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Electrophilic Additions to Dienes. VI.[1] Halogenation of Phenylallene

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Electrophilic bromination, iodination, and chlorination of phenylallene and its derivatives were carried out under various reaction conditions. Products were exclusively monoadducts and the ratios of 1,2 to 2,3 adducts were determined by pmr spectroscopy. Bromination in methanol gave exclusively a 1,2-bromomethoxide at −70° while it resulted in the formation of the 2,3 adduct as well at 0°. Bromination in carbon disulfide yielded both 1,2- and 2,3-dibromides at −70° but the former rearranged completely to the latter at 0°. The fraction of a 1,2 adduct decreased with the electron-donating ability of a substituent of phenylallene derivatives in the bromination in methanol at 0°. Iodination tended to give more 1,2 adduct and chlorination less 1,2 adduct. The former reaction gave exclusively a 1,2 adduct in methanol even at 0°. The product ratios are considered to be determined by the stability of the initially formed 1,2-halonium ion and the reactivity of a nucleophile.

We have previously investigated the hydrochlorination[2] and the sulfenyl chloride addition[1] of phenylallene and its derivatives. It was concluded that the hydrochlorination involves the rate-determining protonation at the central carbon to form a perpendicularly twisted vinylbenzyl cation which easily leads to a conjugated cinnamyl cation by the bond rotation.[2] That is, the reaction takes place *via*

$$C_6H_5CH{=}C{=}CH_2 \xrightarrow[HOAc]{H^+} C_6H_5\overset{+}{C}HCH{=}CH_2 \longrightarrow C_6H_5\overset{+}{C}H{-}CH{=}CH_2 \xrightarrow{Cl^-} C_6H_5CH{=}CHCH_2Cl \quad (1)$$

the internal bond addition to form a terminal bond adduct. By contrast, 2,4-dinitrobenzenesulfenyl chloride proved to add directly (kinetically) to the terminal double bond of phenylallene through an episulfonium ion intermediate.[1]

$$C_6H_5CH{=}C{=}CH_2 \xrightarrow{ArSCl} C_6H_5CH{=}\overset{SAr}{\overset{|}{\overset{+}{C}}}{-}CH_2 \longrightarrow C_6H_5CH{=}\overset{SAr}{\overset{|}{C}}{-}CH_2Cl \quad (2)$$

These contrasting behaviors exhibited by the typical electrophiles in the addition to phenylallene prompted us to examine those to be shown by halogen ions, which are generally considered to be intermediate in nature between the above two extremes of electrophiles.

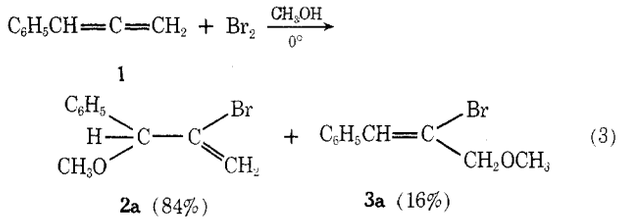
On the other hand, the intermediacy of a cyclic halonium ion is widely considered in the halogenation of olefins.[3] Bromination of optically active allenic compounds has recently been studied in the interest of scrutiny as to whether it takes place through a cyclic bromonium ion or through an open allylic cation. Caserio, *et al.*,[4] found that the bromination of optically active 1,3-dimethylallene gives an optically active product *via* a stable bromonium ion, while Jacobs, *et al.*,[5] observed the loss of optical activity during the bromination of active 2,2-dimethyl-3,4-hexadien-1-ol. The former authors concluded that there was intervention of a stable bromonium ion during the reaction while the latter considered that it was not stable enough to maintain stereochemistry. The direct observation of allenic halonium ions has recently been made in a superacid at lower temperatures.[6]

The present investigation has proved to provide useful information on the intermediacy of cyclic halonium ions and their stabilities.

Results

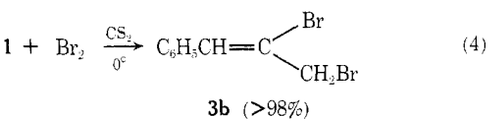
Bromination. Bromination of phenylallene (**1**) was investigated under various reaction conditions. We first carried out the reaction in methanol at 0°. A pmr spectrum of the reaction products revealed the formation of a 1,2

adduct, 2-bromo-3-methoxy-3-phenylpropene (**2a**), and a 2,3 adduct, 2-bromo-3-methoxy-1-phenylpropene (**3a**), in a ratio of 5:1. The 1,2 adduct was isolated by preparative vpc and kept standing at 0° for several hours without any rearrangement being observed.



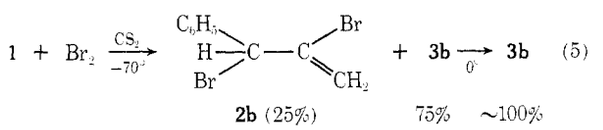
2a (84%) **3a** (16%) (3)

On the other hand, bromination in a nonpolar solvent like CS_2 at higher temperatures (>0°) gave exclusively a 2,3-dibromide **3b**. Similar results were obtained with CCl_4



3b (>98%) (4)

and CH_2Cl_2 as a solvent. However, the control reactions in a nmr sample tube at lower temperatures revealed the formation of a 1,2-dibromide **2b** which was found to rearrange to **3b** on a rise in temperature.

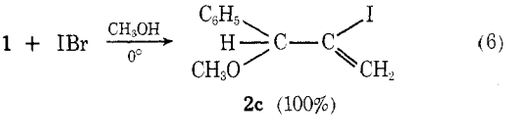


2b (25%) 75% ~100% (5)

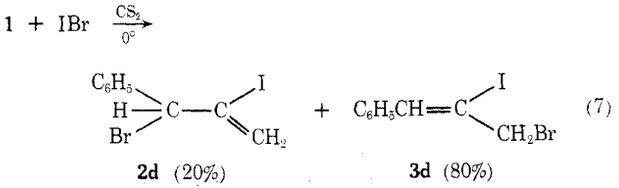
These observations seem to show that bromination of **1** takes place primarily through 1,2-addition. The reaction in a solvent having strong nucleophilicity like methanol results in trapping a 1,2 intermediate to give a stable methoxide. On the other hand, the reaction in a nonpolar solvent like CS_2 might lead to the formation of a 2,3 adduct *via* an allylic cation by the bond rotation of an intermediate.

In order to examine the nature of a reaction intermediate, the bromination of some substituted derivatives of **1** was investigated in methanol at 0°. The fractions of a 1,2 adduct **2a** are summarized in Table I. The yield of **2a** decreases uniformly with the electron-donating nature of a substituent. Furthermore, the pmr spectrum of a reaction mixture of bromination of **1** in methanol-d_4 at −70° showed the exclusive formation of the 1,2 adduct.

Iodination. Iodine bromide addition was carried out in the same way as bromination. At 0°, the reaction gave exclusively a 1,2 adduct in methanol while it gave both 1,2 and 2,3 adducts in CS_2.



2c (100%) (6)



2d (20%) **3d** (80%) (7)

In methanol, all the derivatives of **1** studied here gave exclusively a 1,2 adduct at 0° as summarized in Table I. The pmr spectrum of a reaction mixture from α-methylphenylallene seemed to show the formation of a trace of a 2,3 adduct as well.

Table I
Per cent Fraction of a 1,2 Adduct[a] in Reaction Products of Halogenation of Substituted Phenylallenes[b]

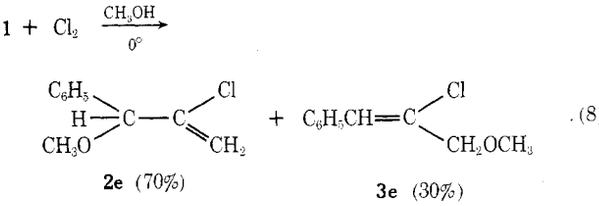
Substituent	Cl_2	Br_2	IBr	Registry no.
m-Cl		89	100	29800-82-6
H	70	84	100	2327-99-3
p-CH_3		78	100	2749-96-4
α-CH_3		58	~100	22433-39-2

[a] 2-Halo-3-methoxy-3-aryl-1-propene or-1-butene. [b] Reactions carried out in methanol at 0°.

Table II
Pmr Data of 1,2 Adducts Obtained by Halogenation

Adduct (substituent)	Chemical shift, δ ppm CH	CH_2	Registry no.
2a (H)	4.59	5.95, 5.58	51493-79-9
2a (*m*-Cl)	4.57	6.00, 5.61	51493-80-2
2a (*p*-CH_3)	4.57	5.97, 5.58	51493-81-3
2a (α-CH_3)		5.97, 5.61	51493-82-4
2b (H)	5.50	6.25, 5.78	51493-83-5
2c (H)	4.35	6.48, 5.91	51493-84-6
2c (*m*-Cl)	4.30	6.48, 5.95	51493-85-7
2c (*p*-CH_3)	4.33	6.45, 5.91	51493-86-8
2c (α-CH_3)		6.42, 6.04	51493-87-9
2d (H)	5.60	6.72, 6.04	51493-88-0
2e (H)	4.57	5.53, 5.32	51493-89-1

Chlorination. Chlorination of **1** was also undertaken in methanol at 0°, yielding 70% of a 1,2 adduct **2e** as well as a 2,3 adduct **3e**.



2e (70%) **3e** (30%) (8)

Pmr Spectra of the Adducts. We should note here pmr characteristics of the adducts obtained. As summarized in Table II, a 1,2 adduct **2** shows one singlet at ~4.5 (methoxide) or ~5.5 ppm (bromide) and two doublets around 6 ppm due to a methine and olefinic methylene protons, respectively.

As listed in Table III, a 2,3 adduct **3** exhibits a singlet at ~7 ppm which is due to an olefinic methine proton. Signals of methylene protons of **3** appear at ~4.2 ppm in two peaks of different intensity. These two peaks should

Table III
Pmr Data of 2,3 Adducts Obtained by Halogenation

Adduct (substituent)	Chemical shift, δ ppm CH	CH_2[a]	Registry no.
3a (H)	6.96	4.20 4.13	51493-90-4
3a (*m*-Cl)	6.98	4.13	51493-91-5
3a (*p*-CH_3)	6.98	4.29	51493-92-6
3a (α-CH_3)		4.09 4.23	51493-93-7
3b (H)	7.01	4.33 (0.6)[b] 4.28 (~0)[b]	23970-90-3
3d (H)	7.02	4.45 (~1)[b] 4.33 (~0)[b]	51493-94-8
3e (H)	6.87 6.80	4.23 4.20	51493-95-9

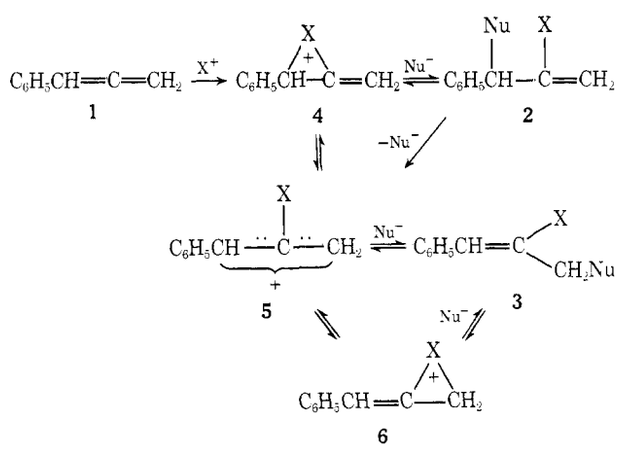
[a] Two signals responsible for geometrical isomers are observed. [b] Long-range coupling constant in hertz.

be ascribed to the methylene group of the geometrical isomers of **3**. When the spectrum was recorded in an expanded scale with a long sweeping time, we found that one of them is a doublet with J = 0.6–1 Hz. Correspondingly, a methine signal was found to be composed of a closely spaced singlet and triplet. Thus, the coupling observed is undoubtedly due to a long-range allylic coupling in one isomer. However, we could not assign the geometrical structure to the isomer. These isomeric ratios seem to be little dependent on the reaction conditions. For example, they are about 8:2 and 4:6 for the 2,3-dibromide **3b** and the 2,3-iodobromide **3d**, respectively, taking the isomer with coupling as a numerator. Further attempts of the assignment was not undertaken because **3** is a secondary product in the present reaction and the observed ratios seem to be determined thermodynamically, thus being less important in the mechanistic considerations.

Discussion

All the observations summarized above appear to be accommodated most adequately by the mechanism shown in Scheme I, where X^+ and Nu^- stand for a halogen ion and a nucleophile, respectively. That is, the electrophilic attack of halogen takes place primarily at the internal bond (1,2 bond) of **1** to form a cyclic 1,2-halonium ion **4** which is trapped by a nucleophile to give a 1,2 adduct **2** or rearranges to an open allylic cation **5** to yield a 2,3 adduct **3** by the collapse with a nucleophile. An open allylic cation of type **5** gives exclusively **3** but not **2** as has been discussed earlier.[2] An initially formed **2** can lead to **5** resulting in its rearrangement to **3** if Nu^- leaves easily. The intervention of a 2,3-halonium ion **6** between **5** and **3** is considered only for the sake of completeness.

Scheme I



At higher temperatures, bromination resulted in the exclusive formation of **3b** in a nonpolar solvent, while methanol could arrest the 1,2 intermediate to lead to stable **2a**. At lower temperatures, bromide ion was also able to arrest the 1,2 intermediate to form **2b**, which rearranged to **3b** on a rise in temperature. It is worth noting that the bromination in methanol-d_4 at −70° gave exclusively a 1,2 adduct **2**.

These observations seem to show that the fraction of **2** increases with lifetime of **4** and nucleophilicity of the medium. That is, the larger the chance of collapse of **4** with a nucleophile prior to its rearrangement, the greater becomes the fraction of **2**. Thus, the bromination should take place primarily at the 1,2 bond of **1**.

Data in Table I show the decrease of the yield of a 1,2-bromomethoxide with the electron-donating character of a substituent. Electron-donating substituents diffuse the positive charge on the α carbon and thus tend to favor an open carbonium ion over the cyclic 1,2-bromonium ion. That is, electron-donating groups lower the rotational barrier of **4** to form **5** (shorten the lifetime of **4**) and thereby make the formation of a 2,3 adduct **3** easy.

Finally, we compare the results for different electrophilic halogens. Table I shows that iodination of **1** gives exclusively a 1,2 adduct **2c** in methanol while chlorination yields only 70% of a 1,2 adduct **2e**. This trend is understandable by considering generally admitted stability order of halonium ions, I > Br > Cl. All the substituted derivatives of **1** studied here give exclusively **2** on iodination in methanol at 0°, showing high stability of a cyclic iodonium intermediate.

In conclusion, halogenation of **1** primarily takes place on the internal bond to form a cyclic halonium ion, in contrast to the results on hydrochlorination and sulfenylation. The product ratio depends both on the stability (lifetime) of a halonium ion and on the reactivity of a nucleophile.

Experimental Section

Materials. Phenylallene (**1**) and its derivatives were obtained as described previously.[2] Bromine and iodine bromide were of reagent grade (Nakarai Chemicals). Liquid chlorine was commercially obtained. Methanol was purified by fractional distillation from magnesium activated with iodine. Carbon disulfide was of spectrograde (Nakarai Chemicals).

Bromination in Methanol. A 200-ml, three-necked, round-bottomed flask was charged with a solution of 3.48 g (0.03 mol) of freshly distilled **1** in 100 ml of anhydrous methanol and the magnetically stirred solution was purged with a slow stream of nitrogen. The solution was cooled to 0° with ice and 4.8 g (0.03 mol) of bromine in 75 ml of methanol was added in darkness through a dropping funnel over 30 min. The reaction mixture was stirred for an additional 5 min, and then taken up in 100 ml of ether and washed with aqueous 10% $Na_2S_2O_3$ and 10% $NaHCO_3$, followed by five washings with water. The ethereal solution was dried over $MgSO_4$ and filtered. The solvent was then removed by rotatory evaporation *in vacuo* to yield 6.72 g of a slightly yellow oil. Analysis of the crude oil by pmr revealed the formation of a mixture of the 1,2 adduct **2a** and the 2,3 adduct **3a**, without any sign of the formation of other products. Pmr data were summarized in Tables II and III along with those of other adducts. The vpc analysis showed the product ratio of **2a:3a** to be 84:16. The adduct **2a** was isolated by preparative vpc. *Anal.* Calcd for $C_{10}H_{11}OBr$: C, 52.89; H, 4.89; Br, 35.18. Found: C, 52.76; H, 4.80; Br, 34.90.

Bromination of other derivatives was carried out in the same way on a smaller scale. The product mixtures were analyzed by pmr as a CCl_4 solution. The products were exclusively monadducts and the product ratios were determined from integration curves, being accurate to within ±5%.

Low-temperature experiments with methanol-d_4 were carried out as described in the following section.

Bromination in Carbon Disulfide. The reactions at higher temperatures were carried out in the same way as above. The reaction mixture was sometimes subjected directly to the pmr analysis. The reactions at lower temperatures were undertaken in an nmr sample tube. A solution of **1** in CS_2 (0.15 M, 0.25 ml) was placed in a tube and solidified by the immersion in liquid nitrogen. The bromine solution in CS_2 (0.15 M, 0.25 ml) was then added slowly with use of a syringe. The pmr spectra were recorded at desired temperatures while the temperature was slowly raised with continuous spinning.

Iodination. The iodination of **1** and its derivatives was carried out with the use of iodine bromide in the same way as bromination. The pmr data of adducts are listed in Tables II and III.

Chlorination. A methanol solution of chlorine was prepared by introducing dry, gaseous Cl_2 into methanol and its concentration (~0.1 M) was determined by the titration of I_2 liberated on the addition of an excess amount of KI. The standard sodium thiosulfate solution was used. This solution was added slowly to a 0.1 M solution of **1** in methanol under magnetic stirring at 0°. The reaction was allowed to proceed for an additional 30 min. The reaction mixture obtained was worked up as in the case of bromination.

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Reactions with α-Diazo Ketones. III.[1] The Stereochemical Course of Cyclization of Some Olefin-Substituted α-Diazo Ketones

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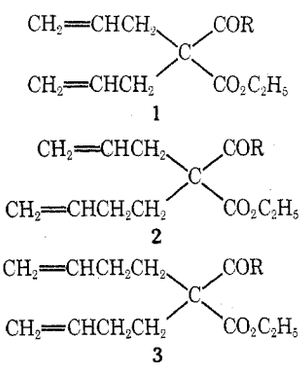
Catalytic decomposition of the suitably substituted ethyl diazoacetoacetates **1b**, **2b**, and **3b** yielded 3-allyl-3-carbethoxybicyclo[3.1.0]hexan-2-one (**4**), 3-(but-3-enyl)-3-carbethoxybicyclo[3.1.0]hexan-2-one (**11**), and 3-(but-3-enyl)-3-carbethoxybicyclo[4.1.0]heptan-2-one (**12**), respectively, all three formed by intramolecular addition of the intermediate ketocarbenoid species to the olefinic bond present in the molecules. The keto esters **4** and **11** were further reduced with $NaBH_4$ and $LiAlH_4$ to the corresponding ester alcohols and diols, respectively. Steric assignment of both the keto esters and the alcohols was based on investigation of their nmr spectra and comparison with spectral data obtained for the simpler model compounds **9a**, **9b**, **10a**, and **10b**, synthesized from 2-carbethoxycyclopentanone. The ring closure of the diazo ketones to the bicyclo[3.1.0]hexan-2-ones seems to be stereoselective, giving preferentially the isomer in which the cyclopropane ring and the carbethoxy group are located trans to each other.

In connection with a project of intramolecular cyclization of bisdiazo ketones,[1,2] it was necessary to investigate the stereochemical course of the ring closure of some related monodiazo compounds.

We wish to report now our results obtained from catalytic decomposition of the monodiazo ketones **1b**, **2b**, and **3b**, prepared by standard procedures from the diesters **1a**, **2a**, and **3a**. The crude diazo compounds, contaminated with chloro ketones, were not purified, but directly decomposed with catalytic amounts of π-allylic palladium chloride complex.[2,3]



1

2

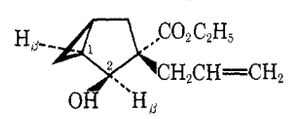
3

a, R = OC_2H_5
b, R = CHN_2

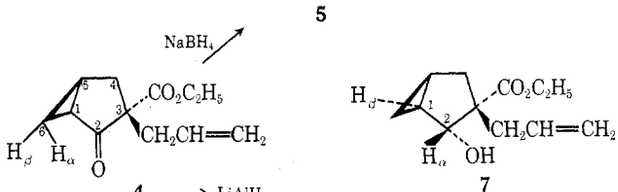
Decomposition of the diallyl compound **1b** gave the 3-allyl-3-carbethoxybicyclo[3.1.0]hexan-2-one (**4**) as the major product.

The configurational assignment of **4** is based on nmr data obtained for compound **4** itself and for the alcohols **5** and **6**. As we showed earlier[2] in detail, the resonance of the geminal cyclopropyl protons is a good indicator of the steric relationship between the cyclopropane ring and a carbonyl group attached at C_3 in the bicyclo[3.1.0]hexane system. In accordance, the presence of the one-proton upfield multiplet centered at δ 0.98 ppm in the spectrum of **4**, due to the endo proton $H_{6\alpha}$, indicates that this proton is anisotropically unaffected by the ester carbonyl group. Thus, the cyclopropane and the carbethoxy group should be trans located to each other.

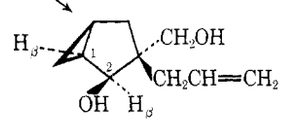
In order to obtain further spectral evidence, small samples of **4** were reduced with $NaBH_4$ and $LiAlH_4$ to the hydroxy ester **5** and the diol **6**, respectively, and their nmr



5



4 **7**



6

spectra were investigated. The most significant feature of the spectra was the presence of a doublet attributed to the tertiary proton $H_{2\beta}$ and observed at δ 4.82 and 4.41 ppm for compounds **5** and **6**, respectively. The splitting of these absorptions to a doublet is reasonably explained as resulting from coupling with the cis proton $H_{1\beta}$;[4] *e.g.*, the C_2 hydroxyl and the cyclopropane ring have to be cis related to each other.[6] It is important to note the large difference (Δ = 4.80 − 4.40 = 0.40 ppm) in the chemical shifts observed for the $H_{2\beta}$ in the spectra of alcohols **5** and **6**. This difference is apparently induced by the anisotropy of the carbonyl group[9] present only in the hydroxy ester **5** and clearly indicates the cis relationship between this proton and the carbethoxy group in this compound.

The reliability of this method in stereochemical investigations of suitably substituted cyclopentane ring systems could be demonstrated on the stereoisomeric model com-