

## Synthesis and Reactions of Sulphuryl Azide, and Aryl and 7,7-Dimethylnorbornan-1-yl Azidosulphates

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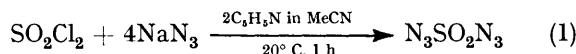
Sulphuryl azide can be made safely and efficiently by the reaction in acetonitrile of sodium azide with sulphuryl chloride in the presence of pyridine. The reactions of solutions of sulphuryl azide with trivalent phosphorus compounds, enamines, norbornene, and dibenzoylmethane have been studied. The synthesis and reactions of 7,7-dimethylnorbornan-1-yl and *p*-nitrophenyl and phenyl azidosulphates have been investigated.

CURTUIS has claimed<sup>1</sup> that sulphuryl azide can be prepared in the absence of solvent by the reaction of sulphuryl chloride with sodium azide. However, the compound is extremely hazardous to handle and its synthesis is unsuited for normal laboratories. Furthermore, only the thermal reactions of this unique and potentially useful synthetic reagent with aromatic compounds have been examined.<sup>1,2</sup> Recently the closely related aryl azidosulphates have been synthesized, but only the reduction of these compounds with copper-methanol has been examined.<sup>3</sup>

We now report a convenient preparation of sulphuryl azide in solution, and the reactions with several reagents to afford compounds with unique functional groups. We have also investigated the synthesis of 7,7-dimethylnorbornan-1-yl and aryl azidosulphates and their reactions with several reagents.

### RESULTS AND DISCUSSION

*Preparation and Reactions of Sulphuryl Azide.*—Pyridine was found to be an effective catalyst for the preparation of sulphuryl azide. When sulphuryl chloride was treated with sodium azide in the presence of pyridine, a solution of sulphuryl azide was obtained [equation (1)].



After addition of the appropriate solvent, the reaction mixture was poured into water, and the organic layer was washed with aqueous potassium hydroxide, followed by hydrochloric acid to remove sulphuryl chloride, chlorosulphonyl azide, and pyridine. After drying over anhydrous sodium sulphate the solutions were used directly for subsequent reactions.

Although we did not isolate or perform a chemical analysis of sulphuryl azide, the following results suggest the formation of the desired compound with sufficient purity for further reaction. The i.r. spectrum of sulphuryl azide (measured in almost 2 mol. equiv. of cyclohexanone or *t*-butylbenzene) ( $\nu_{\text{max}}$ , 2 150, 1 420, 1 180, 1 162, and 793  $\text{cm}^{-1}$ ) is very similar to that of chlorosulphonyl azide ( $\nu_{\text{max}}$ , 2 115, 1 430, 1 190, and 1 155  $\text{cm}^{-1}$ ).<sup>4</sup> The mass spectrum (measured in 2 mol. equiv. of cyclohexanone) ( $m/e$  149 and 148, assignable to protonated sulphuryl azide and the cation radical of sulphuryl azide, respectively) also suggests the formation of sulphuryl azide. Sulphuryl chloride or chloro-

sulphuryl azide could not be detected by i.r. and mass spectroscopy.

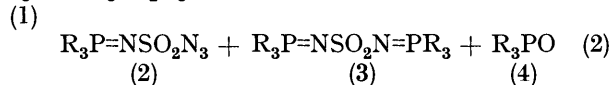
It was previously reported that in the absence of solvent the preparation of sulphuryl azide was almost complete only after 24 h, the products being usually contaminated with small amounts of compounds containing chlorine.<sup>1</sup> The notable catalytic action of pyridine in the preparation may be attributed as follows. Pyridine both increases the solubility of sodium azide and produces highly reactive intermediate complexes such as  $(\text{ClSO}_2\text{NC}_5\text{H}_5)^+\text{Cl}^-$  and  $(\text{N}_3\text{SO}_2\text{NC}_5\text{H}_5)^+\text{Cl}^-$ . A similar effect with dimethylformamide was observed in the preparation of chlorosulphonyl azide.<sup>4,5</sup>

Sulphuryl azide reacted with trivalent phosphorus compounds, enamines, norbornene, and dibenzoylmethane, all of which are known to react with sulphonyl azides<sup>2</sup> (Table 1). When sulphuryl azide, prepared

TABLE I  
Reactions of sulphuryl azide  
Product [% yield]

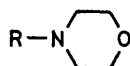
Reagent	Product [% yield]	
(1a)	(2a) [60]	(3a) [20]
(1b)	(2b) [70]	
(1c)	(2c) [30]	(3c) [65]
(1d)	(2d) [5]	(4d) [65]
(1e)	(2e) [7]	(4e) [70]
(5a)	(6a) [42]	
(5b)	(6b) [50]	
(7)	(8) [57]	
(9)	(10) [80]	

from an equimolar amount of sulphuryl chloride, and triphenyl phosphite were allowed to react in refluxing benzene, the *N*-azidosulphonylphosphine imide (2a) (60% yield) and the diphosphazene (3a) (20% yield) were obtained.<sup>6</sup> This result indicates >70% formation of sulphuryl azide in solution. Similar results were obtained in the reactions with tris(2-chloroethyl) phosphite and triethyl phosphite; condensation with loss of nitrogen is predominant in the reaction with electrophilic phosphites. When sulphuryl azide was treated with triphenylphosphine, sulphur dioxide was evolved. After aqueous work-up triphenylphosphine oxide was

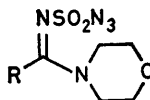


a, R = OPh; b, R = OCH<sub>2</sub>CH<sub>2</sub>Cl; c, R = OEt;  
d, R = Ph; e, R = Bu<sup>n</sup>

isolated in good yield. Tri-*n*-butylphosphine also afforded tri-*n*-butylphosphine oxide in 70% yield, with 7% of the phosphine imide (2e).



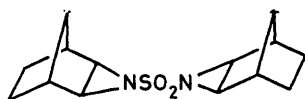
- (5)a; R = cyclohex-1-enyl  
b; R = 2-methylprop-1-enyl



- (6)a; R = cyclopentyl  
b; R = 1-methylethyl



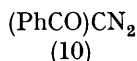
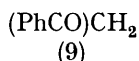
(7)



(8)

The reactions with 1-morpholinocyclohex-1-ene (5a) and 1-morpholino-2-methylpropene (5b) gave the corresponding *N*-azidosulphonylimines (6a and b, respectively).<sup>7</sup>

Sulphuryl azide reacted with 2 mol. equiv. of norbornene to afford the sulphamide (8) in good yield.<sup>8</sup> The diazo-transfer between sulphuryl azide and dibenzoylmethane in the presence of triethylamine is successful.<sup>9</sup>



*Reactions of N-Azidosulphonylphosphine Imides and N-Azidosulphonylimines.*—The *N*-azidosulphonylphosphine imides (2a—c) and the *N*-azidosulphonylimines (6a and b), which belong to a new type of sulphonyl azide, were treated with various reagents in order to ascertain their reactivities. The data are summarized in Table 2.

TABLE 2

Reactions of *N*-azidosulphonylphosphine imides and *N*-azidosulphonylimines

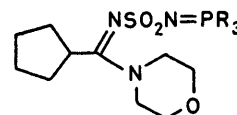
Reactant	Reagent	Product [% yield]
(2a)	(1a) <sup>a</sup>	(11a) [95]
(2b)	(1d) <sup>a</sup>	(11b) [90]
(2c)	(1d) <sup>a</sup>	(11c) [90]
(2a)	(1a) <sup>a</sup>	(3a) [95]
(2c)	(1c) <sup>a</sup>	(3c) [92]
(2a)	(5a) <sup>b</sup>	(12a) [57]
(2b)	(5a) <sup>b</sup>	(12b) [50]
(2c)	(5a) <sup>b</sup>	(12c) [52]
(6a)	(1d) <sup>c</sup>	(13a) [95]
(6b)	(1d) <sup>c</sup>	(13b) [93]

<sup>a</sup> Reaction in benzene for 2 h under reflux. <sup>b</sup> The chloroform solution was refluxed for 3 h. <sup>c</sup> Reaction in benzene for 5 h under reflux.

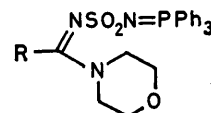
The phosphine imides (2a—c) reacted with triphenylphosphine affording the diphosphazenes (11a—c, respectively) quantitatively. When (2a) treated with triphenyl phosphite, the diphosphazene (3a) was also

obtained quantitatively. The reactions of (2a—c) with (5a) were examined. The corresponding amidines were isolated in good yields. However the reaction with norbornene or the diazo-transfer with dibenzoylmethane did not proceed.

- $\text{R}_3\text{P}=\text{NSO}_2\text{PPh}_3$   
(11)a; R = OPh  
b; R =  $\text{OCH}_2\text{CH}_2\text{Cl}$   
c; R = OEt



- (12)a; R = OPh  
b; R =  $\text{OCH}_2\text{CH}_2\text{Cl}$   
c; R = OEt



- (13)a; R = cyclopentyl  
b; R = Pr<sup>t</sup>

The *N*-azidosulphonylimines (6a and b) reacted with triphenylphosphine to give the expected products (13a and b, respectively). However no reaction with triphenyl phosphite occurred. In the refluxing aqueous potassium hydroxide the imines (6a and b) were hydrolysed giving cyclopentanecarboxylic acid and isobutyric acid, respectively.

*Synthesis and Reactions of 7,7-Dimethylnorbornan-1-yl, p-Nitrophenyl, and Phenyl Azidosulphates.*—The 7,7-dimethylnorbornan-1-yl azidosulphate (14) was prepared by the reaction of 7,7-dimethylnorbornan-1-yl chlorosulphate with sodium azide in the presence of pyridine [equation (3)]. The reaction of chlorosulphonyl azide with *p*-nitrophenol in the presence of pyridine afforded *p*-nitrophenyl azidosulphate (15) [equation (4)]. An attempt to prepare (15) by the reaction of *p*-nitrophenyl chlorosulphate with sodium azide<sup>3</sup> failed. Sulphuryl azide was the major product suggesting that azide ion attacks the sulphur atom of the chlorosulphate with the removal of *p*-nitrophenoxide ion, followed by the displacement of chloride with azide ion.<sup>10</sup>

The results of reactions of (14), (15), and (16) with triphenyl phosphite, triphenylphosphine, 1-morpholinocyclohex-1-ene, norbornene, and dibenzoylmethane are

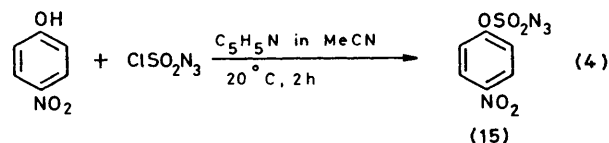
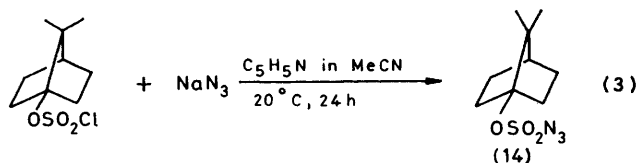


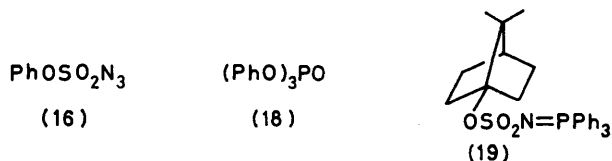
TABLE 3

Reactions of 7,7-dimethylnorbornan-1-yl, *p*-nitrophenyl, and phenyl azidosulphates

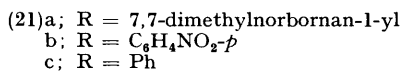
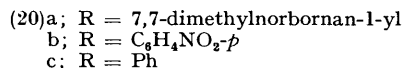
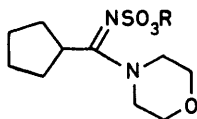
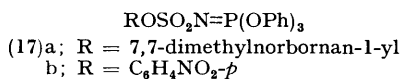
Reactant	Reagent	Product [% yield]
(14)	(1a) <sup>a</sup>	(17a) [95]
(15)	(1a) <sup>a</sup>	(17b) [95]
(16)	(1a) <sup>a</sup>	(18) [80]
(14)	(1d) <sup>a</sup>	(4d) [70], (19) [10]
(15)	(1d) <sup>a</sup>	(4d) [80]
(16)	(1d) <sup>a</sup>	(4d) [75]
(14)	(5a) <sup>b</sup>	(20a) [65]
(15)	(5a) <sup>b</sup>	(20b) [72]
(16)	(5a) <sup>b</sup>	(20c) [60]
(14)	(7) <sup>c</sup>	(21a) [80]
(15)	(7) <sup>c</sup>	(21b) [68]
(16)	(7) <sup>c</sup>	(21c) [60]
(14)	(9) <sup>d</sup>	(10) [34]
(15)	(9) <sup>d</sup>	(10) [60]
(16)	(9) <sup>d</sup>	(10) [40]

<sup>a</sup> Reaction in benzene under reflux for 2 h. <sup>b</sup> The chloroform solution was kept under reflux for 3 h. <sup>c</sup> Reaction in acetonitrile under reflux for 2 h. <sup>d</sup> The ether solution was kept under reflux for 5 h.

summarized in Table 3. The reactions of (14) and (15) with triphenyl phosphite afforded the corresponding phosphine imides (17a and b, respectively), but triphenyl phosphate (18) was the main product in the reaction of (16). When (14) was treated with triphenylphosphine, the phosphine imide (19) was obtained in low yield.



The azides (14—16) reacted with (5a) and norbornene giving the corresponding amidines and *exo*-aziridines, respectively. The diazo-transfer with dibenzoylmethane occurred.



#### EXPERIMENTAL

Mass spectra were obtained with a Hitachi RMU-6H spectrometer, <sup>1</sup>H n.m.r. spectra with a JEOL 3H-60 instrument, and i.r. spectra with a 215 Hitachi grating infrared spectrometer.

Phenyl azidosulphate was prepared by the reported method.<sup>3</sup> Sulphuryl chloride was freshly distilled through an efficient fractionating column (b.p. 69.0—69.5 °C). Pyridine and acetonitrile were carefully purified and dried by standard procedures.

*Sulphuryl Azide*.—To a solution of sodium azide (2.6 g, 40 mmol) and pyridine (1.58 g, 20 mmol) in acetonitrile (50 ml) was added sulphuryl chloride (1.34 g, 10 mmol) in acetonitrile (20 ml) during 10 min at 20 °C and the reaction continued for a further 1 h. After addition of the appropriate solvent, in which the subsequent reaction was performed, the mixture was poured into ice-cold water. The

TABLE 4

Analytical data for new compounds

Compound	Formula	Analysis (%)		
		C	H	N
(2a)	$\text{C}_{18}\text{H}_{15}\text{N}_4\text{O}_5\text{PS}$	50.4 (50.2)	3.6 (3.5)	12.8 (13.0)
(2n)	$\text{C}_6\text{H}_{12}\text{Cl}_3\text{N}_4\text{O}_5\text{PS}$	18.7 (18.5)	3.2 (3.1)	14.4 (14.4)
(2c)	$\text{C}_8\text{H}_{15}\text{N}_4\text{O}_5\text{PS}$	25.4 (25.5)	5.3 (5.3)	19.7 (19.6)
(2d)	$\text{C}_{18}\text{H}_{15}\text{N}_4\text{O}_2\text{PS}$	56.8 (56.5)	4.0 (4.0)	14.5 (14.7)
(2e)	$\text{C}_{12}\text{H}_{27}\text{N}_4\text{O}_2\text{PS}$	44.7 (44.6)	8.4 (8.5)	17.4 (17.4)
(3a)	$\text{C}_{36}\text{H}_{30}\text{N}_2\text{O}_8\text{P}_2\text{S}$	61.7 (6.07)	4.3 (4.2)	3.9 (3.9)
(3c)	$\text{C}_{12}\text{H}_{30}\text{N}_2\text{O}_8\text{P}_2\text{S}$	33.9 (34.0)	7.2 (7.1)	6.6 (6.6)
(6a)	$\text{C}_{10}\text{H}_{17}\text{N}_5\text{O}_3\text{S}$	41.8 (41.8)	5.9 (6.0)	24.4 (24.4)
(6b)	$\text{C}_8\text{H}_{15}\text{N}_5\text{O}_3\text{S}$	36.8 (36.8)	5.8 (5.8)	26.9 (26.9)
(8)	$\text{C}_{14}\text{H}_{20}\text{N}_2\text{O}_2\text{S}$	60.1 (60.0)	7.2 (7.3)	10.0 (10.0)
(11a)	$\text{C}_{36}\text{H}_{30}\text{N}_2\text{O}_5\text{P}_2\text{S}$	65.0 (65.1)	4.6 (4.6)	4.2 (4.2)
(11b)	$\text{C}_{24}\text{H}_{27}\text{Cl}_3\text{N}_2\text{O}_5\text{P}_2\text{S}$	46.0 (46.2)	4.4 (4.4)	4.5 (4.5)
(11c)	$\text{C}_{24}\text{H}_{30}\text{N}_2\text{O}_5\text{P}_2\text{S}$	55.2 (55.4)	5.8 (5.8)	5.3 (5.3)
(12a)	$\text{C}_{28}\text{H}_{32}\text{N}_3\text{O}_6\text{PS}$	58.9 (59.0)	5.7 (5.7)	7.3 (7.4)
(12b)	$\text{C}_{16}\text{H}_{29}\text{Cl}_3\text{N}_3\text{O}_6\text{PS}$	36.3 (36.3)	5.6 (5.5)	7.9 (8.0)
(12c)	$\text{C}_{16}\text{H}_{32}\text{N}_3\text{O}_6\text{PS}$	42.1 (45.2)	7.6 (7.6)	10.1 (9.9)
(13a)	$\text{C}_{28}\text{H}_{32}\text{N}_3\text{O}_3\text{PS}$	64.5 (64.5)	6.2 (6.2)	8.0 (8.1)
(13b)	$\text{C}_{26}\text{H}_{30}\text{N}_3\text{O}_3\text{SP}$	63.0 (63.0)	6.2 (6.1)	8.0 (8.1)
(14)	$\text{C}_9\text{H}_{15}\text{N}_3\text{O}_3\text{S}$	43.9 (44.1)	6.2 (6.2)	17.1 (17.1)
(15)	$\text{C}_6\text{H}_4\text{N}_4\text{O}_5\text{S}$	29.6 (29.5)	1.4 (1.6)	22.7 (22.9)
(17a)	$\text{C}_{27}\text{H}_{30}\text{NO}_6\text{PS}$	61.2 (61.5)	5.8 (5.7)	2.7 (2.7)
(17b)	$\text{C}_{24}\text{H}_{19}\text{N}_2\text{O}_8\text{PS}$	54.5 (54.7)	3.6 (3.6)	5.4 (5.3)
(19)	$\text{C}_{27}\text{H}_{30}\text{NO}_3\text{PS}$	67.6 (67.6)	6.3 (6.3)	2.9 (2.9)
(20a)	$\text{C}_{19}\text{H}_{32}\text{N}_2\text{O}_4\text{S}$	59.1 (59.3)	8.3 (8.5)	7.3 (7.2)
(20b)	$\text{C}_{16}\text{H}_{21}\text{N}_3\text{O}_6\text{S}$	50.0 (50.1)	5.5 (5.5)	11.0 (10.9)
(20c)	$\text{C}_{16}\text{H}_{22}\text{N}_2\text{O}_4\text{S}$	56.8 (56.8)	6.5 (6.5)	8.3 (8.3)
(21a)	$\text{C}_{16}\text{H}_{25}\text{NO}_3\text{S}$	61.4 (61.7)	8.0 (8.1)	4.5 (4.5)
(21b)	$\text{C}_{13}\text{H}_{14}\text{N}_2\text{O}_5\text{S}$	50.1 (50.3)	4.5 (4.5)	9.0 (9.0)
(21c)	$\text{C}_{13}\text{H}_{15}\text{NO}_3\text{S}$	58.4 (58.6)	5.7 (5.5)	5.3 (5.2)

separated organic layer was washed with aqueous potassium hydroxide, water, hydrochloric acid, and water. After drying ( $\text{Na}_2\text{SO}_4$ ), the filtrate was used for the subsequent reaction.

**Reactions of Sulphuryl Azide with Trivalent Phosphorus Compounds.**—A solution of sulphuryl azide in benzene (100 ml) (from 10 mmol of sulphuryl chloride) was kept at 80 °C. To this solution was added the phosphorus compound (10 mmol) in benzene (20 ml) over 10 min, and then the reaction was continued for a further 2 h. After evaporation of the solvent, the products were isolated by chromatography on silica gel. In the reactions with triphenylphosphine and tri-*n*-butylphosphine, the reaction mixtures were worked-up with water before chromatography.

*Azidosulphonylimino(triphenoxy)phosphorane* (2a) had m.p. 67.0–70.0 °C (from benzene–light petroleum),  $\nu_{\text{max}}$  2 135, 1 345, 1 192, 1 182, and 760  $\text{cm}^{-1}$ , *m/e* 430; *azidosulphonylimino(tris-2-chloroethoxy)phosphorane* (2b) was a liquid,  $\delta$  3.50–3.74 (6 H, m) and 4.37–4.66 (6 H, m),  $\nu_{\text{max}}$  2 125 and 1 340  $\text{cm}^{-1}$ ; *azidosulphonylimino(triethoxy)phosphorane* (2c) was a liquid,  $\delta$  1.41 (9 H, t) and 4.23 (6 H, quintet,  $J_{\text{HH}} = J_{\text{PH}} = 7.2$  Hz),  $\nu_{\text{max}}$  2 135, 1 355, 1 182, and 1 160  $\text{cm}^{-1}$ ; *azidosulphonylimino(triphenyl)phosphorane* (2d) had m.p. 150–152 °C (from  $\text{CCl}_4$ –light petroleum), *m/e* 362,  $\nu_{\text{max}}$  2 125, 1 320, and 1 200  $\text{cm}^{-1}$ ; *azidosulphonylimino(tri-*n*-butyl)phosphorane* (2e) had m.p. 64–65 °C (from benzene–light petroleum), *m/e* 322,  $\delta$  0.95 (9 H, t) and 1.15–2.30 (18 H, m),  $\nu_{\text{max}}$  2 100, 1 310, and 1 280  $\text{cm}^{-1}$ ; *bis-(*N*-triphenoxyphosphoranylidene)sulphamide* (3a) had m.p. 137–139 °C (from benzene–light petroleum), *m/e* 712,  $\nu_{\text{max}}$  1 540, 1 360, 1 282, 1 190, 1 180, and 960  $\text{cm}^{-1}$ ; *bis-(*N*-triethoxyphosphoranylidene)sulphamide* (3c) was a liquid,  $\delta$  1.32 (18 H, t) and 4.21 (12 H, quintet,  $J_{\text{HH}} = J_{\text{PH}} = 7.2$  Hz),  $\nu_{\text{max}}$  1 260, 1 200, and 1 025  $\text{cm}^{-1}$ .

**Reactions of Sulphuryl Azide with Enamines.**—To a solution at room temperature of sulphuryl azide in chloroform (100 ml) (prepared from 10 mmol of sulphuryl chloride) was added over 10 min the enamine (10 mmol) in chloroform (20 ml). The reaction was then heated under reflux for 3 h. After evaporation of the solvent, the products were isolated by chromatography on silica gel. *N-(Cyclopentylmorpholinomethylene)azidosulphonamide* (6a) had m.p. 86–88 °C (from ethanol–light petroleum), *m/e* 287,  $\delta$  1.60–2.40 (8 H, m) and 3.73 (8 H, s),  $\nu_{\text{max}}$  2 120, 1 540, 1 350, 1 310, and 1 150  $\text{cm}^{-1}$ . *N-(isopropylmorpholinomethylene)azidosulphonamide* (6b) was a liquid, *m/e* 261,  $\delta$  1.38 (6 H, d), 3.77 (8 H, s), and 3.80 (1 H, m),  $\nu_{\text{max}}$  2 125 and 1 545  $\text{cm}^{-1}$ .

**Reaction of Sulphuryl Azide with Norbornene.**—To a solution of sulphuryl azide in ether (100 ml) (from 10 mmol of sulphuryl chloride), norbornene (20 mmol) in acetonitrile (100 ml) was added at room temperature over 10 min. The ether was evaporated off at 80 °C and the reaction was continued at this temperature for a further 3 h. After normal work-up, the product was isolated by chromatography on silica gel. The sulphamide (8) was a solid, m.p. 124–126 °C (from water–ethanol), *m/e* 280,  $\delta$  0.7–1.63 (12 H, m), 2.55 (4 H, s), and 2.86 (4 H, s),  $\nu_{\text{max}}$  1 320 and 1 156  $\text{cm}^{-1}$ .

**Reaction of Sulphuryl Azide with Dibenzoylmethane.**—A mixture of sulphuryl azide (prepared from 10 mmol of sulphuryl chloride), dibenzoylmethane (2.24 g, 10 mmol), and triethylamine (1.20 g, 12 mmol) in ether (100 ml) was refluxed for 5 h. Chromatography on silica gel gave pure dibenzoyldiazomethane, m.p. 109–110 °C (lit.,<sup>9</sup> 107 °C).

**Products from Reactions of (2a), (2b), and (2c) with Triphenylphosphine or 1-Morpholinocyclohex-1-ene.**—*N-(Triphenylphosphoranylidene)-N'-(triphenoxyphosphoranylidene)sulphamide* (11a) had m.p. 176–178 °C (from  $\text{CH}_2\text{Cl}_2$ –light petroleum), *m/e* 664,  $\nu_{\text{max}}$  1 290, 1 260, 1 190, 1 162, 1 144, and 1 120  $\text{cm}^{-1}$ ; *N-(triphenylphosphoranylidene)-N'-(tris-2-chloroethoxyphosphoranylidene)sulphamide* (11b) had m.p. 132–133 °C (from  $\text{C}_6\text{H}_6$ –light petroleum),  $\delta$  3.50–3.74 (6 H, m), 4.16–4.42 (6 H, m), and 7.30–8.00 (15 H, m),  $\nu_{\text{max}}$  1 260 and 1 121  $\text{cm}^{-1}$ ; *N-(triphenylphosphoranylidene)-N'-(triethoxyphosphoranylidene)sulphamide* (11c) had m.p. 90–92 °C (from  $\text{CCl}_4$ –light petroleum), *m/e* 520,  $\delta$  1.23 (9 H, t), 4.09 (6 H, quintet,  $J_{\text{HH}} = J_{\text{PH}} = 7.2$  Hz), and 7.20–8.00 (15 H, m),  $\nu_{\text{max}}$  1 242, 1 160, 1 120, and 1 020  $\text{cm}^{-1}$ ; *N-(triphenoxyphosphoranylidene)-N'-(cyclopentylmorpholinomethylene)sulphamide* (12a) had m.p. 118–120 °C (from water–ethanol), *m/e* 569,  $\nu_{\text{max}}$  1 540, 1 360, 1 280, 1 210, 1 180, 1 160, and 1 120  $\text{cm}^{-1}$ ; *N-(tris-2-chloroethoxyphosphoranylidene)-N'-(cyclopentylmorpholinomethylene)sulphamide* (12b) had m.p. 105–107 °C (from  $\text{C}_6\text{H}_6$ –light petroleum),  $\nu_{\text{max}}$  1 540 and 1 360  $\text{cm}^{-1}$ ; and *N-(triethoxyphosphoranylidene)-N'-(cyclopentylmorpholinomethylene)sulphamide* (12c), a liquid, showed *m/e* 425,  $\nu_{\text{max}}$  1 540 and 1 360  $\text{cm}^{-1}$ .

**Products obtained from the Reactions of (6a) and (6b) with Triphenylphosphine.**—*N-(Triphenylphosphoranylidene)-N'-(cyclopentylmorpholinomethylene)sulphamide* (13a) had m.p. 245–246 °C (from  $\text{CH}_2\text{Cl}_2$ –light petroleum), *m/e* 521,  $\nu_{\text{max}}$  1 557, 1 255, 1 138, 1 118, and 1 100  $\text{cm}^{-1}$ ; and *N-(triphenylphosphoranylidene)-N'-(isopropylmorpholinomethylene)sulphamide* (13b) had m.p. 212–214 °C (from  $\text{CH}_2\text{Cl}_2$ –light petroleum), *m/e* 495,  $\nu_{\text{max}}$  1 540, 1 250, 1 140, 1 120, and 1 098  $\text{cm}^{-1}$ .

**7,7-Dimethylnorbornan-1-yl Azidosulphate** (14).—A solution of 7,7-dimethylnorbornan-1-yl chlorosulphate<sup>11</sup> (2.38 g, 10 mmol), sodium azide (1.30 g, 20 mmol), and pyridine (1.58 g, 20 mmol) in acetonitrile (100 ml) was kept at room temperature with stirring for 24 h. Conventional work-up and chromatography on silica gel gave the *azidosulphate* (14) (1.47 g, 60%), m.p. 32–35 °C (from water–ethanol), *m/e* 245,  $\delta$  1.08 (6 H, s) and 1.10–2.25 (9 H, m), and  $\nu_{\text{max}}$  2 140, 1 406, and 1 190  $\text{cm}^{-1}$ .

***p*-Nitrophenyl Azidosulphate** (15).—To a solution of sodium azide (20 mmol) and pyridine (20 mmol) in acetonitrile (100 ml) was added sulphuryl chloride (20 mmol) in acetonitrile (50 ml) during 10 min at room temperature; the reaction was continued for 2 h. Into this solution was added a mixture of *p*-nitrophenol (20 mmol) and pyridine (20 mmol) in acetonitrile (50 ml) over 10 min at room temperature, and the reaction was continued for a further 2 h. Recrystallization from ethanol gave the *azidosulphate* (15) (980 mg, 20%), m.p. 69–71 °C, *m/e* 244,  $\delta$  7.5 (2 H, d) and 8.3 (2 H, d),  $\nu_{\text{max}}$  2 150, 1 520, 1 410, 1 350, and 1 150  $\text{cm}^{-1}$ .

**Products obtained from Reactions of (14), (15), and (16) with Several Reagents.**—7,7-Dimethylnorbornan-1-oxysulphonylimino(triphenoxy)phosphorane (17a) had m.p. 100–102 °C (from water–ethanol),  $\nu_{\text{max}}$  1 330, 1 310, 1 204, 1 180, and 1 160  $\text{cm}^{-1}$ ; *p*-nitrophenoxysulphonylimino(triphenoxy)phosphorane (17b) was a liquid, *m/e* 526,  $\nu_{\text{max}}$  1 522, 1 350, 1 280, 1 180, and 1 160  $\text{cm}^{-1}$ ; 7,7-dimethylnorbornan-1-oxysulphonylimino(triphenyl)phosphorane (19) had m.p. 210–211 °C (from water–ethanol), *m/e* 479,  $\delta$  0.74 (6 H, s), 1.0–2.15 (9 H, m), and 7.30–7.90 (15 H, m),  $\nu_{\text{max}}$  1 300, 1 176, 1 160, and 1 150  $\text{cm}^{-1}$ ; 7,7-dimethylnorbornan-1-yl *N*-(cyclopentylmorpholinomethylene)sulphamate (20a) had

m.p. 152—153 °C (from water-ethanol),  $m/e$  384,  $\nu_{\max}$  1 542, 1 358, and 1 154  $\text{cm}^{-1}$ ; *p*-nitrophenyl *N*-(cyclopentylmorpholinomethylene)sulphamate (20b), m.p. 145—147 °C (from ethanol),  $m/e$  383,  $\nu_{\max}$  1 550, 1 520, 1 350, 1 300, and 1 150  $\text{cm}^{-1}$ ; *N*-phenyl *N*-(cyclopentylmorpholinomethylene)sulphamate (20c) had m.p. 152—153 °C (from water-ethanol),  $m/e$  384,  $\nu_{\max}$  1 550, 1 330, and 1 140  $\text{cm}^{-1}$ ; 3-(7,7-dimethylnorbornan-1-oxysulphonyl)-3-azatricyclo[3.2.1.0<sup>2,4</sup>]-octane (21a) had m.p. 150—151 °C (from water-ethanol),  $m/e$  311,  $\delta$  1.0 (6 H, s), 0.70—2.24 (15 H, m), 2.50 (2 H, s), and 2.85 (2 H, s),  $\nu_{\max}$  1 360 and 1 180  $\text{cm}^{-1}$ ; 3-(*p*-nitrophenoxysulphonyl)-3-azatricyclo[3.2.1.0<sup>2,4</sup>]-octane (21b) had m.p. 96—98 °C (from ethanol),  $m/e$  310,  $\delta$  0.78—1.8 (6 H, m), 2.5 (2 H, s), 3.1 (2 H, s), 7.5 (2 H, d), and 8.3 (2 H, d); and 3-(phenoxysulphonyl)-3-azatricyclo[3.2.1.0<sup>2,4</sup>]-octane (21c) had m.p. 101—103 °C (from  $\text{CCl}_4$ ),  $m/e$  265,  $\delta$  0.73—1.84 (6 H, m), 2.52 (2 H, s), 2.98 (2 H, s), and 7.20—7.50 (5 H, m),  $\nu_{\max}$  1 360, 1 170, and 1 142  $\text{cm}^{-1}$ .

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