847. *The Action of Sulphur Monochloride on Amides of Dicarboxylic Acids*

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MONOCARBOXYAMIDES, refluxed in benzene solution with sulphur monochloride, generally undergo replacement of a hydrogen atom of the amide group to form the monosulphide, $(R\cdot CONH)_2S$.[1] The only report on dicarboxyamides is that of Naik [2] who observed no reaction in benzene. We now find that reaction can frequently be induced by increasing the polarity of the solvent. For this purpose nitromethane is most effective. In the aliphatic series oxamide is inactive, as are also the aromatic diamides, isophthalamide, and terephthalamide.

The reactions follow one of three courses: (*a*) substitution of hydrogen by sulphur at a methylene group, and the coupling of two molecules of amide to give a tri- or tetra-sulphide; (*b*) substitution of hydrogen by sulphur at one of the amide groups to give the bisdiamido *NN*-disulphide $(H_2N\cdot CO\cdot[CH_2]_n\cdot CO\cdot NH)_2S_2$; or (*c*) intramolecular elimination of ammonia to form the imide.

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[1] P. Hope and L. A. Wiles, *J.*, 1964, 5679.
[2] K. G. Naik, *J.*, 1921, **119**, 1166.

The evidence for *C*-substitution (*a*) in some amides, and *N*-substitution (*b*) in others, is fairly conclusive. *C*-Substitution occurs if the diamide has an active methylene group, *e.g.*, malonamide or malonanilide. The reaction is more vigorous than with other diamides, and occurs in solvents of lower polarity. The products are polysulphides, and this is the general reaction of sulphur monochloride with active methylene compounds.[3,4] Moreover, dimethylmalonanilide can only react at the methylene group forming a disulphide.[5] The infrared spectra of the sulphides derived from malonamide and malonanilide have each a band at 750 cm.$^{-1}$ (C–S stretching) but they have no CH_2 bands. The nuclear magnetic resonance spectrum of the sulphide from malonanilide gave a ratio of phenyl hydrogens to amide hydrogens of 7 : 1. This is inconclusive in deciding whether the compound was formed by reaction (*a*) or (*b*). The higher aliphatic diamides have inactive methylene groups and, by analogy with monocarboxyamides, form *N*-sulphides. In support of this the infrared spectrum of di-(β-carboxypropionamido) disulphide shows an NH band but no NH_2 doublet.

When the amide groups are favourably situated the products are imides (*c*), *e.g.*, from succinamide and phthalamide.

The relative inactivity to sulphur monochloride of dicarboxyamides compared with monocarboxyamides [1] cannot be attributed to inductive or mesomeric effects since deactivation of the amide group, as in trichloroacetamide, still allows a slow reaction in benezene.[1] Moreover, there is no increase in reactivity in the series $H_2N\cdot CO\cdot[CH_2]_n\cdot CO\cdot NH_2$ as *n* is increased. The inertness must be attributed to the powerful intermolecular forces which bind the amides. These forces must be particularly large in oxamide [6] (m. p. 417°), isophthalamide (m. p. 280°) and terephthalamide (decomp. >350°), none of which reacts with sulphur monochloride. A polar solvent will diminish the intermolecular forces, and it will also increase the polarisation of the sulphur monochloride molecule, $S_2Cl_2 \rightleftharpoons {}^{\delta+}S_2Cl{-}Cl^{\delta-}$. Substitution of hydrogen by the chlorodithio-cation is considered to be an initial stage in forming sulphides.[1] The following Table summarises the results.

The action of sulphur monochloride on dicarboxyamides

Amide	Solvent and product
Oxamide	(*a*), (*b*), (*c*) No reaction
Malonamide	(*a*) No reaction; (*b*) *C*-trisulphide
Malonanilide	(*a*) *C*-tetrasulphide
Succinamide	(*a*) No reaction; (*b*) succinimide; (*c*) *NN*-disulphide
Adipamide	(*a*), (*b*) No reaction; (*c*) *NN*-disulphide
Adipamic acid	(*a*) No reaction; (*c*) *NN*-disulphide
Phthalamide	(*a*) No reaction; (*b*) phthalimide
Isophthalamide	(*c*) No reaction
Terephthalamide	(*c*) No reaction

(*a*) Benzene, (*b*) dioxan, (*c*) nitromethane

Experimental.—The amides were refluxed with sulphur monochloride in solvents of increasing polarity until evolution of hydrogen chloride ceased. Infrared spectra were for mulls in hexachlorobutadiene, or as potassium bromide discs. Melting points were determined on a Kofler hot bench. The *N*-disulphides are highly insoluble compounds and are difficult to purify.

Bisdicarbamoylmethyl trisulphide. Malonamide (10·2 g., 0·1 mole) and sulphur monochloride (13·5 g., 0·1 mole) were refluxed in dioxan (100 ml., 20 hr.). A dark brown solid (8·8 g., 50%) separated. Extraction with hot methanol· gave *bisdicarbamoylmethyl trisulphide* as a buff-coloured solid, m. p. 220°; $\nu_{max.}$ 3390 and 3240 (–NH), 1675 (–CO), and 1560 cm.$^{-1}$ (–CONH) (Found: C, 24·5; H, 3·0; N, 18·5; S, 34·1. $C_6H_{10}N_4O_4S_3$ requires C, 24·2; H, 3·3; N, 18·8; S, 32·2%).

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[3] F. Magnani and A. Angeli, *Gazzetta*, 1894, **24**, (I), 342.
[4] F. Konek-Norwall, *Ber.*, 1918, **51**, 391.
[5] K. G. Naik, *J.*, 1921, **119**, 379.
[6] T. A. Scott and E. L. Wagner, *J. Chem. Phys.*, 1959, **30**, 465.

Bis[di(phenylcarbamoyl)methyl] tetrasulphide. Malonanilide (6·3 g., 0·025 mole) and sulphur monochloride (3·4 g., 0·025 mole) were refluxed in benzene (50 ml., 6 hr.). A buff-coloured solid (6·8 g., 86%) separated and was crystallised from dioxan–water, giving *bis[di(phenylcarbamoyl)methyl] tetrasulphide*, m. p. 246° (decomp.); $\nu_{max.}$ 3300 and 3240 (–NH), 1670 (–CO), and 1560 cm.$^{-1}$ (–CONH) (Found: C, 57·3; H, 4·1; N, 8·6; S, 19·8. $C_{30}H_{26}N_4O_4S_4$ requires C, 56·5; H, 4·1; N, 8·8; S, 20·2%).

Reactions of succinamide with sulphur monochloride. (*a*) Succinamide (11·6 g., 0·1 mole) and sulphur monochloride (13·5 g., 0·1 mole) were refluxed in dioxan (100 ml., 24 hr.). Succinamide (7·9 g., 68%) was recovered unchanged from the hot liquid. On cooling, sulphur (3·1 g.) and succinimide (1 g., 10%), m. p. and mixed m. p. 126°, were obtained.

(*b*) Succinamide (5·8 g., 0·05 mole) and sulphur monochloride (6·8 g., 0·05 mole) were refluxed in nitromethane (50 ml., 18 hr.). A brown solid (6·9 g., 94%) after extractions with dioxan and water gave *di-(β-carbamoylpropionamido) disulphide*, m. p. 237—239° (Found: C, 32·9; H, 4·5; N, 18·2; S, 22·2. $C_8H_{14}N_4O_4S_2$ requires C, 32·7; H, 4·8; N, 19·1; S, 21·8%).

Di-(δ-carbamoylvaleramido) disulphide. Adipamide (7·2 g., 0·05 mole) and sulphur monochloride (6·8 g., 0·05 mole) were refluxed in nitromethane (50 ml., 18 hr.). A dark coloured solid (7·4 g., 84·5%), after extractions with methanol and carbon disulphide, gave *di-(δ-carbamoylvaleramido) disulphide*, m. p. 199° (Found: C, 42·1; H, 5·9; N, 15·1; S, 15·4. $C_{12}H_{22}N_4O_4S_2$ requires C, 41·1; H, 6·3; N, 16·0; S, 18·3%).

Di(β-carboxypropionamido) disulphide. Adipamic acid (7·3 g., 0·05 mole) and sulphur monochloride (6·8 g., 0·05 mole) were refluxed in nitromethane (50 ml., 18 hr.). A dark brown solid (8 g., 90%) gave, after extractions with dioxan and water, *di-(β-carboxypropionamido) disulphide*, which did not melt below 300°; $\nu_{max.}$ 3300 (–NH), 1685 (–CO), and 1570 cm.$^{-1}$ (–CONH) (Found: C, 40·1; H, 5·7; N, 8·5; S, 19·1. $C_{12}H_{22}N_2O_6S_2$ requires C, 49·9; H, 5·7; N, 8·0; S, 18·2%).

Reaction of phthalamide with sulphur monochloride. Phthalamide (8·2 g., 0·05 mole) and sulphur monochloride (13·5 g., 0·1 mole) were refluxed in dioxan (100 ml., 5 hr.). On cooling, a mixture of phthalamide and sulphur (6·6 g.) was recovered. Evaporation of the solution gave phthalimide (2·5 g., 34%) which, crystallised from ethanol, had m. p. and mixed m. p. 238·5—240° [Found: C, 65·2; H, 3·7; N, 9·7%; *M* (Rast), 139. $C_8H_5NO_2$ requires C, 65·3; H, 3·4; N, 9·5%; *M*, 147].

Our thanks are due to Imperial Chemical Industries Limited for gifts of isophthalamide and terephthalamide, to Dr. J. Glazer, National College of Rubber Technology, for a helpful discussion, to Mr. P. J. Waring for assistance with the experimental work, and to Perkin-Elmer Ltd. for nuclear magnetic resonance spectra.

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[*Received, October 29th,* 1964.]