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Abstract

Full Text

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Esters of Phosphinic Acids with Diacetylenic Radicals

(Presented by Academician B. A. Arbuzov, 14 VI 1963)

Recently we showed that α-bromoacetylenes are capable of reacting with trialkyl phosphites to form esters of phosphinic acids with acetylenic radicals ([1],[2]). This Arbuzov rearrangement proceeds especially readily when the acetylenic bond is conjugated with a multiple bond or with a benzene nucleus. Alkyl bromoacetylenes give the expected products in poor yield.

In the present communication it is shown that conjugated bromodiacetylenes also readily enter into the Arbuzov rearrangement, forming esters of phosphinic acids with diacetylenic radicals.

Fig. 1. IR transmission spectra: **1** —1-bromohexadiyne (Ib) (IKS-14 spectrophotometer, layer thickness 37 μ); **2** —1-diethylphosphonopentadiyne-1,3 (IIa); **3** —1-diethylphosphonohexadiyne-1,3 (IIb) (**2** and **3** on an IKS-15 spectrophotometer, layer thickness 7 μ)

The starting bromides were prepared by the action of potassium hypobromite on alkyldiacetylenes in an aqueous alkaline medium ([3]). Bromide (Ia) was described previously in the literature ([4]). In the IR spectrum of bromide (Ib) (Fig. 1, **1**), the triple bond joined to the bromine atom corresponds to an intense band of lowered frequency, 2141 cm^{-1}; the other triple bond corresponds to a band at 2245 cm^{-1}:

$$\underset{(I)}{\mathrm{R{-}C{\equiv}C{-}C{\equiv}C{-}Br}} + \mathrm{P(OC_2H_5)_3} \rightarrow \underset{(II)}{\mathrm{R{-}C{\equiv}C{-}C{\equiv}C{-}P(O)(OC_2H_5)_2}} + \mathrm{C_2H_5Br}$$

Fig. 2. NMR spectra: 1 —1-diethylphosphonopentadiyne-1,3 (IIa); 2 — 1-diethylphosphonohexadiyne-1,3 (IIb)

Figure 2: Fig. 2. NMR spectra: 1 —1-diethylphosphonopentadiyne-1,3 (IIa); 2 —1-diethylphosphonohexadiyne-1,3 (IIb)

(a) R = CH_3, (b) R = C_2H_5.

Esters of phosphinic acids with diacetylenic radicals (II) are colorless mobile liquids, more stable on storage than esters of phosphinic acids with enynic radicals ([2]). Their structure was confirmed by IR spectra and NMR spectra. In the IR spectra of the esters (IIa and IIb) (Fig. 1, **2**, **3**) intense bands at 1260, 1160, and 1030 cm^{-1} are observed, corresponding to the diethylphosphono group ([5]). The frequency of the triple bond in the spectra of both esters (2133 cm^{-1}) is lowered in comparison with that of

in ethers with enyne radicals (2175 cm^{-1} (⌒2)). The frequency of the other triple bond has the usual value (2235 and 3324 cm^{-1}).

In the NMR spectra of the esters (IIa and IIb) (Fig. 2, 1, 2), the diethylphosphonyl groups correspond to a triplet at 3.4 m.d. (standard—H_2O) and a multiplet at 0.7 m.d. (the additional splitting is caused by interaction of the methylene group with the phosphorus nucleus through oxygen). In the spectrum of ester (IIa), the methyl group at the triple bond corresponds to a doublet at 2.8 m.d. (J_{HP} 2.15 Hz); the methylene group at the triple bond in the spectrum of ester (IIb) corresponds to a quartet at 2.2 m.d., and the methyl group connected with it—to a triplet, superimposed on the signal of the methyl group of the ethoxy radical. The chemical shifts in the ^{31}P NMR spectra of both esters are +9 m.d. (external standard 85% H_3PO_4), which is characteristic of diethyl esters of acetylenylphosphinic acids (⌒2).

The presence of a distinct splitting of the signal of the protons of the methyl group in the NMR spectrum of ester (IIa), caused by interaction with the phosphorus nucleus separated by six bonds, may be of considerable interest for elucidating the mechanism of long-range spin-spin interaction. In the literature there are only a few data of this kind concerning proton-proton interaction (⌒6). Therefore it seemed interesting to us to compare the interaction constants in the spectra of the diacetylenic compounds obtained by us with the interaction constants for a number of other organophosphorus compounds, in which the phosphorus atom and the protons interacting with it are separated by an increasing number of bonds (from 1 to 6), and in which there are no groups containing protons or other magnetic nuclei between these atoms.

Fig. 2. NMR spectra: 1 —1-diethylphosphonopentadiyne-1,3 (IIa); 2 — 1-diethylphosphonohexadiyne-1,3 (IIb)

Table 1

Nuclear magnetic resonance of some organophosphorus compounds

Compound	Chemical shift, m.d. H^1	Chemical shift, m.d. P^{31}	Splitting, Hz J_{HP}	Distance, Å R_{HP}	φ
HPO $(OC_2H_5)_2$	−1.8	−3	687	1.4	–
CH_3PO $(OC_2H_5)_2$ (^7)	3.6	−30	17.5	2.4	−0.87
HC CPO $(OC_3H_7$-*iso*$)_2$ (^8)	1.65	–	12.0	4.05	−0.58
CH_3C CPO $(OC_2H_5)_2$	3.6	+9	7.4	5.0	−0.51
CH_3C CC CPO $(OC_2H_5)_2$	2.7	+9	2.15	7.6	−0.50

The data for J_{HP} given in Table 1 can be calculated by the formula

$$J_{HP} = \frac{A \cdot \gamma_H \gamma_P}{R_{HP}^3}(1+\varphi),$$

in which the first term reflects the direct dipole-dipole interaction between the nuclei, inversely proportional to the cube of the distance between them, and the second term represents all other types of interaction. The quantity φ is associated with the internal magnetic fields of molecules and indirectly depends on the dista-

between the nuclei. If $\varphi = 0$ is assumed for directly bonded nuclei, then the product $A \cdot \gamma_H \gamma_P$, characterizing the interaction at a distance of 1 Å, can be determined from the data for the first member of the series; it is equal to 1880. Beginning with the third member of the series, the value of φ assumes a practically constant value.

The possibility of a direct interaction of nuclear spins was pointed out already in the first studies on spin–spin splitting ([9,10]). However, theoretical consideration of simple examples showed that only a small part of the energy can be attributable to this type of interaction. In our case, owing to the anisotropy of the molecule and the substantial difference in the nature of the nuclei H^1 and P^{31}, the direct, non-averaging dipole–dipole interaction may be of substantial importance.

Experimental Part

1-Bromohexadiyne-1,3 (Ib). 3.9 g of ethyldiacetylene was stirred for 1.5 h with a solution of potassium hypobromite (prepared from 8 g of Br_2 and 20 g of KOH in 80 ml of water ([3])) at 10° in a nitrogen atmosphere. The emulsion was then allowed to settle, the lower layer was separated, dried with $CaCl_2$ (in a refrigerator), and distilled in vacuum. Yield 4.65 g (59%).

B.p. 29–31° (1.5 mm), d_4^{20} 1.3461, n_D^{20} 1.5552.

Found, %: Br 50.89; 50.83
$C_6H_5B_2$. Calculated, %: Br 59.92

1-Bromopentadiyne-1,3 ([4]) was prepared analogously and used without purification.

1-Diethylphosphonohexadiyne-1,3 (IIb). To 18 g of 1-bromohexadiyne-1,3, 21 g of triethyl phosphite was added in a nitrogen atmosphere. The temperature of the reaction mixture was regulated by external cooling (30–40°). After 2 h the reaction mixture was heated for 15 min on a boiling water bath and subjected to fractionation. After two distillations in vacuum, 14 g (57%) of substance was obtained.

B.p. 130–131° (∼ 0.5 mm), d_4^{20} 1.0215, n_D^{20} 1.4897.

Found, %: C 55.77; 55.84; H 7.00; 6.97; P 14.57; 14.40
$C_{10}H_{15}O_3P$. Calculated, %: C 56.07; H 7.00; P 14.46

1-Diethylphosphonopentadiyne-1,3 (IIa). From 1-bromopentadiyne-1,3 (prepared from 7 g of methyldiacetylene) and 16.6 g of triethyl phosphite, under conditions analogous to the preceding experiment, 5.7 g of ester was obtained.

B.p. 134.5–136.5° (1.5 mm), d_4^{20} 1.0753, n_D^{20} 1.4930.

Found, %: C 54.30; 54.13; H 6.54; 6.92; P 15.52; 15.35
$C_9H_{13}O_3P$. Calculated, %: C 54.46; H 6.50; P 15.48

The NMR spectra were recorded on a JNM-3 spectrometer at a frequency of 40 MHz; the NMR spectra of (P^{31}) were recorded on the same instrument with an "autodyne" type generator at a frequency of 16.8 MHz with a broadband amplifier.

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