66. *Reactions of Ethylene Oxides. Part II. Reactions with Thioamides, Thiols, and Inorganic Sulphur Salts.*

By C. C. J. Culvenor, W. Davies, and N. S. Heath.

Alkali thioalkoxides react with extreme ease with ethylene oxides to form the 2-hydroxyalkyl sulphides, and alkali sulphides react in a similar manner. With a simple ethylene oxide, potassium *o*-aminothiophenoxide gives a dihydrobenz-1 : 4-thiazine, and with a glycidic ester forms a 3-ketodihydrobenz-1 : 4-thiazine substituted in the 2-position, and this compound is readily hydrolysed to the 3-ketodihydrobenzthiazine. Ethylene oxide reacts with thiosulphates as well as with neutral sulphites to form an isethionate. Some simple ethylene oxides are converted into the corresponding sulphides not only by thiourea but by a number of compounds containing the S:C·NH_2 or HS·C:NH groups, such as xanthamide, thioacetamide, and thiobarbituric acid. Thiourea with stilbene oxide yields stilbene and sulphur and no stilbene sulphide, and this type of reaction, sometimes accompanied by the formation of thiazolidine compounds, can occur with ethylene oxides containing an acyl group.

This paper describes the continuation and extension of the work of Culvenor, Davies, and Pausacker (*J.*, 1946, 1050) on the reactions of some simple ethylene oxide types with thiourea, xanthates, and related compounds. It has now been found that *cyclo*hexene oxide or epichlorohydrin reacts not only with thiourea and thiocarbanilide but also with xanthamide, thioacetamide, thiobenzamide, and thiobarbituric acid to form the ethylene sulphide and the oxygen analogue of the thio-compound used.

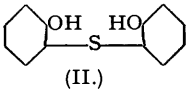
Thiourea with butadiene monoxide and 4-methyl*cyclo*hexene oxide gives the expected sulphides, but stilbene oxide yields only stilbene, sulphur, and urea, no cyclic compound being detected. Apparently, unlike the stable tetraphenylethylene sulphide (Schönberg and Barak, *J.*, 1939, 1074), stilbene sulphide is unstable. The presence of strongly polar groups in ethylene oxides hinders the formation of ethylene sulphides when thiourea in alcoholic or aqueous-alcoholic solution is used. Benzylideneacetone oxide (4-phenyl-3 : 4-epoxybutan-2-one) gives a yellow amorphous solid containing nitrogen and sulphur. Bodforss (*Ber.*, 1918, **51**, 212) found that 1-benzoyl-2-*m*-nitrophenylethylene oxide gave a nitrothiazolidine, m. p. 176°, but a repetition of his work shows that only a small amount of this is formed, most of the pure product obtained being *m*-nitrobenzylideneacetophenone. This, and selenium, are the products from 1-benzoyl-2-*m*-nitrophenylethylene oxide and potassium selenocyanate, and similarly stilbene oxide yields stilbene and selenium only.

The condensation of alcoholic thiourea with ethyl dimethylglycidate produces a thiazolidine derivative, m. p. 285°, which is being investigated, while with ethyl phenylglycidate at ordinary temperatures the products are ethyl cinnamate, sulphur, and urea. Xanthamide, thioacetamide, and thiobenzamide also give ethyl cinnamate and sulphur.

Ethylene oxides are most reactive towards solutions of alkali hydrogen sulphides and alkali derivatives of thiols. Thus *cyclo*hexene oxide and potassium hydrogen sulphide in the cold give 2-*mercapto*cyclo*hexanol* (I) and bis-2-hydroxy*cyclo*hexyl sulphide (II) in almost equal amounts. Contrary to the assumption of Mousseron (*Compt. rend.*, 1943, **216**, 812), who obtained only bis-2-hydroxy*cyclo*hexyl sulphide (II) from sodium sulphide and *cyclo*hexene oxide, the thiol (I) is quite stable and does not condense spontaneously to (II); (II) is produced by further reaction of the potassium salt of (I) with another oxide molecule.

Alkali derivatives of thiols react with ethylene oxide at 0° to give almost quantitative yields of the R·S·CH_2·CH_2·OH derivative. This change has been effected with potassium thioethoxide, thio-*n*-butoxide, and thio*iso*amyloxide on ethylene oxide. Similarly, the dipotassium salt of ethylenedithiol and *cyclo*hexene oxide give 1 : 2-*bis*-(2-*hydroxy*cyclo*hexylthio*)-*ethane* (III).

(I.)



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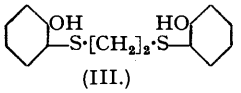

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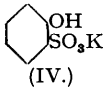
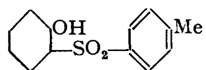


(IV.)

Aqueous sodium sulphite rapidly reacts with ethylene oxide to form sodium hydroxide and sodium isethionate, $CH_2(OH)·CH_2·SO_3Na$. Potassium isethionate is produced by the interaction of potassium thiosulphate and ethylene oxide. In this case, the first product may be $CH_2(OH)·CH_2·S·SO_3K$ which the potassium hydroxide formed would be expected to hydrolyse to potassium sulphite (which then reacts with ethylene oxide to form potassium isethionate) and the sulphenic acid, $CH_2(OH)·CH_2·S·OH$. This mechanism is supported by the detection

in the reaction mixture of a sulphinic acid, into which a sulphenic acid is readily converted (Fromm and Erfurt, *Ber.*, 1909, **42**, 3816). Similarly, *cyclo*hexene oxide and potassium thiosulphate forms the *hydroxy-sulphonate* (IV).

This ready opening of the ethylene oxide ring by sulphites and thiosulphates seems to be brought about, as in the case of sulphides and thioalkoxides, by the presence of a negatively charged sulphur atom. Thus aqueous sodium sulphate is without action. It is noteworthy that sodium selenite also does not react, and this may be due to the charge on the selenite ion not residing on the selenium atom, which is also indicated by the inertness of sodium selenite towards iodine.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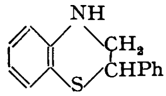
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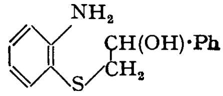
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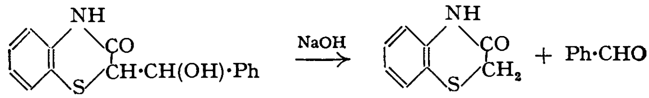
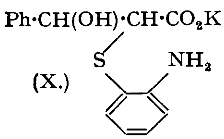
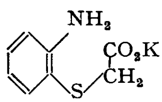

(VIII.) (IX.)




(XI.)

Reaction of Oxides with o-*Aminothiophenol.*—This reaction takes place readily with one molecule of alcoholic alkali. Ethylene oxide condenses to form dihydrobenzthiazine, identified by its phenyl *iso*thiocyanate derivative ("Beilstein," Vol. 27, p. 34).

*cyclo*Hexene oxide forms *hexahydrophenthiazine,* and styrene oxide forms 2-*phenyldihydrobenzthiazine* (VI). This structure has been proved by the synthesis of (VI) from *o*-aminothiophenol and 2-iodo-2-phenylethanol, whereas *o*-aminothiophenol and 2-bromo-1-phenylethanol give o-*aminophenyl* 2-*hydroxy*-2-*phenylethyl sulphide* (VII). The attachment of the S-group to the α-carbon atom of styrene oxide is to be expected from the reactions of styrene oxide outlined by Emerson (*J. Amer. Chem. Soc.*, 1945, **67**, 516).

Benzoylphenylethylene oxide and *o*-aminothiophenol give one of the two possible *benzoylphenyldihydrobenzthiazines,* but no pure product is obtained from benzylideneacetone oxide.

With glycidic esters, $R_1R_2C\overset{\displaystyle O}{\text{——}}CH{\cdot}CO_2Et$, the ring closure occurs on the ester group in preference to the hydroxyl group, and if the ester group is hydrolysed before this can take place (hydrolysis of a glycidic ester is extremely rapid) ring closure does not occur at all. Thus ethyl phenylglycidate produces a mixture of 3-*keto*-2-(α-*hydroxybenzyl*)*dihydrobenzthiazine* (VIII) and *potassium* β-*hydroxy*-α-(o-*aminophenylthio*)-β-*phenylpropionate* (X), together with the well-known 3-ketodihydrobenzthiazine (IX), into which (VIII) is readily converted by being warmed with dilute alkali. From ethyl dimethylglycidate, only (IX) and the corresponding *o*-aminophenylthioacetate (XI) are obtained, the unstable intermediate spontaneously splitting off acetone, the presence of which in the reaction mixture can be shown. Both (X) and (XI) are rapidly converted into the cyclic amides (VIII) and (IX) respectively on acidification. The yields of products from the glycidic ester reactions are greatly reduced by the various hydrolytic transformations to which these compounds are subject in alkaline media. This is particularly marked with ethyl phenylglycidate.

EXPERIMENTAL.

Butadiene Sulphide.—Thiourea (10 g., 1·1 mols.) in methyl alcohol (100 ml.) when stirred with butadiene monoxide (10 g., 1·0 mol.) for 4 hours at 20° yields, when the mixture is poured into water and extracted with ether, *butadiene sulphide* (6·0 g., 50%), b. p. 103—104°. This gradually polymerises even in a sealed tube (Found : S, 37·5. C_4H_6S requires S, 37·2%).

4-*Methyl*cyclo*hexene Sulphide.*—4-Methyl*cyclo*hexene oxide (5 g.) on being stirred with thiourea (5 g.) in methyl alcohol (20 ml.) for 1 hour at 60°, poured into water (150 ml.), and extracted with chloroform, gives a 60% yield of 4-*methyl*cyclo*hexene sulphide*, b. p. 85—86°/25 mm., $n_D^{23°}$ 1·5097 (Found : S, 24·9. $C_7H_{12}S$ requires S, 25·0%).

Reaction of Thiourea with Other Ethylene Oxides.—Thiourea (1·0 g.) in alcohol (20 ml.) reacts with

stilbene oxide (2·0 g.) for 6 days at 35° to produce sulphur (0·2 g., 65%) and stilbene (1·55 g., 80%), the latter being separated by solution in acetone, which also extracts a little unchanged oxide, m. p. 65°. The same reaction proceeds slowly at room temperature. If less than the theoretical amount of thiourea is used, pure urea is obtained by evaporation of the aqueous filtrate.

1-Benzoyl-2-*m*-nitrophenylethylene oxide (1 g.) and thiourea (2·5 g.) are heated with shaking in alcohol (20 ml.) till dissolved, and refluxed for a further 3 minutes before being cooled and freed from alcohol under reduced pressure. The residue, washed with water and recrystallised from alcohol, gives a small amount of white crystals of *m*-nitrobenzylideneacetophenone, m. p. 144°, identified by mixed melting point with an authentic specimen prepared from 1-benzoyl-2-*m*-nitrophenylethylene oxide and potassium iodide. The main product (from mother liquors) is amorphous and complex, but repeated recrystallisation from alcohol gives a very small quantity of a crystalline, yellow powder, m. p. 175°, which shows the same physical properties and colour reaction as the thiazolidine, m. p. 176°, obtained by Bodforss (*loc. cit.*).

Ethyl phenylglycidate (6·4 g.) and thiourea (2·5 g.) in alcohol (20 ml.) are kept at 30° for 16 hours and then at room temperature for 2 days. Filtration gives a mixture of large white crystals of urea (1·1 g.), and yellow crystals of sulphur (0·6 g.), which can be separated mechanically. Dilution of the filtrate precipitates an oil which is extracted with ether and distilled to yield ethyl cinnamate, b. p. 178°/65 mm. (4·0 g.), identified by hydrolysis to cinnamic acid, m. p. 135°, and by the addition of bromine to form the dibromide, Ph·CHBr·CHBr·CO_2Et, m. p. 74—75°.

Reactions of Ethylene Oxides with Other Thioamides.—Thioacetamide. Thioacetamide (5 g.) and *cyclo*hexene oxide (6·5 g.) in methyl alcohol (30 ml.) are refluxed for 5 hours, the solvent removed under reduced pressure, and the product distilled, to give acetamide, b. p. 120—132°/20 mm., solidifying to hygroscopic crystals, m. p. 73—76° (yield, 3·4 g.; 85%), and a large non-distillable sulphur-containing residue.

Thioacetamide and ethyl phenylglycidate in equimolecular amounts are dissolved in alcohol and refluxed for 2 hours or kept at room temperature for 3 weeks. A precipitate of sulphur is removed, and the filtrate diluted with water and extracted with ether. Evaporation of the aqueous layer yields some unchanged thioacetamide, while the extract gives ethyl cinnamate, b. p. 154—159°/26 mm.

Thiobenzamide. Ethyl phenylglycidate (5 g.) and thiobenzamide (3·6 g.) in absolute alcohol (90 ml.), after 4 weeks at room temperature or 3 hours' heating under reflux, give sulphur (0·6 g.; 72%), benzamide (m. p. and mixed m. p. 128—129°), and a little unchanged thiobenzamide, m. p. 115°, and ethyl cinnamate.

Xanthamide. Xanthamide (5·7 g.) and epichlorohydrin (5·9 g.; 1·2 mols.) are refluxed for 1 hour in alcohol (20 ml.); the mixture is then diluted with water and extracted with ether, to give a small amount of chloropropylene sulphide, b. p. 60—85°/100 mm., and an 83% yield of urethane (4·0 g.), b. p. 91°/25 mm., 170—180°/760 mm., with a large non-distillable residue. The identity of the urethane was confirmed by formation of benzylidenediurethane, m. p. 178°, with benzaldehyde and hydrochloric acid. Xanthamide and ethyl phenylglycidate in alcohol give sulphur and ethyl cinnamate.

Thiobarbituric acid. Thiobarbituric acid (3·6 g.) and ethylene oxide (1·3 g.) in water (40 ml.) give, after a week at room temperature, a mixture of solid ethylene sulphide polymer and barbituric acid which is separated with hot water. The barbituric acid was identified by heating it with benzaldehyde to form 5-benzylidenebarbituric acid, m. p. 260°, which loses benzaldehyde again on being heated with dilute sodium hydroxide solution. Thiobarbituric acid gives sulphur and ethyl cinnamate by reaction with ethyl phenylglycidate as above.

Reaction of Alkali Thioalkoxides with Ethylene Oxides.—The additions to ethylene oxide are effected by adding the oxide (2·2 g.) with shaking and cooling to an ice-cold solution of a small excess of thiol in alcoholic potassium hydroxide [2·8 g. (1 mol.) in 30 ml. of 80% alcohol]. After standing overnight, the mixture is diluted with water, acidified with N-sulphuric acid, and extracted with chloroform. Ethylthiol (3·2 g.) gives ethyl 2-hydroxyethyl sulphide (4·8 g.; 91%), b. p. 81°/20 mm.; *n*-butylthiol (4·6 g.) gives 2-hydroxyethyl *n*-butyl sulphide (6·6 g.; 99%), b. p. 103°/16 mm., $n_D^{20°}$ 1·482; and *iso*amylthiol (5·3 g.) gives 2-hydroxyethyl *iso*amyl sulphide (7·3 g.; 99%), b. p. 113°/16 mm., $n_D^{20°}$ 1·475.

When *cyclo*hexene oxide (9·8 g.) is added to a potassium hydrogen sulphide solution prepared by saturating a solution of potassium hydroxide (5·6 g.) in alcohol (50 ml.) with hydrogen sulphide at 0°, the heat of reaction keeps the temperature at about 45° for ½ hour. After standing overnight, the mixture is worked up as above to yield 5·8 g. (44%) of 2-*mercapto*cyclo*hexanol* (I), b. p. 100°/18 mm., and 6·1 g. (53%) of bis-2-hydroxy*cyclo*hexyl sulphide (II), b. p. 148°/0·7 mm., which crystallises on standing, and then has m. p. 60—64° (impure). A small fraction is obtained at 92°/18 mm. and may be the geometrical isomer of (I). If the passage of hydrogen sulphide is continued while the reaction is proceeding, the yield of (I) rises to 70% while that of (II) falls to 29%. 2-Mercapto*cyclo*hexanol is a stable mobile oil and can be completely redistilled after being kept at room temperature for 7 days (Found: S, 23·9. $C_6H_{12}OS$ requires S, 24·24%). Treated with alcoholic potassium hydroxide and chloro-2:4-dinitrobenzene, it gives a bright yellow 2:4-*dinitrophenyl thioether*, m. p. 135° (Found: C, 48·3; H, 5·3. $C_{12}H_{14}O_5N_2S$ requires C, 48·3; H, 4·6%). On being warmed with 50% sulphuric acid, (I) is immediately converted into a solid white polymer with the odour of *cyclo*hexene sulphide (cf. Bennett, *J.*, 1922, **121**, 2144, who records similar behaviour with mercaptoethanol). Boiling with anhydrous magnesium sulphate does not appear to cause dehydration.

*cyclo*Hexene oxide (4·9 g.), added to a solution of potassium hydroxide (2·8 g.; 1 mol.) and ethylenedithiol (2·3 g.; 0·5 mol.) in alcohol (30 ml.), reacts with only small heat evolution; after 2 days in an incubator at 40°, the alcohol is removed under reduced pressure, water is added, and the resulting solution is extracted with chloroform, to give 1:2-*bis*-(2-*hydroxy*cyclo*hexylthio*)*ethane* (III), b. p. 132—136°/0·2 mm. (6·5 g.; 90%). Once purified, it solidifies and can be recrystallised from benzene–light petroleum (1:1) to form large prisms, m. p. 47—49°. It is very soluble in all organic solvents except light petroleum, and readily soluble in water (Found: S, 21·9. $C_{14}H_{26}O_2S_2$ requires S, 22·1%).

Reaction of Ethylene Oxides with Thiosulphates.—Alcohol is added to potassium thiosulphate (10 g.) in water (50 ml.) until a faint milkiness persists, and then excess of ethylene oxide (10 g.) is added

gradually with cooling. The solution rapidly becomes alkaline; after it has been left overnight and concentrated, potassium isethionate crystallises out in 60% yield (based on thiosulphate). On recrystallisation from aqueous alcohol, this melts at 192°; acetylation gives a product, m. p. 258°, agreeing with the observations of Lauer and Hill (*J. Amer. Chem. Soc.*, 1936, **58**, 1873), and it is identical with a sample obtained using potassium sulphite instead of thiosulphate. The aqueous mother liquor, after filtration from the isethionate and neutralisation, gives a strong permanent reddish-brown colouration with ferric chloride, indicating the presence of a sulphinate. A solution of potassium isethionate does not give this colour.

*cyclo*Hexene oxide (5 g.) is added to sodium thiosulphate (10 g.) in water (25 ml.), followed by sufficient alcohol to give solution. After 2 hours' refluxing, the mixture is evaporated to dryness and the sodium 2-hydroxy*cyclo*hexylsulphonate washed with ether and crystallised from aqueous alcohol. Yield, 5·0 g. (50%) (Found: C, 35·1; H, 5·5; S, 16·4; Na, 11·8. Calc. for $C_6H_{11}O_4SNa$: C, 35·6; H, 4·46; S, 15·8; Na, 11·4%*). Evaporation of the ether washings gives *cyclo*hexane-1 : 2-diol (0·3 g.), m. p. 103°.

*Reaction of Ethylene Oxides with Sodium Toluene-*p*-sulphinate.*—Ethylene oxide (20 g.) is added slowly with cooling to sodium toluene-*p*-sulphinate (18 g.) dissolved in aqueous alcohol, and the mixture is left overnight. Ether-extraction gives an oil, b. p. 195°/23 mm. (11 g.; 55%), which solidifies, and after crystallisation from acetone has m. p. 57°. Otto (*J. pr. Chem.*, 1884, **30**, 356) reports *p*-tolyl 2-hydroxyethyl sulphone, m. p. 54—55°, with similar solubilities.

*cyclo*Hexene oxide (9·5 g.) and sulphinate (18 g.) are refluxed in aqueous alcohol for 2 hours and poured into water. Extraction with ether gives o-*hydroxy*cyclo*hexyl* p-*tolyl sulphone* (V) (13 g.; 50%), which separates from alcohol–acetone in white needles, m. p. 123° (Found: C, 61·9; H, 7·9. $C_{13}H_{18}O_3$ requires C, 61·4; H, 7·1%).

Action of Potassium Selenocyanate on Oxides.—When potassium selenocyanate (1·4 g.) and stilbene oxide (1·9 g.) or 1-benzoyl-2-*m*-nitrophenylethylene oxide (2·7 g.) are refluxed in methyl alcohol (25 ml.) for 2 hours, selenium (0·7 g.; 90%) is deposited as a red powder. The alcohol solution is diluted with water and extracted with ether, the extract evaporated, and the residue crystallised from alcohol to give stilbene or *m*-nitrobenzylideneacetophenone according to the oxide used.

Reactions with o-*Aminothiophenol.*—The original method of preparation of *o*-aminothiophenol (reduction of *oo'*-dinitrodiphenyl disulphide with tin and hydrochloric acid) is found to be much inferior to that used by Sullivan and Hesse (*U.S. Public Health Reports*, 1929, **44**, 1599), *viz.*, the fusion of mercaptobenzthiazole with potassium hydroxide. By employing this method essentially but diluting the neutralised fusion mixture from mercaptobenzthiazole (170 g.) and potassium hydroxide (600 g.) with a little carbon tetrachloride and filtering to facilitate a normal extraction, an almost theoretical yield of *o*-aminothiophenol (125 g.) is obtained.

Simple ethylene oxides. The oxide (0·01 mol.) is added with shaking and cooling if necessary (*e.g.*, ethylene oxide causes great heat evolution) to a solution of *o*-aminothiophenol (1·25 g.) and potassium hydroxide (0·56 g.) in alcohol (10 ml.). The mixture is refluxed for ½ hour, then cooled and diluted with water to separate the product. From ethylene oxide is obtained dihydrobenzthiazine, b. p. 203—210°/20 mm., identified by formation of a derivative, m. p. 128—129°, with phenyl *iso*thiocyanate ("Beilstein," Vol. 27, p. 34). *cyclo*Hexene oxide (1 g.) gives *hexahydrophenthiazine* (2·2 g.; 99%), crystallising from aqueous alcohol or light petroleum in colourless needles, m. p. 81° (Found: S, 15·4; N, 6·82. $C_{12}H_{15}NS$ requires S, 15·6; N, 6·83%). Styrene oxide (1·2 g.) gives 2-*phenyldihydrobenzthiazine* (VI), m. p. 103°, which solidifies only after dissolution in dilute hydrochloric acid, filtration of the solution, and reprecipitation with alkali. (VI) crystallises from aqueous alcohol and can be sublimed in a vacuum above its m. p. (Found: S, 14·0, 14·2; N, 6·08. $C_{14}H_{13}NS$ requires S, 14·1; N, 6·17%).

Styrene halohydrins. The two halohydrins required were prepared as follows: 2-iodo-2-phenylethanol by the action of hydriodic acid on styrene oxide (Tiffeneau and Fourneau, *Bull. Soc. chim.*, 1913, **13**, 975); 2-bromo-1-phenylethanol by shaking styrene with hot bromine water (Read and Reid, *J.*, 1928, 1488), and purifying the product by distillation.

A solution of 2-iodo-2-phenylethanol (2·5 g.) in alcohol (15 ml.) added to *o*-aminothiophenol (1·35 g.) and potassium hydroxide (0·56 g.) in alcohol (10 ml.) and refluxed for ½ hour before being cooled and diluted with water, gives an oil which after purification as above solidifies to a crystalline powder, m. p. 101°, identified by mixed m. p. with the product (VI) from styrene oxide. When 2-bromo-1-phenylethanol is treated in the same way, the product is an oil which gives a positive test for a primary aromatic amine (by diazotisation and coupling with β-naphthol). The extracted oil, on treatment with concentrated hydrochloric acid, is converted into a water-soluble hydrochloride which, although quite stable in the dry state, reddens considerably when heated in solution. The *hydrochloride* of (VII) is fairly soluble in alcohol, insoluble in ether and chloroform, and is purified for analysis by dissolution in cold absolute alcohol and precipitation with ether to form feathery needles, m. p. 172° (Found: C, 60·2; H, 5·6. $C_{14}H_{16}ONClS$ requires C, 59·8; H, 5·7%). The hydrochloride also gives the diazotisation test for a primary amine. Attempts at ring-closure by refluxing with acid or alkali yield only oily products.

Benzoylphenyldihydrobenzthiazine is obtained when benzoylphenylethylene oxide (1·1 g.) is kept for 2 days at room temperature with *o*-aminothiophenol (0·6 g.) and potassium hydroxide (0·3 g.) in alcohol (7 ml.). The thiazine separates from the dark red solution, and is crystallised from alcohol to form large yellow prisms, m. p. 187·5° (Found: S, 9·94; N, 4·26. $C_{21}H_{17}ONS$ requires S, 9·67; N, 4·23%).

Glycidic esters. Ethyl dimethylglycidate (14·4 g.) is kept for 24 hours at room temperature with *o*-aminothiophenol (12·5 g.) and potassium hydroxide (5·6 g.) in alcohol (75 ml.), then refluxed for 7 hours. Filtration of the pasty mass obtained gives a mixture of potassium *o*-aminophenylthioacetate (XI) (5·6 g.) and 3-ketodihydrobenzthiazine (IX) (0·9 g.) which are separated by crystallisation from alcohol. Dilution of the filtrate with water yields a further quantity (2·5 g.) of (IX) which crystallises from alcohol in long needles, m. p. 176°, which sublime readily at 140°/15 mm. (Found: C, 58·9;

H, 4·45; N, 8·70; S, 19·8. Calc. for C_8H_7ONS: C, 58·2; H, 4·2; N, 8·50; S, 19·4%). A mixture with 3-ketodihydrobenzthiazine prepared by the method of Hofmann (*Ber.*, 1880, **13**, 1234), by warming *o*-aminothiophenol with chloroacetic acid, gives no depression of the m. p. (IX) is insoluble in hydrochloric acid and cold sodium hydroxide solution but readily soluble in hot sodium hydroxide solution from which it crystallises unchanged if cooled quickly. On being boiled for a few minutes with concentrated potassium hydroxide solution, it is converted into a potassium salt identical with (XI), the second reaction product. This salt is readily soluble in hot alcohol from which it separates in large leafy crystals, m. p. 268° (Found: K, 17·76. Calc. for $C_8H_8O_2NSK$: K, 17·6%). The aqueous solution of (XI) gives no colour with sodium nitroprusside, but, when it is mixed with sodium nitrite and acidified with hydrochloric acid, the resultant solution forms a red dye with alkaline β-naphthol. When a solution of (XI) alone is acidified, the thiazine (IX) separates in a few minutes. The presence of acetone in the aqueous filtrate from the main reaction was demonstrated by means of the Wilbur modification of the Légal test (*Chemist-Analyst*, 1931, **20**, No. 4, 11; *Chem. Abs.*, 1931, **25**, 4202).

When ethyl phenylglycidate (4·8 g.) is added with shaking and cooling to *o*-aminothiophenol (5·1 g.) and potassium hydroxide (1·4 g.) in alcohol (20 ml.), the ester is hydrolysed immediately, and potassium phenylglycidate separates. This salt crystallises from alcohol to form silvery plates, m. p. 285° (decomp.) (Found: K, 19·8. Calc. for $C_9H_7O_3K$: K, 19·6%). Acidification of an aqueous solution of the salt gives phenylacetaldehyde, identified by its 2 : 4-dinitrophenylhydrazone, m. p. 109°. If the reaction mixture is refluxed on a water-bath without removal of the potassium phenylglycidate, the precipitate gradually dissolves. After 3 hours, there separates on cooling a small quantity of the water-soluble *potassium β-hydroxy-α-(o-aminophenylthio)-β-phenylpropionate* (X) (0·25 g.) which crystallises from alcohol in colourless needles, m. p. 209° (Found: C, 55·05; H, 4·55; K, 11·90. $C_{15}H_{14}O_3NSK$ requires C, 55·05; H, 4·32; K, 11·93%). Concentration of the reaction filtrate yields a white solid (1·3 g.) which is a mixture of (IX) and *3-keto-2-(α-hydroxybenzyl)dihydrobenzthiazine* (VIII). The latter compound is also rapidly formed when an aqueous solution of the salt (X) is acidified, and crystallises from aqueous alcohol in colourless needles, m. p. 178—180° (Found: C, 65·9; H, 4·82. $C_{15}H_{13}O_2NS$ requires C, 66·4; H, 4·83%). On being warmed for 5 minutes with dilute sodium hydroxide solution, (VIII) loses benzaldehyde, and acidification then yields 3-ketodihydrobenzthiazine. This decomposition does not occur when (VIII) is boiled with water or dilute acid.

The microanalyses were carried out by N. L. Lottkowitz who reports that the C and H determinations marked with an asterisk were carried out under very humid weather conditions, giving high H results.

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