

RELATIVE REACTIVITIES OF ALKENES TOWARD THE DIPHENYLMETHYL CATION

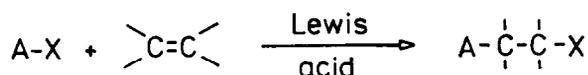
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Summary: The relative reactivities of alkyl and phenyl substituted alkenes toward diphenylmethyl chloride/ZnCl₂/Et₂O in dichloromethane at -78°C have been determined by competition experiments. The transition state structure is discussed.

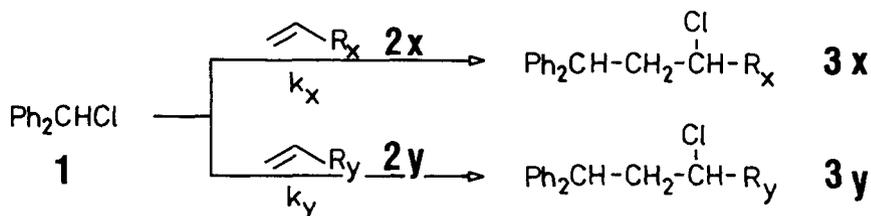
Cationic copolymerisation parameters, which can only be obtained with difficulty, are presently the major source for relative alkene reactivities toward carbenium ions.¹ Only few other approaches to that problem have been undertaken,^{2,3} since carbenium ion additions to alkenes often give complex mixtures of products, including polymers. We have reported recently that Lewis acid catalysed addition reactions of alkyl halides to alkenes may yield 1:1 addition products selectively, if the reactants AX dissociate faster than the products



A-C-C-X.⁴ Alkyl halides with high S_N1 reactivity are therefore suited to give 1:1 adducts with a variety of alkenes with different nucleophilicity.⁵ In this work we selected the zinc chloride catalysed additions of benzhydryl chloride (1) to determine relative alkene reactivities toward the diphenylmethyl cation.

PRODUCTS. At -78°C benzhydryl chloride (1) reacts with 2a-2l in presence of the homogeneous catalyst system ZnCl₂-Et₂O in dichloromethane⁶ to give high yields of 1:1-addition products. On a preparative scale more than 80 % of pure 1:1 products are usually accessible.⁷ The unsymmetrical alkenes of Table 1 undergo regioselective addition reactions in Markownikoff sense. Cis- and trans-2-butene react stereospecifically to give diastereomeric addition products of unknown configuration as well as traces of 1,1-diphenyl-2-methyl-1-butene. Normal addition products are also obtained from cis and trans-1-phenylpropene (2k: stereospecific; 2l: nonspecific), while these reactions have been reported to yield indanes at room temperature.² Under our conditions only 1 and 2h give a cyclised product (1,1,2,2-tetramethyl-3-phenylindane) besides the normal linear adduct. Norbornene reacts with Wagner-Meerwein rearrangement to yield syn-7-benzhydryl-exo-2-chloro-norbornane exclusively.

METHOD. Competition experiments were carried out by adding 1 to a homogeneous solution of ZnCl₂-Et₂O and a mixture of two alkenes in CH₂Cl₂ at -78°C.⁸ After completion of the

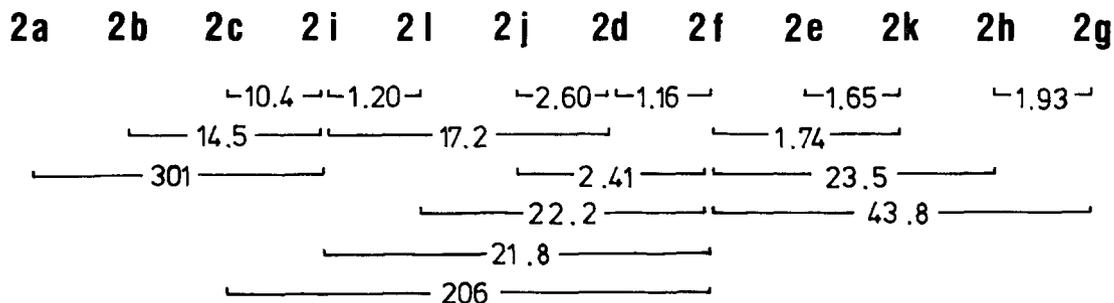


reaction, the catalyst was extracted with aqueous ammonia, and the product ratio (R in eq. 1) was determined by HPLC.⁹ Since the experiments were not carried out under pseudo first order conditions,⁸ eq. 1 was used to evaluate relative reactivities.¹⁰

$$k_x / k_y = \log \left(1 - \frac{[1]_0 R}{[2x]_0 (1+R)} \right) / \log \left(1 - \frac{[1]_0}{[2y]_0 (1+R)} \right) ; \text{ with } R = \frac{[3x]}{[3y]} ; \quad (1)$$

Each rate ratio listed in Scheme 1 was determined 2-5 times with variable relative alkene concentrations. Deviations of less than $\pm 10\%$ were obtained, when the $\frac{2x}{2y}$ ratio was varied within a factor of 10. Reaction time did not influence the product ratio, indicating irreversibility of the addition reactions. When $\text{ZnCl}_2/\text{Et}_2\text{O}$ was replaced by BCl_3 , a rate ratio similar to that in Scheme 1 was obtained for $\frac{2f}{2j}$ (21.6). This finding suggests that the relative reactivities reported in this paper may not be restricted to one specific catalyst system.

The data in Scheme 1 were used to calculate relative rate constants (Table 1). Some k_{rel} values can be obtained in different ways since some of the data in Scheme 1 are redundant. In these cases deviations up to 20% (average 10%) were obtained, indicating the precision of our data.



Scheme 1: Relative Alkene Reactivities toward $\text{Ph}_2\text{CHCl}/\text{ZnCl}_2$ in $\text{Et}_2\text{O}/\text{CH}_2\text{Cl}_2$ at -78°C

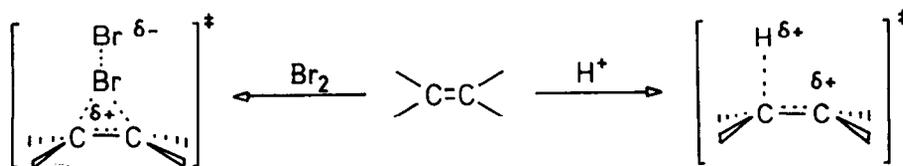
DISCUSSION. The relative olefin reactivities toward diphenylcarbenium ion (Table 1) reflect roughly the stabilities of the carbenium ions formed during addition. $2a-2c$ yield secondary carbenium ions and are 3-5 powers of ten less reactive than $2d-2h$, which give tertiary carbenium ions. The similar reactivity of isobutene ($2d$) and styrene ($2j$) can also be explained by the relative carbenium ion stabilities derived from solvolysis data, which show that phenyl exerts a similar stabilization as two methyl groups.¹⁸ As in other addition reactions,¹⁹ norbornene ($2i$) is found to be more reactive than ordinary 1,2-dialkylated ethylenes ($2b,c$).

Table 1. Reactivities of Alkenes toward Different Electrophiles

		Ph_2CH^+ - Addition ^a	Bromination ^b	Hydration ^c
		k_{rel}	$k_2/3.72 \cdot 10^4$ ($\text{mol}^{-1} \text{sec}^{-1}$)	$k_2/3.71 \cdot 10^{-4}$ ($\text{mol}^{-1} \text{sec}^{-1}$)
<u>2a</u>		$1.8 \cdot 10^{-4}$	0.0108 (11)	$1.33 \cdot 10^{-4}$ (13) $6.42 \cdot 10^{-6}$ (14)
<u>2b</u>		$3.8 \cdot 10^{-3}$	0.640 (11)	$2.24 \cdot 10^{-4}$ (13)
<u>2c</u>		$5.4 \cdot 10^{-3}$	0.349 (11)	$9.46 \cdot 10^{-5}$ (13)
<u>2d</u>		1.0	1.00 (11)	1.00 (13)
<u>2e</u>		1.2	1.62 (12)	1.41 (14)
<u>2f</u>		1.16	0.976 (11)	
<u>2g</u>		51	34.7 (12)	0.580 (13)
<u>2h</u>		27	484 (d)	0.922 (13)
<u>2i</u>		$5.6 \cdot 10^{-2}$		$9.19 \cdot 10^{-2}$ (15)
<u>2j</u>		0.43	0.0411 (11)	$1.00 \cdot 10^{-3}$ (13)
<u>2k</u>		2.0	0.0868 (11)	$3.02 \cdot 10^{-4}$ (13)
<u>2l</u>		$6.2 \cdot 10^{-2}$	0.0213 (11)	$3.29 \cdot 10^{-4}$ (e)

a) This work; b) CH_3OH , 25°C ; c) Acid catalysed hydration in H_2O at 25°C ; d) From rel. rates of 2g and 2h (ref. 16); e) From rel. rates of 2k and 2l in $\text{CF}_3\text{CO}_2\text{H}$ (ref. 17).

Electrophilic additions to alkenes may proceed via bridged or via open transition states.²⁰ For halogenations and sulfenylations of alkylethylenes a bridged transition state was suggested, since these reactions are almost equally accelerated by alkyl groups at both alkene termini (Table 1). In contrast, hydration rates are almost unaffected by β -methyl groups, while they are strongly increased by α -methyl groups (Table 1). These findings indicate a transition state resembling a classical carbenium ion, though the large reactivity difference of isobutene and styrene (10^3 !) is unexplained.



Carbenium ion additions have been postulated to proceed via an open transition state like protonations since in both reactions, alkenes and analogously substituted alkynes show similar reaction rates.²⁰ This conclusion was in agreement with the finding² that introduction of β -methyl groups into styrene (2j \rightarrow 2k, 2l) reduced the reactivity toward diphenylmethyl cation (steric effect).²¹

Except for 2i, which probably has a nonplanar π -system, we find that the reactivity toward the diphenylcarbenium ion is increased by methyl groups at the β -carbon (a/b; d/g; j/k). The similar reactivity of 2g and 2h indicates that the electronic acceleration of the fourth methyl group is compensated by the steric retardation.

These data indicate a transition state which is not solely controlled by the product carbenium ion. If the approach of Ph_2CH^+ to the alkene resembles that of a proton, the transition state must be located earlier on the reaction coordinate, and the acceleration by β -methyl groups can be due to the reduced HOMO (alkene) -LUMO (Ph_2CH^+) energy difference (frontier orbital term²²). Alternatively, a partially bridged transition state, where the β -carbon (attacked position) of the alkene carries part of the positive charge, is in accord with our results.

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