# NOTES.

## *Derivatives of* β-*Naphthaldehyde.* By J. D. Fulton and Robert Robinson.

The substances here briefly described are either new or have previously been obtained in other ways.

β-*Naphthaldehyde.*—This was prepared by Stephen's method (J., 1925, **127**, 1874). β-Naphthonitrile (50 g.) was dissolved in dry ether, saturated with hydrogen chloride, and reduced by anhydrous stannous chloride (250 g.). The aldimine stannichloride was decomposed by steam distillation and the aldehyde, purified through the bisulphite compound, was crystallised from 75% alcohol; m. p. 58° (yield, 38 g.).

The oxime crystallised from methyl alcohol in plates, m. p. 154° (Wuyts and Koeck, *Bull. Soc. chim. Belg.*, 1932, **41**, 196, give m. p. 156°) (Found : N, 7·9. Calc. for $C_{11}H_9ON$ : N, 8·2%).

β-*Naphthoin.*—A mixture of β-naphthaldehyde (12 g.), aqueous alcohol (100 c.c. of 80%), potassium cyanide (1·2 g.), and water (12 c.c.) was refluxed for ½ hour. The *product* (9·4 g.) crystallised from alcohol in rhombic plates, m. p. 125—126° (Found : C, 84·5; H, 5·3. $C_{22}H_{16}O_2$ requires C, 84·6; H, 5·1%). The substance is almost insoluble in ether or light petroleum, moderately soluble in cold acetone or chloroform, and readily soluble in hot alcohol.

The *oxime* crystallised from alcohol and then from benzene in needles, m. p. 172° (Found : N, 4·4. $C_{22}H_{17}O_2N$ requires N, 4·3%).

β-*Naphthil.*—A solution of β-naphthoin in alcohol was added to Fehling's solution. The product, taken up in benzene, crystallised, on addition of alcohol to the concentrated solution, in long, faintly yellow needles, m. p. 158—159° (Gomberg and Bachmann, *J. Amer. Chem. Soc.*, 1928, **50**, 2767, obtained the substance by the reduction of β-naphthoic acid and give m. p. 157—158°) (Found : C, 85·0; H, 4·6. Calc. for $C_{22}H_{14}O_2$ : C, 85·2; H, 4·5%).

2 : 3-*Di*-β-*naphthylquinoxaline.*—A mixture of *o*-phenylenediamine (0·35 g.), β-naphthil (0·9 g.), and acetic acid (8 c.c.) was boiled for a few minutes. The long needles that separated on cooling were recrystallised from alcohol; m. p. 192—193° (Found : N, 7·4. $C_{28}H_{18}N_2$ requires N, 7·3%).

*Hydro*-β-*naphthoin.*—β-Naphthoin was reduced in alcoholic solution with 4% sodium amalgam. The *product* crystallised from nitrobenzene in colourless rhombohedra, m. p. 253° [Found : C, 84·5; H, 5·9; *M* (Rast), 321. $C_{22}H_{18}O_2$ requires C, 84·1; H, 5·7%; *M*, 314].

*Deoxy*-β-*naphthoin.*—Naphthoin was reduced in alcoholic solution by zinc and hydrochloric acid. The *product* crystallised in square, yellow plates, m. p. 155—156° (Found : C, 88·9; H, 5·3. $C_{22}H_{16}O$ requires C, 89·2; H, 5·4%).

β-*Naphthoin Methyl Ether.*—A mixture of β-naphthoin (1 g.), silver oxide (2·4 g.), and methyl iodide (4·26 g.) was kept for several hours and then refluxed for 8 hours. The *product*, isolated by means of ether, crystallised in contact with methyl alcohol. Recrystallised from ether–light petroleum, it formed stellate clusters, m. p. 82° (yield, almost quantitative) (Found : C, 85·0; H, 5·8. $C_{23}H_{18}O_2$ requires C, 84·7; H, 5·5%).

β-*Naphthylidenemalonic Acid.*—A mixture of β-naphthaldehyde (1·56 g.), malonic acid (1·06 g.), and acetic acid (4 c.c.) was heated for 10 hours on the steam-bath; on cooling, a crystalline mass separated. This was collected, washed with chloroform, and recrystallised from ethyl acetate, elongated prisms, which lost lustre in the air or in a vacuum, m. p. 207° (decomp.) (Found : C, 69·7; H, 4·1. $C_{14}H_{10}O_4$ requires C, 69·4; H, 4·1%), being formed. On heating, β-naphthylacrylic acid was obtained.

β-*Naphthylacrylic Acid.*—A mixture of β-naphthaldehyde (2·2 g.), malonic acid (3 g.), and pyridine (6 c.c.) was heated for 1½ hours on the steam-bath and then boiled for 10 minutes. The product was recrystallised from aqueous alcohol; m. p. 208—209°, mixed m. p. with β-naphthylidenemalonic acid, 183° (Rousset, *Bull. Soc. chim.*, 1897, **17**, 815, gives m. p. 196°; Monier-Williams, J., 1906, **89**, 277, gives m. p. 203°).

(β-*Naphthylmethyl*)*malonic Acid.*—A solution of β-naphthylidenemalonic acid (1·2 g.) in alcohol was treated with sodium amalgam (15 g. of 2·5%). The product crystallised from benzene in colourless needles; it decomposed at 150—153° (Mayer and Sieglitz, *Ber.*, 1922, **55**, 1835, give m. p. 94—95°) (Found : C, 68·6; H, 5·3. Calc. for $C_{14}H_{12}O_2$ : C, 68·9; H, 4·9%).

*Ethyl* α-*cyano*-β-*naphthylideneacrylate*, obtained in quantitative yield by gently heating β-naphthaldehyde with ethyl cyanoacetate in presence of a little morpholine, crystallised from alcohol in pale yellow leaflets, m. p. 125—126° after shrinking at 117° (Found : C, 76·3; H, 5·3; N, 5·6. $C_{16}H_{13}O_2N$ requires C, 76·5; H, 5·2; N, 5·6%).

α-*Benzamido*-β-2-*naphthylacrylic Acid.*—β-Naphthylidenephenyl*iso*oxazolone (Kikkoji, *Bio-*

*chem. Z.*, **1911**, **35**, 73) (2 g.) was heated with sodium carbonate solution (50 c.c. of 2%) until a clear solution was obtained; on cooling, the sodium salt separated as pearly plates. The acid (2 g.) crystallised from alcohol in prisms, m. p. 240° with previous softening (Kikkoji, *loc. cit.*, gives m. p. 230°) (Found: C, 75·6; H, 5·1. Calc. for $C_{20}H_{15}O_3N$: C, 75·7; H, 4·7%).

*Methyl α-Benzamido-β-2-naphthylacrylate.*—A solution of the azlactone (1 g.) in methyl alcohol (15 c.c.) was saturated with hydrogen chloride and refluxed for 1 hour. On cooling, colourless needles separated; recrystallised from methyl alcohol, they had m. p. 142° (with previous softening) (Found: C, 76·7; H, 5·3. $C_{21}H_{17}O_3N$ requires C, 76·1; H, 5·1%).

*β-Methylnaphthalene.*—The azlactone (5 g.) was heated with aqueous sodium hydroxide (60 c.c. of 10%) until the evolution of ammonia ceased; the solution was then distilled. β-Methylnaphthalene (0·2 g.) was collected from the distillate; m. p. 32—33°, alone or mixed with an authentic specimen. The picrate (Meyer and Meyer, *Ber.*, 1919, **52**, 1250) had m. p. 115°, alone or mixed with an authentic specimen.

*β-Naphthylpyruvic Acid.*—The azlactone (7 g.) was heated with aqueous sodium hydroxide (35 c.c. of 10%) for 4—5 hours. The acid had m. p. 190° (decomp.) [Kikkoji, *loc. cit.*, gives m. p. 192° (decomp.)] (Found: C, 72·5; H, 4·9. Calc. for $C_{13}H_{10}O_3$: C, 72·9; H, 4·7%). The substance gives a green colour with ferric chloride in alcoholic solution.

*2-Hydroxy-3-(β-naphthylmethyl)quinoxaline.*—A solution of β-naphthylpyruvic acid (0·35 g.) and *o*-phenylenediamine (0·2 g.) in alcohol (4 c.c.) was heated for a few minutes on the steam-bath. The *product* crystallised from alcohol in fine colourless needles, m. p. 222—223° (Found: N, 9·8. $C_{19}H_{14}ON_2$ requires N, 9·8%).

*β-Naphthylacetic Acid.*—A solution of β-naphthylpyruvic acid (1 g.) in aqueous sodium hydroxide (5 c.c. of 10%) was treated with ice-cold perhydrol (1 c.c.) in water (3 c.c.). The solution was kept overnight and then acidified by sulphur dioxide. The precipitated acid (0·75 g.) was crystallised from water; m. p. 141—142° (Gilman and Kirby, *J. Amer. Chem. Soc.*, 1929, **51**, 3476, give m. p. 139—140°) (Found: C, 76·9; H, 5·7. Calc. for $C_{12}H_{10}O_2$: C, 77·4; H, 5·4%).—MANCHESTER UNIVERSITY. DYSON PERRINS LABORATORY, OXFORD UNIVERSITY. [*Received, November* 30*th*, 1938.]

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## *Synthesis of Long-Chain Ketones.* By J. W. H. OLDHAM and A. R. UBBELOHDE.

IN the course of experiments on the structure and melting of long-chain ketones (Oldham and Ubbelohde, in the press) it has been necessary to compare the different synthetical methods available. It is particularly important in preparing long-chain compounds to select a synthesis which does not lead to other long-chain molecules of types difficult to remove from the main product. Since the ketones obtained are of interest for physicochemical and possibly for biochemical investigations, it seems desirable to describe points in the syntheses apparently not mentioned in the literature.

(a) The pyrogenetic synthesis consists in passing the vapour of two acids over a thoria catalyst at about 400° (cf. Pickard and Kenyon, J., 1912, **101**, 629). We have used the reaction for preparing $(C_8H_{15})_2CO$, according to the equation $2C_8H_{15}{\cdot}CO_2H = (C_8H_{15})_2CO + CO_2 + H_2O$, and also for preparing ketones of the series $C_{17}H_{34}O$ ($n = 1, 2, 3$, where $n$ refers to the number of carbon atoms in the shorter alkyl group), and for $C_{18}H_{36}O$ ($n = 2$). In preparing the unsymmetrical ketones a large excess (at least 10 : 1) of the short-chain acid was used, to minimise the loss of long-chain acid in forming the unwanted symmetrical ketone. After washing with 5% hot sodium hydroxide solution and distillation, the yield of crude ketone was about 50% of the long-chain acid used, but it was found to be much more difficult to purify ketones made by this process than by either of the other methods described below.

(b) An acetoacetic ester synthesis has been described by Chibnall and Channon (*Biochem J.*, 1929, **23**, 168). We obtained more satisfactory yields, and a somewhat more easily purified product, by first synthesising the acyl derivative of acetoacetic ester (cf. Bouveault and Bongert, *Bull. Soc. chim.*, 1902, **27**, 1044), which was obtained in yields varying from 44 to 56% of the theoretical. This was then treated with the appropriate alkyl bromide or iodide, to give a final yield of crude ketone varying from 13 to 20% of the theoretical amount calculated from the initial acid chloride.

The alkyl halides should not contain less than 4 carbon atoms, owing to the fact that any acyl acetoacetic ester which fails to react would ultimately give rise to a ketone differing by less than 4 carbon atoms from the main product, and this leads to difficulties and loss in the purification.

Ketones of the series $C_{17}H_{34}O$ were prepared from the following alkyl halides: $C_4H_9I$,

$C_7H_{15}Br$, $C_8H_{17}I$, $C_9H_{19}I$, $C_{11}H_{23}I$, and $C_{12}H_{25}I$. The ketone $C_{17}H_{34}O$ ($n = 1$) was prepared by the direct action of tetradecyl iodide on twice the theoretical amount of acetoacetic ester, and gave a yield of crude ketone of 53%. Ketones of the series $C_{18}H_{36}O$ were prepared from the halides $C_8H_{17}I$, $C_9H_{19}I$, $C_{11}H_{23}I$, and $C_{12}H_{25}I$. In each case the appropriate acyl acetoacetic ester was first prepared and isolated as described by Bouveault and Bongert. The purification of the crude ketone was found to be easier and less wasteful than in the case of method (a), but not so reliable or economical as for the product obtained by method (c).

(c) A reaction between amides and Grignard reagents proposed by Ryan and Nolan (*Chem. Zentr.*, 1913, II, 2050) has been found wasteful and unsatisfactory for long-chain compounds. We have found, however, that long-chain nitriles could be easily obtained as follows: The acyl chloride was converted into the amide by pouring a solution in acetone into excess of dilute aqueous ammonia, with stirring. The amide was recrystallised from light petroleum or acetone, according to chain length, and the dry amide was converted into nitrile by warming for 2 hours with thionyl chloride under reflux on a water-bath, *the temperature being kept below* 85°. The unchanged thionyl chloride was distilled off at 100°, a water-pump being used, and the nitrile was fractionated in a vacuum. Yield, 85—95%, calculated from amide. This method is a modification of the procedure described by Michaelis and Siebert (*Annalen*, 1893, **274**, 312). An attempt to prepare adiponitrile from adipamide was, however, unsuccessful, possibly owing to the insolubility of this amide in thionyl chloride.

To complete the synthesis of the ketone, the nitrile was added to the Grignard reagent, and the mixture boiled under reflux for 2 hours before isolation.

In a few cases [*e.g.*, $C_{17}H_{34}O$ ($n = 7$)] the hydrocarbon by-products of the Grignard reagent (cf. Oldham and Ubbelohde, J., 1938, 201) were difficult to separate from the crude ketone by either distillation or recrystallisation, but such impurities could be removed by dissolving the ketone in warm concentrated sulphuric acid, separating the solution from the undissolved paraffin after cooling, and pouring it on ice to recover the ketone.

The yields after fractional distillation, but before recrystallisation, varied from 63 to 23%, the yield tending to decrease as the nitrile rose in molecular weight. The chief by-products of the reaction between nitrile and Grignard reagent were paraffins, and a very high-boiling residue containing nitrogen.

The same method was employed for the synthesis of a diketone $C_2H_5\cdot CO\cdot[CH_2]_5\cdot CO\cdot C_2H_5$, from the magnesium derivative of the dichloride $[CH_2]_5Cl_2$ and propionitrile. A yield of about 20% of the diketone was obtained on fractionating the products by distillation in a vacuum. In this instance the bulk of the product was a monoketone $C_2H_5\cdot CO\cdot[CH_2]_4\cdot CH_3$ (yield, about 60%). This is probably due to the physicochemical properties of the intermediates. The Grignard derivative of the dichloride $[CH_2]_5Cl_2$ formed a double layer at a concentration of about 2 moles per l. of ether, and the addition product with even 1 molecule of propionitrile formed a compact sticky mass which had to be broken up repeatedly during boiling for about 2 hours, to facilitate completion of the reaction. Higher yields could probably be obtained by varying the solvent for the Grignard reagent, but even as described, the method is one of the most convenient for obtaining certain long-chain diketones.

The ketones were purified by recrystallisation from ethyl alcohol till there was no appreciable difference between the f. p.'s of the crystals and of the ketone recovered from the mother-liquor. For ketones prepared by method (c), this usually required about three recrystallisations, and yielded about 65%, calculated on the basis of the crude ketone.

Tests on the purity of the products involved the use of glacial acetic acid and light petroleum (b. p. 80—100°) as alternative solvents for recrystallisation, followed by molecular distillation, and are discussed in connexion with the physicochemical investigations (Oldham and Ubbelohde, *loc. cit.*). The f. p.'s of the best samples were :

$C_{17}H_{34}O$.

| $n$ | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|---|
| F. p. | 47·9° | 47·7° | 41·5° | 41·2° | 40·9° | 40·6° | 41·7° | 50·0° |

$C_{18}H_{36}O$.

| $n$ | 2 | 3 | 4 | 5 | 6 | 8 |
|---|---|---|---|---|---|---|
| F. p. | 51·0° | 45·6° | 45·0° | 44·8° | 45·0° | 45·6° |

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