Synthesis and Crystal and Molecular Structure of 1-Ethylthio-2-(*p*-nitrophenyl)-2-(triphenylphosphonio)ethenethiolate

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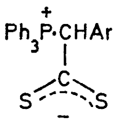
Among the products of the reaction between *p*-nitrobenzylidenetriphenylphosphorane and CS_2 was 1-ethylthio-2-(*p*-nitrophenyl)-2-(triphenylphosphonio)ethenethiolate (9). The structure of (9) was assigned on the basis of an *X*-ray analysis, and its stereochemistry established. A mechanism for the formation of (9) is suggested. Crystals are monoclinic, space group $P2_1/c$, $Z = 4$, $a = 13.506(1)$, $b = 10.134(4)$, $c = 21.615(8)$ Å, $\beta = 120.24(10)°$. The structure was determined by direct methods from diffractometer data and refined to R 6.1% for 3 173 observed reflections.

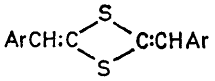
THE reaction of benzylidenetriphenylphosphorane (1a)[1] and some of its *p*-benzylidene substituted derivatives[2] with CS_2 gives rise to the formation of one or more compounds among (2)—(5) depending upon the experimental conditions.[1]

$Ph_3P{:}CHAr$

(1)

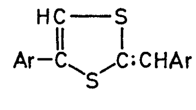


(2)

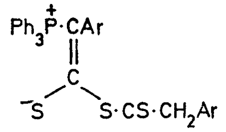


(3)

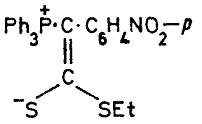
(1)—(8),(10)—(11)
a; Ar = Ph;
b; Ar = p-$O_2NC_6H_4$



(4)

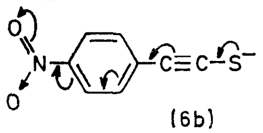


(5)

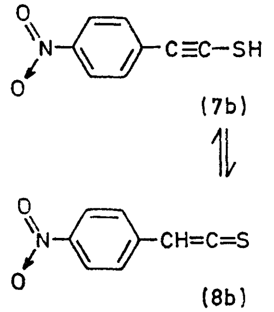


(9)

The reaction of the *p*-nitrobenzylidene derivative (1b) with CS_2 gave (2b), (4b), and (5b) but no (3b);† moreover a new compound (*A*) was obtained. A careful check of the experimental conditions showed that (*A*) was obtained only when the reaction mixture was treated with ethanol during work-up.



(6b)

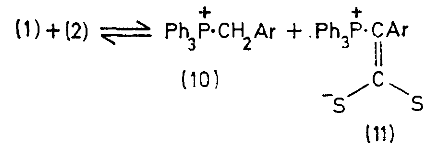


(7b)

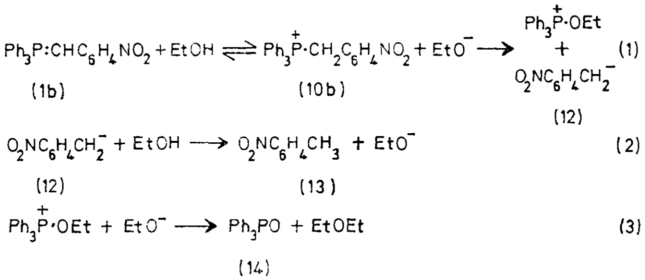
(8b)

The structure (9) of 1-ethylthio-2-(*p*-nitrophenyl)-2-(triphenylphosphonio)ethenethiolate was assigned to (*A*) by means of an *X*-ray analysis which also allowed us to clarify its stereochemistry;‡ n.m.r. and mass spectral results (see Experimental section) confirmed these results.

The formation of (9) can be rationalised by considering the aforementioned[1] presence of (1), (10), and (11) in the reaction mixture of (1) itself with CS_2, due to the equilibrium:



On the other hand it has been reported that (1b) by treatment with ethanol gives rise to reactions (1)—(3).[3]



$$Ph_3P{:}CHC_6H_4NO_2 + EtOH \rightleftharpoons Ph_3\overset{+}{P}{\cdot}CH_2C_6H_4NO_2 + EtO^- \longrightarrow Ph_3\overset{+}{P}{\cdot}OEt + O_2NC_6H_4CH_2^- \quad (1)$$

(1b) (10b) (12)

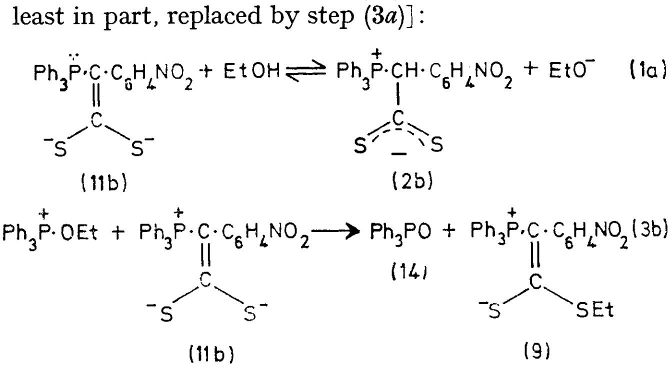
$$O_2NC_6H_4CH_2^- + EtOH \longrightarrow O_2NC_6H_4CH_3 + EtO^- \quad (2)$$

(12) (13)

$$Ph_3\overset{+}{P}{\cdot}OEt + EtO^- \longrightarrow Ph_3PO + EtOEt \quad (3)$$

(14)

In our case, clearly, also (11b) as well as (1b) and (12) can react with ethanol [step (1*a*); step (3) is then, at least in part, replaced by step (3*a*)]:



(1a) (11b) (2b)

(3b) (11b) (14) (9)

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† The lack of (3b) among the reaction products and the higher yield of (4b) over (4a)[1] can be ascribed to the greater stability in this case, of the alkynethiolate species (6b) and (7b), the suggested intermediates[1] to (4b).

‡ Compound (9) is formed also when (2b) reacts with MeI.

[1] G. Purrello and P. Fiandaca, *J.C.S. Perkin I*, 1976, 692.

[2] G. Purrello and P. Fiandaca, unpublished data.

[3] M. Grayson and P. Tarpey Keough, *J. Amer. Chem. Soc.*, 1960, **82**, 3919.

TABLE 1

Final atomic and thermal parameters * of the non-hydrogen atoms (× 10^4), with estimated standard deviations in parentheses

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
P	7 223(1)	2 568(1)	4 482(1)	285(5)	398(5)	335(5)	4(4)	119(4)	−3(4)
S(1)	335(1)	2 171(1)	4 416(1)	364(6)	633(7)	635(7)	30(5)	257(5)	−10(5)
S(2)	785(1)	1 746(1)	3 318(1)	462(6)	712(7)	414(6)	−15(5)	177(5)	−115(5)
O(1)	2 744(3)	2 352(4)	2 949(2)	538(21)	1 171(33)	546(21)	−180(21)	−7(18)	−20(21)
O(2)	2 159(4)	355(5)	2 827(2)	1 152(37)	962(33)	685(25)	172(27)	−16(24)	316(24)
N	2 130(3)	1 450(5)	2 590(2)	443(21)	877(31)	491(23)	116(22)	100(18)	86(23)
C(1)	−410(3)	2 213(4)	444(2)	301(18)	443(21)	396(20)	19(16)	132(16)	9(16)
C(2)	−197(3)	935(4)	711(2)	442(22)	405(21)	505(24)	27(17)	121(19)	11(18)
C(3)	648(4)	666(4)	1 413(2)	525(24)	460(23)	562(26)	76(20)	135(21)	85(20)
C(4)	1 267(3)	1 716(4)	1 840(2)	336(20)	640(26)	408(22)	76(19)	107(17)	40(19)
C(5)	1 101(3)	3 002(4)	1 593(2)	425(22)	575(26)	459(24)	−48(19)	95(19)	−50(20)
C(6)	248(3)	3 237(4)	889(2)	445(22)	475(22)	489(24)	−41(18)	157(19)	6(18)
C(7)	7 172(3)	1 766(4)	247(2)	362(19)	557(23)	416(22)	35(18)	174(17)	30(18)
C(8)	7 524(4)	2 564(5)	843(2)	581(27)	725(31)	466(26)	21(22)	223(22)	−27(22)
C(9)	7 493(5)	2 078(6)	1 438(3)	839(27)	1 081(45)	486(29)	182(34)	386(27)	94(29)
C(10)	7 125(6)	817(7)	1 431(3)	1 062(45)	1 048(47)	642(36)	−13(37)	537(34)	181(33)
C(11)	6 776(4)	34(6)	841(3)	1 198(49)	925(42)	757(39)	−346(37)	560(37)	67(32)
C(12)	6 793(4)	487(5)	244(3)	794(33)	675(30)	550(28)	−177(25)	335(25)	32(23)
C(13)	6 361(3)	3 674(4)	3 749(2)	352(19)	448(21)	364(20)	33(16)	158(16)	6(16)
C(14)	6 854(3)	4 823(4)	3 685(2)	392(21)	602(26)	567(26)	−41(19)	174(20)	96(20)
C(15)	6 208(4)	5 740(5)	3 168(3)	564(27)	596(27)	684(30)	42(22)	285(24)	220(23)
C(16)	5 053(4)	5 511(5)	2 705(2)	513(25)	611(29)	576(28)	125(21)	219(22)	208(22)
C(17)	4 560(4)	4 369(5)	2 757(2)	413(22)	691(29)	502(25)	81(21)	154(19)	90(21)
C(18)	5 202(3)	3 439(4)	3 283(2)	366(20)	484(22)	451(22)	7(17)	128(17)	−6(18)
C(19)	6 564(3)	954(4)	4 350(2)	389(20)	466(22)	412(21)	−44(17)	146(17)	21(17)
C(20)	7 168(4)	−158(4)	4 367(2)	477(23)	454(23)	638(27)	−19(19)	185(21)	6(20)
C(21)	6 682(4)	−1 401(5)	4 291(3)	627(30)	488(26)	964(39)	−68(23)	249(28)	−21(26)
C(22)	5 577(5)	−1 519(5)	4 196(3)	677(33)	558(30)	965(41)	−107(26)	254(30)	62(27)
C(23)	4 992(4)	−410(6)	4 185(3)	522(28)	851(38)	847(36)	−204(26)	265(26)	90(30)
C(24)	5 477(4)	843(5)	4 273(3)	455(23)	635(27)	619(28)	−76(21)	227(21)	59(22)
C(25)	8 668(3)	2 500(3)	4 696(2)	315(19)	380(19)	412(20)	10(15)	137(16)	−1(16)
C(26)	8 878(3)	2 164(4)	4 157(2)	347(19)	399(20)	483(23)	9(16)	177(18)	2(17)
C(27)	395(5)	1 649(8)	3 632(3)	817(38)	1 369(57)	836(41)	112(38)	590(34)	39(39)
C(28)	279(9)	2 674(10)	3 134(6)	1 565(84)	1 476(77)	1 624(85)	−17(62)	1 124(76)	−7(65)

* Thermal parameters, U_{ij} (Å^2 × 10^4) are defined by $\exp[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl)]$.

In accordance with the suggested scheme, the yield of (9) greatly improves when ethanol is added directly to the reaction mixture of (1b) with CS_2, without the customary preliminary treatment.[1] T.l.c. shows the presence of (13) and (14) among the reaction products.

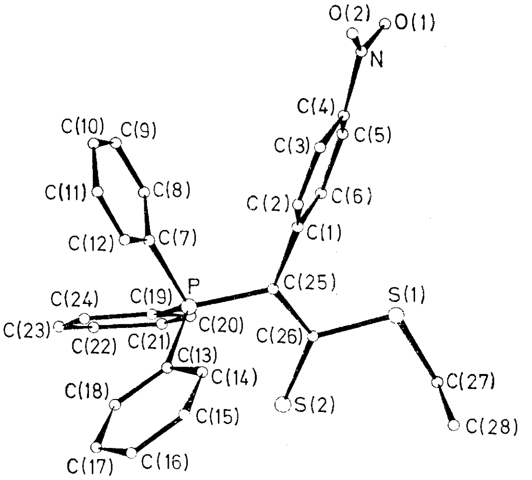

FIGURE 1 The structure of the molecule

The molecular structure of (9) as determined by the X-ray analysis is shown in Figure 1 together with the atom labelling system used. Final parameters for atoms are reported in Tables 1 and 2. Interatomic distances and angles are listed in Table 3, and some significant best planes in the molecule in Table 4. Figure 2 shows the projection of the cell contents along the b axis. Both C(25) and C(26) are sp^2 hybridized so that the atoms which form the skeleton of the molecule [C(20), C(25), C(26), S(1), S(2)] are coplanar. The P–C(Ph) distances are chemically equivalent but are slightly longer (by *ca.*

TABLE 2

Positional parameters of hydrogen atoms (× 10^3), with estimated standard deviations in parentheses

	x	y	z
H(2)	−49(4)	18(5)	39(3)
H(3)	82(4)	−27(5)	161(3)
H(5)	147(4)	379(5)	194(3)
H(6)	11(4)	416(5)	69(3)
H(8)	793(4)	339(5)	87(3)
H(9)	736(5)	242(6)	181(4)
H(10)	697(5)	63(6)	177(3)
H(11)	661(5)	−64(7)	83(3)
H(12)	650(5)	−19(5)	−23(3)
H(14)	759(4)	489(5)	395(3)
H(15)	651(4)	668(5)	312(3)
H(16)	460(4)	622(5)	236(3)
H(17)	377(4)	426(5)	249(3)
H(18)	482(4)	264(5)	332(3)
H(20)	799(4)	−16(5)	439(3)
H(21)	719(5)	−222(6)	427(3)
H(22)	514(5)	−245(6)	419(3)
H(23)	422(5)	−50(5)	415(3)
H(24)	503(4)	189(5)	428(3)

0.04 Å) than the P–C(25) bond distance [1.77 Å]. Bond distances in the nitrophenylene group are as expected, and the C(1)—C(25) bond distance has the predicted value for a C(sp^2) single bond. The nitro-group is inclined at an angle of 9.5° to the phenyl ring which in turn forms an angle of 74.1° with the planar skeleton. The exocyclic C(4)–N bond [1.464(5) Å] which links the nitro-group to the ring system, suggests only limited delocalizing interaction between the π-bond system of the ring and nitro-moieties. The C(25)–C(26) bond [1.365(7) Å] is not very different from a carbon–carbon double bond. The S(1)–C(26) [1.780(4) Å] and S(1)–C(27) bonds [1.802(8) Å] are consistent with the expected values for S–C(sp^2) and S–C(sp^3) single covalent bonds.

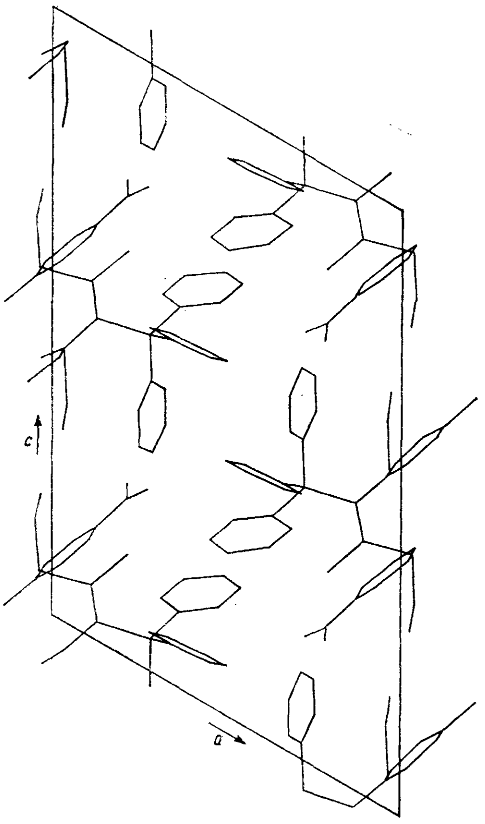

FIGURE 2 Projection of the structure along the *b* axis

However, the S(2)–C(26) distance [1.691(4) Å] compares well with values found in thioacetamide [1.69 Å],[4] ethylenethiourea and thiourea [1.71 and 1.72 Å],[5,6] and carbon disulphide–triethylscarphane [1.69 and 1.68 Å],[7] where this bond has double-bond character or is part of a conjugated system. It may be concluded that C(25), C(26), and S(2) participate in a consistent degree of electron delocalization throughout the chain, so that the molecule can be represented as in (I). However, on the

TABLE 3

Interatomic distances (Å) and angles (°), with estimated standard deviations in parentheses

(*a*) Bonded distances

(i) Involving P

P–C(7)	1.816(5)	P–C(19)	1.814(4)
P–C(13)	1.806(4)	P–C(25)	1.770(4)

(ii) Involving S

S(1)–C(26)	1.780(4)	S(2)–C(26)	1.691(4)
S(1)–C(27)	1.802(8)		

(iii) Phenyl rings

C(7)–C(8)	1.388(6)	C(16)–C(17)	1.367(7)
C(8)–C(9)	1.397(9)	C(17)–C(18)	1.392(5)
C(9)–C(10)	1.368(10)	C(13)–C(18)	1.391(5)
C(10)–C(11)	1.367(9)	C(19)–C(20)	1.381(6)
C(11)–C(12)	1.381(9)	C(20)–C(21)	1.391(7)
C(7)–C(12)	1.393(7)	C(21)–C(22)	1.405(9)
C(13)–C(14)	1.382(6)	C(22)–C(23)	1.367(9)
C(14)–C(15)	1.375(6)	C(23)–C(24)	1.397(8)
C(15)–C(16)	1.385(6)	C(19)–C(24)	1.395(7)

(iv) Involving H

C(2)–H(2)	0.97(5)	C(15)–H(15)	1.06(6)
C(3)–H(3)	1.02(5)	C(16)–H(16)	1.00(5)
C(5)–H(5)	1.03(5)	C(17)–H(17)	0.93(5)
C(6)–H(6)	1.00(5)	C(18)–H(18)	0.98(5)
C(8)–H(8)	0.98(6)	C(20)–H(20)	1.08(6)
C(9)–H(9)	0.96(8)	C(21)–H(21)	1.09(7)
C(10)–H(10)	0.89(8)	C(22)–H(22)	1.11(7)
C(11)–H(11)	0.71(8)	C(23)–H(23)	1.01(7)
C(12)–H(12)	1.12(6)	C(24)–H(24)	1.22(7)
C(14)–H(14))	0.86(5)		

(v) Others bond lengths

C(1)–C(2)	1.388(6)	C(4)–N	1.464(5)
C(2)–C(3)	1.391(5)	N–O(1)	1.215(6)
C(3)–C(4)	1.381(5)	N–O(2)	1.215(7)
C(4)–C(5)	1.383(6)	C(1)–C(25)	1.496(5)
C(5)–C(6)	1.391(5)	C(25)–C(26)	1.365(7)
C(1)–C(6)	1.390(5)	C(27)–C(28)	1.447(14)

(*b*) Important bond angles

P–C(25)–C(1)	118.6(4)	P–C(7)–C(8)	118.5(3
P–C(25)–C(26)	117.8(2)	P–C(8)–C(9)	119.7(5)
C(1)–C(25)–C(26)	123.7(4)	C(7)–C(9)–C(10)	119.8(6)
S(2)–C(26)–C(25)	124.2(3)	C(9)–C(10)–C(11)	120.4(7)
S(2)–C(26)–S(1)	121.5(3)	C(10)–C(11)–C(12)	121.1(6)
S(1)–C(26)–C(25)	114.2(2)	C(11)–C(12)–C(7)	119.0(4)
C(26)–S(1)–C(27)	105.2(2)	C(12)–C(7)–C(8)	119.9(4)
S(1)–C(27)–C(28)	116.4(7)	P–C(13)–C(14)	118.7(2)
		P–C(13)–C(18)	121.5(3)
C(25)–C(1)–C(2)	121.2(3)	C(13)–C(14)–C(15)	120.7(3)
C(25)–C(1)–C(6)	119.9(3)	C(14)–C(15)–C(16)	119.8(5)
C(1)–C(2)–C(3)	121.4(3)	C(15)–C(16)–C(17)	120.1(4)
C(2)–C(3)–C(4)	117.8(4)	C(16)–C(17)–C(18)	120.7(3)
C(3)–C(4)–C(5)	122.8(3)	C(17)–C(18)–C(19)	119.2(4)
C(4)–C(5)–C(6)	117.9(3)	C(18)–C(13)–C(14)	119.6(3)
C(5)–C(6)–C(1)	121.2(4)	P–C(19)–C(20)	119.7(3)
C(6)–C(1)–C(2)	118.8(3)	P–C(19)–C(24)	119.6(3)
C(3)–C(4)–N	118.2(4)	C(19)–C(20)–C(21)	119.9(4)
C(5)–C(4)–N	118.9(3)	C(20)–C(21)–C(22)	119.8(5)
C(4)–N–O(1)	118.3(4)	C(21)–C(22)–C(23)	119.6(5)
C(4)–N–O(2)	118.2(4)	C(22)–C(23)–C(24)	121.1(6)
O(1)–N–O(2)	123.5(4)	C(23)–C(24)–C(19)	118.9(5)
		C(24)–C(19)–C(20)	120.6(4)
C(25)–P–C(7)	108.8(2)		
C(25)–P–C(13)	112.9(2)		
C(25)–P–C(19)	113.3(2)		
C(7)–P–C(13)	105.3(2)		
C(7)–P–C(19)	103.8(2)		
C(13)–P–C(19)	111.9(2)		

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[4] M. R. Truter, *J. Chem. Soc.*, 1960, 997.

[5] P. J. Wheatley, *Acta Cryst.*, 1953, **6**, 369.

[6] M. R. Truter, *Acta Cryst.*, 1967, **22**, 556.

[7] T. N. Margulis and D . H Templeton, *J. Chem. Phys.*, 1962, **36**, 2311.

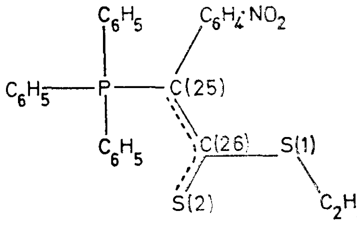
TABLE 4

Deviations (Å) of atoms (in square brackets) from least-squares best planes. Equations of planes are expressed as $Ax + By + Cz = D$ where x, y, and z are fractional co-ordinates

	A	B	C	D
Plane (I):				
P, C(1), C(25), C(26), S(1), S(2)	1.113 7	9.755 8	−5.711 6	0.718 1
[P 0.032, C(1) −0.040, C(25) 0.006, C(26) 0.007, S(1) 0.031, S(2) −0.036]				
Plane (II):				
C(1)—(6)	−12.792 1	−1.251 5	15.839 4	−4.000 4
[C(1) 0.007, C(2) −0.004, C(3) −0.005, C(4) 0.011, C(5) −0.007, C(6) −0.002]				
Plane (III):				
N, O(1), O(2)	−12.592 8	−2.803 4	14.494 2	−5.269 1

Angles (°) between planes: (I)—(II) 74.1, (II)—(III) 9.5, (I)—(III) 66.2

basis of the P–C(25) distance, an extension, at least in part, to the P–C bond, of the double-bond character cannot be excluded.



(I)

EXPERIMENTAL

Preparations.—A 17% solution in benzene–diethyl ether of PhLi (12.5 ml) was added dropwise to the stirred suspension of *p*-nitrobenzyltriphenylphosphonium chloride [8] (10 g) in dry ether. After setting aside for 30 min, dry CS_2 (2.0 g) in dry diethyl ether (10 ml) was added to the stirred reaction mixture and stirring continued for 44 h. The reaction mixture was then diluted with $CHCl_3$ and dried (Na_2SO_4); the solvent was evaporated and the residue fractionated by column chromatography with increasing concentrations of benzene in light petroleum, benzene, and increasing concentrations of ethyl acetate in benzene; yields (%): (4b) 5, (9) 18, (2b) 21, and (5b) 28. In order to increase the yield of (9) the reaction mixture, after being set aside at room temperature, was heated under reflux with ethanol for 2 h; solvent was evaporated and the residue fractionated as before to give yields 30, 30, 10, and 5%. Whatever conditions were used for work-up [1] of the reaction mixture, there was no evidence for (3b).

Physical and Chemical Data.—(2b): red needles (acetone), m.p. 225—226 °C; $\lambda_{max.}$ ($CHCl_3$) 273, 362, and 430 nm (ε 18 350, 7 250, and 4 200); *m/e* 473 (M^+, 5%) (Found: C, 65.80; H, 4.15; N, 2.9; P, 6.65; S, 13.2%. $C_{26}H_{20}NO_2PS_2$ requires: C, 65.95; H, 4.25; N, 2.95; P, 6.55; S, 13.55%).

(4b): amaranth needles (acetone), m.p. 296—298 °C; $\lambda_{max.}$ ($CHCl_3$) 278 and 443 nm (ε 14 050 and 16 200); *m/e* 358 (M^+, 10%) (Found: C, 53.45; H, 3.00; N, 7.95; S, 17.70%. $C_{16}H_{10}N_2O_4S_2$ requires: C, 53.65; H, 2.80; N, 7.80; S, 17.90%).

(5b): violet needles (acetone), m.p. 228—230°; $\lambda_{max.}$ ($CHCl_3$) 265, 324, and 495 nm (ε 20 400, 11 680, and 10 300) (Found: C, 62.35; H, 4.05; N, 4.20; P, 4.95; S, 14.50%. $C_{34}H_{25}N_2O_2PS_3$ requires: C, 62.60; H, 3.85; N, 4.30; P, 4.75; S, 14.70%).

(9): orange needles (acetone), m.p. 285—286 °C; $\lambda_{max.}$ ($CHCl_3$) 280, 356, and 425 nm (ε 24 600, 8 020, and 4 300); δ($C[^2H]Cl_3$) (tetramethylsilane) 7.8—7.0 (m, 19 H), 2.9 (q, 2 H), 0.9 (t, 3 H); *m/e* 501 (M^+, 11, 3%), 472 ($[M - Et]^+$, 4), 440 ($[M - SEt]^+$, 100), 394 ($[440 - NO_2]^+$, 73), 262 (Ph_3P^+, 22), 217 (14), 183 (32), 108 (14) (Found: C, 66.95; H, 4.95; N, 2.80; P, 6.40; S, 13.10%. $C_{28}H_{24}NO_2PS_2$ requires: C, 67.05; H, 4.80; N, 2.80; P, 6.20; S, 12.75%).

Crystal Structure.—Well formed orange crystals of (9) were used for the *X*-ray work. A fragment of dimensions *ca*. 0.2 × 0.5 × 0.4 mm was mounted in a Lindemann capillary with the needle *b* axis parallel to the spindle axis. Laue symmetry and approximate unit-cell parameters were determined from oscillation, Weissenberg, and precession photographs. Final unit-cell parameters were obtained by a least-squares fit to the 2θ angle of 22 independent reflections determined on a Siemens AED diffractometer by use of Cu-K_α radiation ($\lambda = 1.541\ 78$ Å).

Crystal Data.—$C_{28}H_{24}NO_2PS_2$, $M = 502$. Monoclinic, $a = 13.506(1)$, $b = 10.134(4)$, $c = 21.615(8)$ Å, $\beta = 120.24(10)°$, $U = 2\ 556$ Å^3, $D_c = 1.30$ g cm^{-3}, $Z = 4$, $F(000) = 1\ 048$, μ(Cu-K_α) = 30 cm^{-1}. Space group $P2_1/c$ (from systematic absences).

Intensity data were collected on a computer-controlled Siemens AED automated diffractometer by use of Cu-K_α radiation. Of 3 628 unique reflections measured over the range $2° < \theta < 60°$ by the θ—2θ scan and the five-point measuring procedure, 455 having $I < 2\sigma(I)$ were considered unobserved and were given zero weight in the subsequent refinement. Periodic counts were made on a standard peak to provide a check on crystal and electronic stability of the instrument. No significant changes were observed in this standard.

Determination of the Structure.—The structure was solved by the application of direct methods. Program MULTAN was used for the choice of the origin and of symbols, to use as starting data for program TANFIZ.

The set with R_K 16% yielded 283 phases on 285 reflections and the subsequent E map contained 32 peaks which correctly delineated the molecule. Two additional peaks corresponding to the positions of the ethyl carbon atoms were clearly located on the successive Fourier map. The R factor based on the co-ordinates of 32 atoms was 30%. Co-ordinates and thermal parameters of all non-hydrogen atoms were refined in a full-matrix least-squares procedure minimizing the function $\Sigma w(|F_o| - |F_c|)^2$ (initially $w = 1$). Atomic scattering factors used were those listed in ref. 9. After isotropic refinement R was 14.8%.

At this point a difference map was computed which revealed the approximate position of all hydrogen atoms associated with the phenyl groups. Inclusion of these hydrogen atoms with the isotropic temperature factors of their bonded carbon atoms reduced R to 13.5%. Several

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[8] R. Ketcham, D. Jambotkar, and L. Martinelli, *J. Org. Chem.*, 1962, **27**, 4666.

[9] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

cycles of anisotropic refinement in which all positional parameters were refined but the thermal parameters of the hydrogen atoms were included as constants reduced R to 6.8%. Refinement was then continued until convergence with the weighting scheme: $w = 1/(A + F_o + BF_o^2)$, where $A = 2F_{o(\text{min.})} = 7$, and $B = 2/F_{o(\text{max.})} = 0.009\,5$. The resulting R was 6.1% for all observed reflections.

All calculations for the structure determination were performed by use of the '*X*-Ray' system [10] of crystallographic programs. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21666 (3 pp.).*

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[5/1953 *Received, October 6th*, 1975]

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* See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1975, Index issue.

[10] J. M. Stewart, F. A. Kundell, and J. C. Baldwin, Technical Report TR646, Computer Science Centre, University of Maryland, U.S.A., July 1970.