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Ion-Pair Version of the Chemo- and Regioselectivity of Halogen Addition to Double Bond

A. A. Gevorkyan, A. S. Arakelyan, and K. A. Petrosyan

Institute of Organic Chemistry, National Academy of Armenia, Erevan, Russia

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Abstract — Analysis of the stereoselectivity of halogenation of alkenes shows that the notion of the reaction intermediate as a three-membered halogenium state is contrary to fact. It is assumed that the precursors of the halogenation products are the ion pairs formed by step heterolysis of the C=C bond. This allows a logical connection to be revealed between the electronic properties of substituents in substrates and reagents, on the one hand, and the overall stereoselectivity and direction of halogenation, on the other.

Halogenation of alkenes is widely used in organic chemistry [1]. However, the driving forces of the chemo- and stereoselectivity of this reaction are still not revealed conclusively, and their theoretical interpretation is controversial [2–13]. For instance, it is commonly accepted [2] that the additive *anti* addition of halogens at the alkene double bond involves immediate formation of a halogenonium ion from the carbocationoid species resulting from electrophilic halogen addition, which sterically blocks the site of frontal attack of an anionic halogen fragment [3–13]. For this reason, the reaction is completed by nucleophilic attack of the anionic halogen fragment from the back side of the halogenonium ion, yielding the *anti*-addition product.

All the properties assigned to the cationoid state (assumingly, an ion pair), as well as the evidence invoked for substantation of this version, are inconsistent either with experimental data or with some basic principles of organic chemistry. For instance, it is unreasonable to suppose [2–13] that the nucleophilic attack of the anionic halogen fragment can cause halogenonium bond cleavage, since the intermediate species possesses electrophilic properties, and its reaction with nucleophiles should be governed exclusively by the rules of electrophilic substitution. It is also unreasonable to suppose that the formation of a halogenonium ion from 2,3-dibromo-2,3-dimethylbutane is a superacid medium is evidence in favor of the intermediate formation of a species detected in alkene halogenations [10], because carbocationoid species **II**–**IV** formed on halogenation of alkenes **I** have different structure and properties [Scheme (1)]. For instance, the most electrophilic of these species (ion pairs **III** and **IV**) would more readily attack the counterion of the electrophilic fragment of the halogen molecule (type *3* interactions in transition states **III** and **IV**) rather than a still electrophilic halogen atom [this interaction is not shown in Scheme (1)] of the newly formed C–halogen bond. But, what is most important, one can hardly explain in terms of this version why the relative contributions of the *syn* and *anti* additions vary with varied medium polarity and electronic properties of subatituents [1–13] in substrate and reagent, etc. Therefore, it is more probable that the approach accepted in organic chemistry [2] remains actual, since there is no more substantiated and plausible concept of the driving force of the stereoselectivity of such reactions. One faces analogous problems when determining the driving forces of "substitutive" halogenation of alkenes [1, 3–10].

In this connection we considered it interesting to find out (1) whether the problem is clarified when considered in terms of the ion-pair concept [14–17] proposed for elimination; (2) whether the regiochemistry of substitutive halogenation and the stereoselectivity of additive halogenation are associated with the fact that the precursors of products of these reactions are ion pairs of the same types, each, as in elimination [14–22], exhibiting specific reactivity with respect to nucleophiles: in conditions favoring formation of contact ion pair **II**, a *syn*-nucleophilically controlled reactivity (interaction *2*), while in conditions favoring formation of loose and solvent-separated ion pairs **III** and **IV**, respectively *syn*- and *anti*-electrophilically controlled (interactions *1* and *3–6*).

We found that some regularity corresponding to the above-mentioned general principles of donor–acceptor interaction can be revealed [1–13, 23–30] under two assumptions: (1) the double bond of molecule **I** [scheme (1)] is considered as an electro-

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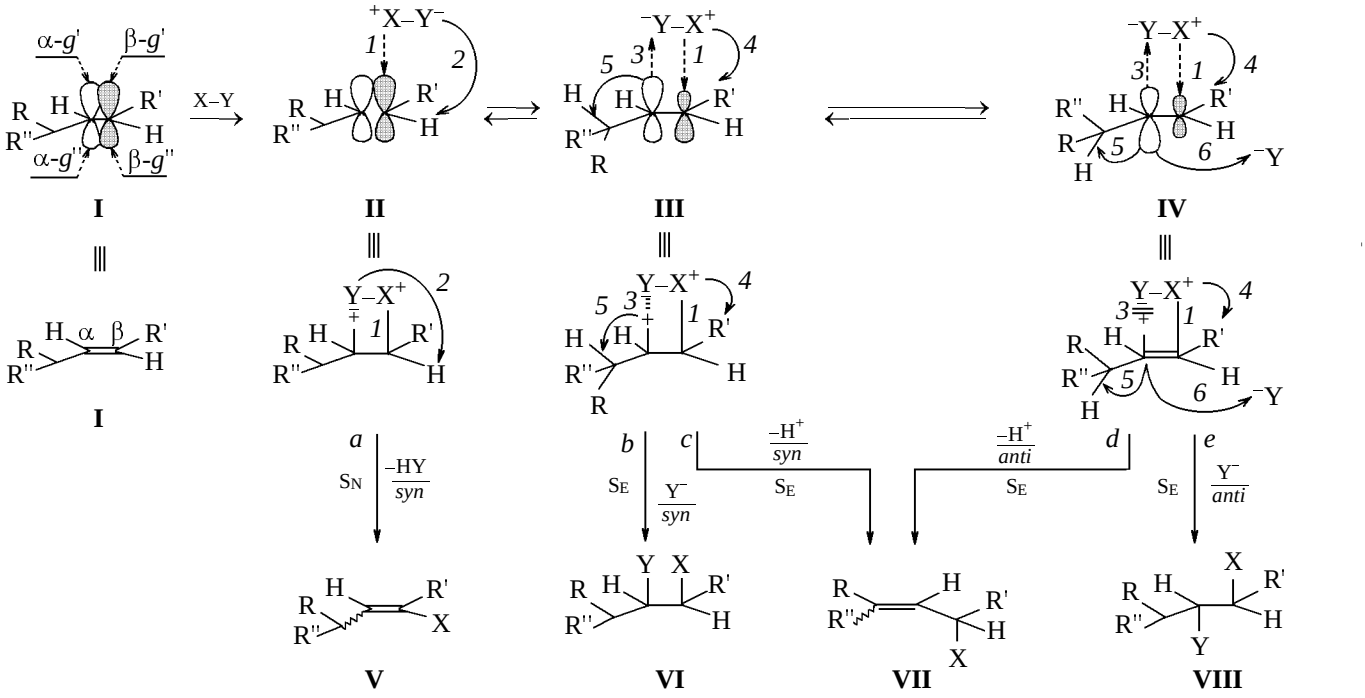
Scheme 1.



fuge–nucleofuge system in which the role of electrofuge belongs to the carbon atom of the RR"CH group, of nucleofuge, the carbon atom of the R'CH group (RR"CH ranks below CHR' in electron-donor acceptor power), of "outgoing electron pair," *p* electrons of the π bond; and (2) electrons of the π bond are involved in reaction stepwise rather than simultaneously: first electrons of one π-bond dumpbell, and then of the other.

For understanding the proposed approach and for convenience, we label the electrofugal and nucleofugal fragments of the reagent, as well as formally electron-donor and formally electron-acceptor orbitals of the substrate in different ways: the electrophilic and electron-donor fragments of the reagent are labeled X and Y, respectively, electron-donor orbitals (i.e. the β-*g*' and β-*g*" dumpbells) of the substrate are shaded, and electrophilic orbitals of the substrate (i.e. the α-*g*' and α-*g*" dumpbells) are unshaded. Take into account that the halogen operates both as the catalyst and the reagent that effects heterolysis of this nonclassical bond C–nucleofuge. Some problems may arise in choosing the stereotopical side of electrophilic attack. However, these problems can be rather easily went around in view of some quantum-chemical results [31, 32] and the results of our independent analysis of the experimental data on the stereochemistry of addition of a series of electrophiles by C=C and C=O bonds. The most important conclusion following from the above quantum-chemical calculations and analysis is that, contrary to commonly accepted views [1, 3–13, 33], there is an asymmetric electron density distribution by the stereotopic sides of the double bond, which controls direction of electrophilic attack. We could find the rule of establishing the stereotopic side of the highest electron density of the substrate, and, consequently, the site of electrophilic attack; this question will be discussed elsewhere.

The reaction begins with halogen attack (interaction *1*) on electrons of that of the two electron-donor π-bond dumpbells (β-*g*' or β-*g*"), which bears the highest electron density (in the scheme, this is the β-*g*' dumpbell). Totally, however, the electron transfer from the double bond of the electrofuge to the nucleofuge (i.e. "heterolysis") and further to an electrophilic halogen atom, by analogy with compounds with a classical C–nucleofuge bond, occurs in three stages (conversions **I** → **II**, **II** → **III**, and **III** → **IV**). Let us consider each of these stages.

The first involves orgination of transition state **II** (contact ion pair). The latter arises when reagent reaction is initiated (i.e. electrophilic act *1* of atom X of halogen molecule X–Y), and, at first, orbitals of the

substate π-bond are slightly stretched (conversion **I** → **II**), which corresponds to the origination of a contact ion pair in a molecule having a classical C–nucleofuge bond. In this reaction stage, i.e. as electrons of the double bond come under the influence of electrophile X, counterion Y, like the nucleofuge in a classical C–nucleofuge bond [1, 3, 4, 6, 9, 10], gradually acquires an anionic character and ability to attack acidic centers of the complex (here the hydrogen atom of the R'CH group (interaction *2*)]. If this hydrogen atom can be accepted, the C–H bond is deprotonated, its electron pair gets free, and halo–alkene **VI** of the vinyl structure is formed by the nucleophilically controlled *syn*-substitution scheme (conversion path *a*).

The second and third stages of C=C heterolysis (conversions **II** → **III** and **III** → **IV**) take place at such reaction conditions and molecular structure (according to [14–17], these conditions do not differ from usual [1, 3, 4, 6, 9, 10]) that the electron transfer from the double bond to electrophile X (fragment of the C–X bond to be formed) is not discontinued in the stretching stage (conversion **I** → **II**). Thus, effective C–X bond origination is initiated, i.e. the *p*-electron cloud of the double bond is really submitted to electrophile X. This process which, as noted above, involves two stages, can be adequately described on the assumption that first the reaction involves electrons of one dumpbell (β-*g*') of the electron-donor orbital (conversion **II** → **III**), and the second dumpbell (β-*g*'') is involved later (conversion **III** → **IV**). Let us illustrate this version by *E*-alkenes **I** and represent variations in the electron density on the *p*-orbital dumpbells by varied area of each of them. Obviously, the charge density on the dumpbells varies in this way as an electrophilic halogen atom reacts with the electron-donor dumpbell β-*g*' (interaction *1*) and the electron deficiency on the α-*g*' dumpbell of substrate **I** and transition states **II**–**IV**. If the proposed version adequately describes the mechanism of reaction of halogens (generally, electrophiles) with alkenes, then it is reasonable to suggest that the electrophilic attack on electrons of the β-*g*' dumpbell (interaction *1*) will unbalance the equilibrium charge density in substrate **I** (α-*g*' = β-*g*' and α-*g*'' = β-*g*''). As a result, first some excess electrophilicity on dumpbell **II**-α-*g*' will arise (where already α-*g*' > β-*g*') and then the stage of counterbalancing the newly induced charge by the electron-donor centers of adjacent groups and the environment (interactions *3* and *5*). Thus, there arise and become prevailing reactions of dumpbell **III**-α-*g*', i.e. of electrophilic centers with the reagent counterion (interaction *3* with Y) with substituent R' (interaction *4*) and group RR''CH (not shown in the scheme), including electrons of the C–H bond (interaction *5*), from the frontal side of the β-C–X bond formed. If the electrophilic power of interaction *3* with counterion Y proves sufficient to cleave the X–Y bond in transition state **III**, then anion Y is pulled over and *syn* adduct **VI** is formed by the frontal electrophilically controlled SE mechanism (conversion path *b*). If this power is insufficient or the X–Y bond in complex **III** is sufficiently strong for the proposed cleavage to occur, the complex can be stabilized in two ways. One of them involves fragmentation and formation of the parent molecule (reverse conversion **III** → **II** → **I**), and the other, reaction development. Depending on the structure of molecule **I** and the nature of the reagent, the reaction can be developed in many ways. One of them involves electrophilic *syn* deprotonation (interaction *5*) and formation of allylic alkene **VII** [one more type of "substitutive" (allylic) halogenation product (path *b*)], and the other involves reaction with electrons of the "reserve" β-*g*'' dumpbell (conversion **III** → **IV**). In the latter case, the deficiency of electrons will also arise on dumpbell **IV**-α-*g*'' (i.e. the equality α-*g*'' = β-*g*'' characteristic of state **III** is disturbed and the inequality α-*g*'' > β-*g*'' characteristic of state **IV** is established) which is in the antifrontal position to the C–X bond to be formed. Dumpbell **IV**-α-*g*'' differs from the frontal dumpbell **III**-α-*g*' in that the former lacks the neighboring-group effect (interaction *3* with the counterion of the X–Y bond in transition state **III**) capable of reducing its electrophilicity. Therefore, dumpbell **IVa**-α-*g*'' is slightly more electrophilic than dumpbell **III**-α-*g*'. For this reason, its reaction with the nucleophile, even if it is intermolecular, occurs easier and gives rise to an *anti*-addition product **VI** (conversion path *d*). And, finally, interaction *5* which apparently gives rise to stereisomer **VII** via substitutive halogenation by path *e*. In other words, this version assumes that the reagent and substrate form a complex in which one of its fragments plays the role of a new reagent and the other, of a new substrate.

The proposed view of the mechanism of halogen addition is fully consistent with published data [1–13, 32] and our data for additive halogen addition (see table). For instance, as follows from the table, the contribution of *anti* addition by the double bond increases with increasing halogen–halogen bond energy, i.e. in the series $F_2 < Cl_2 < Br_2$. For the same reason, the contribution of *anti* chlorination of methylstyrene is 54% [30], while the contribution of its *anti* chlorohydroxylation with hypochlorous acid is 63% [34]; the reaction of deuterostyrene with iodine azide yields an *anti* addition product, while with bromine azide, a mixture of stereoisomeric adducts [35], etc.

Stereoselectivity of halogenation of certain alkenes

No.	Substrate	Halogen	Addition, %		Reference
			syn	*anti*	
1	*cis*-MeCH=CHMe	Br_2	0[a]	100	[24]
2	*trans*-MeCH=CHMe	Br_2	0[a]	100	[24]
3	*cis*-$Me_3CCH=CHCMe_3$	Cl_2	0[a]	100	[25, 26]
4	*trans*-$Me_3CCH=CHCMe_3$	Cl_2	0[b]	100	[25, 26]
5	*trans*-PhCH=CHMe	Cl_2	28–29	55–56	[26, 27]
			46	54	
6	*trans*-PhCH=CHMe	F_2	73	27	[28]
7	*cis*-PhCH=CHMe	Cl_2	21–23	62–63	[27, 29]
			62	38	
8	*cis*-PhCH=CHMe	F_2	78	22	[28]
9	*trans*-PhCH=CHMe	Br_2	12	88	[29]
10	*trans*-4-$MeOC_6H_4CH=CHMe$	Br_2	37	63	[29]
11	*trans*-PhCMe=CHMe	Br_2	63	37	[29]
12	*cis*-PhCMe=CHMe	Br_2	86	14	[29]

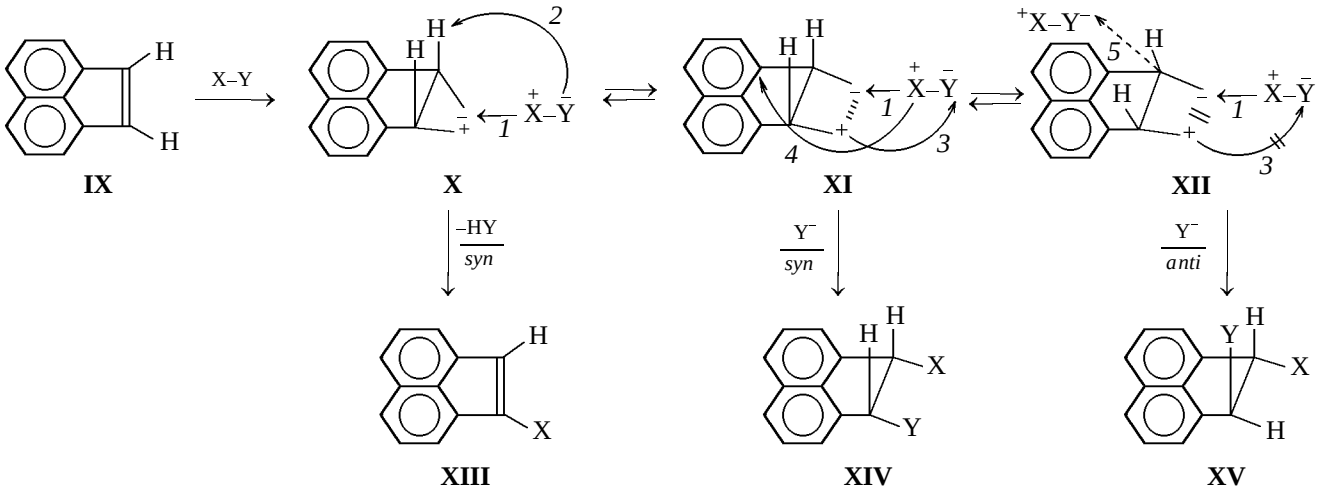
[a] According to [10], this ratio is lower than 1 : 100. [b] Together with 40% of $Me_3CHClCHMeCMe=CH_2$.

Together the above data lead us to conclude that the stereochemistry of addition of halogens and related compounds is controlled by the bond energy of the counterions of the reagent (bond X–Y in transition complexes **III** and **IV**). While this conclusion cannot be considered new (see, for instance, [8]), the proposed "addressing assignment" of electrophilicity and nucleophilicity to the reaction centers of the reagent and substrate imparts to this generalization a greater predictive power. For instance, it follows from this fact that the lower the ionicity of the X–Y bond (i.e. the lower the X–Y bond energy), the higher the probability of *syn* addition. That is why in the complexes formed by alkenes with boron hydrides (the ionicity of the B–H bond is lower than 0.2), *syn*-addition products are formed [36], whereas in the complexes formed by alkenes with mercury alkoxyacetates (the ionicity of the Hg–O bond is higher than 1.4), *anti*-addition products (to cyclohexene but not to norbornene that forms a *syn* adduct) [37, 38], etc. This version is also consistent with known effects of substituents at the C=C bond on the stereoselectivity of halogen addition (see table). Thus, according to these data, dialkylethenes (see table, entry nos. 1–4) [24–27] almost exclusively react by way of *anti* addition, whereas alkylarylethenes (see table, entry nos. 5–12) yield both *anti* and *syn* addition.

This is apparently explained by the fact that an electron-donor substituent (α-alkyl group) in the alkene favors electron density transfer from the α- to β-carbon atom of the double bond and its further transfer to the electrophilic atom X added to the β-carbon atom with subsequent formation of a transition state (solvent-separated ion pair) and its stabilization products. Unlike alkyl, aryl substituents exert their assistance (hidden α-effect [18]) only in the initial stage of C–X bond formation [transition state **II** (contact ion pair)]. Further, when the stage of effective electron density transfer from the C=C bond to the halogen atom (see above) is initiated, aryl groups unfavor (because of their electron-acceptor nature) involvement in reaction of the second β-orbital dumpbell. This retards (while not completely) "heterolysis" of the double bond (see table, entry nos. 5–12) in the stage of origination of loose ion pair **III**, resulting in *syn* addition. Quite expected is also the stereoselectivity difference between β-methylstyrene and its *p*-methoxy derivative (see table, entry nos. 9 and 10): the latter, being better stabilized in acid medium (by forming an oxonium ion), more effectively retards heterolysis and gives more *syn*-addition product (37 against 12%) than β-methylstyrene (see table, entry no. 9).

In terms of the proposed version, one can reasonably explain the effect of solvent polarity on the *syn/anti*-halogenation ratio, specifically increasing fraction of the *syn* adduct with increasing solvent polarity. Obviously, this regularity might be observed if polar solvents favor stretching of the X–Y bond in transition complexes **II**–**IV** rather than of *p*-orbitals of the C=C bond in the latter. This is explainable, since, as shown above, the stereoselectivity of halogenation

Scheme 2.



Here and in Scheme (1), interaction *2* is nucleophilic and interactions *1, 3, 4,* and *5* are electrophilic.

becomes to be controlled by the energetic characteristics of the electrofuge–nucleofuge bond in the reagent. For this reason, for instance, in the low-polarity ethylene chloride *cis*-stylbene gives primarily an *anti*-bromination product (up do 80%), whereas in nitrobenzene (ε ~35) the contribution of *syn* bromination increases sharply, attaining 70% and more [39–41]. The same situation is observed in brominations of 2-butene and β-methylstyrene [26, 41]. For instance, the *anti/syn* ratios for *cis*-β-methylstyrene in methylene chloride and nitrobenzene are 70 : 30 and 45 : 55, respectively [41].

The expected regularity is revealed when comparing the *syn/anti*-addition ratios for stereoisomeric alkenes: The contribution of *syn* addition (as a rule) proves to be higher for *cis* alkenes compared with *trans* alkenes. Thus, for chlorination of β-methylstyrene this ratio is 62 : 38 against 46 : 54, while for fluorination, 78 : 22 and 73 : 27, respectively (see table, entry nos. 5, 7 and 6, 8). Similar ratios are characteristic of bromination of dimethylstyrenes: 86 : 14 against 63 : 37 (see table, entry nos. 11 and 12). Most probably, the latter result is explained by that the transmission of the effect of nonbonded interaction *4* with substituent R' stronger affects (in our case, favor) C=C heterolysis in the transition state of the *trans* isomer of **I** compared with the *cis* isomer [42]. Therefore, in the *cis* isomers, the equilibrium between ion pairs **III** and **IV** is stronger shifted to the left, thus favoring *syn* addition. For the same reason, in compounds related to stylbene, such as acenaphthylene [40] and phenanthrene [43, 44], in which interactions like *4* can stronger shift the equilibrium to the left [scheme (2)], give mostly *syn*-chlorination and -bromination products [43–45]. This metamorphosis is illustrated by the example of acenaphthylene **IX** in scheme (2).

In other words, such reaction path is explained by that interaction *4* markedly reduces the affinity of the halogenonium center to counterion Y, thus facilitating transfer of the latter to the carbocationoid center by the scheme of frontal interaction *3* and formation of a *cis*-dihalo derivative **XIV** rather than its stereoisomer **XV** whose precursor is solvent-separated ion pair **XII**. Correspondingly, the precursor of monohalide **XIII** is contact ion pair **X**. In molecules **I**, where substituent R' (alkyl group) cannot as effectively compensate for the deficit of electrons as aryl groups origination of state **IV** cannot be prevented, and the halogenation product is an *anti* adduct (see above).

As follows from the aforesaid, the principles of donor–acceptor interaction [14–17], which we established for elimination, also apply to the behavior of the ion-pair states formed by molecules with a "nonclassical" C–nucleofuge bond; the carbocationoid centers which are likely to be formed by halogen reactions with alkenes exhibit the same regio- and stereoselectivity as the previously described three types of ion pairs. Consequently, like in elimination reactions, if the observed regio- or stereochemistry of halogenation unfit the above-descrived regularities, one may suspect that the regio- and stereoselectivity are determined with some mistakes or that there is some other

steric manifestation of the electron-donor capacity of the C=C bond or another type of donor–acceptor interaction than those characteristic of model molecules in comparable experimental conditions.

REFERENCES

1. March, J., *Advanced Organic Chemistry*, New York: Wiley, 1994.
2. Roberts, I. and Kimball, G.E., *J. Am. Chem. Soc.*, 1937, vol. 59, no. 5, pp. 947–948.
3. Ingold, C.K., *Structure and Mechanism in Organic Chemistry*, Ithaca: Cornell Univ., 1969, 2nd ed.
4. Becker, H., *Einführung in die Elektronentheorie organisch–chemischer Reaktionen*, Berlin: Wissenschaften, 1974, 3rd ed.
5. Freidlina, R.Kh., Velichko, F.K., Chukovskaya, E.Ts., Khorlina, M.Ya., Krentsel', B.A., Il'ina, D.E., Kruglova, N.V., Mayants, L.S., and Gasanov, R.G., *Metody elementoorganicheskoi khimii. Khlor. Alifaticheskie soedineniya* (Methods of Organoelement Chemistry. Chlorine. Aliphatic Compounds), Moscow: Nauka, 1973.
6. Dneprovskii, A.S. and Temnikova, T.I., *Teoreticheskie osnovy organicheskoi khimii* (Theoretical Fundamentals of Organic Chemistry), Leningrad: Khimiya, 1979.
7. de la Mare, P.B.D., *Electrophilic Halogenation*, Cambridge: Plenum, 1976.
8. de la Mare, P.B.D., and Bolton, R., *Electrophilic Additions to Unsaturated Systems*, Amsterdam: Elsevier, 1966.
9. Lowry, Th.H. and Richardson, S.K., *Mechanism and Theory in Organic Chemistry*, New York: Wiley, 1981, pp. 506–595.
10. Sykes, P., *A Guidbook to Mechanism in Organic Chemistry*, New York: Wiley, 1996.
11. Freeman, F., *Chem. Rev.*, 1975, vol. 75, no. 4, pp. 439–490.
12. Eliel, E.L., Wilen, S.H., and Mander, L.N., *Stereochemistry of Organic Compounds*, New York: Wiley, 1994.
13. Potapov, V.M., *Stereokhimiya* (Stereochemistry), Moscow: Khimiya, 1988.
14. Gevorkyan, A.A., Arakelyan, A.S., Petrosyan, K.A., and Margaryan, A.Kh., *Zh. Obshch. Khim.*, 2001, vol. 71, no. 5, pp. 776–784.
15. Gevorkyan, A.A., Arakelyan, A.A., and Cockerill, A.F., *Tetrahedron*, 1997, vol. 53, no. 23, pp. 7947–7956.
16. Gevorkyan, A.A., Margaryan, A.Kh., and Obosyan, N.G., Abstracts of papers, *Respublikanskaya konferentsiya "Organicheskii sintez"* (Republican Conf. "Organic Synthesis"), Erevan, 1997, p. 21.
17. Gevorkyan, A.A., Arakelyan, A.S., Obosyan, N.G., and Esayan, V.A., *Zh. Org. Khim.*, 1999, vol. 35, no. 2, pp. 315–319.
18. Gevorkyan, A.A. and Sargsyan, M.S., *Zh. Org. Khim.*, 1990, vol. 26, no. 8, pp. 1810–1814.
19. Gevorkyan, A.A., Arakelyan, A.S., and Obosyan, N.G., *Zh. Obshch. Khim.*, 1997, vol. 67, no. 6, pp. 1050–1052.
20. Gevorkyan, A.A., Kazaryan, P.I., Avakyan, S.V., and Simonyan, E.S., *Khim. Geterotsikl. Soedin.*, 1989, no. 3, pp. 309–312.
21. Gevorkyan, A.A., Arakelyan, A.S., and Obosyan, N.G., *Arm. Khim. Zh.*, 1994, vol. 47, nos. 1–3, pp. 152–153.
22. Gevorkyan, A.A., Arakelyan, A.S., Avakyan, O.V., and Obosyan, N.G., *Zh. Org. Khim.*, 1998, vol. 34, no. 2, pp. 315–320.
23. House, H.O., *Modern Synthetic Rections*, New York: Benjamin, 1972, pp. 422–491.
24. Rolston, J.H. and Yates, K., *J. Am. Chem. Soc.*, 1969, vol. 91, no. 6, pp. 1469–1476.
25. Eliel, E.L. and Faber, R.G., *J. Org. Chem.*, 1959, vol. 24, no. 1, pp. 143–151.
26. Fahey, R.C. and Schubert, C., *J. Am. Chem. Soc.*, 1965, vol. 87, no. 22, pp. 5172–5179.
27. Fahey, R.C., *J. Am. Chem. Soc.*, 1966, vol. 88, no. 20, pp. 4681–4684.
28. Merritt, R.F., *J. Am. Chem. Soc.*, 1967, vol. 89, no. 3, pp. 609–612.
29. Fahey, R.C. and Schneider, H.J., *J. Am. Chem. Soc.*, 1968, vol. 90, no. 16, pp. 4429–4434.
30. Fahey, R.C. and Schneider, H.J., *J. Am. Chem. Soc.*, 1965, vol. 87, no. 22, pp. 5172–5179.
31. Royer, J., *Tetrahedron Lett.*, 1978, no. 15, pp. 1343–1346.
32. Paquette, L.A., Larry, W.H., Hertel, R.G., Bohm, M.C., Beno, M.A., and Christoph, G.G., *J. Am. Chem. Soc.*, 1981, vol. 103, no. 24, pp. 7106–7121.
33. *Chemical Reactivity and Reaction Paths*, Klopman, G., Ed., New York: Wiley, 1974.
34. Botot, H., Dieuzeide, E., and Jullien, J., *Bull. Soc. Chim. Fr.*, 1960, no. 6, pp. 1086–1097.
35. Hassner, A., Boerwinrkle, F.P., and Levy, A.B., *J. Am. Chem. Soc.*, 1970, vol. 92, no. 16, pp. 4879–4883.
36. Mikhailov, B.M., *Khimiya borovodorodov* (Chemistry of Boron Hydrides), Moscow: Nauka, 1967.
37. Zefirov, N.S., *Usp. Khim.*, 1965, vol. 34, no. 6, pp. 1272–1292.
38. Reutov, O.A., Beletskaya, I.P., and Sokolov, V.I., *Mekhanizmy reaktsii metalloorganicheskikh soedinenii* (Mechanisms of Reactions of Organometallic

Compounds), Moscow: Khimiya, 1972.

39. Heubein, G., *J. Prakt. Chem.*, 1966, vol. 31, no. 4, pp. 84–91.
40. Bucles, R.E., Bader, J.M., and Thurmajer, R.J., *J. Org. Chem.*, 1962, vol. 27, no. 12, pp. 4523–4527.
41. Yates, K., *J. Am. Chem. Soc.*, 1969, vol. 91, no. 6, pp. 1477–1483.
42. *Chemistry of Alkenes*, Patai, S., Ed., New York: Interscience, 1964. Translated under the title *Khimiya alkenov*, Leningrad: Khimiya, 1969, pp. 409–443.
43. Cristol, S.J., Stermitz, F.R., and Ramay, P.S., *J. Am. Chem. Soc.*, 1956, vol. 78, no. 19, pp. 4939–4941.
44. de la Mare, P.B.D., Klassen, N.V., and Koenigsberger, R., *J. Chem. Soc.*, 1961, no. 12, pp. 5285–5293.
45. de la Mare, P.B.D. and Koenigsberger, R., *J. Chem. Soc.*, 1964, no. 12, pp. 5327–5336.