# Photolysis of Diphenyl- and t-Butyl(phenyl)-phosphinic Azides: Dimethyl Sulphide as a Nitrene Trap, and Its Influence on the Curtius-like Rearrangement[1]

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Photolysis of $Ph_2P(O)N_3$ in benzene containing MeOH gives a high yield (72%) of the phosphonamidate PhP(O)(OMe)NHPh (3) resulting from Curtius-like rearrangement. When some of the benzene solvent is replaced by Me_2S the yield of the rearrangement product (3) is reduced and the sulphilimine $Ph_2P(O)N=SMe_2$ is formed. At higher concentrations of Me_2S, $Ph_2P(O)NHCH_2SMe$ also becomes an important product. The unsymmetrical azide $Bu^tPhP(O)N_3$ behaves in a similar way except that low concentrations of Me_2S do not reduce the amount of rearrangement even though some sulphilimine is formed. At higher concentrations of Me_2S rearrangement is partially suppressed but the ratio of the two rearrangement products PhP(O)(OMe)NHBu^t and Bu^{t}P(O)(OMe)NHPh remains unchanged at 2.05 : 1.

Phosphinic azides such as (1) decompose with loss of N_2 when photolysed in protic solvents.[2,3] In methanol the major product is the methyl phosphonamidate (3) resulting from Curtius-like rearrangement and reaction of the resulting monomeric metaphosphonimidate (2) with the solvent. Notable minor products are the N-methoxy compound (5) and the amide (6), derived from the phosphinyl nitrene (4) (in the singlet or triplet state) by
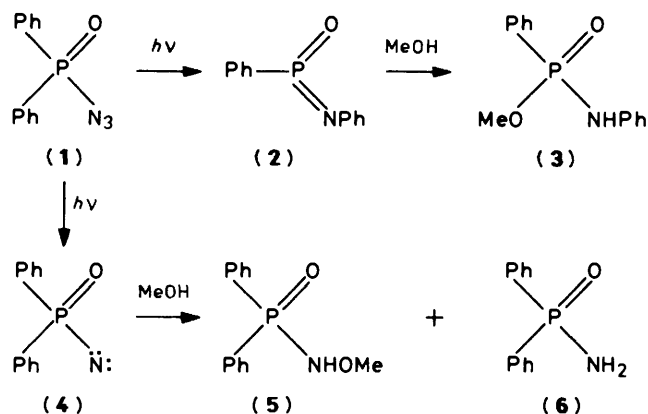

Scheme 1.

insertion or abstraction of hydrogen.[2b] Most phosphinic azides give substantial amounts of amide in methanol, but only rarely has the singlet-derived N-methoxy insertion product been obtained in more than 3% yield.[2] Singlet nitrenes may be intermediates in the Curtius rearrangement; alternatively, the azides may decompose with concerted loss of N_2 and migration of a group from P to N.

The aim of the present investigation was to establish how large a part singlet nitrenes play in the photochemical reactions of phosphinic azides. It made use of dimethyl sulphide, a reagent that has been used to trap efficiently other types of singlet nitrene,[4] including those formed by photolysis of acyl,[5,6] alkoxycarbonyl,[5,7,8] and sulphonyl[8,9] azides.

Results and Discussion

A solution of diphenylphosphinic azide (1) in dimethyl sulphide (100 ml per g of azide) was irradiated with a medium-pressure mercury lamp until *ca.* 90% of the azide had been consumed (3.3 h).† Chromatography then afforded the sulphilimine (7) in 20% yield [*m/z* 277 (M^+, 31%) and 262 (M^+ − Me, 100%); δ

(CDCl₃) 7.9—7.2 (10 H, m) and 2.66 (6 H, s)]. Its identity was confirmed by comparison with a sample prepared from diphenylphosphinic amide (6) and the Me_2S-N-chlorosuccinimide reagent used by Dawson and Swern[10] for making other types of sulphilimine. Two other photolysis products were also isolated, diphenylphosphinic amide (6) (11%) and a compound seen by mass spectrometry (M^+ 277, 1%) and elemental analysis to be an isomer of the sulphilimine. This isomer was assigned the N-(methylthiomethyl)phosphinic amide structure (9) (17.5%)
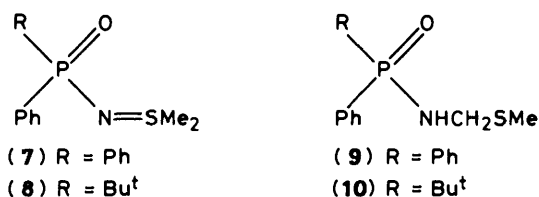
on the evidence of an NH absorption in the i.r. spectrum ($v_{max.}$ 3 160 cm⁻¹), an abundant ion (35%) corresponding to M^+ − SMe in the mass spectrum, and ¹H n.m.r. signals at δ 8.0—7.3 (10 H, m), 4.05 (2 H), 3.3br (NH), and 2.21 (3 H, s, SMe). The signal at δ 4.05 appeared as a dd (J_{PH} 11, J_{HH} 8 Hz) and collapsed to a d (J_{PH} 11 Hz) when the NH proton was exchanged with deuterium.
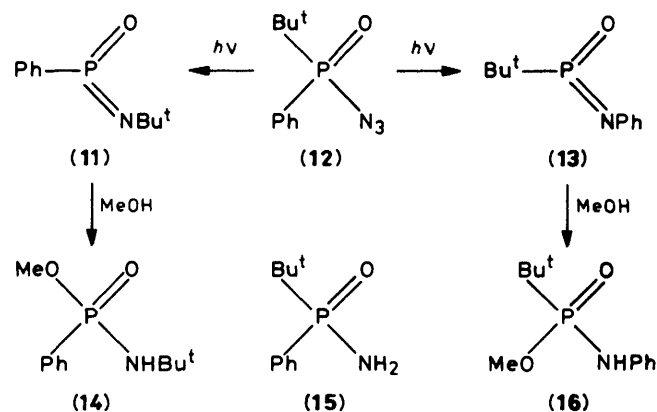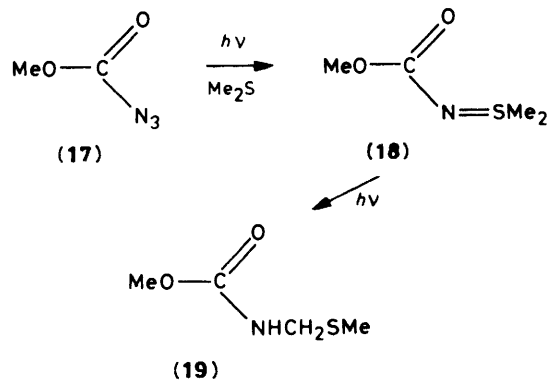

Scheme 2.

† In most of the reactions described in this paper there was some azide remaining when irradiation was stopped. The quoted yields of products are based on the amount of azide consumed.

A similar experiment with t-butyl(phenyl)phosphinic azide (12) (taken to *ca.* 60% completion) gave the sulphilimine (8) in 34% yield, together with the amide (15) (13%) and the *N*-(methylthiomethyl) amide (10) (21%) (see footnote on preceding page). Apparently this azide behaves in the same way as the diphenyl compound (1) except that the yield of sulphilimine is appreciably higher. Also, because of chirality at phosphorus, the two Me groups attached to the S atom in the sulphilimine (8) are non-equivalent and give rise to distinct ^{1}H n.m.r. signals ($\Delta\delta$ 0.04 in CDCl$_3$, 0.16 in CCl$_4$). In this case the authentic sample required for confirmation of the structure of the sulphilimine was prepared from the amide (15) using Swern's Me$_2$SO–(CF$_3$CO)$_2$O reagent.[11]

A remarkable feature of these azide photolyses is the formation of substantial amounts of the *N*-(methylthiomethyl) amides (9) and (10). Although these are formally the products of insertion of the singlet nitrenes into a C–H bond of Me$_2$S, it would be surprising if insertion were to compete effectively with the electrophilic attack of the nitrenes at sulphur. We know of only one report of an analogous product being formed in an azide photolysis. Thus Ando[7] obtained some of the *N*-(methylthiomethyl) compound (19) from methyl azidoformate (17) in Me$_2$S. This, however, was not a primary product, being

Scheme 3.

formed only on prolonged irradiation; apparently it resulted from a Stevens-like rearrangement of the sulphilimine (18) (Scheme 3).[7] By contrast, when the present azide photolyses were followed by ^{31}P n.m.r. spectroscopy it was seen that the *N*-(methylthiomethyl) amides were present even in the very early stages, and that they, at least as much as the sulphilimines, suffered decomposition on prolonged irradiation. It seems clear that the *N*-(methylthiomethyl) compounds are not derived from the sulphilimines, but are primary products of the photochemical reactions of the azides with Me$_2$S.

Having isolated and characterised the products resulting from the photochemical reactions of the phosphinic azides (1) and (12) with Me$_2$S, we turned to the question of how Me$_2$S affects their Curtius rearrangement. In an aprotic solvent like Me$_2$S the monomeric metaphosphonimidates [*e.g.* (2)] that would result from rearrangement would be unlikely to give well-defined products. We therefore introduced a small amount of methanol (10 mmol per mmol of azide; *ca.* 1.65% by volume of the reaction medium) to intercept any metaphosphonimidate that might be formed, and carried out a series of experiments in which benzene was used as a diluent so that the concentration of Me$_2$S could be varied. The compounds investigated as possible products are shown in Table 1 and details of the methods of analysis are given in the Experimental section. The principal results from this series of experiments are shown in Table 2.

With benzene as solvent and no Me$_2$S the dominant products

Table 1. Analysis of photochemical reaction mixtures. G.l.c. retention times (R_t) and ^{31}P n.m.r. chemical shifts (δ_P)

	R_t/min^a	δ_P/p.p.m.^{b}
Ph$_2$P(O)OMe	3.7	33.1
Ph$_2$P(O)N$_3$^{c}		29.9
PhP(O)(OMe)NHPh	6.3	19.1
Ph$_2$P(O)NH$_2$	8.9	22.6
Ph$_2$P(O)NHCH$_2$SMe^d		23.4
Ph$_2$P(O)N=SMe$_2$^{e}	29.5	26.5—28.5
Ph$_2$P(O)NHOMe^f	8.9	27.4
Ph$_2$P(O)NHPh^{f,g}		18.4

	R_t/min^h	δ_P/p.p.m.^{b}
Bu^{t}PhP(O)OMe^f	1.8	52.0
Bu^{t}PhP(O)N$_3$^{i}	2.8	51.4
PhP(O)(OMe)NHBu^t	3.2	21.6
Bu^{t}P(O)(OMe)NHPh	5.0	37.3
Bu^{t}PhP(O)NH$_2$	10.7	41.4
Bu^{t}PhP(O)NHCH$_2$SMe^j		41.9
Bu^{t}PhP(O)N=SMe$_2$	19.9	46.5—48.5

^{a} On 3% silicone OV 17 at 245 °C. ^{b} In CH$_2$Cl$_2$ or CDCl$_3$. Chemical shifts varied slightly from sample to sample; values of δ_P shown are average values. ^{c} Decomposes on g.l.c. $\nu_{max.}$ (benzene) 2 140 cm^{-1}. ^{d} On g.l.c. gives only decomposition peaks having R_t 5.5 (small) and 8.9 min (very small). ^{e} Possibly some decomposition on g.l.c.; not used quantitatively. ^{f} Data for authentic sample; not a significant reaction product. ^{g} R_t 15.6 min at 264 °C. ^{h} On 3% silicone OV 225 at 195 °C. ^{i} $\nu_{max.}$ (benzene) 2 150 cm^{-1}. ^{j} On g.l.c. gives only decomposition peaks having R_t 2.8 (small) and 10.7 min (very small). Where appropriate allowance was made for this enhancing slightly the peaks due to Bu^{t}PhP(O)N$_3$ and Bu^{t}PhP(O)NH$_2$.

Table 2. Principal products from photolysis of phosphinic azides as 0.041 M-solutions in benzene—Me$_2$S containing MeOH (10 mmol/mmol azide; 1.65 vol%)^a

Me$_2$S (vol %)	0	3	6	12	24	48	100
Me$_2$S (mmol/mmol azide)	0	10	20	40	80	160	334

	Yield (%) from Ph$_2$P(O)N$_3$ (1)						
PhP(O)(OMe)NHPh (3)	72	64	58	46	39	28	28
Ph$_2$P(O)N=SMe$_2$ (7)		10	14	18	23	26	25
Ph$_2$P(O)NHCH$_2$SMe (9)		0	0	Some	7	13	28
Ph$_2$P(O)NH$_2$ (6)	3	4	4	8	10	9	11

	Yield (%) from Bu^{t}PhP(O)N$_3$ (12)						
PhP(O)(OMe)NHBu^t (14) ⎱^{b} Bu^{t}P(O)(OMe)NHPh (16) ⎰	59	59	59	55	50	33	26
Bu^{t}PhP(O)N=SMe$_2$ (8)		14	19	24	32	30	32
Bu^{t}PhP(O)NHCH$_2$SMe (10)		0	0	Some	9	18	22
Bu^{t}PhP(O)NH$_2$ (15)	13	8	7	10	9	20	17

^{a} Yields are based on the amount of azide undergoing N$_2$-eliminating decomposition. With azide (1), but not the more hindered (12), a small amount ($\leqslant$8%) of the substrate was always lost by methanolytic conversion into Ph$_2$P(O)OMe. This, as well as unchanged azide, has been allowed for in calculating the yields shown. ^{b} Ratio (14)/(16) always 2.05 ± 0.05.

were, as expected, the methyl phosphonamidates resulting from Curtius rearrangement. Even a very low concentration of Me$_2$S causes the sulphilimines to be formed in appreciable yield. In the case of diphenylphosphinic azide (1), increasing the concentration of Me$_2$S increases the yield of sulphilimine and reduces the amount of rearrangement. This is what might be expected if the rearrangement proceeds *via* a singlet nitrene. At the highest concentrations of Me$_2$S there is still some re-

arrangement. It could be that Me$_2$S is not efficient enough to trap out all the singlet nitrene, or (more obviously in accord with the smallness of the increase in the sulphilimine yield on going to the highest concentrations of Me$_2$S) that the residual rearrangement occurs by a non-nitrene (concerted) mechanism. It was recognition of the possibility that rearrangement might occur by more than one mechanism that prompted the inclusion of t-butyl(phenyl)phosphinic azide (12) in our investigation. This unsymmetrical azide can undergo Curtius rearrangement with migration of either t-butyl or phenyl (Scheme 2).[2c] In benzene in the absence of Me$_2$S the two methyl phosphonamidates (14) and (16) are produced in a 2.05:1 ratio, indicating a small but definite preference for migration of the t-butyl group. High concentrations of Me$_2$S reduce the amount of rearrangement but leave the ratio of the products unchanged. If Me$_2$S were suppressing rearrangement by the singlet nitrene but not by the concerted pathway, the product ratio would remain unchanged only if the relative migratory aptitudes of t-butyl and phenyl were exactly the same for the two mechanisms. This seems most unlikely. Much more likely is that rearrangement occurs by a single mechanism that is only partially suppressed by Me$_2$S. As to the nature of the mechanism, it is noteworthy that in the case of t-butyl(phenyl)phosphinic azide (12) low concentrations of Me$_2$S cause no decrease in the amount of rearrangement even though substantial amounts of sulphilimine are formed. Also, at higher concentration of Me$_2$S, when rearrangement does become less prominent, the decline correlates more with the formation of the N-(methylthiomethyl) amide than with any increase in the yield of sulphilimine. This behaviour suggests that with the azide (12) practically all the rearrangement occurs by a non-nitrene concerted mechanism. It must also cast doubt on the suggestion that some of the rearrangement of diphenyl-phosphinic azide (1) occurs via the singlet nitrene, since there is no obvious reason why Ph$_2$P(O)N̈: should rearrange if Bu^{t}PhP(O)N̈: does not.

The mechanistic picture is greatly complicated by the formation of the N-(methylthiomethyl)phosphinic amides. Having already eliminated the possibility that these are formed by isomerisation of the sulphilimines, it seems we must now also exclude the possibility that they are formed by insertion of singlet nitrenes. As shown in Table 2, the ratio of N-(methylthiomethyl) amide to sulphilimine varies greatly with changes in the concentration of Me$_2$S, whereas it would surely be constant if both products were derived directly from the singlet nitrene. Several possibilities remain, including the combination of radicals formed by reaction of Me$_2$S with the

chemistry of phosphinic azides. As regards the Curtius rearrangement, the results for t-butyl(phenyl)phosphinic azide point strongly to a concerted mechanism but those for diphenylphosphinic azide leave open the possibility that some, at least, proceeds via the singlet nitrene.

Experimental

Instrumentation was as previously described.[13] G.l.c. analyses were performed on a Pye 104 flame-ionisation chromatograph fitted with 1.5 m × 4 mm internal diameter glass columns packed with the stated stationary phase coated on silanised 100—120 mesh diatomite C 'Q'. Chromatography employed neutral alumina. Methanol was dried by distillation from its magnesium salt, dimethyl sulphide was dried over molecular sieves and distilled, and AnalaR benzene was dried over sodium. Diphenyl-[2b] and t-butyl(phenyl)-phosphinic[2c] azides were prepared as before.

Preparation of Authentic Samples of N-Phosphinyldimethyl-sulphilimines.

N-*Diphenylphosphinyldimethylsulphilimine* (7). Dimethyl sulphide (0.28 g, 4.5 mmol) in dichloromethane (1 ml) was added with stirring to a solution of N-chlorosuccinimide (0.60 g, 4.5 mmol) in dry dichloromethane (11 ml) at 0 °C.[10] A precipitate formed but gradually disappeared as diphenylphosphinic amide (0.65 g, 3.0 mmol) in dichloromethane (15 ml) was added. Stirring was continued at 0 °C for 20 min and at room temperature for 50 min. The solution was washed with 10% aqueous sodium hydroxide (12 ml) and water, the washings were extracted with chloroform, and the combined organic portions were dried (MgSO$_4$) and concentrated. Crystallisation from toluene afforded the *sulphilimine* (7) (0.43 g, 1.6 mmol, 52%), m.p. 155—159 °C, raised to 160.5—162 °C by re-crystallisation; m/z 277 (M^+, 31) and 262 (M^+ − Me, 100%); δ (CDCl$_3$) 7.9—7.2 (10 H, m) and 2.66 (6 H, s); ν$_{max.}$ (Nujol) 1 180 cm^{-1} (P=O) (Found: C, 61.05; H, 6.0; N, 5.0. C$_{14}$H$_{16}$NOPS requires C, 60.6; H, 5.8; N, 5.05%).

N-[*t-Butyl(phenyl)phosphinyl*]*dimethylsulphilimine* (8).—A solution of dimethyl sulphoxide (0.78 g, 10 mmol) in dichloromethane (5 ml) was stirred and maintained at ⩽ −50 °C while trifluoroacetic anhydride (2.1 g, 10 mmol)[11] and then t-butyl(phenyl)phosphinic amide (1.0 g, 5.0 mmol) in dichloromethane were slowly added. After a further 1 h at −50 °C the mixture was stirred at room temperature for 2 h. Volatile
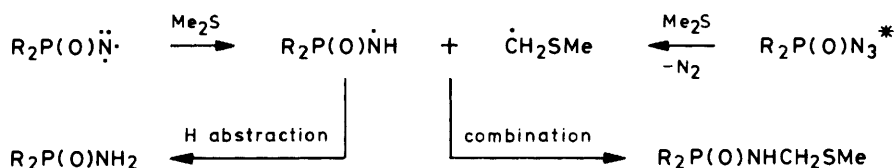
Scheme 4.

triplet nitrene or the triplet excited state of the azide (Scheme 4). Unless the presence of Me$_2$S actually increases the amount of triplet formed (a possibility we would certainly not discount), the latter seems more consistent with our results. Another possible mechanism involves electron transfer from Me$_2$S to an excited state of the azide.[12]

Uncertainty as to the origin of the N-(methylthiomethyl) compounds (and also to some extent the amides) limits the conclusions that can be drawn from this investigation. The formation of sulphilimines does, however, clearly demonstrate the substantial involvement of singlet nitrenes in the photo-

material was pumped off and the residue was dissolved in dichloromethane. The solution was washed with 2M-sodium hydroxide, dried, and the solvent evaporated. The resulting oil was dissolved in ether and light petroleum was added to precipitate a solid. Crystallisation from benzene–light petroleum (b.p. 60—80 °C) gave the *sulphilimine* (8) (0.45 g, 1.8 mmol, 35%) as a hydrate. After removal of water, by azeotropic distillation with benzene and drying at 50 °C at 0.1 mmHg, it had m.p. 128—130 °C; m/z 257 (M^+, 5) and 201 (M^+ − C$_4$H$_8$, 100%); δ (CDCl$_3$) 7.9—7.2 (5 H, m), 2.64 (3 H, s), 2.60 (3 H, s), and 1.05 (9 H, d, J_{PH} 15 Hz); δ (CCl$_4$) includes 2.81 (3 H, s) and

2.65 (3 H, s); $v_{max.}$ (Nujol) 1 155 cm^{-1} (P=O) (Found: C, 55.6; H, 7.8; N, 5.4. $C_{12}H_{20}NOPS$ requires C, 56.0; H, 7.8; N, 5.4%).

Preparative Photochemical Reactions of Phosphinic Azides in Dimethyl Sulphide.—These employed a 125-W medium-pressure mercury lamp in a water-cooled quartz envelope immersed in the stirred reaction mixture. The isolated products were identified as detailed below or (where no details are given) by comparison with the samples available from earlier work [2b,c] and the sulphilimines prepared above.

Diphenylphosphinic azide in dimethyl sulphide. The azide (0.65 g, 2.7 mmol) dissolved in dimethyl sulphide (65 ml) was irradiated for 3.3 h, after which time ^{31}P n.m.r. spectroscopy showed ca. 9% unchanged azide. The bulk (97%) of the product was chromatographed on alumina. Elution with ether containing an increasing proportion of methanol (0—12%) gave, in order, the following (yields based on azide consumed): N-(*methylthiomethyl*)*diphenylphosphinic amide* (9) (0.115 g, 17.5%), crystallised from toluene, m.p. 123—127 °C; m/z 277 (M^+, 1), 230 (M^+ − SMe, 35), 202 (30), and 201 (100%); δ (CDCl$_3$) 8.0—7.3 (10 H, m), 4.05 (2 H, dd, J_{PH} 11, J_{HH} 8 Hz), 3.3 br (1 H), and 2.21 (3 H, s) (the signal at 4.05 collapsed to d, J_{PH} 11 Hz, on shaking with D$_2$O); $v_{max.}$ (Nujol) 3 160 (NH) and 1 180 cm^{-1} (P=O) (Found: C, 60.5; H, 5.8; N, 4.9. $C_{14}H_{16}NOPS$ requires C, 60.6; H, 5.8; N, 5.05%); *N-diphenylphosphinyl-dimethylsulphilimine* (7) (0.133 g, 20%); and diphenylphosphinic amide (0.056 g, 11%).

When the photolysis was repeated with methanol (10 mmol/mmol azide) present, chromatography afforded two additional products: methyl diphenylphosphinate (8%) (eluted first) and methyl NP-diphenylphosphonamidate (3) (15%) (eluted third). Many of the fractions contained more than one product; their composition was established by ^{1}H n.m.r. spectroscopy.

t-Butyl(phenyl)phosphinic azide in dimethyl sulphide. The azide (1.00 g, 4.5 mmol) dissolved in dimethyl sulphide (100 ml) was irradiated for 8 h, when ^{31}P n.m.r. spectroscopy showed ca. 42% unchanged azide. Chromatography afforded the following, in order of elution with ether containing methanol (0—8%) (yields based on azide consumed): N-(*methylthiomethyl*)*-t-butyl(phenyl)phosphinic amide* (10) (0.116 g, 21%), crystallised from toluene–light petroleum (b.p. 60—80 °C), m.p. 143—145 °C (some decomp. above 135 °C); m/z 257 (M^+, 1), 210 (M^+ − SMe, 15), 209 (12), 153 (60), and 125 (100%); δ (CDCl$_3$) 8.0—7.3 (5 H, m), 3.98 (2 H, m), 2.90br (1 H), 2.17 (3 H, s), and 1.10 (9 H, d, J_{PH} 15 Hz) (irradiation at 2.90 simplified the signal at 3.98); $v_{max.}$ (Nujol) 3 180 (NH) and 1 170 cm^{-1} (P=O) (Found: C, 55.95; H, 7.9; N, 5.25. $C_{12}H_{20}NOPS$ requires C, 56.0; H, 7.8; N, 5.4%); *N-[t-butyl(phenyl)phosphinyl]dimethylsulphilimine* (8) (0.19 g, 34%); and t-butyl(phenyl)phosphinic amide (0.054 g, 13%).

When the photolysis was repeated with methanol (10 mmol/mmol azide) present, chromatography gave a mixture of methyl N-t-butyl-P-phenylphosphonamidate (14) and methyl N-phenyl-P-t-butylphosphonamidate (16) (total 23%, ratio 2:1) followed by the three compounds obtained previously.

Photochemical Reactions of Phosphinic Azides in Benzene–Dimethyl Sulphide Mixtures.—The phosphinic azide (0.7—0.9 mmol) and methanol (10 mol equiv.) were dissolved in benzene, dimethyl sulphide, or a mixture of these solvents, to give a solution having [azide] = 0.041 M. The solution was placed in a quartz tube, stoppered securely, and irradiated at 254 nm in a Rayonet reactor. Because of the limited photostability of some of the products (see below) samples (0.40 ml) were withdrawn at intervals (typically corresponding to 40, 55, 70, and 80% consumption of azide) and analysed by i.r. spectroscopy

(2 300—2 000 cm^{-1}; 0.1 mm path-length cell) and g.l.c. (Table 1).* The rate of consumption of the azide was seen to decrease as the proportion of dimethyl sulphide in the reaction mixture increased, except that in 100% dimethyl sulphide it was greater than in some of the benzene–dimethyl sulphide mixtures. Most product yields were deduced by g.l.c., comparing peak areas for the reaction mixture with those for calibration solutions of known concentration. Irradiation was continued until > 70%, and usually ca. 90%, of the azide had been consumed, this requiring 1.1—8.5 h. The final reaction mixture was analysed by ^{1}H and ^{31}P n.m.r. spectroscopy as well as i.r. and g.l.c. For the sulphilimines (7) and (8) the yields shown in Table 2 refer to material isolated by extraction (see below).

Photostability of reaction products. (a) Methyl phosphonamidates. During photolysis the yields (based on azide consumed) of the N-phenyl compounds (3) and (16), but not the N-t-butyl compound (14), decreased somewhat in the later stages of reaction, and the ratio (14):(16) increased accordingly (cf. ref. 2c). In experiments where this was appreciable the yield and the ratio (14):(16) shown in Table 2 relate to the situation at ca. 50% completion.

(b) Sulphilimines. In control experiments both N-phosphinyl-sulphilimines (7) and (8) suffered slight decomposition (ca. 1.5%/h by ^{31}P n.m.r. analysis) on irradiation in dimethyl sulphide but this appeared to be too slow to have been important in the azide photolyses.

(c) N-(Methylthiomethyl)phosphinic amides. When the photolysis of diphenylphosphinic azide (1) in dimethyl sulphide was followed by ^{31}P n.m.r. spectroscopy it was seen that the N-(methylthiomethyl) amide:sulphilimine ratio remained at ca. 1.1:1 to 50% completion but then gradually declined to 0.7:1 at 80% completion as a result of decomposition of the N-(methylthiomethyl) compound. The yields in Table 2 relate to the situation at ⩽ 50% completion, but may still understate the amounts actually formed. Similar monitoring of the photolysis of t-butyl(phenyl)phosphinic azide (12) in dimethyl sulphide showed that the N-(methylthiomethyl) amide:sulphilimine ratio did not decrease significantly during the reaction (both compounds probably suffered slight decomposition).

Isolation of N-phosphinylsulphilimines by extraction. On completion of the period of irradiation, the bulk of the reaction mixture (corresponding to 0.6—0.8 mmol of azide) was evaporated down and the residue was dissolved in chloroform. This solution was extracted with 1M aqueous HCl (2 × 2 ml) and water (3 × 1 ml) and the extracts were combined, washed with chloroform (1 ml), and made alkaline with 4M-aqueous NaOH. The liberated free sulphilimine was then extracted with chloroform (4 ml, 4 × 2 ml) and the combined extracts were dried (Na$_2$SO$_4$). After complete removal of the solvent the product was weighed and examined by ^{1}H n.m.r. spectroscopy. It was seen to be entirely the sulphilimine in experiments with diphenylphosphinic azide (1), but the sulphilimine contaminated with a little amide (15) in experiments with t-butyl(phenyl)phosphinic azide (12). In these cases the proportion of amide was deduced from the ^{1}H n.m.r. spectrum (Bu^t signals) and the weight of sulphilimine in the isolated material was calculated.

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* It was not possible to follow accurately the elimination of N$_2$ from the azide with a gas burette because of interference from volatile Me$_2$S photodecomposition products.

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