181. *Reactions of Ethylene Oxides. Part IV. The Reaction of Epichlorohydrin with Some Aromatic Amines.*

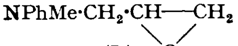
By W. Davies and W. E. Savige.

Epichlorohydrin with one mole or two moles of methylaniline gives good yields of 1-chloro-3-*N*-methylanilinopropan-2-ol (II) and 1 : 3-di-(*N*-methylanilino)propan-2-ol, respectively. Modification of the conditions brings about the production of dimethylaniline, 1-methyltetrahydroquinoline, and 3-hydroxy-1-methyltetrahydroquinoline (which readily loses water to form 1-methyl-1 : 2-dihydroquinoline). The basic group in the oxide derived from the chlorohydrin (II) has little effect on its general properties and reactions, which are essentially those of a normal $\alpha\beta$-oxide.

Reaction of methylaniline and epichlorohydrin, described chiefly in the patent literature, has been reinvestigated in order to prepare, and examine the properties of, a compound such as

3-*N*-methylanilinopropylene oxide (I) containing a basic centre separated by one methylene group from an αβ-oxide ring. The reaction is found to give a variety of products depending on the experimental conditions. For example, Eisleb (D.R.-P. 473,219/1929; U.S.P. 1,790,042/1931) obtained (I) by interaction of equimolar quantities of epichlorohydrin and methylaniline in aqueous alcohol, followed by treatment with alkali. On the other hand, Lange (D.R.-P. 619,825) obtained 3-hydroxy-1-methyl-1 : 2 : 3 : 4-tetrahydroquinoline (III) when the reaction was carried out in chlorobenzene. It is now found that in hot aqueous alcohol or in boiling xylene the chief product is 1-*chloro*-3-N-*methylanilinopropan*-2-*ol* (II), which is converted by alkali into the oxide (I).

Further differences are found when the condensation occurs in the absence of solvent and when the temperature is varied. 1 : 3-Di-(*N*-methylanilino)propan-2-ol was the only pure compound isolated, and that in very small yield, by Wedekind and Bruch (*Annalen*, 1929, **471**, 94) from equimolar amounts of reactants without a solvent, on the water-bath. This diamine is now found to be produced almost quantitatively from two moles of methylaniline at rather higher temperatures, a process which recalls the formation of 1 : 3-dianilinopropan-2-ol from epichlorohydrin and aniline (Fouconnier, *Compt. rend.*, 1888, **107**, 250; Fukagawa, *Ber.*, 1935, **68**, *B*, 1344).

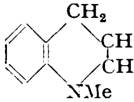


$NPhMe{\cdot}CH_2{\cdot}\overbrace{CH{-}CH_2}^{}{>}O$

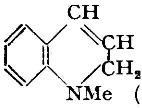
(I.)

$NPhMe{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2Cl$

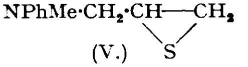
(II.)



(III.)

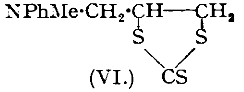


(IV.)



$NPhMe{\cdot}CH_2{\cdot}\underset{\diagdown S \diagup}{CH{-}CH_2}$

(V.)



$NPhMe{\cdot}CH_2{\cdot}\underset{S\diagdown CS \diagup S}{CH{-}CH_2}$

(VI.)

However, if equimolar amounts of the reactants are refluxed without a solvent for a short time, the reaction becomes violently exothermic, and the products, after treatment with concentrated alkali, are dimethylaniline, kairoline (1-methyl-1 : 2 : 3 : 4-tetrahydroquinoline), and 3-hydroxykairoline (III) in yields of 8, 10, and 45% respectively, the remainder consisting of small intermediate fractions and higher-boiling material. If the subsequent alkali treatment is omitted, it is very difficult to separate 3-hydroxykairoline by distillation from the chlorohydrin (II) present in the reaction mixture. When the conditions of the reaction are more controlled, dimethylaniline, the oxide (I), 3-hydroxykairoline (III), and 1 : 3-di-(*N*-methylanilino)propan-2-ol are isolated in yields of 2, 35, 10, and 2% respectively. The kairoline obtained is identified in the usual way. Little information is given by Lange (*loc. cit.*) about the main heterocyclic product 3-hydroxykairoline. It has the high viscosity and boiling point characteristic of tertiary ethanolamine derivatives, and the presence of the hydroxy-group is shown by reaction with methylmagnesium iodide and phenyl *iso*cyanate. The position of the hydroxy-group has not been proved, but the 3-position is to be expected if the nitrogen ring is formed by intramolecular reaction of either (I) or (II). Similarly, 3-hydroxy-1-phenyl-1 : 2 : 3 : 4-tetrahydroquinoline is considered (D.R.-P. 284,291) to be the product from the reaction of epichlorohydrin and diphenylamine under pressure, which, if catalysed by sodium iodide, is now found to occur at ordinary pressure; the presence of the hydroxy-group is shown by the formation of a crystalline *phenylurethane*.

3-Hydroxykairoline is converted by distillation over solid potassium hydroxide into a lower-boiling liquid, 1-*methyl*-1 : 2-*dihydroquinoline* (IV), readily reduced to kairoline by zinc and sulphuric acid. This dihydro-compound, like 1-methyl-2-propyl-1 : 2-dihydroquinoline (von Braun and Aust, *Ber.*, 1914, **47**, 3023), polymerises readily when kept, thus favouring the 1 : 2- rather than the 1 : 4-dihydro-structure.

The mechanism of the production of 3-hydroxykairoline (III) is deduced from known reactions of epichlorohydrin. Thus, in the presence of hydroxylic solvents or at high temperatures, epichlorohydrin generally combines with amines to form first the 1-chloropropan-2-ol, and it has now been confirmed that with an equimolecular quantity of *p*-toluidine it gives the crystalline *p*-tolyl analogue of (II) (Cohn and Friedlander, *Ber.*, 1904, **37**, 3034); Drefus (F.P. 702,553) claims a similar preparation of the α-naphthyl analogue. Lange (U.S.P. 2,150,001/1939) also reports that primary aromatic amines can yield tertiary amines of the type $Ar{\cdot}N[CH_2{\cdot}CH(OH){\cdot}CH_2Cl]_2$. Thus, methylaniline probably produces initially (II) which then cyclises to (III) with loss of hydrogen chloride. This view is supported by the decomposition of (II) at 180—200°, to give 50% of (III) together with dimethylaniline and a polymer. A similar ring closure is involved in the formation of lilolidine by heating 1-3′-chloropropyldihydroindole (von Braun, Heider, and Wyczatkowska, *Ber.*, 1918, **51**, 1219), and in the mechanism postulated by Lange (I.G. Farbenind., Zetco Reports, Jan., 1946, F.I.A.T. Microfilm Reel C 60, PB L 64079) for the production of 3-hydroxytetrahydroquinoline derivatives from epichlorohydrin and α- or β-naphthylamine or secondary arylalkylamines. Further analogous reactions involving primary and secondary aromatic amines are set out by Lange and Helberger (D.R.-P. 634,038) and Lange (U.S.P. 2,194,399/1940).

The condensation of methylaniline or similar amines with epichlorohydrin to produce kairoline (or analogous bases) and dimethylaniline (or similar amines) is apparently novel, and the mechanism is not yet clearly understood. Dunlop and Jones (*J.*, 1909, **95**, 420) showed that methylaniline was converted into dimethylaniline by methyl bromide which is produced when ethylene dibromide and methylaniline form 1 : 4-diphenylpiperazine. (For similar fissions of alkyl groups attached to nitrogen see Wedekind and Bruch, *loc. cit.*, p. 76, and Thorpe and Wood, *J.*, 1913, **103**, 1611.) The somewhat analogous conversion of methylaniline into dimethylaniline may occur *via* methyl chloride during the condensation with epichlorohydrin, but it is probable that an intermediate compound (*e.g.*, II) undergoes fission at the link between the $\mathrm{N{\cdot}CH_2}$ and the CH(OH). That this link can be unstable in halogen-free compounds related to (II) is shown by the production of dimethylaniline in 50% yield on decomposition of the crude *trithiocarbonate* (VI) by heat. Moreover, the production of dimethylaniline during the inter-action of methylaniline and epichlorohydrin seems to be associated with the formation of kairoline. This and associated reactions are being further investigated.

The oxide (I) has been examined in order to verify its structure, since condensations of epichlorohydrin with certain reagents have been found to give the unsaturated alcohol rather than the expected oxide. Thus, with sodium acetylide epichlorohydrin gives pent-2-en-4-yn-1-ol, $\mathrm{CH{\vdots}C{\cdot}CH{:}CH{\cdot}CH_2{\cdot}OH}$ (Haynes, Heilbron, Jones, and Sondheimer, *J.*, 1947, 1610) and with sodium sulphinates gives sulphones $\mathrm{R{\cdot}SO_2{\cdot}CH{:}CH{\cdot}CH_2{\cdot}OH}$ (Culvenor, Davies, and Savige, *J.*, 1949, 2200) which are also formed by the action of cold dilute alkali on the chloro-alcohols, $\mathrm{R{\cdot}SO_2{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2Cl}$. The dioxan type of dimer from the unsaturated alcohol is also sometimes formed, but that possibility is discarded in the case of the methylaniline product, because the latter has great chemical activity and a low boiling point. The following reactions of (I) are characteristic of αβ-oxides, and are unlikely to occur readily with the unsaturated alcohol, $\mathrm{NPhMe{\cdot}CH{:}CH{\cdot}CH_2{\cdot}OH}$ unless its double bond is far more reactive than the formula indicates.

Methylaniline gives with (I) the expected crystalline diamine 1 : 3-di-(N-methylanilino)-propan-2-ol; Eisleb (*loc. cit.*; also U.S.P. 1,845,403/1932) obtained analogous products from (I) with ammonia and with ethylamine. The oxide (I) is converted by dilute sulphuric acid into the crystalline *glycol*, $\mathrm{NPhMe{\cdot}CH_2CH(OH){\cdot}CH_2{\cdot}OH}$, by sodium sulphite into an *isethionate*, probably $\mathrm{NPhMe{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}SO_3Na}$, and by thiourea into the corresponding *sulphide* (V). Potassium methyl xanthate (cf. Culvenor, Davies, and Pausacker, *J.*, 1946, 1051) with (I) forms the corresponding impure trithiocarbonate (VI) characterised as its *picrate*. Finally, the absence of active hydrogen was shown by failure to react with methylmagnesium iodide, and absence of a hydroxy-group by infra-red analysis, indicating that the compound is the oxide (I) and not the unsaturated alcohol.

It is to be expected that salt formation involving the nitrogen in (I) would favour the formation of the unsaturated alcohol, but it has not been possible to obtain a crystalline methyl iodide derivative of (I), and dry hydrogen chloride at 0° yields an oily hydrochloride which cannot be purified and readily isomerises on warming to give a chlorohydrin, probably (II). However, the corresponding sulphide (V) does give a crystalline *monomethiodide*, which is regarded as an ammonium and not a sulphonium salt (cf. Culvenor, Davies, and Heath, *J.*, 1949, 282) and shows evidence of the retention of the thiairene ring. The properties of αβ-oxides containing an electrophilic group are being further studied.

Experimental.

Interaction of Epichlorohydrin with Methylaniline.—1-*Chloro*-3-N-*methylanilinopropan*-2-*ol* (II), a pale yellow viscous liquid, b. p. 132—134°/0·8 mm., 140°/2·5 mm., n_{D}^{16} 1·572, was obtained when epichlorohydrin (25 ml., 0·32 mol.), methylaniline (25 ml., 0·23 mol.), water (20 ml.), and alcohol (30 ml.) were heated under reflux for 2 hours and then treated with water (20 ml.), the product being extracted with ether, dried, and distilled (Found : C, 61·3, 61·25; H, 7·2, 7·0; N, 7·4. $\mathrm{C_{10}H_{14}ONCl}$ requires C, 60·2; H, 7·0; N, 7·0%). The high values for carbon and nitrogen are attributed to slight contamination of the product with 3-hydroxykairoline (III) into which (II) was partly converted at the temperature of distillation. When (II) was redistilled at 167°/15 mm., sufficient (III) was produced to be identified as its methiodide, and the last few viscous drops of the distillate gave the blue coloration in air and other reactions indicative of the presence of dimethylaniline hydrochloride. The chlorohydrin (II), b. p. 152—155°/4·5 mm., was also obtained on refluxing epichlorohydrin (18 ml.) and methylaniline (22 ml.) in xylene (35 ml.) for 6 hours, the product being again contaminated with (III), but no reaction occurred in boiling acetone with or without potassium iodide. Methylmagnesium iodide gave methane by interaction with (II), which yielded no crystalline derivative with picric or picrolonic acid, phenyl *iso*cyanate, methyl iodide, or dry hydrogen chloride.

1 : 3-Di-(*N*-methylanilino)propan-2-ol, b. p. 195—198°/0·25 mm., m. p. 80°, short needles from benzene–light petroleum (Found : C, 76·4; H, 8·25; N, 10·15. Calc. for $C_{17}H_{22}ON_2$: C, 75·6; H, 8·15; N, 10·4%), previously made by Wedekind and Bruch (*loc. cit.*, who record m. p. 82°, b. p. 180—240°/20 mm.), was formed almost quantitatively from methylaniline (2·5 g.) and epichlorohydrin (0·9 g.) at 155° (1 hour) and then 170° (1 hour), the viscous acid product being then dissolved in dilute hydrochloric acid (5 ml.) and treated with aqueous sodium hydroxide.

In the absence of solvents, equimolecular amounts of methylaniline and epichlorohydrin gave 1-methyltetrahydroquinoline derivatives, the formation of which was favoured by high temperatures. Residual viscous material was also produced, and this can be the main product if the temperature of the reaction is too high. The following are typical condensations. (i) Epichlorohydrin (34·8 ml.) was heated under reflux, and methylaniline (43·6 ml.) added in small portions during ½ hour. Five minutes later, an exothermic reaction occurred, the temperature rising to >200°. The mixture was warmed on the water-bath for a further hour, cooled, and stirred with ether and a solution of sodium hydroxide (25 g.) in water (50 ml.) for 1 hour. The dried ethereal extract gave, after two refractionations, the following chlorine-free fractions, together with unchanged epichlorohydrin (5 ml.) and a viscous residue (20 ml.) : (*a*) b. p. 74—77°/13 mm. (6 ml.), identified by its picrate as dimethylaniline; (*b*) b. p. 62°/0·15 mm., 243°/756 mm., n_D^{21} 1·585 (8 ml.), kairoline (Found : C, 81·65; H, 9·0; N, 9·7. Calc. for $C_{10}H_{13}N$: C, 81·65; H, 8·85; N, 9·5%), a mobile liquid insoluble in water; and (*c*) b. p. 134—136°/0·18 mm., 290°/760 mm., n_D^{20} 1·595 (35 ml.), 3-hydroxykairoline (III), an extremely viscous liquid for which Lange (D.R.-P. 619,825) gives b. p. 165—166°/12 mm. (Found : C, 73·0, 73·6; H, 7·9, 8·2; N, 8·3. Calc. for $C_{10}H_{13}ON$: C, 73·6; H, 8·0; N, 8·6%).

(ii) Epichlorohydrin (21·8 ml.) and methylaniline (26·2 ml.), after reaction as described above except that adequate external cooling was applied at the onset, were heated at 180° for 1½ hours, to give : (*a*) dimethylaniline, b. p. 82°/12 mm. (1 ml.), which exhibited slight fluorescence; (*b*) 3-*N*-methylanilinopropylene oxide (I), b. p. 140—146°/12 mm. (18 ml.), identified as picrate; (*c*) 3-hydroxykairoline, b. p. 156—161°/12 mm. (5 ml.), identified as picrolonate; and (*d*) 1 : 3-di-(*N*-methylanilino)propan-2-ol, b. p. 195—198°/0·25 mm., m. p. 80°, identified by a mixed m. p. No kairoline was isolated in this case, although formation of a very small amount is not precluded. Much residue was again obtained.

Kairoline was identified as methiodide, m. p. 171·5°, and picrate, m. p. 137·5°, both m. p.s being undepressed on admixture with the respective derivatives of commercial (Schuchardt) material. The m. p. of the picrate of the commercial base could not be raised above 125° by the use of neutral organic solvents, but crystallisation from dilute acetic acid gave material of m. p. 134—135°; the impurity was quinoline, and the presence of this or similar substances may be the reason for the wide variation in the m. p. (125° to 145°) recorded in the literature. 3-Hydroxykairoline with nitrous acid gave an orange colour which changed to green on neutralisation with aqueous ammonia. With methylmagnesium iodide 3-hydroxykairoline gave methane, and with phenyl *iso*cyanate in benzene at 100° (1 hour) gave an uncrystallisable oil. No precipitate was formed on treatment with alcoholic picric acid, but with picrolonic acid a sparingly soluble *picrolonate*, m. p. 185° (decomp.), yellow needles from acetone, was obtained (Found : C, 55·85; H, 4·9. $C_{10}H_{13}ON,C_{10}H_8O_5N_4$ requires C, 56·15; H, 4·9%). Warming the base with excess of methyl iodide gave a *methiodide*, m. p. 157° (slight decomp.) (prisms from acetone–ether) considerably variable according to the rate of heating (Found : C, 43·1; H, 5·35; N, 4·45; I, 41·8. $C_{11}H_{16}ONI$ requires C, 43·3; H, 5·25; N, 4·6; I, 41·65%).

1-*Methyl*-1 : 2-*dihydroquinoline* (IV).—This *base*, b. p. 128°/15 mm., was obtained in theoretical yield when 3-hydroxykairoline (5 g.) was heated with powdered potassium hydroxide (5 g.) in a distilling flask at 190°/20 mm., the distillate being redistilled immediately (Found : C, 83·0; H, 7·65; N, 9·6. $C_{10}H_{11}N$ requires C, 82·7; H, 7·6; N, 9·65%). It is a mobile water-insoluble liquid, aqueous-alcoholic solutions of which fluoresce. It formed a methiodide, m. p. 205° (with sublimation), rapidly developed a red colour, and became cloudy and viscous after 24 hours, even in a sealed tube or in the presence of a trace of quinol. It was not re-formed by heating the viscous material, which partly solidified during 7 days. The polymer was insoluble in alcohol, but acetone dissolved the adhering oil, leaving a white powder which dissolved in hot alcohol and was re-precipitated on cooling. Two repetitions of this treatment gave an amorphous *polymer*, m. p. 100° (Found : C, 82·1; H, 8·0%), which darkened during several days, while the m. p. fell to 94—97°.

Conversion of (IV) *into Kairoline.*—To monomeric (IV) (3 g.) in dilute sulphuric acid (15 ml.) at 100° zinc dust (10 g.) was added in portions during 1½ hours, with occasional shaking. The mixture was filtered, made alkaline with aqueous sodium hydroxide, and extracted with ether. The dried extract on distillation gave a stable mobile liquid, identified as kairoline, b. p. 110°/15 mm. (0·5 g.), by a mixed m. p. determination of its picrate.

Production of 3-*Hydroxykairoline from* 1-*Chloro*-3-N-*methylanilinopropan*-2-*ol* (II).—The chlorohydrin (II) (5 g.) was heated at 190—200° for 2 hours, gaseous products being evolved. The dark, viscous residue was shaken with a mixture of ether and 5% aqueous sodium hydroxide. The dried ethereal extract yielded dimethylaniline, b. p. 110°/20 mm. (0·5 ml.) (identified as picrate), and 3-hydroxykairoline, b. p. 130—135°/1 mm. (2·5 g.), identified as picrolonate. The remainder was high-boiling material.

Preparation and Reactions of 3-N-*Methylanilinopropylene Oxide.*—The crude undistilled chlorohydrin (II) was converted by cold 50% sodium hydroxide solution into 3-*N*-methylanilinopropylene oxide (I), b. p. 120—122°/3 mm., 107°/0·5 mm., n_D^{19} 1·562 (Found : C, 73·6; H, 7·8; N, 8·8. Calc. for $C_{10}H_{13}ON$: C, 73·6; H, 7·95; N, 8·6%), in 74% yield. Eisleb (*loc. cit.*) records b. p. 132—134°/8 mm., 160—162°/30 mm. A 10% yield of 1 : 3-di-(*N*-methylanilino)propan-2-ol was also formed.

The oxide was characterised as *picrate*, m. p. 109°, yellow prisms from alcohol (Found: N, 14·0. $C_{10}H_{13}ON,C_6H_3O_7N_3$ requires N, 14·3%), did not produce methane with methylmagnesium iodide, and gave no precipitate with aqueous *p*-nitrophenylhydrazine hydrochloride. Infra-red analysis (for which we thank Dr. J. B. Willis) showed the absence of hydroxy-groups. The product formed on heating (I) (1·63 g.) and methylaniline (1·25 g.) at 160° for 2 hours solidified on cooling; washing the product with light petroleum gave 1 : 3-di-(*N*-methylanilino)propan-2-ol (IV), m. p. 80°, without recrystallisation.

3-N-*Methylanilinopropylene Glycol.*—The *glycol*, b. p. 156—158°/0·5 mm., m. p. 74—75°, plates from benzene–light petroleum, was prepared by heating (I) (5 g.) in 5N-sulphuric acid (10 ml.) under gentle reflux for ½ hour, cooling, and carefully neutralising the mixture with concentrated aqueous ammonia (Found: C, 66·55; H, 8·35. $C_{10}H_{15}O_2N$ requires C, 66·3; H, 8·3%). In a first experiment, crystallisation of this glycol, which was difficult to extract from aqueous medium with ether, was effected only after evaporation to dryness and extraction with alcohol–ether, followed by distillation and digestion of the distillate with cold ether; in a second experiment crystallisation was effected by seeding the crude reaction mixture. The glycol was readily soluble in alcohol or benzene, slightly soluble in ether or water, and sparingly so in light petroleum.

Sodium 3-N-*Methylanilino*-2-*hydroxypropane*-1-*sulphonate.*—This *salt* (Found: Na, 8·65. $C_{16}H_{14}O_4SNa$ requires Na, 8·6%), m. p. 266°, lustrous plates from 90% alcohol, was obtained when the oxide (I) (1·63 g.) in alcohol was mixed with sodium sulphite (3 g.) and the mixture buffered to neutrality (phenolphthalein) with acetic acid and aqueous sodium acetate. The mixture was then kept at 30° for 18 hours and concentrated. This isethionate is readily soluble in water (cf. Lauer and Hill, *J. Amer. Chem. Soc.*, 1936, **58**, 1873).

Attempts to make pure salts, other than the picrate, from (I) were unsuccessful. An uncrystallisable oil was obtained when (I) was heated with excess of methyl iodide for ½ hour. Dry hydrogen chloride was passed into a solution of (I) (1·63 g.) in dry benzene at 0°, with cooling, until the weight had increased by 0·36 g. The mobile oil which separated dissolved by warming to 60° and was not reprecipitated on cooling. Distillation gave a main fraction b. p. 140°/1·2 mm., n_D^{15} 1·572, which contained non-ionic chlorine and was probably the chlorohydrin (II) or an isomer.

N-*Methylanilinomethyl-thiairene*(-*propylene Sulphide*) (V).—This *compound*, a pale yellow liquid, b. p. 107—108°/0·1 mm., 154°/12 mm., n_D^{11} 1·606, possessing a slight offensive odour, was obtained (3 g.) when thiourea (2·5 g.) and (I) (4·1 g.) in methanol (20 ml.) were stirred at 60° for 1¼ hours, the mixture being then poured into water (100 ml.), extracted with chloroform, dried, distilled, and fractionated to remove unchanged oxide (Found: N, 7·7. $C_{10}H_{13}NS$ requires N, 7·8%). It forms a sparingly soluble *picrate*, yellow pyramid-like crystals (from alcohol), m. p. 76·5° (Found: S, 7·8. $C_{10}H_{13}NS,C_6H_3O_7N_3$ requires S, 7·85%). When the sulphide (V) was heated under reflux with a large excess of methyl iodide for 15 minutes, a crystalline *methiodide* was rapidly precipitated, recrystallisation from alcohol–benzene giving plates, m. p. 147·5° (Found: S, 9·9; I, 40·25. $C_{11}H_{16}NIS$ requires S, 9·95; I, 39·6%), soluble in water, but rapidly polymerised when heated in alkali (cf. Dachlauer and Jackel, D.R.-P. 636,708). Nitrogen was readily evolved on treatment of the methiodide with a solution of sodium azide, iodine, and potassium iodide in water.

3-N-*Methylanilinopropylene Trithiocarbonate* (VI).—This was obtained as a viscous, malodorous, non-distillable, yellow oil when the oxide (I) (4·1 g.) and excess of potassium methylxanthate were kept in methyl alcohol for 18 hours. The oil was extracted with benzene, the extract washed well with water and methanol and dried, and the benzene evaporated off. Like most trithiocarbonates, it was only sparingly soluble in alcohol, ether, or acetone, but readily soluble in benzene or chloroform. A benzene solution of the undistilled ester was warmed with an excess of alcoholic picric acid and the reddish oil set aside until crystallisation occurred. Recrystallisation from alcohol, in which it is not very soluble, gave yellow crystals of the *picrate*, m. p. 124—125° (Found: S, 19·9. $C_{11}H_{13}NS_3,C_6H_3O_7N_3$ requires S, 19·85%). On attempted distillation of the ester at 0·6 mm., decomposition occurred at 200°, the distillate consisting mainly of dimethylaniline, as shown by its conversion in high yield by picrolonic acid into *dimethylaniline picrolonate*, small yellow prisms (Found: N, 18·05. $C_8H_{11}N,C_{10}H_8O_5N_4$ requires N, 18·2%), m. p. 200° (from alcohol) not depressed on admixture with the authentic picrolonate.

Reaction of Epichlorohydrin with Diphenylamine.—No reaction occurred when a mixture of these compounds was refluxed without a catalyst. Diphenylamine (16·9 g.), epichlorohydrin (13·9 g.), and sodium iodide (10 g.) were refluxed for 5 hours, cooled, decanted from inorganic material, and distilled, first at 15 mm. whereupon a mixture of gaseous hydrogen chloride and iodide distilled together with unchanged epichlorohydrin below 140°, and then at 1·5 mm. whereupon unchanged diphenylamine, b. p. 130—170°, and crude 3-hydroxy-1-phenyl-1 : 2 : 3 : 4-tetrahydroquinoline, b. p. 175—183°, were collected. The latter was purified by redistillation and solidified on storage. Recrystallisation from benzene–light petroleum gave a halogen-free product (7 g.), m. p. 78—79°; m. p. 79° is recorded in D.R.-P. 284,291. This compound (1 g.) and phenyl *iso*cyanate (1·4 g.) in dry benzene, when kept in a sealed tube for 3 days at 30°, gave a *carbanilate*, m. p. 127° (Found: N, 8·35. $C_{22}H_{20}O_2N_2$ requires N, 8·15%), needles from alcohol.

Reaction of Epichlorohydrin with p-*Toluidine.*—The use of aqueous alcohol as in the method of Cohn and Friedlaender (*loc. cit.*) gave 1-chloro-3-*p*-toluidinopropan-2-ol, leaflets (from alcohol), m. p. 81—82°. No distillate was obtained when this product was heated at 220°/0·8 mm.; there was a small sublimate of a basic hydrochloride. On cooling, the contents of the flask set to a hard resin which was only sparingly soluble in aqueous or organic solvents. When the chlorohydrin was stirred in benzene with 30% sodium hydroxide solution for 1 hour and the benzene was evaporated off at room temperature, a similar glassy resin was obtained, which has possible technical applications.

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