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CERTAIN TRANSFORMATIONS OF

2-ALKYL(ARYL)-2-THIONO-1,2-OXA-4-PHOSPHOLENE DERIVATIVES

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2-Oxo-1,2-oxa-4-phospholene derivatives, the properties of which were studied in detail [1-3], react with aliphatic alcohols with ring opening and formation of γ -ketoalkyl phosphonates or phosphinates [1]. It could be expected that derivatives of 2-alkyl(aryl)-2-thiono-1,2-oxa-4-phospholene (TOPh), the preparation of which was reported earlier [4], will react with alcohols with formation of γ -ketoalkyl thionophosphinates.



UDC 542.91:547.1:118

Reaction of TOPh with alcohols occurs with evolution of heat. Elemental composition of the obtained compounds corresponds to products of addition of one equivalent of alcohol. However, from IR and ³¹P NMR spectral data, the obtained compounds are 2-alkyl(aryl)-2-thiono-5-alkoxy-1,2-oxaphospholanes, and not γ -ketoalkyl thionophosphinates. Consequently, alcohols react without opening of the phospholene ring and add to the double bond.



Absorption bands are absent in IR spectra of the obtained compounds in the region of $1600-1750 \text{ cm}^{-1}$, characteristic for C=C bond and C=O group. ³¹P NMR spectra have a singlet in the region of -106 to -126 ppm (relative to 85% H₃PO₄), which is characteristic for compounds containing a thiophosphoryl group of similar structure [4].

Aliphatic mercaptans add analogously to alcohols at the double bond of TOPh with formation of 2-alkyl-(aryl)-2-thiono-5-thioalkyl-1,2-oxaphospholanes.

Institute of Organic and Physical Chemistry, Kazan Branch of the Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 7, pp. 1589-1592, July, 1976. Original article submitted July 9, 1975.

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Results of the acidic and basic hydrolyis of these compounds also confirm the structure of 2-alkyl-2thiono-5-alkoxy (thioalkyl)-1,2-oxaphospholanes. Thus, we isolated ethyl- $(\alpha, \alpha$ -dimethyl- γ -ketobutyl) phosphinic acid [1] upon acidic hydrolysis of 2-ethyl-2-thiono-3,3,5-trimethyl-5-ethoxy (thioethyl)-1,2-oxaphospholanes



Its IR spectrum was identical to the spectrum of ethyl- $(\alpha, \alpha$ -dimethyl- γ -ketobutyl)phosphinic acid obtained by the method of [3], i.e., not only saponification of the alkoxyl(thioalkyl) group and opening of the oxaphospholene ring but also cleavage of H₂S occurred during hydrolysis. The latter fact agrees with data of [5].

The difference in behavior of TOPh and 2-oxo-1,2-oxa-4-phospholene in relation to such nucleophilic reagents as alcohols and mercaptans is explained as follows: Substitution of the phosphoryl group by a thio-phosphoryl group evidently hinders nucleophilic substitution on the tetrahedral P atom and together with this facilitates occurrence of reaction at the double bond.

We obtained interesting results during the study of the reaction of TOPh with chloral: their desulfurization and transformation to 2-alkyl(aryl)-2-oxo-1,2-oxa-4-phospholenes occur in this case. Constants of the obtained compounds coincide with data of [2, 6]. Values of δ_{31} also agree with the structure of the obtained compounds.

Reaction of thiono-4-phospholene derivatives with chloral can be presented by the scheme proposed for the reaction of thione phosphate with chloral [7].



Formation of the phosphonium betaine occurs at the first stage of the reaction. Desulfurization occurs intramolecularly via formation of an unstable compound with a four-membered ring as the intermediate product.

EXPERIMENTAL

<u>2-Ethyl-2-thiono-3,5-dimethyl-5-ethoxy-1,2-oxaphospholane (II)</u>. Analogously from 15.2 g of 2-ethyl-2-thiono-3,5-dimethyl-1,2-oxa-4-phospholene and 4 g of ethanol was obtained 10 g (54.6%) of (II), bp 77° (0.04 mm), n_D^{20} 1.5010, d_4^{20} 1.0588, δ_{31} P -119 ppm. Found: P 13.90; S 14.37%; MR 61.82. $C_9H_{19}O_2PS$. Calculated: P 13.94; S 14.43%; MR 61.28.

 $\frac{2-\text{Ethyl}-2-\text{thiono}-3,3,5-\text{trimethyl}-5-\text{ethoxy}-1,2-\text{oxaphospholane (III)}}{3,3,5-\text{trimethyl}-1,2-\text{oxa}-4-\text{phospholene by reaction with 4.4 g of ethanol was obtained 18 g (79.3\%) of (III)},$

bp 75° (0.03 mm); n_D^{20} 1.5022; d_4^{20} 1.0588; $\delta_{31}P$ -122 ppm. Found: P 13.52; S 13.49%; MR 65.88. $C_{10}H_{21}O_2PS$. Calculated: P 13.21; S 13.57%; MR 65.89.

<u>2-Ethyl-2-thiono-3,3,5-trimethyl-5-butoxy-1,2-oxaphospholane (IV)</u>. From 8.5 g of 2-ethyl-2-thiono-3,3,5-trimethyl-1,2-oxa-4-phospholene and 3.3 g of n-butanol was obtained 7.5 g (62.7%) of (IV), bp 80-81.5° (0.003 mm); n_D^{20} 1.4977; d_4^{20} 1.0301. Found: P 11.68; C 54.65; H 9.52%; MR 75.19. $C_{12}H_{25}O_2PS$. Calculated: P 11.71; C 54.50; H 9.53%; MR 75.13.

 $\frac{2-\text{Ethyl}-2-\text{thiono}-4,5-\text{dimethyl}-5-\text{propoxy}-1,2-\text{oxaphospholane (V)}. \text{ Reaction of 17.6 g of 2-ethyl}-2-\text{thiono}-4,5-\text{dimethyl}-1,2-\text{oxa}-4-\text{phospholene with 6 g of n-propanol yielded 16 g (67.8\%) of (V), bp 87-88° (0.02 mm); n_D^{20} 1.4980; d_4^{20} 1.0494. \text{ Found: P 12.90; S 13.40\%; MR 66.00. } C_{10}H_{21}O_2PS. \text{ Calculated: P 13.15; S 13.57\%; MR 65.89.}$

 $\frac{2 - \text{Ethyl} - 2 - \text{thiono} - 3.5 - \text{dimethyl} - 5 - \text{ethoxy} - 1.2 - \text{oxaphospholane (VI)}. \text{ From 13 g of 2 - ethyl} - 2 - \text{thiono} - 3.5 - \text{dimethyl} - 1.2 - \text{oxa} - 4 - \text{phospholene and 4.5 g of n-propanol was obtained 10 g (57.5\%) of (VI), bp 82° (0.04 mm); n_D^{20} 1.4970; d_4^{20} 1.0473; \delta^{31} \text{ p} - 120 \text{ ppm}. \text{ Found: P 12.85; S 14.08\%; MR 66.02. C}_{10}\text{H}_{21}\text{O}_2\text{PS. Calculated: P 13.15; S 13.57\%; MR 65.89.}$

 $\frac{2 - \text{Phenyl} - 2 - \text{thiono} - 3,3,5 - \text{trimethyl} - 5 - \text{propoxy} - 1,2 - \text{oxaphospholane (VII).}}{2 - \text{phenyl} - 2 - \text{thiono} - 3,3,5 - \text{trimethyl} - 1,2 - \text{oxa} - 4 - \text{phospholene and 3 g of n-propanol was heated with stirring for 3 h at 100°.}$ Distillation separated 8.5 g (57.0%) of (VII), bp 140° (0.02 mm); n_D^{20} 1.5460; d_4^{20} 1.1013; δ_{31} -113 ppm. Found: P 10.10; S 10.79%; MR 85.76. $C_{15}H_{23}O_2$ PS. Calculated: P 10.39; S 10.75%; MR 85.93.

 $\frac{2-\text{Ethyl-2-thiono-3,5-dimethyl-5-thioethyl-1,2-oxaphospholane (VIII).}{2-\text{Cyntheorem}} \text{ A mixture of 8.4 g of 2-ethyl-2-thiono-3,5-dimethyl-1,2-oxa-4-phospholene and 3 g of ethyl mercaptan was heated in a tube for 4 h at 130°.} \text{ Distillation in vacuum separated 7.2 g (63.1%) of (VIII), bp 110° (0.02 mm); n_D^{20} 1.5500; d_4^{20} 1.1146; \delta_{31} \text{ p} -88 \text{ ppm}. Found: P 12.98; S 26.95\%; MR 68.10. C_9H_{19}OPS_2. Calculated: P 13.00; S 26.91\%; MR 67.63.}$

2-Ethyl-2-thiono-4,5-dimethyl-5-thioisopropyl-1,2-oxaphospholane (X). From 11 g of 2-ethyl-2-thiono-4,5-dimethyl-1,2-oxa-4-phospholene and 4.7 g of isopropyl mercaptan was obtained 8.5 g (54.1%) of (X), bp 85° (0.015 mm); n_D^{20} 1.5640; d_4^{20} 1.338; δ_{31} p -91 ppm. Found: P 12.64; S 25.45%; MR 72.39. C₁₀H₂₁OPS₂. Calculated: P 12.28; S 25.42%; MR 72.25.

2-Phenyl-2-thiono-3,3,5-trimethyl-5-thioethyl-1,2-oxaphospholane (XII). Analogously to the experiment described above from 7.9 g of 2-phenyl-2-thiono-3,3,5-trimethyl-1,2-oxa-4-phospholene and 2 g of ethyl mercaptan was obtained 5.4 g (54.5%) of (XII), bp 153° (0.01 mm); n_D^{20} 1.5910; d_4^{20} 1.1648; δ_{31} p -74 ppm. Found: P 10.32; S 21.20%; MR 87.12. C₁₄H₂₁OPS₂. Calculated: P 10.32; S 21.35%; MR 87.66.

Acidic Hydrolysis of (III) and (XI). We heated 7 g of (III) or (XI) with a threefold excess of 10% HCl for 6 h. The solution was evaporated and the residue was extracted with benzene and dried with Na₂SO₄. After removal of benzene the residue crystallized. Recrystallization from ether yielded correspondingly 4.2 or 4.8 g (73.6 or 82.8%) of ethyl(α , α -dimethyl- γ -ketobutyl)phosphonic acid with mp 111°; mixed sample with the acid obtained by the method of [3] did not show a melting point depression. Found: C 49.55; H 9.21; P 15.75%. C₈H₁₇O₃P. Calculated: C 49.97; H 8.84; P 16.07%.

Basic Hydrolysis of (III). We heated 10 g of (III) with a threefold amount of 10% NaOH at 130° for 6 h. The solution was neutralized with HCl, evaporated, and the residue was dissolved in methanol. The NaCl was filtered and the filtrate was evaporated again. The residue was recrystallized from an acetone - methanol mixture. We obtained 6.7 g (68.3%) of the Na salt of ethyl(α , α -dimethyl- γ -ketobutyl)thiophosphinic acid with mp 222°. Found: C 41.63; H 6.84; P 13.86; S 13.76%. C₈H₁₆O₂PSNa. Calculated: C 41.72; H 6.99; P 13.44; S 13.91%.

<u>Reaction of 2-Ethyl-2-thiono-3,3,5-trimethyl-1,2-oxa-4-phospholene with Chloral.</u> To 30 g of chloral (fourfold excess) slowly was added 9.6 g of oxa-4-phospholene; the temperature of the mixture increased to 80°. After boiling the reaction mixture (1 h) the excess chloral was distilled and the residue was distilled

in vacuum. We obtained 7.9 g (90.8%) of 2-ethyl-2-oxo-3,3,5-trimethyl-1,2-oxa-4-phospholene [3], bp 59° (0.04 mm); n_D^{20} 1.4760; d_4^{20} 1.0588; $\delta_{31}P$ -76 ppm.

 $\frac{\text{Reaction of } 2-\text{Ethyl-2-thiono-4,5-dimethyl-1,2-oxa-4-phospholene with Chloral.}}{\text{of oxa-4-phospholene and 30 g of chloral was obtained 7.1 g (86.2%) of 2-ethyl-2-oxo-4,5-dimethyl-1,2-oxa-4-phospholene [2], bp 73° (0.01 mm); n_D^{20} 1.4840; d_4^{20} 1.0985; \delta_{31} p = 70 ppm.}$

 $\frac{\text{Reaction of } 2-\text{Phenyl-2-thiono-3,3,5-trimethyl-1,2-oxa-4-phospholene with Chloral. From 11.9 g of oxa-4-phospholene and 30 g of chloral was obtained 9 g (81.0%) of 2-phenyl-2-oxo-3,3,5-trimethyl-1,2-oxa-4-phospholene [6], bp 130° (0.06 mm); n_D^{20} 1.5440; d_4^{20} 1.1296; \delta_{31}p - 60 ppm.$

CONCLUSIONS

1. 2-Alkyl(aryl)-2-thiono-1,2-oxa-4-phospholenes react with alcohols and mercaptans without ring opening, forming products of addition at the double bond.

2. 2-A lkyl(aryl)-2-thiono-1, 2-oxa-4-phospholenes react with chloral with formation of <math>2-a lkyl(aryl)-2-oxo-1, 2-oxa-4-phospholenes.

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REACTIONS OF π -CYCLOPENTADIENYL IRON DICARBONYL

DIMERS WITH β -IODACRYLIC ACID AND ITS ESTERS

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 UDC 542.91:541.49:547.514.

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In the preceding works [1, 2] the preparation of trans- σ -(β -acylvinyl)cyclopentadienyl iron carbonyl complexes by the direct reaction of trans- β -iodovinylketones with the [C₅H₅Fe(CO)₂]₂ (I) dimer was reported:

trans $-RCOCH = CHI + [Fe(CO)_2C_5H_5]_2 \rightarrow trans - RCOCH = CHFe(CO)_2C_5H_5 + IFe(CO)_2C_5H_5$

Furthermore, it was shown that other dimeric complexes of the transition metals can be used successfully in this reaction, specifically $[\text{Re}(\text{CO})_5]_2$ [2].

In this article we study the problem of extending this reaction to various derivatives of vinyl iodide, and also their stereochemistry. In attempts at using organic compounds containing the iodine atom on the sp^2 -hybridized carbon atom (trans-diiodoethylene, m-diiodobenzene, and acetyl iodide) in reactions with (I), the

Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 7, pp. 1592-1596, July, 1976. Original article submitted July 4, 1975.

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