

STUDIES IN NAPHTHALENE SERIES

Part XV. The Preparation and Properties of 4-Phenylacetyl-1-Naphthol and 2-Phenylacetyl-1-Naphthol

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THE condensation of α -naphthol with phenylacetyl chloride gave a mixture of 4-phenylacetyl- and 2-phenyl-acetyl-1-naphthols, the latter being in preponderant amount. As the yield of the 4-isomer was not good, the Fries migration of 1-naphthyl phenylacetate was tried, but this method also gave a poor yield. The condensation of methoxy naphthalene gave a good yield of 4-phenylacetyl-1-methoxy naphthalene, but attempts to demethylate it by hydrogen bromide, hydrogen iodide and anhydrous aluminium chloride were not successful. As only a small quantity of 4-phenylacetyl-1-naphthol was available, only its bromination was studied.

As considerable quantity of 2-phenylacetyl-1-naphthol was formed, we undertook its reduction, bromination, nitration, and bromination of the chromone prepared by Cheema and Venkataraman by its vigorous acetylation.

EXPERIMENTAL

4-Phenylacetyl-1-naphthol

To a solution of α -naphthol (20 g.) in nitrobenzene (60 c.c.) containing finely powdered anhydrous zinc chloride (20 g.) in suspension, the solution of phenylacetyl chloride (40 g.) in nitrobenzene (40 c.c.) was gradually added. After allowing the mixture to stand at the room temperature for 24 hours, it was decomposed by ice-cold hydrochloric acid, and the nitrobenzene removed by steam. The brown solid that was obtained was alternately extracted with water (thrice) and 5 per cent. sodium carbonate solution remove α -naphthol and phenylacetic acid. The residue on extraction with 5 per cent. sodium hydroxide solution left an insoluble solid, and the alkaline extract on acidification with hydrochloric acid gave the product most of which went in solution when treated with petroleum ether (b.p. 60–80°). The insoluble product crystallised from alcohol in brownish red needles, m.p. 92–93° (yield 5%). Its alcoholic solution gave an intense red coloration with ferric chloride. (Found: C, 82.6; H, 5.3; $C_{18}H_{14}O_2$ requires C, 82.4; H, 5.3 per cent.)

The petroleum-ether soluble product crystallised in small white needles, m.p. 100–01° C. This was identified as 2-phenyl-acetyl-1-naphthol (yield 10%).

The alkali-insoluble product was crystallised from chloroform and acetic acid mixture, m.p. 130–32° C. Its alcoholic solution gave green coloration with ferric chloride. This was probably 2-4 diphenyl acetyl-1-naphthol.

The Fries migration of 1-naphthol-phenyl acetate. Preparation of 1-naphthol-phenyl-acetate.—1-Naphthol (50 g.) dissolved in sodium hydroxide (10%; 500 c.c.) and phenylacetyl chloride (60 g.) was very gradually added with constant shaking to the ice-cooled alkaline solution. The mixture was shaken well and kept for four hours and poured in water. The product on washing and crystallising through acetic acid gave small colourless plates, m.p. 46–47° C.

4-Phenyl-acetyl-1-naphthol.—An intimate mixture of dry 1-naphthol-phenylacetate (10 g.) and anhydrous aluminium chloride (25 g.) was heated in an oil-bath at 150° C. for one hour. The reaction mixture was decomposed in the cold, and the product on treatment with alkali gave alkali-soluble and insoluble substances.

The alkali-soluble material was acidified and the brownish product was treated with petroleum-ether (b.p. 60–80° C). The soluble portion crystallised in white needles, m.p. 100–01° C. undepressed by 2-phenyl-acetyl-1-naphthol (yield 5 per cent.).

The petrol-insoluble product was crystallised from alcohol in short needles, m.p. 92–93° C. undepressed by 4-phenyl-acetyl-1-naphthol (yield 5 per cent.).

2:4-Dinitrophenyl-hydrazone of 4-phenyl-acetyl-1-naphthol.—The ketone (0.5 g.) was dissolved in glacial acetic acid (10 c.c.) and 2:4-dinitrophenyl-hydrazine (0.5 g.) dissolved in glacial acetic acid (10 c.c.) was added and the mixture was heated under reflux for six hours. On cooling the product crystallised in small red needles, m.p. 177–78°. (Found: N, 12.6. $C_{24}H_{18}O_5N_4$ requires N, 12.7 per cent.)

Condensation of 1-naphthyl methyl ether with phenylacetyl chloride by Friedel and Crafts method.

Preparation of 1-methoxy-4-phenyl acetyl-naphthalene.—1-Naphthyl-methyl ether (10 c.c.) dissolved in dry benzene (20 c.c.) and phenyl acetyl-chloride (18 g.) dissolved in dry benzene (20 c.c.) were alternately added with constant shaking, to a cooled suspension of powdered anhydrous zinc chloride (10 g.) in dry nitrobenzene (30 c.c.). After keeping the reaction

at room temperature for 24 hours, it was decomposed by dilute hydrochloric acid in the cold. The nitrobenzene was steam-distilled and the product was purified and crystallised from alcohol in long white needles, m.p. 80–81° C. Its alcoholic solution gave no coloration with ferric chloride. (Found: C, 82.5; H, 5.6; $C_{19}H_{16}O_2$ requires C, 82.6; H, 5.8 per cent.)

Demethylation of 1-methoxy-4-phenyl acetyl naphtholene by hydrogen bromide and pyridic acid in glacial acetic acid also by anhydrous aluminium chloride.—Demethylation of 1-methoxy-4-phenyl acetyl naphthalene by 50% hydrogen bromide was carried out for 8 hours and only the original product was obtained.

The demethylation of this compound was tried with 50% hydrogen iodide without any success. Heating the methoxy product (3 gm.) with anhydrous aluminium chloride in dry benzene (50 c.c.) for one hour gave phenyl-acetic acid.

Bromination of 4-phenylacetyl-1-naphthol with one mol. of bromine: Preparation of 2-bromo-phenyl-acetyl-1-naphthol.—4 Phenyl-acetyl-1-naphthol (0.4 gm.) was dissolved in glacial acetic acid (10 c.c.) to which a solution of bromine (0.15 c.c.) in glacial acetic acid (5 c.c.) was added drop by drop with constant shakings. The reaction mixture was kept for 24 hours and then poured into large quantity of ice-cold water. The red substance which separated out was crystallised from alcohol in long red needles m.p. 76–78° C., and was unaffected by heating with 10 per cent. alkali. (Found: Br, 11.50. $C_{18}H_{13}O_2$ Br requires Br 11.7 per cent.)

Derivatives of 2-phenylacetyl-1-naphthol-4-nitrophenylhydrazone.

This was prepared by heating the mixture of the ketone (0.5 gm.) and 4-nitrophenyl-hydrazine (0.5) in alcohol (25 c.c.) for 6 hours, and crystallised from alcohol in short, orange-red needles m.p. 249–50° C. (Found: N, 10.8. $C_{24}H_{19}O_3N_3$ requires N, 10.6 per cent.)

The 2:4-dinitrophenyl-hydrazone crystallised from alcohol in small, orange-red needles, m.p. 275–77°. (Found: N, 12.5. $C_{24}H_{18}O_5N_4$ requires N, 12.7 per cent.)

Bromination of 2-phenyl acetyl-1-naphthol with one mol. of bromine: Preparation of 4-bromo-2-phenyl acetyl-1-naphthol.—The ketone (1 gm.) was dissolved in acetic acid (20 c.c.) and to this, a solution of bromine (0.25 c.c.) in acetic acid (5 c.c.) was added drop by drop with constant shaking. The mixture was kept for 24 hours and then poured in water. The yellow substance that separated out was crystallised from alcohol in

yellow needles m.p. 97–98° C. (depressed to 72° C. by the original ketone). (Found: Br, 11.9. $C_{18}H_{13}O_2$ Br, requires Br, 11.8 per cent.)

Bromination of 2-phenyl acetyl-1-naphthol with two and three mols. of bromine gave only 4-bromo-2-phenyl acetyl α -naphthol. The bromo product was unaffected by heating with 10 per cent. alkali.

Nitration of 2-phenyl acetyl-1-naphthol with one mol. of fuming nitric acid: Preparation of 4-nitro-2-phenyl-acetyl-1-naphthol.—To the solution of the ketone (2 gm.) in acetic acid (30 c.c.) a solution of fuming nitric acid (d. = 1.5; 0.4 c.c.) in acetic acid (5 c.c.) was added drop by drop with constant shaking and the mixture was kept for 24 hours at room temperature. It was poured in water and the product was crystallised from alcohol in orange yellow needles m.p. 156–157° C. (Found: N, 4.3; $C_{18}H_{13}O_4N$, requires N, 4.6 per cent.)

Nitration of 2-phenylacetyl-1-naphthol with two and three mols of fuming nitric acid gave only the mono nitroderivative.

Clemmensen Reduction of 2-phenyl-acetyl-1-naphthol: Preparation of 2-(β -phenyl-ethyl)-1-naphthol.—A mixture of 2-phenyl acetyl-1-naphthol (2 gm.) amalgamated zinc (7 gm.) and hydrochloric acid (1: 1; 60 c.c.) was heated on sand-bath under reflux for 20 hours.

On neutralizing the alkaline solution, a brownish product was obtained which was crystallised from alcohol in yellow needles, m.p. 106–107° C. This alcoholic solution gave no coloration with ferric chloride. (Found C, 86.9; H, 6.4; $C_{18}H_{16}O$ requires C, 87.1; H, 6.5 per cent.)

Formation of 2-(β -phenyl-ethyl)-ac-tetrahydro-1-naphthol.—On evaporation, the ethereal layer gave the neutral hydroxylic compound which was crystallised from alcohol in white shining needles, m.p. 196–98° C. Its alcoholic solution gave no coloration with ferric chloride. (Found: C, 85.9; H, 8.05; $C_{18}H_{20}O$ requires C, 85.71; H, 7.9 per cent.)

Kostanecki Reaction with 2-phenyl-acetyl-1-naphthol: Preparation of 2-methyl-3-phenyl-1:4- α -naphthopyrone.—The ketone (3 gm.) was heated with acetic anhydride (25 c.c.) and sodium acetate (3 gm.) in an oil-bath at 180–90° C. for eight hours. The mixture was poured in water and separated solid was purified and crystallised from alcohol in pale yellow needles m.p. 210–11° C. (Venkataraman and Cheema give 204°). It was soluble in the usual organic solution. (Found: C, 84.0; H, 4.7; call. for $C_{20}H_{16}O_2$ C, 83.9, H, 4.9 per cent.)

Hydrolysis of the above pyrone.—The above pyrone (0.2 gm.) was refluxed on water for three hours with caustic soda (10%, 15 c.c.). On

acidifying the alkaline solution pale yellow substance was obtained which was soluble in 5% sodium-bicarbonate solution. This was crystallised from alcohol, m.p. 186–87° C., undepressed by 1-hydroxy-2-naphthoic acid.

Bromination of the pyrone with one mol. of bromine: Preparation of diperbromide of the pyrone.—A solution of bromine (0.2 c.c.) in chloroform (10 c.c.) was added to the solution of 2-methyl-3-phenyl-1:4- α -naphthapyrone (1 gm.) in chloroform (30 c.c.). On keeping the mixture for 24 hours the product crystallised out in white needles, m.p. 160° C. (Found: Br 35.7; $C_{20}H_{14}O_2Br_2$ requires Br, 35.9 per cent.)

Action of sulphur dioxide solution on the diperbromide of 2-methyl-3-phenyl-1:4- α -naphthapyrone.—The diperbromide of the pyrone (0.2 gm.) was kept in SO_2 solution (50 c.c.) for 24 hours, the product was then washed and crystallised from chloroform in white needles, m.p. 210–11° and was 2-methyl-3-phenyl-1:4- α -naphthapyrone.

Action of glacial acetic acid on the diperbromide of 2-methyl-3-phenyl-1:4- α -naphthapyrone.—The diperbromide of the pyrone (0.2 gm.) was heated with glacial acetic acid (10 c.c.) on water-bath under reflux for three hours and the solution was then poured in water. The solid was filtered and crystallised through chloroform in white needles, m.p. 160° C. undepressed by the diperbromide of 2-methyl-3-phenyl-1:4- α -naphthapyrone.

SUMMARY

The condensation of α -naphthol and phenyl acetyl chloride gave mainly 2-phenyl acetyl-1-naphthol and 4-phenyl acetyl-1-naphthol in small quantity. The former was brominated, nitrated, reduced, and acetylated by the Kostanecki method to give the pyrone. An attempt to prepare 4-phenylacetyl-1-naphthol the latter by dimethylation of 1-methoxy-4-phenylacetyl-naphthalene did not meet with success.

REFERENCE

1. K. Venkataraman and Cheema .. *J. C. S.*, 1932, 918.