ACETOXY DERIVATIVES IN THE ARBUZOV REACTION

B. E. Ivanov, S. S. Krokhina,
L. A. Valitova, N. P. Anoshina,
and É. I. Gol'dfarb

UDC 542.91:547.1'118

The reactions of amidophosphites with (acetoxymethyl)diethylamine proceed at room temperature, are exothermic, and lead to the formation of high yields of the corresponding amides of aminomethylphosphonic acids [1]. To solve the problem of the direction of the reactions we studied the kinetics of the reaction of (acetoxymethyl)diethylamine with mono-(I), bis-(II), and tris(diethylamido)phosphites by P^{31}-NMR and thermographic methods. Signals for the phosphorus nuclei were observed in the P^{31}-NMR spectrum obtained for the reaction mixture (including (III)) at room temperature and had the following chemical shifts (relative to 85% phosphoric acid): −122 ppm (triamidophosphite) and −54 ppm. The product with a chemical shift of −54 ppm is relatively stable, since no change in the signal was observed at room temperature in the course of 15-20 min. At 30-40°, the signal at −54 ppm vanished, and a new signal with a phosphorus nuclei chemical shift of −32 ppm appeared. We observed the same chemical shift for the signal of the final product of the reaction, viz., diethylaminomethylphosphonic acid bisdiethylamide.

The NMR spectra for the reaction mixtures of (I) and (II) were obtained at −50° and −20°, respectively, in a special cooling chamber of the apparatus. Peaks with chemical shifts of −132 ppm (bisdiethylamidophosphite), −54 ppm (at −20°), and −32 ppm (at room temperature) appeared in the spectrum for the reaction mixture of (II). Only a signal at −148 ppm (0,0-diethyldiethylamidophosphite) was observed for the reaction mixture of (I) at −50°, while at room temperature a signal was observed at −23 ppm (final reaction product – diethyl diethylaminomethylphosphonate). A sudden jump (by three orders of magnitude) in the change in the electrical conductivity was observed when the reaction mixture of (III) was poured into CH_2Cl_2 at −70°.

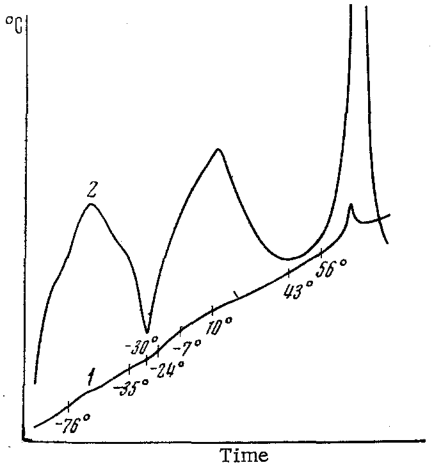


Fig. 1. Thermogram of a mixture of $Et_2NCH_2 \cdot OCOCH_3$ and $P(NEt_2)_3$ at a heating rate of 2.2 deg/min: 1) simple recording; 2) differential recording.

The set of data in [2] and our experimental results make it possible to relate the chemical shift of −54 ppm to an intermediately formed product of the quasiphosphonium type. Reaction mixtures of (I), (II), and (III) were studied by means of thermography [3] to confirm the possibility of the formation of an intermediate quasiphosphonium compound.

If the reaction proceeded via a two-step mechanism, two exothermic effects, one of which would correspond to the formation of the product of the addition of (acetoxymethyl)diethylamine to the amidophosphite, the second of which would correspond to the decomposition of the intermediate addition product with the formation of the reaction products, should have been expected on the differential-thermal curve (DTC). The start of the exothermic effect of the crystallization of the triamidophosphite at −76° and an endothermic effect for its melting are seen on the thermogram (Fig. 1) for the (acetoxymethyl)diethylamine–tris(diethylamido)phosphite system (at a heating rate of 2.2 deg/min). On further heating an exothermic effect commences at −24° and ceases at 43° with a maximum at 10°. This effect is related to

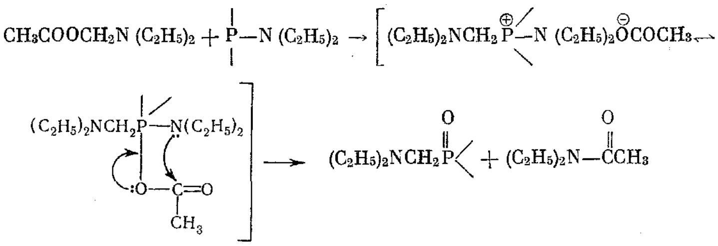
---

A. E. Arbuzov Institute of Organic and Physical Chemistry, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 3, pp. 597-599, March, 1972. Original article submitted March 15, 1971.

the formation of an addition product. An intense exothermic effect, which is associated with the decomposition of the addition product, is observed at 56°.

The sharp pattern of a two-step process could not be observed on the thermograms for mixtures of (I) (heating rate 1.9 deg/min) and (II) (heating rate 0.9 deg/min). This is probably associated with the fact that the rate of decomposition of the intermediate product in the case of (II) is commensurable and even higher (in the case of (I)) than its rate of formation. It is therefore impossible to register the addition product by P^{31}-NMR (for (I)) or by thermography (for (I) and (II)). For (III), however, the time that the intermediate product exists turned out to be no less than 15-20 min at room temperature, i.e., its rate of formation is higher than the rate of its decomposition. This probably also enabled us to obtain a sharp pattern on both the P^{31}-NMR spectrum and the DTC.

Thus, on the basis of the results obtained, these reactions can be described by the scheme



The fact that the formation of the final product occurs through an intermediate covalent form can be considered to be essential in the proposed scheme.

EXPERIMENTAL METHOD

An equimolar amount of one of the amidophosphites was added to liquid-nitrogen cooled (acetoxymethyl)diethylamine, and the reaction mixture was then placed in a chamber cooled to −100° and heated at 1.9 or 2.2 deg/min.

CONCLUSIONS

The reaction of (acetoxymethyl)diethylamine with mono-, bis-, and tris(diethylamido)phosphites proceeds through the intermediate formation of compounds of the quasiphosphonium type, as shown by P^{31}-NMR and thermography.

LITERATURE CITED

1. B. E. Ivanov, L. A. Valitova, and S. S. Krokhina, Izv. Akad. Nauk SSSR, Ser. Khim., 1502 (1971).
2. L. V. Nesterov, A. Ya. Kessel', Yu. Yu. Samitov, and A. A. Musina, Dokl. Akad. Nauk SSSR, 180, 116 (1968).
3. B. A. Arbuzov and A. V. Fuzhenkova, Dokl. Akad. Nauk SSSR, 114, 89 (1957).