541. 3 : 4-*Dihydro*-2-*ketonaphtho*(1′ : 2′-5 : 6)-1 : 3-*oxazine*.

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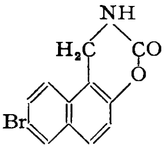
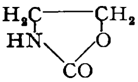
The preparation of 6′-bromo- and 3′ : 6′-dibromo-3 : 4-dihydro-2-ketonaphtho(1′ : 2′-5 : 6)-1 : 3-oxazine is described. The unbrominated compound was not obtained by a similar method.

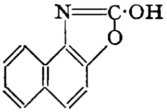
WHEN a solution of 1-aminomethyl-2-naphthol hydrochloride was mixed with excess of warm sodium hydrogen carbonate solution the corresponding base was set free (Haworth, MacGillivray, and Peacock, *J.*, 1950, 1493) but 1-aminomethyl-6-bromo-2-naphthol hydrochloride behaved differently. Cold aqueous sodium hydrogen carbonate solution set free the base, but a hot solution formed a product $C_{12}H_8O_2NBr$, probably 6′-bromo-3 : 4-dihydro-2-ketonaphtho(1′ : 2′-5 : 6)-1 : 3-oxazine (I). This type of compound does not appear to have been described hitherto, but the oxazolones, containing a somewhat similar structure in a five-membered ring, are quite well-known and 2-ketoxazolidine (II) was prepared by Gabriel and Eschenbach (*Ber.*, 1897, **30**, 2494) by the action of warm sodium hydrogen carbonate on 2-bromoethylamine hydrobromide.



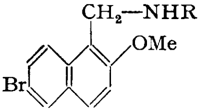
(I)



(II)



(III)



(IV)

The compound (I) was stable to boiling water but was decomposed by dilute sodium hydroxide solution to the sodium salt, and by acid to the corresponding salt, of 1-aminomethyl-6-bromo-2-naphthol, but 2-hydroxy-β-naphthoxazole (III) (Desai, Hunter, and Khalidi, *J.*, 1938, 321), unlike (I), was stable to cold 30% potassium hydroxide solution. 1-Aminomethyl-3 : 6-dibromo-2-naphthol hydrochloride reacted similarly to the monobromo-compound with hot aqueous sodium hydrogen carbonate, to give a compound regarded as the 3′-bromo-derivative of (I). The presence of a free hydroxyl group is necessary for the formation of (I) and its derivatives, and 1-aminomethyl-6-bromo-2-methoxynaphthalene hydrochloride when treated with hot aqueous sodium hydrogen carbonate gave only the expected base (IV; R = H).

EXPERIMENTAL

6′-Bromo-3 : 4-dihydro-2-ketonaphtho(1′ : 2′-5 : 6)-1 : 3-oxazine (I).—To a solution of 1-aminomethyl-6-bromo-2-naphthol hydrochloride (1 g.) (Haworth, MacGillivray, and Peacock, *loc. cit.*) in hot water (40 c.c.), sodium hydrogen carbonate (2 g.) was added with stirring, and the mixture warmed on a water-bath for several minutes. The precipitated *naphtho-oxazine* was filtered off, washed well with hot water, dried, and washed with ether. It crystallised from hot glacial acetic acid, in small cubes (0·9 g.), m. p. 206—208° [Found : C, 51·6; H, 2·8; N, 4·9; Br, 28·7%; *M* (in camphor) 290. $C_{12}H_8O_2NBr$ requires C, 51·6; H, 2·9; N, 5·1; Br, 28·7%; *M*, 278]. The compound was soluble in hot ethanol and insoluble in chloroform, ether, or benzene.

3′ : 6′-Dibromo-3 : 4-dihydro-2-ketonaphtho(1′ : 2′-5 : 6)-1 : 3-oxazine, prepared similarly to the foregoing compound from 1-aminomethyl-3 : 6-dibromo-2-naphthol (Haworth, MacGillivray, and Peacock, *loc. cit.*), crystallised from hot acetic acid as a microcrystalline powder, m. p. 180° (Found : C, 40·2; H, 2·2. $C_{12}H_7O_2NBr_2$ requires C, 40·3; H, 2·0%).

6-Bromo-2-methoxy-1-phenylacetamidomethylnaphthalene (IV; R = $CH_2Ph{\cdot}CO$).—A solution of 6-bromo-1-phenylacetamidomethyl-2-naphthol (2 g.) in methyl alcohol (25 c.c.) and 20% potassium hydroxide solution (5 c.c.) was mixed with methyl sulphate (1·5 c.c.); after 10 minutes at room temperature the mixture solidified. The *ether* (IV; R = $CH_2Ph{\cdot}CO$) crystallised from hot ethanol in colourless needles (1·8 g.), m. p. 196° (Found : C, 62·7; H, 4·7; N, 3·7. $C_{20}H_{18}O_2NBr$ requires C, 62·5; H, 4·7; N, 3·7%).

1-Aminomethyl-6-bromo-2-methoxynaphthalene (IV; R = H).—The acyl derivative (IV; R = $CH_2Ph{\cdot}CO$) (1·0 g.) was boiled under reflux for 3 hours with concentrated hydrochloric acid (6 c.c.) and ethanol (20 c.c.). The crystalline *hydrochloride* separated on cooling, and was filtered off, washed with alcohol, and crystallised from hot water, from which it separated as colourless needles (0·4 g.), m. p. 256° (decomp.) (Found: C, 46·2; H, 4·2; N, 4·6. $C_{12}H_{13}ONClBr$ requires C, 46·3; H, 4·3; N, 4·6%). The *base* (IV; R = H), liberated from the hydrochloride by hot or cold aqueous sodium carbonate, crystallised in colourless needles, m. p. 172° (Found: Br, 30·2. $C_{12}H_{12}ONBr$ requires Br, 30·1%).

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