

212. *The Condensation of $\alpha\alpha'$ -Dibromo-dicarboxylic Esters with Thioureas and the Synthesis of Dithiazolidylmethane Derivatives.*

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ALTHOUGH the condensation of thioureas with α -halogenated monocarboxylic acids and their esters has frequently been utilised as a source of ψ -thiohydantoin derivatives, the corresponding reaction with $\alpha\alpha'$ -dihalogenated dicarboxylic acids does not appear to have been previously studied.

Dibenzthiazolylmethane and some derivatives have been synthesised by Mills (J., 1922, **121**, 456), but no derivative of dithiazolylmethane itself appears to have been previously described.

Ethyl $\alpha\alpha'$ -dibromoglutarate reacts with thiocarbanilide and with phenylthiourea in the presence of alcoholic pyridine, giving 2 : 2'-diphenylimino-4 : 4'-diketo-3 : 3'-diphenyl-5 : 5'-dithiazolidylmethane, $\text{CH}_2\left(\text{CH}\left\langle\begin{array}{l} \text{S}-\text{C}:\text{NPh} \\ \text{CO}\cdot\text{NPh} \end{array}\right.\right)_2$, and 2 : 2'-di-imino-4 : 4'-diketo-3 : 3'-diphenyl-5 : 5'-dithiazolidylmethane respectively, but similar condensation could not be effected with ethyl $\alpha\alpha'$ -dibromocyclopentane-1 : 1-diacetate.

EXPERIMENTAL.

Glutaric acid (m. p. 95°) was conveniently prepared in 90—95% yield (compare *Annalen*, 1893, **275**, 320; J., 1921, **119**, 316) by

gradually adding *cyclopentanone* to nitric acid (10 vols.) heated under reflux, evaporating the mixture to dryness on a water-bath, extracting the residue with aqueous sodium hydroxide, and freeing the neutralised solution from succinic acid by addition of barium hydroxide; the filtrate was evaporated to dryness, and the glutaric acid isolated by extraction with chloroform.

The yield of ethyl $\alpha\alpha'$ -dibromoglutarate obtained in the Hell-Volhard-Zelinsky process (Ingold, J., 1921, **119**, 313) by means of thionyl chloride was increased from 45% to 75% by conducting the bromination in a special apparatus containing an electric light bulb, rich in ultra-violet light, immersed in the reaction mixture.

2 : 2'-*Diphenylimino*-4 : 4'-*diketo*-3 : 3'-*diphenyl*-5 : 5'-*dithiazolidylmethane*.—10.5 G. of ethyl $\alpha\alpha'$ -dibromoglutarate were gradually added to a boiling solution of thiocarbanilide (2 mols.) and pyridine (5 g.) in alcohol and the solution was heated under reflux for a further 6 hours. The *dithiazolidylmethane* separated from the cooled solution and was recrystallised from alcohol; m. p. 210° (Found: N, 10.1; S, 11.8. $C_{31}H_{24}O_2N_4S_2$ requires N, 10.2; S, 11.8%). Yield, 4 g.

2 : 2'-*Di-imino*-4 : 4'-*diketo*-3 : 3'-*diphenyl*-5 : 5'-*dithiazolidylmethane*, similarly obtained from phenylthiourea and the dibromoglutaric ester, formed a microcrystalline powder, m. p. 276° (decomp.), on recrystallisation (Found: S, 16.5. $C_{19}H_{16}O_2N_4S_2$ requires S, 16.2%). Yield, 18%.

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