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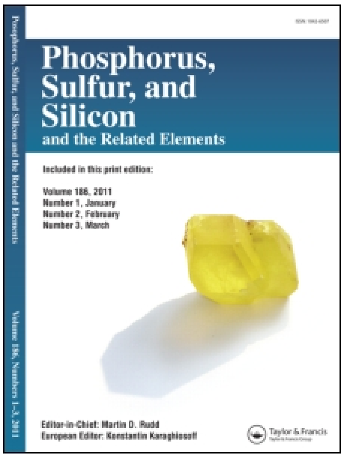

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THE STEREOCHEMISTRY OF DEALKYLATION STEP IN THE ARBUZOV REACTION INVOLVING FIVE-COORDINATE INTERMEDIATE. EVIDENCE FOR EQUILIBRIUM BETWEEN PHOSPHORANE AND PHOSPHONIUM SPECIES

Jan Michalski[a]; Jerzy Mikołajczak[a]; Marek Pakulski[a]; Aleksandra Skowronska[a]
[a] Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Boczna, Poland

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THE STEREOCHEMISTRY OF DEALKYLATION STEP IN THE ARBUZOV REACTION INVOLVING FIVE-COORDINATE INTERMEDIATE. EVIDENCE FOR EQUILIBRIUM BETWEEN PHOSPHORANE AND PHOSPHONIUM SPECIES

JAN MICHALSKI, JERZY MIKOŁAJCZAK, MAREK PAKULSKI and ALEKSANDRA SKOWROŃSKA
Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Łódź, Boczna 5, Poland

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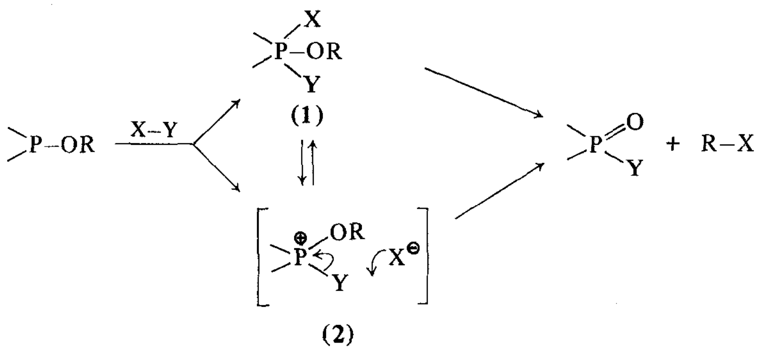
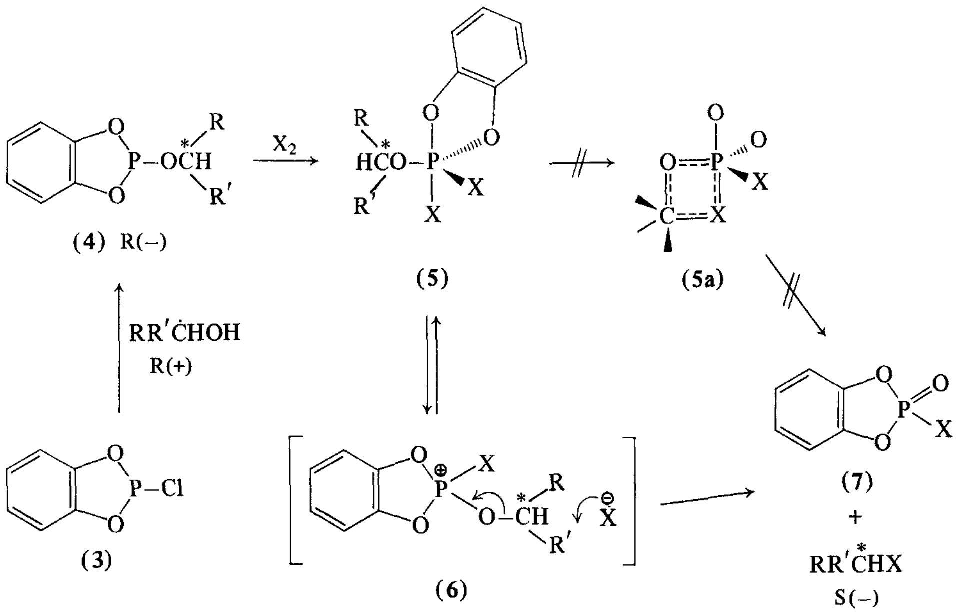
The oxidative addition of molecules X–Y to three-coordinated phosphorus compounds is of considerable general interest. If one of the groups attached to the phosphorus atom is an alkoxy, OR, the final product is almost always $>$P(O)Y with the formation of an alkyl halide RX. The above process is known as Arbuzov reaction, the mechanism of which can be represented, in the light of our present knowledge, as follows:



The formation of an intermediate phosphonium salt (**2**) is well documented in a number of cases.[1] When optically active secondary alcohol ROH was used highly inverted alkyl halide was obtained in agreement with an S_N2 reaction of displaced anion on the alkyl group of the phosphonium intermediate (**2**).[2] The formation of five-coordinate species in the Arbuzov reaction of phosphites derived from pyrocatechol has recently been established in this Laboratory.[3] Consequently the following question arose: whether in this case the dealkylation step could proceed by concerted elimination of R–X from the five-coordinate intermediate (**1**). A study of stereochemical changes at the chiral carbon atom of the alkoxy group, RO, was undertaken, in the hope of gaining insight into this fundamental mechanistic problem for the Arbuzov reaction.

The R(−)phosphite (**4**) was prepared from R(+)2-octanol of 95% opt. purity, $[\alpha]^{20}_{D}$ +9.4° (neat) and the chlorophosphite (**3**) by standard condensation in the presence of tertiary amine and purified by distillation *in vacuo*, δ^{31}P −127.5 ppm, $[\alpha]^{D}_{20}$ −25.6° (neat). Equimolar amounts of the phosphite (**4**) and the corresponding halogen in CH_2Cl_2 solution were allowed to react at −85°C. The reaction was monitored by ^{31}P nmr and the spectra showed only the presence of the five-coordinate intermediates with a characteristic high-field chemical shifts: X=Cl, δ^{31}P +35 ppm; X=Br, δ^{31}P +195 ppm. On warming to above −40°C new peaks appeared corresponding to phosphorohalidates (**7**): X=Cl, δ^{31}P −19 ppm; X=Br, δ^{31}P −3.5 ppm. The reaction mixture, after standard working up, was separated by distillation which gave: phosphorohalidates (**7**); S(−)2-chlorooctane of 82% optical purity, $[\alpha]^{20}_{D}$ −27.7° (neat) and S(−)2-bromooctane of 95% optical purity, $[\alpha]^{20}_{D}$ −32.2° (neat).

It was anticipated that in a concerted dealkylation of the five-coordinate intermediate (**5**) configuration at the carbon atom of the alkyl halide formed should be



the same as in the starting optically active alcohol. The structural combination of halogens and alkoxy group for a feasible transition state for concerted elimination, with the least distortion of bond angles is the one involving the carbon atom and the partly formed carbon-halogen bond and the partly broken carbon-oxygen bond, the inter bond angle being close to 90°. Such a transition state (**5a**) should result in retention of configuration at the carbon atom and not in an almost full inversion as observed in this study. We can therefore rule out the direct dealkylation of the five-coordinate intermediate (**5**) and suggest as a plausible explanation of our stereochemical results the existence of a fast equilibrium between (**5**) and (**6**). The dealkylation of the phosphonium intermediate (**6**) should follow the S_N2 type displacement at the chiral carbon atom accompanied by optical inversion.

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