

149. The Formation of $\beta\beta'$ -Thiodipropionitrile (Di-2-cyanoethyl Sulphide) and a Study of its Derivatives.

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The formation of $\beta\beta'$ -thiodipropionitrile (di-2-cyanoethyl sulphide) during the reaction of viscose and acrylonitrile and its separation from the reaction mixture at low temperatures are reported. Preparation of the corresponding acid and a number of its derivatives is described. Polycondensation products of the acid and of the derived sulphone with glycols and diamines, such as polyesters and polyamides, have no useful fibre-forming properties.

WHEN acrylonitrile reacts with viscose (a solution of sodium cellulose xanthate in dilute aqueous sodium hydroxide) the viscose changes from its normal golden-brown shade to olive-green within a few minutes (cf. MacGregor and Pugh, *J. Soc. Dyers and Col.*, 1948, **64**, 71). Hollihan and Moss (*Ind. Eng. Chem.*, 1947, **39**, 222) attributed this colour change to the reaction of the acrylonitrile with by-products such as sodium thiocarbonate and sodium sulphide present in the viscose, with formation of $\beta\beta'$ -thiodipropionitrile (di-2-cyanoethyl sulphide), although they did not isolate this product from the reaction mixture.

During a recent investigation (cf. Courtaulds Ltd., MacGregor and Pugh, B.P. Appln. No. 31,659/1947) into the production of partial ethers by treatment of viscose with acrylonitrile at $<16^\circ$ we isolated $\beta\beta'$ -thiodipropionitrile in bulk. With this readily available material we have investigated the production and properties of a number of its derivatives.

Synthesis of $\beta\beta'$ -thiodipropionitrile has been described previously (cf. *e.g.*, Nekrasov, *J. Russ. Phys. Chem. Soc.*, 1927, **59**, 921; D.R.-P. 669,961; Gershbein and Hurd, *J. Amer. Chem. Soc.*, 1947, **69**, 241). Although closely related to mustard gas, it is not vesicant. Hydrolysis with boiling concentrated hydrochloric acid (cf. Nekrasov, *loc. cit.*) produced the corresponding acid, $\beta\beta'$ -thiodipropionic acid (di-2-carboxyethyl sulphide), in almost quantitative yield. The acid is of similar strength to adipic acid ($K_1 = 8.4 \times 10^{-5}$ and $K_2 = 2.1 \times 10^{-5}$, determined by electrometric titration; cf. Britton, "Hydrogen Ions," London, 1929, p. 144). Various alkyl- and aryl-amides, and esters were prepared by standard methods (cf. Experimental). Oxidation of the acid with bromine water gave a good yield of the corresponding sulphone, which, unlike the parent acid, afforded a crystalline dimethyl ester.

$\beta\beta'$ -Thiodipropionic acid and the derived sulphone were condensed in various ways with ethylene and trimethylene glycols and with hexamethylenediamine (see Experimental), but the fibre-forming properties of the products were not encouraging.

EXPERIMENTAL.

Isolation of $\beta\beta'$ -Thiodipropionitrile.—Viscose (30 kg.), containing 7.75% by wt. of cellulose (1 mol. as anhydroglucose) and 6.2% by wt. of sodium hydroxide and having a "salt index" figure of 5.5, was cooled to 10° and mixed with acrylonitrile (995 c.c., 1.05 mols.). The reaction mixture was stirred at 10—15° for 3 hours and then filtered at 40 lb./sq. in. through one plate (300 sq. in.) of a filter press wrapped with a layer of swansdown and a fine calico filter-cloth. The residue was stirred with water at 15° and filtered at the pump through a Whatman No. 54 filter paper. Washing of the residue with water (at 15°) was continued until the filtrate was free from sodium hydroxide. The crude nitrile was purified (a) by recrystallisation by cooling the aqueous solution slowly from 25° to 5° or (b) by fusing and heating it to ca. 140° (most of the water evaporating) and then filtering it through a Whatman No. 1 filter paper. The clear liquid (250 g.) was allowed to solidify. Recrystallisation of this product from ether gave colourless odourless needles, m. p. 28° (Nekrasov, *loc. cit.*, gives m. p. 24—25°) [Found: N (Kjeldahl), 19.9; S, 22.9. Calc. for $C_6H_8N_2S$: N, 20.0; S, 22.9%].

$\beta\beta'$ -Thiodipropionic Acid.— $\beta\beta'$ -Thiodipropionitrile (180 g.) and concentrated hydrochloric acid (700 c.c.) were shaken vigorously at room temperature and then heated under reflux for 2 hours on a steam-bath. After cooling, the solid was filtered off, washed with cold water, and dried at 105°, giving $\beta\beta'$ -thiodipropionic acid as colourless crystals, m. p. 131—132°. Recrystallisation from water ("Acticarbon") raised the m. p. to 134° (Nekrasov, *loc. cit.*, gives m. p. 128°) (Found: S, 18.2. Calc. for $C_6H_{10}O_4S$: S, 18.0%). The disodium salt, colourless crystals (from ethanol), did not melt below 300° (Found: S, 14.3; Na, 20.7. $C_6H_8O_4SNa_2$ requires S, 14.4; Na, 20.7%). The bisethylenediamine salt formed colourless crystals (from ethanol), m. p. 154° (Found: N, 11.6. $C_8H_{18}O_4N_2S$ requires N, 11.8%). The dimethyl ester, prepared by methanol and sulphuric acid in 90% yield, was a pale straw-coloured liquid, b. p. 158—159°/10 mm., with a rather unpleasant smell (Found: S, 15.2. $C_8H_{14}O_4S$ requires S, 15.5%).

The acid (178 g., 1 mol.) and urea (60 g., 1 mol.) were intimately mixed and heated at 160—170° for 6 hours. Three recrystallisations of the crude product (150 g., 85%) from ethanol ("Acticarbon") gave the diamide in colourless lustrous plates m. p. 182° (Bennett and Scolah, *J.*, 1927, 194, give m. p. 177—178.5°) (Found: N, 15.8; S, 18.2. Calc. for $C_6H_{12}O_2N_2S$: N, 15.9; S, 18.2%).

When prepared from the diamide (0.05 mol.) and the appropriate alcohol (0.1 mol.), the didodecyl and dihexadecyl esters formed colourless waxy crystals, m. p. 39° (Found: S, 6.4. $C_{30}H_{58}O_4S$ requires S, 6.2%), and m. p. 53.5° (Found: S, 5.2; $C_{38}H_{74}O_4S$ requires S, 5.1%), from ethanol and acetone respectively (cf. B.P. 592, 106).

The diamide (8.8 g., 0.05 mol.) and *n*-dodecylamine (18.5 g., 0.1 mol.), when heated for 5 hours at 170—180°, gave NN'-*di-n*-dodecyl- $\beta\beta'$ -thiodipropionamide as a colourless micro-crystalline substance (from ethanol) with a waxy feel, m. p. 140° (Found: N, 5.4; S, 6.3. $C_{30}H_{60}O_2N_2S$ requires N, 5.5; S, 6.3%).

The NN'-*di-n*-hexadecyl-amide, m. p. 131° (Found: N, 4.4. $C_{38}H_{76}O_2N_2S$ requires N, 4.5%), was similarly prepared.

$\beta\beta'$ -Thiodipropionanilide.—Heating $\beta\beta'$ -thiodipropionic acid (8.9 g., 0.05 mol.), aniline (9.3 g., 0.1 mol.), pyridine (10 c.c.), and phosphorus trichloride (6 c.c.) for 4 hours at 115° (cf. Hopper, MacGregor, and Wilson, *J. Soc. Dyers and Col.*, 1939, 55, 449), and recrystallisation of the product from ethanol ("Acticarbon") gave the dianilide as colourless crystals, m. p. 165° (Bennett and Scolah, *loc. cit.*, give m. p. 163.5°) (Found: N, 8.4; S, 9.8. Calc. for $C_{18}H_{20}O_2N_2S$: N, 8.5; S, 9.8%).

*$\beta\beta'$ -Thiodipropio-*p*-toluidide.*—The *di-p*-toluidide was prepared as above. Recrystallisation from ethanol ("Acticarbon") gave colourless crystals, m. p. 199° (Found: N, 7.7; S, 9.0. $C_{20}H_{24}O_2N_2S$ requires N, 7.9; S, 9.0%).

$\beta\beta'$ -Thiodipropionanilic Acid.— $\beta\beta'$ -Thiodipropionic acid (17.8 g., 0.1 mol.) and aniline (9.3 g., 0.1 mol.) were heated with fused zinc chloride (2 g.) at 150—160° for 2 hours (cf. Pressman *et al.*, *J. Amer. Chem. Soc.*, 1948, 70, 1352). The warm, fluid reaction mixture was poured into 220 c.c. of *n*-sodium hydroxide, and the whole refluxed for 1 hour. The mixture was filtered hot and the filtrate acidified with concentrated hydrochloric acid. This precipitated the monoanilide, which was cooled, filtered at the pump, and washed free from Cl⁻ and Zn²⁺. Recrystallisation from water gave the acid as small lustrous plates, m. p. 128° (Found: N, 5.3; S, 12.7%; equiv., 250. $C_{12}H_{15}O_3NS$ requires N, 5.5; S, 12.6%; equiv., 253).

*$\beta\beta'$ -Thiodipropio-*p*-toluidinic acid*, prepared similarly, and recrystallised from water, formed fine colourless needles, m. p. 134° (Found: N, 5.2; S, 11.8%; equiv., 263. $C_{13}H_{17}O_3NS$ requires N, 5.2; S, 12.0%; equiv., 267).

Di-(2-carboxyethyl) Sulphone.— $\beta\beta'$ -Thiodipropionic acid (44 g.) was covered with 440 c.c. of water, and 25 c.c. of bromine were added gradually. The reddish-orange solution was set aside at room temperature for 1 hour and then heated on a steam-bath for 30 minutes, filtered hot, and allowed to cool. The solid product was washed with water and dried at 110°; the sulphone (86%) melted at 219—220° (Found: S, 15.0. Calc. for $C_6H_{10}O_6S$: S, 15.2%).

The acid (30.4 g.), methanol (304 c.c.), and concentrated sulphuric acid (15 c.c.) were refluxed for 12 hours and then allowed to cool slowly. The dimethyl ester which crystallised was filtered off, pressed dry, washed with dilute sodium carbonate solution, and then water. Recrystallisation from methanol gave a product melting at 115° (Found: S, 13.4. $C_8H_{14}O_6S$ requires S, 13.4%).

Polymers.

Polyesters.—(a) $\beta\beta'$ -Thiodipropionic acid (8.9 g.) and ethylene glycol (2.82 c.c., 1.05 mols.) were heated in a metal bath at 190°/15 mm. for 3 hours. A slightly viscous golden liquid was obtained. The liquid was then heated at 220°/2 mm. for 5 hours, giving a golden-yellow viscous oil, insoluble in water.

(b) Trimethylene glycol, brought into reaction similarly, gave a highly viscous oil whence very small colourless crystals, m. p. 40°, were obtained by means of acetone and "Acticarbon." The polymers from both glycols yielded no fibres and were probably of relatively low molecular weight.

(c) Di-(2-carbomethoxyethyl) sulphone (11.9 g.), ethylene glycol (4.2 g., 1.35 mols.), and anhydrous potassium carbonate (0.01 g.) were heated for 2 hours at 180—200°, then for 2 hours at 220—240°/3 mm. and for 6 hours at 250—260°/3 mm. The product was a dark brown solid, m. p. >285°. Poor fibres could be drawn from the melt.

With lithium methoxide as catalyst, pronounced decomposition of the sulphone occurred at the reaction temperature (280—300°), giving a black porous brittle product.

In both cases, but more markedly with the lithium methoxide catalyst, unpleasant-smelling volatile by-products were obtained.

(d) Di-(2-carboxyethyl) sulphone (10.5 g.), ethylene diacetate (10.5 g., 1.44 mols.), and toluene-*p*-sulphonic acid (0.05 g.) were heated for 2 hours at 190—210° in nitrogen, and then for 6.5 hours at 230—240°/1—2 mm. An unpleasant-smelling volatile by-product was detected. The product was a black solid, m. p. ca. 320—330° (decomp.), with only a poor fibre-forming capacity.

Polyamides.—(a) $\beta\beta'$ -Thiodipropionic acid (17.8 g., 0.1 mol.) and hexamethylenediamine (11.6 g., 0.1 mol.) were heated at 190° for 3 hours and then for a further 3 hours at 220°/2 mm. The product was dissolved in *m*-cresol, and the polymer precipitated as a colourless granular powder by pouring the solution into a large volume of ethanol. The dry powder contained 10.8% of nitrogen, as required by a polymer of $(-\text{HN}(\text{CH}_2)_6\text{NH}\cdot\text{CO}(\text{CH}_2)_2\text{S}(\text{CH}_2)_2\text{CO}-)_x$. The thiopolyamide had an intrinsic viscosity of 1.1 and yielded poor fibres of low tenacity at 217—226°. The polymer was soluble in *m*-cresol and dimethylformamide and had m. p. ~210° (decomp.). The fibres exhibited dichroic properties.

(b) The hexamethylenediamine salt of $\beta\beta'$ -thiodipropionic acid (crystals, m. p. 181—182°, from ethyl alcohol) was prepared by mixing equimolar quantities of the acid and the diamine in 50% aqueous alcohol. The salt was heated at 220—230°/1—2 mm. for 3 hours. The polymer was purified by dissolution in *m*-cresol and pouring into a large volume of ethanol. The precipitated thiopolyamide was a colourless substance which yielded fibres of poor strength but having intrinsic viscosity of 1.2. These fibres and those recorded in the previous paragraph can be "cold-drawn" and give highly crystalline X-ray diffraction patterns.

An attempt was made to wet spin the thiopolyamides from *m*-cresol solution, using a hypodermic needle and spinning into 10, 20, 25, and 35% aqueous sodium hydroxide (ethanol was unsatisfactory), 25% appearing to be the most useful concentration. No stretch was put on the fibre as spun. The fibres obtained, however, were excessively brittle and disintegrated on the lightest touch.

(c) The salt, m. p. 160°, obtained from di-(2-carboxyethyl) sulphone and hexamethylene diamine, was heated in boiling xylenol through which a stream of nitrogen was passed. In the first run, a black sticky resinous material was obtained, and, in the second, a solid which had not melted at 290° but showed appreciable signs of decomposition.

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