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Elvi MUKS

SYSTEMATIZATION OF INTRAMOLECULAR INTERACTIONS IN CATIONIC REACTIONS

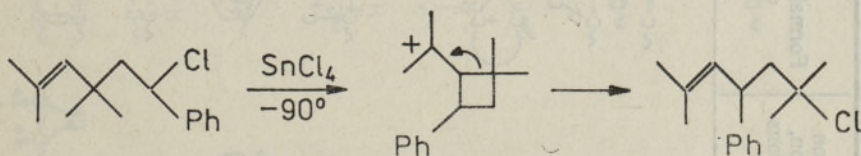
(Presented by K. Lääts)

In a previous review [1] competing paths of intermolecular interactions of the carbocationic intermediate with π -, n - and σ -donors such as $>C=C<$, ArH, ROH, RHIg, R_3CH , etc., were discussed. The present review systemizes intramolecular interactions of the carbocationic centre with the above atoms or groups.

The neighbouring group participation stabilizing the cationic intermediate is revealed by the higher reaction rate and in many cases by the formation of isomeric products. The nature of an intramolecular interaction depends on the distance of the donor group to the cationic centre. Intramolecular interactions are systematically presented in the Table.

As the intermediate with delocalization (column II) corresponds to both isomeric molecules (columns I and III in the table), inverse isomerization may also take place. In principle, the formation of isomers is formally reversible. The result of a given reaction depends on electron and steric factors which determine the partial charge and availability of the cationic centre by interaction with a nucleophile.

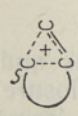
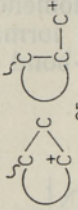
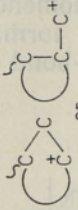

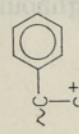
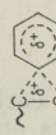
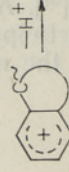
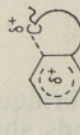
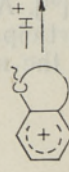
The intramolecular reaction of the cationic centre with a π - or n -donor may lead to cycloproducts [10]. On the other hand, cyclic oxonium cations are the active species in numerous ring opening processes, for example, polymerization of cyclic ethers, cyclic acetals, oxiranes, etc., in the presence of acidic catalysts [31]. A complex phenomenon of 1,3-alkenyl migration is explained by π -participation with the formation of a cyclobutylcarbiny cation followed by the neighbouring σ -bond opening [32]:



The formation of bridged carbocations and corresponding isomeric products due to σ -bonds shifts and the closure or opening of cyclic structures is characteristic for cyclopropane derivatives and complex polycyclic compounds (derivatives of camphene, norbornene cholesterol, α - and β -pinene, etc.) [2, 8, 9, 33, 34].

While 1,2-shifts of atoms or groups are well-known, only a few cases of carbocationic rearrangement due to 1,3-, 1,4-, 1,5- or 1,6-migration of hydrogen [9, 28–30] or halogen [7, 22, 23, 35] atoms over bridged intermediates are observed for the compounds meeting certain electronic and steric requirements. Possibilities of 1,6- (1,5-) alkyl shift still need the elucidation.

Neighbouring group participation in cationic reactions

Carbocation formally formed (n=3,4,1,2,5...)	Stabilization (conjugation, bridged cations [2-9])	Formally isomeric cation	Isomeric products	Notes
$\overset{+}{\sim}C-C=C$	$\overset{\delta+}{\sim}C=C=C$	$\sim C=C-C^+$	Multiple bond shift (allylic isomers)	Triple bond participation gives propargylic isomers or derivatives of cyclopentene, cyclohexene, etc. [10, 12]
$\overset{+}{\sim}C-C-C=C$	$\overset{\delta+}{\sim}C-C=C$	$\overset{+}{\sim}C-C-C$	Cyclopropane ring formation (including poly-cyclic cations) [2, 3, 8, 9]	
$\overset{+}{\sim}C(C)_n-C=C$		 or 	Derivatives of cyclopentane, cyclohexane, etc. [10, 11]	
$\overset{+}{\sim}C$ (with phenyl ring)			1,2-Phenyl shift [2, 3, 8, 9, 13, 14]	Analogous participation of different aromatic groups
$\overset{+}{\sim}C$ (with benzene ring)			Derivatives of indane, tetrahydronaphthalene, etc. [10, 15, 16]	
$\overset{+}{\sim}C(C)_n$ (with phenyl ring)			Carbonyl compounds [11, 13]	R=H, Alk, Ph, Ac. Analogous participation of O-, N- and S-containing groups [20, 21]
$\overset{+}{\sim}C-OR$	$\overset{\delta+}{\sim}C=OR$	$\overset{+}{\sim}C=OR \xrightarrow{-H^+}$	Cyclic ethers, lactones, etc. [3, 10, 17-19]	
$\overset{+}{\sim}C(C)_n-OR$	$\overset{\delta+}{\sim}C-OR$	$\overset{+}{\sim}C-OR \xrightarrow{-R^+}$		

Halogen atom as *n*-donor [7]

Halogen atom as *n*, σ -donor

Few cases if the cation formed is unstable

Contribution of α -substituents: R=Alk, Ph, Hlg

Contribution of β -electron-donor substituents: R'=Alk, Ph, OH

Contribution of γ -donor substituents: R''=OH, NR₂, R₃

$\sim\overset{\delta+}{\text{C}}-\text{Hlg}$	$\sim\overset{\delta+}{\text{C}}=\overset{\delta+}{\text{C}}-\text{Hlg}$	$\sim\overset{\delta+}{\text{C}}-\overset{\delta+}{\text{C}}-\text{Hlg}$	$\sim\overset{\delta+}{\text{C}}-\overset{\delta+}{\text{C}}-\text{Hlg}$	$\sim\overset{\delta+}{\text{C}}-\overset{\delta+}{\text{C}}-\text{Hlg}$	1,2-Halogen shift [7]	Halogen atom as <i>n</i> -donor [7]
$\sim\overset{\delta+}{\text{C}}(\text{C})_n-\text{Hlg}$	$\sim\overset{\delta+}{\text{C}}(\text{C})_n-\text{Hlg}$	$\sim\overset{\delta+}{\text{C}}-\overset{\delta+}{\text{C}}-\text{Hlg}$	$\sim\overset{\delta+}{\text{C}}-\overset{\delta+}{\text{C}}-\text{Hlg}$	$\sim\overset{\delta+}{\text{C}}-\overset{\delta+}{\text{C}}-\text{Hlg}$	1,4-(1,5)Halogen shift [7, 22, 23]	Few cases if the cation formed is unstable
$\sim\overset{\delta+}{\text{C}}-\overset{\delta+}{\text{C}}-\text{H}$	a) $\sim\overset{\delta+}{\text{C}}\text{R}=\overset{\delta+}{\text{C}}-\text{H}$	b) $\sim\overset{\delta+}{\text{C}}-\overset{\delta+}{\text{C}}\text{R}'-\text{H}$	a) $\sim\overset{\delta+}{\text{C}}-\overset{\delta+}{\text{C}}\text{R}'-\text{H}$	$\sim\text{C}=\text{C} + \text{H}^+$	Deprotonation by nucleophile [1, 24]	Contribution of α -substituents: R=Alk, Ph, Hlg
$\sim\overset{\delta+}{\text{C}}-\text{C}-\text{R}$	a) $\sim\overset{\delta+}{\text{C}}-\overset{\delta+}{\text{C}}\text{R}'-\text{R}$	b) $\sim\overset{\delta+}{\text{C}}-\overset{\delta+}{\text{C}}\text{R}'-\text{H}$	$\sim\overset{\delta+}{\text{C}}-\overset{\delta+}{\text{C}}\text{R}'$	$\sim\overset{\delta+}{\text{C}}-\overset{\delta+}{\text{C}}\text{R}'$	1,2-Hydride shift [2, 9, 13, 24]	Contribution of β -electron-donor substituents: R'=Alk, Ph, OH
$\sim\overset{\delta+}{\text{C}}-\text{C}-\text{SiR}_3$	b) $\sim\overset{\delta+}{\text{C}}=\overset{\delta+}{\text{C}}-\text{R}^3\text{C}$	$\sim\overset{\delta+}{\text{C}}-\overset{\delta+}{\text{C}}\text{R}'$	$\sim\overset{\delta+}{\text{C}}-\overset{\delta+}{\text{C}}\text{R}'$	$\sim\text{C}=\text{C} + \text{R}^3\text{C}^+$	1,2-Alkyl shift [2, 9, 13, 24]	
$\sim\overset{\delta+}{\text{C}}(\text{C})_n-\text{H}$	$\sim\overset{\delta+}{\text{C}}=\overset{\delta+}{\text{C}}-\text{R}_3\text{Si}$	$\sim\overset{\delta+}{\text{C}}-\overset{\delta+}{\text{C}}-\text{H}$	$\sim\text{C}=\text{C} + \text{R}_3\text{Si}^+$	$\sim\text{C}=\text{C} + \text{R}^3\text{C}^+$	Fragmentation [2, 9]	Contribution of γ -donor substituents: R''=OH, NR ₂ , R ₃
					β -Silyl effect [25-27]	
					1,3-, 1,4-, 1,5- or 1,6-Hydride shift [9, 28-30]	Few special cases

The effect of π - or n -participation on the rate and isomeric product composition is more significant than that of σ -participation. The lower the degree of stabilization (the greater the electron demand) of the initial cation formed, the more significant the neighbouring group contribution [5, 7, 9].

The Table reveals a similarity between the interactions of the cationic centre with β -hydrogen atoms or β -alkyl groups. The electron-donating ability of C—H bonds, known as hyperconjugation, may result in the β -proton elimination by a nucleophile. In the case of the β -alkyl group with donating substituent(s) the hyperconjugative effect of β, γ C—C bond, known as frangomeric effect, may also result in the β -group elimination (fragmentation). As the β -proton elimination is supported by α -substituents (Alk, Ph, Cl . . .) [1, 24], it may be assumed that these α -substituents contribute also to β -fragmentation.

The stereo-electronic substituent effects in the carbocation formation may be divided into steric, inductive and nucleophilic participation. The above systematization (the Table) of internal nucleophilic participation effects (conjugation, hyperconjugation, anchimeric assistance) may contribute to the orientation in this particular field.

REFERENCES

1. Muks, E. Comparison of electrophilic addition reactions. Reactions of the carbocationic intermediate // Proc. Estonian Acad. Sci. Chem., 1990, 39, N 2, 94—102.
2. Берел Д., Голд В. Карбониевые ионы. М., 1970.
3. Harishorn, S. R. Aliphatic nucleophilic substitution. Cambridge, 1973.
4. Polla, E., Boršič, S., Sunko, D. E. Secondary deuterium isotope effects in solvolysis of 1-aryl-5-methyl-5-hepten-1-yl chlorides. Comparison of π and n participation mechanisms // J. Org. Chem., 1979, 44, N 23, 4096—4100.
5. Orlović, M., Polla, E., Boršič, S. π -Participation and stereoselectivity. Solvolysis rates of (E)- and (Z)-1-aryl-5-heptenyl chlorides // J. Org. Chem., 1983, 48, Nr. 13, 2278—2280.
6. Kronja, O., Polla, E., Boršič, S. A case of extended π -participation // J. Chem. Soc., Chem. Comm., 1983, N 18, 1044—1945.
7. Modena, G., Scorrano, G. Directing, activating and deactivating effects // The chemistry of the carbon-halogen bond. Part 1. London-New York, 1973.
8. Стори П., Кларк Б. Гомоаллильные и гомоароматические катионы; Ричи Г. Дж. Циклопропилкарбониевые ионы; Ланселот Ч., Крам Д., фон Шлейел П. Фенольные ионы // В кн.: Карбониевые ионы. М. 1976, 54—153; 268—370; 427—577.
9. Марч Дж. Органическая химия. Т. 1—4. М. 1987, 1988.
10. Мукс Э. Сопоставление реакций электрофильного присоединения. Образование циклических продуктов // Изв. АН ЭССР. Хим., 1988, 37, № 2, 100—111.
11. Heilmann, W., Koschinsky, R., Mayr, H. [3+2]- and [5+2]-cycloadditions of the cyclohepta-2,4-dienyl cation // J. Org. Chem., 1987, 52, N 10, 1989—1993.
12. Rizzo, C. J., Dunlap, N. K., Smith, A. B. A convenient preparation of 4- and 5-substituted cyclopentenons // J. Org. Chem., 1987, 52, N 23, 5280—5283.
13. Вьюнов К. А., Гунак А. И. Механизм электрофильного присоединения галогенов к кратной связи // Успехи химии, 1981, 50, № 2, 273—295.
14. Vittinghoff, K., Griesbaum, K. A 1,2-phenyl shift to the double bond of a vinyl cation // Tetrahedron Lett., 1981, 22, N 20, 1899—1890.
15. Martens, H., Hornaert, G. Stereochemistry of polar additions to acetylenes // Tetrahedron Lett., 1970, N 21, 1821—1824.
16. Erhard, H., Klaus, H., Mayr, H. Preparation of indans // Ger. Offen DE 3626227 (1988); Chem. Abs., 1988, 108, 167129.
17. Reitz, A. B., Nortey, S. O., Maryanoff, B. E. Stereoselectivity of electrophile-promoted cyclizations // J. Org. Chem., 1987, 52, N 19, 4191—4202.
18. Garbers, C. F., Buekes, M. S., Ehlers, C., McKenzie, M. J. Electrophilic addition reactions in terpenoid synthesis // Tetrahedron Lett., 1978, N 1, 77—80.
19. Chamberlin, A. R., Mulholland, R. L., Kahn, S. D. Modeling chemical reactivity // J. Amer. Chem. Soc., 1987, 109, N 3, 672—677.
20. Ренгевич Е. Н., Станинец В. И., Шилов Е. А. К вопросу о значении циклических переходных комплексов в механизме органических реакций // Докл. АН СССР, 1962, 146, № 1, 111—114.

21. Bland, J. M., Stammer, C. H. An intramolecular bromonium to thiiranium ion rearrangement // *J. Org. Chem.*, 1983, 48, N 23, 4393—4394.
22. Olah, G. A. Halonium ions. New York, 1975.
23. Bienvenüe-Goetz, E., Dubois, J. E., Pearson, D. W., Willams, D. Participation by neighbouring groups in addition reactions // *J. Chem. Soc. (B)*, 1970, N 7, 1275—1278.
24. Мукс Э. Сопоставление реакций электрофильного присоединения. Конкурирующие направления, определяемые строением алкена // *Изв. АН ЭССР. Хим.*, 1987, 36, № 2, 103—113.
25. Mayr, H., Pock, R. Electrophilic attack at allylsilanes: a quantitative determination of the β -silyl effect // *Tetrahedron*, 1986, 42, N 4211—4214.
26. Hayashi, T., Konishi, M., Ito, H., Kumada, M. Optically active allylsilanes // *J. Amer. Chem. Soc.*, 1982, 104, N 18, 4962—4963.
27. Kahn, S. D., Pau, C. F., Clamberlin, A. R., Hehre, W. J. Modeling chemical reactivity // *J. Amer. Chem. Soc.*, 1987, 109, N 3, 650—663.
28. Okazawa, N. E., Sorensen, T. S. Solution carbocation stabilities measured by internal competition for hydride ion // *Can. J. Chem.* 1982, 60, N 17, 2180—2193.
29. Saba, J. A., Fry, J. L. Carbocationic rearrangements originating from the 2-tert-butyl-2-adamantyl system // *J. Amer. Chem. Soc.* 1983, 105, N 3, 533—537.
30. Proudfoot, J. R., Djerassi, C. Stereochemical effects in cyclopropane ring openings // *J. Amer. Chem. Soc.* 1984, 106, N 19, 5613—5622.
31. Penczek, S., Kubisa, P. Structures and reactivities in the ring opening and vinyl cationic polymerization; Jedlinski, Z. J. The cationic ring opening polymerization and copolymerization of some heterocyclic monomers // *Cationic polymerization and related processes*. London 1984, 139—154; 181—187.
32. Bäuml, E., Kolberg, C., Mayr, H. A carbocationic 1,3-alkenyl shift // *Tetrahedron Lett.* 1987, 28, N 4, 387—390.
33. Pock, R., Klein, H., Mayr, H. Electrophile Alkylierung von Norbornen // *Chem. Ber.* 1986, 119, N 3, 929—942.
34. Лысенков В. И., Ударов Б. Г., Пехк Т. И. Изучение состава гидрохлоридов — продуктов взаимодействия α -пинена с хлористым водородом // *Вестн АН БССР, сер. хим. наук*, 1985, № 4, 62—66.
35. Toman, L., Pokorny, S. Cationic polymerization initiated with system 2,5-dichloro-2,5-dimethylhexane- BCl_3 // *J. Polym. Sci., Polym. Chem.* 1989, 27, N 7, 2217—2238.

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INTRAMOLEKULAARSETE PROTSESSIDE SÜSTEMATISEERIMINE KATIOONSETE REAKTSIOONIDE KORRAL

Nukleofiilsete rühmade intramolekulaarne toime intermediaadi stabiliseerimisel ja isomeersetel produktidel moodustumisel on süstematiseeritud olenevalt asendusrühma iseloomust ja tema kaugusest katioonsest tsentrist.

Эльви МУКС

СИСТЕМАТИЗАЦИЯ ВНУТРИМОЛЕКУЛЯРНЫХ ВЗАИМОДЕЙСТВИЙ ПРИ КАТИОННЫХ РЕАКЦИЯХ

Систематизированы эффекты участия соседней электронодонорной группы при стабилизации интермедиата или при образовании изомерных продуктов в зависимости от химического характера этой группы и от ее удаленности от катионного центра.