44. *The Hydrogenation of Tutin.*

By S. N. Slater.

Bromohydrotutin and bromohydropicrotoxinin have been further investigated and assigned the formulæ $C_{15}H_{17}O_6Br$ and $C_{15}H_{15}O_6Br$ respectively. Hydrogenation of tutin in acetic acid with a platinum oxide catalyst yields *a-dihydrotutin*, but with palladised charcoal and ethyl alcohol as solvent, gives an isomeric form, *β-dihydrotutin*.

The author recently reported (this vol., p. 50) the preparation of two substances described as bromohydrotutin and bromohydropicrotoxinin. In attempts to repeat those experiments tutin and picrotoxinin were hydrogenated with a palladium–charcoal catalyst and with ethyl alcohol as solvent, but the products did not give insoluble bromo-derivatives when treated with bromine water. As the melting points of bromohydrotutin and α-bromotutin are so close, it might be suggested that they are in fact identical and that no hydrogenation of tutin had taken place originally under the conditions used. The substances obtained in the previous investigation were therefore re-examined. The conclusion reached from melting-point and optical determinations is that they are undoubtedly different compounds. Bromohydropicrotoxinin also must be regarded as a distinct substance, for it remains unchanged after further crystallisation: were it a mixture of α- and β-bromopicrotoxinin, β-bromopicrotoxinin would readily be isolated from it by fractional crystallisation.

These facts may perhaps be correlated with the difficulty experienced by other workers in obtaining reproducible results when hydrogenating picrotoxinin by means of a palladium–charcoal catalyst; *e.g.*, Mercer and Robertson (J., 1936, 288) obtained as the sole product of this reaction β-dihydropicrotoxinin, but O'Donnell, Robertson, and Harland (J., 1939, 1261) were unable to repeat this preparation. In view of the experiments recorded by these workers on the bromination of picrotoxinin it seems certain that the double bond is the seat of reaction and it is therefore unlikely that " bromohydrotutin " and " bromohydropicrotoxinin " are derived from hydrogenated tutin or hydrogenated picrotoxinin. Further analyses support the formulæ $C_{15}H_{17}O_6Br$ and $C_{15}H_{15}O_6Br$ respectively, these substances possibly being derived from isomerisation products of tutin and picrotoxinin formed under the influence of the catalyst and hydrogen.

When platinum oxide was used as catalyst and acetic acid as solvent, picrotoxinin gave exclusively α-dihydropicrotoxinin, as described by the above workers, and tutin gave a dihydro-derivative which, by analogy, has been termed *α-dihydrotutin*. When tutin in alcohol was hydrogenated with a palladium–charcoal catalyst, a different product, termed *β-dihydrotutin*, was obtained.

These results furnish a further indication of the close connection between tutin and picrotoxinin.

Experimental.

Bromohydrotutin.—After further recrystallisation bromohydrotutin melted at 260° (decomp.) (Found: C, 48·4; H, 4·8; Br, 21·6. Calc. for $C_{15}H_{17}O_6Br$: C, 48·3; H, 4·6; Br, 21·4%). It depressed the m. p. of a-bromotutin (259°, decomp.) by *ca.* 20°. Dr. F. J. Turner kindly undertook an examination of the optical properties of the two substances. Measurement of the optic axis angle gave: a-bromotutin, $2V = 48° \pm 3°$, sign $-$; bromohydrotutin, $2V = 50° \pm 2°$, sign $+$.

Bromohydropicrotoxinin.—Further recrystallisation failed to change the m. p. (254—255°, decomp.) and the mother-liquors when concentrated yielded only material melting at the same temperature (Found: C, 48·9; H, 4·5; Br, 21·4. Calc. for $C_{15}H_{15}O_6Br$: C, 48·5; H, 4·1; Br, 21·6%).

a-Dihydrotutin.—Tutin (0·5 g.) in acetic acid (10 c.c.) was shaken with platinum oxide (0·1 g.) in hydrogen at atmospheric pressure; 44 c.c. were absorbed in 15 minutes (theo. for one double bond, 38 c.c.). The acetic acid was removed in a vacuum at 50°, and the product taken up in alcohol. On cooling, a white powder was obtained, which was crystallised from chloroform–benzene. *a-Dihydrotutin* formed small felted needles, m. p. 224—226° (decomp.) (Found: C, 60·7; H, 7·3. $C_{15}H_{20}O_6$ requires C, 60·8; H, 6·8%).

a-Dihydropicrotoxinin.—Hydrogenation of picrotoxinin in acetic acid with a platinum oxide catalyst yielded a-dihydropicrotoxinin, m. p. 253—254° (decomp.).

β-Dihydrotutin.—Tutin in ethyl alcohol was shaken with palladised norit in hydrogen at atmospheric pressure.

Absorption of hydrogen was slow and fresh catalyst was added after 4 hours' shaking. When absorption was complete, the catalyst was filtered off, the solvent removed, and the product crystallised from water, *β-dihydrotutin* being obtained in needles, m. p. 232—233° (decomp.) (Found : C, 60·9; H, 7·1. $C_{15}H_{20}O_6$ requires C, 60·8; H, 6·8%).

The last three compounds were stable to bromine water and reduced ammoniacal silver nitrate on heating, but only the last two reduced Fehling's solution on heating.

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