CCLIX.—*The Reactions of Divinyl Sulphide, Sulphoxide, and Sulphone.*

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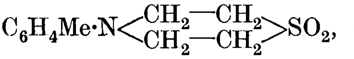
It has been shown by Bales and Nickelson (J., 1922, **121**, 2137; 1923, **123**, 2486) that when divinyl sulphide is treated with hydrogen chloride, αα′-dichlorodiethyl sulphide, $(CHClMe)_2S$, results. The constitution of this substance is established by its preparation from α-trithioacetaldehyde and either sulphur monochloride or dichloride (Mann and Pope, J., 1923, **123**, 1175). In the same way, Bales and Nickelson showed that divinyl sulphide added on hydrogen bromide, and the present authors have established that this is also an α-compound because it passes to trithioacetaldehyde very readily on treatment with alkali. Bales and Nickelson found it impossible to isolate an additive compound from divinyl sulphide and *dry* hydrogen iodide. The authors, however, by using aqueous hydriodic acid, obtained an addition compound which proved to be ββ′-diiododiethyl sulphide. Another substance with which divinyl sulphide yielded a β-addition product was thiophenol, which readily gave di-β-phenylthioldiethyl sulphide, $(SPh\cdot CH_2\cdot CH_2)_2S$, previously prepared by Helfrich and Reid (*J. Amer. Chem. Soc.*, 1920, **42**, 1231).

Divinyl sulphoxide, in contrast to the sulphide, yields no additive compounds with the halogen acids, but with aqueous sodium hydroxide it yields the oxide of 1 : 4-thioxan, $SO(CH_2\cdot CH_2)_2O$, and with sodium methoxide ββ′-dimethoxydiethyl sulphoxide,

$$(MeO\cdot CH_2\cdot CH_2)_2SO.$$

In both these cases β-addition products result.

Divinylsulphone proves to be extremely reactive, and readily yields additive compounds with a large number of different substances. The compounds resulting may be either straight-chain compounds or six-membered rings; in all cases, however (except with bromine), a hydrogen atom is added in the α-position. Hydrogen bromide and hydrogen iodide yield the β-halogenosulphones; phenol, thiophenol, and aniline also yield open-chain β-derivatives. The case of aniline is interesting because Helfrich and Reid (*loc. cit.*) found that ββ′-dichlorodiethylsulphone when treated with *p*-toluidine yielded 4-*p*-tolyl-1 : 4-sulphonazan,  $C_6H_4Me{\cdot}N{<}\begin{matrix}CH_2{-}CH_2\\CH_2{-}CH_2\end{matrix}{>}SO_2$, whereas the present authors have found that divinylsulphone and aniline readily yield ββ′-*dianilinodiethylsulphone*, $(NHPh{\cdot}CH_2{\cdot}CH_2)_2SO_2$. Examples of ring formation with divinylsulphone are furnished by the behaviour of this substance towards aqueous alkali, glycine ester, hydrogen sulphide, and phenylhydrazine.

The action of tertiary amines on ββ′-dichlorodiethyl sulphide, sulphoxide, and sulphone has been studied by Lawson and Reid (*J. Amer. Chem. Soc.*, 1925, **47**, 2821). In most cases quaternary ammonium salts were formed. The attention of the authors was drawn by Dr. E. Walker to the fact that, when ββ′-dichlorodiethylsulphone is treated with triethylamine, the hydrochloride of this amine separates rapidly, and with his consent we have investigated the action of this base on various halogeno-sulphides, -sulphoxides, and -sulphones. With ββ′-dichlorodiethyl sulphide and sulphoxide, triethylamine has practically no reaction in the cold; ββ′-di-iododiethyl and αββ′-trichlorodiethyl sulphoxide, however, react readily with the formation of the divinyl sulphoxides. With triethylamine, ββ′-dichlorodiethylsulphone reacts almost instantaneously in the cold, and divinylsulphone, $(CH_2{:}CH)_2SO_2$, can be readily prepared by this method.

The reaction between ββ′-dichlorodiethyl sulphide and potassium cyanide was studied by Davies (J., 1920, **117**, 297). A compound was obtained to which the formula $CN{\cdot}[CH_2]_2{\cdot}S{\cdot}[CH_2]_2{\cdot}S{\cdot}[CH_2]_2{\cdot}CN$ was given. This reaction with the sulphoxide and sulphone has been found to yield respectively divinyl sulphoxide and dicyanodiethylsulphone, $(CN{\cdot}CH_2{\cdot}CH_2)_2SO_2$, which was converted into ββ′-dicarboxyethylsulphone, m. p. 210°, previously prepared by Lovén (*Ber.*, 1896, **29**, 1138).

EXPERIMENTAL.

A. *Reactions of Divinyl Sulphide.*

The divinyl sulphide employed in these experiments was prepared by the method of Bales and Nickelson (J., 1922, **121**, 2137).

Addition of Halogens.—αβ-*Dichloroethyl vinyl sulphide*,

$CH_2Cl{\cdot}CHCl{\cdot}S{\cdot}CH{:}CH_2$, was prepared from divinyl sulphide by the addition of the calculated quantity of chlorine in carbon tetrachloride solution. It was a brownish oil, b. p. 84—85°/20 mm. (Found : C, 30·8; H, 3·8; Cl, 44·9. $C_4H_6Cl_2S$ requires C, 30·6; H, 3·8; Cl, 45·2%).

When this compound was treated with alcoholic potassium hydroxide it yielded β-*chlorodivinyl sulphide*, CHCl:CH·S·CH:CH_2, b. p. 123—124°/760 mm. (Found: S, 26·3; Cl, 29·3. C_4H_5ClS requires S, 26·6; Cl, 29·5%).

αβα′β′-*Tetrachlorodiethyl sulphide*, $(CH_2Cl{\cdot}CHCl)_2S$, was prepared by treating divinyl sulphide with 2 mols. of chlorine. It was a pale yellow liquid, b. p. 132—133°/15 mm. (Found : Cl, 62·2. $C_4H_6Cl_4S$ requires Cl, 62·3%). When dissolved in benzene and treated with slightly more than 1 mol. of triethylamine, it yielded αβ-*dichloroethyl*-β′-*chlorovinyl sulphide*, $CH_2Cl{\cdot}CHCl{\cdot}S{\cdot}CH{:}CHCl$, b. p. 103—104°/20 mm. (Found : Cl, 55·2. $C_4H_5Cl_3S$ requires Cl, 55·6%).

With bromine and with iodine, divinyl sulphide yielded undistillable fuming oils.

Addition of Halogen Acids.—It has been shown by Bales and Nickelson (*loc. cit.*) that with hydrogen chloride and hydrogen bromide, divinyl sulphide yields di-α-halogeno-diethyl sulphide. We have now found that when it is warmed in alcoholic solution with a concentrated aqueous solution of hydriodic acid, it affords ββ′-di-iododiethyl sulphide, m. p. 56—60°.

Other Additive Reactions.—When divinyl sulphide was warmed with two molecular proportions of thiophenol, there resulted di-β-phenylthioldiethyl sulphide, $(SPh{\cdot}CH_2{\cdot}CH_2)_2S$, m. p. 57°, identical with the compound prepared by Helfrich and Reid (*loc. cit.*). In the same way phenol gives an additive compound with divinyl sulphide.

Divinyl sulphide when treated with aniline, with sodium hydroxide, or with sodium methoxide gave only polymerisation products.

B. *Reactions of Divinyl Sulphoxide*, $(CH_2{:}CH)_2SO$.

This compound was prepared by the following method : ββ′-Di-iododiethyl sulphoxide (40 g.) was dissolved in dry benzene (600 c.c.) and treated with slightly more than 2 molecular proportions of triethylamine. The mixture was kept for 8 days, the triethylamine hydriodide removed, the benzene distilled off, and the residual oil distilled in a vacuum. Divinyl sulphoxide was obtained in 75% yield as a colourless stable oil, b. p. 86—87°/18 mm. This compound is identical with that obtained by Lewin (*J. pr. Chem.*, 1930, **127**, 77) by oxidation of divinyl sulphide with perbenzoic acid.

αβα′β′-*Tetrachlorodiethyl sulphoxide*, $(CH_2Cl{\cdot}CHCl)_2SO$, was prepared in carbon tetrachloride solution, and when crystallised from alcohol gave white needles, m. p. 121° (Found : S, 13·1. $C_4H_6OCl_4S$ requires S, 13·1%). Similarly, *αβα′β′-tetrabromodiethyl sulphoxide*, when recrystallised from carbon tetrachloride, gave hard white needles, m. p. 119° (Found : C, 11·2; H, 1·5. $C_4H_6OBr_4S$ requires C, 11·3; H, 1·4%).

Divinyl sulphoxide did not react under any conditions with hydrogen chloride; with hydrogen bromide it gave insoluble polymerisation products, and it was decomposed by hydrogen iodide.

When divinyl sulphoxide was heated with 5% aqueous sodium hydroxide for 6 hours it yielded the oxide of 1 : 4-thioxan, m. p. 30°. This compound has been described by Cashmore (J., 1923, **123**, 1738) as being formed when ββ′-dichlorodiethyl sulphoxide is treated with aqueous sodium hydroxide.

Divinyl sulphoxide when boiled with sodium methoxide in dry methyl alcohol gave ββ′-dimethoxydiethyl sulphoxide, a colourless oil, b. p. 164—165°/17 mm. The constitution of this compound was established by preparing it by the action of methyl-alcoholic sodium methoxide on ββ′-dichlorodiethyl sulphoxide. In a similar manner it was found that divinyl sulphoxide and sodium ethoxide interacted to give the corresponding diethoxy-compound (compare Cashmore, *loc. cit.*).

No reaction occurred between divinyl sulphoxide and thiophenol, phenylhydrazine, or aniline.

β-Chlorodivinyl sulphoxide, $CH_2:CH\cdot SO\cdot CH:CHCl$, was prepared by the action of triethylamine on trichlorodiethyl sulphoxide (Pope and Mann, J., 1922, **121**, 603) in ethereal solution. It is a liquid boiling at 73—74°/15 mm. (Found : C, 35·2; H, 3·5. C_4H_5OClS requires C, 35·2; H, 3·6%).

C. *Reactions of Divinylsulphone*, $(CH_2:CH)_2SO_2$.

This compound was prepared by the following method : ββ′-Dichlorodiethylsulphone (20 g.) was dissolved in dry benzene (250 c.c.), and triethylamine (21 g.) added. The triethylamine hydrochloride separated immediately, and the reaction was completed in 24 hours. After removal of the hydrochloride and the benzene, the sulphone was obtained in 80% yield as a colourless oil, b. p. 120—121°/18 mm. This compound was prepared by Lewin (*loc. cit.*) by the oxidation of divinyl sulphide with perbenzoic acid. It polymerises on standing for several months.

Addition of Halogens.—It was impossible to obtain an additive compound from chlorine and divinylsulphone. With bromine, however, this sulphone readily yielded *αβα′β′-tetrabromodiethylsulphone*, which, when crystallised from carbon tetrachloride, gave white needles, m. p. 138° (Found : C, 11·1; H, 1·4. $C_4H_6O_2Br_4S$ requires C, 11·1; H, 1·4%).

Addition of Halogen Acids.—Divinylsulphone and hydrogen chloride do not react under any conditions. On the other hand, when the sulphone was heated with a concentrated aqueous solution of hydrogen bromide, ββ'-dibromodiethylsulphone, m. p. 110—111°, was obtained. The constitution of this compound is established by the fact that the same substance was obtained by Lewin (*loc. cit.*) by oxidising ββ'-dibromodiethyl sulphide with perbenzoic acid. In a similar manner, divinylsulphone and hydrogen iodide react to give ββ'-di-iododiethylsulphone.

When divinylsulphone was heated with 5% aqueous sodium hydroxide there resulted the dioxide of 1 : 4-thioxan, m. p. 130° (compare Baumann and Walter, *Ber.*, 1893, **26**, 1124).

ββ'-*Dimethoxydiethylsulphone*, $(MeO\cdot CH_2\cdot CH_2)_2SO_2$, was prepared by boiling either divinylsulphone or ββ'-dichlorodiethylsulphone with sodium methoxide in dry methyl alcohol. It is a colourless oil, b. p. 170—171°/17 mm., which solidifies to a very hygroscopic crystalline mass, m. p. 35° (Found: C, 39·4; H, 7·6. $C_6H_{14}O_4S$ requires C, 39·5; H, 7·7%).

In a similar manner, divinylsulphone yields the diethoxy- and the di*iso*amyloxy-diethylsulphone when treated with the sodium alkyloxide in the appropriate alcohol.

With phenol, divinylsulphone condenses readily to yield ββ'-diphenoxydiethylsulphone, m. p. 105—106° (Helfrich and Reid, *loc. cit.*). Similarly, thiophenol and divinylsulphone react in the cold to give ββ'-diphenylthioldiethylsulphone.

ββ'-*Dianilinodiethylsulphone*, $(NHPh\cdot CH_2\cdot CH_2)_2SO_2$, was prepared by warming divinylsulphone and aniline for 6 hours on a water-bath, pouring the mixture into water, and shaking it with acetic acid; the substance solidified slowly, and after recrystallisation from alcohol melted at 94—95° (Found : C, 62·6; H, 6·6; S, 10·6. $C_{16}H_{20}O_2N_2S$ requires C, 63·1; H, 6·6; S, 10·5%).

When divinylsulphone is warmed with glycine ester in alcoholic solution, ethyl 1 : 4-sulphonazan-4-acetate (m. p. 67°; picrate, m. p. 190°) resulted (compare Cashmore and McCombie, J., 1923, **123**, 2884).

4-*Anilino*-1 : 4-*sulphonazan* was obtained when divinylsulphone or ββ'-dichlorodiethylsulphone and phenylhydrazine were warmed for 3 hours in alcoholic solution. When recrystallised from alcohol, it melted at 192° (Found: S, 14·2. $C_{10}H_{14}O_2N_2S$ requires S, 14·2%).

Divinylsulphone reacted neither with acid chlorides, such as acetyl chloride, thionyl chloride, and carbonyl chloride, nor with ammonia, hydrazine, phthalimide, benzaldehyde, or formic acid.

When divinylsulphone is treated with hydrogen sulphide, a small quantity of the *dioxide* of 1 : 4-*dithian*, $SO_2<(CH_2{\cdot}CH_2)_2>S$, was formed, together with a large quantity of polymerisation products. This substance when crystallised from alcohol melted at 206°; its constitution was established by its preparation from the interaction of ββ′-dichlorodiethyl sulphide and sodium sulphide (Found : C, 31·6; H, 5·4. $C_4H_8O_2S_2$ requires C, 31·6; H, 5·3%).

β-Chloroethylvinylsulphone, $CH_2Cl{\cdot}CH_2{\cdot}SO_2{\cdot}CH{:}CH_2$, was prepared from the dichloro-sulphone by treatment with one molecular proportion of triethylamine in benzene solution; b. p. 152—154°/17 mm. (Found : Cl, 22·7; S, 21·1. Calc. for $C_4H_7O_2ClS$: Cl, 22·9; S, 20·8%). This compound has been prepared by Kretov (*J. Russ. Phys. Chem. Soc.*, 1930, **62**, 1) by the reduction of ββ′-dichlorodiethylsulphone.

β-*Chloro*-β′-*iododiethylsulphone*, $CH_2Cl{\cdot}CH_2{\cdot}SO_2{\cdot}CH_2{\cdot}CH_2I$, was obtained from the chloroethylvinylsulphone by treatment with aqueous hydriodic acid. It melted at 125—126° (decomp.) (0·1247 G. gave 0·1653 g. AgCl + AgI. $C_4H_8O_2ClIS$ requires 0·1669 g.). The constitution of this substance was established by its ready conversion, by means of sodium iodide, into ββ′-di-iododiethylsulphone.

ββ′-Dichlorodiethylsulphone reacts with potassium cyanide to give ββ′-*dicyanodiethylsulphone*, plates from alcohol, m. p. 84° (Found : C, 40·9; H, 4·5; N, 16·23. $C_6H_8O_2N_2S$ requires C, 41·7; H, 4·4; N, 16·3%). This compound on hydrolysis with dilute acid yields ββ′-dicarboxyethylsulphone, previously obtained by Lovén (*loc. cit.*), plates, m. p. 210°.

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