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 cm^{-1}; nmr (CCl_4) δ 5.06 (2 H, d, $=CH_2$), 6.07 (1 H, t, $-CH=$), 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 cm^{-1}; nmr (CCl_4) δ 2.26 (3 H, s, CH_3), 5.04 (2 H, d, $=CH_2$), 6.03 (1 H, t, $-CH=$), J_{13} = 7.1 Hz. *m*-Methylphenylallene: bp 54° (4 mm); ir (thin film) 1948, 852 cm^{-1}; nmr (CCl_4) δ 2.29 (3 H, s, CH_3), 5.06 (2 H, d, $=CH_2$), 6.03 (1 H, t, $-CH=$), J_{13} = 7.0 Hz. *p*-Chlorophenylallene: bp 60° (4 mm); ir (thin film) 1944, 850 cm^{-1}; nmr (CCl_4) δ 5.09 (2 H, d, $=CH_2$), 6.03 (1 H, t, $-CH=$), J_{13} = 7.0 Hz. *m*-Chlorophenylallene: bp 73° (5 mm); ir (thin film) 1943, 854 cm^{-1}; nmr (CCl_4) δ 5.13 (2 H, d, $=CH_2$), 6.03 (1 H, t, $-CH=$), J_{13} = 7.0 Hz. α-Methylphenylallene (**2**): bp 58° (6 mm); ir (thin film) 1946, 852 cm^{-1}; nmr (CCl_4) δ 2.07 (3 H, t, CH_3), 4.95 (2 H, q, $=CH_2$), $J_{3\mathrm{Me}}$ = 3.35. γ-Methylphenylallene (**3**): bp 58° (4 mm); ir (thin film) 1955, 875 cm^{-1}: nmr (CCl_4) δ 1.77 (3 H, q, CH_3), 5.44 (1 H, m, $=CHMe$), 6.01 (1 H, m, $PhCH=$), J_{13} = 6.96 Hz, $J_{3\mathrm{Me}}$ = 7.22 Hz, $J_{1\mathrm{Me}}$ = 3.43 Hz.

Styrene and α-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 cm^{-1}; nmr (CCl_4) δ 4.14 (2 H, d, CH_2Cl), 6.07 and 6.36 (1 H, m, $=CHC$), 6.61 (1 H, d, $PhCH=$), J_{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.

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

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

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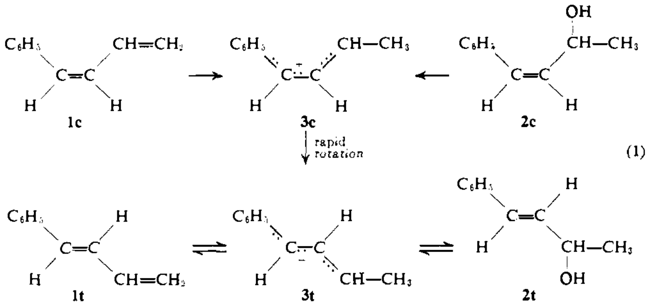
[1] Part III: T. Okuyama, K. Izawa, and T. Fueno, *J. Amer. Chem. Soc.*, **95**, 6749 (1973).

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

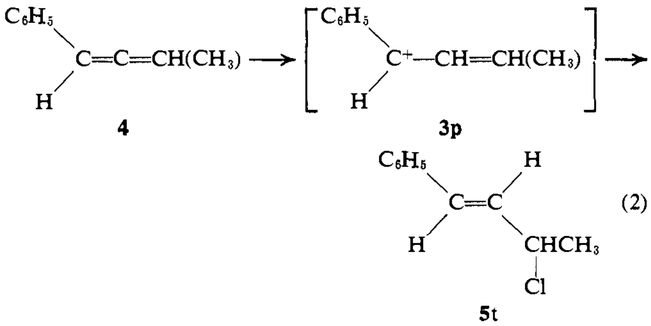
[3] W. G. Young and J. S. Franklin, *ibid.*, **88**, 785 (1966), and papers cited therein.

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

3-phenylallyl alcohol (**2c**) in aqueous media. Their careful studies led them to conclude that the reaction proceeds through the rate-determining formation of a cis allylic cation (**3c**), followed by rapid rotation about its C_1–C_2 bond, giving the trans cation (**3t**) prior to its collapse with a water molecule of the solvent.



The direct isomerization of **3c** to **3t**, as involved in reaction 1, should necessarily pass through a perpendicular allylic cation (**3p**) having a localized olefinic bond. We have shown in the preceding paper[1] that this cation **3p** can be regarded as a model of the intermediate for the hydrochlorination of 1-phenyl-1,2-butadiene (**4**) to give *trans*-1-methyl-3-phenylallyl chloride (**5t**). Examination of the relative stabilities of **3c**, **3t**, and **3p** is expected to present a useful guide for assessing the conclusion of Pocker and Hill.[4]



We have thus undertaken to investigate the kinetics of hydrochlorination of the isomeric 1-phenylbutadienes (**1c**, **1t**, and **4**) under essentially the identical condition. All the dienes gave the same product **5t**. The observed kinetic features have illuminated the mechanism of geometrical isomerization of **3c** to **3t**.

Experimental Section

Materials. *trans*-1-Phenyl-1,3-butadiene (**1t**) and its ring-substituted derivatives were prepared by the method of Grummitt and Christoph.[5] Their boiling points were: **1t**, 70° (7 mm) (lit.[5] 83° (11 mm)); *p*-CH_3, 90.5° (7 mm); *m*-CH_3, 98° (7 mm); *p*-Cl, 99° (7 mm); and *m*-Cl, 97° (7 mm). Infrared spectra of these compounds showed absorption at *ca.* 10.5 μ (lit.[5] 10.56 μ for **1t**). Nmr spectra were consistent with the structure but full analysis was not practiced. *cis*-1-Phenyl-1,3-butadiene (**1c**) was obtained by the photoisomerization[5] of **1t** and fractionated by preparative vpc; ir 14.2 μ (lit.[5] 14.20 μ). Preparation of 1-phenyl-1,2-butadiene (**4**) was described in the preceding paper.[1] All the dienes were chromatographically pure.

Reactions in HCl–HOAc. The procedure was the same as described before.[1] Reaction products were extracted with *n*-pentane, isolated by fractionation, and identified by nmr and ir spectra: *trans*-1-methyl-3-phenylallyl chloride (**5t**); nmr (CCl_4) δ 1.68 (3 H, d, CH_3) 4.62 (1 H, m, -CH(Cl)-), 6.18 (1 H, q, =CH-), 6.52 (1 H, d, PhCH=).

Reactions in DCl–DOAc. A solution of DCl in DOAc was prepared according to the literature.[6] Nmr analysis showed that acetic acid-*O-d* contained less than 2% of hydroxylic protons. Kinetic measurements were carried out in the same way as in the protium medium. Deuterium distribution in the product was determined by nmr spectroscopy after work-up as in the case of the HCl–HOAc reaction.

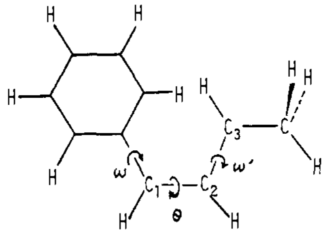


Figure 1. The rotation angles θ, ω, and ω' defined for the 1-phenyl-3-methylallyl cation. In the hypothetical planar cis cation, $\theta = \omega = \omega' = 0°$.

Theoretical Calculations. The total energy and charge density of the 1-phenyl-3-methylallyl cation (**3**) were calculated as the function of the rotation angles θ, ω, and ω' (Figure 1) around the C_1–C_2, C(phenyl)–C_1, and C_2–C_3 bonds, respectively, by the extended Hückel molecular orbital method.[7] Conformation of the methyl group was assumed to be the same as in propylene.[8] For the sake of simplicity, the rotation angle ω' was in most cases fixed at 0°. The bond angles for the sp^2 and sp^3 carbon atoms were assumed to be 120 and 109°28′, respectively. The carbon–carbon bond distances were taken as 1.51 (C_3–CH_3), 1.43 (C_1–C_2 and C_2–C_3), 1.49 (C(phenyl)–C_1), and 1.397 Å (C(phenyl)–C(phenyl)), respectively. The carbon–hydrogen bond distances were assumed to be 1.09 (CH_3), 1.08 (olefinic CH), and 1.084 Å (aromatic CH). Calculations were carried out on a NEAC-2200/500 at the Osaka University Computation Center.

Results

Product Studies. Hydrochlorination of **1t** takes place readily in glacial acetic acid at 18° to give *trans*-1-methyl-3-phenylallyl chloride (**5t**) quantitatively (>98%). The cis isomer **1c** gave the same product **5t** (>97%) though more slowly under the same conditions. The reaction of **1c** was carried out also in the deuterium medium (DCl–DOAc) in order to determine the protonation site. Nmr analysis of the product showed the presence of D at the terminal carbon only, indicating that the reaction takes place through protonation at the C_4 atom exclusively.

Kinetic Studies. The compounds studied here include **1c**, **1t**, and the ring-substituted derivatives of the latter (*p*-CH_3, *m*-CH_3, *p*-Cl, and *m*-Cl) as well as 1-phenyl-1,2-butadiene **4**. Hydrochlorination of **1** was found to be first order with respect to both **1** and HCl in the region of the initial acid concentration $[HCl]_0$ = 0.07–0.20 *M*. Figure 2 shows that the pseudo-first-order decay of **1t** holds usually down to *ca.* 20% conversion when $[HCl]_0 = 1.5[\mathbf{1t}]_0$. The pseudo-first-order rate constants k_1 determined in the conversion range of 15% or less were precisely proportional to $[HCl]_0$. The second-order rate constants k_2 were obtained as $k_1/[HCl]_0$ at temperatures 18.0–28.3°. The results are given in Table I.

In the same way, the rate constants k_2 for the ring-substituted derivatives of **1t** were obtained at 18.0°. The effects of substituents on the rate of **1t** obeyed the Hammett-type relationship with Brown–Okamoto's

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(5) O. Grummitt and F. J. Christoph, *J. Amer. Chem. Soc.*, **73**, 3479 (1951).

(6) R. C. Fahey, M. W. Monahan, and C. A. McPherson, *ibid.*, **92**, 2810 (1970).

(7) R. Hoffmann, *J. Chem. Phys.*, **40**, 2480 (1964).

(8) D. R. Herschbach and L. C. Krisher, *ibid.*, 28, 728 (1955).

Table I. Second-Order Rate Constants for the Hydrochlorination of Phenylbutadienes

Substrate	Temp, °C	[HCl], M	[PBD], M	10^3k_2, M^{-1} sec^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
1c	15.2	0.133	0.20	0.0393	21.3	−5.36
	28.3	0.133	0.20	0.168		
	35.0	0.133	0.20	0.451		
1t	14.7	0.198	0.138	3.40	16.4	−11.2
	16.8	0.133	0.20	4.38		
	18.0	0.072	0.092	4.98		
	18.0	0.133	0.092	4.95		
	18.0	0.140	0.092	4.92		
	28.3	0.133	0.20	10.7		
p-CH$_3$	18.0	0.140	0.091	46.2		
m-CH$_3$	18.0	0.140	0.091	7.25		
p-Cl	18.0	0.140	0.092	3.18		
m-Cl	18.0	0.140	0.091	0.357		
4	14.7	0.198	0.138	0.615	17.8	−16.5
	15.9	0.133	0.20	0.639		
	28.3	0.133	0.20	2.08		
	35.0	0.133	0.20	4.68		

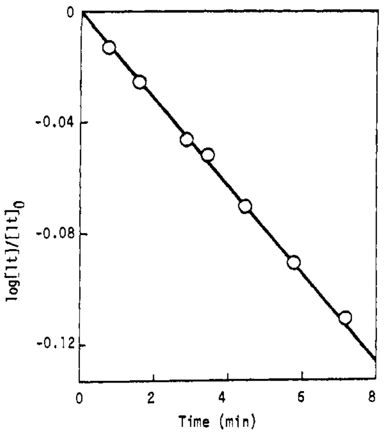


Figure 2. Pseudo-first-order plots for the hydrochlorination of **1t** at 18.0°; [**1t**]$_0$ = 0.092 M; [HCl]$_0$ = 0.140 M.

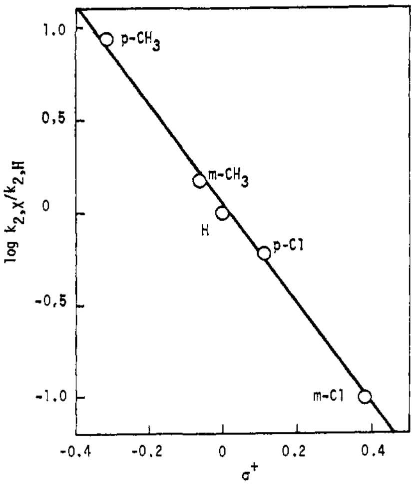


Figure 3. The Hammett-type correlation of the hydrochlorination rates of ring-substituted **1t** at 18.0°.

σ^+ (Figure 3). The reaction constant ρ^+ was −2.98 with a correlation coefficient r = 0.987.

The rates of hydrochlorination of **1c** and **4** were also measured at varying temperature. The data listed in Table I show that **4** is clearly less reactive than **1t** but is far more reactive than **1c**.

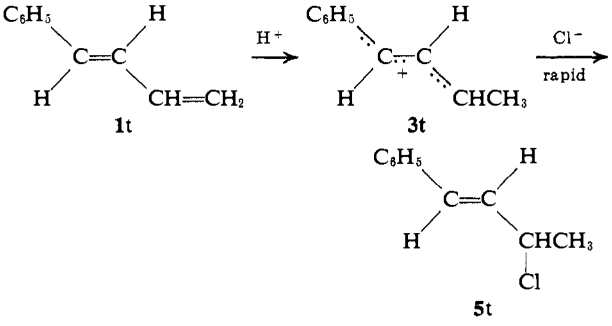
From the k_2 values listed in Table I, activation parameters, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, were calculated for **1c**, **1t**, and **4** in a usual manner. The results are included in Table I.

The kinetic deuterium isotope effects on the reaction of **1c** and **1t** were measured in DCl–DOAc at 28.3°. The second-order rate constants k_2 of 0.109 and 4.65 × 10^{-3} M^{-1} sec^{-1} were obtained for **1c** and **1t**, respectively. That is, the reaction was retarded in the deuterium medium by a factor of 1.54 and 2.30 for **1c** and **1t**, respectively.

EHMO Calculations. The total energies (relative to **3t**) and charge distributions (over the allyl carbons) calculated for various conformations of **3** are given in Table II. The rotation angles of θ = 90 and 180° correspond to the intermediate phenylallyl cations, **3p** and **3t**, respectively. For the cation **3c**, the rotation angles are somewhat uncertain. Implications of the results given in Table II will be discussed in the section that follows.

Discussion

The observed kinetic isotope effect of $k_H/k_D \simeq 2$ shows most convincingly that the hydrochlorination of both **1c** and **1t** proceeds through the rate-determining protonation,[9] as is generally accepted for related reactions.[10,11] No doubt, the reaction of **1t** can be represented by the two-step 3,4-addition scheme as follows.



(3)

The rates of hydrochlorination of the ring-substituted derivatives of **1t** obeyed the Hammett-type relationship with σ^+ giving ρ^+ = −2.98. This ρ^+ value is very close to that (ρ^+ = −3.1) found[12] for the acid-

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[9] K. B. Wiberg, *Chem. Rev.*, **55**, 713 (1955).

[10] Y. Pocker and M. J. Hill, *J. Amer. Chem. Soc.*, **91**, 7154 (1969).

[11] R. C. Fahey and C. A. McPherson, *ibid.*, **91**, 3865 (1969).

[12] The ρ^+ value was calculated from the data given in the literature.[13]

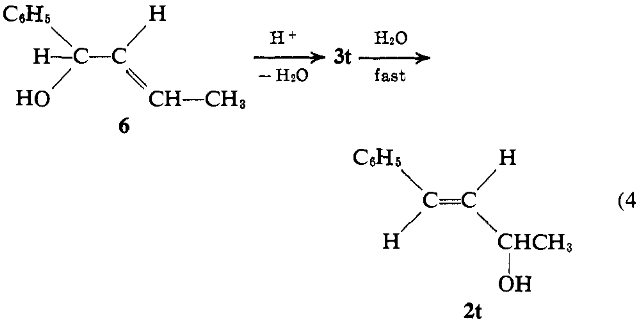
[13] E. A. Braude and E. S. Stern, *J. Chem. Soc.*, 1096 (1947).

Table II. Results of the EHMO Calculations on 1-Phenyl-3-methylallyl Cation[a]

No.	θ, deg	ω, deg	ω', deg	Charge density[b]			ΔE, kcal/mol
				C_1	C_2	C_3	
1	0	0	0	−517	−141	24	107.8
2	0	30	0	155	−144	209	38.0
3	0	45	0	207	−146	270	12.0
4	0	60	0	244	−149	299	2.78
5	0	30	30	53	−122	358	17.2
6	30	0	0	168	−152	193	38.6
7	30	30	0	224	−142	232	4.26
8	30	45	0	263	−145	236	1.24
9	45	0	0	255	−149	161	15.9
10	60	0	0	343	−138	56	10.1
11 (**3p**)	90	0	0	449	−125	−95	10.6
12	120	0	0	362	−134	37	7.33
13	135	0	0	290	−141	153	4.49
14	150	0	0	232	−149	225	2.04
15 (**3t**)	180	0	0	85	−160	292	0

[a] For the conformation, see Figure 1. [b] $(4.000 - q) \times 10^3$.

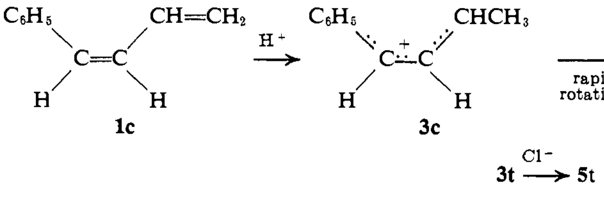
catalyzed rearrangement of 1-phenyl-3-methylallyl alcohol (**6**).[13,14] This agreement of the ρ^+ values im-



(4)

plies that the transition states for both the reactions 3 and 4 have the electronic structure which closely resembles that of the trans allylic intermediate cation **3t**.

As for the reaction of **1c**, the product was also **5t**. Thus the overall reaction should involve the rate-determining protonation plus a complete isomerization with respect to the C_1–C_2 bond. The possibility that the isomerization may occur through the protonation of the C_1–C_2 bond was ruled out by the results of the deuterium incorporation experiments.[15] Therefore, it is very likely that the hydrochlorination of **1c** proceeds by the mechanism involving the direct isomerization of **3c** to **3t**, as was proposed by Pocker and Hill (eq 1).[4] Whether this isomerization can indeed be a rapid process or not should depend on how high the rotational barrier of **3c** would be.



(5)

A piece of information which can answer the above question is obtained from our rate data of **1c**, **1t**, and **4**. The rotation of **3c** (eq 5) should proceed by way of the perpendicular allylic cation **3p**. Probably, **3p** is in the vicinity of the top of the energy profile for the process **3c** → **3t**, so the barrier height of **3c** is, to a first approximation, equal to the thermochemical stability (enthalpy) of **3c** relative to **3p**. By the same token, the rotational barrier of **3t** may be approximated to the enthalpy difference between **3p** and **3t**. These differences in enthalpy can be estimated from the activation heats of **1c**, **1t**, and **4** (Table I) combined with their relative ground-state stabilities.

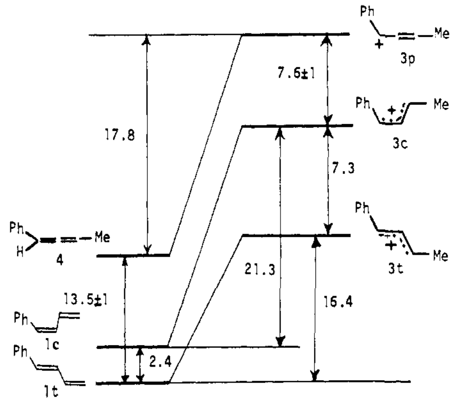
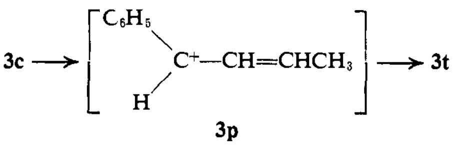


Figure 4. Enthalpy diagram for the hydrochlorination of phenylbutadienes.



$$3c \longrightarrow \left[\begin{array}{l} C_6H_5 \\ \quad \diagdown \\ \quad\; C^+\text{—}CH{=}CHCH_3 \\ \quad \diagup \\ H \end{array} \right] \longrightarrow 3t \qquad (6)$$

3p

The difference in enthalpy between **1t** and **4** in the ground state may be assumed equal to that known between a pair of 1,3- and 1,2-diene isomers. It is 12.44 and 14.50 kcal/mol for butadienes and pentadienes, respectively.[16] Taking the average, we have 13.5 ± 1.0 kcal/mol; **4** is considered to be less stable than **1t** by this much. The enthalpy difference between **1t** and **1c** is probably equal to one-half that (4.8 kcal/mol[16]) between the trans,trans and cis,cis isomers of 1,4-diphenyl-1,3-butadiene. Thus, **1c** will be 2.4 kcal/mol less stable than **1t**.

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(14) Y. Pocker and M. J. Hill, *J. Amer. Chem. Soc.*, **91**, 3243 (1969).

(15) The same conclusion was reached for the acid-catalyzed hydration of **1c** in the aqueous medium.[4] It should be noted, however, that this is not generally true with all *cis*-diene derivatives. For instance, T. Okuyama, T. Sakagami, and T. Fueno [*Tetrahedron*, **29**, 1503 (1973)] have found that *cis*-1-ethoxy-1,3-butadiene protonated partly at the C_2 atom despite the exclusive C_4 protonation of its trans isomer.

(16) M. Sakiyama, *et al.*, "Kagaku Binran (Handbook of Chemistry)," S. Seki, Ed., Maruzen, Tokyo, 1966, p 811.

Figure 4 shows an approximate enthalpy diagram obtained as above. It is assumed there that the level heights of **3c**, **3t**, and **3p** can be approximated by those of the transition states for the protonation of **1c**, **1t**, and **4**, respectively. This assumption would introduce no serious error into the estimation of the enthalpy differences between the intermediates, because any difference in energy between the transition state and the succeeding intermediate will essentially be identical for the substrates undergoing a given type of reaction. Thus, **3c** should be thermochemically less stable than **3t** by 7.3 kcal/mol but more stable than **3p** by 7.6 ± 1 kcal/mol. The rotational barrier for the conversion **3c** → **3t** should then be 7.6 ± 1 kcal/mol, while that for the reverse process **3t** → **3c** should be 14.9 ± 1 kcal/mol.

The results of the EHMO calculations given in Table II show that the perpendicular cation **3p** (no. 11) is less stable than the trans cation **3t** (no. 15) by *ca.* 11 kcal/mol, which is to be compared with the observed value of 14.9 ± 1 kcal/mol. The planar cis cation (no. 1) is highly unstable because of a large steric repulsion between the phenyl and vinyl groups situated cis to each other. This repulsion decreases with the increase in the rotation angle θ but remains to be appreciably large until θ exceeds 45°. The most likely structure of **3c** must be some compromise among the three angles θ, ω, and ω'. Variation of ω under the restriction that $\theta = \omega' = 0$ (no. 1–4) gave an energy minimum when ω is taken as 60° (no. 4). When $\theta = 30°$ and $\omega' = 0°$ (no. 6–8), a rotation of $\omega = 45°$ (no. 8) was enough to minimize the calculated energy. We have not attempted to locate the energy minimum in the three-dimensional space precisely, but it is very likely that it will be *ca.* 1 kcal/mol relative to **3t**. The rotational barrier of **3c** is thus calculated to be *ca.* 10 kcal/mol, which is in reasonable agreement with the observed value of 7.6 ± 1 kcal/mol.

The unimolecular reaction rate theory[17] predicts that the rate constant k for a cis–trans isomerization is given approximately by

$$k = 10^{13}e^{-E/RT}\ \text{sec}^{-1} \tag{7}$$

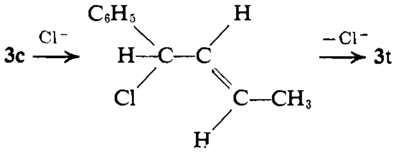
where E stands for the rotational barrier height. Adopting our experimental values of 7.6 ± 1 and 14.9 ± 1 kcal as the barrier heights for **3c** and **3t**, respectively, we obtain the isomerization rate constants at ordinary temperature

$$k_{3c\rightarrow 3t} = 10^{7.5\pm0.7}\ \text{sec}^{-1} \tag{8}$$

$$k_{3t\rightarrow 3c} = 10^{2.2\pm0.7}\ \text{sec}^{-1} \tag{9}$$

The direct isomerization **3c** → **3t** (eq 5) is certainly a rapid process, its half-time being of the order of 10^{-7} sec. The reverse process **3t** → **3c**, whose half-time is of the order of 10^{-2} sec, is probably slower than its competing ion–recombination reaction, **3t** + Cl^- → **5t**. All these results lend strong support to the mechanisms (1 and 5) which involve a rapid direct isomerization of **3c** to **3t**.

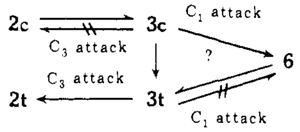
It should be noted, however, that the above argument cannot entirely negate the possibility that the isomerization of **3c** may proceed by assistance of a nucleophile. According to Pocker and Hill,[4] the



7

(10)

rates of the acid-catalyzed isomerization and ^{18}O exchange of **2c** are identical, indicating that no water attack at C_3 of **3c** prior to its isomerization takes place. They state that it is hard to justify attack of C_1 of **3c** to the complete exclusion of attack at C_3. The fate



(11)

of **3c** will then be to isomerize unimolecularly to **3t**, which in turn undergoes the water attack at C_3 exclusively.[15] This reasoning has been used as the basis of the mechanism shown in eq 1.

We suspect that, while **3t** reacts with a nucleophile at C_3 excusively, nucleophilic attack to **3c** can occur at its C_1 in prevalence over C_3. Because of its nonplanarity, the electronic structure of **3c** should be different from that of **3t**. Table II shows that in **3t** the C_3 atom takes a greater positive charge than does the C_1 atom, in agreement with the greater amenability of the former site to a nucleophile. In the domain of **3c** (no. 4, 7, and 8), the charge densities are nearly equal at the C_1 and C_3 positions. As θ increases, the positive charge at C_1 tends to increase while that at C_3 decreases (no. 6–11). Thus, **3c** may trap a nucleophile at its C_1 position, before it reaches the top of the rotational barrier. The adduct **7** thus formed is unstable under the present experimental conditions,[18] and hence will liberate Cl^-, leaving **3t** (eq 10). The C_1 attack similar to eq 10 was in fact noted for the 1-phenylallyl cation.[19]

In conclusion, the rotational barrier of **3c** is low enough to permit its direct isomerization to **3t**, but this isomerization may well be assisted by a nucleophile.

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[17] S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968, pp 72–75.

[18] It was confirmed by a separate experiment that the authentic sample of **7** is extremely unstable in HCl–HOAc and rearranges to **5t**.

[19] (a) H. L. Goering and R. E. Dilgren, *J. Amer. Chem. Soc.*, 82, 5744 (1960); (b) *ibid.*, 81, 2556 (1959); (c) Y. Pocker, *Chem. Ind.* (*London*), 195 (1959); (d) C. A. Bonton, Y. Pocker, and H. Dahn, *ibid.*, 1516 (1958).