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SUBSTITUTED 1-PHOSPHABICYCLO[3.2.0]HEPT-4-ENES

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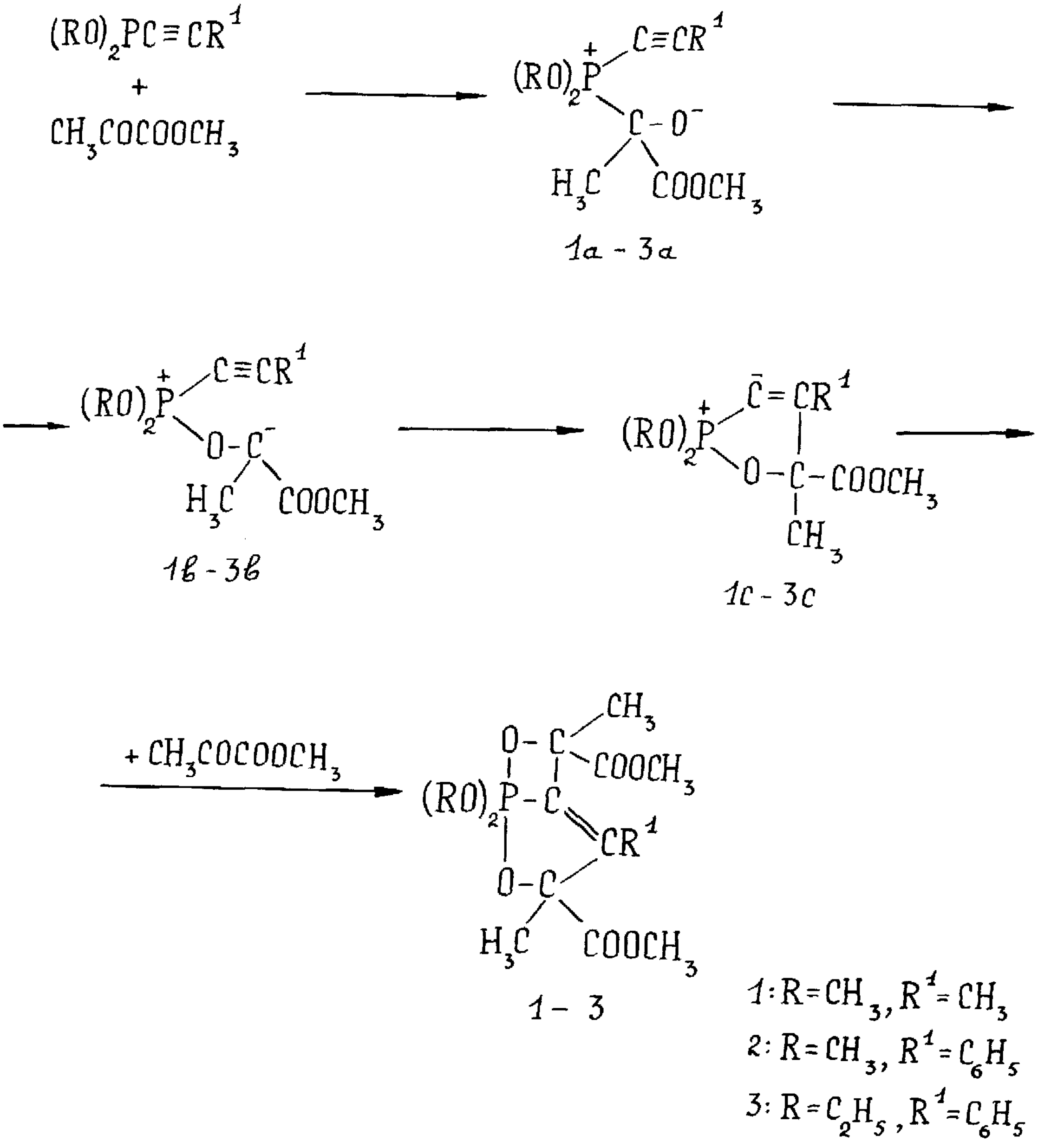
Abstract.The interaction between dialkyl alkynylphosphonites and pyruvic acid methyl ester in boiling benzene afforded 1,1-dialkoxy-3,6-dimethyl-3,6-di(methoxycarbonyl)-4R-2,7-dioxa-1-phosphabicyclo[3.2.0]hept-4-enes.

Trialkyl phosphites and dialkyl phosphonites react with pyruvic acid esters to form 1,3,2-dioxaphospholanes at 0 ÷ -10°C and at 100°C the mixtures of 1:1 and 1:2 adducts of the open chain or dioxaphospholane structure respectively [1,2].The interaction between dialkyl isocyanatophosphites, hetero-α,β-unsaturated P(III)compounds, and pyruvic acid esters leads to 1:1 heterocyclic adducts - substituted $1,4,3,\lambda^5$-oxazaphospholidines resulting from the involvment in the reaction both phosphorus atom and isocyanate multiple bond [3].

The results obtained show, that in contrast to isocyanatophosphites,dialkyl phosphonites containing triple C≡C bond react with pyruvic acid methyl ester to form 1:2 adducts - 1,1-dialkoxy-3,6-dimethyl-3,6-di(methoxycarbonyl)-4R-2,7-dioxa-1-phosphabicyclo[3.2.0]hept-4-enes (1-3). The latter are representatives of new type unsaturated heterocycles containing phosphorus.

The reaction are likely to start with the nucleophilic attack of a phosphorus atom to the carbon of a carbonyl group.The resulting bipolar ion (1a-3a) transforms into ion (1b-3b) in a manner of phosphonate-phosphate rearrangement. The carbanion of the bipolar ion (1b-3b) adds to β-carbon atom of the activated C≡C bond to give cyclic ylide (1c-3c). Addition of the second molecule of pyruvic acid ester leads to ylide stabilization.In a similar manner the interaction of diphenylvinylphosphine with hexafluoroacetone is known to occur [4].

The reactions of dialkyl alkynylphosphonites with pyruvic acid methyl ester were conducted under the reagent ratios both 1:1 and 1:2. In either case identical compounds have been formed. Using a standard procedure 0.05 mole of pyruvic acid methyl ester in 10 ml of benzene was added dropwise to the solution of 0.05 mole dialkyl alkynylphosphonite in 15 ml of boiling benzene under argon atmosphere for 20-30 min. The reaction mixture was boiled with reverse condenser, the solvent and the phosphonite excess being removed in vacuum. The residue slowly crystallizing while standing was recrystallized from the mixture of benzene-hexane (1:1).



1a - 3a

1в - 3в

1c - 3c

1 - 3

1: $R=CH_3, R^1=CH_3$
2: $R=CH_3, R^1=C_6H_5$
3: $R=C_2H_5, R^1=C_6H_5$

Elemental analysis data as well as those of ^{1}H NMR spectra integral intensity signals show the formation of 1:2 adducts.

The compound structure (1-3) was determined by the infra-red, ^{1}H- and ^{31}P NMR spectroscopy as well as by x-ray structure analysis (Table).

Table. Substituted 1-phosphabicyclo[3.2.0]hept-4-enes (1-3) yields, melting points and spectral characteristics.

Compound No	Yield (%)	Mp °C	IR, cm^{-1}		^{31}P NMR (relatively 85% H_3PO_4, δ, ppm
			C=C	C=O	
1	65	93-94.5	1650	1750	-11.7
2[b]	74	98-101	1680	1738	-10.7
3[b]	80	103-105	1680	1740	-13.3

Table (to be continued)

^{1}H NMR, in C_6D_6 (80 MHz)				
RO		R^1	$CH_3OC(O)$	-C-CH_3
δ, ppm	^{3}J(PH), Hz, ppm	δ, ppm	δ, ppm	δ, ppm
3.67 d	14.0	1.67 d [a]	3.17 s	1.40 s
3.62 d	14.0		3.25 s	1.50 s
3.73 d	14.0	7.10 m	3.20 s	1.75 s
3.55 d	13.8		3.23 s	1.84 s
1.14 m		7.15 m	3.16 s	1.70 s
(CH_3)			3.21 s	1.82 s
4.14 m				
(OCH_2)				

a) ^{4}J(PH) 3.5 Hz

b) NMR characteristics are given for the prevailing stereoisomer.

No C≡C bond absorption was observed in i.r. spectrum of the substituted 1-phosphabicyclo[3.2.0]hept-4-enes (1-3) but there was intensive absorption of the C=O group (1738-1750 cm^{-1}) and middle intensity absorption of the

C=C bond (1650-1680 cm^{-1}). In ^{31}P NMR spectra the chemical shift of phosphorus is placed in the comparatively mild field $\delta\,^{31}P$ $-11 \div -13$ ppm (high field relatively to 85% H_3PO_4), which is not quite typical for the pentacoordinated phosphorus atom. According to ^1H NMR spectra the compound (1) is obtained as one stereoisomer while phosphabicycloheptenes (2,3) as two stereoisomers, one of them strongly dominating. The NMR $^1H\{^{31}P\}$ signal integration indicates that there are two magnetically non-equivalent alkoxy groups at a phosphorus atom. The chemical shift of protons in these groups and $^3J(PH)$ have standard values. Non-equivalent methoxycarbonyl groups are observed as two singlets of the same intensity in the compound (1), while in the compound (2,3) they give two pairs of singlets with 3.16-3.25 ppm. The proton signals of methyl groups, bounded with the cyclic carbon atoms are presented in the similar way. In the Table are given NMR characteristics for the prevailing stereoisomer.Using 1,1-dimethoxy-3,6-di(methoxycarbonyl)-2,7-dioxa-3,4,6-trimethyl-1-phosphabicyclo[3.2.0]hept-4-ene (1) the compound structure was proved by x-ray crystal analysis.The molecule of this compound was found to contain the bicycle frame of the substituted bicyclo-[3.2.0]heptene. The phosphorus atom is pentacoordinated. The oxygen atoms of methoxy groups are positioned equatorially while the oxygen atoms involved in a cycle axially. More data of x-ray crystal analysis will be reported later.

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