azole and 129° for 1-vinylbenzimidazole. The compound samples studied were purified by recrystallization from organic solvents or repeated vacuum distillation.

CONCLUSIONS

Photoelectron spectroscopy data and quantum chemical calculations for imidazoles and their benzologs indicate that the fusion of the five-membered heterocycle with a benzene ring leads to the inversion of the highest occupied molecular orbitals.

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SYNTHESIS AND MOLECULAR STRUCTURE OF O-ISOPROPYLCHLOROFORMIMINODIPHENYLPHOSPHINATE

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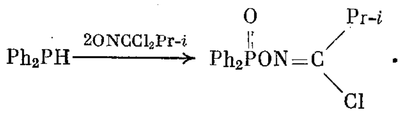
547.558.1

In previous work [1], we showed that diphenylphosphorous acid reacts with 1,1-dichloro-1-nitrosoalkanes to form the corresponding O-alkylchloroformiminodiphenylphosphinates. In order to expand the scope of this reaction, we studied the reaction of diphenylphosphine with 1,1-dichloro-1-nitrosoisobutane and carried out an x-ray diffraction structural analysis of the corresponding O-phosphoryloxime. We should note that the molecular structure of phosphoryloximes, which hold interest as a promising class of pesticides [2], had not been studied previously.

We found that diphenylphosphine reacts with two equivalents of 1,1-dichloro-1-nitrosoisobutane to give O-isopropylchloroformiminodiphenylphosphinate (I) in 58% yield.



$$Ph_2PH \xrightarrow{2ONCCl_2Pr\text{-}i} Ph_2\overset{O}{\overset{\|}{P}}ON{=}C(Pr\text{-}i)Cl \; .$$

Phosphinate (I) is a colorless, crystalline compound, whose composition and structure were supported by elemental analysis and ^1H and ^{31}P NMR spectroscopy.

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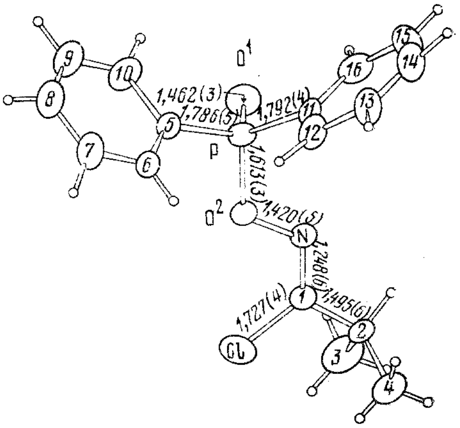

Fig. 1. Molecular structure of (I) as indicated by x-ray structural analysis. The nonhydrogen atoms are shown by thermal oscillation probability ellipsoids (p = 35%).

TABLE 1. Atomic Coordinates ($\times 10^4$, $\times 10^3$ for H) for the Structure of (I)

Atom	X	Y	Z	Atom	X	Y	Z
Cl	0	1168(2)	0	C^{15}	3317(4)	6900(6)	1662(5)
P	668(1)	5589(1)	534(1)	C^{16}	2453(4)	6586(5)	1000(4)
O^1	606(3)	6292(4)	−562(3)	H^2	214(4)	182(7)	−81(6)
O^2	487(2)	3926(3)	479(3)	$H^{3.1}$	64(6)	9(9)	−200(9)
N	1180(3)	3245(4)	−19(4)	$H^{3.2}$	166(6)	24(9)	−234(9)
C^1	995(3)	1996(4)	−264(4)	$H^{3.3}$	95(6)	157(9)	−248(9)
C^2	1640(4)	1140(5)	−825(4)	$H^{4.1}$	154(6)	−68(8)	−1(8)
C^3	1177(6)	726(8)	−2018(6)	$H^{4.2}$	248(6)	−59(8)	−30(8)
C^4	2013(5)	−116(6)	−96(6)	$H^{4.3}$	227(6)	40(8)	71(8)
C^5	−233(3)	6074(5)	1291(4)	H^6	−14(5)	448(6)	241(6)
C^6	−439(3)	5331(5)	2192(4)	H^7	−136(5)	501(9)	323(7)
C^7	−1120(4)	5803(7)	2786(5)	H^8	−211(5)	715(8)	273(7)
C^8	−1594(4)	7020(7)	2431(6)	H^9	−171(5)	861(8)	141(7)
C^9	−1404(4)	7778(6)	1526(6)	H^{10}	−51(4)	793(7)	38(6)
C^{10}	−725(4)	7314(5)	958(5)	H^{12}	149(4)	493(7)	292(6)
C^{11}	1794(3)	5845(4)	1425(4)	H^{13}	296(5)	532(7)	398(7)
C^{12}	1996(3)	5393(5)	2568(4)	H^{14}	412(5)	693(9)	312(7)
C^{13}	2868(4)	5725(6)	3223(5)	H^{15}	377(5)	742(8)	129(7)
C^{14}	3516(4)	6456(7)	2803(5)	H^{16}	229(4)	693(8)	19(6)

The molecular structure of (I) is shown in Fig. 1, which gives the lengths of the major bonds. Selected bond and torsion angles in (I) are as follows: O^1PO^2, 115.8(2)°; O^1PC^5, 114.1(2)°; O^1PC^{11}, 111.5(2)°; O^2PC^5, 98.5(2)°; O^2PC^{11}, 106.4(2)°; C^5PC^{11}, 109.5(2)°; PO^2N, 110.3(3)°; O^2NC^1, 113.6(4)°; ClC^1N, 123.2(4)°; ClC^1C^2, 116.5(3)°; NC^1C^2, 120.3(4)°; O^1PO^2N, 62.7°; PO^2NC^1, −168.5°; O^2NC^1Cl, −1.1°; $O^2NC^1C^2$, 178.3°; $NC^1C^2C^3$, −114.0; and $NC^1C^2C^4$, 119.9°. This indicates a gauche conformation for the $O^1{=}P{-}O^2{-}N$ fragment and Z-configuration of the oxime fragment $O^2{-}N{=}C^1{-}Cl$.

EXPERIMENTAL

The ^1H and ^{31}P NMR spectra were taken on a Bruker CXP-200 spectrometer in $CDCl_3$ relative to TMS as an internal standard and H_3PO_4 as an external standard.

O-Isopropylchloroformiminodiphenylphosphinate (I). A sample of 15.6 g (0.1 mole) of 1,1-dichloro-1-nitrosoisobutane was added with stirring to a solution of 9.3 g (0.05 mole) Ph_2PH in 100 ml benzene at 10-15°C in an argon atmosphere. Stirring was continued for 1 h and benzene was distilled off. The residue was recrystallized from hexane to give 9.4 g (58.4%) crystalline phosphinate (I), mp 69-70°C. ^1H NMR spectrum (δ, ppm): 1.10 d (6H, $2CH_3$, J = 7 Hz), 2.84 m (1H, CH), 7.58 m (6H, 2Ph), 7.92 m (4H, 2Ph). ^{31}P NMR spectrum: 36.83 ppm. Found, %: C 59.78, H 5.20, N 4.20, P 9.54. $C_{16}H_{17}ClNO_2P$. Calculated, %: C 59.73, H 5.33, N 4.35, P 9.63.

The x-ray diffraction structural analysis of (I) was carried out on an Enraf–Nonius CAD4-LSI11/02-PDP11/23 automatic diffractometric system using MoK_α radiation and a graphite monochromator. The unit cell parameters for the colorless, transparent, monoclinic crystals of (I) are as follows: $C_{16}H_{17}ClNO_2P$, M = 321.75, a = 14.507(4), b = 9.573(3), c = 11.973(4) Å, β = 100.82(3)°, V = 1633(2) Å³, Z = 4, d_{calc} = 1.308 g/cm³, $\mu(MoK_\alpha)$ = 3.31 cm⁻¹, space group Cc.

The intensities of 2200 systematically nonextinguished reflections were measured in an inverse space quadrant ($2\theta \leq 57°$) by $\omega/2\theta$ scanning. In the final calculations, 1575 independent observed reflections with $I \geq 2\sigma(I)$ were used. Absorption was not taken into account. The structure of (I) was solved by direct methods using the MULTAN 11/82 program and magic numbers and refined by the full-matrix method of least squares anisotropically for the nonhydrogen atoms. The positions of all the hydrogen atoms were found from the Fourier electron density difference map and these coordinates were refined by the method of least squares with fixed isotropic temperature factors (Table 1).

The final R factors were calculated using 1575 observed reflections: $R = 5.28$, $R_w = 6.66\%$, fit quality $S = 1.20$. The calculations were carried out on a PDP 11/23 minicomputer using the Enraf–Nonius SDP-PLUS program system.

CONCLUSIONS

Diphenylphosphine reacts with two equivalents of 1,1-dichloro-1-nitrosoisobutane to give O-isopropylchloroformiminodiphenylphosphinate. The molecular structure of this product was determined by x-ray diffraction structural analysis.

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REACTION OF TRIETHYL TRITHIOPHOSPHITE WITH AROMATIC ALDEHYDES IN THE PRESENCE OF N-PHENYLTHIOUREA

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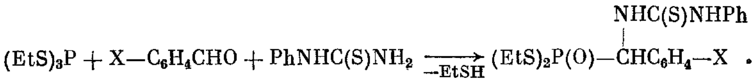
Trialkyl and thiphenyl phosphites react with aldehydes in the presence of N-substituted and unsubstituted ureas and thioureas to form 1-ureoalkylphosphonates and diphosphonates [1-3]. Trialkyl esters of thio acids $(R_1S)_3P$ were not tested in this reaction.

We have found that triethyl trithiophosphite (I) reacts with benzaldehyde (II) and anisaldehyde (III) in the presence of N-phenylthiourea (IV) with the elimination of EtSH and the formation of substituted benzyldithiophosphonates (V) and (VI).



$$(EtS)_3P + X{-}C_6H_4CHO + PhNHC(S)NH_2 \xrightarrow[-EtSH]{} (EtS)_2P(O){-}\overset{NHC(S)NHPh}{\overset{|}{C}}HC_6H_4{-}X$$

(V), (VI)

$X = H$ (V), p-OMe (VI).

The structures of phosphonates (V) and (VI) were supported by ^1H and ^{31}P NMR and IR spectroscopy. The N-phenylthiourea fragment in (V) and (VI) is attached to the sterically less-hindered NH group.

PMR spectrum of (V) in DMSO-d_6 (δ, ppm): 1.17 t and 1.22 t (6H, CH_3CS, $^3J_{HH} = 7.5$ Hz), 2.37-3.02 m (4H, CH_2SP), 6.47 d.d (1H, PCH, $^3J_{HH} = 10.0$, $^2J_{PH} = 11.5$ Hz); upon deuterium exchange of the NH groups in 1:1 DMSO-d_6–CD_3OD, this signal appears at 6.47 d ($^2J_{PH} = 11.5$ Hz), 6.98-7.68 m (9H, Ph), 8.53-8.82 m (1H, PCNH), 9.87 s (1H, PhNH). ^{31}P NMR spectrum: δ 67 ppm.

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