PREPARATION AND SOME PROPERTIES OF INTERMEDIATE PRODUCTS OF THE ARBUZOV REARRANGEMENT

1957

SovietRxiv

Abstract

Full Text

CHEMISTRY

A. I. RAZUMOV and N. N. BANKOVSKAYA

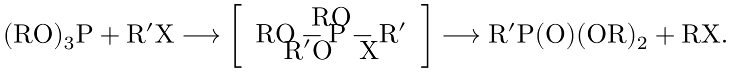
PREPARATION AND SOME PROPERTIES OF INTERMEDIATE PRODUCTS OF THE ARBUZOV REARRANGEMENT

(Presented by Academician A. E. Arbuzov on V 6, 1957)

The rearrangement known in the world chemical literature as the Arbuzov rearrangement proceeds in two phases, with formation of an intermediate product. The general scheme of the rearrangement was proposed by its author in the following form (^{1}):

Esters of trivalent phosphorus with compounds containing a mobile halide enter into the rearrangement. About 400 varied examples of such a rearrangement have been described in the literature (^{2}).

There are, however, also other views on the mechanism of the rearrangement—as on a reaction of ionic (^{3}) or radical type ($^{4-6}$).



$$\mathrm{(RO)_3P} + \mathrm{R'X} \longrightarrow \left[\ \mathrm{RO}\underset{\mathrm{R'O}}{-}\overset{\mathrm{RO}}{\mathrm{P}}\underset{\mathrm{X}}{-}\mathrm{R'}\ \right] \longrightarrow \mathrm{R'P(O)(OR)_2} + \mathrm{RX}.$$

The possibility of an ionic or radical type of course of the indicated reaction in individual cases is not excluded; however, there is very little experimental evidence for this.

One of the best proofs of the two-phase nature of the process is the isolation of intermediate products and their thermal decomposition into a halogen compound and a derivative of phosphinic acids.

The first proof was given by A. E. Arbuzov, the author of this rearrangement, who thermally decomposed iodous triphenylmethylphosphonium, obtained by A. Michaelis and Kaehne (^{7}), into iodobenzene and phenyl ester of methylphosphinic acid.

By the present time several intermediate products have been isolated in an analytically pure state ($^{8-11}$).

All identified intermediate products were obtained by addition only to aromatic esters of trivalent phosphorus. Five of the indicated compounds have been thermally decomposed in complete agreement with the Arbuzov rearrangement scheme (^{1}, ^{10}, ^{11}).

With regard to intermediate products obtained from aliphatic esters of trivalent phosphorus, there existed the opinion that they could not be isolated because of their instability (1) and capacity for spontaneous decomposition (12). It is true that V. S. Abramov and co-workers, by a number of indirect proofs, succeeded in showing the formation of intermediate products in the interaction of aliphatic esters of phosphorous acid with α-, β-dibromoalkyl ethers and in carrying out their subsequent thermal decomposition in accordance with the scheme of A. E. Arbuzov. However, it was not possible to isolate these intermediate products in pure form (13, 14).

Quite recently an interesting communication appeared by G. Kh. Kamai and V. A. Kukhtina on the preparation of a cyclic intermediate product in the course of

interactions of an aliphatic phosphite with an α,β-unsaturated aldehyde. They were unable to identify this product (15).

The study of the Arbuzov rearrangement by B. A. Arbuzov and co-workers using physical methods also confirms the two-phase process of the rearrangement (16–17).

The authors of the present work assumed that, if the intermediate products are unstable, heating—under which the Arbuzov rearrangement most often proceeds between aliphatic phosphites and alkyl halides—facilitates this all the more. It seemed more probable to hope to obtain intermediate products with those aliphatic derivatives of trivalent phosphorus which are capable of entering into rearrangement without heating, i.e., in which the tendency toward the addition reaction is stronger.

The esters of dialkylphosphinous acids taken for this purpose showed that they are capable of reacting with alkyl halides without heating. Moreover, addition of methyl iodide to the ethyl ester of ethylphosphinous acid at room temperature leads to a violent explosion with decomposition of the products and evolution of iodine vapors.

When the same reaction is carried out at $-6°$, the reaction proceeds calmly and is completed after about 30 min with formation of a crystalline product. After washing the crystals with dry ether, they are analytically pure, have m.p. 56–58°, and correspond in composition to methyl diethylethoxyphosphonium iodide. The yield is quantitative.

Found, %:	C 30.94; 30.83;	H 6.68; 6.70;	P 11.00; 10.90
$C_7H_{18}OPI$. Calculated, %:	C 30.43;	H 7.24;	P 11.23

The interaction of ethyl iodide with the same ester proceeds at room temperature (21°) and is completed after 22-23 hours with formation of a crystalline product. After washing, the crystals were analytically pure, had m.p. 79–81°, and corresponded in composition to triethylethoxyphosphonium iodide.

Found, %:	C 33.30; 33.22; H 7.09; 7.10; P 10.40; 10.22
$C_8H_{20}OPI$. Calculated, %:	C 33.10; H 6.86; P 10.68

The interaction of *n*-propyl iodide with the same ester was completed at room temperature (18°) after 42-44 hours with formation of crystals having m.p. 73–75°, analytically pure and corresponding in composition to *n*-propyldiethylethoxyphosphonium iodide.

Found, %:	C 35.60; 35.65; H 7.24; 7.21; P 10.54; 10.48
$C_9H_{22}OPI$. Calculated, %:	C 35.55; H 7.23; P 10.19

All three products dissolve well in polar solvents, and also in benzene. They are insoluble in carbon tetrachloride.

To determine their stability, all three products were placed in vacuum desiccators over phosphorus anhydride. Observation showed that the products obtained are unstable and decompose spontaneously. Their lifetimes are not the same and depend on structure. The first exists for 24-25 days at room temperature (18°), the second for 15 days (21°), and the third for 10 days (18°).

Of interest for the kinetics of the process is the fact that during their lifetime the crystalline structure of the product does not visibly change, and then, rapidly, within a day, liquefaction begins, and all the crystals turn into a homogeneous liquid mass, which we regarded as the end of phase II of the rearrangement. It is not excluded that the dissociation process begins earlier as well, but it is beyond doubt that in that case it proceeds very slowly and only at the very end is completed rapidly.

Probably, in the near future we shall succeed in determining the order of reaction of phases I and II, which still remains not entirely clear. With more high-

At high temperatures the rate of both the first and second phases of the reaction increases considerably. Thus, carrying out the reaction in a thermostat at 45° (±0.1°) shows that formation of triethylethoxyphosphonium iodide is completed after 20 min, and complete completion of the rearrangement after 5 h 45 min; at 55°, respectively, after 10 min and 2 h.

After decomposition of the phosphonium compounds, phosphine oxides are formed, in accordance with the Arbuzov rearrangement. Apparently, the latter are present in solution in the alkyl halides that have separated. Opening the desiccators reveals the disappearance or weakening of the vacuum and a strong odor of alkyl halide. After removal of the latter by means of vacuum, crystalline phosphine oxides remain. However, analysis of the oxides is very difficult because of their exceptionally high hygroscopicity. Therefore the oxides were identified in the form of their complex compounds with gold chloride. Thus, triethylphosphine oxide, mixed with gold chloride in acidified aqueous solution, formed golden-yellow crystals of a complex compound with m.p. 53-54°. Literature data: 54-56° (18).

The dipole moment measured for *n*-propyldiethylethoxyphosphonium iodide is rather high (5.03 D*). A similar value was also obtained for methyltriphenoxyphosphonium iodide (16). The nature of the bond in quasi-phosphonium compounds is probably not purely covalent or ionic.

Kazan Chemical-Technological
Institute named after S. M. Kirov

Received
3 IV 1957

CITED LITERATURE

1. A. E. Arbuzov, *On the Structure of Phosphorous Acid and Its Derivatives*, Dissertation, 1905.
2. B. A. Arbuzov, *Reactions and Methods of Investigation of Organic Compounds*, 3, Moscow, 1954.
3. B. Smith, A. Burger, *J. Am. Chem. Soc.*, **75**, 5891 (1953).
4. P. Rumpf, V. Chavane, *C. R.*, **224**, 919 (1947).
5. V. Chavane, *Bull. Soc. Chim.*, **27**, 774 (1948).
6. P. Rumpf, *Bull. Soc. Chim.*, 128 C (1951).
7. A. Michaelis, R. Kaehne, *Ber.*, **31**, 1048 (1898).
8. A. Michaelis, W. La-Coste, *Ber.*, **18**, 2109 (1885).
9. A. E. Arbuzov, G. Kh. Kamai, L. V. Nesterov, *Transactions of the Kazan Chem.-Techn. Institute*, **16**, 17 (1952).
10. A. E. Arbuzov, L. V. Nesterov, *Izv. AN SSSR, OKhN*, 1954, 431.
11. K. A. Petrov, G. A. Sokol' skii, *ZhOKh*, **26**, 3379 (1956).
12. G. Kosolapoff, *Organophosphorus Compounds*, 1950.

13. V. S. Abramov, G. Karp, *DAN*, **91**, 1095 (1953).

14. V. S. Abramov et al., *ZhOKh*, **24**, 1823 (1954); **26**, 163 (1956); **26**, 2014 (1956).

15. G. Kh. Kamai, V. A. Kukhtin, *DAN*, **112**, 868 (1957).

16. B. A. Arbuzov, A. V. Fuzhenkova, V. S. Vinogradova, T. G. Tolkacheva, *Chemistry and Application of Organophosphorus Compounds*, Moscow, 1957.

17. B. A. Arbuzov, A. V. Fuzhenkova, M. K. Saikina, V. M. Zaroastrova, Abstracts of reports at the conference *Problems of the Structure of Organic Compounds*, Kazan, 1957.

18. R. H. Pickard, J. Kenyon, *J. Chim. Soc.*, **89**, 262 (1906).

* The measurements were made by T. G. Tolkacheva (laboratory of Academician B. A. Arbuzov), to whom the authors express their gratitude.

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.