CONCLUSIONS

Potentiometric titration was used to elucidate that enantioselectivity of the complexation of APA with cupric salts in aqueous solution.

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ACID CATALYSIS OF THE REACTIONS OF N-ACETOXYMETHYLAMIDES OF BENZOIC AND ACETIC ACIDS WITH DIETHYLAMIDODIETHYLPHOSPHITE

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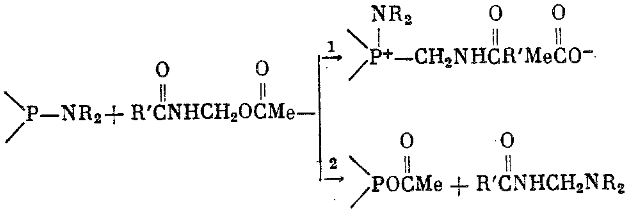
547.1'118

Two pathways have been reported for the reactions of mono-, di-, and triamidophosphites with the N-acetoxymethylamides of carboxylic acids: at the phosphorus atom with the formation of the products of the substitution of the amide group [1]:



The product ratio depends on the nature of the electrophile and type of amide of the P(III) acid. The yields of products along pathway 2 increase in going from triamido- to di- and monoamidophosphites [1].

In previous work [2], we showed that the reaction of the amides of P(III) acids with the cleavage of the P—N bond are, as a rule, acid-catalyzed due to impurities such as amine hydrochlorides in the amidophosphites and hydrolysis and oxidation products in the electrophilic reagents. Cleavage of the P—N bond also occurs in the reaction of P(III) acid amides with the N-acetoxymethylamides of carboxylic acids along pathway 2. Thus, acid catalysis presumably occurs in these reactions due to impurities in the starting compounds. In such a case, the purification of these reagents to remove acidic impurities should lead to suppression of the replacement of the amide group and exclusive formation of Arbuzov reaction products. In order to check this hypothesis, we studied the reactions of diethylamidodi-

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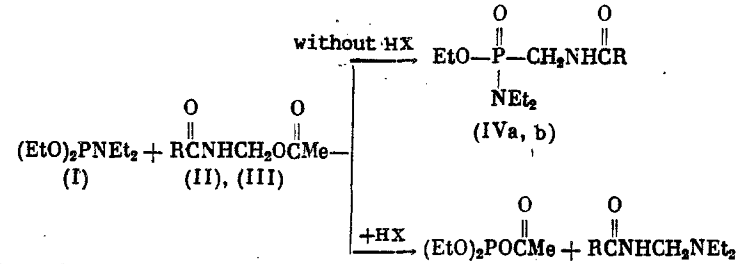
ethylphosphite (I) with N-acetoxymethylbenzamide (II) and N-acetoxymethylacetamide (III), for which the greatest yields of the substitution product, namely, diethylacetylphosphite (up to 55%) were observed [1].

Starting (I) was purified by triple distillation in the presence of 5% bis(trimethylsilyl)acetamide according to our previous procedure [3]. N-Acetoxymethylamides (II) and (III) were repeatedly crystallized from benzene and ether. The final crystallization was carried out from vinyl n-butyl ether used to remove traces of acids [4]. The experiments were performed in a dry argon atmosphere.

Starting reagents purified in this manner react exothermally and give only Arbuzov reaction products. The only organophosphorus product in the reaction with (II) is N-diethylamido-O-ethyl-N'-(benzamido)methylphosphonate (IVa). Monitoring of the reaction using ^{31}P NMR spectroscopy showed no formation of diethylacetylphosphite. However, if up to 5% acetic acid is added to the reaction mixture of purified (I) and (II), ^{31}P NMR spectroscopy indicates the formation of products through both pathways. The ratio of the signals for phosphonate (IVa) (δP 28 ppm) and diethylacetylphosphite (δP 132 ppm) in the presence of acetic acid is 1:2. Analogous behavior is observed if purified (I) is maintained for ~12 h in the air and the ratio of the signals for the products along pathways 1 and 2 is 1:1.3. In the two latter cases, the ^{31}P NMR spectra of the reaction mixtures also show low-intensity signals at δP 23 and 8 ppm.



$$\underset{\text{(I)}}{(EtO)_2PNEt_2} + \underset{\text{(II), (III)}}{RC(O)NHCH_2OC(O)Me} \xrightarrow{\text{without HX}} \underset{\text{(IVa, b)}}{EtO-P(O)(NEt_2)-CH_2NHC(O)R}$$

$$\xrightarrow{+HX} (EtO)_2POC(O)Me + RC(O)NHCH_2NEt_2$$

R = Ph (a), Me (b).

Similarly, the only product in the reactions of (I) and (III) purified according to our procedure [3] and the method of Gazizov [4] is N-diethylamido-O-ethyl-N'-(acetamido)methylphosphonate (IVb) (Arbuzov reaction product) as indicated by ^{31}P NMR spectroscopy.

EXPERIMENTAL

The ^{31}P NMR spectra were taken on a KGU-4 spectrometer at 10.2 MHz relative to 85% H_3PO_4. The IR spectra were taken on a UR-20 spectrophotometer.

Reaction of Diethylamidodiethylphosphite (I) with N-Acetoxymethylamides of Carboxylic Acids (II) and (III). a) A sample of 4.0 g (20 mmoles) (I) was added to 4.0 g (20 mmoles) (II). The mixture was carefully warmed to 40°C. Spontaneous warming to 70-80°C was observed and (II) dissolved. The ^{31}P NMR spectrum showed a single signal with δP 28 ppm corresponding to (IVa) [1]. The crystals which formed over 12 h were washed with hexane and recrystallized from ether to give 4.6 g phosphonate (IVa), mp 96.5-97.5°C. IR spectrum in vaseline mull (ν, cm^{-1}): 3250 (NH), 1657 (C=O), 1204 (P=O), 1045 (P=O=C). Evaporation of the hexane extract in vacuum gave a colorless oil with δP 28 ppm which crystallized to give 0.6 g (IVa). The total yield of (IVa) was 5.2 g (88.6%).

b) Equimolar amounts of (I) and (III) were mixed at ~20°C. An exothermal effect was observed. The ^{31}P NMR spectrum of the reaction mixture has a signal with δP 28 ppm corresponding to phosphonate (IVb) [1].

c) A sample of 3.1 mg (0.05 mmole) acetic acid was introduced into an ampul containing 0.2 g (1 mmole) (I) and 0.2 g (1 mmole) (II). A sample of 0.2 g (II) maintained for ~12 h in the air was added to 0.2 g (1 mmole) (I) in a second ampul. The ampuls were sealed, heated for 20 min at 70°C, and their ^{31}P NMR spectra were taken (see text).

CONCLUSIONS

The reactions of amides of P(III) acids with N-acetoxymethylamides of carboxylic acids with the formation of products of the substitution of the amide group was found to be catalyzed by acids.

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ELECTROCHEMICAL BROMINATION OF DMSO IN ALKALINE MEDIA: THE SYNTHESIS OF 1,1,1-TRIBROMO- AND HEXABROMODIMETHYLSULFONES

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The reaction of DMSO with chlorine and bromine in aqueous media leads to oxidation of the organic substrate. In acid media, the reaction product is dimethylsulfone [1]. In slightly basic media, the completely halogenated derivative $(CX_3)_2SO_2$ is obtained (the yield for X = Br is 70% [2]).

The electrolysis of aqueous bromide solutions containing DMSO leads to the same products. The yield of $(CBr_3)_2SO_2$ (I) in this case, however, is less than upon chemical bromination and decreases with increasing alkali content in the electrolyte, which corresponds to the evidence for the cleavage of (I) by concentrated alkali [3]. The use of sodium carbonate instead of alkali in the electrosynthesis permits an increase in the yield of (I) to 50%. However, carrying out the reaction in the presence of $NaHCO_3$ unexpectedly led to previously unreported 1,1,1-tribromodimethylsulfone $CBr_3SO_2CH_3$ (II). The structure of this product was confirmed by convergent synthesis by the oxidation of CBr_3SCH_3 using CrO_3 in acetic acid. Sulfone (I) is formed, in all likelihood, as the result of purely bulk bromination of DMSO through a base catalysis mechanism by analogy to the electrosynthesis of $CHBr_3$ from acetone [4]. In both cases, the yield of the bromo derivatives increases with decreasing temperature and increasing substrate concentration. The same pH range is optimal. Sodium bicarbonate apparently cannot have a specific effect on the bromination reaction which proceeds in the electrolyte bulk, since $NaHCO_3$ has been used to optimize the bromination of various sulfur compounds to give (I) [3, 5], while the formation of "unsymmetrical" derivatives, i.e., products containing bromine at only one methyl group, was not observed. Hence, we may assume that the electrochemical synthesis of (II) proceeds through the formation of an intermediate, apparently a complex of DMSO with halogens [6] in the adsorption layer and the subsequent electrochemical oxidation of this intermediate.

EXPERIMENTAL

The PMR spectra were obtained on a Tesla BF-467 spectrometer at 60 MHz with TMS as the internal standard in CCl_4 solution. A sample of CBr_3SCH_3 which is the starting compound for the convergent synthesis of (II) was obtained according to Truce [7] and Boberg [8].

Electrosynthesis of Hexabromodimethylsulfone (I). A 600 ml aqueous solution containing 120 g KBr, 100 g $Na_2CO_3 \cdot 10H_2O$, and 23.4 g DMSO was added to a diaphragmless electrolyzer containing a 100-cm^2 ruthenium–titanium oxide anode and 20-cm^2 stainless steel cathode and a 6 A current was passed at 7-10°C (19 A·h was introduced). The precipitate was filtered off, dried over P_2O_5, and extracted with benzene. The solvent was distilled off in vacuum to give 14.4 g (50% current yield) (I), mp 135°C [5]. When the reaction was carried out in the presence of 5.6 g KOH instead of Na_2CO_3, the yield of (I) is 6.8 g (24% current yield).

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