

CCXIII.—*Monothioethylene Glycol. Part III. Nitrophenyl Thioethers.*

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IN continuation of the examination of monothioethylene glycol and its derivatives (J., 1921, **119**, 1860; 1922, **121**, 2139), we have now prepared the three isomeric nitrophenyl β -hydroxyethyl

sulphides and a number of related substances. The direct conversion of the parent mercaptan into each of these nitrophenyl thioethers was realised, the *o*-isomeride being obtained in good yield by the action of *o*-bromonitrobenzene and alcoholic potassium hydroxide, and the *m*- and *p*-isomerides by the action of the respective nitrobenzenediazonium salts (compare Stadler, *Ber.*, 1884, **17**, 2073). The most economical method for preparing each of these substances is, however, by the action of ethylene chlorohydrin upon the salt of the nitrothiophenol. The corresponding *p*-nitrobenzyl thioether was obtained in a similar manner from *p*-nitrobenzyl mercaptan, the preparation of which has been improved. The isomeric *p*-nitrophenyl γ -hydroxypropyl sulphide is also described.

From these hydroxy-sulphides, the chloro-, bromo-, and iodo-sulphides have been produced by known methods. The replacement of the hydroxyl group by chlorine was appreciably less easy in *p*-nitrophenyl γ -hydroxypropyl sulphide than in the β -series (compare Bennett and Hock, *J.*, 1925, **127**, 2671; this vol., p. 477).

The isolation of three of these compounds has been announced by other authors during the course of our work—*o*-nitrophenyl β -chloroethyl sulphide by Lecher and Simon (*Ber.*, 1925, **58**, 409) and *p*-nitrophenyl β -hydroxy- and β -bromo-ethyl sulphides by Waldron and Reid (*J. Amer. Chem. Soc.*, 1923, **45**, 2399).

The results of a crystallographic examination of some of these compounds are summarised in the following table :

Substance.	$a : b : c$.	β .	Cleavage.
1 : 2(NO ₂)C ₆ H ₄ ·S·C ₂ H ₄ ·OH	0·5445 : 1 : 1·1416	—	(010)
1 : 2(NO ₂)C ₆ H ₄ ·S·C ₂ H ₄ Cl	0·9584 : 1 : 0·5126	—	(010)
1 : 2(NO ₂)C ₆ H ₄ ·S·C ₂ H ₄ Br	0·9590 : 1 : 0·5250	—	(010)
1 : 2(NO ₂)C ₆ H ₄ ·S·C ₂ H ₄ I	3·143 : 1 : 2·513	99° 16'	(010) & (100)
1 : 4(NO ₂)C ₆ H ₄ ·S·C ₂ H ₄ Cl	0·4752 : 1 : 0·4026	96° 54'	(100)
1 : 4(NO ₂)C ₆ H ₄ ·S·C ₂ H ₄ Br	1·8113 : 1 : 1·1187	96° 18'	—
1 : 4(NO ₂)C ₆ H ₄ ·S·C ₂ H ₄ I	0·5081 : 1 : 0·5160	104° 45'	—

EXPERIMENTAL.

Action of Sodium and Potassium Salts of Monothioethylene Glycol on o- and p-Chloro- and Bromo-nitrobenzenes.—The *o*-nitrophenyl thioether was first isolated from the products of the interaction of *o*-nitrochlorobenzene and monothioethylene glycol. *o*-Nitrophenyl β -hydroxyethyl sulphide was thus obtained in deep yellow, orthorhombic tables, m. p. 100° (Found: C, 48·2; H, 4·5; N, 7·1. C₈H₉O₃NS requires C, 48·2; H, 4·5; N, 7·05%).

A better yield and a purer product were obtained by gradually heating *o*-nitrochlorobenzene in spirit with monothioethylene glycol and potassium hydroxide, but the most convenient method

of preparation of this substance is through *o*-nitrothiophenol as described below.

When these preparations were repeated using *p*-chloronitrobenzene and *p*-bromonitrobenzene, reduction or some other subsidiary reaction was still more marked; the yellow product isolated, being practically indifferent to phosphorus pentachloride, was not *p*-nitrophenyl β -hydroxyethyl sulphide.

Preparation of the p-Nitrophenyl Thioether of Monothioethylene Glycol.—The *p*-compound was first isolated by a reaction analogous to that noted by Stadler (*loc. cit.*). The product was an oil, but it solidified after 3 weeks. It was dried on porous earthenware and recrystallised from dilute alcohol, and was identical with the material obtained more conveniently by the following method: *p*-Nitrochlorobenzene (31.5 g.) was covered with alcohol, a warm solution of sodium sulphide (48 g. of $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$) in dilute alcohol (60 c.c., 1 : 1) was added, and the mixture heated on the steam-bath until a vigorous reaction occurred. When this reaction had subsided, the mixture was heated for a further 5 minutes. Prolonged heating at this stage causes a decrease in the yield owing to oxidation of the thiophenol to disulphide (compare Willgerodt, *Ber.*, 1885, **18**, 331). The mixture was then poured into about 500 c.c. of water and cooled in a coal-gas atmosphere until the precipitated unchanged *p*-nitrochlorobenzene had solidified, and the liquid was rapidly filtered into an excess of sulphurous acid to precipitate the thiophenol and prevent oxidation. The thiophenol was quickly filtered off, dissolved in alcohol (30 c.c.), and added to a solution of potassium hydroxide (6 g. in 40 c.c. of water). The mixture was heated under reflux on the steam-bath with ethylene chlorohydrin (15 c.c.) until the dark colour faded, and the alcohol and volatile impurities were then removed in steam. The product (18 g.), which solidified on cooling, was *p*-nitrophenyl β -hydroxyethyl sulphide, which crystallised well from ether or carbon disulphide-petroleum as a pale yellow, finely crystalline solid, m. p. 62° (Found : C, 48.0; H, 4.6; N, 7.25. Calc. : C, 48.2; H, 4.5; N, 7.05%). Waldron and Reid (*loc. cit.*) give m. p. 59° .

Convenient Method of Preparation of the o-Nitrophenyl Thioether.—The analogous method can be shortened satisfactorily for the preparation of *o*-nitrophenyl β -hydroxyethyl sulphide. *o*-Nitrochlorobenzene and sodium sulphide are heated as described above and the product is poured into water. The precipitated nitrochlorobenzene, which does not solidify readily, is extracted with benzene, and the remaining solution is heated with the requisite amount of ethylene chlorohydrin for 15 minutes. It is not advisable to heat for longer than this, owing to the possible reduction of the

nitro-group by the sodium sulphide present in the solution. The yield is 17 g.

Preparation of m-Nitrophenyl β -Hydroxyethyl Sulphide.—An attempt to prepare this compound by the Stadler diazo-reaction (*loc. cit.*) gave an oil which did not crystallise. The *m*-nitrophenyl thioether was therefore made from *m*-nitrothiophenol, prepared as described by Leuckart (*J. pr. Chem.*, 1890, **41**, 179). The awkward diazotisation at great dilution was avoided thus: *m*-Nitroaniline (50 g.), dissolved in 150 c.c. of concentrated hydrochloric acid and 750 c.c. of water and cooled to 10°, was diazotised by adding sodium nitrite (26.5 g. in a little water) all at once, the temperature not being allowed to rise above 15°. This mixture was kept in ice for about 30 minutes, and the liquid was then filtered into a solution of potassium xanthate (75 g.) and borax (150 g.) in water (750 c.c.) at 70–75°. (It is necessary to add the diazo-solution cautiously, otherwise an explosive evolution of gas may be caused.) The mixture was finally heated until effervescence ceased. After cooling, the precipitated oil was removed in ether, the ether evaporated, and the crude xanthogenic ester hydrolysed. The dinitrodiphenyl disulphide, obtained by adding potassium ferricyanide to the resulting solution, was purified by recrystallisation and reduced with glucose and alkali (compare Lecher and Simon, *Ber.*, 1922, **55**, 2427), and the resulting thiophenol was converted into *m*-nitrophenyl β -hydroxyethyl sulphide in the same way as the *o*- and *p*-isomerides. The crude product was a dark oil which did not solidify. As the compound could not be distilled, even at pressures of 1 mm., it was heated at 150° with the equivalent of *p*-nitrobenzoyl chloride. The product solidified and, after recrystallising from toluene, *m*-nitrophenyl β -(*p*-nitrobenzoyl)oxyethyl sulphide was obtained as a pale yellow solid, m. p. 86° (Found: N, 8.25. $C_{15}H_{12}O_6N_2S$ requires N, 8.05%). This nitrobenzoyl derivative was hydrolysed by boiling alcoholic sodium hydroxide, the mixture poured into water, the oil which separated removed in ether, the extract dried, and the ether evaporated. The remaining oil solidified on being cooled in a freezing mixture, and *m*-nitrophenyl β -hydroxyethyl sulphide was obtained in pale yellow needles, m. p. 42.5°, by crystallisation from light petroleum (b. p. 40–60°) or warm water (Found: C, 48.0; H, 4.7; N, 7.0. $C_8H_9O_3NS$ requires C, 48.2; H, 4.6; N, 7.0%).

Little difficulty was encountered in getting the *mm'*-dinitrodiphenyl disulphide into a solid workable condition during the winter months, but when the preparation was repeated in warmer weather the disulphide solidified so slowly that it could not easily be obtained pure in quantity. The preparation of the *m*-compound has there-

fore been carried out without the isolation of the disulphide, as follows: The xanthogenic ester (20 g.) was hydrolysed with an alcoholic solution of sodium hydroxide (5 g. of sodium, 50 c.c. of alcohol, and 10 c.c. of water), and the reaction liquor was poured into water and extracted with carbon tetrachloride. The remaining solution was filtered, the filtrate dropping into water saturated with sulphur dioxide, and the precipitated thiophenol was removed in ether. The filtered ethereal solution was extracted with a solution of potassium hydroxide (10 g.) in two portions, and the extract heated on the steam-bath with ethylene chlorohydrin (10 c.c.) until the solution became clear. The precipitated oil, after being steam-blown, solidified when cooled and nucleated (yield, 9 g. of dry crude product).

Preparation of p-Nitrobenzyl β -Hydroxyethyl Sulphide.—*p*-Nitrobenzyl thiocyanate (m. p. 84°; compare Henry, *Ber.*, 1869, 2, 638) was converted into *p*-nitrobenzyl thiocarbamate by Meyer's method ("Analyse und Konstitutions Ermittlung Organischen Verbindungen," 3rd Ed., p. 678), but it was subsequently found more convenient to use the method described by Gabriel and others (*Ber.*, 1895, 28, 1027; 1896, 29, 160: compare also Poggi, *Atti R. Accad. Lincei*, 1925, 2, 423). A solution of the thiocyanate (50 g.) in concentrated sulphuric acid (250 c.c.) was kept in the ice-chest for 10 hours and then poured on ice. The precipitated thiocarbamate was filtered off and purified (m. p. 146°). The thiocarbamate was hydrolysed by boiling it under reflux with hydrochloric acid (10 parts of 20% acid) for 2 hours (compare Gabriel and Stelzner, *Ber.*, 1896, 29, 160). On cooling, the oil, *p*-nitrobenzyl mercaptan, solidified.

The alternative method of preparation of *p*-nitrobenzyl mercaptan described by Price and Twiss (*J.*, 1909, 95, 1725) was found to be less satisfactory than the description would lead one to expect and certainly gave a product inferior both in yield and in purity to that obtained by the method described above.

The conditions for the condensation of the sodium salt of *p*-nitrobenzyl mercaptan and ethylene chlorohydrin are important, in that too great a concentration of alkali and heating to too high a temperature must be avoided, or else subsidiary reactions occur. The method used was as follows: To the mercaptan prepared from the thiocarbamate (12 g.) as described above, a solution of sodium hydroxide (3 g. in 60 c.c. of water) and ethylene chlorohydrin (7 c.c.) were added and the mixture was heated, in a flask provided with a stirrer, to 50° (thermometer dipping into the reaction liquid). The mixture was kept at this temperature for 15 minutes, during which an oil separated. 2*N*-Sodium hydroxide (10 c.c.) and ethylene chlorohydrin (3 c.c.) were then added and the mixture was heated

for a further 10 minutes. The reaction liquid was steam-blown to remove volatile impurities and cooled, the oil removed in ether, the extract dried, and the ether evaporated. After being kept for several days in a desiccator, the oil solidified (9 g.).

p-Nitrobenzyl β -hydroxyethyl sulphide, which is soluble in alcohol, ether, and benzene and slightly soluble in water, crystallises best from a mixture of equal volumes of carbon disulphide and light petroleum (b. p. 40–60°) in almost colourless needles, m. p. 37·5° (Found: C, 50·6; H, 5·4; N, 6·5. $C_9H_{11}O_3NS$ requires C, 50·7; H, 5·2; N, 6·6%).

In subsequent preparations, this compound was obtained as a solid by inoculating the steam-blown reaction liquor.

Preparation of p-Nitrophenyl γ -Hydroxypropyl Sulphide.—This compound was prepared by a method analogous to that used for the *p*-nitrophenyl β -hydroxyethyl sulphide and was isolated as an oil which solidified after a few days. It was recrystallised from carbon disulphide–light petroleum and obtained in pale yellow needles, m. p. 41·5°, which are slightly soluble in water and easily soluble in ether, alcohol, benzene, and acetone (Found: C, 50·5; H, 5·5; N, 6·6. $C_9H_{11}O_3NS$ requires C, 50·7; H, 5·2; N, 6·6%).

Preparation of Halogen Derivatives.

I. *Chloro-compounds.*—The *o*- and *p*-nitrophenyl β -chloroethyl sulphides were prepared by the action of phosphorus pentachloride on the hydroxy-compound (yield, 75%).

When this method was used for the preparation of *p*-nitrophenyl γ -chloropropyl sulphide, the yield was poor (45%), owing to a large amount of phosphoric ester being formed as a by-product. The preparation of this compound was therefore repeated using the Darzens reaction (*Compt. rend.*, 1911, 152, 1314). The hydroxy-compound was dissolved in dimethylaniline (1·5 mols.), and thionyl chloride (1·5 mols.) gradually added, the mixture being kept cool. After 15 minutes, the mixture was heated on the steam-bath for 15 minutes and poured into dilute hydrochloric acid. The chloro-compound separated, and solidified on being cooled and scratched (yield, 87%). It was subsequently found that this method was preferable to the phosphorus pentachloride reaction for the preparation of the β -chloroethyl sulphides, in that the reaction product was much cleaner and solidified more readily (yield, 80–85%).

These ω -chloroalkyl sulphides are soluble in alcohol, acetone, benzene, and glacial acetic acid, and are best recrystallised from light petroleum or methyl alcohol.

Preparation of the Sulphoxides of the Halogenated Sulphides.—After the halogenated sulphide had been boiled for 15 minutes

with concentrated nitric acid (d 1.40), the product obtained on neutralising the solution had, even after several recrystallisations, an indefinite melting point.

The sulphide was dissolved in a little glacial acetic acid, and bromine (a slight excess above 1 mol.) added to the warm solution. As a dibromide ($R \cdot SBr_2 \cdot R'$) did not crystallise, the solution was neutralised and a slight excess of aqueous sodium hydroxide added. The product in this case also had a diffuse melting point.

By adding a slight excess of hydrogen peroxide (30%) to a glacial acetic acid solution of the sulphide and keeping the mixture for 24 hours, compounds of sharp melting points were obtained. The sulphoxides crystallise well from either light petroleum or dilute acetic acid.

When oxidation of the iodoethyl sulphides was attempted with hydrogen peroxide, iodine was liberated and the pure sulphoxide was not isolated.

o-Nitrophenyl β -chloroethyl sulphide crystallises in deep yellow, orthorhombic needles, m. p. 51° (Found : C, 44.0; H, 3.8; Cl, 16.3. Calc. : C, 44.1; H, 3.7; Cl, 16.3%). The *sulphoxide* forms pale yellow needles, m. p. 84° (Found : N, 6.0. $C_8H_8O_3NCIS$ requires N, 6.0%).

p-Nitrophenyl β -chloroethyl sulphide crystallises in pale yellow, monoclinic needles, m. p. 62° (Found : Cl, 16.3, 16.2. $C_8H_8O_2NCIS$ requires Cl, 16.3%). The *sulphoxide* crystallises in colourless needles, m. p. 80° (Found : C, 41.2; H, 3.6; N, 6.0. $C_8H_8O_3NCIS$ requires C, 41.1; H, 3.4; N, 6.0%).

m-Nitrophenyl β -chloroethyl sulphide forms pale yellow needles, m. p. 31° (Found : Cl, 16.2%).

p-Nitrophenyl γ -chloropropyl sulphide forms pale yellow needles, m. p. 50° (Found : N, 6.1; Cl, 15.4. $C_9H_{10}O_2NCIS$ requires N, 6.1; Cl, 15.4%).

p-Nitrobenzyl β -chloroethyl sulphide forms almost colourless needles, m. p. 46 — 47° (Found : N, 6.1; Cl, 15.2. $C_9H_{10}O_2NCIS$ requires N, 6.1; Cl, 15.4%).

II. *Bromo-compounds*.—These compounds were prepared by the action of phosphorus pentabromide on the hydroxy-compounds (see corresponding preparation of the chloro-compounds; p. 1671.) They are soluble in alcohol, benzene, acetone, and ether, and are best recrystallised from light petroleum.

o-Nitrophenyl β -bromoethyl sulphide crystallises in deep yellow, orthorhombic needles, m. p. 63° (Found : Br, 30.3. $C_8H_8O_2NBrS$ requires Br, 30.45%), and the *sulphoxide* in pale yellow needles, m. p. 112° (Found : N, 5.0%).

p-Nitrophenyl β -bromoethyl sulphide forms pale yellow, mono-

clinic needles, m. p. 59° (Found : Br, 30.1. Calc. : Br, 30.45%). Waldron and Reid (*loc. cit.*), who prepared this compound by the action of hydrobromic acid on the hydroxy-compound, give the melting point as 58°. The *sulphoxide* forms colourless needles, m. p. 100° (Found : Br, 28.6. $C_8H_8O_3NBrS$ requires N, 5.0; Br, 28.7%).

m-Nitrophenyl β -bromoethyl sulphide forms almost colourless, orthorhombic plates, m. p. 32° (Found : Br, 30.3%).

III. *Iodo-compounds*.—The interaction of phosphorus tri-iodide or phosphorus and iodine with the hydroxy-sulphides causes reduction and not simple replacement of the hydroxyl group. *o*- and *p*-Nitrophenyl β -iodoethyl sulphides have been obtained by heating the bromo-compound with a slight excess of sodium iodide in acetone solution for about 8 hours. They crystallise well from either methyl alcohol or light petroleum. The former crystallises in deep yellow plates, m. p. 64° (Found : I, 40.8. $C_8H_8O_2NIS$ requires I, 41.0%), and the latter in pale yellow plates, m. p. 67° (Found : I, 40.8%).

m-Nitrophenyl β -iodoethyl sulphide was obtained in a similar manner as a dark brown oil which did not crystallise and was not analysed. After it had been kept for a long time in the expectation of its solidifying, it was found in fact to be depositing crystals. These, on recrystallisation from petroleum (b. p. 90—120°), gave pale yellow plates, m. p. 136°, which contained sulphur and nitrogen but no iodine (Found : N, 8.2%; *M*, cryoscopic in molten camphor, 393). Sufficient of this substance was not obtained for a more detailed examination, but it seems probable that it was *di*-*m*-nitro-diphenylthiolcyclobutane,
$$NO_2 \cdot C_6H_4 \cdot S - \begin{array}{c} \text{CH} - \text{CH}_2 \\ | \quad | \\ \text{CH}_2 - \text{CH} \cdot S \cdot C_6H_4 \cdot NO_2 \end{array}$$
 which requires N, 7.7%; *M*, 362.

Crystallographic Measurements.

o-Nitrophenyl β -hydroxyethyl sulphide crystallises from acetone in deep yellow, orthorhombic crystals with $a : b : c = 0.5445 : 1 : 1.1416$. The forms observed are $b(010)$, $c(001)$, $r(101)$ and $q(011)$, the habit being tabular with c large (Fig. 1). The mean angular values obtained by measurement of seven crystals on a single-circle goniometer are : $cq^*48^\circ 47'$, $cr^*64^\circ 30'$, $rq 73^\circ 37'$ (calc. $73^\circ 31'$), $bc 89^\circ 59'$. There is a perfect cleavage in the plane (010). d_1^s (vac.) 1.472. The substance has strong positive double refraction. The plane of the optic axes is (100), the acute bisectrix emerging perpendicular to (010), and there is large dispersion of the axes.

o-Nitrophenyl β -chloroethyl sulphide was obtained in suitable crystals, after many trials, by slow crystallisation from cold ethyl

alcohol or from ethylene dichloride-ethylene chlorohydrin, in orthorhombic crystals with $a : b : c = 0.9584 : 1 : 0.5126$. The following are the forms observed and the respective mean angular values from eight crystals :

	a (100).	m (110).	x ($21\bar{2}$).	y (232).
ϕ	$0^{\circ} 0'$	$*43^{\circ} 47'$	$*24^{\circ} 47'$	$57^{\circ} 54'$
ρ	$90^{\circ} 0'$	$90^{\circ} 0'$	$*29^{\circ} 27'$	$43^{\circ} 2'$

The crystals are uniterminal and of prismatic habit similar to that shown in Fig. 2. d^{18} , 1.480.

There is an excellent cleavage in the plane (010). Examination of cleavage planes in convergent polarised light shows that the substance has strong crossed axial dispersion. The optic picture is apparently uniaxial for the D line of sodium : red light (lithium flame) gives a biaxial picture with the axes well separated in the

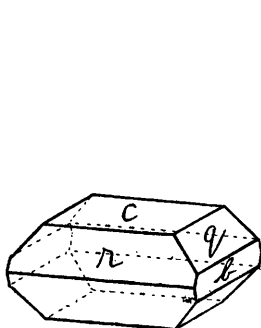


FIG. 1.

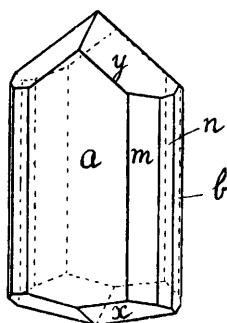


FIG. 2.

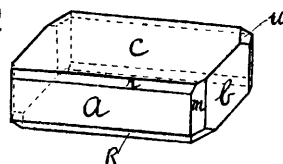


FIG. 3.

plane (100), whilst for green light (thallium) they are in the plane (001), the acute bisectrix remaining normal to (010) throughout.

o-Nitrophenyl β -bromoethyl sulphide separates from acetone in prisms (Fig. 2) belonging to the hemimorphic class of the orthorhombic system isomorphous with the foregoing, having $a : b : c = 0.9590 : 1 : 0.5250$. The following are the mean angular values (from six crystals) :

	a (100).	m (110).	n (120).	b (010).	x ($21\bar{2}$).	y (232).
ϕ	$0^{\circ} 0'$	$*43^{\circ} 48'$	$62^{\circ} 25'$	$90^{\circ} 0'$	$*23^{\circ} 53'$	$56^{\circ} 57'$
ρ	$90^{\circ} 0'$	$90^{\circ} 0'$	$90^{\circ} 0'$	$90^{\circ} 0'$	$*29^{\circ} 52'$	$43^{\circ} 10'$

There is an excellent cleavage in the plane (010). d^{17} 1.742. A straight extinction was observed on (100). The acute bisectrix emerges perpendicular to (010), the axes being widely separated in the plane (001). The dispersion is large.

o-Nitrophenyl β -iodoethyl sulphide separates from acetone in large, deep yellow, monoclinic crystals (Fig. 3) with $a : b : c =$

3.143 : 1 : 2.513; $\beta = 99^\circ 16'$. The following are the mean angular values (four crystals) :

	a (100).	m (110).	b (010).	r (101).	c (001).	R ($\bar{1}01$).	u ($\bar{1}12$).
ϕ	$0^\circ 0'$	$*72^\circ 8'$	$90^\circ 0'$	$0^\circ 0'$	$0^\circ 0'$	$180^\circ 0'$	$100^\circ 32'$
ρ	$90^\circ 0'$	$90^\circ 0'$	$90^\circ 0'$	$*44^\circ 13'$	$9^\circ 16'$	$33^\circ 45'$	$47^\circ 53'$

There is a marked tendency for b to be replaced by a pair of vicinal faces. There are poor cleavages in the planes (010) and (100). $d^{16^\circ} 2.026$. The position of the optic axes could not be observed.

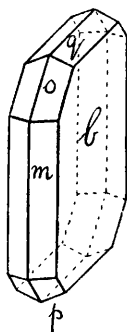


FIG. 4.

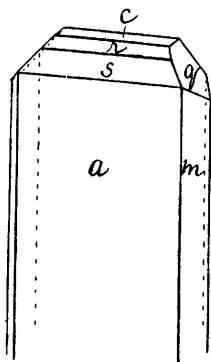


FIG. 5.

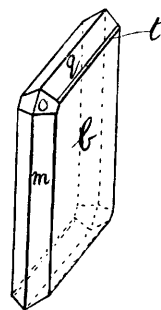


FIG. 6.

p-Nitrophenyl β -chloroethyl sulphide crystallises in the monoclinic system with $a : b : c = 0.4752 : 1 : 0.4026$; $\beta = 96^\circ 54'$. The following are the mean angular values (4 crystals), the habit being as in Fig. 4.

	b (010).	m (110).	q (011).	o (111).	p (11)
ϕ	$0^\circ 0'$	$*64^\circ 45'$	$*16^\circ 43'$	$67^\circ 52'$	$298^\circ 39'$
ρ	$90^\circ 0'$	$90^\circ 0'$	$*22^\circ 48'$	$47^\circ 15'$	$40^\circ 28'$

There is a poor cleavage in the plane (100). $d^{18^\circ} 1.486$. The extinction appears to be straight on (010). The position of the optic axes was not observed.

p-Nitrophenyl β -bromoethyl sulphide crystallises in the monoclinic system with $a : b : c = 1.8113 : 1 : 1.1187$; $\beta = 96^\circ 18'$, the habit being as in Fig. 5. The following are the mean angular values (4 crystals) :

	a (100).	c (001).	m (110).	q (011).	s (201).	r (101).
ϕ	$0^\circ 0'$	$0^\circ 0'$	$*60^\circ 57'$	$84^\circ 54'$	$0^\circ 0'$	$0^\circ 0'$
ρ	$90^\circ 0'$	$*6^\circ 18'$	$90^\circ 0'$	$*48^\circ 18'$	$36^\circ 19'$	$53^\circ 45'$

No marked cleavage was found. $d^{16^\circ} 1.742$. The extinction was straight on (100), but the position of the optic axes was not observed.

p-Nitrophenyl β -iodoethyl sulphide crystallises in the monoclinic system with $a : b : c = 0.5081 : 1 : 0.5160$; $\beta = 104^\circ 45'$, the habit

being as in Fig. 6. The following are the mean angular values (3 perfect crystals):

	<i>b</i> (010).		<i>t</i> (021).		<i>q</i> (011).		<i>m</i> (110).		<i>o</i> (111).	
ϕ	0°	0'	45°	11'	*63°	29'	*27°	24'	68°	21'
ρ	90°	0'	90°	0'	90°	0'	*29°	47'	54°	5'

There is no marked cleavage. d^{17} 1.938. The extinction on *b* is oblique at 17° 20' to the edge *bm*. The optic axial plane coincides with (010), one optic axis being seen in the centre of the field when the observation is normal to the plane (100). The dispersion is extremely high.

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