α-Cyano-sulphonyl Chlorides: Their Preparation and Reactions with Amines, Alcohols, and Enamines

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Cyanomethanesulphonyl chloride has been prepared, and some aspects of its chemistry have been investigated. Reactions with primary and secondary amines led to the expected sulphonamides, but sulphonates derived from reactions with alcohols were in most cases too unstable to be isolated. Reactions with enamines gave either substituted thietan 1,1-dioxides or acyclic sulphones, depending upon whether the enamine was derived from an aldehyde or a cyclic ketone. Sulphonamides derived from cyanomethanesulphonyl chloride contain an acidic methylene group, and were found to condense with aldehydes and with isopentyl nitrite in the normal fashion to give, respectively, substituted olefins and an oxime. The course of the coupling reaction with diazonium salts, however, appeared to depend upon whether the sulphonamide was derived from a primary or a secondary amine. Homologues of cyanomethanesulphonyl chloride having an alkyl group attached to the α-carbon atom were markedly less reactive towards nucleophiles than was the parent compound, reactivity decreasing with increase in chain length. A number of sulphonamides were prepared from each homologue.

SEVERAL sulphonyl chlorides having unsaturated electron-withdrawing groups attached to the α-carbon atom are known,[1-5] but to date, no authentic examples of α-cyano-sulphonyl chlorides have been reported. Michalski and Tulimovski [6] have reported α-cyanoethanesulphonyl chloride (2) as a product of the oxidative chlorination of the phosphorus ester (5) under aqueous conditions. It was not isolated, but was characterised as its anilide (m.p. 71—72 °C). A sample of compound (2) prepared by us as described later was found to be extremely labile in the presence of water, and to yield an anilide of m.p. 83—84 °C. Clearly the compound prepared by Michalski and Tulimovski was different from our own.

We report the synthesis of four novel sulphonyl chlorides (1)—(4), examples of sulphonamides derived from each, and some reactions characteristic of cyano-methanesulphonyl chloride (1).

$ClSO_2{\cdot}CHR{\cdot}CN$ (1) R = H (2) R = Me (3) R = Et (4) R = Pr^n

$(EtO)_2P(Se)S{\cdot}CHMe{\cdot}CN$ (5)

The reaction between chloroacetonitrile (7; R = H) and sodium sulphite under aqueous conditions gave an essentially quantitative yield of the sodium sulphonate (8; R = H). This, on treatment with phosphorus pentachloride in phosphoryl chloride under strictly anhydrous conditions gave a mixture from which compound (1) was isolated as an unstable oil by distillation under high vacuum.

The three sulphonyl chlorides (2)—(4) were prepared in an analogous fashion. The α-chloro-nitriles (7; R = Me, Et, or Pr) were obtained by the action of thionyl chloride (1 equiv.) and pyridine (1 equiv.) on the corresponding aldehyde cyanohydrins (6). Yields were reduced considerably if an excess of thionyl chloride was used. The chloro-nitriles (7; R = Pr^i, Bu^s, or cyclohex-3-enyl) did not react with sodium sulphite under a variety of conditions; neither did α-bromobenzyl cyanide. This appears to be a steric effect.

$$HO{\cdot}CHR{\cdot}CN \xrightarrow{} ClCHR{\cdot}CN \xrightarrow{} NaO{\cdot}SO_2{\cdot}CHR{\cdot}CN \xrightarrow{} (1)\text{—}(4)$$

(6) (7) (8)

The sulphonyl chlorides (1)—(4) are very reactive towards nucleophiles; their reactivity decreases with increase in chain length of R. Hinman and Locatell [7] attributed the lability of chlorosulphonylacetic acid to the presence of the adjacent electron-withdrawing carbonyl group. This suggestion is borne out by the high lability of compound (1), and the even greater lability of α-nitropropanesulphonyl chloride.[5]

Compound (1) reacted vigorously with cold water after a brief induction period, and violently with aqueous ammonia and methylamine. No identifiable products were isolated, and the latter two reactions were accompanied by tar formation. Sulphonamides (9; R^1 = H) could be isolated however from the reaction between compound (1) and 2 equiv. of primary or secondary amine in anhydrous ether or dioxan at 0 °C, the precipitate of amine hydrochloride being readily removed. Sometimes (*e.g.* with 2-methyl-4-nitroaniline), both the amine salt and the sulphonamide precipitated from solution, but they were readily separated by stirring with acetone. Benzene was also found to be a suitable solvent, but the use of chloroform led to low yields. Generally, yields varied within wide limits, being affected both by the pK_b of the amine and by steric factors. Reactions of compound (1) with primary aliphatic amines gave low yields of sulphonamides, contaminated with a dark tarry substance having a characteristic sharp i.r. absorption at 2170 cm^{-1}, 80 cm^{-1} to lower wavelength than the CN absorption in most derivatives of (1). This material has

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[1] R. Vieillefosse and C. Viellefosse, *Bull. Soc. chim. France*, 1947, 351.
[2] C. Ziegler and J. M. Sprague, *J. Org. Chem.*, 1951, **16**, 621, and references cited therein.
[3] G. Opitz, *Angew. Chem. Internat. Edn.*, 1967, **6**, 107.
[4] R. Fusco, S. Rossi, S. Maiorana, and G. Pagani, *Gazzetta*, 1965, **95**, 774.
[5] B. Loev, F. Dowalo, I. M. Fried, and M. M. Goodman, *Tetrahedron Letters*, 1968, 817.
[6] J. Michalski and Z. Tulimovski, *Bull. Acad. polon. Sci., Sér. Sci. chim.*, 1966, **14**, 303.
[7] R. L. Hinman and L. Locatell, *J. Amer. Chem. Soc.*, 1959, **81**, 5655, see especially footnote (10).

not yet been identified. Substituted anilines reacted smoothly without formation of the tarry substance, though if 1 equiv. of the aniline was replaced by one of triethylamine, the by-product was present and the yield of sulphonamide was low.

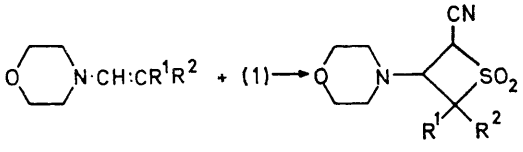
Sulphonamides (9; R^1 = Me, Et, or Pr) were also prepared by analogous methods from the corresponding sulphonyl chlorides (2)—(4). Yields were higher than with compound (1), and in no case was the tarry substance observed. All sulphonamides prepared showed characteristic i.r. absorption near 2250 (CN), near 1340 and 1150 (SO_2), and near 930 cm^{-1} (S–N).[8] Data for a number of sulphonamides are summarised in the Table.

$R^2R^3N{\cdot}SO_2{\cdot}CHR^1{\cdot}CN$ (9) $\qquad$ $RO{\cdot}SO_2{\cdot}CH_2{\cdot}CN$ (10)

Phenylhydrazine and its derivatives reacted with compound (1) to give low yields of sulphonohydrazides; the crude products decomposed spontaneously at room temperature with the evolution of sulphur dioxide, though the purified materials were stable under the same conditions.

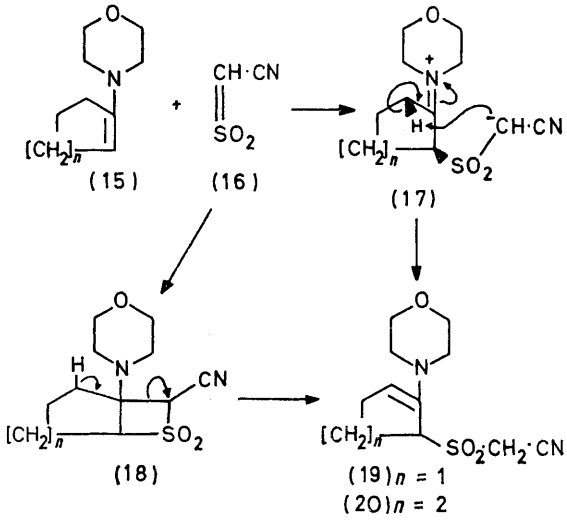
Sulphonates (10; R = Bu^n or Bu^i) derived from compound (1) and the appropriate alcohol were unstable, decomposing slowly at room temperature with the evolution of sulphur dioxide. Those derived from phenols were too unstable to be isolated. Generally, 1 equiv. each of the alcohol and pyridine were treated with 1 equiv. of compound (1) in benzene. The sulphonates could be identified, after removal of solvent and major impurities, by i.r. absorption near 1370 and 1180 cm^{-1}. None was obtained pure.

The work of Stork and Borrowitz,[9] and of Opitz,[10] on the reaction between enamines and sulphonyl chlorides having α-hydrogen atoms led us to attempt to prepare substituted thietan 1,1-dioxides from compound (1). Equivalent amounts of enamine and triethylamine in dioxan were treated with the calculated quantity of compound (1) under nitrogen. Enamines (11) and (12) gave the expected products (13) and (14) together with the tarry substance having i.r. absorption at 2170 cm^{-1}. Enamines (15; n = 1 or 2), however, gave rise to the



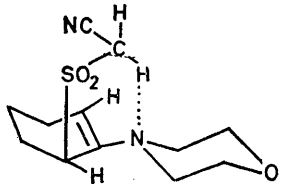
(11) $R^1 = R^2$ = Me
(12) R^1R^2 = $CH_2{\cdot}CH{:}CH{\cdot}CH_2{\cdot}CH_2$
(13) $R^1 = R^2$ = Me
(14) R^1R^2 = $CH_2{\cdot}CH{:}CH{\cdot}CH_2{\cdot}CH_2$

open chain sulphones (19) and (20). Presumably the intermediate sulphene (16) adds to the enamines (15) to give the intermediates (17) or (18) before rearrangement to the products. Evidence presented by Looker [11] for an analogous reaction would point to (18) as being the most likely intermediate. However, the half-life of the zwitterion (17) may be sufficiently long, owing to resonance stabilisation of the negative charge, to permit the alternative mechanism. Models show that the stereochemistry could allow such a mechanism. The active (acidic) methylene protons in (19) and (20)



(15) (16) (17) (18) (19) n = 1 (20) n = 2

situated between the sulphonyl and nitrile groups were found to be non-equivalent, giving rise to quartets in their n.m.r. spectra. Looker [11] reported a similar effect in a number of compounds where an active methylene group was separated from an asymmetric carbon atom by a sulphonyl group. (The corresponding sulphides did not show this effect.) In addition the n.m.r. spectra of (19) and (20) show that the 2- and 6-methylene groups in the morpholine residue are non-equivalent, and that the olefinic protons absorb respectively at τ 4·83 and 4·50. In an analogous compound prepared by Borrowitz,[12] (20; CN replaced by H), the 2- and 6-methylene groups in the morpholine residue are equivalent, and the olefinic proton signal is reported at τ 2·85. These observations can be explained if we postulate a weak electrostatic bond between one of the active methylene protons in (19) or (20) and the nitrogen atom of the morpholine residue. The resulting configuration of the molecule (21) would prevent free rotation of the



(21)

morpholino-group, rendering the 2- and 6-methylene-groups non-equivalent, and would hold the nitrile group close to the olefinic proton, thus helping to account for

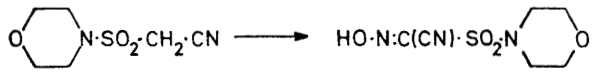
[8] D. Hadži, *J. Chem. Soc.*, 1957, 847.
[9] G. Stork and I. J. Borrowitz, *J. Amer. Chem. Soc.*, 1962, **84**, 313, and subsequent work.
[10] G. Opitz and H. Adolph, *Angew. Chem. Internat. Edn.*, 1962, **1**, 113, and subsequent work.
[11] J. J. Looker, *J. Org. Chem.*, 1966, **31**, 2973.
[12] I. J. Borrowitz, *J. Amer. Chem. Soc.*, 1964, **86**, 1146.

its shift in absorption to higher field in the n.m.r. A similar weak electrostatic interaction might explain the splitting of the active methylene protons in Looker's compounds, and the absence of splitting when the activating sulphonyl group is absent. This suggestion needs further experimental support, but it is worth noting that the active methylene protons in (19) and (20) exchange extremely rapidly with deuterium oxide in the absence of added base. It appears that the morpholine nitrogen atom is assisting this process.

The sulphonamides (9; $R^1 = H$) have an active methylene group, and show reactions characteristic of it.

$R^1CH{:}C(CN){\cdot}SO_2{\cdot}NHR^2$

(22)



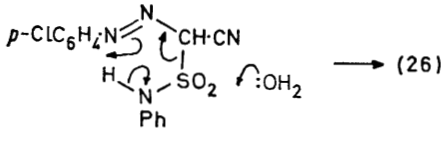
(23) (24)

For example, 4-formylcyclohexene and a number of aromatic aldehydes condensed readily with a variety of sulphonamides in the presence of an acidic catalyst to give high yields of substituted olefins (22). Water was removed by means of a Dean–Stark apparatus. Nitrosation of morpholinosulphonylacetonitrile (23) with isopentyl nitrite under basic conditions gave on acidification a high yield of the oxime (24). An interesting variation in behaviour was observed during the coupling reaction between certain sulphonamides and aromatic diazonium salts. The addition of *p*-chlorobenzenediazonium chloride to a buffered solution of *N*-methyl-*N*-phenylsulphamoylacetonitrile (9; $R^1 = H$, $R^2 = Me$, $R^3 = Ph$) led to the expected hydrazone (25). However, addition of the same reagent to a buffered solution of phenylsulphamoylacetonitrile (9; $R^1 = R^2 = H$, $R^3 = Ph$) resulted in the elimination of the sulphamoyl group and formation of the hydrazone (26). The use of

$p\text{-}ClC_6H_4{\cdot}NH{\cdot}N{:}C(CN){\cdot}SO_2{\cdot}NMePh$ (25)

$p\text{-}ClC_6H_4{\cdot}NH{\cdot}N{:}CH{\cdot}CN$ (26)

cyanoacetic acid in place of the sulphonamide also led to the formation of (26). It is likely that the elimination takes place *via* the intermediate (27), the mechanism being related to that of the Japp–Klingemann reaction.



(27)

EXPERIMENTAL

Light petroleum refers to the fraction b.p. 80—100 °C. I.r. spectra were determined for liquid films or Nujol mulls. N.m.r. spectra were determined for solutions in deuteriochloroform, with tetramethylsilane as internal reference, unless otherwise stated.

α-Halogeno-nitriles.—*α-Chloropropiononitrile* (7; R = Me). α-Hydroxypropiononitrile (6; R = Me) (71 g, 1 mol) and pyridine (79 g, 1 mol) were mixed, and cooled to below 10°. Thionyl chloride (119 g, 1 mol) was added with stirring during 2 h, the temperature being maintained below 25°. Stirring was continued for a further 2 h. The product was poured on crushed ice (300 g), chloroform (250 cm³) was added, and the mixture was stirred until the ice had melted. The chloroform layer was separated, the aqueous layer was washed with chloroform, and the combined organic layers were dried (Na_2SO_4). Removal of the solvent, and distillation of the residue at atmospheric pressure (Vigreux column) gave the chloronitrile (35 g, 39%), b.p. 123—124° at 756 mmHg, n_D^{21} 1·4110.

The other chloronitriles (excepting chloroacetonitrile, which is available commercially) were prepared in a similar fashion. α-Bromobenzyl cyanide was prepared by the reaction between equimolar amounts of bromine and benzyl cyanide at 105—110°.

Sodium Salts of Sulphonic Acids.—Generally, the halogenonitrile (7) (1 mol) was added to a suspension of hydrated sodium sulphite (250 g, 1 mol) in water (250 cm³), and the mixture was stirred until a clear homogeneous solution was obtained. Conditions varied from 3 h at room temperature to 3 days at 70° as R increased in chain length from H to Pr. Removal of water under reduced pressure, and recrystallisation from 98% ethanol gave the product in high yield, though the crude dry product containing sodium chloride was suitable for the preparation of sulphonyl chlorides. Physical properties and yields of individual sodium sulphonates were as follows.

Sodium α-cyanomethanesulphonate (8; R = H) (98%), m.p. 290° (decomp.) (80% aqueous ethanol) (Found: C, 16·9; H, 1·15; S, 22·6. $C_2H_2NNaO_3S$ requires C, 16·8; H, 1·4; S, 22·4%), $\nu_{max.}$ 2240m, 1240s, and 1060s cm⁻¹, τ (D_2O) 5·32 (s).

Sodium α-cyanoethanesulphonate (8; R = Me) (93%; containing combined water), $\nu_{max.}$ 2240m, 1230vs, 1060s, and 630s cm⁻¹, τ (D_2O) 5·83 (1H, q, *J* 7 Hz) and 8·35 (3H, d, *J* 7 Hz).

Sodium α-cyanopropanesulphonate (8; R = Et) (53%; containing combined water), $\nu_{max.}$ 2240m, 1220vs, and 1070 cm⁻¹.

Sodium α-cyanobutanesulphonate (8; R = Pr) (60%; containing combined water), $\nu_{max.}$ 2240m, 1220vs, and 1070s cm⁻¹.

Sulphonyl Chlorides.—*Cyanomethanesulphonyl chloride* (1). Crude sodium cyanomethanesulphonate (195 g, 1 mol; containing sodium chloride) was suspended in phosphoryl chloride (350 cm³), and powdered phosphorus pentachloride (208 g, 1 mol) was added. The mixture was stirred vigorously at 70° for 2½ h with exclusion of moisture, cooled, and filtered to remove sodium chloride; the phosphoryl chloride was removed under reduced pressure. The residual oil was distilled *via* a short Vigreux column, and the *sulphonyl chloride* (70 g, 50%) was collected as a pale yellow oil, which decomposed over a few days at room temperature; b.p. 74—75° at 0·06 mmHg, n_D^{20} 1·4799 (Found: C, 17·1; H, 1·65; N, 10·1; S, 23·1. $C_2H_2ClNO_2S$ requires C, 17·3; H, 1·45; N, 10·0; S, 22·9%), $\nu_{max.}$ 2260m, 1390s, and 1180s cm⁻¹, τ 5·30 (s).

α-Cyanoethanesulphonylchloride (2). Sodium α-cyanoethanesulphonate (77 g, 0·46 mol) was suspended in phosphoryl chloride (180 cm³), and phosphorus pentachloride (104 g, 0·5 mol) was added in small portions during 10 min at 25° with stirring. Stirring was continued for a

further 2 h, and the *product* (42 g, 54%) was isolated as described for compound (1); b.p. 61—62° at 0·02 mmHg, n_D^{21} 1·4689 (Found: C, 23·4; H, 2·6; N, 8·9; S, 20·8. $C_3H_4ClNO_2S$ requires C, 23·45; H, 2·6; N, 9·1; S, 20·9%), $\nu_{max.}$ 2240w, 1390s, and 1170s cm^{-1}, τ 5·39 (1H, q, J 7 Hz) and 8·04 (3H, d, J 7 Hz).

α-Cyanopropanesulphonyl chloride (3). Prepared similarly (52%) from sodium α-cyanopropanesulphonate, the *product* had b.p. 106—108° at 0·5 mmHg, n_D^{30} 1·4640 (Found: C, 29·0; H, 3·9; N, 8·65; S, 19·4. $C_4H_6ClNO_2S$ requires C, 28·7; H, 3·6; N, 8·35; S, 19·15%), $\nu_{max.}$ 2240w, 1380s, and 1165s cm^{-1}.

α-Cyanobutanesulphonyl chloride (4). Sodium α-cyanobutanesulphonate in a similar fashion gave a *sulphonyl chloride* (35%), b.p. 70° at 0·1 mmHg, n_D^{22} 1·4659 (Found: C, 33·1; H, 4·4; N, 7·55; S, 17·7. $C_5H_8ClNO_2S$ requires C, 33·1; H, 4·45; N, 7·7; S, 17·65%), $\nu_{max.}$ 2240w, 1390s, and 1170s cm^{-1}.

Sulphonamides.—A general method of preparation is described, together with variations in the conditions during work-up where these are important. Data for twenty-one sulphonamides are summarised in the Table.

Sulphonamides (9) derived from primary and secondary amines

						Found (%)			Required (%)		
R^1	R^2	R^3	Reaction solvent	M.p. (T/°C)	Yield (%)	C	H	N	C	H	N
H	H	Bu^i	Ether	45—49 [d]	49	40·9	6·9	15·9	40·7	6·9	15·7
H	$CH_2{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}CH_2$		Ether	79—80 [c]	53	38·1	5·3	14·5	37·9	5·3	14·7
H	H	Ph	Ether	78—79 [a]	60	48·8	4·3	14·0	49·0	4·1	14·3
H	Me	Ph	Ether	81 [d]	32	51·0	4·9	13·1	51·4	4·8	13·3
H	H	4-ClC_6H_4	Ether	88—89 [e]	52	41·4	3·2	12·3	41·7	3·1	12·1
H	H	2,4-$Cl_2C_6H_3$	Ether	132—136 [a]		36·3	2·3	10·6	36·25	2·3	10·6
H	H	2,5-$(MeO)_2C_6H_3$	Dioxan	121—125 [c]	72	46·9	4·9	10·8	46·9	4·7	10·9
H	H	2-Me-4-$O_2N{\cdot}C_6H_3$	Dioxan	152—153 [c]	44	42·4	3·9	16·3	42·35	3·55	16·45
H	H	Thiazol-2-yl	Dioxan	186—187 [f]		29·3	2·9	20·7	29·55	2·5	20·7
Me	H	Bu^i	Ether	47—48 [d]	58	44·1	7·6	14·5	44·2	7·4	14·75
Me	$CH_2{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}CH_2$		Ether	91 [b]	78	41·5	5·8	13·7	41·2	5·9	13·7
Me	H	Ph	Ether	83—84 [d]	81	51·5	4·9	13·3	51·4	5·1	13·3
Me	H	2,4-$Cl_2C_6H_3$	Ether	93—94 [d]	43	38·5	2·9	9·9	38·7	2·9	10·0
Et	H	Bu^i	Ether	64—65 [b]	59	47·1	7·9	13·4	47·1	7·8	13·7
Et	$CH_2{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}CH_2$		Ether	72 [b]	59	43·9	6·3	12·8	44·0	6·4	12·8
Et	H	Ph	Ether	72 [d]	54	53·8	5·7	12·6	53·55	5·4	12·5
Et	H	2,4-$Cl_2C_6H_3$	Ether	100 [d]	48	40·7	3·4	9·55	40·95	3·4	9·55
Pr	H	Bu^i	Ether	51—52 [d]	46	49·4	7·9	13·1	49·5	8·3	12·85
Pr	H	Ph	Ether	54—55 [d]	79	55·2	5·6	11·7	55·4	5·9	11·8
Pr	H	4-ClC_6H_4	Ether	66—68 [d]	66	48·4	4·6	10·3	48·4	4·8	10·3
Pr	H	2,4-$Cl_2C_6H_3$	Ether	87—88 [d]	68	43·1	3·7	9·2	43·0	3·9	9·1

Solvents for recrystallisation: [a] benzene; [b] light petroleum; [c] ethanol; [d] benzene–light petroleum; [e] chloroform–ethanol; [f] acetone–ethanol.

The sulphonyl chloride (0·05 mol), dissolved in anhydrous diethyl ether or dioxan (50 cm^3), was added with vigorous stirring during 1 h to a cooled (<10°) solution of the amine (0·1 mol) in the same solvent (50 cm^3). Stirring was continued for a further 2 h. In the case of amines which form water-soluble hydrochlorides, the product was diluted with water (100 cm^3), stirred vigorously, and separated, and the ether layer was dried (Na_2SO_4). Removal of the ether, followed by recrystallisation, gave the pure product. In the case of amines which form hydrochlorides of low solubility in water, the solvent was evaporated off (reduced pressure) and the residue was stirred with acetone and filtered to remove the insoluble hydrochloride. Evaporation of the acetone, and recrystallisation of the residue, gave the pure product.

On occasions, *e.g.* with 2-methyl-4-nitroaniline, both the desired sulphonamide and the amine salt of the sulphonic acid were isolated. I.r. and n.m.r. data are given for both compounds as representative examples:

2-Methyl-4-nitrophenylsulphamoylacetonitrile (9; R^1 = R^2 = H, R^3 = 2-Me-4-$O_2N{\cdot}C_6H_3$) (44%), m.p. 152—153°, $\nu_{max.}$ 3200m, 2250w, 1340s, 1145s, and 920m cm^{-1}, τ 0·93 (1H, s), 1·76—2·36 (3H, m), 5·24 (2H, s), and 7·40 (3H, s).

2-Methyl-4-nitrophenylammonium cyanomethanesulphonate (26%), m.p. 178—179°, $\nu_{max.}$ 3000br,m, 2600m, 2250w, 2010br,m, 1220vs, and 1055s cm^{-1}, τ ([$^2H_6$]acetone) 1·6—2·5 (4H, m, NH_3^+ exchanged with solvent), 6·41 (2H, s), and 7·47 (3H, s).

2,5-Dichlorophenylhydrazosulphonylacetonitrile (9; R^1 = R^2 = H, R^3 = 2,5-$Cl_2C_6H_3{\cdot}NH$).—A solution of compound (1) (3·9 g, 0·036 mol) in dry benzene (50 cm^3) was added to 2,5-dichlorophenylhydrazine (10 g, 0·07 mol) in the same solvent, below 10°, during 30 min. Stirring was continued for 2 h, the mixture was filtered, and the residue was shaken with water (250 cm^3). Filtration left a residue, which was recrystallised from benzene to give the *hydrazide* (41%), m.p. 104—108° (decomp.) (Found: C, 34·0; H, 2·5; N, 14·7; S, 11·4. $C_8H_7Cl_2N_3O_2S$ requires C, 34·3; H, 2·5; N, 15·0; S, 11·45%), $\nu_{max.}$ 3300m, 2270w, 1340s, 1150s, and 900m cm^{-1}. When dioxan was used as reaction solvent in place of benzene, evaporation yielded a dark oil which evolved sulphur dioxide spontaneously at room temperature.

Butyl Cyanomethanesulphonate (10; R = Bu).—A solution of compound (1) (7·0 g, 0·05 mol) in anhydrous benzene (30 cm^3) was added during 20 min to a solution of butanol (8·9 g, 0·06 mol) and triethylamine (6·6 g, 0·065 mol) in the same solvent (100 cm^3), the temperature being maintained below 10° throughout. Stirring was continued for 2 h, the precipitate was filtered off, and the filtrate was shaken with active charcoal (5 g) and water (20 cm^3). The charcoal was removed, the water layer separated, and the benzene layer dried ($CaCl_2$). The solvent was removed at below 40° to yield a straw-coloured oil (4·8 g), containing some benzene (*ca.* 15% from n.m.r.), and slowly evolving sulphur dioxide;

$\nu_{max.}$ 2260w, 1370s, 1180s, and 940s cm^{-1}, τ 5·5 (2H, t, J 6·5 Hz), 5·80 (2H, s), 7·9—8·9 (4H, m), and 9·05 (3H, t, J 6 Hz).

Reactions with Enamines.—*2-Cyano-4,4-dimethyl-3-morpholinothietan 1,1-dioxide* (13). A solution of compound (1) (8·4 g, 0·06 mol) in dry dioxan (10 cm^3) was added during 30 min to a solution of 2-methyl-1-morpholinopropene (8·5 g, 0·06 mol) and triethylamine (6·2 g, 0·06 mol) in the same solvent (70 cm^3) at 15° under nitrogen. Stirring was continued for 24 h, acetone (50 cm^3) was added, the mixture was filtered, and the filtrate was evaporated under reduced pressure. The resulting oil was heated with an equal volume of ethanol and cooled, with scratching, to give the cyclic *sulphone* (3 g, 21%), m.p. 132—134° (ethanol) (Found: C, 48·8; H, 6·65; N, 11·3; S, 13·1. $C_{10}H_{16}N_2O_3S$ requires C, 49·15; H, 6·6; N, 11·45; S, 13·2%), $\nu_{max.}$ 2240w, 1330s, and 1140s,d cm^{-1}, τ 5·30 (1H, d, J 9 Hz), 6·27 (4H, m), 6·95 (1H, d, J 9 Hz), 7·53 (4H, m), 8·35 (3H, s), and 8·39 (3H, s).

2-Cyano-3-morpholino-1-thiaspiro[3,5]non-6-ene 1,1-dioxide (14). Prepared similarly from compound (1) and cyclohex-3-enylidene(morpholino)methane, the *product* (30%) had m.p. 155—156° (benzene) (Found: C, 55·0; H, 6·75; N, 9·9; S, 11·1. $C_{13}H_{18}N_2O_3S$ requires C, 55·3; H, 6·4; N, 9·9; S, 11·35%), $\nu_{max.}$ 2250w, 1650vw, 1340s, and 1130s cm^{-1}, τ 4·13 (2H, m), 5·25 (1H, d, J 9 Hz), 6·23 (4H, m), 6·95 (1H, d, J 9 Hz), and 7·1—8·4 (10H, m, morpholine at τ 7·50).

3-Cyanomethylsulphonyl-2-morpholinocyclopentene (19). Prepared from compound (1) and 1-morpholinocyclopentene (15; n = 1) under conditions identical to those in the two previous examples, the *enamine sulphone* (20%) had m.p. 132° (ethanol) (Found: C, 51·4; H, 6·55; N, 11·1; S, 12·5. $C_{11}H_{16}N_2O_3S$ requires C, 51·55; H, 6·3; N, 10·95; S, 12·5%), $\nu_{max.}$ 2240w, 1620m, 1320s, and 1120s cm^{-1}, τ 4·83br (1H, s), 5·52br (1H, s), 5·75 (1H, d, J 9 Hz), 5·89 (1H, d, J 9 Hz), 6·23 (4H, m), and 7·08 (4H, m).

3-Cyanomethylsulphonyl-2-morpholinocyclohexene (20). Prepared similarly from compound (1) and 1-morpholinocyclohexene (15; n = 2), the *product* (14%) had m.p. 143—145° (ethanol) (Found: C, 53·3; H, 6·7; N, 10·4; S, 11·8. $C_{12}H_{18}N_2O_3S$ requires C, 53·4; H, 6·5; N, 10·4; S, 11·85%), $\nu_{max.}$ 3050w, 2250w, 1645m, 1310s, and 1120s cm^{-1}, τ 4·50 (1H, t, J 4 Hz), 5·31 (1H, d, J 15·5 Hz), 5·85br (1H, s), 5·88 (1H, d, J 15·5 Hz), 6·23 (4H, m), and 7·19 (4H, m).

Condensation of Sulphonamides with Aldehydes.—*2-(p-Chlorophenyl)-1-cyano-1-phenylsulphamoylethylene* (22; R^1 = p-ClC_6H_4, R^2 = H, R^3 = Ph). p-Chlorobenzaldehyde (2·81 g, 0·02 mol), phenylsulphamoylacetonitrile (3·8 g, 0·02 mol), glacial acetic acid (0·3 cm^3), and β-alanine (0·02 g) were heated together under reflux with use of a Dean–Stark water separator. After 5 h, when the calculated amount of water had been collected, the solution was cooled, the product was filtered off, and the residue was washed with ethanol (50 cm^3). Recrystallisation (ethanol) gave the *olefin* (86%), m.p. 156—159° (Found: C, 56·3; H, 3·5; N, 8·9; S, 9·9. $C_{15}H_{11}N_2O_2S$ requires C, 56·5; H, 3·5; N, 8·8; S, 10·05%).

2-(Cyclohex-3-enyl)-1-cyano-1-(2,4-dichlorophenylsulphamoyl)ethylene (22; R^1 = cyclohex-3-enyl, R^2 = H, R^3 = 2,4-$Cl_2C_6H_3$). Prepared similarly from 4-formylcyclohexene and 2,4-dichlorophenylsulphamoylacetonitrile, the *olefin* (55%) had m.p. 146° (ethanol) (Found: C, 50·1; H, 4·0; N, 7·9; S, 8·7. $C_{15}H_{14}Cl_2N_2O_2S$ requires C, 50·4; H, 3·95; N, 7·85; S, 8·95%).

Hydroxyimino(morpholinosulphonyl)acetonitrile (24). Isopentyl nitrite (6·0 g, 0·052 mol) was added during 5 min to a stirred solution of sodium (1·2 g, 0·05 mol) and morpholinosulphonylacetonitrile (9·5 g, 0·05 mol) in ethanol (50 cm^3). The solution became very hot during the addition. Stirring was continued for 2 h, and the yellow precipitate of the sodium salt of the oxime was separated and washed with anhydrous ether; yield 83%, $\nu_{max.}$ 2200s, 1360s, and 1180s cm^{-1}. The sodium salt (2·41 g, 0·1 mol) was dissolved in water (15 cm^3), and hydrochloric acid (conc.) was added dropwise until the yellow colour of the solution was discharged. The resulting buff-coloured precipitate was separated by filtration. Recrystallisation [benzene–ethyl acetate (1 : 1)] gave the *oxime* (82%), m.p. 144—146° (decomp.) (Found: C, 32·6; H, 4·55; N, 18·85; S, 14·7. $C_6H_9N_3O_4S$ requires C, 32·85; H, 4·15; N, 19·15; S, 14·6%), $\nu_{max.}$ 2900s,vbr, 2230vw, 1600m, 1370s, 1180s, and 970s cm^{-1}.

Coupling Reactions between Sulphonamides and Diazonium Salts.— *p-Chlorophenylhydrazono-N-methyl-N-phenylsulphamoylacetonitrile* (25). A diazonium salt solution (30 cm^3), prepared by the standard procedure from p-chloroaniline (1·0 g, 0·008 mol) and sodium nitrite (0·6 g, 0·008 mol), was added during 10 min to a stirred mixture of N-methyl-N-phenylsulphamoylacetonitrile (1·55 g, 0·0075 mol) in ethanol (10 cm^3), and sodium acetate (3·5 g) in water (3 cm^3), the mixture being maintained at 4°. The mixture was allowed to warm to room temperature (2 h), and the precipitated product was separated. Recrystallisation (acetone) gave the *hydrazone* as orange prisms (15%), m.p. 134—136° (Found: C, 51·4; H, 3·6; N, 16·4; S, 8·8. $C_{15}H_{13}ClN_4O_2S$ requires C, 51·6; H, 3·75; N, 16·1; S, 9·2%), $\nu_{max.}$ 3220w, 2220m, 1550s, 1360s, and 1170s cm^{-1}.

p-Chlorophenylhydrazonoacetonitrile (26). This was prepared by use of the conditions described in the previous example, but with phenylsulphamoylacetonitrile as the active methylene compound. The crude red precipitate was triturated with acetone and recrystallised from ethanol to give the *hydrazone* (85%) (Found: C, 53·7; H, 2·8; N, 23·2. $C_8H_6ClN_3$ requires C, 53·5; H, 3·4; N, 23·4%), $\nu_{max.}$ 3230m, 2220m, and 1530s cm^{-1}. No attempt was made to isolate the sulphonamide residue. When the reaction was repeated with cyanoacetic acid in place of phenylsulphamoylacetonitrile, a product with the same i.r. spectrum was obtained.

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