**Reactions Procedures.** Reactions of 2-butyl halides and tosylate with the various base–solvent solutions were carried out using either an ampoule technique[32] or a nitrogen gas sweep method[33] (10-min reaction time) as indicated in the tables. Elimination products were analyzed by glpc as before.[32,33]

**Control Experiments.** Negligible amounts of butenes resulted from the solvolysis of 2-butyl bromide and tosylate in *tert*-BuOH at 50° in the presence of 2,6-lutidine[34] for reaction periods comparable with those employed in reactions with *t*-BuOK–*t*-BuOH. Formation of butenes by solvolysis of 2-butyl bromide and iodide in various other solvents was shown to be insignificant when compared with the corresponding base-promoted reactions.

**Acknowledgment.** A portion of this research was supported by a Grant-in-Aid of Research from the Society of the Sigma Xi.

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[32] R. A. Bartsch, *J. Org. Chem.*, **35**, 1334 (1970).
[33] R. A. Bartsch, *ibid.*, **35**, 1023 (1970).
[34] Present to prevent acid-catalyzed reactions of substrate or products.

# Electrophilic Additions to Dienes. III.[1,2] Hydrochlorination of Phenylallene and Its Derivatives

**Tadashi Okuyama,* Kunisuke Izawa, and Takayuki Fueno**

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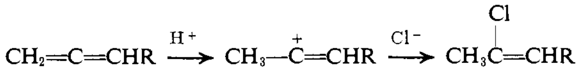
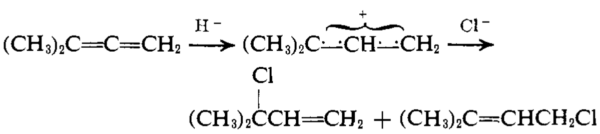
**Abstract:** The hydrochlorination of phenylallene and its derivatives (*p*-$CH_3$, *m*-$CH_3$, *p*-Cl, *m*-Cl, $\alpha$-$CH_3$, and $\gamma$-$CH_3$) has been investigated in glacial acetic acid. The product of each reaction was exclusively cinnamyl chloride or its derivative. The kinetic order of the reaction with respect to hydrogen chloride was one at lower concentrations ([HCl] = 0.10–0.25 *M*) and two at higher concentrations ([HCl] = 0.64–1.33 *M*). The effects of ring substituents on the reaction rate obey the Hammett-type relationship with Brown–Okamoto's $\sigma^+$ giving $\rho^+ = -4.20$ ([HCl] = 0.955 *M*, 30.4°). The $\alpha$- and $\gamma$-methyl substitutions accelerate the reaction by a factor of 4000 and 200, respectively. These results led us to conclude that the hydrochlorination of phenylallene proceeds through a transition state which structurally resembles the perpendicularly twisted $\alpha$-vinylbenzyl cation.

Although the electrophilic addition reactions to allenic compounds have been studied fairly widely,[3] factors which determine the course of reaction are not at all understood. The investigations so far available are concerned only with the orientation[4] and the stereochemistry[5] of addition. Surprisingly, no information is available with regard to the kinetic phase of the reaction.[6]

The orientation of addition depends both on the structure of allene and on the nature of electrophile. In the case of hydrochlorination, a proton, the simplest electrophile, attacks the terminal methylene of allene and monoalkylallenes to give vinylic cation while it attacks the central carbon of 1,1-dimethylallene leading to allylic cation.[3,4a] Because of the conjugative nature of an intermediate allylic cation, the product studies of the latter type of reaction cannot establish which double bond is attacked first by the proton.



$$\mathrm{CH_2{=}C{=}CHR \xrightarrow{H^+} CH_3{-}\overset{+}{C}{=}CHR \xrightarrow{Cl^-} CH_3\overset{\overset{\displaystyle Cl}{|}}{C}{=}CHR} \tag{1}$$



$$\mathrm{(CH_3)_2C{=}C{=}CH_2 \xrightarrow{H^-} (CH_3)_2C\overbrace{{\cdots}CH{\cdots}}^{+}CH_2 \xrightarrow{Cl^-}}$$
$$\mathrm{(CH_3)_2\overset{\overset{\displaystyle Cl}{|}}{C}CH{=}CH_2 + (CH_3)_2C{=}CHCH_2Cl} \tag{2}$$

The present paper reports the results of kinetic studies on the hydrochlorination of phenylallene and its derivatives and establishes the orientation of addition in the rate-determining step. Furthermore, the nature of the transition state in the protonation of phenylallene will be clarified.

## Results

**Product Analysis.** Hydrochlorination of phenylallene **1** was undertaken in glacial acetic acid at [HCl] = 0.955 *M*. The reaction proceeds at a moderate rate at room temperature. The reaction for 2 days gave exclusively cinnamyl chloride (>99% by nmr; isolated in 95% yield). The product isolated by distillation was compared with an authentic sample. No sign of the formation of the isomeric chlorides was observed. Careful examination of the product revealed formation of a small amount of an acetate (<0.5% by nmr).

**Kinetic Studies.** Initial rates *R* for the reaction were gas chromatographically measured as a function of the concentrations of **1** and HCl. Logarithmic plots of *R vs.* [HCl] at [**1**] = 0.455 *M* are shown in Figure 1. The slope was calculated by the method of least squares to be 1.97. Similar plots of *R vs.* [**1**] at [HCl] = 0.955

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[1] Part I: T. Okuyama, K. Izawa, and T. Fueno, *Tetrahedron Lett.*, 3295 (1970); preliminary communication of the present paper.
[2] Part II: T. Okuyama, T. Sakagami, and T. Fueno, *Tetrahedron*, **29**, 1503 (1973).
[3] For reviews, see K. Griesbaum, *Angew. Chem., Int. Ed. Engl.*, **5**, 933 (1966); D. R. Taylor, *Chem. Rev.*, **67**, 317 (1967).
[4] (a) T. L. Jacobs and R. N. Johnson, *J. Amer. Chem. Soc.*, **82**, 6397 (1960); (b) H. G. Peer, *Recl. Trav. Chim. Pays-Bas*, 81, 113 (1962); (c) W. L. Waters and E. F. Kiefer, *J. Amer. Chem. Soc.*, **89**, 6261 (1967); (d) T. L. Jacobs and R. Macomber, *J. Org. Chem.*, **33**, 2988 (1968).
[5] (a) T. L. Jacobs, R. Macomber, and D. Zunker, *J. Amer. Chem. Soc.*, **89**, 7001 (1967); (b) W. L. Waters, W. S. Linn, and M. C. Caserio, *ibid.*, **90**, 6741 (1968); (c) R. D. Bach, *ibid.*, **91**, 1771 (1969); (d) M. C. Findlay, W. L. Waters, and M. C. Caserio, *J. Org. Chem.*, **36**, 275 (1971).
[6] The kinetic discussion is reported only in ref 4a. Unfortunately, the investigation without solvent and at low temperature made it qualitative.

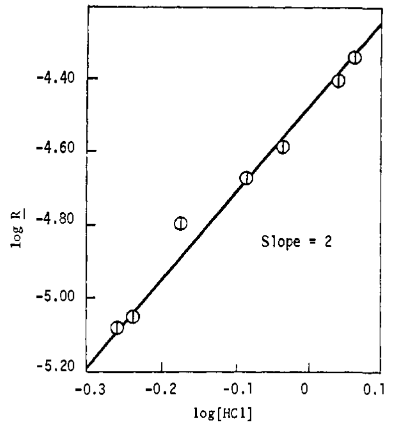


Figure 1. Log–log plots of the initial rate $R$ as a function of [HCl]; [**1**] = 0.455 $M$, 30.4°.

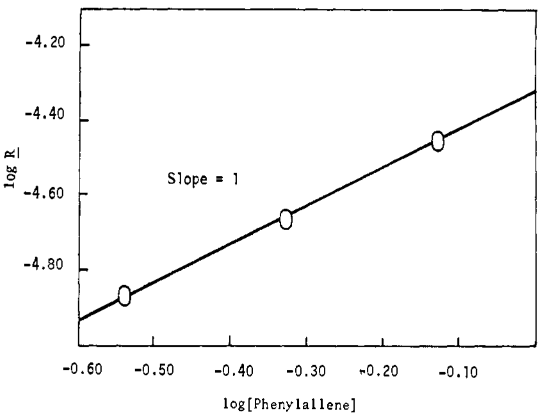


Figure 2. Log–log plots of the initial rate $R$ as a function of [**1**]; [HCl] = 0.955 $M$, 30.4°.

$M$ gave a slope of 1.10 as is seen in Figure 2. Thus, in the region of [HCl] = 0.64–1.33 $M$, the reaction is first order with respect to **1** and second order in acid. The same kinetic order of two in HCl was observed previously in the hydrochlorination of acetylenes[7] and olefins[8] under similar conditions. The rate equation is given by

$$\text{rate} = k_3[\mathbf{1}][\text{HCl}]^2 \qquad (3)$$

The third-order rate constants $k_3$ were calculated by the integrated form of eq 3[9] for each run of reaction.

Kinetic measurements for ring-substituted derivatives have also been carried out at 30.4° and [HCl] = 0.955 $M$. The $k_3$ values as the averages of three runs are given in Table I. The error is less than 5%.

**Table I.** Third-Order Rate Constants for the Hydrochlorination of Ring-Substituted Phenylallenes[a]

| Substituent | $10^4k_3$, $M^{-2}$ sec$^{-1}$ |
|---|---|
| $p$-CH$_3$ | 32.7 |
| $m$-CH$_3$ | 3.99 |
| H | 1.47[b]<br>1.12<br>0.534[c] |
| $p$-Cl | 0.469 |
| $m$-Cl | 0.0365 |

[a] [HCl] = 0.955 $M$; [allene] = 0.455 $M$; 30.4°. [b] At 34.3°. [c] At 25.1°.

From the temperature-dependence data, the activation parameters at 30° were calculated for **1**: $\Delta H^{\ddagger} = 19.4$ kcal/mol and $\Delta S^{\ddagger} = -12.7$ eu.

The reactions of $\alpha$- and $\gamma$-methylphenylallenes (**2** and **3**) were too fast to be followed under the same conditions. Therefore, the rate measurements of these compounds as well as **1** have been carried out at a lower acid concentration of [HCl] = 0.198 $M$. In this region of acid concentration, the reaction was first order both in an allene and acid. The second-order rate constants $k_2$ are summarized in Table II. The product was again exclusively cinnamyl chloride or a methylcinnamyl chloride,[10] depending on the starting material. The mechanism of reaction is regarded to be essentially the same as that at higher acid concentrations.

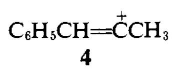
**Table II.** Second-Order Rate Constants for the Hydrochlorination of Phenylallene Derivatives[a]

| Substrate | $k_2$, $M^{-1}$ sec$^{-1}$ | Relative rate |
|---|---|---|
| $C_6H_5CH{=}C{=}CH_2$ | $3.05 \times 10^{-6}$ | 1 |
| $C_6H_5C(CH_3){=}C{=}CH_2$ | $1.23 \times 10^{-2}$ | 4000 |
| $C_6H_5CH{=}C{=}CH(CH_3)$ | $6.15 \times 10^{-4}$ | 200 |
| $C_6H_5CH{=}CHCH{=}CH_2$[b] | $3.4 \times 10^{-3}$ | 1100 |

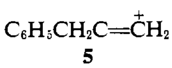
[a] 14.7°; [HCl] = 0.198 $M$; [substrate] = 0.138 $M$. [b] Reference 13.

## Discussion

Finding of a cinnamyl chloride as an exclusive reaction product excludes the possibility of the terminal-carbon protonation, *i.e.*, the formation of vinylic cations like **4** and **5**. This observation is in contrast

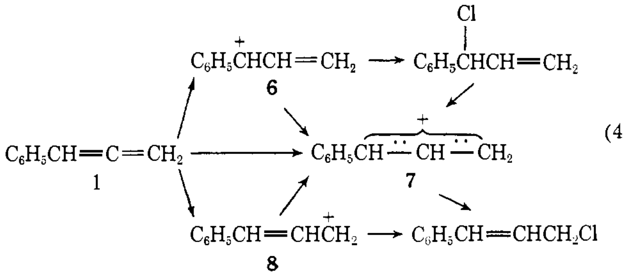

$C_6H_5CH{=}\overset{+}{C}CH_3$

**4**


$C_6H_5CH_2C{=}\overset{+}{C}H_2$

**5**

with the result for hydrochlorination of monoalkylallenes in which the protonation occurs at the terminal methylene to form a vinylic cation.[4a] The remaining pathways that can be conceived for the present reaction are as follows



(4)

where the cations **6** and **8** are both different from the allylic intermediate **7** in that the p$\pi$-atomic orbital of the charged-center atom in the former two ions still

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[7] R. C. Fahey and D. J. Lee, *J. Amer. Chem. Soc.*, 88, 5555 (1966); 90, 2124 (1968).

[8] R. C. Fahey, M. W. Monahan, and C. A. McPherson, *ibid.*, **92**, 2819 (1970); R. C. Fahey and M. W. Monahan, *ibid.*, **92**, 2816 (1970); R. C. Fahey and C. A. McPherson, *ibid.*, **93**, 2445 (1971).

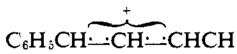
[9] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, Wiley, New York, N. Y., 1961, p 20.

[10] Although in the preliminary communication[1] the product from **2** or **3** was assigned as a methylcinnamyl acetate, it was found that the acetate was a secondary product derived from the initially formed chloride during long standing in acetic acid.

remains orthogonal to the $\pi$ orbital of the intact ethylenic bond.

**Effects of Ring Substituents.** Plots of log $k_3$ of several ring-substituted derivatives against Brown–Okamoto's $\sigma^+$ values show fairly good linear relationship as compared with those against Hammett's $\sigma$ values (Figure 3). The reaction constant $\rho^+$ was $-4.20$ with $r = 0.996$. The correlation with $\sigma^+$ values and the high negative $\rho^+$ value indicates that a positive center is in direct conjugation with the phenyl ring in the transition state. Thus, the possibility that **8** is involved as an intermediate can be ruled out. The vacant p$\pi$ orbital of the terminal carbon of **8** has no conjugative interaction with the phenyl ring.

The $\rho^+$ values of around $-4$ have been observed for the SN1 solvolyses of benzyl-type compounds[11] like $ArC(CH_3)_2Cl$ and $ArCH(CH_3)Cl$ and for various electrophilic additions to styryl compounds[12] leading to a benzylic cation. As will be reported in the succeeding paper,[13] the $\rho^+$ value of $-2.98$ was found for the hydrochlorination of *trans*-1-phenyl-1,3-butadienes.[14] This reaction is considered to proceed through the transition state close to the conjugated allylic cation **9**. The relatively low $\rho^+$ value of $-2.98$ must be due to the effective delocalization of positive charge (by allylic conjugation) in the side chain of **9**. Since the cation **7** is structurally



$$C_6H_5CH\overset{+}{\overbrace{\cdots CH\cdots}}CHCH_3$$

**9**

analogous to **9**, a reaction with the transition state resembling **7** should have a $\rho^+$ value of about $-3$. The considerably large negative $\rho^+$ value of $-4$ to $-5$ for the present reaction will be well interpreted by the reaction through the transition state like **6**, a nonconjugatively vinyl-substituted benzyl cation, rather than **7**, a conjugated allylic benzylic cation.

**Effects of $\alpha$- and $\gamma$-Methyl Substitutions.** It is well known that $\alpha$-methyl substitution at the positive center of a carbonium ion effectively stabilizes the ionic species.[15] $\alpha$-Methyl substitution would profoundly stabilize the $\alpha$ cation **6** but influence very little the stability of **8**. Correspondingly, it would accelerate the reaction through **6** but little the one through **8**. In the same manner, $\gamma$-methyl substitution would enhance the reactivity in the reaction *via* **8** but little the one *via* **6**. The relative effects of $\alpha$- and $\gamma$-methyl substitution on the stability of the conjugated allylic cation **7** are not straightforward. The $\gamma$ substitution would be at least as effective as the $\alpha$ substitution. Probably, the former is even more effective than the latter.[16]

The relative rates summarized in Table II show that the rate enhancement of an $\alpha$-methyl group is by a factor of as great as 4000 while that of a $\gamma$-methyl group is by a factor of 200. A significantly greater reactivity of $\alpha$-methylphenylallene as compared with the $\gamma$-methyl isomer (20 times) lends strong support to the exclusion of a possible transition-state structure resembling **8** and suggests again the cation **6** rather than **7** as an intermediate most closely resembling the transition state of the present reaction. The relatively large effects of $\gamma$-methyl substitution (200 times) seem to suggest some conjugative character of the side chain in the transition state. Possibly the transition state for **1** itself is not completely orthogonal and/or alternatively some transition state shift by substitution might take place and enhance the rate; $\gamma$-methyl substitution would increase the conjugative allylic character of the transition state.

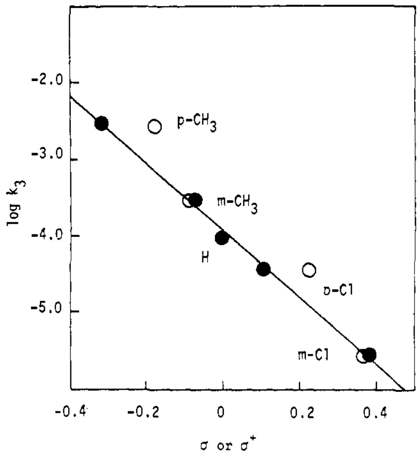


Figure 3. Hammett-type correlation of the hydrochlorination rates of ring-substituted phenylallenes: (○) Hammett's $\sigma$; (●) Brown–Okamoto's $\sigma^+$.

The results discussed here coupled with those of ring-substituted derivatives lead us to conclude that the transition state in question is structurally similar to the localized vinylbenzyl cation **6** and the reaction proceeds as follows

$$\mathbf{1} \xrightarrow[\text{slow}]{H^+} \underset{\mathbf{6}}{C_6H_5\overset{+}{C}HCH{=}CH_2} \longrightarrow \underset{\mathbf{7}}{C_6H_5CH\cdots\overset{+}{C}H\cdots CH_2} \xrightarrow{Cl^-} C_6H_5CH{=}CHCH_2Cl \quad (5$$

Although the possible formation of the $\alpha$ chloride, $C_6H_5CHClCH{=}CH_2$, as an intermediate is not completely excluded, it is highly unlikely. The perpendicularly twisted cation **6** is very unstable and easily rotates without barrier to the conjugated allylic cation **7**, which would be much faster than the collapse of **6** with nucleophile.[17]

**Comparison with the Reactivity of 1,3-Diene.** The hydrochlorination of 1-phenyl-1,3-butadiene, a prototropic isomer of **3**, has been investigated as will be detailed in the succeeding paper.[13] The comparison of the reactivity between *trans*-1-phenyl-1,3-butadiene (**10**) and the 1,2-diene **3** provides useful information about the transition state in the hydrochlorination of **3** and hence that of **1**.

The 1,3-diene **10** reacts 5.5 times faster than **3**. The conjugated diene **10** is estimated to be more stable than

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[11] *E.g.*, H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, **79**, 1913 (1957).

[12] T. Okuyama, N. Asami, and T. Fueno, *Bull. Chem. Soc. Jap.*, **43**, 3353 (1970).

[13] K. Izawa, T. Okuyama, T. Sakagami, and T. Fueno, *J. Amer. Chem. Soc.*, **95**, 6752 (1973).

[14] The $\rho^+$ value of $-5.0$ was found for phenylallenes ($p$-$CH_3$, $m$-$CH_3$, and H) at the lower acid concentration ([HCl] = 0.198 *M*) applied to the reaction of 1-phenyl-1,3-butadienes.

[15] *E.g.*, J. L. Fry, J. M. Harris, R. C. Bingham, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **92**, 2540 (1970).

[16] D. H. DeWolfe and W. G. Young, *Chem. Rev.*, **56**, 786 (1956). The $\gamma$-methyl substitution accelerates more effectively the ethanolysis of $\alpha$-methylallyl chloride than does the $\alpha$-methyl substitution.

[17] See ref 13 for further discussion about the rotation problem. The first-order rate constant for a unimolecular reaction without barrier would be of the order of $k_1 \simeq 10^{13}$ sec$^{-1}$. Thus, the fastest possible (diffusion-controlled) bimolecular reaction ($k_2 \simeq 10^{10}$ $M^{-1}$ sec$^{-1}$) could never be faster than the rotation of **6**. Furthermore, a *trans*-allylic cation gives exclusively the $\gamma$ chloride.

the allene **3** by at least 10 kcal/mol.[18] This observation indicates that the hydrochlorination of the allene **3** occurs through a transition state far less stable than that of **10**. The transition state for the reaction of **10** is established to be close to the conjugated allylic cation **9**. These comparisons are compatible with the conclusion that the transition state in the protonation of the allene is very close to the orthogonal cation **6**.[19]

## Experimental Section

**Materials.** Phenylallene (**1**) was prepared by the method of Skatteböl[20] from 1,1-dibromo-2-phenylcyclopropane, which was obtained by dibromocarbene addition to styrene:[21] bp 64° (11 mm) (lit.[20] bp 64° (11 mm)); ir (thin film) 1950, 850 $\mathrm{cm^{-1}}$; nmr ($\mathrm{CCl_4}$) $\delta$ 5.06 (2 H, d, $=\mathrm{CH_2}$), 6.07 (1 H, t, $-\mathrm{CH}=$), $J_{13}$ = 7.1 Hz.

The following allenes were also synthesized by the same method. *p*-Methylphenylallene: bp 58° (4 mm); ir (thin film) 1945, 855 $\mathrm{cm^{-1}}$; nmr ($\mathrm{CCl_4}$) $\delta$ 2.26 (3 H, s, $\mathrm{CH_3}$), 5.04 (2 H, d, $=\mathrm{CH_2}$), 6.03 (1 H, t, $-\mathrm{CH}=$), $J_{13}$ = 7.1 Hz. *m*-Methylphenylallene: bp 54° (4 mm); ir (thin film) 1948, 852 $\mathrm{cm^{-1}}$; nmr ($\mathrm{CCl_4}$) $\delta$ 2.29 (3 H, s, $\mathrm{CH_3}$), 5.06 (2 H, d, $=\mathrm{CH_2}$), 6.03 (1 H, t, $-\mathrm{CH}=$), $J_{13}$ = 7.0 Hz. *p*-Chlorophenylallene: bp 60° (4 mm); ir (thin film) 1944, 850 $\mathrm{cm^{-1}}$; nmr ($\mathrm{CCl_4}$) $\delta$ 5.09 (2 H, d, $=\mathrm{CH_2}$), 6.03 (1 H, t, $-\mathrm{CH}=$), $J_{13}$ = 7.0 Hz. *m*-Chlorophenylallene: bp 73° (5 mm); ir (thin film) 1943, 854 $\mathrm{cm^{-1}}$; nmr ($\mathrm{CCl_4}$) $\delta$ 5.13 (2 H, d, $=\mathrm{CH_2}$), 6.03 (1 H, t, $-\mathrm{CH}=$), $J_{13}$ = 7.0 Hz. $\alpha$-Methylphenylallene (**2**): bp 58° (6 mm); ir (thin film) 1946, 852 $\mathrm{cm^{-1}}$; nmr ($\mathrm{CCl_4}$) $\delta$ 2.07 (3 H, t, $\mathrm{CH_3}$), 4.95 (2 H, q, $=\mathrm{CH_2}$), $J_{3\mathrm{Me}}$ = 3.35. $\gamma$-Methylphenylallene (**3**): bp 58° (4 mm); ir (thin film) 1955, 875 $\mathrm{cm^{-1}}$; nmr ($\mathrm{CCl_4}$) $\delta$ 1.77 (3 H, q, $\mathrm{CH_3}$), 5.44 (1 H, m, $=\mathrm{CHMe}$), 6.01 (1 H, m, $\mathrm{PhCH}=$), $J_{13}$ = 6.96 Hz, $J_{3\mathrm{Me}}$ = 7.22 Hz, $J_{1\mathrm{Me}}$ = 3.43 Hz.

Styrene and $\alpha$-methylstyrene were commercially obtained. Other substituted styrenes were prepared by dehydration of the corresponding secondary alcohols[22] which were obtained by the Grignard method from an appropriate bromobenzene.

Cinnamyl chloride was prepared by the action of thionyl chloride on *trans*-cinnamyl alcohol in ether: bp 85° (6 mm); ir (thin film) 960 $\mathrm{cm^{-1}}$; nmr ($\mathrm{CCl_4}$) $\delta$ 4.14 (2 H, d, $\mathrm{CH_2Cl}$), 6.07 and 6.36 (1 H, m, $=\mathrm{CHC}$), 6.61 (1 H, d, $\mathrm{PhCH}=$), $J_{\mathrm{trans}}$ = 17 Hz, $J_{2,3}$ = 7 Hz.

**Hydrochlorination.** All the allenes were distilled under a nitrogen atmosphere immediately before use. They were over 99% pure by vpc analysis. Glacial acetic acid was refluxed overnight over triacetyl borate and distilled.[23] Solutions of hydrogen chloride in glacial acetic acid were prepared by weight. Their concentrations were determined by the following method. A solution of lithium acetate in acetic acid was added to the hydrochloric solution and the excess lithium acetate was titrated potentiometrically with standard *p*-toluenesulfonic acid in acetic acid.

The reaction solutions were prepared in a 20-ml volumetric flask by dissolving an allene (9.1 mmol) and tetralin (0.3 ml) as internal standard in a stock solution of the acid. The solutions were then immersed in a thermostated bath after vigorous shaking. A 0.3-ml aliquot was withdrawn at appropriate intervals and added with pentane (2 ml) and water (5 ml). An organic layer was separated after thorough shaking and analyzed by vpc. A Shimadzu Model 4APT gas chromatograph with a 1-m column (polyethylene glycol) was operated at 100–120° with hydrogen as carrier gas. The internal standard method coupled with the half-height width evaluation of peak area sufficed for the determination of allene concentrations. The vpc analysis was made at least two times for each sample, and the calibration revealed the data so obtained to be accurate to within ±5%.

For product analyses an extract of the reaction products was evaporated to the complete removal of solvent and applied to nmr analysis (JNM-4H-100 spectrophotometer) or fractional distillation followed by spectroscopic characterization. Nmr spectra of reaction solutions were also recorded directly.

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[18] G. B. Kistiakowsky, J. R. Ruboff, H. A. Smith, and W. E. Vaughan, *J. Amer. Chem. Soc.*, **58**, 146 (1936); M. Sakiyama, *et al.*, "Kagaku Binran," S. Seki, Ed., Maruzen, Tokyo, 1966, p 811.

[19] See the succeeding paper[13] for further discussion.

[20] L. Skatteböl, *Acta Chem. Scand.*, 17, 1683 (1963).

[21] W. von E. Doering and A. K. Hoffmann, *J. Amer. Chem. Soc.*, **76**, 6162 (1954).

[22] (a) W. S. Emerson, *Chem. Rev.*, **45**, 347 (1949); (b) C. G. Overberger and J. H. Saunders, *Org. Syn.*, **28**, 31 (1949).

[23] L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath, Boston, Mass., 1955.

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# Electrophilic Additions to Dienes. IV.[1] Hydrochlorination of 1-Phenyl-1,3- and 1-Phenyl-1,2-butadienes

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*Contribution from the Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560, Japan.* *Received March 23, 1973*

**Abstract**: Hydrochlorination of *cis*- and *trans*-1-phenyl-1,3-butadienes (**1c** and **1t**) and 1-phenyl-1,2-butadiene (**4**) has been investigated kinetically in glacial acetic acid. All the isomeric dienes gave the same product, *trans*-1-methyl-3-phenylallyl chloride (**5t**). The reactions of both **1t** and **1c** were retarded in DCl–DOAc by a factor of *ca.* 2. The second-order rate constants of ring-substituted derivatives of **1t** obeyed the Hammett-type $\rho^+\sigma^+$ relationship with $\rho^+ = -2.98$. Clearly, the reaction involves the rate-determining protonation of dienes to give intermediate allylic cations. The heats of activation observed for **1t**, **1c**, and **4** were 16.4, 21.3, and 17.8 kcal/mol, respectively. The height of the rotational barrier for the cis allylic cation (**3c**) formed from **1c** was estimated to be 7.6 ± 1 kcal/mol, which is sufficiently low to permit its rapid isomerization to the trans allylic cation (**3t**). It is suggested that the isomerization can take place through the chloride attack at the $\mathrm{C_1}$ atom as well.

The structure of allylic cations has recently stimulated interest of organic chemists. High rotational barriers of the cations have been demonstrated experimentally and reproduced by theoretical calculations.[2] Solvolysis studies on allylic compounds also indicate the geometrical stability of allylic cations.[3]

Recently, Pocker and Hill[4] reported the results of their investigations on the acid-catalyzed isomerization of *cis*-1-phenyl-1,3-butadiene (**1c**) and *cis*-1-methyl-

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[1] Part III: T. Okuyama, K. Izawa, and T. Fueno, *J. Amer. Chem. Soc.*, **95**, 6749 (1973).

[2] V. Buss, R. Gleiter, and P. v. R. Schleyer, *ibid.*, **93**, 3927 (1971), and papers cited therein.

[3] W. G. Young and J. S. Franklin, *ibid.*, **88**, 785 (1966), and papers cited therein.

[4] Y. Pocker and M. J. Hill, *ibid.*, **93**, 691 (1971).