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REACTIVITY OF ALKENES IN CATIONIC TELOMERIZATION WITH ALLYLIC AND ALKOXYMETHYL CHLORIDES. A NEGATIVE ELECTRONIC EFFECT IN THE REACTIONS OF CONJUGATED ALKENES WITH "HARD" TELOGENS

For a more detailed quantitative study of complicated reaction systems of cationic telomerization, creation of a databank of standard telogens and taxogens with determination of their relative reactivity was highly necessary. Standard ingredients must not give side reactions accompanying dehydrochlorination, isomerization, etc. [1-5]. According to literature data, of telogens methyl-substituted allylic and alkoxymethyl chlorides meet the above requirements, of taxogens — isoalkenes, conjugated alkenes, styrene [6-10]. Moreover, the differences in the relative reactivities of the compared compounds for the conversion models should not exceed each other five times.

On the basis of the above ideas as well as on preliminary experimental data, 1-chloro-3-methyl-2-butene (X_1 — a kinetic equilibrium mixture with its allyl isomer [3]), 2-chloro-3-pentene (X_2), 2-chloro-4-methyl-3-pentene (X_3 — a kinetic equilibrium mixture with its allyl isomer [5]), methoxy- (X_4), isobutoxy- (X_5) and isopropoxy- (X_6) — methylchlorides served as model telogens. As taxogens, 2-methyl-2-butene (Y_1), 2-methyl-1,3-butadiene (Y_2), styrene (Y_3) and 1-chloro-3-methyl-2-butene (Y_4) were studied. The dry $SnCl_4$ was used as a catalyst, the reaction was run at 296 K.

The relative reactivity of ingredients was calculated by the gas-liquid chromatographic (GLC) method of determining the ratio of the resulting monoadducts at low conversion of ingredients [11].

Table 1 presents the relative reactivity values of the compounds under study according to the formation of monoadducts. A correlation analysis of the reactivity of taxogens with allylic chlorides yields a satisfactory descriptive equation $K_{ij} = a_i \cdot b_j$, where a_i — the reactivity of telogen X_i with taxogen Y_1, b_j — the reactivity of taxogen Y_j with telogen X_1.

However, in the reactions of conjugated alkenes with alkoxymethyl chlorides a considerable reduction in the reactivity of ingredients was observed, being 30-fold for styrene and methoxymethyl chloride as compared with 2-methyl-2-butene. This effect is graphically illustrated in Figs 1, 2.

Mathematical data processing permitted the derivation of a correlation equation for the reactivity of alkenes with alkoxymethyl chlorides:

$$K_{ij}(1 \pm 0.1) = a_i \cdot b_j \left(\frac{K_{0j}}{a_0 \cdot b_j} \right)^{\left(\frac{a_0}{a_i} \right)^{n_j}} \text{, where}$$

a_i — the relative reactivity of telogens with 2-methyl-2-butene (Y_1); b_j — the relative reactivity of taxogens with allylic chlorides ($X_1 - X_3$); K_{0j} — the relative reaction rate of taxogen (Y_j) with standard alkoxymethyl chloride (methoxymethyl chloride (X_4)); a_0 — the relative reactivity of standard alkoxymethyl chloride (X_4) with 2-methyl-2-butene (Y_1); n_j — the exponent of a decrease in the negative effect of taxogen (Y_j) with increasing telogen activity of alkoxymethyl chlorides (a_i).

According to the above correlation equation if $a_i \to \infty$, then $K_{ij} \to a_i \cdot b_j$, i. e. the reduction effect of reactivity disappears at high reactivities of X_i.
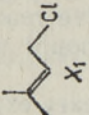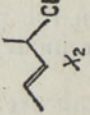
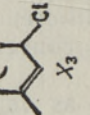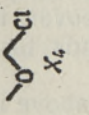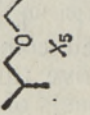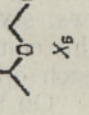The following values were calculated:

for 2-methyl-1,3-butadiene (Y_2) $K_{02} = 0.197$; $n_2 = 0.52$;

for styrene (Y_3) $K_{03} = 0.035$; $n_3 = 0.21$;

for 2-chloro-3-methyl-2-butene (Y_4) $K_{04} = 0.094$; $n_4 = 0.25$.

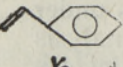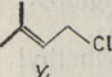A decrease in the reactivity of taxogens with electron-donative resonance substituents in the reactions with "hard" telogens $-\overset{..}{\underset{..}{O}}-\overset{|}{\underset{|}{C}}-\overset{..}{\underset{..}{Cl}}$: is probably due to the "asymmetry" of coulomb and covalent (resonance)

Table 1

Relative reactivity (K_{ij}) of alkenes with substituted allylic and alkoxymethyl chlorides. Catalyst $SnCl_4$, temperature 296 K

Taxogens Y_j	Telogens X_i					
	X_1	X_2	X_3	X_4	X_5	X_6
Y_1	1.00	4.3 ± 0.4	56 ± 5	45 ± 5	82 ± 8	175 ± 17
Y_2	0.56 ± 0.05 *	2.4 ± 0.2	31 ± 3	5.0 ± 0.5	15 ± 2	44 ± 4
Y_3	0.77 ± 0.07	3.3 ± 0.3	43 ± 4	1.2 ± 0.1	3.5 ± 0.3	11 ± 1
Y_4	0.04 ± 0.004 *	0.17 ± 0.02	2.2 ± 0.2	0.17 ± 0.02	0.5 ± 0.05	1.2 ± 0.1

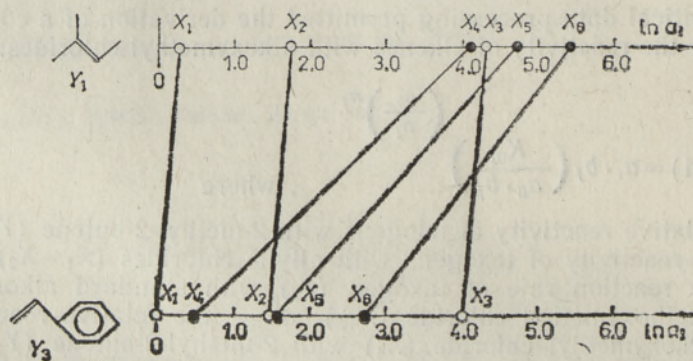* The relative reactivity values were determined by the model of cotelomerization [12].

Fig. 1. Relative reactivity of telogens with 2-methyl-2-butene and styrene.
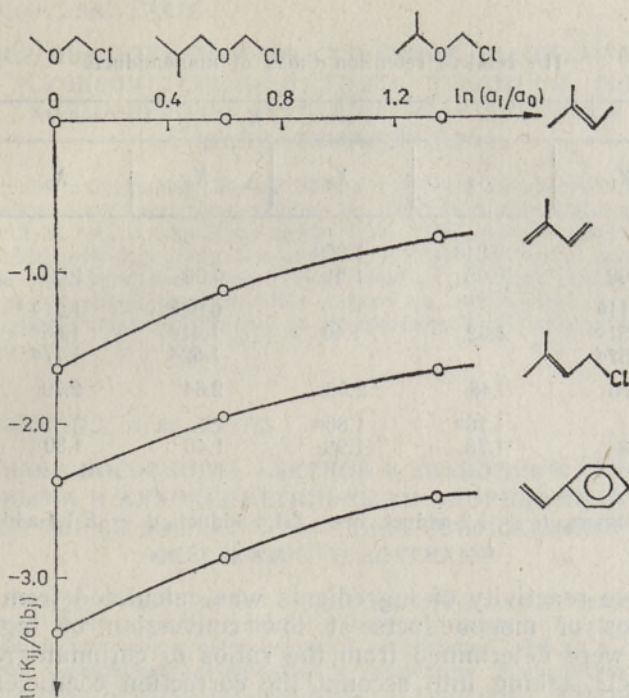
Fig. 2. Reduction in the relative reactivity of alkoxymethyl chlorides.

components of the electro- and nucleophilic reaction centres of the intermediates formed. In the reaction complexes with "softer" telogens of allylic structure, no such "asymmetric" barrier arises and the reactivity is conditioned only by the total polarizability of reagents.

As a result, the relative reactivities of isoalkenes and conjugated alkenes with chlorotelogens of allylic and alkoxymethyl structure have been determined. A negative electronic effect has been established in the reactions of conjugated alkenes with alkoxymethyl chlorides and the correlation equations of the reactivity of telogens and taxogens have been derived. The data obtained may be used to determine the relative reactivity of components in the reactions of cationic telomerization with the compounds under study used as standard ingredients.

Experimental

The initial substances were obtained and prepared according to the methods described in [2, 3, 5, 13].

The reaction of cotelomerization was carried out without solvent at 296 K using a solution of $SnCl_4$ in dichloroethane. The methods, isolation and analysis of the reaction products have been described in [3, 11].

The temperature-programmed GLC method was used to analyze the reaction systems as the mixtures analyzed contain components with highly different boiling temperatures. GLC was performed using a "Chrom 4" chromatograph with a flame ionization detector, capillary borosilicate glass column (13000 · 0.03 mm), liquid phase TCEP, initial column temperature 40°C, isothermal regime 2 min., linear temperature rise 20°C/min., evaporator temperature 190°C, carrier gas flow rate 1.2 ml/min. The relative retention times of the monoadducts are presented in Table 2.

1*

The relative retention times of monoadducts

Y_j	X_i					
	X_1	X_2	X_3	X_4	X_5	X_6
Y_1	1.00	0.84a 0.95	1.05a 1.21	0.66	1.06	0.81
Y_2	1.11b 1.51c 1.57d	1.32	1.40	0.93b 1.41c 1.52d	1.21b 1.65c 1.77d	1.01b 1.42c 1.54d
Y_3	2.76	2.45	2.58	2.64	2.79	2.65
Y_4	1.84	1.70a 1.78	1.86a 1.98	1.46	1.80	1.54

a — diastereoisomers, b — 1,2-adduct, c — Z-1,4-adduct, d — E-1,4-adduct.

The relative reactivity of ingredients was calculated from the corresponding ratios of monoadducts at low conversion of ingredients [11]. These ratios were determined from the ratios of chromatographic peaks of monoadducts, taking into account the correction coefficients preliminarily determined by the model mixtures of these chlorides.

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ALKEENIDE REAKTSIOONIVÕIME KATIOONSEL TELOMERISATSIOONIL ALLÜÜL- JA ALKOKSÜMETÜÜLKLORIIDIDEGA. NEGATIIVNE ELEKTRONEFEKT KONJUGEERITUD ALKEENIDE REAKTSIOONIDES «KARMIDE» TELOGEENIDEGA

Konkureerivate reaktsioonide meetodi abil on määratud isoalkeenide ja konjugeeritud alkeenide suhteline reaktsioonivõime allüülse ja alkoksümetüülse ehitusega klorotelogeenidega. On kindlaks tehtud negatiivne elektronefekt konjugeeritud alkeenide reaktsioonides alkoksümetüülkloriididega ning tuletatud korrelatsioonivõrrandid uuritud telogeenide ja taksogeenide reaktsioonivõime kohta. Leitud efekt on seletatav täiendava potentsiaalibarjääri tekkega reaktsiooniintermediaatide elektro- ja nukleofiilsete reaktsioonitsentrite vahel ning tingitud viimaste kuloniliste ja kovalentsete (resonantsete) osamoodustajate «asümmeetriast».

Николай САЛЬНИКОВ, Койт ЛЭЭТС

РЕАКЦИОННАЯ СПОСОБНОСТЬ АЛКЕНОВ В КАТИОННОЙ ТЕЛОМЕРИЗАЦИИ С АЛЛИЛЬНЫМИ И АЛКОКСИМЕТИЛЬНЫМИ ХЛОРИДАМИ. ОТРИЦАТЕЛЬНЫЙ ЭЛЕКТРОННЫЙ ЭФФЕКТ В РЕАКЦИЯХ СОПРЯЖЕННЫХ АЛКЕНОВ С «ЖЕСТКИМИ» ТЕЛОГЕНАМИ

Методом конкурирующих реакций определены относительные реакционные способности изоалкенов и сопряженных алкенов с хлортелогенами аллильного и алкоксиметильного строения. Установлен отрицательный электронный эффект в реакциях сопряженных алкенов с алкоксиметилхлоридами и выведены корреляционные уравнения реакционной способности изученных телогенов и таксогенов. Обнаруженный эффект объяснен возникновением дополнительного потенциального барьера в реакциях катионного присоединения вследствие «асимметрии» кулоновских и ковалентных (резонансных) составляющих электро- и нуклеофильных реакционных центров образующихся интермедиатов реакции.