333. *Condensation of Phenols with Unsaturated Ketones or Aldehydes. Part I. β-Naphthol and Vinyl Methyl Ketone.*

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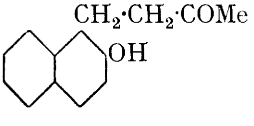
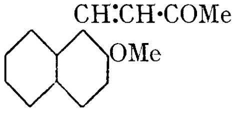
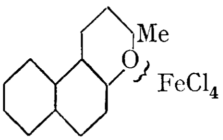
A collateral investigation (Robinson and Walker, this vol., p. 1435) describes the synthesis of benzopyrylium salts by the condensation of reactive phenols with unsaturated ketones in *acid* solution and in the presence of an oxidising agent; the object of the present series is to study the condensation of phenols with αβ-unsaturated carbonyl compounds in the presence of *basic* catalysts. As a typical case we examined the condensation of β-naphthol and vinyl methyl ketone in the hope of obtaining β-2-*hydroxy*-1-*naphthylethyl methyl ketone* (I): the substance is produced from these generators in cold alcoholic solution containing sodium ethoxide or potassium ethoxide.



(I.)



(II.)



(III.)

The methyl ether of the phenolic ketone is readily obtained and is identical with a specimen made by catalytic reduction of 2-methoxynaphthylideneacetone (II). The oxidative ring-closure of (I) in the presence of hydrogen chloride should give a methylnaphthopyrylium chloride, and indications of this reaction were obtained in many experiments. However, most of the methods gave tarry products or mixtures containing further condensed material and a satisfactory conversion was only made possible by the combined action of phosphoryl chloride and chloranil. The resulting oxonium salt was characterised as the ferrichloride (III).

Experimental.

β-2-*Hydroxy*-1-*naphthylethyl Methyl Ketone* (I).—(A) The substance was first obtained by the use of sodium ethoxide. It crystallised from aqueous alcohol in colourless needles, m. p. 84° (Found: C, 78·3; H, 6·5. $C_{14}H_{14}O_2$ requires C, 78·5; H, 6·5%).

(B) Vinyl methyl ketone (11 g., free from formaldehyde and its polymerides) was added to a solution of β-naphthol (20 g.) in alcoholic potassium ethoxide (from 5 g. of potassium and 70 c.c. of anhydrous alcohol) and the mixture was kept for 4 days in the ice-chest. The alcohol was removed under diminished pressure, water added to the residue, and the phenols precipitated by the passage of carbon dioxide as an oil, which was washed with aqueous alcohol (1 : 1) in order to remove unchanged β-naphthol. The substance ultimately crystallised and was recrystallised from aqueous alcohol (yield, 7 g.), m. p. 84° alone or mixed with the analysed specimen. The substance is readily soluble in alcohol, benzene, or chloroform; also in aqueous sodium hydroxide, but it is insoluble in aqueous sodium carbonate.

In the course of attempts to bring about the oxidative ring-closure to a pyrylium salt, the phenolic ketone was dissolved in acetyl chloride and anhydrous ferric chloride added. An orange *ferrichloride* separated in prismatic crystals and this is a curiously stable compound of ferric chloride and the *O*-acetyl derivative of the hydroxy-ketone. It appears to be possible to crystallise this substance from formic acid, but it could not be obtained in an analytically pure condition. On decomposition with water or alcohol it yields a colourless crystalline substance insoluble in cold aqueous alkalis but capable of hydrolysis under mild conditions and consequently soluble on heating with formation of the starting material.

The *methyl* ether was readily obtained by methylation of the phenolic ketone with methyl sulphate and aqueous sodium hydroxide. The oil, b. p. 205°/10 mm., crystallised from methyl alcohol, containing a little water, in white needles, m. p. 54° (it is better to omit the distillation) (Found: C, 79·0; H, 7·1. $C_{15}H_{16}O_2$ requires C, 78·9; H, 7·0%).

2-*Methoxy*-1-*naphthylideneacetone* (II).—Aqueous sodium hydroxide (1·5 c.c. of 5%) was added to a solution of 2-methoxy-1-naphthaldehyde (7 g.) in pure acetone (50 c.c.), and the mixture kept for 24 hours. The excess of acetone was then removed, and the oily product isolated by means of ether and distilled, b. p. 195—205°/1 mm. The distillate crystallised from aqueous acetone in light yellow needles, m. p. 146·5—147·5° [Found: C, 79·9; H, 6·3; *M* (Rast), 219. $C_{15}H_{14}O_2$ requires C, 79·6; H, 6·2%; *M*, 226]. The substance is readily soluble in alcohol, acetic acid, or acetone.

Hydrogenation. A solution of the unsaturated ketone (0·2 g.) in acetic acid (10 c.c.) to which palladous chloride solution (2·5 c.c. of 0·5%) had been added was agitated with hydrogen at 30—40° until decolorised. The product was β-2-methoxy-1-naphthylethyl methyl ketone, which, after crystallisation from aqueous methyl alcohol, had m. p. 54°, alone or mixed with a specimen obtained by methylation of the product of condensation of β-naphthol and vinyl methyl ketone. The yield was almost quantitative.

2-*Methyl*-5 : 6-*naphtha*(1 : 2)*pyrylium Ferrichloride* (III).—A mixture of hydroxynaphthylethyl methyl ketone (2 g.), chloranil (2·5 g.), and phosphoryl chloride (25 c.c.) was cautiously heated to its boiling point; a vigorous reaction then occurred and this was allowed to subside; the process was repeated 4 times. The reaction mixture was then at once added to 5% hydrochloric acid (100 c.c.), cooled, quickly filtered, and mixed with ferric chloride (20 g., crystallised) in concentrated hydrochloric acid (30 c.c.). The precipitated *ferrichloride* was collected, dried (3·5 g.), and crystallised from acetic acid, forming greenish-yellow prismatic needles, m. p. 151° but not to a clear liquid (Found: C, 42·8; H, 2·5; Cl, 36·2. $C_{14}H_{11}OCl_4Fe$ requires C, 42·7; H, 2·8; Cl, 36·1%). The yellow solution in sulphuric acid exhibits a brilliant bluish-green fluorescence, and this is also exhibited to a slightly less striking extent by solutions in acetic acid, alcohol, or even dilute aqueous acids. Aqueous solutions of the salt gradually decompose with deposition of an indigo-blue precipitate. The colourless pseudo-base may be taken up in ether or ethyl acetate after the addition of sodium acetate to an aqueous solution; the organic layer may then be washed with 5—10% hydrochloric acid and the yellow chloride regenerated. This salt is not stable in aqueous solution containing less than 5% of hydrogen chloride.

On hydrolysis with boiling aqueous alcoholic sodium hydroxide and acidification of the diluted solution with acetic acid a very sparingly soluble, crystalline, pale greenish-yellow substance was precipitated. This becomes deep blue (dichroic-red) on heating with acetic acid and it could be reconverted into the original ferrichloride by careful heating with a mixture of acetic and hydrochloric acids and addition of ferric chloride. Perhaps the sparingly soluble substance is a dimeride of 2-hydroxy-1-naphthylideneacetone, or this whole series of substances contains less hydrogen than we now suggest. Oxidative coupling at the methyl group is a possibility which the analyses do not exclude.

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