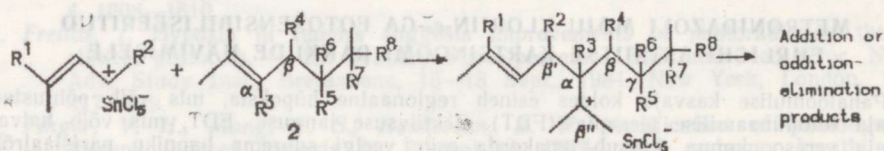


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## CARBOCATIONIC ADDITIONS OF ALLYLIC CHLORIDES TO ISOALKENES. STERIC EFFECTS OF SUBSTITUENTS

In general, isoalkenes ( $R^1 > C=C < R^2$ ,  $R^1 > C=C < R^2$ ,  $>C=C < R$ ) in electrophilic additions, except ionic chlorination, readily give regular adducts, provided that the structures of the products do not become too ramified [1,2]. When groups R are bulky, the addition rate decreases and the addition-elimination products may become predominant [1–4]. We report now on the relative  $\text{SnCl}_4$ -catalyzed addition rates of a primary (1a) or secondary (1b) allylic chloride with ramified isoalkenes (2):



1a:  $R^1 = \text{Me}$ ;  $R^2 = \text{H}$   
 1b:  $R^1 = \text{H}$ ;  $R^2 = \text{Me}$

$R^3, R^4, R^5, R^6 = \text{H}$  or  $\text{Me}$ ;  
 $R^7 = \text{Me}$ ,  $\pi\text{Pr}$  or  $i\text{Pr}$ ;  $R^8 = \text{Cl}$

The relative reactivities of isoalkenes (2) towards 1-chloro-3-methyl-2-butene (1a) or E-2-chloro-3-pentene (1b) were determined by competition experiments. The results listed in the Scheme show that electronic accelerating effect of a methyl group in  $\alpha$ -position is nearly compensated by steric decelerating effect if primary chloride (1a) is involved and overcompensated in case of secondary chloride (1b). The steric retardation by a more distant  $\gamma$ -methyl group is negligible in 1a additions, while in 1b additions it increases with the progressive introduction of methyl groups. The steric retarding contribution of a  $\beta$ -methyl group is important in both additions: with 1a about 10 times and with 1b about 50 times.

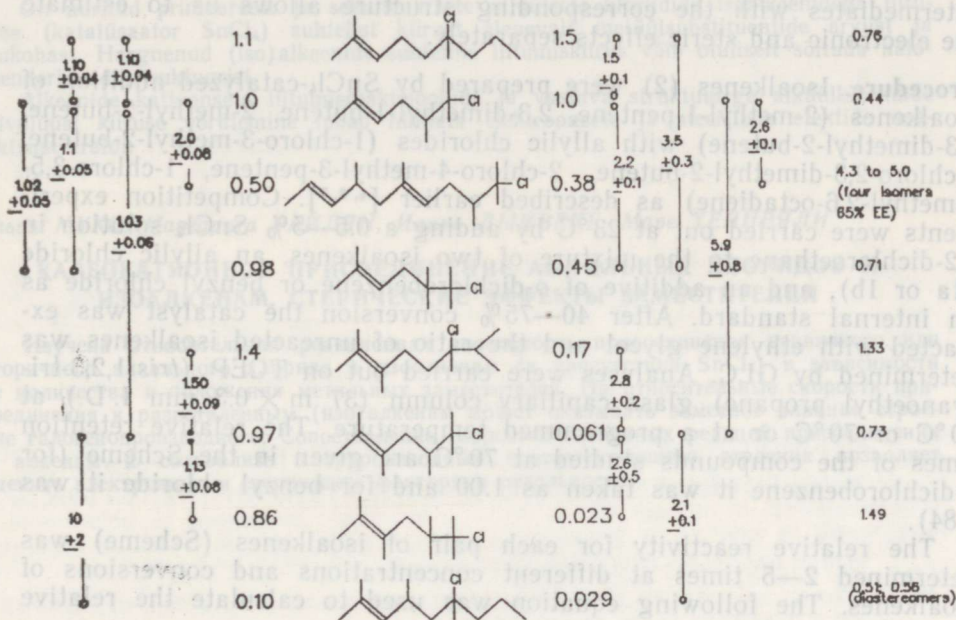
So, the substituents adjacent to the reaction centre in the transition state ( $\beta$ -,  $\beta'$ -, and  $\beta''$ -positions) introduce the most considerable steric effects and the accumulation of the neighbouring substituents results in an increasingly important steric contribution. Thus, if ramified structures are involved in the (iso)alkene additions, the relative rates may depend markedly on the branching of an electrophilic reagent.

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Relative reactivity  
in relation to 1a

Relative reactivity  
in relation to 1b

Relative retention  
time (see  
procedure)



Scheme. Relative rates of isoalkene addition with allylic chlorides 1a or 1b (catalyzed by  $\text{SnCl}_4$  at  $23^\circ\text{C}$ ).

The opposite effects of branching have been observed in solvolysis reactions of tertiary alkyl chlorides [5]. The examples below [2, 3, 6, 7] illustrate the steric effects ( $\text{R}=\text{Ph}_2\text{CH}$ ):

	$\text{R}^1=\text{Me}$	Et	$n\text{Pr}$	$i\text{Pr}$	$t\text{Bu}$	$n\text{soP}\theta$	
	$10^4 k_{sol.v}$	0.77	1.4	1.5	2.6	6.1	29*
$\text{RCl} + \text{C}=\text{C}$ (alkene with R1 substituent)	$k_{ad} / k_{od}$	23.3	18.4	25.8	6.08	1.21	28.6*
	$k_{rel} / k_{ad}$	0.841	1.16	1.0(1.0)	(0.47)		
	$\text{R}^1, \text{R}^2=\text{H, Me}$						
	$10^4 k_{sol.v}$		8.7				86
$\text{RCl} + \text{C}=\text{C}$ (alkene with R1 and R2 substituents)	$k_{od} / k_{ad}$		247		<0.25		>5.6
	$k_{rel} / k_{od}$		44.2(1.9)				23.3(2.4)

$k_{sol.v}$  — the rate of solvolysis in 80% ethanol at  $50^\circ\text{C}$ ;

$k_{ad}$  — the rate of  $\text{BCl}_3$ -catalyzed addition at  $-70^\circ\text{C}$ ;

$k_{rel}$  — the relative rate of  $\text{ZnCl}_2$ -catalyzed addition by the competition method (in brackets  $\text{SnCl}_4$ -catalyzed at  $23^\circ\text{C}$  if  $\text{RCl}$  is  $(\text{CH}_3)_2\text{C}=\text{CHCH}_2\text{Cl}$ ).

\* also a frangomeric effect.

In both cationic processes the electronic factors are similar, while the steric strains are eased in ionisation reactions, but are formed in addition reactions. Therefore, a comparison of the rates of cationic addition reactions of alkenes and solvolysis of chloroderivatives giving cationic intermediates with the corresponding structure allows us to estimate the electronic and steric effects separately.

**Procedure.** Isoalkenes (2) were prepared by  $\text{SnCl}_4$ -catalyzed addition of isoalkenes (2-methyl-1-pentene, 2,3-dimethyl-1-butene, 2-methyl-2-butene, 2,3-dimethyl-2-butene) with allylic chlorides (1-chloro-3-methyl-2-butene, 1-chloro-2,3-dimethyl-2-butene, 2-chloro-4-methyl-3-pentene, 1-chloro-3,5-dimethyl-2,6-octadiene) as described earlier [4, 6, 7]. Competition experiments were carried out at 23°C by adding a 0.5–5%  $\text{SnCl}_4$  solution in 1,2-dichloroethane to the mixture of two isoalkenes, an allylic chloride (1a or 1b), and an additive of *o*-dichlorobenzene or benzyl chloride as an internal standard. After 40–75% conversion the catalyst was extracted with ethylene glycol and the ratio of unreacted isoalkenes was determined by GLC. Analyses were carried out on TCEP (*tris*-1,2,3-tricyanoethyl propane) glass capillary column (37 m × 0.3 mm I. D.) at 60°C or 70°C or at a programmed temperature. The relative retention times of the compounds studied at 70°C are given in the Scheme (for *o*-dichlorobenzene it was taken as 1.00 and for benzyl chloride it was 1.84).

The relative reactivity for each pair of isoalkenes (Scheme) was determined 2–5 times at different concentrations and conversions of isoalkenes. The following equation was used to calculate the relative reactivity:

$$\frac{k_{\text{II}}}{k_{\text{I}}} = \frac{\lg(S_{\text{II}}^0 \cdot S_{\text{st}}^p / S_{\text{II}}^p \cdot S_{\text{st}}^0)}{\lg(S_{\text{I}}^0 \cdot S_{\text{st}}^p / S_{\text{I}}^p \cdot S_{\text{st}}^0)},$$

where  $S_{\text{I}}^0$ ,  $S_{\text{II}}^0$ , and  $S_{\text{st}}^0$  are areas of GLC peaks of isoalkene I, isoalkene II, and an internal standard in the initial mixture, respectively; and  $S_{\text{I}}^p$ ,  $S_{\text{II}}^p$ , and  $S_{\text{st}}^p$  are the corresponding areas after the reaction was stopped.

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## KARBOKATIOONNE ALLÜULSETE KLORIIDIDE LIITUMINE ISOALKEENIDEGA. SUBSTITUENTIDE STEERILISED EFEKTID

On uuritud primaarsete ja sekundaarsete allüülsete kloriidide isoalkeenidega liitumise (katalüsaator  $\text{SnCl}_4$ ) suhtelist kiirust olenevalt metüülsubstituentide arvust ja asukohast. Hargnenud (iso)alkeenide suhteline liitumiskiirus võib oluliselt sõltuda halogeenderivaadi struktuurist.

Alkeenide katioonsete liitumisreaktsioonide ja vastava struktuuriga alküülkloriidide solvolüüsi kiiruse võrdlemine lubab hinnata elektroonsete ja steeriliste efektide osatähtsust eraldi.

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## КАРБОКАТИОННОЕ ПРИСОЕДИНЕНИЕ АЛЛИЛЬНЫХ ХЛОРИДОВ К ИЗОАЛКЕНАМ. СТЕРИЧЕСКИЕ ЭФФЕКТЫ ЗАМЕСТИТЕЛЕЙ

Изучена относительная реакционная способность присоединения первичного или вторичного аллильного хлорида к изоалкенам (в присутствии  $\text{SnCl}_4$ ) в зависимости от количества и положения метильных заместителей. На относительные скорости присоединения к разветвленным (изо)алкенам может оказывать заметное влияние строение галогенопроизводного. Сопоставление скоростей катионных реакций присоединения к алкенам и сольволиза хлорпроизводных соответствующего строения позволяет оценить электронные и стерические факторы в отдельности.