

154. *The Structure of Aromatic Compounds. Part III. The Action of Acetyl Chloride on α - and β -Naphthylmethylmagnesium Halides.*

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α -Naphthylmethylmagnesium chloride reacts with acetyl chloride to give 1 : 3-*di- α -naphthyl-2-methylpropylene*, the structure of which was established by ozonolysis. The isomeric hydrocarbon derived from β -naphthylmethylmagnesium chloride probably has an analogous structure.

CERTAIN reagents with benzylmagnesium chloride and cinnamyl chloride give unexpected products due to molecular rearrangement (Tiffeneau and Delange, *Compt. rend.*, 1903, **137**, 573; Gilman and Harris, *J. Amer. Chem. Soc.*, 1927, **49**, 1825; Gilman and Kirkby, *ibid.*, 1932, **54**, 345; Austin and Johnston, *ibid.*, p. 647; Coleman and Forrester, *ibid.*, 1936, **58**, 27; Young, Ballou, and Nozaki, *ibid.*, 1939, **61**, 12). Compounds containing the fragment $C_6H_5\cdot CH_2\cdot MgCl$ may therefore be expected under certain conditions to undergo rearrangement. The observation that α -naphthylmethylmagnesium chloride gives "abnormal" products accordingly affords evidence that the $\alpha\beta$ -linkage possesses decided double-bond

character. In continuation of the work on the fine structure of naphthalene (McLeish and Campbell, J., 1937, 1103) it was of interest to study the interaction of α - and β -naphthylmethylmagnesium halides with acetyl chloride.

We found that α -naphthylmethylmagnesium chloride reacts with acetyl chloride to give 1 : 3-di- α -naphthyl-2-methylpropylene, $C_{10}H_7 \cdot CH : CMe \cdot CH_2 \cdot C_{10}H_7$, the structure of which was established by ozonolysis, α -naphthoic acid and α -naphthylacetone being produced. The isomeric hydrocarbon derived from β -naphthylmethylmagnesium chloride probably has an analogous structure. These products are doubtless formed from intermediate carbinols. In neither case were ketonic compounds due to rearrangement detected.

Analogous results were obtained by the dehydration of dibenzylmethylcarbinol : the product was 1 : 3-diphenyl-2-methylpropylene, since oxidation with chromic acid gave benzyl methyl ketone. Sabatier and Murat (*Compt. rend.*, 1913, **156**, 1430) studied the dehydration of dibenzylmethylcarbinol, but did not analyse the carbinol or the hydrocarbon and made no attempt to determine the structure of the latter.

EXPERIMENTAL.

M. p.'s were determined in Kofler's apparatus (*Mikrochem.*, 1934, **15**, 242), and analyses were done by Dr. Weiler (Oxford) and Mr. W. Brown (Edinburgh).

Preliminary experiments showed that it is necessary to obtain pure β -naphthylmethyl halide in order to prepare the Grignard reagent. It was difficult to obtain a good yield of bromo-compound by the bromination of β -methyl-naphthalene (Schulze, *Ber.*, 1884, **17**, 1527), and in most of the experiments β -naphthylmethyl chloride prepared from the carbinol was used.

β -Naphthylcarbinol.— β -Naphthaldehyde was prepared from β -naphthonitrile by Stephen's method (Robinson and Fulton, J., 1939, 200). In preparing the stannous chloride it was found advisable to use the method of Stephen (J., 1930, 2786) and recrystallise the product from glacial acetic acid, the crystalline form obtained dissolving readily in ether. The naphthaldehyde invariably contained a considerable quantity of unchanged nitrile. Reduction of the aldehyde with a palladium-barium sulphate catalyst yielded β -methyl-naphthalene (m. p. 36°; picrate, m. p. 118°). Reduction of the aldehyde (6.2 g.) in ethyl alcohol (50 c.c.) with Adams's platinum catalyst and ferric chloride as promoter (0.5 c.c. of 0.1M-ferric chloride) gave the carbinol, which formed colourless needles from light petroleum (b. p. 60—80°), m. p. 80° (lit., 80°); yield, 80%. When excess of the promoter was used, further reduction occurred.

Attempts were made to prepare the carbinol by other methods. The method of Byron West (*J. Amer. Chem. Soc.*, 1920, **42**, 1662) gave only a 27% yield from β -naphthoamide. Ziegler's method (*Ber.*, 1921, **54**, 737) was unsuccessful, although this worker obtained the corresponding carbinol from α -bromonaphthalene in good yield. A mixture of magnesium turnings (1 g.), dry ether (10 c.c.), and ethyl iodide (0.3 g.) was stirred and boiled, and β -iodonaphthalene (10 g.) in ether (40 c.c.) added. When the reaction had moderated, the solution was cooled in a freezing mixture, and formaldehyde, generated from trioxymethylene, led in. The black mass obtained was treated with water and extracted with ether, which on evaporation yielded a brown solid (4.5 g.). This after crystallisation from methyl alcohol (twice) was found to be $\beta\beta'$ -dinaphthyl, m. p. 185° (lit., 188°); picrate, m. p. 184° (lit., 184°).

β -Naphthylmethyl Chloride.— β -Naphthylcarbinol (12 g.) was dissolved in dry toluene (50 c.c.), thionyl chloride (25 c.c.) gradually added, and the mixture boiled under reflux for 3 hours. After removal of the toluene and the excess of thionyl chloride by distillation the residue was distilled in a vacuum, the fraction, b. p. 170°/20 mm., being collected; m. p. 47° (lit., 48°).

β -Naphthylmethyl Bromide.—The method of Schulze (*loc. cit.*) had to be modified. β -Methyl-naphthalene was brominated at 240—260° in a quartz flask exposed to radiation from a mercury vapour lamp. If no such radiation were used, a glassy black solid was obtained from which no β -naphthylmethyl bromide could be isolated. In a series of experiments the yield of the bromide never exceeded 22%, a large amount of the methyl-naphthalene being recovered. The compound was best purified by distillation in a vacuum (b. p. 214°/100 mm.) and subsequent crystallisation from ethyl alcohol; m. p. 54° (lit., 56°).

β -Naphthylmethylmagnesium Halide and Acetyl Chloride.—The formation of the Grignard reagent was extremely capricious, and occurred in only three cases (one of the bromide and two of the chloride). β -Naphthylmethyl bromide (9 g.) in dry ether (40 c.c.) was added to a mixture of magnesium turnings (1 g.) in ether (40 c.c.). Two drops of ethyl iodide were added to start the reaction, which became vigorous and was moderated by cooling. The mixture was then

boiled for $\frac{1}{4}$ hour, and after being cooled in carbon dioxide-ether was filtered through glass wool into a cooled solution of acetyl chloride (5 g.) in ether. The white precipitate which immediately formed was decomposed with ice-cold dilute hydrochloric acid, and the solution extracted with ether, which on evaporation yielded 1 : 3-*di*- β -*naphthyl*-2-*methylpropylene* (4.5 g.), m. p. 184—185° after recrystallisation from glacial acetic acid (Found : C, 93.6; H, 6.5. $C_{24}H_{20}$ requires C, 93.5; H, 6.5%). It did not decolorise alkaline permanganate or bromine in carbon tetrachloride. Compounds containing a double bond, however, frequently do not react with these reagents, especially when one of the carbon atoms attached to the double bond holds no hydrogen (Gilman's "Organic Chemistry," vol. 1, p. 546).

α -Naphthylmethylmagnesium Chloride and Acetyl Chloride.— α -Naphthylmethyl chloride was prepared by the method of Coles and Dodds (*J. Amer. Chem. Soc.*, 1938, **60**, 853); b. p. 164—167°/16 mm. (lit., 158—159°/14 mm.). When the mixture of naphthalene, formaldehyde, and concentrated hydrochloric acid was kept at room temperature for 48 hours before the addition of sulphuric acid, a better yield was obtained and less unchanged naphthalene remained. The preparation of the Grignard reagent and the addition of acetyl chloride to it were carried out as described above, except that the mixture was finally heated under reflux for 4 hours. Evaporation of the ether yielded an oil, which was purified by dissolving it in light petroleum (b. p. 40—60°) and immersing the solution in carbon dioxide-ether. An impurity separated, and the clear solution was decanted and on evaporation gave a white solid, m. p. 162—163°, in very poor yield (Found : C, 93.4; H, 6.6. $C_{24}H_{20}$ requires C, 93.5; H, 6.5%). Ozonisation of the hydrocarbon in carbon tetrachloride solution gave α -naphthoic acid (m. p. and mixed m. p. with an authentic sample) and an oil which on the usual treatment with 2 : 4-dinitrophenylhydrazine gave a 2 : 4-dinitrophenylhydrazone which was shown to be identical with that of α -naphthylacetone (see below); m. p. 174—176° after purification by sublimation. No formaldehyde was detected. The hydrocarbon is therefore 1 : 3-*di*- α -*naphthyl*-2-*methylpropylene*.

α -Naphthylacetone-2 : 4-dinitrophenylhydrazone.—A mixture of α -naphthylacetic acid and barium acetate was intimately mixed and distilled. The oily solid formed readily yielded a 2 : 4-dinitrophenylhydrazone, which crystallised from tetralin in orange plates, m. p. 174—176° (Found : N, 15.1. $C_{19}H_{16}O_4N_4$ requires N, 15.4%).

Dibenzylmethylcarbinol.—Methyl iodide (29 g.) was converted into the Grignard reagent and cooled to -5° . Dibenzyl ketone (21 g.) in ether was then slowly added, and the product isolated in the usual manner. The oil (13 g.) obtained was dissolved in light petroleum (b. p. 40—60°), and the solution cooled in carbon dioxide-ether. Impurity separated and the clear solution was decanted. Evaporation yielded a solid. The process was repeated several times and *dibenzylmethylcarbinol* was finally obtained as a white crystalline mass (8 g.), m. p. 26—27° (Found : C, 84.9; H, 8.0. $C_{16}H_{18}O$ requires C, 85.0; H, 7.9%).

Dehydration of Dibenzylmethylcarbinol.—The carbinol (3 g.) was added to phthalic anhydride (5 g.) and heated to 160°, and phosphoric oxide (1 g.) added in small portions during 1 hour. The mixture was heated for a further $\frac{1}{2}$ hour, cooled, boiled with sodium hydroxide solution, and then extracted with ether. From the extract an oil was obtained which distilled at 180°/15 mm. (Sabatier and Murat, *loc. cit.*, record 304°/760 mm.) (Found : C, 92.3; H, 7.7. $C_{16}H_{16}$ requires C, 92.3; H, 7.7%).

The unsaturated compound (2 g.) was suspended in glacial acetic acid (30 c.c.), and chromic acid (4 g.) in water (8 c.c.) added. The mixture was gently heated for 1 minute, and the brisk reaction which ensued was moderated by cooling. After $\frac{1}{2}$ hour the mixture was distilled in steam, and the distillate extracted with ether. The ethereal solution was shaken with caustic soda and evaporated. The oil obtained yielded a 2 : 4-dinitrophenylhydrazone, m. p. 147—149°, identical with that obtained from benzyl methyl ketone (mixed m. p.). The hydrocarbon is therefore 1 : 3-*diphenyl*-2-*methylpropylene*.

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