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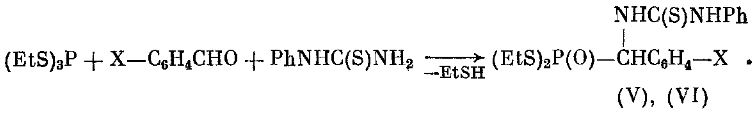
Trialkyl and thiphenyl phosphites react with aldehydes in the presence of N-substituted and unsubstituted ureas and thioureas to form 1-ureoalkylphosphonates and diphosphonates [1-3]. Trialkyl esters of thio acids $(R_1S)_3P$ were not tested in this reaction.

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).



$$(EtS)_3P + X{-}C_6H_4CHO + PhNHC(S)NH_2 \xrightarrow[-EtSH]{} (EtS)_2P(O){-}\underset{\text{(V), (VI)}}{\overset{\overset{\textstyle NHC(S)NHPh}{|}}{C}HC_6H_4}{-}X\ .$$

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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EXPERIMENTAL

The ^{31}P NMR spectra were taken on a KGU-4 NMR spectrometer at 10.2 MHz relative to 85% H_3PO_4. The PMR spectra were taken on a Varian T-60 spectrometer at 60 MHz relative to TMS. The IR spectra were taken on a UR-20 spectrometer for Vaseline mulls.

S,S'-Diethyl-1-(N-phenylthioureo)-N'-p-methoxybenzyldithiophosphonate (VI). A sample of 3.6 g (26 mmoles) (III) was added in portions with agitation to a mixture of 4.0 g (26 mmoles) (IV) and 5.6 g (26 mmoles) (I) in 4 ml abs. toluene; the reaction mixture warmed to 50°C. Then the mixture was heated for an additional 45 min at 50°C. The crystalline precipitate was separated, washed with toluene, and recrystallized in portions from acetonitrile and benzene to give 8.6 g (74.8%) (VI), mp 161°C. PMR spectrum in DMSO-d_6 (δ, ppm, J, Hz): δ_1 1.19 t, δ_2 1.24 t (6H, CH_3CS, $^3J_{HH}$ = 7.5), 2.38-2.96 m (4H, CH_2SP), 3.72 s (3H, OCH_3), 6.34 d.d (1H, PCH, $^3J_{HH} = {}^2J_{PH}$ = 10.0; upon deuterium exchange of the NH groups in 1:1 DMSO-d_6:CD_3OD, this signal appears at 6.34 d (1H, PCH, $^2J_{PH}$ = 10.0)), 6.76-7.62 m (9H, Ar), 8.73-8.45 m (1H, PCNH), 9.78 s (1H, ArNH)). ^{31}P NMR spectrum: δ 69 ppm. IR spectrum (ν, cm^{-1}): 3290 v.s, 3210 m, 3170 s (NH), 3020 w (=C—HAr), 1538 v.s (NCS-I), 1457 v.s (NCS-II), 1245 v.s (P=O), 1153 v.s (NCS-III), 647 m (S—C), 585 v.s, 571 v.s (P—S). Found, %: C 51.30, H 5.68, N 6.31, P 7.22, S 21.99. $C_{19}H_{25}N_2O_2PS_3$. Calculated, %: C 51.80, H 5.72, N 6.36, P 7.03, S 21.83. The filtrate yielded 1.0 g (62.5%) ethyl mercaptan, bp 35-36°C, n_D^{20} 1.4305 [4].

S,S'-Diethyl-1-(N-phenylthioureo)-N'-benzyldithiophosphonate (V) was obtained by analogy in 40.1% yield, mp 148°C. IR spectrum (ν, cm^{-1}): 3310 s, 3280 sh, 3235 sh, 3173 m, 3133 m (NH), 3040 w, 3060 w (=C—HAr), 1603 w (C=CAr), 1533 v.s (NCS-I), 1456 s (NCS-II), 1247 s (P=O), 1160 s (NCS-III), 645 w (S—C), 590 s, 548 s (P—S). Found, %: C 52.86, H 5.67, N 6.91, P 6.72, S 23.04. $C_{18}H_{23}N_2OPS_3$. Calculated, %: C 52.66, H 5.65, N 6.82, P 7.54, S 23.43.

CONCLUSIONS

Triethyl trithiophosphite reacts with benzaldehyde and anisaldehyde in the presence of N-phenylthiourea to form S,S'-diethyl-1-(N-phenylthioureo)-N'-benzyldithiophosphonates.

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