 cm^{-1} (m). The general appearance of this spectrum is very similar to the ir spectrum of the isomer **10**. However, the occurrence of some additional adsorptions points to a symmetry lower than D_{3h}, caused by substitution patterns around the double bonds and/or nonplanarity (see below). Particularly illustrative is the observation of the A_1' vibration at 1840 cm^{-1} which is ir inactive in D_{3h}[4a] and is not observed with **10**.

Uv (CH_2Cl_2) 283 nm (ϵ 2900), 263 (25 060). In comparison with the isomer **10** there is a pronounced blue shift of the longest wavelength absorption which points to serious deviation of the vinyl substituents from coplanarity. NMR ($CDCl_3$) τ 2.40 (center of m, 3 H), 7.81 (center of m, 18 H).

Anal. Calcd for $C_{15}Cl_6H_{21}Sb$: C, 33.58; H, 4.10. Found: C, 33.59; H, 3.82.

In one run *n*-hexane was added to the reaction mixture about 30 min after addition of *cis*-2-butene. A dark green oil deposited which was collected and freed of volatile components in vacuo at room temperature. The NMR spectrum ($CDCl_3$) of this product was essentially compatible with intermediate **11**. It consisted of two complex multiplets centered at τ 5.80 and 8.30 in an approximate ratio 1:3. These signals can be reasonably attributed to the single protons α and β to the cyclopropenium ring and the methyl groups of **13**, respectively. Furthermore, during standing in $CDCl_3$ at room temperature both groups of signals gradually disappeared in favor of the spectrum of **12**. The latter salt could be isolated in pure form after 12 h standing of the $CDCl_3$ solution by addition of ether. With *trans*-2-butene as starting olefin the observed sequence of events was entirely analogous. However, isolated yields of **12** were much lower (20%).

1,2-Di[(1-methyl-2-chloro)-1-propenyl]-3-chlorocyclopropenium Hexachloroantimonate (13). To a suspension of 2.36 g (5 mmol) of **1b** in 50 ml of dry CH_2Cl_2 was dropped within 5 min at room temperature 0.9 g (16 mmol) of 2-butyne dissolved in 20 ml of dry CH_2Cl_2. During this operation **1b** was consumed and replaced by a voluminous precipitate of **13**. After filtration and three washings with CH_2Cl_2 1.53 g (60%) of **13** was obtained as almost colorless, analytically pure microcrystals: mp 137 °C dec; ir (KBr) 1600 (s), 1450 (s, broad), 1300 (m), 1100 (w), 960 (w), 830 (w), 695 cm^{-1} (w); uv (CH_2Cl_2) 292 nm (ϵ 30 300). NMR (CD_3CN) indicates a 82/18 mixture of two stereoisomers. Component I (82%) has signals at τ 7.33 [q, J = 1 Hz (long-range coupling), 3 H] and 7.69 [q, J = 1 Hz (long-range coupling), 3 H]. Component II (18%) has signals at τ 7.47 (s, broad) and 7.69 (hidden under the high-field peak of component I) in a 1:1 ratio. The low-field signals of both components are assigned to the terminal methyls both because of allylic resonance involving and Cl substitution of the carbon atom to which they are attached.

Anal. Calcd for $C_{11}Cl_9H_{12}Sb$: C, 22.65; H, 2.05. Found: C, 22.85; H, 2.31.

Di[(1-methyl-2-chloro)-1-propenyl]cyclopropenone (14). A suspension of 2.0 g (3.42 mmol) of **13** in 50 ml of CH_2Cl_2 was vigorously stirred together with 100 ml of 5% aqueous $NaHCO_3$ solution. After 2 h the organic phase was separated and dried over $MgSO_4$. After evaporation of the solvent there remained 0.78 g (99%) of pure **14**: mp 102 °C; ir (KBr) 1850 (s, broad), 1590, 1620 (s, intensity 1:1), 1440 (m), 1360, 1380 (s, intensity 1:1), 1210 (w), 1080, 1105 (s, intensity 1:1), 950 (m), 820 (w), 725 cm^{-1} (m); uv (CH_2Cl_2) 293 nm (ϵ 26 800). NMR ($CDCl_3$) indicates two isomers: I (82%) τ 7.29 [q, J = 1 Hz (long range), 3 H], 7.81 [q, J = 1 Hz (long range), 3 H]; 7.63 (s, broad), 7.86 (partly hidden under the 7.81 signal of I) with ratio 1:1; mass spectrum *m/e* (assignment, rel intensity) 230 (M^+, 3), 202 ($M^+ - CO$, 100).

Anal. Calcd for $C_{11}Cl_2H_{12}O$: C, 57.25; H, 5.22. Found: C, 57.01; H, 5.35.

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Registry No.—**1b**, 10421-73-5; **3a**, 58815-76-2; **3b**, 58815-78-4; **10**, 58815-80-8; **12**, 58815-82-0; **13**, 58815-84-2; **14**, 58815-89-4; tetrachlorocyclopropene, 56-23-5; $AgCF_3SO_3$, 2923-28-6; isobutylene, 115-11-7; *cis*-2-butene, 590-18-1; *trans*-2-butene, 624-64-6; 2-butyne, 503-17-3.

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Substituent Effects in the Homolytic Brominolysis of Substituted Phenylcyclopropanes

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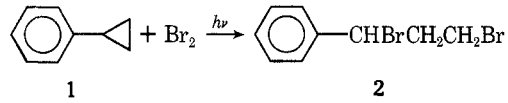
Competitive photochemical brominolyses of substituted phenylcyclopropanes in carbon disulfide at 20 °C gave linear Hammett plots with σ^+ ($\rho = -1.84$, correlation coefficient −0.996) or with σ ($\rho = -2.16$, correlation coefficient −0.982). The substituent effect is similar to that found in homolytic bromination of toluenes, and is similarly interpreted in terms of a polar transition state for the displacement reaction.

Bimolecular homolytic substitutions at carbon (SH2 reactions) are seldom encountered. The best known examples are cleavages of cyclopropane rings by halogen atoms.[1] Although this process has been investigated with respect to its kinetic order,[2] stereochemistry,[1,3,4] and regiospecificity,[3,5] it has not been studied with respect to the electron demands at the involved carbon atoms in the transition state, except for one preliminary study[2b] which gave some gross (not site-specific) substituent effects. The present study provides this information for the leaving carbon radical by a Hammett study of brominolysis of substituted phenylcyclopropanes.

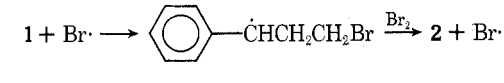
The bromination of phenylcyclopropane (**1**) under a variety of conditions has been studied by LaLonde, Ferrara, and Debboli,[6] who found a light-induced bromination in carbon tetrachloride at 25 °C to give exclusively 1,3-dibromo-1-phenylpropane (**2**). Although the simplest and most obvious



1 **2**

mechanism for this process is a conventional free-radical chain (Scheme I), those authors were unwilling to endorse that

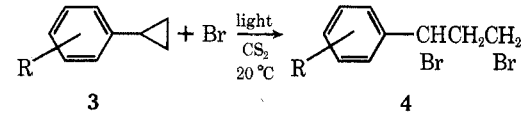
Scheme I



mechanism, partly because they could not demonstrate inhibition with nitrobenzene or trinitrobenzene and partly because of the general unreactivity of cyclopropanes toward free-radical ring opening. Our preference was to accept Scheme I as the mechanism in view of the abundant evidence cited above for homolytic halogenolysis of cyclopropanes, and we have in fact found that although the reaction of **1** with bromine is not retarded by nitrobenzene (in agreement with LaLonde), it is strongly inhibited by isoamyl nitrite. Without isoamyl nitrite, a solution of **1** and bromine decolorized fully in 7 min of illumination. With added isoamyl nitrite, an identical mixture showed no visible decoloration after 1 h of illumination.

A series of substituted phenylcyclopropanes were prepared by conventional methods, some by way of electrophilic substitutions on **1** and some from substituted acetophenones through a Mannich condensation and subsequent pyrazoline formation and thermolysis.[7] Details are in the Experimental Section. Substituents were chosen to avoid reactions of the substituent with bromine, to avoid activation of the aromatic ring toward electrophilic substitution, and to avoid charged groups which might reduce solubility in nonpolar solvents.

All of the phenylcyclopropanes (**3**) reported here underwent light-induced addition of bromine in carbon disulfide at 20



3 **4**

a, R = *p*-phenyl
b, R = *p*-Cl
c, R = *p*-Br
d, R = *m*-Br
e, R = *p*-I
f, R = *p*-CN
g, R = *p*-NO_2

°C to give the 1,3-dibromo-1-arylpropanes (**4**). The NMR spectra of the 1,3-dibromides were very similar, all showing the benzylic doublet of doublets at δ 4.93–5.10, the central methylene multiplet at δ 2.1–3.0, and the terminal methylene multiplet at δ 3.0–3.6. Control reactions in the absence of light showed no significant reaction for any of the compounds **3** in 30 min or longer, except that **3a** gave a 22.5% yield of **4a** in 1 h in the dark. All but **3f** and **3g** gave 100% yields of **4** in 18 min or less when illuminated with a sunlamp. The reaction of **3a** in the light was complete in 2 min. **3f** and **3g** gave reactions only 70% (1 h) and 19% (2 h) complete, respectively, under illumination, but no products other than **4f** and **4g** were detected. It is important that no exchange of aryl halogen for bromine was observed in recovered **3b** and **3e** (dark reactions) or **4b** and **4e** (from photoreactions).

To obtain relative rate constants for the brominolyses of compounds **3**, it was found necessary for practical reasons to measure each in competition with *p*-chlorotoluene (which gives α-bromination) rather than in competition with one another. The mixtures obtained from more than one of the phenylcyclopropanes were not easily analyzed by NMR or gas chromatography, whereas the NMR signals from *p*-chlorobenzyl bromide (δ 4.27) and *p*-chlorobenzal bromide (δ 6.52) were cleanly resolved with respect to the spectra of compounds **3** and **4**, and permitted accurate quantitative analysis. It was shown that the hydrogen bromide formed in bromination of the *p*-chlorotoluene does not react with either **1** or **3f** under the conditions used in the competitive reactions.

Table I lists the results of competitive brominations of the phenylcyclopropanes against *p*-chlorotoluene, with k_2 being the rate constant for brominolysis of the cyclopropane and k_1