167. *The Condensation of 2-Methylnaphthalene with Acetyl Chloride.*

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The condensation of 2-methylnaphthalene with acetyl chloride in nitrobenzene solution constitutes a good method of preparation of 6-acetyl-2-methylnaphthalene; a smaller amount of the 2 : 8-compound is also produced. The 2 : 6-ketone has been reduced to *2-methyl-6-ethylnaphthalene.*

The Friedel–Crafts reaction between 2-methylnaphthalene and acetyl chloride was investigated by Dziewoński and Brand (*Bull. Int. Acad. Polon.*, 1933, *A*, 99), who obtained a mixture of products from which both 6- and 8-acetyl-2-methylnaphthalene (methylacetonaphthones) were isolated by a tedious fractional crystallisation of their oximes; the process did not appear suitable for the preparation of large quantities of the 2 : 6-ketone, which we required for another investigation. Haworth and Bolam (J., 1932, 2248) have, however, shown that substantially pure 2 : 6-derivatives are formed from 2-methylnaphthalene in the presence of nitrobenzene when condensed with propionyl chloride and with succinic anhydride; we therefore adapted their procedure to the reaction with acetyl chloride.

The product was a semi-solid mixture, from which the desired solid 2 : 6-ketone could be separated by filtration, a further amount being recovered in the form of the very sparingly soluble semicarbazone, m. p. 237° (compare Dziewoński and Brand, *loc. cit.*). From the mother-liquors of this we isolated another, much more soluble *semicarbazone*, m. p. 181°, giving rise to a liquid ketone. As the semicarbazone of the 2 : 8-ketone is described by Dziewoński and Brand as melting at 228—230°, this was thought to be a new isomeride. However, it gave on oxidation with hypobromite an acid, m. p. 147—148°, and on reduction by Clemmensen's method 2-methyl-8-ethylnaphthalene (Brunner and Grof, *Monatsh.*, 1934, **64**, 33); it must therefore be the 2 : 8-ketone.

We have repeated Dziewoński and Brand's preparation of the two ketones and separated them through the semicarbazones; here again the more soluble compound melted at 181° and no trace of a compound of m. p. 228—230° was isolated; it would appear that the latter must have contained a high proportion of the 2 : 6-isomeride. It can also be concluded that some of the 2 : 8-ketone is formed under both sets of conditions.

Haworth and Bolam's preparation of 2-methyl-6-propionaphthone was repeated, but we were unable to detect the formation of another isomeride in this instance.

2-Methyl-6-acetonaphthone has been reduced to 2-*methyl*-6-*ethylnaphthalene*, which has been characterised by the formation of derivatives.

EXPERIMENTAL.

2-*Methyl*-6- *and* -8-*acetonaphthones*.—92 G. of 2-methylnaphthalene were added to a cold solution of 176 g. of aluminium chloride in 400 c.c. of nitrobenzene, and the mixture cooled in ice and mechanically stirred while 46 g. of acetyl chloride were added dropwise. After 24 hours at room temperature, ice and dilute hydrochloric acid were added, the mixture extracted with ether, and the dark purple ethereal layer washed with alkali, dried, and evaporated. When the residue was distilled under reduced pressure to remove the nitrobenzene (this method was preferable to the lengthy steam distillation recommended by Haworth and Bolam, *loc. cit.*), finally with the aid of an oil-pump, 76 g. of the mixed ketones (64%) were obtained, b. p. mainly 154°/0·8 mm.; the last runnings solidified readily. The mixture became semi-solid overnight. The pasty solid obtained on filtration was drained on a porous plate, giving 10 g. of practically pure 2-methyl-6-acetonaphthone. The filtrate (53 g.) was treated with semicarbazide acetate and enough alcohol to give a homogeneous solution. The very sparingly soluble semicarbazone of the 2 : 6-ketone separated at once (34 g.) and was pure (m. p. 237°) after one extraction with about 250 c.c. of hot alcohol. The mother-liquors from this first crop were diluted with water (2 vols.); a sticky solid separated overnight. This was rubbed successively with petroleum, ether, and methyl alcohol, and crystallised from a small quantity of the last solvent; fine plates were obtained, the m. p. of which gradually rose to the constant value of 181°. The *semicarbazone* of 2-methyl-8-acetonaphthone was freely soluble in hot alcohol and was easily distinguished from the 2 : 6-isomeride; the yield was 5·3 g., but the losses in purification were necessarily high (Found : N, 17·9. $C_{14}H_{15}ON_3$ requires N, 17·4%). The ketone regenerated from the semicarbazone boiled at 150—154°/1·5 mm. and did not solidify (Found : C, 84·6; H, 6·7. Calc. for $C_{13}H_{12}O$: C, 84·7; H, 6·6%).

Oxidation.—1 G. of the solid 2 : 6-ketone was shaken with a solution of hypobromite prepared from 10 g. of sodium hydroxide, 50 c.c. of water, and 2·5 c.c. of bromine; the mixture was finally warmed to the b. p. The sodium salt of 2-methyl-6-naphthoic acid was gradually precipitated and was collected; it yielded the acid, m. p. 230°, on acidification. The 2 : 8-ketone was similarly oxidised; the sodium salt of the acid was more soluble in this case and the acid was precipitated on saturation of the solution with sulphur dioxide; m. p. 147—148° after crystallisation from much water containing a little alcohol.

Reduction of the Isomeric Ketones.—4 G. of the ketone in a little alcohol were boiled with amalgamated zinc (10 g.), 7·5 c.c. of water and 17·5 c.c. of hydrochloric acid, more of the last being added at intervals. After 24 hours, the mixture was extracted with ether, and the dried solution distilled. The liquid ketone gave under these conditions 2·5 g. of 2-methyl-8-ethylnaphthalene, which was identified by means of the picrate, m. p. 106°, and the styphnate, m. p. 143—144° (Brunner and Grof, *loc. cit.*); it also gave a trinitrotoluene *derivative*, canary-yellow needles from alcohol, m. p. 77—78° (Found : C, 60·7; H, 4·7. $C_{13}H_{14},C_7H_5O_6N_3$ requires C, 60·4; H, 4·8%), and a *s*-trinitrobenzene *derivative*, slightly paler needles from alcohol, m. p. 127—128° (Found : C, 59·7; H, 4·4. $C_{13}H_{14},C_6H_3O_6N_3$ requires C, 59·5; H, 4·5%).

The solid ketone similarly yielded 2-*methyl*-6-*ethylnaphthalene*, which crystallised from methyl alcohol in plates, m. p. 44—45° (Found : C, 91·6; H, 8·2. $C_{13}H_{14}$ requires C, 91·7; H, 8·3%); an attempt to prepare the hydrocarbon by treating the semicarbazone of the 2 : 6-ketone with sodium in benzyl alcohol at 180—190° (compare Ruzicka and Goldberg, *Helv. Chim. Acta*, 1935, **18**, 672) was unsuccessful. The derivatives of this hydrocarbon were more soluble than those of the 2 : 8-isomeride; the *picrate* formed orange needles from alcohol, m. p. 109° (Found : C, 57·0; H, 4·1. $C_{13}H_{14},C_6H_3O_7N_3$ requires C, 57·1; H, 4·3%); the *styphnate*, deep yellow needles, m. p. 119° (Found : C, 55·2; H, 4·0. $C_{13}H_{14},C_6H_3O_8N_3$ requires C, 55·0; H, 4·1%); the *s*-trinitrobenzene *derivative*, yellow needles, m. p. 116—117° (Found : C, 59·5; H, 4·5. $C_{13}H_{14},C_6H_3O_6N_3$ requires C, 59·5; H, 4·5%); the trinitrotoluene *derivative*, yellow needles, m. p. 62° (Found : C, 60·7; H, 5·0. $C_{13}H_{14},C_7H_5O_6N_3$ requires C, 60·4; H, 4·8%).

Condensation of 2-*Methylnaphthalene with Acetyl Chloride in Carbon Disulphide*.—This was carried out exactly as described by Dziewoński and Brand (*loc. cit.*), 11·5 g. of mixed ketones being obtained from 25 g. of hydrocarbon; the mixture did not solidify and was converted into the semicarbazones, from which the 2 : 6-derivative, m. p. 237°, and the 2 : 8-derivative, m. p. 181°, could be isolated, the 2 : 6-compound greatly predominating. As a preparative method, that described above is to be preferred.

2-*Methyl*-6-*propionaphthone*.—Haworth and Bolam's preparation was repeated, the modified method of working up given on p. 793 being used; 13 g. of ketone were obtained from 15 g. of 2-methylnaphthalene. The solid ketone was recrystallised from petroleum (b. p. 40—60°) and had the correct m. p. (61°). The mother-liquor was evaporated, and the ketone converted into the *semicarbazone*, which was very sparingly soluble, forming small plates from alcohol, m. p. 224—225° (Found : N, 16·4. $C_{15}H_{17}ON_3$ requires N, 16·5%); no other semicarbazone could be isolated from the mother-liquors, although some indications of the existence of a second substance were obtained. The amount must in any case have been very small.

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