

ELECTROPHILIC ADDITIONS TO ALLENES. THE NATURE OF THE TRANSITION STATE
IN THE PROTONATION OF PHENYLALLENES

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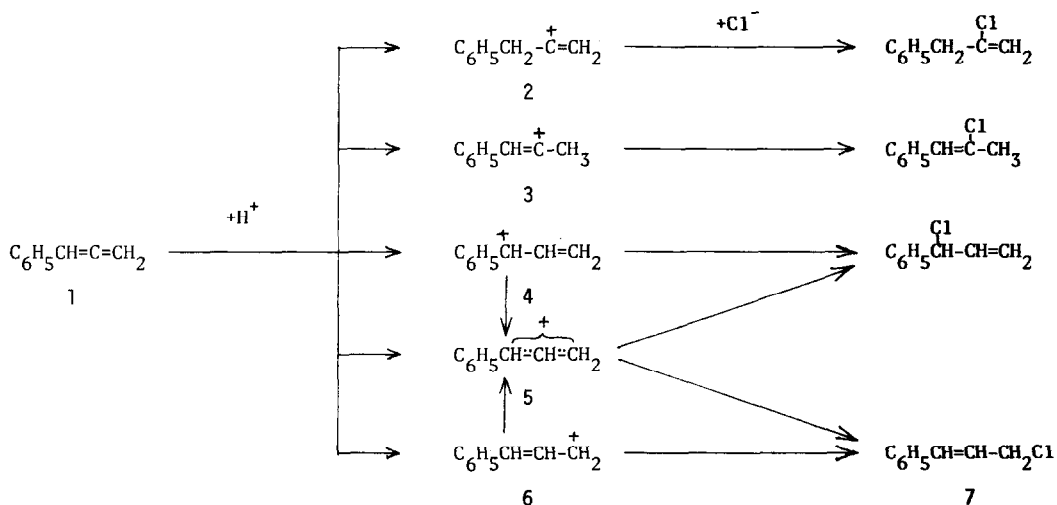
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We wish to report here the results of kinetic studies on the hydrochlorination of phenylallene 1 and its derivatives, and discuss about a salient characteristic of this reaction in its transition state.

Electrophilic additions to allenic compounds have already been investigated fairly widely by a number of workers.¹⁻³ However, the scope of investigation has so far been confined to the orientation¹ and stereochemistry² of the addition, and little information is available with regard to the kinetic phase of the reaction, still less to the nature of its transition state. The following are aimed at clarifying a transition state model of the hydrochlorination of a series of phenylallenes.

The pathways that can be conceived for the present reaction are essentially as follows:

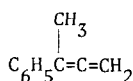
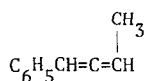


In analogy to the case of the hydrochlorination of 1-phenylpropyne⁴ and styrene,⁵ the structure of the transition state is considered to be close to a carbonium ion (or more precisely ion pair^{4,5}) resulting from the protonation, and be closest to some particular one of the possible intermediate cations 2 to 6. The cations 4 and 6 are both different from the allylic intermediate 5 in that the $p\pi$ atomic orbital of the charged-center carbon atom in the former two ions still remains orthogonal to the π orbital of the intact ethylenic bond.

Hydrochlorination of **1** in glacial acetic acid ($[HCl] = 0.955M$) at 30.4° gave cinnamyl chloride **7** exclusively, the yield being over 98%. Thus, the first two possibilities, involving the formation of the vinyl cation intermediates **2** and **3**, must be excluded. Under the same conditions, the reaction was first order in **1** and second order in hydrochloric acid,⁶ as has been observed in the hydrochlorination of acetylenes.⁴ The third-order rate constant, k_3 , for **1** was $1.12 \times 10^{-4} \text{ l}^2 \text{ mole}^{-2} \text{ sec}^{-1}$.

Next, the effect of ring substituents ($p\text{-CH}_3$, $m\text{-CH}_3$, $p\text{-Cl}$, and $m\text{-Cl}$) on the rate was examined under the same reaction condition as above. The observed effect of substituents obeyed a Hammett-type relationship with Brown-Okamoto's σ^+ as the substituent constants ($\rho = -4.20$, $r = 0.996$). This observation suggests that a positive center be in direct conjugation with the phenyl ring in the transition state. Hence, the cationic intermediate **6** can be ruled out as a model of the transition state.

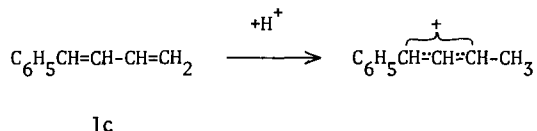
In order to decide which of the remaining two intermediates **4** and **5** is the closer to the transition state, we have undertaken to investigate the effects of α - and γ -methyl substitutions on the rate.

**1a****1b**

Both α - and γ -methylphenylallenes, **1a** and **1b**, were found to be too reactive to be followed kinetically in the above HCl-HOAc solution at 30.4° . Under these circumstances, the rates of disappearance of **1a** and **1b** have been measured in an HCl-HOAc solution of $[HCl] = 0.198 M$ at 14.7° . In this region of acid concentration, the reaction was first order in both allene and acid, and the products were essentially methylcinnamyl acetates instead of chlorides.⁷ The second-order rate constants, k_2 , for **1a** and **1b** were 1.23×10^{-2} and $6.15 \times 10^{-4} \text{ l mole}^{-1} \text{ sec}^{-1}$, respectively. Under these conditions, the k_2 value for **1** was $3.05 \times 10^{-6} \text{ l mole}^{-1} \text{ sec}^{-1}$.

The α -methyl substitution thus enhances the rate of protonation of phenylallene by a factor of as great as ca. 4000, while the γ -methyl group by a factor of ca. 200. The significantly greater reactivity (ca. 20 times) of α -methylphenylallene in comparison with that of the γ -methyl isomer suggests that the transition state in question is somewhat closer to the localized allylic cation 4 than to the delocalized cation 5. If it were very close to 5, the rate-enhancing effect of the γ -methyl substitution should at least be comparable in magnitude with, or even be greater⁸ than, that of the α -methyl substitution.

Finally, trans-1-phenyl-1,3-butadiene 1c, a prototropic isomer of 1b, has been subjected to the rate measurement under the same conditions as adopted for 1a and 1b. The k_2 value was $3.4 \times 10^{-3} \text{ l mole}^{-1} \text{ sec}^{-1}$, a value which was ca. 5.5 times greater than that for 1b. No doubt, an electrophilic addition of a 1,3-diene proceeds through the delocalized allylic cation, with a transition state close to a structure similar to 5.⁹



According to the literature,¹⁰ a 1,3-diene is thermochemically more stable than the corresponding 1,2-diene by 10 — 15 kcal/mole. The smaller reactivity of 1b despite its lesser stability as compared with 1c clearly indicates that the protonation of the former compound proceeds through a transition state of higher energy than that of the latter. The indication is compatible with the above suggestion concerning the transition state of 1.

In conclusion, the three observations described above indicate that the hydrochlorination (protonation) of phenylallenes proceeds through a transition state closely related to the localized allylic cation 4 in structure. Further details will shortly be presented elsewhere.

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4. R. C. Fahey and D.-J. Lee, ibid., 88, 5555 (1966).
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6. Rates were measured by a gaschromatographic method analogous to that adopted by Fahey et al.^{4,5} Tetralin was used as internal standard.
7. During the reaction, the formation of conjugated dienes (rearranged products) was observed. However, the observed rates must be those of protonation of allenes.
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