CONCLUSIONS

1. The thermal and photoinduced reactions of Cp_2MMMe_2 (M = Ti, Zr) with Et_3EH (E = Ge, Sn) produce 1 mole of Et_6E_2, 2 moles of methane, and 1 mole of Cp_2M. Compounds with the general formula $Cp_2M(EEt_3)_2$ could not be obtained.

2. The exchange reaction of Cp_2MCl_2 (M = Ti, Zr) with Et_3ELi (E = Ge, Sn) in THF or toluene at −40°C results in the formation of compounds with the general formula $Cp_2M(EEt_3)_2$, which decompose at 20°C, yielding 1 mole of Et_6E_2 and an adduct of the biscyclopentadienyl derivative of the metal with THF.

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1,3-DIPOLAR CYCLOADDITION OF C-BENZOYL-N-PHENYL- AND C,N-DIPHENYLNITRONES TO β-SUBSTITUTED VINYLPHOSPHONATES

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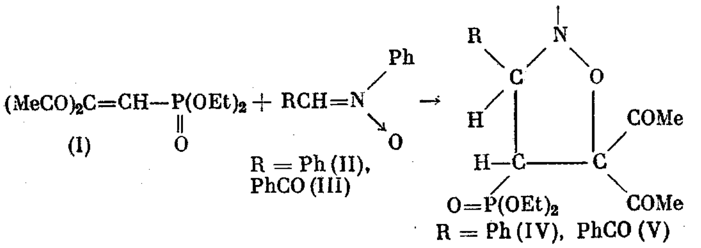
UDC 542.91:547.1'118

It has previously [1, 2] been shown that C,N-diphenyl- and C-benzoyl-N-phenylnitrones react with diethyl vinylphosphonates having strong electron-acceptor substituents (CN, $COOCH_3$) in the β position to form 4-phosphonoisoxazolidines with a trans–trans configuration.

In the present work we investigated the orientation of the cycloaddition of vinylphosphates with various types of substituents in the β position.

Diethyl β,β-diacetylvinylphosphonate (I) readily reacts with C,N-diphenylnitrone (II) and C-benzoyl-N-phenylnitrone (III) at room temperature to form crystalline 2,3-diphenyl-4-diethoxyphosphono-5,5-diacetylisoxazolidine (IV) and 2-phenyl-3-benzoyl-4-diethoxyphosphono-5,5-diacetylisoxazolidine (V):



(I)

R = Ph (II), PhCO (III)

R = Ph (IV), PhCO (V)

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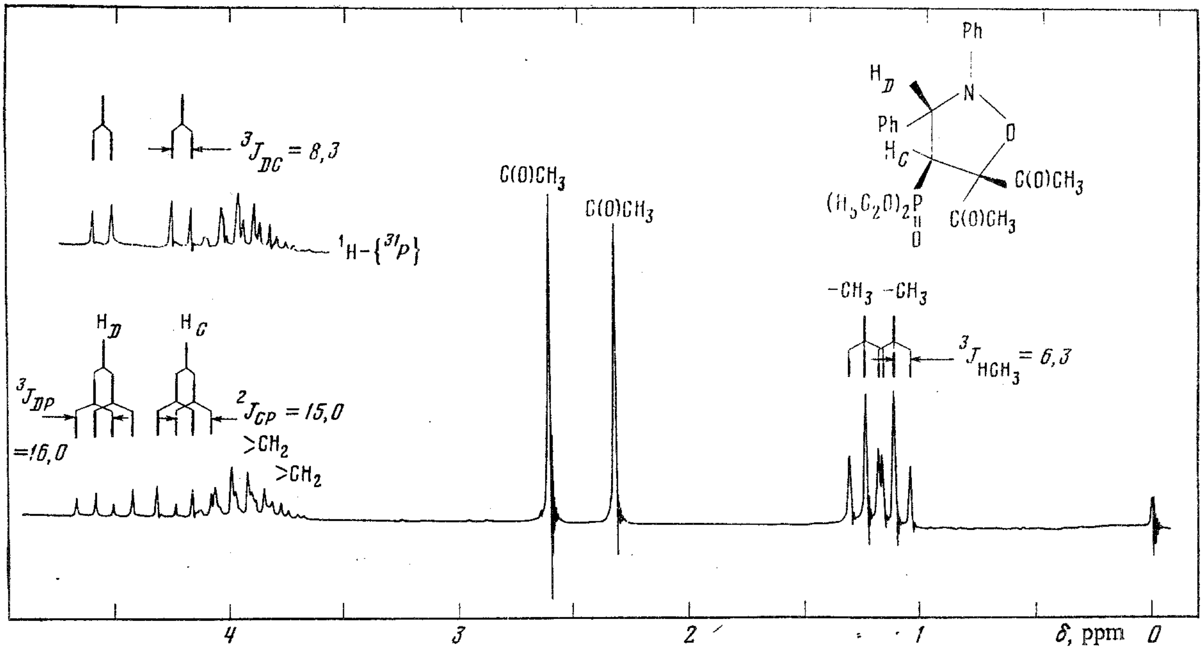


Fig. 1. Proton magnetic resonance and $^1H-\{^{31}P\}$ double resonance spectra of isoxazolidine IV, 5% solution in C_6H_6, 27°C.

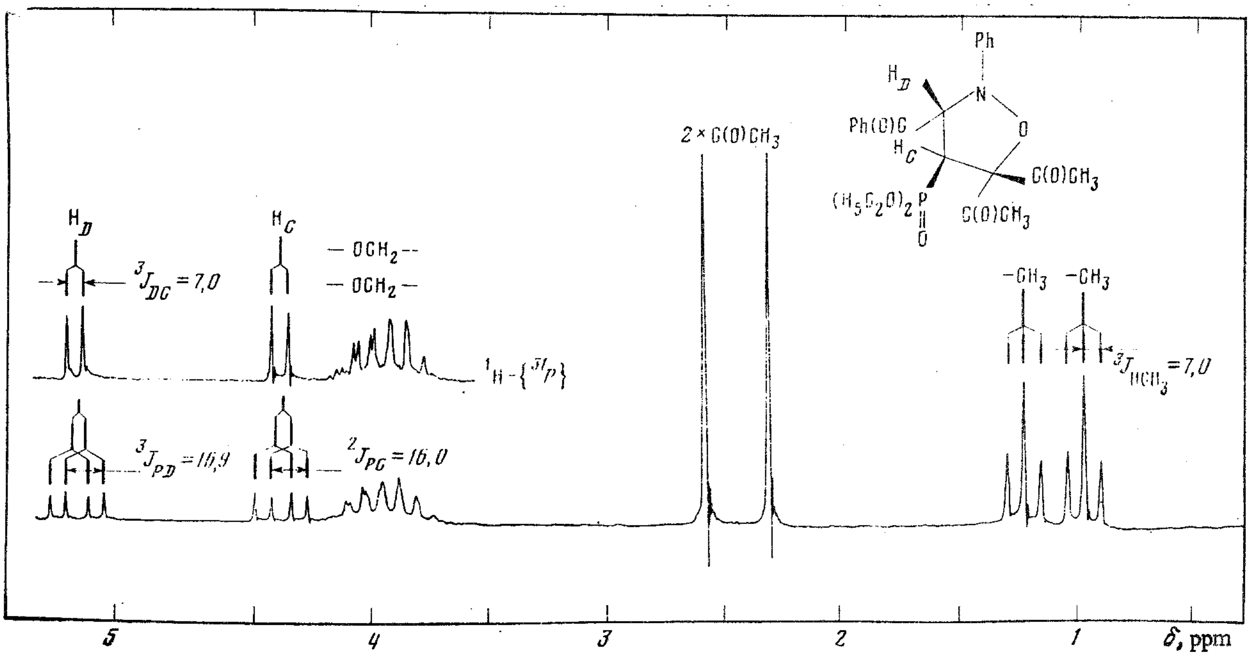


Fig. 2. Proton magnetic resonance and $^1H-\{^{31}P\}$ double resonance spectra of isoxazolidine V, 5% solution in $CHCl_3$, 27°C.

The structure of isoxazolidines IV and V was proved by the data from elemental analysis and the IR and NMR spectra. The values of δ ^{31}P, viz., –23 for IV and –27 ppm for V, demonstrate the phosphonate surroundings of the P atom. The IR spectra of IV and V have the following absorption bands (ν, cm^{-1}): 1030, 1060 vs (P–O–C), 1180 m (P–O–Et), 1260 (P=O), 1490, 1600 m (Ph), 1713, 1735 vs (C=O in IV), 1687, 1703, 1730 vs (C=O in V). The ^1H NMR and $^1H-\{^{31}P\}$ NMDR spectra prove that the phosphorus-containing fragment $P(O)(OEt)_2$ is located on the ^4C atom of the heterocycle, since the proton on the C^3 atom (H_D) is manifested in the PMR spectrum in the form of four lines with a center at δ 4.53 in the case of IV (Fig. 1) and 5.17 ppm in the case of V (Fig. 2), which are simplified to doublets in the $^1H-\{^{31}P\}$ double resonance spectra. The vicinal constants $^3J_{CD} = 8.3$ and $^3J_{PD} = 16.0$ Hz for IV and $^3J_{CD} = 7.0$ and $^3J_{PD} = 16.9$ Hz for V are similar to those for the previously investigated [1] trans-2,3-diphenyl-4-diethoxyphosphono-5-cyanoisoxazolines (and carbomethoxy analogs). These findings allow us to assign a trans orientation to the substituents on C^3 and C^4 in IV and V.

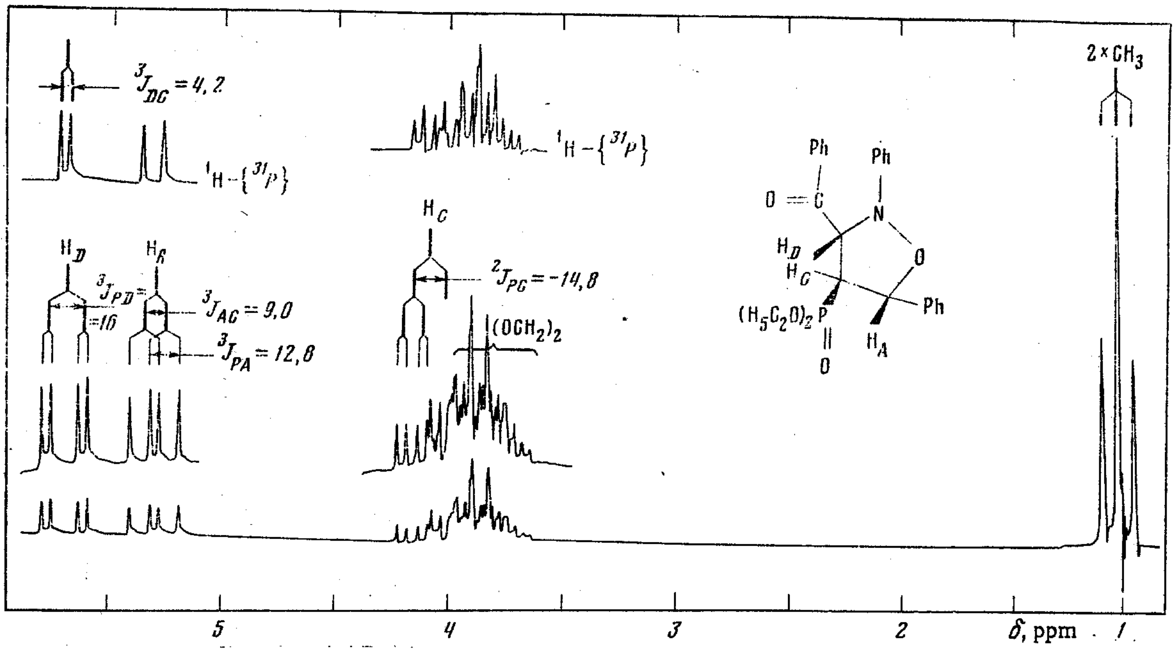
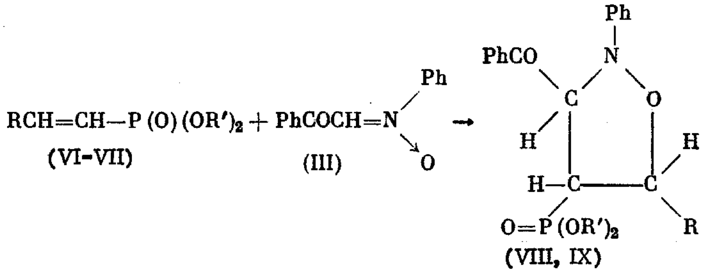


Fig. 3. Proton magnetic resonance and $^1H-\{^{31}P\}$ double resonance spectra of isoxazolidine VIII, 5% solution in C_6H_6, 28°C.

The dipolarophiles [diethyl β-phenylvinylphosphonate (VI) and dimethyl β-ethoxyvinylphosphonate (VII)] were found to be less reactive in the reactions with the nitrones than the β,β-disubstituted ester (I). Ester VI does not react with nitrone II even upon boiling in xylene for 3 h. The thermogram of the reaction mixture of VI with II shows an exothermic effect with an initial temperature of 137°C and a temperature at the maximum equal to 160°C. Ester VI reacts with nitrone III at ∿20°C.

Ester VII is even less reactive. The thermogram of the reaction mixture of VII with nitrone III has an exothermic effect with an initial temperature of 65°C and a temperature at the maximum equal to 93°C. Thus, as the electrophilic nature of the double bond is enhanced, the reactivity of the vinylphosphonates with respect to nitrones increases.

The 1,3-dipolar cycloaddition of C-benzoyl-N-phenylnitrone (III) to VI and VII produced the crystalline compounds 2,5-diphenyl-3-benzoyl-4-diethoxyphosphonoisoxazolidine (VIII) and 2-phenyl-3-benzoyl-4-dimethoxyphosphono-5-ethoxyisoxazolidine (IX). The direction of the addition of III to VI does not depend on the conditions under which the experiment is carried out. Isoxazolidine VIII forms both at room temperature and upon heating.



$RCH{=}CH{-}P(O)(OR')_2 + PhCOCH{=}N(Ph){\rightarrow}O \rightarrow$

(VI-VII) (III) (VIII, IX)

R = Ph, R' = Et (VI), R = Ph, R' = Et (VIII), R = EtO, R' = Me (VII) R = OEt, R' = Me (IX)

The structure of products VIII and IX was proved by the data from the elemental analysis, as well as the IR and NMR spectra. The chemical shifts δ ^{31}P, viz., –27 for VIII and –25 ppm for IX, are evidence of the phosphonate surroundings of the phosphorus. The ^1H NMR spectra and the $^1H-\{^{31}P\}$ double resonance spectra of VIII and IX prove that the P=O group is located at C^4, since the H_D proton is manifested in the ^1H NMR spectrum in the form of our lines with δ 5.69 (VIII) and 5.61 ppm (IX), which are simplified to a doublet in the $^1H-\{^{31}P\}$ double resonance spectrum (Fig. 3). The trans–trans configuration of the substituents on the three chiral centers C^3, C^4, and C^5 is proved by the values of the vicinal constants $^3J_{HH}$ and $^3J_{PCCH}$ presented in Table 1. The conclusions regarding the configuration were drawn on the basis of the analysis of the spin–spin coupling constants presented in [1, 3].

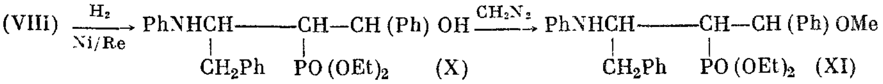
TABLE 1. Chemical Shifts and Spin—Spin Coupling Constants of Isoxazolidines VIII and IX

Compound	δ¹H, ppm			J, Hz			
	H_A	H_C	H_D	$^3J_{AC}$	$^3J_{CD}$	$^3J_{PD}$	$^3J_{PA}$
(VIII)	5,29	4,00	5,69	9,0	4,2	16,0	12,8
(IX)	4,97	3,90	5,61	7,3	3,5	17,2	10,0

The anomalously large values of the chemical shift of the proton on C^4 (H_C), which reach a value of δ 4.39 ppm in V, should be noted. A similar effect has been described for isoxazolidines containing an esteric substituent instead of a phosphono group [4].

In all the cases we studied of the cycloaddition of nitrones to β-substituted vinylphosphonates with different degrees of electrophilic character of the double bond, we obtained isoxazolidines with the same orientation of the phosphono group in the ring. The electronic factors are apparently not responsible for the orientation of the cycloaddition. In the example case of isoxazolidine VIII, high thermal stability was demonstrated, the decomposition of VIII beginning only at 210°C.

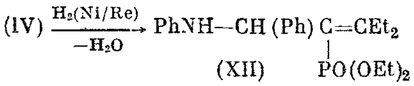
The hydrogenation of isoxazolidines on Raney Ni results in the cleavage of the ring at the N—O bond, since the IR spectra of the hydrogenation products show a broad band in the 3200-3450-cm^{-1} region (NH, OH). The hydrogenation of VIII followed by methylation by diazomethane clearly takes place according to the following scheme:



$$\text{(VIII)} \xrightarrow[\text{Ni/Re}]{H_2} \underset{CH_2Ph}{PhNHCH}—\underset{PO(OEt)_2}{CH}—CH(Ph)OH\ \text{(X)} \xrightarrow{CH_2N_2} \underset{CH_2Ph}{PhNHCH}—\underset{PO(OEt)_2}{CH}—CH(Ph)OMe\ \text{(XI)}$$

Aminoalcohol X and ether XI were isolated in the form of crystalline compounds. Their structure was proved by the data from the elemental analysis and the IR spectra. The IR spectrum of (X) has the following bands (ν, cm^{-1}): 1030, 1060 vs (P—O—C), 1160 m (P—O—C_2H_5), 1220 s, br (P=O), 1500, 1600 s (C_6H_5), 3300-3400 vbr (NH, OH). The IR spectrum of XI contains the following absorption bands (ν, cm^{-1}): 1020, 1040 vs (P—O—C), 1160 w (P—O—C_2H_5), 1243 s (P=O), 1511, 1600 m (C_6H_5), and 3310 narrow (NH). The PMR spectra were found to be difficult to interpret because of the broadening of the signals, which was probably due to the formation of intermolecular assoiates and inter- and intramolecular hydrogen bonds.

In the case of the hydrogenation of IV, V, and IX, it was not possible to obtain analytically pure products. They were isolated in the form of powders, which were not methylated by diazomethane. The IR spectra of the hydrogenation products and of the products of the subsequent methylation were totally identical. The IR spectra contain the following absorption bands (ν, cm^{-1}): 1030, 1060 vs (P—O—CO), 1165 m (P—O—C_2H_5), 1220 s (P=O), 1500, 1600 s (C_6H_5), 1635 m (C=C), 3400 br (NH and OH region). The presence of $\nu_{C=C}$ suggests that dehydration of the hydrogenation products takes place during the reaction:



$$\text{(IV)} \xrightarrow[-H_2O]{H_2(Ni/Re)} PhNH—CH(Ph)\underset{PO(OEt)_2}{C}{=}CEt_2\ \text{(XII)}$$

EXPERIMENTAL

The PMR spectra of 5% solutions of V and IX in $CHCl_3$ and of IV and VIII in C_6H_6 were recorded on a Varian HA-100 D NMR spectrometer. The chemical shifts δH were measured relative to TMS as an internal reference with an accuracy of ±0.005 ppm. The IR spectra were recorded on a VR-10 spectrophotometer.

Reaction of C,N-Diphenylnitrone (II) with Diethyl β,β-Diacetylvinylphosphonate (I). A solution of 7.1 g of II and 9 g of I [5] in abs. CH_2Cl_2 was held for one week at 20°C. After removal of CH_2Cl_2 in a vacuum and the addition of absolute ether, 0.5 g (3%) of a fine powder with mp 138-141°C was recovered. The product was soluble in ethanol, CH_2Cl_2, and nitromethane and insoluble in hexane and ether. δ ^{31}P = 0 ppm (CH_2Cl_2). IR spectrum (ν cm^{-1}): 1040-1060 s (P—O—C), 1230 s (P=O), 1505, 1605 m (C_6H_5), 1560. There was no $\nu_{C=O}$ frequency. The structure of the product was not established. After filtration of the crystalline product, removal of the ether in a vacuum, and chromatography of the remaining viscous mass on silica gel (140 g of type KSK, 0.25 mesh), 7.7 g (47%) of isoxazolidine IV with mp 105- 106°C (from a 1:1 hexane—ether mixture), 3 g of unreacted I, and 1 g of nitrone II were isolated.

Isoxazolidine IV was eluted by a 10:1 benzene—ether mixture. R_f 0.25 (ether). Found: C 62.01; H 6.40; P 7.31; N 3.26%. Calculated for $C_{23}H_{28}O_6NP$: C 62.01; H 6.33; P 6.95; N 3.14%.

Reaction of C-Benzoyl-N-phenylnitrone (III) with Diethyl β,β-Diacetylvinylphosphonate (I). A solution of 2.27 g of nitrone III and 2.3 g of I in abs. CH_2Cl_2 was held at 20°C for 3 days. Removal of the solvent in a vacuum and the addition of absolute ether resulted in the isolation of 0.3 g (6%) of a fine powder (mp 139-140°C), whose IR spectrum contained the following absorption bands (ν, cm^{-1}): 1030, 1050 (P—O—C), 1230 (P=O), 1493, 1595 (C_6H_5), 1680 (C_6H_5CO). However, there were no $\nu_{C=O}$ frequencies of acyl groups. The structure of the product was not established. After filtration of the latter, the viscous mass was crystallized by treatment with ether and hexane. This yielded 2.7 g (60%) of isoxazolidine V, mp 103-104°C (from 1:1 hexane—ether). R_f 0.20 (ether). Found: C 60.85; H 6.25; N 3.01; P 6.53%. Calculated for $C_{24}H_{28}O_7NP$: C 60.87; H 5.96; N 2.95; P 6.54%.

Reaction of C-Benzoyl-N-phenylnitrone (III) with Diethyl β-Phenylvinylphosphonate (VI). a. A solution of equimolar amounts of 2.5 g of III and 2.7 g of VI [6] in CH_2Cl was held for 3 days at ∿20°C. Removal of the solvent in a vacuum and treatment of the residue with a 1:1 ether—hexane mixture yielded 3.02 g (58%) of isoxazolidine (VIII) in the form of white crystals, mp 139-140°C (from ether). R_f 0.17 (ether). Found: C 67.30; H 6.23; N 3.36; P 6.49%. Calculated for $C_{26}H_{28}NO_5P$: C 67.07; H 6.07; N 3.01; P 6.66%.

b. A solution of 1.5 g of III and 1.6 g of VI in CH_2Cl_2 was boiled for 3 h. Removal of the solvent and treatment of the residue with a 1:1 ether—hexane mixture yielded 1.8 g (58%) of isoxazolidine VIII, mp 139-140°C.

Reaction of C-Benzoyl-N-phenylnitrone (III) with Dimethyl β-Ethoxyvinylphosphonate (VII). A solution of equimolar amounts of 1.5 g of III and 1.2 g of VII [7] in benzene was boiled for 3 h. Removal of the solvent in a vacuum and treatment of the residue with ether at ∿20°C yielded 1.43 g (53%) of isoxazolidine IX in the form of colorless crystals, mp 96-97°C (from 4:1 ether—CH_2Cl). Found: C 59.30; H 6.22; N 3.49; P 7.53%. Calculated for $C_{20}H_{24}NO_6P$: C 59.24; H 5.97; N 3.46; P 7.64%.

Hydrogenolysis of 2,5-Diphenyl-3-benzoyl-4-diethoxyphosphonoisoxazolidine (VIII). A 1-g portion of VIII in ethyl acetate was hydrogenated on W-6 Raney Ni [8] in a flat-bottomed flask with a magnetic stirrer. Removal of the solvent in a vacuum yielded 0.87 g (86%) of 1,4-diphenyl-2-diethoxyphosphono-3-phenylaminobutan-1-ol (X) in the form of colorless crystals, mp 46-48°C. Found: N 2.84; P 6.47%. Calculated for $C_{26}H_{31}NO_4P$: N 3.09; P 6.83%.

Methylation of Aminoalcohol X by Diazomethane. A solution of 0.14 g of X in ether was treated with an ethereal solution of diazomethane. After the completion of the evolution of nitrogen, 0.11 g (78%) of the methyl ether of 1,4-diphenyl-2-diethoxyphosphono-3-phenylaminobutan-1-ol (XI) precipitated from the reaction mass in the cold in the form of white crystals, mp 178-179°C (from ether). Found: C 69.04; H 6.89; N 3.26; P 6.68%. Calculated for $C_{27}H_{33}NO_4P$: C 69.49; H 7.13; N 3.00; P 6.64%.

CONCLUSIONS

1. The 1,3-dipolar cycloaddition of C,N-diphenyl- and C-benzoyl-N-phenylnitrones to diethyl β,β-diacetylvinylphosphonate yields trans-2,3-diphenyl-4-diethoxyphosphono-5-5-diacetylisoxazolidine and trans-2-phenyl-3-benzoyl-4-diethoxyphosphono-5,5-diacetylisoxazolidine, respectively.

2. C-Benzoyl-N-phenylnitrone reacts with diethyl β-phenylvinylphosphonate to form trans-trans-2,5-diphenyl-3-benzoyl-4-diethoxyphosphonoisoxazolidine, and it reacts with dimethyl β-ethoxyvinylphosphonate to form trans-trans-2-phenyl-3-benzoyl-4-dimethoxyphosphono-5-ethoxyisoxazolidine.

3. As the electrophilic character of the double bond in the β-substituted vinylphosphonates is enhanced, their reactivity in 1,3-dipolar cycloaddition to nitrones increases.

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MECHANISM OF THE REACTIONS OF TRIALKYL PHOSPHITES WITH α-HALOCARBONYL COMPOUNDS

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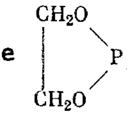
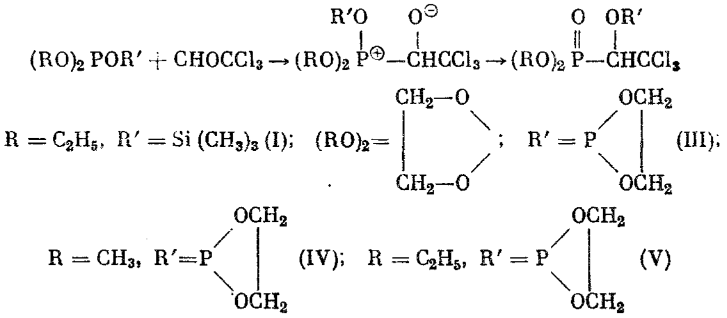
A number of mechanisms have been proposed for the reactions of trialkyl phosphites with α-halocarbonyl compounds. It has been postulated that the reaction begins with the nucleophilic attack of the P atom at the carbonyl carbon, the carbonyl oxygen, the α carbon atom, or the positively polarized halogen atom of the halocarbonyl compound [1]. Therefore, in considering the mechanism of these reactions the determination of the reaction center of the molecule of the α-halocarbonyl compound is of great importance.

We have previously studied the reactions of diethyl trimethylsilyl phosphite [2] and of pyrophosphites [3] containing the  group with chloral. As a result we obtained diethyl α-trimethylsiloxy-β,β,β-trichloroethylphosphonate (I) with a 92% yield and α-dialkylphosphono-β,β,β-trichloroethylethylene phosphites with a yield >90%:



$$(RO)_2POR' + CHOCCl_3 \rightarrow (RO)_2\overset{R'O}{\overset{|}{P}}{}^{\oplus}\text{—}\overset{O^{\ominus}}{\overset{|}{C}}HCCl_3 \rightarrow (RO)_2\overset{O}{\overset{\|}{P}}\text{—}\overset{OR'}{\overset{|}{C}}HCCl_3$$

The reaction of diethyl trimethylsilyl phosphite with trichloroacetaldehyde resulted in the formation of diethyl α-trimethylsiloxy-β-chloroethylphosphonate (II) with a 59% yield. Dialkyl acyl phosphites reacted similarly with mono-, di-, and trichloroacetaldehyde in [4]. The occurrence of these reactions in only one direction to form products with a P—C bond indicated that the reactions of P(III) derivatives with chloral begin with the nucleophilic attack of the P atom on the carbonyl C atom of chloral.

We have recently shown that at −70°C trialkyl phosphites react with chloral to form 2,2,2-trialkoxy-3,5-bis(trichloromethyl)-1,4,2-dioxaphospholanes (E) [5], which are stable at < −40°C:

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