Proc. Estonian Acad. Sci. Chem., 1990, 39, N 2, 94—102
https://doi.org/10.3176/chem.1990.2.05
УДК 547.31

Elvi MUKS

COMPARISON OF ELECTROPHILIC ADDITION REACTIONS. REACTIONS OF THE CARBOCATIONIC INTERMEDIATE

(Presented by K. Lääts)

A conception of the formation of carbocationic intermediates in the rate-determining step is successfully used by interpreting processes of electrophilic addition to alkenes [1–6]. A whole range of possible structures and ways of formation of the above cationic intermediates have been suggested. Despite the specific features, the lack of electrons in the intermediate is common and, hence, its high reactivity by interaction with different molecules which may serve as nucleophiles.

The present review considers the formation of end products, i. e. competing paths by the interaction of the carbocationic intermediate with n-, π- and σ-donors. A more detailed discussion of chain transfer processes will be given. Products formed in subsequent reactions, e. g. stepwise addition, have not been dealt with.

The electrophilic reactions of addition of reactive reagents (EY), such as halogen hydrides, halogens, inter- and pseudohalogens, lead mainly to normal adducts ($ECCY$) and in O-, N- or S-containing solvents [7–11] to the corresponding mixed products. In many cases, depending on the alkene structure, side reactions take place:

$$EY + C{=}C \xrightarrow{EY;\ SolOH;\ MX_n} E{-}C{-}C{-}Y +$$

$$+ \underset{\text{(in hydroxylic solvents)}}{E{-}C{-}C{-}OSol} + \underset{\text{(β-substituted and bifunctional alkenes)}}{\text{isomeric products}} + \underset{\text{(α-substituted alkenes)}}{\text{products of substitution and subsequent addition}}$$

$EY = HCl, HBr, Cl_2, Br_2, ICl, BrN_3, ClOH, ClOR, ClNO \ldots$
$MX_n = ZnCl_2, HgCl_2, SnCl_4, I_2 \ldots$ and $SolOH = H_2O, CH_3OH, CH_3COOH \ldots$

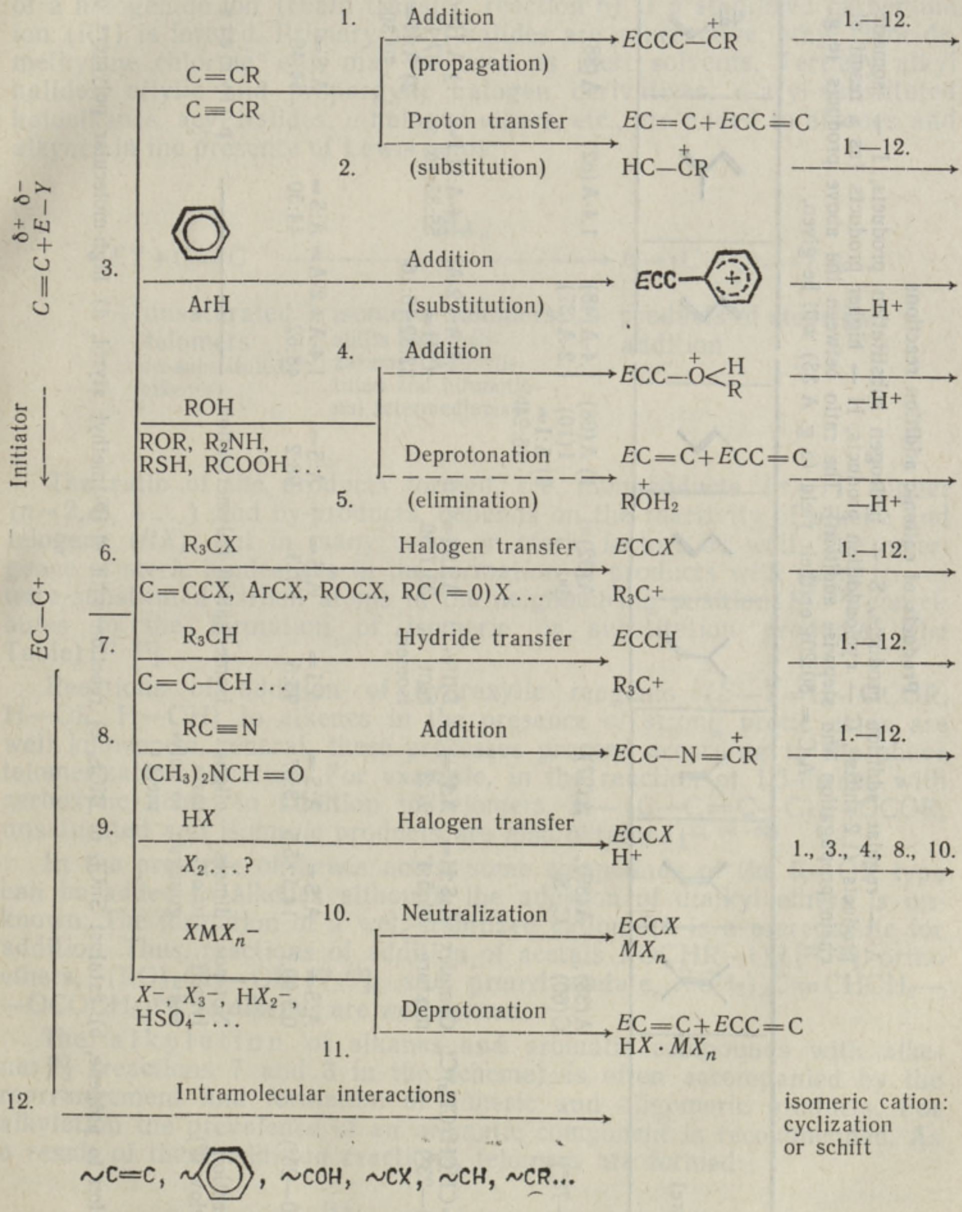
The ionic chlorination of isoalkenes (α-substituted) such as isobutene, 2-methyl-1-(or -2)butene, etc., gives unsaturated allylic monochloroderivatives (85—99%) and products of addition of HCl to alkene [11–15] (transfer of the proton from the cation to the alkene molecule, reaction 2 in the scheme):

$$> \underset{\alpha'}{C}{=}\underset{\alpha}{C}R{-}CH_2{-} + Cl_2 \rightarrow\ > CCl{-}CR{=}CH{-} +\ > CH{-}CRClCH_2{-} + \ldots$$

Substantial amounts of hydrogen substitution products (splitting of the proton in the β-position to the cationic centre [12]) are obtained by chlorination of 2-methyl- and 2,3-dimethyl-1,3-butadiene (up to 55%) [16–18], 1,3-dichloro-2-butene (up to 92%) [19] and cyclohexene (20%) [15]. By chlorination of 1- and 2-butenes and 1,3-butadiene the amount of substitution products does not exceed 3% (the Table) [10, 15, 20]. The highest amount of unsaturated substitution products is obtained in the reactions of ionic chlorination of alkenes, as well as in the addition of ClOH or ClOR [35–39].

The ionic bromination of methylenecyclohexane affords 85% dibromide and 15% allylic bromides [40]. However, by bromination of sterically hindered alkenes such as 2,2, 3,4, 5,5-hexamethyl-3-hexene of octamethylcyclopentene no normal adducts are formed [41, 42].

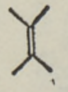
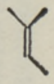
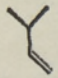
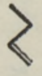
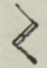
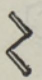
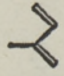
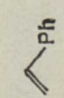
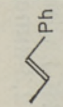
In the reactions of hydrohalogenation of asymmetric isoalkenes as a result of the hydrogen-hydrogen substitution reaction, (reaction 2) isomerization of the starting alkene owing to the shift of the double bond takes place [43–46]. For example, in the reaction of HCl with 1,2-dimethylcyclo-1-hexene together with the addition products 2,3-dimethylcyclo-1-hexene is also formed [43].



Reaction paths of carbocationic intermediates.
The counterion is not shown. X=Hlg.

Products of cationic addition reactions

A — regular addition products, S — hydrogen substitution products, I — isomeric products (1,2-shifts), C — cycloaddition products, H — higher products (as a result of chain propagation and stepwise addition). The ratio between the above products (e. g. A:C = 80:20) or their yield (e. g. A 33) will be given.

Reagent (catalyst, temperature)											References
Ph_2CHCl ($ZnCl_2$; −78°)	A(33), C(60)	A(89), C, S	A(97)		A(92)[a] I[a]	1) A(68) I(10) 2) A:I=76:24[b]	1,4-A(48) 1,2-A(37)	1,4-A(82)	A(88)	1) A(61) 2) A:C=80:20[b]	[21–24]
$CH_3CH{=}CHCH(CH_3)Cl$ ($SnCl_4$; 0—23°)	Complex mixture	A:S:H=91:5:4	A:H=97:3	Different isomers	A:I:H=33:7:50		1,4-A:1,2-A::C:H=32:32:16:16	1,4-A:H:I=55:35:10	1) A:H=87:13 2) A:H=70:30[c]		[25–29]
Cl_2 (Cl_2; −20—25°)	A:S=0.3:99.7	A:S=14.5:85.5	A:S=13:87	A:I=95:5	A:S=97:3	A:S=98:2	1,4-A:1,2-A=48:52	A:S=44:50	A:S=54:46	A:S=84:16	[10–18, 30–32]
Polymerization (MX_n; below 0°)	Not polymerized	dimers to oligomers	oligomers to polymers[d]	isomerisation polymerization			polymers				[3, 4, 33, 34]

a) addition to propene, b) catalyst $SnCl_4$ or $BiCl_3$, c) reaction with *m*-(*p*-)methyl styrol, d) high-molecular polymers only at low temperature, below −100°.

It is known that in the reactions of halogenation or hydrohalogenation of easily polymerizable alkenes such as substituted 1,3-butadienes, styrenes and vinyl ethers, together with a 1:1 adduct, higher products (reaction 1) are also obtained [47–49]. The reaction of nitrosyl chloride with alkenes in the presence of $AlCl_3$ has been described as telomerization [50].

The influence of the alkene structure on the composition of cationic reaction products will be briefly described in the conclusive part of this work (see also reviews [12, 51]).

In the last decades reactions of cationic telomerization of alkenes with halogen derivatives ($EY=RX$) [12, 21–29, 52–59] have been investigated more thoroughly. The halogen derivatives serve as donors of a halogenide ion (chain transfer, reaction 6) if a stabilized carbenium ion (R^+) is formed. Primary alkyl halides are nonreactive: ethyl chloride, methylene chloride, etc., may be used as inert solvents. Tertiary alkyl halides, allylic and propargylic halogen derivatives, α-aryl-substituted haloalkanes, acyl halides, α-halogen ethers, etc., are added to alkenes and alkynes in the presence of Lewis acids:

$$EY+\mathrm{C{=}C} \xrightarrow{\qquad MX_n \qquad} E\mathrm{-(C-C)}_n\mathrm{-}Y+$$

+ unsaturated telomers (α-substituted alkenes) + isomeric telomers: shifts and cyclizations (β-substituted and bifunctional intermediates) + products of stepwise addition

The ratio of the products formed, i. e. monoadducts ($n=1$), higher ($n=2, 3, 4 \ldots$) and by-products, depends on the reactivity of alkene and telogene (RX), but in many cases on steric factors as well. The emergence of steric hindrances in the formation of products with some tri- or tetra-substituted carbon atoms in the neighbouring positions [25, 59] contributes to the formation of isomeric or substitution products (the Table) [52–59].

Reactions of addition of hydroxylic reagents ($E{-}Y=\mathrm{H{-}OCOR}$, H—OR, H—OH) to alkenes in the presence of strong protic acids are well known. In general, these processes proceed according to the above telomerization equation. For example, in the reaction of 1,3-dienes with carboxylic acids, in addition to telomers, $\mathrm{H{-}(C{-}C{=}C{-}C)_n{-}OCOR}$, unsaturated and isomeric products are also obtained [52, 60–62].

In the presence of Lewis acids, some compounds of the R—OR type can be added to alkenes although the addition of dialkyl ethers is unknown. The formation of a well-stabilized cation R^+ is a prerequisite for addition. Thus, reactions of addition of acetals ROCHR—OR [52, 63], ortho ethers, $\mathrm{(RO)_2CH{-}OR}$ [52, 63], and prenyl acetate, $\mathrm{(CH_3)_2C{=}CHCH_2{-}OCOCH_3}$ [64], to alkenes are well known.

The alkylation of alkanes and aromatic compounds with alkenes [5] (reactions 7 and 3 in the scheme) is often accompanied by the rearrangement and formation of dimeric and oligomeric products. For alkylation the prevalence of an aromatic component is recommended. As a result of these addition reactions, telomers are formed:

$$\mathrm{C{=}C+R_3CH} \xrightarrow{\mathrm{H^+}} \mathrm{R_3C(C{-}C)}_n\mathrm{H} + \text{isomeric products}$$

$$\mathrm{C{=}C+HAr} \xrightarrow{\mathrm{H^+}} \mathrm{H(C{-}C)}_n\mathrm{Ar} + \text{isomeric products}$$

Cationic polymerization of alkenes [3, 4] may be described by the following general formula:

$$\mathrm{C{=}C} \xrightarrow[\text{or } \mathrm{H}^+]{EY\cdot MX_n} E\text{—}(\mathrm{C\text{—}C})_n\text{—}\mathrm{C{=}C} + E\text{—}(\mathrm{C\text{—}C})_n\text{—}Y' + \text{isomeric polymers}$$

$EY = \mathrm{HOH},\ \mathrm{HOR},\ \mathrm{H}X,\ X_2,\ \mathrm{R_3C}X \ldots$ and $E'Y' = EY$ and $\mathrm{HAr},\ \mathrm{R_3CH} \ldots$ For the cationic polymerization of isobutylene with $\mathrm{R_aAlCl_b}$ it is reported that in the presence of tertiary RCl or HCl additives [3, 4, 65–70] the polymers are obtained in good yields but with lower molecular weight than in the absence of these additives. Both alkyl halides and HCl serve as coinitiators and chain transfer agents (reactions 6 and 9) in this system. In order to obtain polymers with a reactive end group of halogen $\mathrm{Cl_2}$ ($\mathrm{Br_2}$ is less suitable) is also used as a coinitiator and transfer agent (inifer) [4, 71]. Unfortunately, no data are available on the influence of halogens on the molecular weight of polymers. In principle, the formation of addition products is possible by the transfer of the halogenide ion from the halogen molecule to the cation (reaction 9) in polymerization as well as in addition of halogens to alkenes.

In several investigations [3, 4, 72–74] on the cationic polymerization of isobutylene it has been established that the admixtures of *n*-alkenes decrease the yield of polymers, but do not influence their molecular weight. The influence of *n*-alkenes was explained by the transfer of allylic hydrogen (reaction 7) from the alkene molecule to the polyisobutylene cation with the formation of a more stable allylic cation:

$$\sim\overset{+}{\mathrm{C}}(\mathrm{CH_3})_2 + \mathrm{RCH_2CH{=}CHR'} \longrightarrow \sim\mathrm{CH(CH_3)_2} + \mathrm{R}\overset{+}{\mathrm{C}}\mathrm{HCH{=}CHR'}.$$

Chain transfer (with participation of σ-bonds C—X, C—H, H—X, ...) or termination (with participation of O-, N- and S-containing compounds or reactive aromatic compounds) competing with propagation may be minimized by purifying the initial substances and using inert solvents. But the contribution of proton transfer from the cation to the alkene molecule (reaction 2) may be somewhat decreased depending upon the temperature and other conditions. Thus, by polymerization of isoolefins chain propagation is decreased because of this reaction and high-molecular polymers are obtained only from a less-substituted isoolefin, isobutylene, at low temperatures (the Table) [3, 4, 33]. Intramolecular interactions (reaction 12) such as hydride and alkyl shifts (for example, isomerization polymerization of 3-methyl- and 3,3-dimethyl-1-butenes [3, 4, 34]) or cyclization polymerization with participation of the other double bond in the case of 1,5- or 1,6-dienes [3, 4, 75] lead to isomeric polymers but, in principle, do not lead to chain breaking. 1,3-Butadiene, styrene, vinyl ether and their sterically unhindered alkyl- and phenyl-substituted and other derivatives (the Table) are easy-to-polymerize [3, 4] (reaction 1 is prevailing).

A comparison of the chemical structure of the products of cationic addition, telomerization and polymerization gives evidence of a similarity in the initiating step as well as in competing paths of the above reactions in the formation of the end products. The head group is fixed in the initiating step. Then, success or failure of synthesis depend on the ability of the main reaction to compete with side processes. In the scheme possible competing paths are shown which lead to the fixation of the end group. The scheme depicts the reaction with only one representative of a whole group of reagents which in principle react similarly. Intramolecular interactions are analogous to intermolecular ones [51, 76].

In conclusion it can be said that competing paths in the reactions of cationic addition to alkenes are mainly determined by the chemical structure of alkene, but the ratio of regular to irregular products depends greatly on the chemical nature of the reagent to be added. Thus, high-reactivity alkenes with negligible steric hindrances (i. e. conjugation of the double bond with the neighbouring n- or π-donor) easily give chain propagation. High-reactivity alkenes with considerable steric hindrances [77, 78], i. e. with substituents (Alk, Ph) at the double bond easily afford unsaturated substitution products [12, 54]. Electron-donor substituents (Alk, Ph, OH) in the β-position to the cationic centre [12, 76] contribute to the intramolecular interaction of the cationic centre with the neighbouring σ-donor, leading to 1,2-shifts of atoms or groups (H, Alk, Ph, Cl). Intramolecular interactions with *n*- or π-donors in positions 5, 6, 7, 4 ... from the cationic centre may result in cycloaddition if steric factors do not counteract [51, 76]. The formation of a cation more stabilized than the initial one is a precondition for the inter- or intramolecular interaction of the cationic centre with the nucleophilic one. The formation of irregular by-products is often associated with the emergence of steric hindrances in the formation of products with several tri- and tetra-substituted carbon atoms in the neighbouring positions [25].

REFERENCES

1. *Бетел Д., Голд В.* Карбониевые ионы. М., 1970.
2. *Сергеев Г. Б., Смирнов В. В., Ростовщикова Т. Н.* Гидрохлорирование ненасыщенных соединений // Успехи химии, 1983, **52**, № 3, 455—482.
3. *Кеннеди Дж.* Катионная полимеризация олефинов. М., 1978.
4. *Kennedy, J. P., Marechal, E.* Carbocationic Polymerization. New York, 1982.
5. *Olah, G. A.* Friedel-Crafts Chemistry. New York, 1973.
6. *De la Mare, P. B. D.* Electrophilic Halogenation. Cambridge, 1976.
7. *Bertrand, M., Dulcere, J.-P., Rodrigues, J., Zahra, J.-P.* Cohalagénation de cetones, α, β-éthyléniques dans le THF // Tetrahedron Lett., 1983, N 19, 1967—1970.
8. *Boerwinkle, F., Hassner, A.* Solvent participation in additions to olefins // Tetrahedron Lett., 1968, N 36, 3921—3924.
9. *Uemura, S., Fukuzawa, S., Toshimitsu, A., Okano, M.* Iodine-induced formation of bicyclo[3.3.0]octane derivatives from 1,5-cyclooctadiene // J. Org. Chem., 1983, **48**, N 2, 270—273.
10. *Акопян С. К., Котикян Ю. А., Миракян С. М., Мартиросян Г. Т.* Хлорирование бутадиена в среде растворителей в присутствии катализаторов // Арм. хим. ж., 1979, **32**, № 11, 890—895.
11. *Мкрян Г. Г., Акопян С. К., Мартиросян Г. Т.* Исследование жидкофазного галогенирования ненасыщенных соединений // Арм. хим. ж., 1982, **35**, № 4, 241—246.
12. *Мукс Э.* Сопоставление реакций электрофильного присоединения. Конкурирующие направления, определяемые строением алкена // Изв. АН ЭССР. Хим., 1987, **36**, № 2, 103—113.
13. *Мукс Э., Эрм А., Кабрал С., Лээтс К.* Продукты хлорирования 2-метил-2-бутена // Изв. АН ЭССР. Хим., 1979, **28**, № 1, 46—48.
14. *Weill, J., Carapon, J., Silleon, B.* Ionic reaction of chlorine on branched olefins: synthesis of allylic chlorides // C. R. Acad. Sc. C., 1980, **290**, N 11, 207—209.
15. *Poutsma, M. L.* Chlorination studies of unsaturated materials in nonpolar media // J. Amer. Chem. Soc., 1965, **87**, N 19, 4285—4293.
16. *Jones, G. D., Tefertiller, N. B., Raley, C. F., Runyon, I. R.* Isoprene chlorination // J. Org. Chem., 1968, **33**, N 7, 2946—2951.
17. *Said, E. Z., Tipping, A. E.* Reactions of 2,3-dimethyl-1,3-butadiene with chlorine and with iodine monochloride // J. Chem. Soc. Perkin Trans. 1, 1972, N 16, 1986—1991.
18. *Тищенко Д., Абрамова А., Яржемская Е.* Аддитивная способность двойной связи при четвертичном углероде. Действие хлора на 1,3-диены // Ж. общ. хим., 1957, **27**, № 1, 227—233.
19. *Мкрян Г. Г., Капланян Э. Е., Мкрян Г. М.* Об аномальной реакции хлорирования этиленовых соединений, содержащих атом хлора у двойной связи // Ж. орг. хим., 1981, **17**, № 8, 1575—1580.
20. *Stoyanova-Antoszczyn, M., Zielinski, A. Z., Chojnicki, E.* Catalytic chlorination of butadiene in a liquid phase // Przem. Chem., 1979, **58**, N 3, 160—162.
21. *Mayr, H., Pock, R.* Relative Reaktivität Alkyl-substituerter Alkene und Cycloalkene gegenüber Diarylcarbenium-Ionen // Chem. Ber., 1986, **119**, N 8, 2473—2496.
22. *Pock, R., Mayr, H.* Relative Reaktivität konjugierter Alkene gegenüber Diarylcarbenium-Ionen // Chem. Ber., 1986, **119**, N 8, 2497—2509.

23. *Pock, R., Mayr, H., Rubow, M., Wilhelm, E.* Do carbenium ion additions toward alkenes proceed via π-complexes? A stereochemical investigation // J. Amer. Chem. Soc., 1986, **108**, N 24, 7767—7772.
24. *Mayr, H., Striepe, W.* Scope and limitations of aliphatic Friedel—Crafts alkylations // J. Org. Chem., 1983, **48**, N 8, 1159—1165.
25. *Мукс Э. А., Эрм А. Ю., Лыйвеке И. А., Тенг С. Э., Крумм Л. Л., Лээтс К. В.* К изучению ионно-каталитической теломеризации. XXV. Стерический эффект алкильных заместителей // Ж. орг. хим., 1988, **24**, № 9, 1838—1842.
26. *Лээтс К. В., Чернышев В. О., Пехк Т. И., Ранг Х. А., Эрм А. Ю.* К изучению ионно-каталитической теломеризации. XV. Теломеризация гем.-диалкил и β-алкилзамещенных 1-алкенов // Ж. орг. хим., 1978, **14**, № 5, 913—920.
27. *Чернышев В. О., Пехк Т. И., Ранг Х. А., Лээтс К. В.* Теломеризация 2-хлор-*транс*-3-пентена с 1-пентеном // Ж. орг. хим., 1977, **13**, № 11, 2300—2304.
28. *Петров А. А., Разумова Н. А., Генусов М. Л.* Присоединение 2-хлор-пентена-3 к дивинилу // Ж. общ. хим., 1958, **28**, № 8, 2132—2138.
29. *Лээтс К., Чернышев В., Ранг Х.* О теломеризации 4-хлор-2-пентена с арилзамещенными этена // Изв. АН ЭССР. Хим., 1988, **37**, № 2, 88—91.
30. *Bilke, H., Collin, G., Duschek, Ch., Hoebold, W.* Electrophile Additionen an umlagerungsfähige aliphatische Olefine // J. Prakt. Chem., 1969, **311**, N 6, 1037—1057.
31. *Negoro, T., Ikeda, Y.* Bromochlorination of alkenes with dichlorobromate (1)-ion // Bull. Chem. Soc. Jap., 1984, **57**, N 8, 2111—2115.
32. *Fahey, R. C., Schubert, C.* Chlorination of 2-butene and 1-phenylpropene // J. Amer. Chem. Soc., 1965, **87**, N 22, 5172—5179.
33. *Van Lohuizen, O. E., Devries, K. S.* Cationic polymerization of some 1,1-dialkylethylenes and methylencycloalkanes // J. Polym. Sci. C, 1965 (Pub. 1968), N 16 (Pt. 7), 3943—3956.
34. *Kennedy, J. P., Johnston, J. E.* The cationic isomerization polymerization of 3-methyl-1-butene and 4-methyl-1-pentene // Adv. Polym. Sci., 1975, **19**, 57—95.
35. *Hegde, S. G., Vogel, M. K., Oliver, M., Wolinsky, J.* The reaction of hydrochlorous acid with olefins // Tetrahedron Lett., 1980, N 5, 441—444.
36. *Willis, B. J., Eilerman, R. G., Christenson, P. A., Yurecko, J. M.* Functionalization of terminal trisubstituted alkenes and derivatives // U. S. US 4510319 (1985); Chem. Abs., 1985, **103**, 178477.
37. *Сийрде К., Эрм А., Тенг С., Лээтс К.* Синтез компонентов феромонов щелкуна кубанского и калифорнийской щитовки // Изв. АН ЭССР. Хим., 1988, **37**, № 2, 145—147.
38. *Бодриков И. В., Спиридонова С. В., Смолян З. С.* Электрофильное галогенирование олефинов // Ж.. орг. хим., 1977, **13**, № 3, 486—493.
39. *Карташов В. Р., Пушкарев В. П., Бодриков И. В., Тишков К. Н.* Кинетика реакции 2,3-диметил-3-бутен-2-ола с *трет.*-бутилгипохлоритом // Ж. орг. хим., 1971, **7**, № 8, 1570—1574.
40. *Arnold, R. T., Lee, W. W.* The low temperature halogenation of isobutylenes // J. Amer. Chem. Soc., 1953, **75**, N 21, 5396—5400.
41. *Lenoir, D.* Synthese und Reaktionen eines sterisch gehinderten Olefins, *trans*-2,2,3,4,5,5-Hexamethyl-3-hexen // Chem. Ber., 1978, **111**, N 1, 411—414.
42. *Mayr, H., Will, E., Heigl, U. W., Schade, C.* Bromination of octamethylcyclopentene // Tetrahedron, 1986, **42**, N 9, 2519—2522.
43. *Fahey, R. C., McPherson C. A.* Kinetics and stereochemistry of the hydrochlorination of 1,2-dimethylcyclohexene // J. Amer. Chem. Soc., 1971, **93**, N 10, 2245—2253.
44. *Wolinsky, J., Novak, R. W., Erikson, K. L.* The reaction of bromine with disubstituted terminal olefins // J. Org. Chem., 1969, **34**, N 3, 490—495.
45. *Snider, B. B., Rodini, D. J., Karras, M., et al.* Alkylaluminium halides. Lewis acid catalysts which are Brønsted bases // Tetrahedron, 1981, **37**, N 23, 3927—3934.
46. *Лысенков В. И., Ударов Б. Г., Пехк Т. И.* Изучение состава гидрохлоридов — продуктов взаимодействия α-пинена с хлористым водородом // Весці АН БССР. Сер. хім. навук, 1985, № 4, 62—66.
47. *Губин С. П., Голоунин А. В.* Диены и их π-комплексы. Новосибирск, 1983.
48. *Trifan, D. S., Bartlett, P. D.* Four reactions between iodine and styrene // J. Amer. Chem. Soc., 1959, **81**, N 21, 5573—5581.
49. *Денисов Е. Н., Морозов Ю. Д., Шурупов Е. В., Расулев З. Г.* Получение 4-хлорпентена-2 гидрохлорированием пиперилена абгазным хлористым водородом // Хим. пром., 1985, № 11, 654—655.
50. *Титов А. И.* Нитрозохлорирование олефинов и их производных по ионному механизму // Докл. АН СССР, 1963, **149**, № 3, 619—622.
51. *Мукс Э.* Сопоставление реакций электрофильного присоединения. Образование циклических продуктов // Изв. АН ЭССР. Хим., 1988, **37**, № 2, 100—111.
52. *Петров А. А., Генусов М. Л.* Ионная теломеризация. Л., 1968.
53. *Мукс Э., Райлян М., Тенг С., Эрм А., Лээтс К.* Аллильные хлориды в качестве таксогенов при катионной теломеризации // Изв. АН ЭССР. Хим., 1988, **37**, № 4, 255—258.

54. *Мукс Э. А., Лээтс К. В.* К изучению ионно-каталитической теломеризации. XXII. О перераспределении галогеноводорода при теломеризации изоалкенов // Ж. орг. хим., 1985, **21**, № 6, 1177—1180.
55. *Dubois, J. E., Saumtally, I., Lion, C.* Acylation de quelques olefines substituées selon Friedel—Crafts // Bull. Soc. Chim. Fr., 1984, N 3—4, Pt. 2, 133—138.
56. *Mayr, H., Heilman, W.* Steric control of regiochemistry in the reactions of methyl substituted pentadienyl cations with isobutene // Tetrahedron, 1986, **42**, N 24, 6657—6662.
57. *Mayr, H., Klein, H., Sippel, E.* Synthese von 1,2,3,3,6,6-Hexamethyl-1-cyclohexen — eine Umlagerungskaskade von $C_{12}H_{32}^+$-Kationen // Chem. Ber., 1983, **116**, N 11, 3624—3630.
58. *Mayr, H., Klein, H., Kolberg, G.* Lewis-Säure-katalysierte Additionen 1,3-Alkyl-substituierter Allylkloride an Alkene // Chem. Ber., 1984, **117**, N 8, 2555—2579.
59. *Baran, J., Mayr, H.* Synthesis of hexamethylglutaric acid: an approach to compounds with adjacent quaternary carbon centers // J. Org. Chem., 1988, **53**, N 19, 4626—4628.
60. *Tanaka, J., Katagiri, T., Okawa, H.* Reactions of isoprene with acetic acid by the action of polyphosphoric acid // Nippon Kagaku Zasshi, 1970, **91**, N 2, 156—159; 159—161; Chem. Abs., 1970, **73**, 25672; 45612.
61. *Лээтс К., Эрм А., Липпмаа Э., Пускар Ю.* О составе продукта реакции теломеризации изопрена с уксусной кислотой // Изв. АН ЭССР. Хим. Геол., 1968, **17**, № 4, 427—428.
62. *Nordlander, J. E., Haky, J. E., Landino, J. P.* Mechanism of addition of neat trifluoroacetic acid to protoadamantene // J. Amer. Chem. Soc., 1980, **102**, N 25, 7487—7493.
63. *Van der Brüggen, U., Lammers, R., Mayr, H.* Relative reactivities of acetals and orthoesters in Lewis acid catalyzed reactions with vinyl ethers // J. Org. Chem., 1988, **53**, N 13, 2920—2925.
64. *Takabe, K., Katagiri, T., Tanaka, J.* Cationic telomerization of isoprene with prenyl acetate // Kogyo Kagaku Zasshi, 1971, **74**, N 6, 1162—1164; Chem. Abs. 1971, **75**, 129947.
65. *Kennedy, J. P., Bank, S., Squires, R. G.* Contributions to the mechanism of isobutene polymerization. VI. Effect of halides // J. Macromol. Sci., 1967, **A1**, N 6, 977—993.
66. *Kennedy, J. P., Squires, R. G.* Contributions to the mechanism of isobutene polymerization. VII. Effect of HCl and chloroethylbenzene and a brief summary of the data // J. Macromol. Sci., 1967, **A1**, N 6, 995—1004.
67. *Kennedy, J. P.* Novel sequential copolymers by elucidating the mechanism of initiation and termination of carbocationic polymerizations // J. Polym. Sci.: Polym. Symp., 1977, N 56, 1—11.
68. *Musch, R., Pask, S., Mottweiler, R., Nuyken, O.* Preparation of polymers with reactive end groups // Ger. Offen, DE 3542000, 1987; Chem. Abs., 1987, **107**, 176701.
69. *Verstrate, G., Baldwin, F. P.* Low molecular weight terminally-functional saturated hydrocarbon polymer // U. S. 4278822, 1981; Chem. Abs., 1981, **95**, 187880.
70. *Mayr, H., Schneider, R., Pock, R.* Addition reactions of carbocations with alkenes: studies on the mechanism of carbocationic polymerization // Makromol. Chem., Macromol. Symp., 1986, **3**, 19—31.
71. *Kennedy, J. P., Sivaram, S.* Olefin polymerization. VII. Initiation by electrophilic halogens // J. Macromal. Sci., 1973, **A7**, N 4, 969—989.
72. *Kennedy, J. P., Squires, R. G.* Contributions to the mechanism of isobutene polymerization. I. Theory of allylic termination and kinetic considerations // J. Macromol. Sci., 1967, **A1**, N 5, 805—829.
73. *Kennedy, J. P., Squires, R. G.* Contributions to the mechanism of isobutene polymerization. II. Effect of *n*-alkenes // J. Macromol Sci, 1967, **A1**, N 5, 831—845.
74. *Cheradame, H., Razzouk, H., Rousset, E., Gandini, A.* Unsaturated telechelic oligoisobutylenes: appraisal of the transfer efficiency of some dienes // Makromol. Chem., Macromol. Symp. 1988, **13—14**, 417—431.
75. *Marek, M., Roosova, M., Doskočilova, D.* Cationic polymerization of 2,5-dimethyl-1,5-hexadiene // J. Polym. Sci. C, 1967, N 16, 971—976.
76. *Muks, E.* Systematization of intramolecular interactions in cationic reactions // Proc. Estonian Acad. Sci. Chem., 1990, **39**, N 2.
77. *Grosjean, D., Mouvier, G., Dubois, J.-E.* Bromination of ethylenic compounds // J. Org. Chem., 1976, **41**, N 24, 3869—3872.
78. *Grosjean, D., Mouvier, G., Dubois, J.-E.* Predominance of steric effects on the reactivity of tetrasubstituted alkenes // J. Org. Chem., 1976, **41**, N 24, 3872—3876.

Estonian Academy of Sciences,
Institute of Chemistry

Received
Aug. 19, 1989

Elvi MUKS

ELEKTROFIILSED ÜHINEMISREAKTSIOONID. KARBOKATIOONSE INTERMEDIAADI REAKTSIOONID

On esitatud ülevaade reaktsiooniproduktidest alkeenide elektrofiilse ühinemise, katioonse telomerisatsiooni ja polümerisatsiooni protsessides ning toodud üldskeem katioonse tsentri reaktsioonidest nukleofiilidega. Konkureerivad reaktsioonisuunad on määratud põhiliselt alkeeni keemilise ehitusega, kusjuures regulaarsete ja kõrvalproduktide suhteline sisaldus sõltub nukleofiilse reagendi omadustest. Lähemalt on käsitletud reaktsiooniahela ülekande protsesse.

Эльви МУКС

СОПОСТАВЛЕНИЕ РЕАКЦИЙ ЭЛЕКТРОФИЛЬНОГО ПРИСОЕДИНЕНИЯ. РЕАКЦИИ КАРБОКАТИОННОГО ИНТЕРМЕДИАТА

Приведен обзор литературных данных по продуктам реакции электрофильного присоединения к алкенам, по их катионной теломеризации и полимеризации. Представлена общая схема взаимодействий катионного центра с нуклеофилами. Конкурирующие направления реакций катионного интермедиата определяются, в основном, химическим строением алкена, соотношение же регулярных и побочных продуктов реакции зависит от химической природы нуклеофильного реагента. Обсуждены процессы переноса реакционной цепи.