STUDIES IN NAPHTHALENE SERIES

Part IX. Properties of 4-Propionyl-1-Naphthol and the Preparation of 4-Propyl-1-Naphthol

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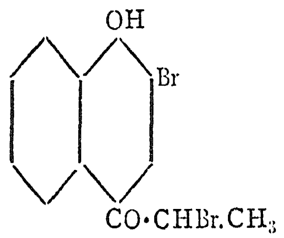
4-Propionyl-1-naphthol can best be prepared by the action of propionyl chloride on α-naphthol in the presence of zinc chloride, though other less satisfactory methods are also described in the experimental portion. It readily gave the picrate, the semicarbazone, the methyl ether and the acetyl derivative. The condensation of this hydroxy-ketone with acid chlorides takes place easily in the presence of anhydrous aluminium chloride but not zinc chloride with the formation of 2:4-diacyl-1-naphthols. The application of the Nencki Reaction to 4-propionyl-1-naphthol is interesting in the fact that if sufficient time is given (six to eight hours), the resulting products are always 2-acyl-1-naphthols, whilst if the reaction is allowed to proceed only for a short time (two to three hours), it is possible to isolate either α-naphthol or 2:4-diacyl-1-naphthol which is supposed to be the intermediate product.

Bromination of 4-propionyl-1-naphthol gave the monobromo- and the dibromo-derivatives. As the monobromo-derivative is unaffected by hot alkali solution, the bromine must be situated in the nucleus. Therefore, its constitution is 2-bromo-4-propionyl-1-naphthol. One of the bromine atoms of the dibromo-derivative can be replaced by hydroxyl by the action of dilute alkali; therefore, this bromine must be situated in the side-chain, and the constitution of the dibromo-derivative must be 2-bromo-4-α-bromopropionyl-1-naphthol (I).

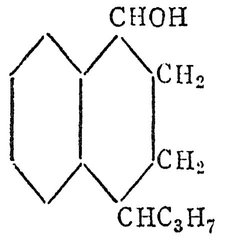
Nitration with one mol of fuming nitric acid gave 2-nitro-4-propionyl-1-naphthol together with small quantities of 2-nitro-1-naphthol and 2:4-dinitro-1-naphthol. When two mols or excess of nitric acid was used, the sole product was 2:4-dinitro-1-naphthol, showing that the propionyl group was eliminated.

The Clemmenson Reduction gave 4-propyl-1-naphthol, together with a neutral, hydroxylic compound supposed to be 4-propyl-*ac*-tetrahydro-1-naphthol (II). It was characterised by the picrate, and underwent the Nencki

Reaction with ease. On coupling it with benzenediazonium chloride in alkaline solution, 4-propyl-2-benzene-azo-1-naphthol, as well as the phenylhydrazone of 4-ethyl-β-naphthaquinone (III) was obtained. Further work regarding the action of diazosalts on 4-propionyl-1-naphthol is being actively pursued.



(I)



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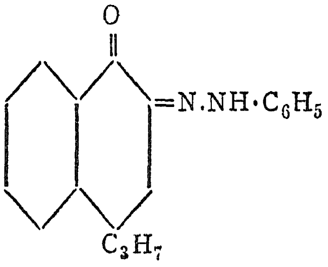

(III)

Experimental

4-*Propionyl*-1-*naphthol*.—(1) The mixture obtained by adding propionyl chloride (15 g.) to a mixture of α-naphthol (20 g.), powdered anhydrous zinc chloride (20 g.) and nitrobenzene (125 c.c.) with efficient shaking and cooling was worked up as usual after forty-eight hours. The solid obtained on cooling is dried and exhaustively extracted with hexane which dissolves only 2-propionyl-1-naphthol (6 g.), while the insoluble residue is recrystallised from alcohol when white, silky needles (m.p. 188°) are obtained (12 g.). It is soluble even in warm sodium bicarbonate solution and its alcoholic solution does not give any colour with ferric chloride. (Found: C, 77·8; H, 5·9. $C_{13}H_{12}O_2$ requires C, 78·0; H, 6·0 per cent.)

(2) The above method was repeated using propionic anhydride in place of propionyl chloride. As warming of the mixture on the water-bath is necessary, the products obtained are coloured and the yield is not as good as in case (1).

(3) The condensation was carried out using anhydrous aluminium chloride and propionyl chloride but the yield of 4-propionyl-1-naphthol was poor.

(4) The reaction was repeated using anhydrous aluminium chloride and acetic anhydride, but even here the yield was not as good as in case (1).

The Acetyl derivative obtained by heating the compound (1 g.) with acetic anhydride (5 c.c.) for three hours crystallised from dilute alcohol in lustrous leaflets (m.p. 92°). Warming with dilute alkali solution regenerated the original hydroxy-ketone. (Found: C, 74·0; H, 5·9. $C_{15}H_{14}O_3$ requires C, 74·4; H, 5·8 per cent.)

The Picrate prepared by mixing equal weights of the components in warm benzene, crystallised in orange needles (m.p. 158°). (Found: C, 53·0; H, 3·4. $C_{19}H_{14}O_9N_3$ requires C, 53·2; H, 3·2 per cent.)

The Methyl ether obtained by shaking the alkaline solution of the naphthol (1 g. in 10 c.c. of 10 per cent. NaOH) with dimethyl sulphate (3 c.c.) crystallised from hexane in lustrous plates (m.p. 58°). It was identical with the product described by Gattermann, Ehrhardt and Maisch.[1]

The Semi-carbazone crystallised from alcohol in small needles (m.p. 223°). (Found: C, 65·1; H, 6·0. $C_{14}H_{15}O_2N_3$ requires C, 65·4; H, 5·8 per cent.)

Action of glacial acetic and propionic acids in presence of zinc chloride and formation of 4-propionyl-2-acetyl-1-naphthol, 2-acetyl-1-naphthol; α-naphthol and 2-propionyl-1-naphthol.—A mixture of 4-propionyl-1-naphthol (2 g.), anhydrous zinc chloride (2 g.) and acetic acid (20 c.c.) was heated on sand-bath for three hours. The solid obtained by pouring the mixture into a large quantity of water was purified through dilute alkali, dried, and extracted with hexane. The insoluble portion was the original 4-propionyl-1-naphthol, while the soluble portion was fractionally crystallised from alcohol. The first fraction gave needles (m.p. 130°), identified as 2-acetyl-4-propionyl-1-naphthol by comparison with an authentic specimen prepared by Akram and Desai,[2] while the second fraction (m.p. 101°) was proved to be 2-acetyl-1-naphthol.

If the heating of the original mixture was carried out for six to seven hours, 2-acetyl-1-naphthol constituted the only isolable product. The same reaction was repeated using propionic acid. Though much of the original product remained unchanged after three hours, an appreciable amount of α-naphthol was isolated (25 per cent.) while 2-propionyl-1-naphthol was the sole product after seven hours.

2-Bromo-4-propionyl-1-naphthol was obtained by adding the chloroform (5 c.c.) solution of bromine (0·5) to the chloroform (25 c.c.) solution of 4-propionyl-1-naphthol (2 g.). The solid, after the removal of chloroform-crystallised from hexane in colourless needles (m.p. 111°) (depressed to 86° by 2:4-dibromo-1-naphthol (m.p. 110°). The product was recovered unchanged after heating with 5 per cent. caustic soda solution. (Found: Br, 28·1. $C_{13}H_{11}O_2Br$ requires Br, 28·3 per cent.)

2-Bromo-4-α-bromopropionyl-1-naphthol was obtained as above by using double the quantity of bromine and exposing the mixture to sunlight for twenty-four hours, and crystallised from alcohol in pale-yellow needles (m.p. 132°). (Found: Br, 44·6. $C_{13}H_{10}O_2Br_2$ requires Br, 44·7 per cent.)

On heating with 5 per cent. caustic soda solution it gave a brown solid (m.p. 223°) and containing 27·0 per cent. of bromine.

2-*Nitro*-4-*propionyl*-1-*naphthol.*—A solution of fuming nitric acid (*d.* = 1·5; 1 c.c.) in glacial acetic acid was gradually added with constant shaking and cooling to the solution of 4-propionyl-1-naphthol (5 g.) in glacial acetic acid (50 c.c.). The contents were poured into water after four hours, and the solid that gradually separated out was treated with 5 per cent. alkali. The insoluble reddish orange sodium salt was filtered off, dissolved in water and decomposed with concentrated hydrochloric acid. The solid crystallised from hexane in deep yellow needles (m.p. 100°). (Found: C, 63·5; H, 4·6. $C_{13}H_{11}O_4N$ requires C, 63·7; H, 4·5 per cent.)

The hexane insoluble portion crystallised from dilute alcohol in yellow needles m.p. 128°, and was identified as 2-nitro-1-naphthol.

The alkali-soluble sodium salt, on decomposition with hydrochloric acid gave 2:4-dinitro-1-naphthol (m.p. 138°), which was the sole product of nitration if the reaction was carried out using two mols of nitric acid.

Reduction of 4-*propionyl*-1-*naphthol to* 4-*propyl*-1-*naphthol and* 4-*propyl*-ac-*tetrahydro*-1-*naphthol.*—A mixture of 4-propionyl-1-naphthol (20 g.), amalgamated zinc (30 g.) and dilute hydrochloric acid (100 c.c.) was heated on sand-bath under reflux for six hours. The oily product was extracted with ether, and separated into acidic and neutral components with dilute alkali. The acidic product, b.p. 150°/ 6 mm., was a viscous liquid with a phenolic smell and solidified if cooled in ice (yield = 50 per cent.). (Found: C, 83·6; H, 7·6. $C_{13}H_{14}O$ requires C, 83·9; H, 7·5 per cent.)

The Picrate prepared in benzene solution crystallised in orange-red needles (m.p. 138°). (Found: C, 54·5; H, 4·2. $C_{19}H_{17}O_8N_3$ requires C, 54·9; H, 4·1 per cent.)

The neutral product of reduction, b.p. 126–28°/ 6 mm., was a yellowish brown liquid that did not solidify. It did not give a picrate, but its benzene solution reacted with sodium liberating hydrogen. (Found: C, 81·9; H, 9·7. $C_{13}H_{18}O$ requires C, 82·1; H, 9·5 per cent.)

Nencki Reaction with 4-*propyl*-1-*naphthol, and formation of* 2-*acetyl*-4-*propyl*-1-*naphthol.*—The mixture of the naphthol (1 g.), zinc chloride (1 g.) and glacial acetic acid (15 c.c.) was heated on sand-bath under reflux for three hours, and the solid that was obtained on pouring the mixture into water was purified through dilute alkali. It crystallised from hexane in thick, prismatic needles (m.p. 185°). (Found: C, 78·7; H, 7·1. $C_{15}H_{16}O_2$ requires C, 79·0; H, 7·0 per cent.)

Its alcohol solution gave dark-green coloration with ferric chloride.

Coupling of 4-*propyl*-1-*naphthol with benzene-diazonium chloride and formation of* 4-*propyl*-2-*benzeneazo*-1-*naphthol and the phenylhydrazone of* 4-*propyl-β-naphthaquinone.*—An ice-cold diazotised solution of aniline (1 g.) in hydrochloric acid was gradually added to the alkaline solution of 4-propyl-1-naphthol (2 g.). A deep red precipitate which was immediately formed was filtered off, and separated into 5 per cent. alkali-soluble and insoluble components. The alkali-soluble portion crystallised from hexane in deep red needles (m.p. 186°). (Found: C, 78·4; H, 6·4. $C_{19}H_{18}ON_2$ requires C, 78·6; H, 6·2 per cent.)

The neutral product crystallised from dilute alcohol in microcrystalline, dark-red plates (m.p. 150°). (Found: C, 78·3; H, 6·3. $C_{19}H_{18}ON_2$ requires C, 78·6; H, 6·2 per cent.)

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Summary

The best method of preparing 4-propionyl-1-naphthol has been worked out. Its simple chemical properties like bromination, nitration, reduction, as well as the formation of functional derivatives have been studied. 4-Propyl-1-naphthol has also been subjected to some chemical reactions.

REFERENCES

1. Gattermann, Ehrhardt and Maisch	*Ber.*, 1890, **23**, 1209.
2. Akram and Desai	*Proc. Ind. Acad. Sci.*, (A), 1940, **11**, 156.