

A NOTE ON THE ACTION OF CHLORINE AND BROMINE ON
2-ACETYL-1-NAPHTHOL AND OF BROMINE ONLY
ON 2-HYDROXY-3-NAPHTHOIC ACID

By A. V. REGH AND S. V. SHAH

Hantzsch (*Ber.*, 1906, **39**, 3097) obtained by the action of bromine on 2-acetyl-1-naphthol a monobromo derivative in which bromine had entered into the naphthalene nucleus, whereas Ullmann (*Ber.*, 1897, **30**, 1468) had obtained a bromo derivative in which the hydrogen of acetyl only was replaced by a bromine atom. By the action of chlorine in excess on the same compound, the present authors have obtained a tetrachloro derivative, trichloromethyl-2-(1-hydroxy-4-chloro)-naphthyl ketone and by the action of bromine in excess dibromomethyl-2-(1-hydroxy-4-bromo)-naphthyl ketone. By the action of bromine in excess on 2-hydroxy-3-naphthoic acid, a dibromo derivative has been obtained, whilst Gradenwitz (*Ber.*, 1894, **27**, 2622) obtained only a monobromo derivative.

Trichloromethyl-2-(1-hydroxy-4-chloro)-naphthyl Ketone.—When 2-acetyl-1-naphthol (5 g.) in acetic acid (50 c.c.) is treated with excess of dry chlorine till the product turns yellow and then poured into water, a yellow solid separates out which on crystallisation from alcohol melts at 141° . [Found: Cl, 15.21; equiv. (Ba salt), 232.9. $C_{12}H_7O_2Cl$ requires Cl, 14.17 per cent. Equiv., 250.5].

Dibromomethyl-2-(1-hydroxy-4-bromo)-naphthyl Ketone.—When 2-acetyl-1-naphthol is heated to 110° in an oil-bath and bromine (25 c.c.) is added dropwise, white fumes of hydrogen bromide are evolved and a yellow solid separates out. It is washed first with dilute sodium thiosulphate solution and then with water and crystallised from chloroform, m. p. 201° . (Found: Br, 57.28. $C_{12}H_7O_2Br_2$ requires Br, 56.74 per cent). When refluxed with NaOH solution, the bromine in the side-chain is decomposed and bromine in the filtrate from the decomposed product estimated. (Found: Br, 38.24. $C_{12}H_7O_2Br_2$ requires Br, 37.83% for two bromine atoms in the acetyl group).

1:6-Dibromo-2-hydroxy-3-naphthoic Acid.—The acid (5 g.) taken with acetic acid (50 c.c.) is treated with bromine (15 c.c.) with constant shaking. On cooling the product crystals appear. They are washed with dilute sodium thiosulphate solution and crystallised from alcohol, m. p. 251° . (Found: Br, 46.10; equiv., 342.6. $C_{11}H_8O_3Br_2$ requires Br, 46.24 per cent. Equiv., 346.0]. The product on oxidation with alkaline $KMnO_4$ solution for 6 hours on a sand-bath, concentrated, acidified, and then extracted with ether gives a white solid, m. p. 168° , identical with 4-bromophthalic acid. (Found: equiv., 120.1. $C_8H_5O_4Br$ requires equiv., 122.5).