HETEROCYCLIC COMPOUNDS

Part XIII. Abnormal Alkaline Hydrolysis of Some 4-Isopropyl-1:2-α-Naphthapyrones

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By the acetylation of 2-isobutyryl-1-naphthol according to Kostanecki’s method, we obtained a compound having the composition $C_{14}H_{16}O_2$. In the absence of a $CH_2R$ group ortho to the hydroxyl, this method cannot give a chromone, and therefore, we have assumed the coumarin structure for it. However, when we hydrolysed it by heating with 5 per cent. caustic soda, only 1-hydroxy-2-naphthoic acid was obtained. The formation of an $o$-hydroxy-carboxylic acid by this method has been usually accepted as the criterion of the chromone structure, but never that of the coumarin which is supposed to give usually $o$-hydroxy-cinnamic acid or, in rare cases, $o$-hydroxy-ketone as recently shown by Sethna and Shah. However, if the hydrolysis of the coumarin (I) takes the course indicated as follows, the formation of $o$-hydroxy-carboxylic acid can be easily explained.

2-Isobutyryl-1-naphthol is not the intermediate product during the hydrolysis of this coumarin, as this hydroxy-ketone can be recovered unchanged under identical conditions. 4-Bromo-2-isobutyryl-1-naphthol, and 4-acetyl-2-isobutyryl-1-naphthol gave 4-isopropyl-6-bromo-1:2-α-naphthapyrone ($\text{II, } R = \text{Br}$) and 4-isopropyl-6-acetyl-1:2-α-naphthapyrone ($\text{II, } R = \text{Ac}$).
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$R = \text{CoCH}_3$), which underwent alkaline hydrolysis to 4-bromo-1-hydroxy-2-naphthoic (III, $R = \text{Br}$) and 4-acetyl-1-hydroxy-2-naphthoic acids (III, $R = \text{CoCH}_3$) respectively.

These observations serve to emphasise the fact that the results of the alkaline hydrolysis cannot be always relied upon as an unequivocal method for the identification of coumarins and chromones. However, we wish to collect more examples of such abnormal hydrolysis by extending these observations to 4-isopropylbenzo-$\alpha$-pyrone, as well as its substitution products which are easily obtainable by the Pechmann condensation of isobutyryl-acetic ester and its C-alkyl derivatives with the phenols.

Before concluding, we wish to make a passing reference to a new method which we have evolved for the diagnosis of the coumarins and chromones. When bromine in glacial acetic acid solution is added to the coumarin or the chromone dissolved in the same solvent, the former invariably gives the bromo-substitution derivative while the latter gives the di-per-bromide from which the original chromone can be regenerated by the action of aqueous sulphurous acid. However, we wish to make this a subject of future communication.

**Experimental**

2-Isobutyryl-1-naphthol was prepared by the modification of the method of Goldzweig and Kaiser. To a solution of anhydrous zinc chloride (20 g.) in isobutyric acid (20 g.), $\alpha$-naphthol (20 g.) was added and the mixture was poured into water after heating to boiling on the sand-bath for two hours. The black, semi-solid mass was purified through 5 per cent. alkali when a considerable quantity of neutral products was removed. The acidic material was exhaustively extracted with hexane which dissolved 2-isobutyryl-1-naphthol, leaving impurities of a dinaphthol type insoluble. Finally the crystallisation from alcohol gave pale-yellow, square plates, m.p. 87–88° (literature gives 77°). Mixed m.p. with an authentic specimen of 2-butyryl-1-naphthol was 65°. (Yield = 25 per cent.) (Found: C, 78.4; H, 6.6. C$_{14}$H$_{12}$O$_2$ requires C, 78.5; H, 6.5 per cent.)
Its alcoholic solution gave dark green colouration with ferric chloride.

**Kostanecki Reaction with 2-Isobutyryl-1-naphthol and Formation of 4-Isopropyl-1:2-a-naphthapyrone.**—A mixture of 2-isobutyryl-1-naphthol (10 g.), anhydrous sodium acetate (20 g.) and acetic anhydride (50 c.c.) was heated at 175-80° for 12 hours, and poured into water. The solid after being triturated with 5 per cent. alkali, crystallised from hexane in thick white plates, m.p. 105°. (Yield = 90 per cent.) (Found: C, 80.4; H, 6.1, \( \text{C}_{16}\text{H}_{14}\text{O}_{2} \) requires C, 80.7; H, 5.9 per cent.)

It was soluble in alcohol, acetone, acetic acid, and benzene, and dissolved in concentrated sulphuric acid without any colour or fluorescence.

**Hydrolysis of the Coumarin to 1-Hydroxy-2-naphthoic Acid.**—A suspension of the coumarin (1 g.) in 5 per cent. NaOH (50 c.c.) was heated on sand-bath under reflux for four hours when a clear solution was obtained. The cooled filtered solution gave, on acidification with concentrated HCl, a solid which was purified through sodium bicarbonate solution, and crystallised from alcohol in needles, m.p. 195°, undepressed by admixture with an authentic specimen of 1-hydroxy-2-naphthoic acid.

**4-Bromo-2-isobutyryl-1-naphthol.**—When Bromine (2.5 c.c.) was gradually added to the solution of 2-isobutyryl-1-naphthol (10 g.) in glacial acetic acid (150 c.c.), copious fumes of HBr were evolved. The mixture was exposed to sunlight for two hours and kept overnight before pouring into water. The solid that slowly separated out crystallised from alcohol in square plates, m.p. 71° (depressed to 34° by 4-bromo-2-butyryl-1-naphthol). (Found: Br, 27.0. \( \text{C}_{14}\text{H}_{13}\text{O}_{2} \) Br, requires Br, 27.3 per cent.)

**Kostanecki Reaction with 4-Bromo-2-isobutyryl-1-naphthol and Formation of 6-Bromo-4-isopropyl-1:2-a-naphthapyrone.**—The reaction was carried out at 175-80° for 12 hours using 4-bromo-2-isobutyric acid (4 g.), sodium acetate (8 g.) and acetic anhydride (20 c.c.) and the coumarin isolated as usual. It crystallised from alcohol in small, colourless plates m.p. 98°. (Yield = 3.5 g.) (Found: Br, 25.1; \( \text{C}_{16}\text{H}_{13}\text{O}_{2} \) Br requires Br, 25.2 per cent.)

**Hydrolysis of the Coumarin to 4-Bromo-1-hydroxy-2-naphthoic Acid.**—The hydrolysis was carried out as usual. The acid, purified through sodium bicarbonate solution crystallised from alcohol in white needles, m.p. 244-45°, and was identified as 4-bromo-1-hydroxy-2-naphthoic acid by comparison with an authentic specimen.

**4-Acetyl-2-isobutyryl-1-naphthol.**—Acetyl chloride (9 g.) was gradually added with constant shaking to a mixture of powdered anhydrous zinc
chloride (20 g.) 2-isobutyryl-1-naphthol (20 g.) and nitrobenzene (120 c.c.). After 30 hours, the mixture was worked up as usual, and the solid that separated out after the removal of nitrobenzene in steam crystallised from alcohol in pale-yellow needles, m.p. 80° (depressed to 60° by 4-acetyl-2-butyryl-1-naphthol). The substance is soluble in dilute (2–3 per cent.) alkali, but forms an insoluble sodium salt in concentrated solutions (5–10 per cent.). Its alcoholic solution gave a violet colouration with ferric chloride. (Found: C, 74.7; H, 6.4. \( \text{C}_{16}\text{H}_{16}\text{O}_{3} \) requires C, 75.0; H, 6.3 per cent.)

**Kostanecki Reaction with 4-Acetyl-2-isobutyryl-1-naphthol and Formation of 6-Acetyl-4-isopropyl-1 : 2-\( \alpha \)-naphthapyrone.**—The mixture of the naphthol (3 g.), sodium acetate (6 g.) and acetic anhydride (25 c.c.) was heated at 175–80° for 12 hours. The product isolated as usual crystallised from hexane in small plates, m.p. 85°. (Found: C, 76.8; H, 5.8. \( \text{C}_{18}\text{H}_{18}\text{O}_{3} \) requires C, 77.1; H, 5.7 per cent.)

The coumarin was hydrolysed as usual, and the acid which after purification melted at 215°, was identified as 4-acetyl-1-hydroxy-2-naphthoic acid by comparison with an authentic specimen. This acid gave, on decarboxylation, 4-acetyl-1-naphthol, m.p. 200°, already described by Akram and Desai.²

**Summary**

4-Isopropyl-1 : 2-\( \alpha \)-naphthapyrone is hydrolysed by dilute alkali to 1-hydroxy-2-naphthoic acid. It is further observed that 6-bromo- and 6-acetyl-4-isopropyl-1 : 2-\( \alpha \)-naphthapyrones are also hydrolysed to 4-bromo- and 4-acetyl-1-hydroxy-2-naphthoic acids. As the hydrolysis of the coumarins to \( \alpha \)-hydroxy carboxylic acids is unusual, these cases provide interesting exceptions to the usual behaviour.

**REFERENCES**