



The thiosulphonates of divalent selenium are pale greenish, and so are the selenium disulphinates, whereas the thiosulphonates of divalent tellurium are yellow. When kept in a dry, neutral atmosphere, shielded from light, the crystals remain unchanged for months.

In the following, the symbols Bs and Ts denote the benzenesulphonyl and *p*-toluenesulphonyl group, respectively.

Compound	M.p., °C (preheated bath, dec.)	% Se or Te	
		Calc.	Found
SeBs ₂	132–3	21.85	21.94
SeTs ₂	121–2	20.29	20.16
Se(SBs) ₂	152–4	19.00	19.04
Se(STs) ₂	Ca. 200	17.41	17.53
Te(SBs) ₂	Ca. 170	26.91	26.73
Te(STs) ₂	Ca. 215	25.41	25.28

The crystals of the selenium disulphinates, SeBs₂ and SeTs₂, are monoclinic prismatic, and are isomorphous with those of the corresponding sulphur derivatives, the crystal structure of which was described recently by Mathieson and Robertson⁵.

The unit cells and space group of the benzene- and *p*-toluenethiosulphonates of divalent sulphur, S(SBs)₂ and S(STs)₂, have been reported by Dawson, Mathieson and Robertson⁶. The crystals are tetragonal trapezohedral. The crystals of the following four compounds are isomorphous with those of the sulphur thiosulphonates: Selenium di(benzenethiosulphonate), selenium and tellurium di(*p*-toluenethiosulphonate), and triselenium di(*p*-toluenesulphinate), *i.e.*, Se(SBs)₂, Se(STs)₂, Te(STs)₂, and Se₃Ts₂. Tellurium di(benzenethiosulphonate), Te(SBs)₂, is orthorhombic, whereas triselenium di(benzenesulphinate), Se₃Bs₂, is triclinic.

Work on the crystal structure of the *p*-toluene compounds, Se(STs)₂, Te(STs)₂ and Se₃Ts₂, is in progress in this Institute.

1. Foss, O. *Acta Chem. Scand.* **5** (1951) 115.
2. Otto, R., and Troeger, J. *Ber.* **24** (1891) 1125.
3. Troeger, J., and Hornung, V. *J. prakt. Chem.* [2] **60** (1899) 113.
4. Foss, O. *Acta Chem. Scand.* **4** (1950) 1499.
5. Mathieson, A. McL., and Robertson, J. M. *J. Chem. Soc.* (1949) 724.
6. Dawson, I. M., Mathieson, A. McL., and Robertson, J. M. *J. Chem. Soc.* (1948) 322.

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Explosions in the Preparation of Diethylaminoethyl Dinitrate

JØRGEN FAKSTORP and JYTTE CHRISTIANSEN

Research Laboratory, "Pharmacia",
Copenhagen, Denmark

In the preparation of diethylaminoethyl dinitrate, O₂NO · CH₂ · CH₂ · N(C₂H₅)₂, HNO₃ according to the directions given by Barbière¹, we have experienced several very violent explosions.

Hence we feel compelled to call attention to the potential danger of this compound.

The procedure as described by Barbière (*l.c.*) calls for addition of 23.4 g of diethylaminoethanol to 75.6 g of fuming nitric acid under stirring in an ice bath and evaporating excess nitric acid *in vacuo* being careful not to let the bath temperature exceed 40° C.

When most of the nitric acid had evaporated our mixture invariably exploded. This explosion could not be prevented by nitrating in the presence of urea.

The following alternative procedure is suggested: After addition of the reagents,

which should take at least two hours, the reaction mixture is diluted with 200 ml of methanol and precipitated with 2 l of ether.

After a night in the icebox the solvents are decanted from the oily precipitate, which is washed with ether and dissolved in 50 ml of anhydrous ethanol. This solution is evaporated to half its volume *in vacuo* keeping a bath temperature of no more than 30° C. Upon cooling, and addition of a small amount of ether, a crystalline precipitate starts to settle, which is removed, washed with ether and dried over conc. sulphuric acid and paraffin.

The prisms melted at 60° C (Barbière finds 63° C). Yield 22 g = 50 % of the theoretical.

We have prepared other similar compounds without difficulty according to Barbière's directions.

1. Barbière, J. *Bull. Soc. Chim.* [5] 11 (1944) 473.

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The Structure of Pauly's Dibromo-diethyl Ketone

LENNART SCHOTTE

Chemical Institute, University of Uppsala, Uppsala, Sweden

A dibromo-diethyl ketone with the bromine atoms in the α -position of the keto group has been prepared by Pauly¹, and he assumed the substance to be symmetrically substituted. No structure proof is given, however, and he made his conclusions from the attributed similarity to 1,3-dichloroacetone.

When a ketone is brominated, it is well known that the first bromine atom will substitute at the α -carbon atom and the

second one, if possible, in most cases at the same α -position.² Acetone and methyl ethyl ketone are thus brominated according to the given rule, and it is surprising to find that diethyl ketone gives a symmetrical dibromide. This substance was needed in connection with other work, and a structure proof and an examination of the dibromide of diethyl ketone was therefore performed.

The usual way to get evidence about the structure of a dibromo substituted ketone is to hydrolyze the substance.³ The dibromide was thus hydrolyzed in an alkaline medium, and from the products acetylpropionyl could be isolated. The hydrolysis is very rapid and has been performed with potassium hydroxide in cooled alcohol as well as with potassium carbonate in water solution. Acetylpropionyl was easily identified by the dioxime and the orange-coloured nickel precipitate, formed from the dioxime, a well known reagent of aliphatic α -diketones. Duroquinone was also obtained from acetylpropionyl and dilute alkali hydroxide,³ and if a mixture of the dibromide and potassium carbonate in water solution is refluxed, until the dibromide is dissolved, duroquinone can be isolated from the reaction products. A similar investigation has once been performed by Faworsky on α,α -dichloropropyl methyl ketone.⁴

From the results it is obvious that the dibromide must be unsymmetrically substituted, as the hydrolysis gives an α -diketone and not α,α' -dioxi-diethyl ketone. The author is conscious, however, of the possibility of a rearrangement of the dibromo ketone from α,α' - to α,α -substitution during the hydrolysis, but it must be emphasized that such an isomerisation is not very probable in an alkaline medium and not found in analogous reactions; the Faworsky rearrangement² only results in other products of hydrolysis and is specially studied for α,α' -dibromo ketones. *The dibromide is thus α,α -dibromo-diethyl ketone.*