

metallic compounds. π -Nucleophiles of widely varying structure can, therefore, be compared with respect to the same electrophiles.

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Supplementary Material Available: Tables with concentrations and rate constants at different temperatures for the reactions of 2-X,Y-BCl_4^- with **3** (8 pages). Ordering information is given on any current masthead page.

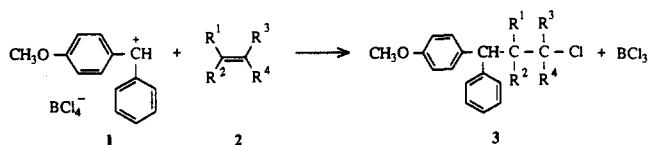
Kinetics of the Reactions of the *p*-Methoxy-Substituted Benzhydryl Cation with Various Alkenes and 1,3-Dienes

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Abstract: The kinetic method described in the preceding article has been used to determine the rate constants for the reaction of $(p\text{-CH}_3\text{OC}_6\text{H}_4)(\text{C}_6\text{H}_5)\text{CH}^+\text{BCl}_4^-$ with 30 alkenes and 1,3-dienes in dichloromethane at -80 to -30 °C. The second-order rate constants, which reflect the rate of attack of $(p\text{-CH}_3\text{OC}_6\text{H}_4)(\text{C}_6\text{H}_5)\text{CH}^+$ at these π -systems strongly depend on the electron-releasing ability of the substituents at the developing carbenium center ($\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{R}$: R = H, 9.39×10^{-4} ; R = vinyl, 15.6; R = CH₃, 23.3; R = Ph, 1450; R = cyclopropyl, 5650 L mol⁻¹ s⁻¹ at -70 °C). The steric effects of substituents at this position are of minor importance ($\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{R}$: R = Me, 23.3; R = Et, 18.4; R = *i*-Pr, 6.08; R = *t*-Bu, 1.21 L mol⁻¹ s⁻¹ at -70 °C). Methyl groups at the electrophilically attacked vinylic position usually lower ΔH^\ddagger and ΔS^\ddagger , while a uniform effect on the rate constants is not found.

In the preceding article we have reported that colorless, covalent products are formed when 2-methyl-1-pentene is added to the colored ionic solutions of several diarylcarbenium tetrachloroborates in CH_2Cl_2 ,¹ and we have shown that the rate of disappearance of the diarylcarbenium ions, which can be measured photometrically and conductimetrically, equals the rate of attack of the carbenium ions at the alkenes. We report now on the



relationship between the structure and reactivity of alkenes and 1,3-dienes employing the *p*-methoxy-substituted benzhydryl cation **1** as the reference electrophile. This is the first report on absolute rate constants of various vinyl derivatives toward carbenium ions since Dorfman's pioneering work on the reactivity of radiolytically generated benzyl and benzhydryl cations toward some unsaturated hydrocarbons.² A smaller set of data on relative reactivities of alkenes has previously been published by us.³

Experimental Section

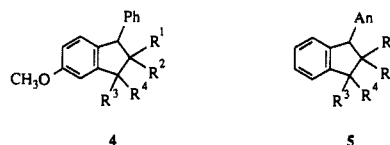
The kinetic method has been described in the preceding article,¹ and the results of the individual kinetic experiments are given in the supplementary material. All reaction products obtained from $1\cdot\text{BCl}_4^-$ with **2** were characterized by ¹H NMR and/or ¹³C NMR spectroscopy. Spectral and other physical data of the reaction products are documented in ref 4.

Reaction Products.

The combination of $1\cdot\text{BCl}_4^-$ with compounds **2a–dd** yields 1:1 products in almost quantitative yields, as previously described for analogous reactions of other benzhydryl chlorides.^{3,5} For un-

symmetrical alkenes, the electrophilic attack of **1** takes place regioselectively to give the most stabilized carbenium ion,⁶ and the adducts **3** are usually the exclusive or the predominant products. When secondary alkyl cations are involved as intermediates, 1,2-hydrogen shifts often cannot be avoided, and in the reactions of $1\cdot\text{BCl}_4^-$ with **2a–d**, the main products **3a–d** are accompanied by some rearranged material. The stereoselectivities of the addition reactions with the *E,Z*-isomeric 2-butenes **2b,c** and 1-phenylpropenes **2s,t** are comparable to the results reported for the analogous reactions of diphenylmethyl chloride and di-*p*-tolylmethyl chloride.⁷ By analogy with an earlier report,⁸ norbornene **2e** reacts with complete Wagner–Meerwein rearrangement to give a 7-(diarylmethyl)-2-chloronorbornane, and 2-cyclopropylpropene **2dd** undergoes the well-known cyclopropylcarbinyl/homoallyl rearrangement with exclusive formation of 1,1-diaryl-6-chloro-3-methyl-3-hexene.^{3b}

The ordinary addition products **3** are accompanied by the indans **4** and **5**, when $1\cdot\text{BCl}_4^-$ is combined with the alkenes **2l–p,s,t**. While **4** and **5** are formed in approximately equal amounts in all cases, the ratio **3**/(**4** + **5**) strongly depends upon the reaction conditions as described for the reaction of bis(*p*-methoxyphenyl)carbenium tetrachloroborate with trimethylethylene.¹ The alkenes **2m** and **2p** react with exclusive or predominant formation of the indans **4** and **5** (*gem*-dialkyl effect⁹).



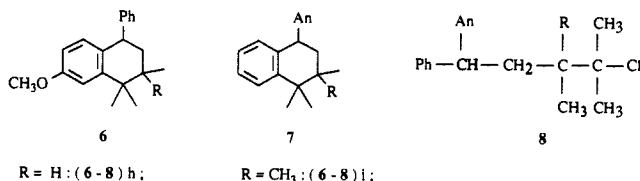
- (4) (a) Schneider, R. Dissertation, Universität Erlangen-Nürnberg, 1987. (b) Schade, C. Dissertation, Medizinische Universität zu Lübeck, 1988. (c) Irrgang, B. Dissertation, Medizinische Universität zu Lübeck, 1990. (5) Mayr, H.; Striepe, W. *J. Org. Chem.* **1983**, *48*, 1159. (6) Unsymmetrical π -systems are attacked at the left sp² carbon of the formula drawings in Table I. (7) Pock, R.; Mayr, H.; Rubow, M.; Wilhelm, E. *J. Am. Chem. Soc.* **1986**, *108*, 7767. (8) Pock, R.; Klein, H.; Mayr, H. *Chem. Ber.* **1986**, *119*, 929. (9) Review: Capon, B.; McManus, S. P. *Neighboring Group Participation*; Plenum Press: New York, 1976. Vol. 1, p 58.

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While indan formation is not observed from terminal alkenes under these reaction conditions, the olefins **2h** and **2i** yield the tetrahydronaphthalenes **6** and **7** in addition to the regular adducts **3** and the rearrangement products **8**, indicating that cyclizations with formation of six-membered rings are favored over formation of five-membered rings.¹⁰



Mixtures (1:1) of 1,2- and 1,4-addition products are obtained in the reaction of $1 \cdot \text{BCl}_4^-$ with **2u** and **2v**. While the 1,2- and 1,4-addition products obtained from **2u** do not isomerize under the reaction conditions (kinetic control), the product mixture obtained from **2v** appears to be thermodynamically controlled. With all other dienes (**2w–cc**) the predominant formation of 1,4-adducts (>90%) is observed. Since the 1,4-adducts obtained from **2y–cc** incorporate three chiral centers, mixtures of diastereoisomers are produced, which show complex ¹³C NMR spectra.^{4c}

Kinetic Investigations

Second-order kinetics were found for the reactions of $1 \cdot \text{BCl}_4^-$ with most nucleophiles listed in Table I. The reactions of $1 \cdot \text{BCl}_4^-$ with **2a** and **2b** did not follow the second-order rate law, and the k_2 values derived from the initial slopes of the second-order plots were greater than those calculated at a higher degree of conversion. Since the electrophilic attack at these alkenes yields secondary carbenium ions, the curvature of the graphs was explained by the reversibility of the addition step, which gains importance as the BCl_4^- concentration decreases toward the end of the conversion. As discussed in the previous article,¹ this complication can be overcome by studying the reactions in the presence of $\text{PhCH}_2\text{NEt}_3^+ \cdot \text{BCl}_4^-$ ($\sim 10^{-2} \text{ mol L}^{-1}$). Linear second-order plots to more than 80% conversion are now observed, and since the k_2 values derived from these plots are identical with those observed for the reaction of $1 \cdot \text{SnCl}_5^-$ with **2b** in the presence of $\text{PhCH}_2\text{NEt}_3^+ \cdot \text{SnCl}_5^-$, we conclude that the observed reaction rates are identical with the rates of attack of the carbenium ion **1** at these alkenes.

Consequently, all reactions of $1 \cdot \text{BCl}_4^-$, which proceed through secondary carbenium ions or which involve alkenes with a high polymerization tendency (e.g. **2r**) have been investigated in the presence of $\text{PhCH}_2\text{NEt}_3^+ \cdot \text{BCl}_4^-$ ($\sim 10^{-2} \text{ mol L}^{-1}$). Since the reaction of $1 \cdot \text{BCl}_4^-$ with tetramethylethylene (**2p**) gave the indans **4** and **5** almost exclusively, variation of $[\text{BCl}_4^-]$ did not influence the reaction rate. There is indirect evidence, however, that the attack of **1** at the tetrasubstituted ethylene **2p** is a reversible process,¹¹ and the k_2 value given in Table I has to be considered as a lower limit for the rate of attack of **1** at **2p**.

Usually, no complications arise when HBCl_4 is generated during the reactions along with the cyclized products **4–7**, as HBCl_4 reacts very slowly with the alkenes. Since HBCl_4 only dissociates to a very small extent in CH_2Cl_2 , this side reaction does not interfere with measurements obtained by the conductimetric method.

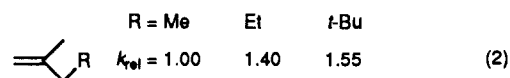
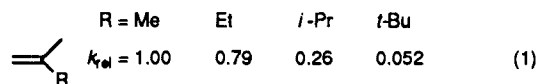
Structure–Reactivity Relationships

Activation Entropies. Table I shows that enthalpic and entropic effects are responsible for the variations of the k_2 values, which cover a range of 6×10^6 . Some regularities of the ΔS^\ddagger values

are noticeable: All 1,1-dialkylated ethylenes possess ΔS^\ddagger values of $(-117 \pm 5) \text{ J mol}^{-1} \text{ K}^{-1}$, and in all classes of compounds ΔS^\ddagger becomes more negative when an alkyl group is introduced at the electrophilically attacked carbon. The effect of a trans substituent is generally greater than that of a cis substituent (Table II).

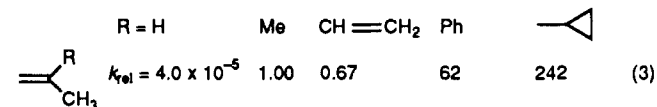
α -Substituent Effects. The predominant role α -substituents, i.e., substituents at the developing carbenium center is manifested by the fact that the k_2 values of Table I allow the alkyl-substituted ethylenes to be divided into two sets: Compounds **2a–d**, which yield secondary carbenium ions, and compounds **2f–p**, which yield tertiary carbenium ions. If the sterically shielded compound **2m** is omitted, norbornene (**2e**) is located in between these two groups.

Comparison of compounds **2f–k** shows that branching of an α -alkyl group has a moderate influence on the addition rate constants. The reduction of reactivity created by branching in the allylic position (series 1) indicates the predominance of the steric effect, while the slight reactivity increase caused by branching in the homoallylic position (series 2) can be attributed to hyperconjugative stabilization of the generated carbenium ion.



The modest magnitude of the effect in both series suggests, however, that steric effects of α -substituents can be neglected in the following discussion, when substituents with different electronic properties are compared.

Replacement of hydrogen by a methyl group at the developing carbenium center increases the reactivity by a factor of 25 000 (series 3, R = H vs CH_3) and an acceleration by 5 orders of magnitude is observed when a vinylic hydrogen in 2-butene (**2l/2b**, **2l/2c**) or cyclopentene (**2n/2d**) is substituted by methyl. The relative activating effects of methyl and vinyl groups are opposite at tertiary (series 3) and at secondary positions (series 4): Whereas butadiene (**2u**) is 21 times more reactive than propene (**2a**), the reactivity of isoprene (**2w**) is only 0.67 times that of isobutene (**2f**). A phenyl group activates considerably better than methyl



when located at a secondary center (1.2×10^4) but only somewhat better than methyl when located at a tertiary center (62). This trend may be explained by the different electron demand.¹³ The activating effect of cyclopropyl is greater than that of vinyl and phenyl, further evidence for the unique electron-releasing ability of the cyclopropyl group.¹⁴

β -Substituent Effects. Methyl groups at the initially attacked vinylic position do not have a uniform effect on the rate constants. Activating as well as deactivating effects are observed (Table II). When we disregard *cis*- β -methylstyrene (**2t**), the low reactivity of which may be explained by the nonplanarity of the π -system, we realize that methyl groups at the attacked vinylic position generally reduce ΔS^\ddagger as well as ΔH^\ddagger . While the reduction of ΔH^\ddagger is relatively small for the 2-butenes, big effects on ΔH^\ddagger are found in the comparisons **2l/2f** and **2y/2v** (Table II).

PMO theory may be used to explain the enthalpic effects. Since the second-order perturbation energy (ΔE_1 and ΔE_2 , Figure 1)

(10) As these cyclizations can either be classified as *exo*-trig or *endo*-trig processes. Baldwin's rules do not allow a prediction: Baldwin, J. E. *J. Chem. Soc., Chem. Commun.* **1976**, 734.

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Table I. Rate Constants ($-70.0\text{ }^{\circ}\text{C}$) and Activation Parameters for the Reactions of *p*-Methoxydiphenylcarbenium Tetrachloroborate ($\text{I}\cdot\text{BCl}_4^-$) with Various Alkenes and Dienes in Dichloromethane





































		k_2 ($-70\text{ }^{\circ}\text{C}$), ^{a,b} $\text{L mol}^{-1}\text{ s}^{-1}$	ΔH^\ddagger , kJ mol^{-1}	ΔS^\ddagger , $\text{J mol}^{-1}\text{ K}^{-1}$	$k_{\text{H}_2\text{O}^+}$ ($25\text{ }^{\circ}\text{C}$), ^c $\text{L mol}^{-1}\text{ s}^{-1}$
Mono- and 1,2-Dialkylated Ethylenes					
	2a	9.39×10^{-4}	32.6 ± 0.2	-139 ± 1	2.38×10^{-9} (ref 12a)
	2b	1.26×10^{-3}	29.9 ± 0.5	-150 ± 2	3.51×10^{-8} (ref 12b)
	2c	1.01×10^{-3}	31.4 ± 0.4	-145 ± 2	8.32×10^{-8} (ref 12b)
	2d	7.0×10^{-3}			
	2e	7.82×10^{-1}	23.9 ± 0.3	-126 ± 1	3.41×10^{-5} (ref 12a)
1,1-Dialkylated Ethylenes					
	2f	2.33×10^1	21.1 ± 0.4	-112 ± 2	3.71×10^{-4} (ref 12a)
	2g	1.84×10^1	21.4 ± 0.2	-112 ± 1	5.22×10^{-4} (ref 12c)
	2h	6.08			
	2i	1.21	24.4 ± 0.5	-120 ± 3	2.04×10^{-4} (ref 12c)
	2j^d	2.58×10^1	19.5	-119	
	2k	2.86×10^1	18.6 ± 0.3	-122 ± 1	
Tri- and Tetraalkylated Ethylenes					
	2l	2.47×10^2	7.5 ± 0.1	-159 ± 0.3	2.14×10^{-4} (ref 12a)
	2m^e	$\leq 2.47 \times 10^{-1}$	(19.9 ± 0.1)	(-156 ± 1)	
	2n	5.2×10^2			9.15×10^{-4} (ref 12a)
	2o	8.70	17.7 ± 0.2	-136 ± 1	3.05×10^{-4} (ref 12a)
	2p^f	> 5.62	(8.0 ± 0.2)	(-188 ± 1)	3.42×10^{-4} (ref 12b)
Styrenes					
	2q	1.09×10^1	19.3 ± 0.3	-127 ± 1	2.40×10^{-7} (ref 12a)
	2r	1.45×10^3			9.67×10^{-5} (ref 12c)
	2s	3.87	15.5 ± 0.4	-154 ± 2	1.12×10^{-7} (ref 12b)
	2t	8.29×10^{-2}	26.1 ± 0.3	-134 ± 1	
1,3-Dienes					
	2u	1.93×10^{-2}			3.96×10^{-8} (ref 12d)
	2v	4.62×10^1	22.4 ± 0.3	-99 ± 2	
	2w	1.56×10^1	23.0 ± 0.4	-106 ± 2	3.19×10^{-5} (ref 12d)
	2x	2.83×10^1			
	2y	1.82×10^2	15.1 ± 0.6	-124 ± 3	
	2z	1.74×10^3			$\sim 7.0 \times 10^{-7} \text{ s}$
	2aa	2.75×10^1	18.5 ± 0.7	-123 ± 4	$\sim 7.0 \times 10^{-6}$ (ref 12a)
	2bb	3.04	22.1 ± 0.8	-123 ± 4	$\sim 1.4 \times 10^{-8} \text{ s}$

Table I (Continued)

		k_2 (-70 °C), ^{a,b} L mol ⁻¹ s ⁻¹	ΔH^\ddagger , kJ mol ⁻¹	ΔS^\ddagger , J mol ⁻¹ K ⁻¹	$k_{\text{H}_3\text{O}^+}$ (25 °C), ^c L mol ⁻¹ s ⁻¹
	2cc	3.26×10^{-1}			$\sim 3.5 \times 10^{-9} \epsilon$
Cyclopropylpropene					
	2dd	5.65×10^3			2.0×10^{-1} (ref 12c)

^a Not corrected for statistical factors. ^b If activation parameters have been determined, the k_2 values presented in this column are based on ΔH^\ddagger and ΔS^\ddagger , which are given with more digits in the supplementary material. ^c Rates of acid-catalyzed hydration. ^d Data from ref 1. ^e **2m** may isomerize into the more reactive **2k**. ^f Addition step reversible. see text. ^g From $k(\mathbf{2aa})$ and the relative rate of hydration of this cycloalkadiene and **2aa** at 80 °C; ref 12e.

Table II. Effect of Methyl Groups at the Electrophilically Attacked Vinylic Carbon

alkenes		$k_{\text{CH}_3}/k_{\text{H}}$ (-70 °C)	$\Delta H_{\text{CH}_3}^\ddagger - \Delta H_{\text{H}}^\ddagger$	$\Delta S_{\text{CH}_3}^\ddagger - \Delta S_{\text{H}}^\ddagger$
	2b/2a	1.3	-2.7	-11
	2c/2a	1.1	-1.2	-6
	2l/2f	10.6	-13.6	-47
	2s/2q	0.36	-3.8	-27
	2t/2q	0.0076	+6.8	-7
	2y/2v	3.9	-7.3	-25

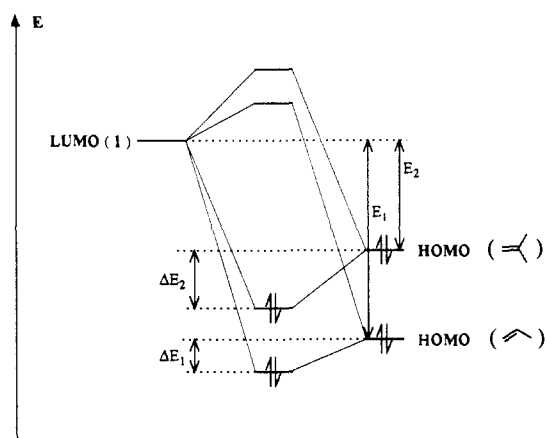
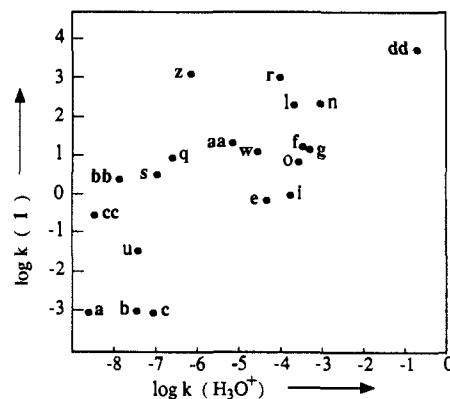


Figure 1. Frontier orbital interactions in reactions of alkenes with a carbenium ion.

is inversely proportional to the energy difference between the interacting orbitals (E_1 and E_2), one can rationalize the increase of nucleophile reactivity with increasing height of the HOMO level ($E_2 < E_1 \rightarrow \Delta E_2 > \Delta E_1$). The inverse proportionality $\Delta E \sim 1/E$ furthermore implies that the effect of a perturbation increases with decreasing magnitude of E , i.e., a perturbation of E_2 will affect ΔE_2 to a greater extent than the same perturbation of E_1 will affect ΔE_1 .¹⁵ Therefore, a greater reduction of ΔH^\ddagger is observed when a β -methyl group is introduced into isobutene (**2f** \rightarrow **2l**) than into propene (**2a** \rightarrow **2b,c**). In accord with this interpretation, the accelerating effect of β -methyl groups increases as the energy of the carbenium LUMO is lowered; i.e. the activating effect of β -methyl groups grows with increasing reactivity of the reference carbenium ion.¹⁶

The higher reactivity of trimethylethylene (**2l**) compared with isobutene (**2f**) shows that the steric retardation by the additional

Figure 2. Correlation of the reactivities of alkenes and dienes **2** toward H_3O^+ (H_2O , 25 °C) and the carbenium ion **1** (CH_2Cl_2 , -70 °C).

methyl group is overcompensated by its electronic acceleration. As expected, the steric effect outweighs the electronic effect in the case of *tert*-butyl, and **2m** is at least 2 orders of magnitude less reactive than isobutene. Since the degree of reversibility is not known for the reaction of **1** with **2p**,¹¹ the data given for **2p** cannot be discussed in structural terms.

1,3-Dienes. While the electrophilic attack at 1,3-butadiene (**2u**) generates a terminally monoalkylated allyl cation, all other dienes listed in Table I yield terminally dialkylated allyl cations. Since the stabilization of allyl cations predominantly depends on the number and not on the position of the terminal alkyl groups,¹⁷ the similar order of magnitude for the reactivities of the dienes **2v**–**y** can be explained. The decrease of k_2 with increase of ring size of the cycloalkadienes can qualitatively be attributed to the increase of deviation of the π -system from planarity. A more detailed analysis is given below.

Transition-State Structure—Comparison with Proton Additions

Comparison with Protonation Rates. Electrophilic additions toward alkenes may proceed through bridged or through open transition states. While bridged transition states are usually encountered in electrophilic brominations, chlorinations, and sulfonyl halide additions,¹⁸ proton additions are assumed to take place through open transition states.^{12,19} Ruasse, Dubois, and Argile have employed methyl effects to differentiate the two modes of attack.²⁰ Whereas bridged transition states are stabilized by methyl groups at both vinylic termini, open transition states are

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

























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Table III. Calculation of the Addition Enthalpy ΔH_{add} According to Scheme 1 and Equation 6

adducts	ΔH_{a} , kJ mol ⁻¹ ^a	$10^4 k_{\text{solv}}$ ^b	$\Delta G_{\text{solv,P}}$, kJ mol ⁻¹	ΔH_{add} , ^c kJ mol ⁻¹	adducts	ΔH_{a} , kJ mol ⁻¹ ^a	$10^4 k_{\text{solv}}$ ^b	$\Delta G_{\text{solv,P}}$, kJ mol ⁻¹	ΔH_{add} , ^c kJ mol ⁻¹		
	3a	-105.7	$\sim 1.4 \times 10^{-5}$ ^d	134	-30		3n	-92.6	~ 1100 ^e	85	-72
	3b	-96.5	$\sim 1.4 \times 10^{-5}$ ^d	134	-21		3o	-85.3	6.3	99	-49
	3c	-94.2	$\sim 1.4 \times 10^{-5}$ ^d	134	-19		3p	-57.1	86	92	-29
	3d	-98.4	$\sim 6.3 \times 10^{-3}$ ^e	118	-41		3q	-90.8	0.058	112	-41
	3e	-109.9	~ 0.095 ^e	110	-61		3r	-88.1	~ 3500 ^d	82	-71
	3f	-97.0	0.77	105	-55		3s	-79.8	0.083	111	-31
	3g	-94.5	1.4	103	-54		3t	-110.7	0.075	111	-61
	3h	-91.7	2.6	102	-53		3u	-72.5	0.064	111	-23
	3i	-87.6	6.1	99	-51		3v	-70.4	~ 56	93	-41
	3j	-95.0	1.5	103	-55		3w	-75.2	1.2	104	-34
	3k	-79.0	29	95	-48		3z	-84.7	~ 9100 ^f	80	-70
	3l	-85.7	8.7	98	-51		3aa	-88.0	13	97	-54
							3bb	-73.4	~ 20 ^f	96	-41
							3cc	-82.5	~ 0.15 ^f	109	-35

^a From force field calculations;²⁵ in all cases, the enthalpy of the most stable conformer of 3 has been used for the calculations. Experimental values for ΔH_{a} : 3j, -84.5 ± 3.6 ; 3l, -78.9 ± 3.8 ; 3q, -83.4 ± 3.2 ; 3s, -78.1 ± 4.4 ; 3w, -74.2 ± 2.9 kJ mol⁻¹; ref 26. ^b Solvolysis rates of compounds 3a–cc (R = Ph₂CH) in 80% ethanol at 50 °C; this work. These rates deviate only insignificantly from those of compounds with R = (*p*-CH₃OCH₂H₂)PhCH; ref 1. ^c From eq 6 with $\Delta G_{\text{solv,R}}^{\ddagger} = 67.1$ kJ mol⁻¹. This number is based on the solvolysis rate of AnPhCHCl (50 °C, 80% EtOH) = 97 s⁻¹, which was derived from the activation parameters of the ethanolysis reaction of AnPhCHCl (ref 28) and the assumption that the LFER (ref 28, Table 11, entry 10) also holds at 50 °C. ^d Estimated from *k* (3f, R = Ph₂CH) and the relative ethanolysis rates (25 °C) of 3f (R = H, $\equiv 1.0$), 3a (R = H, 1.8×10^{-5} , also used for 3b,c), and 3r (R = H, 4580); ref 29. ^e Estimated from *k* (3o, R = Ph₂CH) and the relative ethanolysis rates (25 °C) of 3o (R = H, $\equiv 1.0$), 3d (R = H, 1.0×10^{-3}), 3e (R = H, 0.015), and 3n (R = H, 181); ref 29. ^f Estimated from *k* (3aa, R = Ph₂CH) and the relative reactivities of the corresponding allyl bromides (R = H) in 80% ethanol at 25 °C; ref 30.

predominantly stabilized by methyl groups at the developing carbenium center. Melloni, Modena, and Tonellato have shown that alkenes are more reactive than alkynes in reactions involving bridged transition states, while analogously substituted alkenes and alkynes show similar reactivity toward nonbridging electrophiles.²¹ Both criteria led to the conclusion that carbenium ion additions are closely related to proton additions, though partial bridging in additions of diarylcarbenium ions toward *E,Z*-isomeric 2-butenes has been derived from stereochemical investigations.⁷

The data in Table I now allow a comprehensive comparison between proton and carbenium ion addition rates. Figure 2 shows that there is a moderate correlation between the two sets of data which refer to different temperatures. It is evident that conjugated π -systems (1,3-dienes and styrenes) react considerably faster with the carbenium ion 1 than expected from their reaction rates with protons. This deviation has to be seen in context with the previously reported, unexpectedly low reactivity of styrene toward protons.^{12e} While in limiting S_N1 solvolyses, the rate enhancement of a phenyl group is comparable to that of two methyl groups,²²

the acid-catalyzed hydration of styrene was found to be three orders of magnitude slower than the corresponding reaction of isobutene. Higher resonance stabilization of the ground state of styrene has been suggested to account for this reactivity difference.^{12e} This explanation cannot be appropriate, however, since the heats of hydrogenation of isobutene and of styrene are identical within experimental error.²³ As 1 attacks these two π -systems with similar rates (2f, 2q, Table I), though the same ground-state effects must be encountered as in proton additions, an unknown transition-state effect must be responsible for the low reactivity of conjugated π -systems toward protons.

Rate equilibrium relationships can be employed for characterizing transition-state structures.²⁴ As the rate-determining step of the reaction sequence under consideration corresponds to

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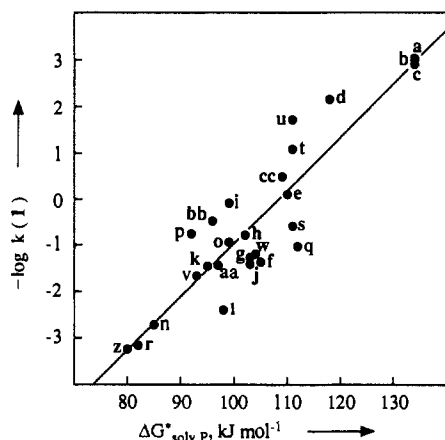
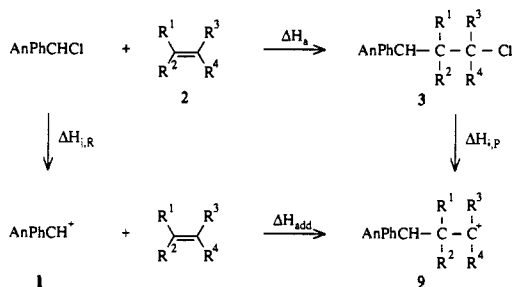


Figure 3. Correlation of the reactivities of alkenes and dienes **2** toward the carbenium ion **1** (CH_2Cl_2 , -70°C) with the free energies of activation for ethanolsis of the adducts **3**.

Scheme I



the attack of the carbenium ion **1** at the alkene **2**, the rate constants have to be compared with the free energy or the enthalpy of this step (ΔH_{add} in Scheme I). According to Scheme I, ΔH_{add} can be calculated from a Hess cycle by using eq 5. The enthalpies

$$\Delta H_{\text{add}} = \Delta H_a + (\Delta H_{i,P} - \Delta H_{i,R}) \quad (5)$$

ΔH_a , given in Table III, have been obtained by force field calculations.²⁵ Comparison with some ΔH_a values determined calorimetrically²⁶ shows the typical errors of this computational method (see footnote *a* of Table III). As the difference of the ionization enthalpies of reactants and products ($\Delta H_{i,P} - \Delta H_{i,R}$)

cannot be determined directly, this term has been replaced by $(\Delta G_{\text{solv,P}}^* - \Delta G_{\text{solv,R}}^*)/0.89$ making use of the Arnett-Schleyer correlation.²⁷ According to this correlation, 89% of the differences of the ionization enthalpies of alkyl chlorides in nonnucleophilic media are reflected by the differences of the activation free energies of the ethanolsis reactions.²⁷ The correlation between the ad-

$$\Delta H_{\text{add}} = \Delta H_a + (\Delta G_{\text{solv,P}}^* - \Delta G_{\text{solv,R}}^*)/0.89 \quad (6)$$

dition rate constants ($\log k_2$, Table I) and the addition enthalpies ΔH_{add} given in Table III is rather poor, however ($r = 0.71$), which is explained by the errors introduced by the force field calculations. This interpretation is supported by the observation that the free energies of activation for the ethanolsis of the products ($\Delta G_{\text{solv,P}}^*$, Table III) are fairly correlated with the corresponding addition rate constants ($r = 0.91$, Figure 3). The existence of this correlation implies that ΔH_a , the term in eq 6, which accounts for the different ground states of the π -systems, can be neglected, i.e., the reactivities of π -systems toward the electrophile **1** can roughly be estimated from the stabilization of the carbenium ions **9**. Multiplication of the slope of the correlation in Figure 3 with $(-2.3 \times RT)$ yields a value of 0.45, indicating that in the transition state roughly 50% of carbenium character is developed at the α carbon of the alkene.

Conclusion

The rate constants for the additions of **1** to the alkenes **2** roughly reflect the thermodynamics of the rate-determining step, in accord with a transition state, which is not strongly bridged.⁷ Though some analogy between the substituent effects on proton and carbenium ion additions is evident, diversities between the transition states of the two reaction series are indicated by the deviations from the correlation of Figure 2.

It remains to examine, whether the reactivity order measured for the carbenium ion **1** will also hold for other carbenium ions. For diarylcarbenium ions this question will be treated in the following paper.

Acknowledgment. We thank Ute Grabis for experimental assistance and the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support.

Supplementary Material Available: Tables with concentrations and rate constants of the kinetic experiments described in Table I (8 pages). Ordering information is given on any current masthead page.

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