Tetrahedron Vol 39, No 19, pp 3145 to 3149, 1983
Printed in Great Britain.

0040-4020/83 $3.00 + .00

STEREOCHEMICAL STUDIES—XXIX

STEREOCHEMISTRY OF THE ADDITION OF PHOSPHOROUS TRIBROMIDE TO OLEFINS

NIKOLAI S. ZEFIROV*, NIKOLAI V. ZYK, ANATOLII A. BORISENKO and MIKHAIL YU. KRYSIN
Department of Chemistry, Moscow State University, Moscow 117234, U.S.S.R.

and

TAMARA G. SCHESTAKOVA
Novomoskovsk Branch of Mendeleev Institute of Chemical Technology, Novomoskovsk, Tula Region, U.S.S.R.

(*Received in UK 14 December 1982*)

Abstract—The stereochemical course of PBr_3 addition to a series of cycloolefins has been found to depend crucially on the olefinic structure and the reaction proceeds in highly stereoselective fashion either as *trans*- (cyclohexene) or as *cis*- (norbornene and related compounds) addition without skeletal and homoallylic rearrangements.

The utility of addition reactions of compounds containing P–Hal bond/s to olefins in the preparation of organophosphorous compounds is well recognized.[1-12] Different types of initiation of these addition process were employed including Lewis acids[2] or the typical initiators of free-radical addition such as UV light,[3,7] radiation,[5,6] peroxides[3] and thermal.[7] It is remarkable, that oxygen can also play the role of catalyst to these reactions.[1,7-10] The simple examination of bonds energies[13] indicates that PBr_3 should more easily dissociate into radicals and hence should be better chain-transfer agent, than PCl_3.

In spite of the intensive studies many problems still remain open. First, the major question to be answered concerns the role of the oxygen. Indeed, the PCl_3 additions in presence of O_2 lead to the product/s of oxidative phosphorylation with the incorporation of the O_2 into structure/s of product/s.[1] In the opposite, the additions of the PBr_3 to a double bond follows the simple 1, 2-addition pathway in accordance with eqn (1) *without* incorporation of the O_2.[7-11]

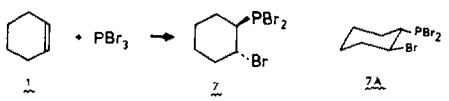
$$PBr_3 + C{=}C \xrightarrow{[O_2]} Br\text{–}C\text{–}C\text{–}PBr_2. \qquad (1)$$

Thus, the "invisible" participation of O_2 in PBr_3 reactions remains obscure and the nature of transition state/s and intermediate/s have yet to be established. Secondly, it is surprising that the stereochemical course of PBr_3 addition to olefins is also unknown[7,8] (for the addition to triple bond see refs. 9–12). The absence of a knowledge of stereochemistry of PBr_3 additions precludes from specification of any possible mechanism. It was of interest, therefore, to investigate more systematically the stereochemistry of PBr_3 addition to a series of cycloolefins, and that was the purpose of present study (preliminary communication see Ref. 14).

RESULTS AND DISCUSSION

The model olefins **1–6** have been chosen to clarify the following problems: (a) the stereochemistry dependence of the PBr_3 addition on the olefin structure and the double bond strain, and (b) evaluation of the "effective electrophilicity"[15] of these reactions *via* possible isolation of the rearranged products, typical for carbocationic-like pathways.

Reaction of PBr_3 *with cyclohexene* (**1**). As reported by Fontal and Goldwhite[7] the PBr_3 addition to cyclohexene initiated by UV or $(t\text{-}BuO)_2$ proceeds non-stereospecifically to give 1:1 mixture of isomers. Later it was shown[8] that this reaction initiated by oxygen proceeds to give a single adduct, which exhibits the peak near 200 ppm in its NMR ^{31}P spectrum. However, its configuration has not been determined. We reproduced these data and also show that PBr_3 addition to 1 with the slow stream of O_2 proceeds to give a single adduct **7** (δ_P = 201 ppm), isolated in 44% yield. However, the absence of another addition products, including oxygenated derivatives has been proven by NMR ^{31}P spectra of the reaction mixtures. If the reaction has been performed without special addition of O_2, but in the usual dry air atmosphere, the only adduct **7** has also been identified with the completion of the addition being substantially lower for the same period.



1 2 7A

Scheme 1.

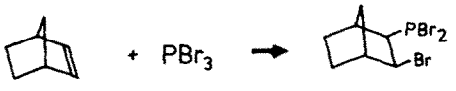
The H–CBr signal in the NMR ^1H spectrum of **7** containing nine lines was simplified into triplet of doublets ($J_1 = J_2 = 10.8$ Hz, $J_3 = 4.4$ Hz) by H–P decoupling ($^3J_{HP} = 3.3$ Hz). The large vicinal coupling constant fits perfectly for the *trans ee*-isomer **7A**. Thus, the PBr_3 reaction with cyclohexene in presence of O_2 is obviously

highly stereoselective since the *trans*-adduct is isolated and there is no indication of the formation of any significant amount of the *cis*-adduct.

In free-radical additions to cyclohexene there is usually a strong preference for both axial attack of a radical on the double bond[17,18] and also axial transfer of the second portion of the addend to the resulting cyclohexyl radical.[17-19] If one assumes as suggested in literature a free-radical chain mechanisms for PBr_3 addition[7,8] the high degree of *trans*-selectivity means that intermediate radical, formed by axial attack of Br · on cyclohexene, must undergo chain transfer rapidly compared with the rate of the conformational ring flip. The stereochemistry of the reaction studied is not unprecedental and is similar to that of the free-radical addition of arenesulfonyl iodides[20] and areneselenosulfonates[18] to cyclohexene.

Reaction of PBr_3 *with norbornene* (**2**). Norbornene is a typical strained olefin which has been widely used for studies of the course of addition processes due to the exceptional characteristics of its reactivity: (a) occurence of Wagner–Meerwein rearrangement for Ad_E additions of the "effectively strong electrophyles",[15a,21] (b) high preference for *exo*-attack on the double bond[22] and (c) increased rate constants in all addition reactions.[23] What is more, addition to the norbornene and related bicyclic olefins often follows a different stereochemical course from that of monocyclic and acyclic olefins.[18,21,22]

We have found that PBr_3 addition to **2** proceeds

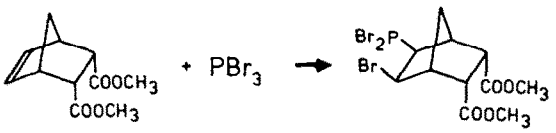


2 Scheme 2. **8**

smoothly in the air atmosphere at 0° to give the adduct **8** (δ_P = 178 ppm) in 70% yield. However, the NMR ^{31}P spectra of the reaction mixtures revealed the formation of the minor by-product ($\delta_P \cong 181$ ppm; ≤4%), which has not been isolated. The DNMR ^1H–{^{31}P} spectrum of **8** includes the multiplets of H–CBr and H–$CPBr_2$ signals with $^3J_{H_2H_1}$ = 7.2 Hz, $^3J_{H_1H_4}$ = 2.1 Hz, and $^3J_{H_1H_2}$ = 1.6 Hz, which clearly evidences the *cis*-configuration of the adduct (we accepted *exo*-configuration in accordance with usually observed stereochemical course). Thus, the addition of PBr_3 to norbornene proceeds (i) without skeletal rearrangement and (ii) in sufficiently selective manner to give *cis*-adduct, which is in contrast with adduct configuration observed for the addition to cyclohexene.

Reaction of PBr_3 *to the diester* **3**. The addition of electrophilic agents to the diester **3**[24] involves the participation of the ester moiety in the final step of the addition to give the corresponding γ-lactones. Few examples of the addition to analogs of **3** exhibited the *cis-exo*-addition to the double bond without the intramolecular cyclization.[25] Hence, the structure of the addition product can shed light on on the basic characteristic of the addition process.

We have found that PBr_3 addition to **3** proceeds to give the single adduct **9** (δ_P = 177 ppm) as a crystal solid in the total yield of 51% (92% calculated on the reacted ester **3**). The NMR ^1H spectrum of **9** contains two multiplets of H–CBr and H–$CPBr_2$ signals with the vicinal coupling constant ^3J = 7.4 Hz. This value of ^3J clearly indicates *exo-cis* configuration. Thus the reaction of PBr_3 with the diester **3** proceeds as *exo-cis*-addition



3 Scheme 3. **9**

without participation of COOR group, which is similar to the addition to norbornene.

Reaction of PBr_3 *with norbornadiene* (**4**). The majority of free-radical additions to norbornadiene (e.g. Refs. 18a, 26, 27) give mainly the product/s with nortricyclenic structures and nortricyclic radical **11** is favored in the equilibrium which includes the interconversion of norbornenyl (**10**) and nortricyclyl (**11**) radicals.[27]

We have found that the reaction of PBr_3 with norbornadiene in 1:1 ratio proceeds to give the mixture with 85% content of the adduct **12**. However, the NMR ^{31}P spectrum reveals the presence of the minor product in 14% yield. Unfortunately, we could not separate these compounds and the structural and stereochemical assignment have been achieved using the mixture of the products. The decoupling ^1H–{^{31}P} study revealed that the major product has the structure **12** which was confirmed by the presence of the signals of olefinic protons as well as of vicinal coupling constant ^3J = 7.2 Hz. Thus, these data confirm that the addition of PBr_3 to **4** proceeds as 1, 2-*exo-cis*-addition to the one double bond without allylic participation of the second double bond. The observation that 1, 2-adduct is the major product evidences that PBr_3 should be an extremely reactive chain-transfer agent such as, for example, arenesulfonyl iodide.[26a]

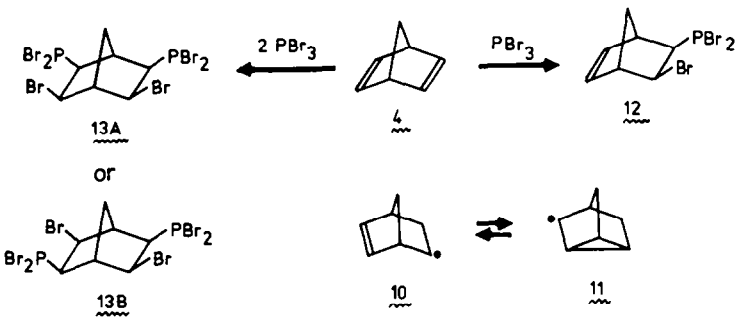
The addition of PBr_3 to **4** in 4:1 ratio proceeds to give diadduct as a crystal solid in the 68% yield. The NMR data (single resonance in NMR ^{31}P at 170 ppm, NMR ^1H: J_{vic} = 7.3 Hz, absence of olefinic protons) support the structure of the diadduct **13**, but do not permit to make choice between the structures **13A** vs **13B**. Thus, the addition of excess of PBr_3 also proceeds as *exo-cis*-addition in agreement with above obtained data.

Reaction of PBr_3 *with diester* (**5**). The addition to the tricyclo[4, 2, 2, $0^{2,5}$]deca-3, 7-diene derivatives has been extensively studied.[16,28-32] In general, the addition of effectively strong electrophiles[15] involves the cross-type participation of the C_7–C_8 double bond[16,28-30] and δ-lactone closure.[29,30] However, the addition of effectively weak electrophiles[16,31] and radical addition[29,32] involves the strained cyclobutene double bond to give *trans* and *cis* (discussion see[16]) addition products.

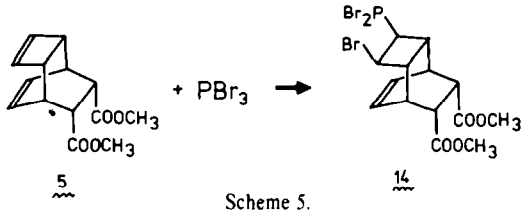
The reaction of PBr_3 with ester **5** (2.7:1 ratio) in CH_2Cl_2 proceeds to give the adduct **14** in 71% yield. However, the NMR ^{31}P of the reaction mixtures reveals the formation of the minor product (≤7%) which has not been isolated.

The DNMR ^1H–{^{31}P} spectrum of **14** contains the signal of H_4 which appears to as a doublet of doublets with $J_{H_3H_4}$ = 8.8 Hz and $J_{H_4H_5}$ = 3.8 Hz. In accordance with literature data this set of coupling constants seems to indicate the *cis*-configuration of the Br–C–C–PBr_2 framework. Thus, the addition of PBr_3 to the diester **5** proceeds at cyclobutene double bond in *cis*-fashion without the participation of the second double bond (*cf* Ref. 29).

Reaction of PBr_3 *with methylidenecyclobutane* (**6**). The interconversion of cyclobutyl (**15**) and cyclopropylmethyl (**16**) cationic intermediates is well documented.[33,34] For example, electrophilic additions to **6**



Scheme 4.



Scheme 5.

often lead to a mixture of cyclobutane (**17**) and cyclopropane (**18**) derivatives.[34,35]

The addition of PBr_3 to **6** proceeds regiospecifically to give a single adduct **19** (δ_P = 190 ppm). The assignment of the structure **19** (vs **20**) is based on the downfield chemical shift of the CH_2 signal (δ 3.91 ppm) in NMR ^1H spectrum of the adduct which is attributed to that of CH_2Br group rather than to that of CH_2PBr_2 one. The DNMR ^{13}C-{^1H} spectrum shows the presence of the three carbons with geminal ^{13}C-^{31}P coupling constant ($J_1 = J_2 = 16.6$ Hz, $J_3 = 13.7$ Hz) and the absence of the signals of t-CBr in the region of 65–80 ppm, which confirms the structure **19** and rejects the structure **20**. Thus, the addition of PBr_3 to **6** proceeds regiospecifically with the Br atom bonded with methylene group and without rearrangement. The structure of adduct **19** may be regarded to as the indication of the transfer of chain reaction by Br · rather than PBr_2 ·.

CONCLUSIONS

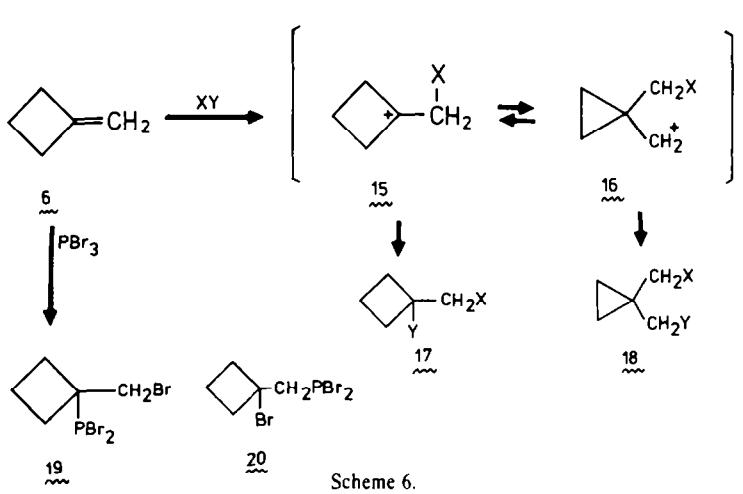
First, the formation of non-rearranged products in all cases provides the best evidence for an absence of discrete cationic intermediate and supports any non-electrophillic schemes of the addition (*cf* the addition of PX_5[36]).

Second, we have found that PBr_3 addition to a series of cycloolefins proceeds in either stereospecific or at least in highly stereoselective manner. If one assumes the previously suggested stepwise chain-radical mechanism[7,8] our observation requires, in turn, to accept the sufficiently rapid chain transfer to intercept the intermediate radical, which is potentially capable of undergoing a number of transformations including conformational ring reversal, rearrangements, etc.

Third, the stereochemistry of PBr_3 addition was found to depend crucially on the olefin structure. Undoubtedly, that high stereoselectivity, which may be easily predicted empirically, sharply enforces the synthetical utility of PBr_3 addition to olefins. Of course, the circumstances surrounded the observed changeable stereochemistry of the PBr_3 addition are not completely understood, because free-radical additions has been shown to depend on "the complex interplay of polar, steric and bond strength terms".[37] Nevertheless, a wide variety of radical reactions, contrary to the general belief, may proceed in stereospecific (and regiospecific) fashion.[37] The rationalization of such a behavior has to be based on the knowledge of the mechanisms of reactions. The observation of stereospecificity of PBr_3 addition as well as the stereochemical course in general is not obviously sufficient to specify the mechanism. While more works, especially kinetics concerning the role of the oxygen, are needed to evaluate the whole mechanistic picture, every suggested mechanism must be able to explain the observed stereochemical regularities.

EXPERIMENTAL

PBr_3 as well as the olefins **1**, **2**, **4** and **6** were the commercial chemicals which were distilled before using. Esters **3** and **5** were



Scheme 6.

obtained following published procedures.[38-39] NMR spectra were recorded on Varian T-60 and Varian XL-100 spectrometers in $CDCl_3$ unless otherwise specified with TMS as the internal standard. The ^{31}P NMR spectra (^1H decoupled) were recorded using Varian CFT-20 (40.5 MHz) spectrometer in $CHCl_3$ with 85% phosphoric acid as external standard. The ^{13}C NMR spectra (^1H decoupled) were recorded on Varian CFT-20 spectrometer (25.16 MHz) in $CDCl_3$ and chemical shifts were given in ppm from TMS.

General procedure for the addition of PBr_3 *to olefins.* The reagents (PBr_3 and olefin) were mixed dropwise at 0° in a dry atmosphere and a moderate flow of dried O_2 was passed through the mixture at a suitable temp. during 10–12 hr. The unreacted olefin and PBr_3 were removed *in vacuo* (10–12 mm Hg) and residue was distilled (1 mg of Hg). In the case of solid adducts they were isolated by washing with a suitable solvent after removing unreacted PBr_3.

trans-2-*Bromocyclohexyldibromophosphine* (**7**) From 32.5 g of PBr_3 (0.12 mmol) and 5 g (0.06 mol) of **1** the adduct **7** was obtained (8.8 g; 44%) following the general procedure, b.p. 134–135° (1 mm), n_D^{20} = 1.6322 (lit. data[8] b.p. 172–176°/15 mm, n_D^{20} = 1.6325); δ_P 201.3; DNMR ^1H-{^{31}P} (δ): 1.28–2.65 (m, 9H), 4.08 (td, 1H, HCBr, $^3J_1 = {}^3J_2 = 10.8$ Hz, $^3J_3 = 4.4$ Hz). $^3J_{HP} = 3.3$ Hz; $^2J_{HP} = 26.9$ Hz. The yield of **7** without passing of O_2 is 31%.

cis-2-*Bromonorbornyldibromophosphine* (**8**). From 1.86 g of **2** and 8.13 g of PBr_3 at 0° the adduct **8** (5.11 g; 70%) was obtained as a crystalline solid (during distillation), b.p. 148–150°/1 mm, m.p. 89–90° (from $CHCl_3$). (Found: C, 23.00; H, 2.73; Br, 65.11. Calc. for $C_7H_{10}PBr_3$: C, 23.04; H, 2.76; Br, 65.70). δ_P = 177.9 ppm. ^1H-{^{31}P} NMR (δ): 4.41 (dq, 1H, HCBr, $^3J_1 = 7.2$ Hz, $^3J_2 = 2.1$ Hz and $^4J_3 = 0.8$ Hz), 3.08 (dd, 1H, HCPBr$_2$, $^3J_1 = 7.2$ Hz, $^3J_2 = 1.6$ Hz), 2.78 (m, 2H, H_1 and H_4), 1.30–2.52 (m, 6H). $^3J_{(H_1P)} = 1.2$ Hz; $^2J_{(H_4P)} = 8.8$ Hz. δ_P of the minor product was at 181.2 ppm.

Adduct of PBr_3 *and ester* **3** (**9**). 2.1 g (0.01 mol) of **3** and 5.42 g (0.02 mol) of PBr_3 gave 2.45 g (51%) of **9** as colourless crystals following the general procedure with subsequent washing with Et_2O (yield on reacted ester **3** is 92%), m.p. 103–104° (from ether). δ_P = 177.1 ppm. ^1H NMR (δ): 5.05 (m, 1H, HCBr, ^3J = 7.4 Hz), 3.71 and 3.68 (two singlets of COOCH$_3$), 2.97–3.26 (m, 4H), 2.48 and 1.60 (two one-proton doublets of H_7, $|^2J|$ = 11 Hz). $^3J_{HP} = 1.9$ Hz; $^2J_{HP} = 9.1$ Hz. (Found: C, 27.62; P, 6.51; Br, 49.24. Calc. for $C_{11}H_{14}O_4PBr_3$: C, 27.47; P, 6.44; Br, 49.85%).

Reaction of PBr_3 *with norbornadiene*

(a). From 2.56 g (0.03 mol) of **4** and 8.13 g (0.03 mol) of PBr_3 at room temp. using the general procedure, 8.9 g of the mixture of four compounds was obtained as a viscous colourless oil with δ_P at 183.2, 182.0, 180.9 (main product, **12**, 86% by integrating) and 175.0 ppm, b.p. (mixt) 131–132°/1 mm. NMR data for the major product: DNMR ^1H-{^{31}P} (δ): 6.42 (m, 1H, =CH), 6.14 (m, 1H, =CH), 4.19 (dd, 1H, HCBr, $^3J_1 = 7.2$, $^3J_2 = 2.0$), 3.38 (m, 2 H, H_1 and H_4), 2.96 (dd, 1H, HCPBr$_2$, $^3J_1 = 7.2$ Hz, $^3J_2 = 2.0$ Hz), 2.18 and 1.69 (two one-proton multiplets of H_7; $|^2J| = 10$ Hz). (Found for mixture: C, 23.45; P, 8.52; Br, 65.87. Calc. for $C_7H_8PBr_3$: C, 23.17; P, 8.54; Br, 66.07%).

(b). From 35.2 g (0.13 mol) of PBr_3 and 2.56 g (0.03 mol) of **4** using the general procedure 11.5 g (68%) of diadduct **13** was obtained after distilling off the unreacted reagents and washing the residue with $CHCl_3$ (2 × 7 ml). The crystalline solid rapidly becomes dark in sunlight, m.p. 131–132.5° (washing with $CHCl_3$). δ_P = 170.0 ppm. ^1H NMR (CD_2Cl_2, δ): 4.61 (m, 2H, 2HCBr, ^3J = 7.3 Hz), 3.30 and 2.75 (two multiplets of H_1, H_4 and 2HCPBr$_2$), 2.46 (m, 2H, H_7). (Found: Br, 74.12. Calc. for $C_7H_8P_2Br_6$: Br, 75.68%).

Adduct of PBr_3 *and ester* **5** (**14**). Following the above procedure, 1.09 g (10.8 mmol) of PBr_3 and 1.0 g (4.03 mmol) of **5** in 2 ml CH_2Cl_2 gave 1.5 g (71%) of **14** after the washing the residue with Et_2O, m.p. 131–132° (from Et_2O). δ_P = 175.0 ppm; δ_P of a minor product is 203.5 ppm). ^1H NMR (^{31}P decoupled, δ): 6.56 (m, 2H, olefinic protons), 4.22 (dd, 1H, HCBr, $^3J_1 = 8.8$ Hz, $^3J_2 = 3.8$ Hz), 3.58 (s, 6H, COOCH$_3$), 2.66–3.64 (m, 7H); $^3J_{H_1P} = 5.4$ Hz. (Found: C, 33.01; P, 6.06; Br, 46.01. Calc. for $C_{14}H_{16}O_4PBr_3$: C, 32.40; P, 5.97; Br, 46.19%).

Adduct of PBr_3 and **6** (**19**). Following the general procedure, from 16.3 g (0.06 mol) of PBr_3 and 3.4 g (0.05 mol) of **6** the adduct **19** (10.7 g, 63%) was obtained as a colourless oil with b.p. 103–105°/1 mm, n_D^{20} = 1.6254. δ_P = 190.0 ppm. ^1H NMR (δ): 1.62–2.78 (broad multiplet, 6H), 3.91 (d, 2H, CH$_2$Br, $J_{HP} = 8$ Hz). ^{13}C NMR (^1H decoupled): 14.14 (d, $^3J_{CP} = 5.0$ Hz), 27.96 (d, $^2J_{CP} = 16.6$ Hz), 40.60 (d, $^2J_{CP} = 13.7$ Hz), 45.38 (d, $^1J_{CP} = 21.7$ Hz). (Found: C, 18.51; Br, 69.54. Calc for $C_5H_8PBr_3$: C, 17.72; Br, 70.75%). Yield of **19** without passing O_2 is 49%.

REFERENCES

[1] Yu. M. Zinov'ev and L. Z. Soborovsky, *Reaktsii i Metody Issledovanija Org. Soed.* (*Reactions and Research Methods of Organic Comp.*) Vol. 21. "Khimija", Moscow (1970).

[2] J. T. McBride, B. Jungermann, J. V. Killheffer and R. J. Clutter, *J. Org. Chem.* **27**, 1833 (1962).

[3] J. R. Little and P. F. Hartman, *J. Am. Chem. Soc.* **88**, 96 (1966).

[4] G. A. Zagorets, A. G. Shostenko and A. M. Dodonov, *Zh. Ob. Khim.* **41**, 2171 (1971).

[5] E. I. Babkina and U. V. Vereshchinsky, *Ibid.* **38**, 1772 (1968).

[6] V. A. Kozlov, A. A. Borisenko, A. F. Grapov, E. I. Babkina and N. N. Mel'nikov, *Ibid.* **49**, 279 (1979).

[7] B. Fontal and H. Goldwhite, *J. Org. Chem.* **31**, 3804 (1966).

[8] S. V. Fridland, T. M. Shchukareva and R. A. Salakhutdinov, *Zh. Ob. Khim.* **46**, 1232 (1976).

[9] A. S. Kruglov, E. L. Oskotsky, A. V. Dogadina, B. I. Ionin and A. A. Petrov, *Ibid.* **48**, 705, 1495 (1978).

[10] M. V. Sendurev, A. V. Dogadina, B. I. Ionin and A. A. Petrov, *Ibid.* **50**, 1651 (1980).

[11] M. V. Sendurev, T. N. Beljaeva, A. V. Dogadina, V. E. Kholmogorov, B. I. Ionin and A. A. Petrov, *Ibid.* **51**, 2803 (1981).

[12] M. A. Kazankova, I. G. Trostjanskaja, A. R. Kudinov and I. F. Lutsenko, *Ibid.* **49**, 469 (1979).

[13] S. B. Hartley, W. S. Holmes, J. F. Jacqnes, M. F. Mole and J. C. McCoubrey, *Quart. Rev.* **17**, 204 (1963).

[14] N. V. Zyk, M. Yu. Krysin, A. A. Borisenko, T. G. Shestakova and N. S. Zefirov, *Dokl. Akad. Nauk SSSR* **265**, 882 (1982).

[15a] It is worthy to clarify additionally this term. For the *multistage* electrophilic additions the total rate ("kinetic electrophilicity") describes only the rate limiting step. We suggested [15b,16] that the ratio of rearranged and non-rearranged products may be regarded as the measure of the electrophility of intermediates and hence of "effective electrophilicity" of reagents. In other words, an "effectively" strong electrophile generates a relatively large positive charge on C atom/s of intermediate' [b] N. S. Zefirov, N. K. Sadovaja, A. M. Maggeramov, I. V. Bodrikov and V. R. Kartashov, *Tetrahedron* **31**, 2948 (1975); N. S. Zefirov, N. K. Sadovaja, A. M. Maggeramov and I. V. Bodrikov, *Zh. Org. Khim.* **13**, 245 (1977).

[16] N. S. Zefirov, A. S. Koz'min, V. N. Kirin, V. V. Zhadankin and R. Caple, *J. Org. Chem.* **46**, 5264 (1981).

[17] J. G. Traynham, A. G. Lane and N. S. Bhacca, *Ibid.* **34**, 1302 (1969); N. Lebel and A. DeBoer, *J. Am. Chem. Soc.* **89**, 2784 (1967).

[18a] R. A. Cancarz and J. L. Kice, *J. Org. Chem.* **46**, 4899 (1981); [b] T. G. Black and S. Kollins, *Ibid.* **46**, 3249 (1981).

[19] F. D. Greene, C. C. Chu and J. Walia, *Ibid.* **29**, 1285 (1964).

[20] L. Kao Liu, Y. Chi and Kwan-Yue Jen, *Ibid.* **45**, 406 (1980).

[21] R. S. Fahey, *Topic in Stereochemistry* (Edited by E. L. Eliel) Vol. 3, p. 237 (1968).

[22] T. G. Traylor, *Acc. Chem. Res.* **2**, 152 (1969); N. S. Zefirov, N. K. Sadovaja, L. A. Novgorotseva, R. Sh. Achmedova, S. V. Baranov and I. V. Bodrikov, *Tetrahedron* **35**, 2759 (1979).

[23] R. Huisgen, R. H. J. Ooms, M. Mingin and N. L. Allinger, *J. Am. Chem. Soc.* **102**, 3951 (1980).

[24] C. D. Vernood and C. S. Rondestvedt, *Ibid.* **77**, 3538 (1955).

[25] J. Meinwald, Y. C. Meinwald and T. N. Baker, *Ibid.* **86**, 4074 (1964).

[26a] S. J. Cristol and D. I. Davies, *J. Org. Chem.* **29**, 1282 (1964); [b] S. J. Cristol, J. K. Harrington and M. S. Singer, *J. Am. Chem. Soc.* **88**, 1529 (1966).

[27] M. S. Alnajjar and H. G. Kuivila, *J. Org. Chem.* **46**, 1053 (1981);

S. J. Cristol and R. W. Gleanson, *Ibid.* **34**, 1762 (1969); S. R. Warner, R. J. Strunk and H. G. Kuivila, *Ibid.* **31**, 3381 (1966).
[28]T. Sasaki, K. Kanematsu and A. Kondo, *Ibid.* **39**, 2246 (1974); G. Mechta and P. N. Pandey, *Ibid.* **40**, 3631 (1975).
[29]A. Kondo, T. Yamane, T. Ashida, T. Sasaki and K. Kanematsu, *Ibid.* **43**, 1180 (1978).
[30]N. S. Zefirov, V. N. Kirin, A. S. Koz'min, I. V. Bodrikov, I. V. Potekhin and E. N. Kurkutova, *Tetrahedron Lett.* 2617 (1978).
[31]N. S. Zeifirov, A. S. Koz'min, V. N. Kirin, V. V. Zhdankin, G. V. Lagodzinskaja, K. A. Potekhin and E. N. Kurkutova, *Nouv. J. Chim.* **4**, 475 (1980).
[32]G. I. Fray, R. Geen, D. I. Davies, L. T. Parfitt and M. J. Parrott, *J. Chem. Soc.* Perkin I, 654 (1973).
[33]M. Saunders and J. Rosenfeld, *J. Am. Chem. Soc.* **92**, 2548 (1970).
[34]D. E. Applequist and J. D. Roberts, *Ibid.* **78**, 874 (1956).
[35]S. N. Anfilogova, E. B. Frolov and E. S. Balenkova, *Vestnik Mosk. Univ.*, ser "Khimija" **21**, 611 (1980); S. N. Anfilogova, E. B. Frolov, Yu. N. Luzikov and E. S. Balenkova, *Zh. Org. Khim.* **15**, 1432 (1979).
[36]Y. Okamoto and H. Sakurai, *Bull. Chem. Soc. Jap.* **43**, 2613 (1970); V. V. Rybkina, V. G. Rosinov and E. F. Grechkin, *Zh. Ob. Khim.* **43**, (1973); A. F. Kolomiets, A. V. Fokin, A. A. Krolevets, P. V. Petrovsky and O. V. Verenikin, *Izvest. Akad. Nauk SSSR, ser. Khim.* 2108 (1979).
[37]A. L. J. Beckwith, *Tetrahedron* **37**, 3073 (1981); J. M. Tedder and J. C. Walton, *Acc. Chem. Res.* **9**, 183 (1976).
[38]H. Koch, *Monatsch.* **93**, 292 (1962).
[39]W. Reppe, O. Schichting, K. Klager and T. Toepel, *Liebigs Ann.* **560**, 1 (1948); A. G. Anderson and P. R. Fagerburg, *Tetrahedron* **29**, 2973 (1973).