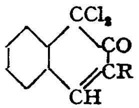
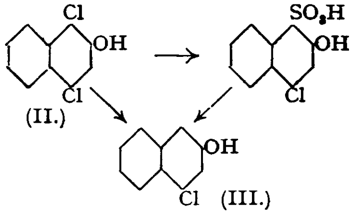
73. *The Chlorination of β-Naphthol and Ethyl 2-Hydroxy-3-naphthoate in Presence of Sodium Acetate. 4-Chloro-β-naphthol and its Derivatives.*

By Harold Burton.

The conversion of 1 : 1-dichloro-2-keto-1 : 2-dihydronaphthalene (I, R = H) into 1 : 4-dichloro-β-naphthol (II) by hydrogen chloride in acetic acid (Fries and Schimmelschmidt, *Annalen*, 1930, **484**, 295) has been modified to give a 45—50% overall yield from β-naphthol. Attempted application of the method to ethyl 2-hydroxy-3-naphthoate was not successful.

Chlorination of β-naphthol in presence of acetic acid and sodium acetate was shown by Fries and Schimmelschmidt (*loc. cit.*) to give 1 : 1-dichloro-2-keto-1 : 2-dihydronaphthalene (I, R = H), which, under the influence of hydrogen chloride in acetic acid, was converted into 1 : 4-dichloro-β-naphthol (II), a compound first obtained in poor yield by Zincke (*Ber.*, 1888, **21**, 3387) by reduction of 1 : 1 : 3 : 4-tetrachloro-2-keto-1 : 2 : 3 : 4-tetrahydronaphthalene, and later by Armstrong and Rossiter (*Proc.*, 1891, **7**, 32) by the action of sulphuryl chloride on β-naphthol. Investigation of the former method has led to (II) in 45—50% yield from the β-naphthol used.

(I.)


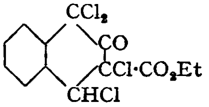


(IV.)

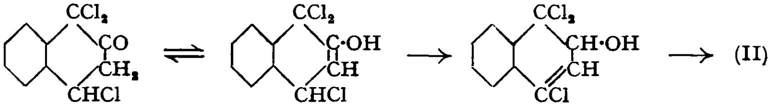
The 1-chlorine atom of (II) is not very reactive and is not removed by the usual acid or alkaline reducing agents; with stannous chloride in acetic acid–hydrogen chloride at 100° under pressure, as recommended by Fries and Schimmelschmidt (*loc. cit.*), conversion into 4-chloro-β-naphthol (III) occurs. Prolonged treatment of (II) with sodium sulphite in boiling aqueous alcohol gave 15% of *4-chloro-β-naphthol-1-sulphonic acid* (IV), the sulphonic acid group of which was readily eliminated under the influence of boiling dilute sulphuric acid, thus giving (III) by an alternative route. *4-Chloro-2-hydroxy-1-naphthaldehyde* could not be obtained from (III) by means of *N*-methylformanilide and phosphoryl chloride, but was presumably obtained (see Experimental) by the Reimer–Tiemann reaction.

Chlorination of 2-hydroxy-3-naphthoic acid under conditions similar to those used for β-naphthol gave a product which, as expected of a β-ketonic acid, rapidly decomposed. Ethyl 2-hydroxy-3-naphthoate, on the other hand, afforded the stable *ethyl* 1 : *1-dichloro-2-keto-1* : *2-dihydro-3-naphthoate* (I, R = CO_2Et), which was not rearranged smoothly by acetic acid–hydrogen chloride. The use of ethyl-alcoholic hydrogen chloride gave ethyl 1-chloro-2-hydroxy-3-naphthoate as the main identifiable product (*ca.* 20%), together with much amorphous material, and a small amount (4%) of a *dichlorohydroxynaphthoic acid* which might well be the 1 : 4-dichloro-derivative, although an attempt to obtain (II) from it by decarboxylation was inconclusive. Further chlorination of ethyl 2-hydroxy-3-naphthoate or of the dichloroketo-ester gave *ethyl* 1 : 1 : 3 : *4-tetrachloro-2-keto-1* : 2 : 3 : *4-tetrahydro-3-naphthoate* (V), but attempted reductions (compare Zincke, *loc. cit.*) of this to the 1 : 4-dichloro-derivative were unsuccessful; ethyl 1-chloro-2-hydroxy-3-naphthoate was again the main identifiable product.

The relatively facile conversion of (I, R = H) but not of (I, R = CO_2Et) into a 1 : 4-dichloro-β-naphthol suggests that the first stage in the process might be the addition of hydrogen chloride across the 3 : 4-double linking to give 1 : 1 : 4-trichloro-2-keto-1 : 2 : 3 : 4-tetrahydronaphthalene (VI). Such a compound could enolise in one direction only, namely to (VII), and if this underwent a prototropic change to the trichlorocarbinol (VIII), followed by loss of hydrogen chloride, 1 : 4-dichloro-β-naphthol would result.



(V.)



Such a mechanism for the action of hydrogen bromide on (I, R = H) is not applicable, since the final product is 1-chloro-6-bromo-β-naphthol. In this case it is probable that bromine chloride is an intermediate (compare Fries and Schimmelschmidt, *loc. cit.*).

Alternatively, 1 : 4-elimination of hydrogen chloride from (VI) would give (II) (in its ketonic form) directly.

Experiments to test the inter- or intra-molecular nature of the rearrangement are not easy to devise. The choice of a readily chlorinated compound to decide whether the reaction is intermolecular, *viz.*, $\cdot CCl_2\cdot CO\cdot + HCl \longrightarrow \cdot CCl{:}C(OH)\cdot + Cl_2$, is very limited. The use of an amine (*e.g.*, aniline) is impracticable, since the concentration of hydrogen chloride is so high that the base must be largely or wholly removed from solution as the hydrochloride. The use of a phenol overcomes this objection, but condensation of the phenol with the initial reactant is not precluded. It has been found that when the change (I, R = H) ⟶ (II) is carried out in presence of phenol itself, the yield of (II) is reduced but the formation of chlorophenol could not be detected. Traces of unchanged phenol may have been present in the reaction mixture, which after separation of the 1 : 4-dichloro-β-naphthol in the usual manner (see Experimental), contained a large amount of a tarry product soluble in aqueous sodium hydroxide. It must be concluded that almost the whole of the phenol had undergone condensation. The mechanism of the rearrangement thus remains obscure.

The production of 1 : 4-dichloro-β-naphthol from β-naphthol and sulphuryl chloride (Armstrong and Rossiter, *loc. cit.*) undoubtedly involves the intermediate production of 1 : 1-dichloro-2-keto-1 : 2-dihydronaphthalene, which is now shown to be produced in small but definite amount from β-naphthol and 2·5 molecules of the chloride.

EXPERIMENTAL.

1 : 1-*Dichloro-2-keto*-1 : 2-*dihydronaphthalene* (I, R = H).—The procedure of Fries and Schimmelschmidt (*loc. cit.*) was modified as follows. A solution of *β*-naphthol (72 g.; recrystallised from benzene) and crystalline sodium acetate (200 g.) in glacial acetic acid (400 c.c.) was stirred, cooled in ice, and treated with chlorine (71 g.) during not less than 2½ hours (a shorter time causes production of tar). A distinct colour change was noted when the total weight of chlorine had been absorbed. After 15 minutes, a small amount was poured on ice and stirred until solidification occurred; the remainder of the solution was then added. The mixture was stirred for 45 minutes, the solid filtered off, washed with water, ground into a paste with acetic acid, refiltered, and finally washed with a little light petroleum (b. p. 80—100°). This material (*A*) was used for conversion into 1 : 4-dichloro-*β*-naphthol. Further purification (as above) and recrystallisation of this product from light petroleum (b. p. 40—60°) gave massive prisms, m. p. 48—50°, unaltered by further crystallisation. Fries and Schimmelschmidt (*loc. cit.*) give m. p. 54°.

1 : 4-*Dichloro-β-naphthol* (II).—The material (*A*) was shaken vigorously in a wide-mouthed bottle with a saturated solution (80 c.c.) of hydrogen chloride in glacial acetic acid for 2—3 minutes. The mixture was then cooled in ice-water, stirred, and dry hydrogen chloride slowly passed in for 30 minutes. The bottle was stoppered and kept in a cool place for *ca.* 18 hours. The resulting solid was filtered off, washed repeatedly with successive small amounts of acetic acid until the filtrate was nearly colourless, and finally with light petroleum (b. p. 80—100°). Recrystallisation from light petroleum (b. p. 80—100°; 300 c.c.; little charcoal) gave 50±2 g. of 1 : 4-dichloro-*β*-naphthol, m. p. 122—123°.

When this experiment (see p. 281) was carried out in the presence of phenol (23·5 g.), the yield of recrystallised 1 : 4-dichloro-*β*-naphthol was 25 g. Neutralisation of the filtrate with sodium carbonate and steam-distillation gave a further quantity of the dichloronaphthol as the sole volatile product.

4-*Chloro-β-naphthol*-1-*sulphonic Acid* (IV).—A mixture of 1 : 4-dichloro-*β*-naphthol (10·7 g.), crystalline sodium sulphite (25·2 g.), water (250 c.c.), and 95% alcohol (150 c.c.) was boiled for 72 hours. On cooling, unchanged dichloronaphthol (5·5 g.) crystallised. Evaporation of the alcohol and extraction of the aqueous residue with ether gave a further 2·6 g. of dichloronaphthol. The aqueous solution was evaporated to small bulk, acidified with sulphuric acid, and boiled to expel sulphur dioxide. The *sulphonic acid* (2 g.) crystallised, and after being washed with water and a little alcohol, was recrystallised from water, separating in nearly colourless plates, which sintered at *ca.* 200° but did not melt up to 260°, and appeared to contain 0·5 mol. of water of crystallisation (not lost at 100° in a vacuum) (Found: Cl, 13·2; S, 11·9. $C_{10}H_7O_4ClS,0{\cdot}5H_2O$ requires Cl, 13·3; S, 12·0%).

4-*Chloro-β-naphthol* (III).—(*a*) The above sulphonic acid (5·2 g.), water (150 c.c.), and concentrated sulphuric acid (50 c.c.) were boiled for 20 minutes. On cooling, the chloronaphthol (3·2 g.) crystallised; recrystallisation from light petroleum (b. p. 80—100°) gave needles, m. p. 102—103°.

(*b*) A mixture of 1 : 4-dichloro-*β*-naphthol (15 g.), stannous chloride dihydrate (70 g.), and 300 c.c. of a saturated solution of hydrogen chloride in acetic acid was heated in a pressure bottle in a boiling water-bath for 8 hours. The solution was poured, when cold, into ice-water, and the crystalline material (12 g.), m. p. 95°, filtered off. (If this product had m. p. 83—87°, the above treatment had to be repeated, indicating incomplete removal of the 1-chlorine atom.) Recrystallisation from light petroleum (b. p. 80—100°) gave nearly colourless, silken needles (9·2 g.), m. p. 103—104°, unchanged by admixture with a specimen prepared as in (*a*).

4-Chloro-*β*-naphthol could not be obtained from the dichloronaphthol by means of tin and a mixture of boiling concentrated hydrochloric and acetic acids or by zinc dust in boiling aqueous potassium hydroxide.

4-Chloro-*β*-naphthol was characterised as the acetate, colourless plates from light petroleum (b. p. 40—60°), m. p. 58—59° (Hodgson and Birtwell, J., 1943, 468, give m. p. 56°) (Found: Cl, 16·1. Calc. for $C_{12}H_9O_2Cl$: Cl, 16·1%), and as the *benzoate*, colourless needles from alcohol, m. p. 83—84° (Found: C, 72·0; H, 4·0; Cl, 12·75. $C_{17}H_{11}O_2Cl$ requires C, 72·2; H, 3·9; Cl, 12·6%).

4-*Chloro*-2-*hydroxy*-1-*naphthaldehyde*.—A solution of 4-chloro-*β*-naphthol (25 g.) and sodium hydroxide (40 g.) in water (100 c.c.) and alcohol (80 c.c.) was heated under reflux to 65°, and chloroform (20 g.) added dropwise. A deep green colour, changing to brown, developed and the temperature rose to 75° and then fell to 70°. After 30 minutes, the alcohol was removed by distillation, and the aqueous residue acidified with concentrated hydrochloric acid. The solid residue (29 g.) obtained from the dried ethereal extract was dissolved in the minimum amount of boiling alcohol; on cooling, the aldehyde (6·5 g.), m. p. 118°, separated. Evaporation of the alcoholic filtrate gave much purple material, from which unchanged 4-chloro-*β*-naphthol (4 g.) was extracted with light petroleum. Recrystallisation of the aldehyde from alcohol or acetic acid gave a colourless product, m. p. 118—119° (slight previous shrinking), which was apparently not homogeneous but could not be fractionated by alcohol. The *aldehyde* [Found: (i) C, 64·0; H, 3·5; Cl, 17·6; (ii) C, 64·1; H, 3·5; Cl, 17·5. $C_{11}H_7O_2Cl$ requires C, 63·9; H, 3·4; Cl, 17·2%] does not react with sodium bisulphite; it gives the characteristic yellow colour of an *o*-hydroxy-aldehyde with aqueous ammonia.

An attempt to obtain the aldehyde from 4-chloro-*β*-naphthol (8·6 g.), *N*-methylformanilide (17 g.), and phosphoryl chloride (21 g.) at 75—78° for 2 hours was unsuccessful. The product gave hardly any precipitate with semicarbazide acetate, whereas the above aldehyde reacts readily to give the insoluble semicarbazone, which does not melt up to 280°.

Ethyl 1 : 1-*Dichloro-2-keto*-1 : 2-*dihydro*-3-*naphthoate* (I, R = CO₂Et).—A solution of ethyl 2-hydroxy-3-naphthoate (54 g.) and crystalline sodium acetate (100 g.) in acetic acid (600 c.c.) was treated in the cold with chlorine (36 g.) during 1½ hours. The solution was poured on ice (450 g.), and the mixture stirred. The resulting solid (70 g.), m. p. *ca.* 70°, was dried, and recrystallised from light petroleum (b. p. 60—80°), forming colourless prisms, m. p. 85—86° (Found: Cl, 24·8. $C_{13}H_{10}O_3Cl_2$ requires Cl, 24·9%). The *ester* is more stable than 1 : 1-dichloro-2-keto-1 : 2-dihydronaphthalene; it liberates iodine from potassium iodide in acetic acid and is reduced by sulphur dioxide in aqueous-alcoholic solution to ethyl 1-chloro-2-hydroxy-3-naphthoate, m. p. 113—114° (from alcohol).

Attempted Rearrangement of Ethyl 1 : 1-*Dichloro-2-keto*-1 : 2-*dihydro*-3-*naphthoate*.—Solutions of the ester in acetic acid saturated with hydrogen chloride contained unchanged material (potassium iodide test) after 72 hours. After 14 days, the only crystalline product isolable after dilution with water was ethyl 1-chloro-2-hydroxy-3-naphthoate, m. p. 111—112°, identified by hydrolysis to the free acid, m. p. 230°.

The crude ester (70 g.), suspended in absolute alcohol (200 c.c.), was treated with dry hydrogen chloride until it dissolved, and the mixture was then cooled in ice and saturated with hydrogen chloride (if solid separated during this process, the mixture was removed from the cooling bath until redissolution occurred). After 18 hours at room temperature, yellow needles of ethyl 1-chloro-2-hydroxy-3-naphthoate (12 g.) had separated. Evaporation of the filtrate to about one-third of its bulk gave a further 4 g. of this ester, m. p. 111—112°. The new filtrate was hydrolysed with sodium hydroxide (50 g. in 200 c.c. of water) during 3 hours and then acidified with concentrated hydrochloric acid. The resulting air-dried solid (35 g.) was extracted with three successive portions (100 c.c.) of benzene, and the solid which separated from the combined extracts was recrystallised from water (yield, 6 g.). Four recrystallisations from xylene then gave yellow needles (3 g.), m. p. 192—193° after slight previous softening, which appear to be a *dichloro-*

hydroxynaphthoic acid (Found: Cl, 27·5. $C_{11}H_6O_3Cl_2$ requires Cl, 27·6%). Attempted decarboxylation in boiling quinoline containing a little copper-bronze gave no crystalline product.

The above benzene extracts contained a large amount of an acid oil and a neutral resin.

Ethyl 1 : 1 : 3 : 4-*Tetrachloro-2-keto-*1 : 2 : 3 : 4-*tetrahydro-3-naphthoate* (V).—A solution of ethyl 2-hydroxy-3-naphthoate (25 g.) and crystalline sodium acetate (50 g.) in acetic acid (400 c.c.) was treated in the cold with chlorine (25 g.) during 1½ hours. The sticky product obtained by adding the mixture to ice gradually solidified; the air-dried material (40 g.), recrystallised from ligroin (b. p. 60—80°), gave colourless prisms, m. p. 73—74°, which were probably not quite pure (Found: Cl, 37·2. $C_{13}H_{10}O_3Cl_4$ requires Cl, 39·9%).

The *ester* liberated iodine from potassium iodide in acetic acid and thereby yielded ethyl 1-chloro-2-hydroxy-3-naphthoate, m. p. and mixed m. p. 113—114°. Sulphur dioxide in aqueous-alcoholic solution had no effect. Reduction of the tetrachloro-ester with stannous chloride in acetic–concentrated hydrochloric acids also gave ethyl 1-chloro-2-hydroxy-3-naphthoate. Tarry or amorphous products were obtained when the tetrachloro-ester was treated with pyridine, pyridine and sulphur dioxide, or alkali under various conditions.

Chlorination of β-Naphthol with Sulphuryl Chloride.—A mixture of β-naphthol (18 g.), sulphuryl chloride (42 g., 2·5 mols.), and dry carbon tetrachloride (50 c.c.) was warmed until reaction set in. After the initial phase (cooling in water was necessary), the mixture was heated on the steam-bath for 1 hour. The residue obtained by evaporation was kept in a vacuum desiccator, and a small amount of crystalline material separated. Recrystallisation from light petroleum (b. p. 40—60°) gave 1 : 1-dichloro-2-keto-1 : 2-dihydronaphthalene, m. p. and mixed m. p. 48—50°.

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