35. *Preparation of Analogous Organic Derivatives of Sulphur, Selenium, and Tellurium.*

By N. M. CULLINANE, A. G. REES, and C. A. J. PLUMMER.

The preparation of diphenylene sulphide (two methods), selenide (two methods), and telluride is described.

DIAZOTISATION of 2-aminodiphenyl sulphide, followed by treatment of the product with 50% sulphuric acid, affords a fair yield of diphenylene sulphide (I). Courtot and Bastani (*Compt. rend.*, 1936, **203**, 198) obtained the same compound in unstated yield by heating diphenylene telluride (IV) with sulphur. Sulphur likewise replaces selenium in diphenylene selenide (II), giving a 56% yield of diphenylene sulphide.

Diphenylene sulphide reacts with acetyl chloride in presence of aluminium chloride to give a *diacetyl* derivative. Although the constitution of this substance has not been established,* comparison with other substitution derivatives in this series indicates that the acetyl groups are attached at the 3- and 6-positions (compare, *e.g.*, Cullinane, Davies, and Davies, J., 1936, 1436; Chaix and De Rochebouët, *Bull. Soc. chim.*, 1935, **2**, 273). 3-Acetyldiphenylene oxide is similarly formed from acetyl chloride and diphenylene oxide (Mayer and Krieger, *Ber.*, 1922, **55**, 1659).

2-Nitrodiphenyl selenide can be obtained in small yield by the condensation of *o*-nitrobenzenediazonium chloride and sodium selenophenoxide, the intermediate unstable diazo-selenoether losing nitrogen on being heated :

$$C_6H_5{\cdot}SeK + ClN_2{\cdot}C_6H_4{\cdot}NO_2 \longrightarrow C_6H_5{\cdot}Se{\cdot}N_2{\cdot}C_6H_4{\cdot}NO_2 \longrightarrow C_6H_5{\cdot}Se{\cdot}C_6H_4{\cdot}NO_2$$

A much better yield results from the condensation of *o*-chloronitrobenzene and potassium selenophenoxide; this method has not hitherto been employed for the synthesis of diaryl selenides.

The diazonium salt derived from 2-aminodiphenyl selenide, when boiled with 50% sulphuric acid, affords no diphenylene selenide (contrast that of the corresponding sulphide); by choosing a suitable concentration of acid, however, a very small quantity can be obtained. Both diphenyl diselenide and benzeneseleninic acid are simultaneously produced. This shows that scission of the selenium bond occurs, for each of these substances is readily formed from the selenophenol resulting from the rupture.

Copper-bronze reacts readily with thianthren to give diphenylene sulphide (Cullinane,

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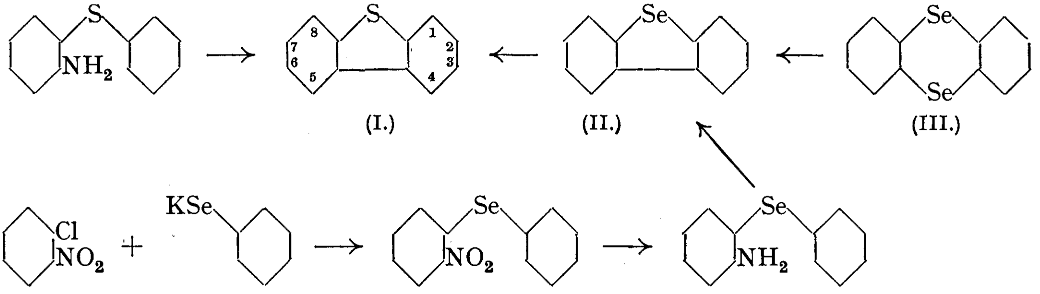
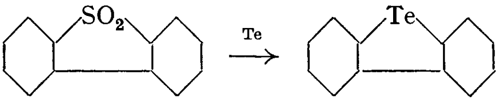
* (*Note added in proof.*) Burger, Wartman, and Lutz (*J. Amer. Chem. Soc.*, 1938, **60**, 2630) have now established the constitution of this substance, for which they give m. p. 208—209°, by the series of reactions: diacetyl compound -> dioxime -> diacetamido-compound -> 3 : 6-diaminodiphenylene sulphide.

Morgan, and Plummer, *Rec. Trav. chim.*, 1937, **56**, 629). Selenanthren (III) is converted with equal ease into diphenylene selenide.



(I.) (II.) (III.)

Diphenylenesulphone is converted by the action of sulphur and selenium into diphenylene sulphide (Cullinane and Davies, *Rec. Trav. chim.*, 1936, **55**, 884) and selenide (Cullinane, Morgan, and Plummer, *loc. cit.*) respectively. Contrary to the statement of Courtot and Bastani (*loc. cit.*), the action of heat on a mixture of diphenylenesulphone and tellurium gives diphenylene telluride; the yield, however, diminishes progressively from sulphide to telluride.



(IV.)

EXPERIMENTAL.

Diphenylene Sulphide.—(a) A solution of 2-aminodiphenyl sulphide (4 g.) (Cullinane and Davies, *loc. cit.*) in hot dilute sulphuric acid (60 c.c.) was rapidly cooled, and the finely divided sulphate diazotised at 0° with sodium nitrite (1·7 g.) in water (10 c.c.), the mixture being stirred during 2 hours; the diazonium salt separated in yellow needles. The mixture was then poured gradually into sulphuric acid (300 c.c.) so that the ultimate concentration of acid was 50%, and, after boiling under reflux for 7 hours, the product was distilled with steam. Diphenylene sulphide was precipitated from the distillate with sodium hydroxide solution, washed with water, and crystallised from alcohol, colourless needles (1·5 g.), m. p. and mixed m. p. 99°, being obtained.

(b) Diphenylene selenide (4 g.) and sulphur (0·8 g.) were well mixed and heated gradually to gentle boiling, crystals which sublimed on the condenser walls being melted down from time to time. After 6 hours, when addition of concentrated sulphuric acid to a test portion showed that there was scarcely any selenide present (the sulphide gives no coloration), the product was distilled with steam, and the solid distillate recrystallised from alcohol. The yield of diphenylene sulphide, m. p. 99°, was 56%.

3 : 6-*Diacetyldiphenylene Sulphide.*—Treatment of diphenylene sulphide with acetyl chloride and anhydrous aluminium chloride under various conditions furnished no monoacetyl derivative.

Diphenylene sulphide (5 g.) was dissolved in dry carbon disulphide (50 c.c.), aluminium chloride (5 g.) and acetyl chloride (2·5 g.) added, and the mixture boiled under reflux with frequent shaking for 2 hours, hydrogen chloride being evolved. The oily solid remaining after removal of the solvent and addition of dilute hydrochloric acid to the residue was washed with ether, and the undissolved portion extracted with boiling acetone. Several crystallisations from the same solvent gave pale yellow needles (about 1 g.), m. p. 210° (Found: S, 12·2. $C_{16}H_{12}O_2S$ requires S, 11·9%).

Diphenylenesulphone-3 : 6-*dicarboxylic Acid.*—A mixture of the diacetyl compound (4·2 g.), bleaching powder (18 g.), and dilute sodium hydroxide solution (140 c.c.) was stirred mechanically for 3 hours at 70°. A further 2 g. of bleaching powder were then added, and the experiment continued for 2 hours more, while the water-bath was raised gradually to the b. p. The liquid was filtered, the residue extracted with boiling aqueous sodium hydroxide, and the filtrates combined and acidified with concentrated hydrochloric acid. The precipitate of small needles (3 g.), which did not melt below 400°, was redissolved in alkali solution and reprecipitated [Found: equiv., 156. $C_{12}H_6SO_2(CO_2H)_2$ requires equiv., 152]. The *acid* was insoluble in most organic solvents.

2-*Nitrodiphenyl Selenide.*—Repetition of the synthesis of Keimatsu, Yokota, and Satoda (*J. Pharm. Soc. Japan*, 1932, **52**, 531) gave only a small yield. Potassium hydroxide (5·9 g.), heated with water (1·5 c.c.), was added to a solution of *o*-chloronitrobenzene (13·5 g.) and selenophenol (15 g.) in hot alcohol. The brownish solution was boiled under reflux in a nitrogen atmosphere for 12 hours. The light brown solid deposited on cooling was washed with a little cold alcohol and with water and recrystallised from acetone–alcohol. The required nitro-compound (18 g.; 75% yield, calculated on the chloronitrobenzene) was deposited in bright yellow needles, m. p. 92°. The product of the Japanese authors melted at the same temperature.

2-Aminodiphenyl Selenide.—Keimatsu, Yokota, and Satoda reduced the nitro-compound with zinc dust and dilute sulphuric acid. An 80% yield of the amine was afforded by reduction with iron filings, ferric chloride, and water. The amine was extracted in much dilute hydrochloric acid, liberated with sodium hydroxide solution, and distilled in steam. An ethereal extract of the distillate yielded colourless needles, m. p. 36°. The hydrochloride formed colourless needles, m. p. 163° (decomp.).

Diphenylene Selenide.—(a) 2-Aminodiphenyl selenide (2·75 g.) was ground with dilute sulphuric acid (12 c.c.) and diazotised at 0° with sodium nitrite (0·92 g.) in water (10 c.c.). The clear solution of the diazonium salt was poured after 30 minutes into sulphuric acid (200 c.c.), the ultimate concentration of acid being 50%. The mixture was boiled under reflux for 4 hours, and the product distilled with steam. Excess of aqueous sodium hydroxide precipitated from the distillate a solid, which, crystallised from alcohol, gave yellow needles of diphenyl diselenide, m. p. 63°. Acidification of the alkaline filtrate gave a deposit, which, when recrystallised from alcohol, afforded benzeneseleninic acid in yellow needles, m. p. 124°. No diphenylene selenide could be isolated. In another experiment, 85% sulphuric was used, the mixture stirred at 45—50° for 1½ hours, cooled, and poured on ice, and excess of solid sodium carbonate added. Distillation with steam yielded a minute quantity of diphenylene selenide in colourless needles, m. p. 71°, identified by comparison with an authentic sample. The other products mentioned above were also isolated.

Diphenylene selenide becomes deep blue on addition of concentrated sulphuric acid; on warming, it dissolves to a purplish-red solution, which becomes colourless on further heating or on addition of a drop of concentrated nitric acid.

(b) In the preparation of selenanthren * from selenium and diphenylenedisulphone (Krafft and Kaschau, *Ber.*, 1896, **29**, 443) the temperature has to be regulated very carefully if a satisfactory yield is to be obtained. When the heating is too vigorous, resulting in rapid evolution of sulphur dioxide, the selenanthren formed is largely decomposed and a small quantity only is isolated. The formation of selenophenol, which rapidly changes into diphenyl diselenide, m. p. 63°, is observed. The following method gives a yield of 44%. The disulphone and selenium are well mixed and heated gradually to the m. p. A crust forms on the surface of the liquid and this is melted down at intervals. After several hours the crust ceases to form, all the reaction mixture remaining molten. As the reaction progresses, the flame is gradually lowered, the evolution of gas being maintained at a rather slow rate. When sulphur dioxide has almost ceased to be formed, the product is worked up as described by Krafft and Kaschau.

Selenanthren (3 g.) was heated with copper-bronze (12 g.) under a long air condenser while nitrogen was passed through the vessel. The temperature was gradually raised to 230° (bath temperature) and maintained at this point for 4 hours. The product was extracted with hot acetone, the solvent removed, and the residue distilled with superheated steam. The white solid obtained on recrystallisation from alcohol was diphenylene selenide (yield, 60%).

Diphenylene Telluride.—Diphenylenesulphone (Cullinane and Davies, *loc. cit.*) (8 g.) and tellurium (6 g.) were mixed thoroughly and heated in an atmosphere of carbon dioxide until evolution of sulphur dioxide indicated that reaction had begun. The temperature was regulated so that the evolution of gas was continuous, the sublimate of sulphone being melted down from time to time. After 36 hours the product was extracted with boiling acetone, and the extract evaporated to dryness. The solid residue was washed with cold alcohol, in which the telluride dissolved, the sulphone remaining unaffected. The product resulting from evaporation of the alcohol was distilled in steam and recrystallised from light petroleum, colourless needles (about 1 g.), m. p. 93°, being obtained. The crystals became violet on addition of cold concentrated sulphuric acid and then gave a colourless solution.

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THE TATEM LABORATORIES, UNIVERSITY COLLEGE, CARDIFF. [*Received, November 30th,* 1938.]

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* Preliminary experiments indicate that the two isomeric dioxides melt at 249° and 266°. This work is being continued.