STUDIES IN CHLORALAMIDES

Part II. Chloral Nitro- and Chloral Bromo-Salicylamides

BY (THE LATE) N. W. HIRWE, (MISS) K. D. GAVANKAR
AND
B. V. PATIL

Received November 17, 1938
(Communicated by Dr. Mata Prasad, D.Sc., F.I.C.)

A detailed study of chloral salicylamide and its methyl ether has been made by previous authors. The present paper deals with a study of nitro substitution products and the bromo substitution products of these compounds. The constitutions of the various nitro chloral salicylamides obtained by the nitration of chloral salicylamide and its methyl ether and of the various bromo chloral salicylamides obtained by the bromination of chloral salicylamide and its methyl ether were established by hydrolysing them to the known salicylic acids and their constitutions were further confirmed by directly condensing the various known nitro- and bromo-salicylamides and their methyl ethers with chloral.

It has been found by the present authors that during nitration and bromination of chloral salicylamide the para-directing influence of the OH group which is clearly obvious in nitration of salicylic acid is considerably lessened by the presence of CONH·CH·(OH)·CCl₃ group in the ortho position. Thus chloral salicylamide when nitrated gives mainly chloral 3-nitro salicylamide together with only a small quantity of 5-nitro-salicylamide instead of its chloral condensation product and chloral salicylamide when brominated gives very little 5-bromochloral salicylamide the main product being a compound which gives 3-bromo salicylic acid on hydrolysis.

Further if chloral-3-nitro salicylamide is brominated in order to get chloral-3-nitro-5-bromo-salicylamide, bromine enters position 5 with a simultaneous detachment of the chloral group and 3-nitro-5-bromo-salicylamide is obtained. 5-nitro salicylamide and 5-bromo-salicylamide cannot be condensed with chloral in order to get chloral-5-nitro-salicylamide and chloral-5-bromo-salicylamide respectively; while the 3-nitro salicylamide and 3-bromoc-
salicylamide condense easily. However, it may be noted with interest that if the nuclear OH group is changed into a -OCH₃ group, then the product of nitration and of bromination of chloral O-methoxy benzamide are exclusively 5-nitro chloral 2-methoxy benzamide and 5-bromo chloral-2-methoxy benzamide respectively. This is undoubtedly due to the stronger para directing influence of the methoxyl group.

**Experimental**

**Chloral-3-nitro salicylamide**—

1. A mixture of chloral salicylamide (20 g.) and dilute nitric acid (40 c.c., sp. gr. 1.2) was kept at room temperature for four days when a yellow solid, a mixture of chloral-3-nitro salicylamide and 5-nitro salicylamide was obtained. On fractionation from alcohol yellow cubes separated (yield 10 g.) m.p. 154°. It gave red colour with ferric chloride. (Found : Cl 32·1, N 8·5; C₉H₆O₅N₂Cl₃ requires Cl 32·3, N 8·5 per cent.)

The mother liquor from the above experiment on further concentration gave yellow needles, m.p. 224-25° identified as 5-nitro salicylamide.

**Hydrolysis.**—The foregoing chloral compound (0.5 g.) was refluxed with sodium hydroxide solution (10 per cent. 10 c.c.) for two hours. On acidification a solid was obtained which crystallised from water in needles, m.p. 128°, identified as 3-nitro salicylic acid.

2. A mixture of 3-nitro salicylamide (5 g.) and choloral (5 g.) was heated on a flame till a clear solution was obtained. It was kept overnight at room temperature when it set to a transparent sticky mass, which gave a solid (7 g.) on being washed with water. It was recrystallised from alcohol in yellow cubes m.p. 154° identical with above.

**Sodium Salt.**—(NO₂·C₆H₃·ONa·CO·NH·CH·ONa·CCl₃).

A red solid, very soluble in water. (Found : Na 11·1, H₂O 8·5; C₉H₆O₅N₂Na₂Cl₃, 2H₂O requires Na 11·2 and H₂O 8·8 per cent.)

**Potassium Salt.**—(NO₂C₆H₃OK·CO·NH·CH·OK·CCl₃).

A red solid very soluble in water. (Found : K 19·1; C₉H₆O₅N₂Cl₃K₂ requires K 19·2 per cent.)

**Calcium Salt.**—To a solution of chloral 3-nitro salicylamide in dilute ammonium hydroxide was added a solution of calcium chloride when a yellow solid separated which crystallised from water in yellow granules with five molecules of water. This water of crystallisation could not be removed at lower temperatures and even under reduced pressure. At higher