

**160. The Action of Methanol on Naphthalene in the Presence of Catalysts of the Alumina-Silica Type. Formation of 2-Methylnaphthalene.**

By N. M. CULLINANE and S. J. CHARD.

A new method has been devised for the preparation in satisfactory yield of 2-methylnaphthalene by causing methanol and naphthalene to react in contact with aluminosilicate catalysts in the vapour phase. The 1-methyl isomer does not appear to be present among the products. In fact, when this compound is passed over the catalyst it is converted into 2-methylnaphthalene, smaller quantities of naphthalene and dimethylnaphthalenes being also produced.

THIS work was undertaken in order to ascertain if methanol and naphthalene could be induced to react in the vapour phase in contact with certain catalysts to yield 2-methylnaphthalene, which is the initial material for the synthesis of the anti-hæmorrhagic vitamin K, and of which the oxidation product, 2-methyl-1 : 4-naphthaquinone, likewise possesses considerable activity; the hydrocarbon itself is also reported to be slightly active (Tishler, Fieser, and Sampson, *J. Amer. Chem. Soc.*, 1940, **62**, 1881).

The catalysts employed included activated alumina and aluminosilicates. In addition to recovered naphthalene, 2-methylnaphthalene was obtained together with smaller quantities of dimethylnaphthalenes.

The silicates were found to be much more effective catalysts than alumina, contrary to what had been previously observed in the reaction between methanol and phenol (Cullinane and Chard, *J.*, 1945, 821). Langside stone, British Guiana bauxite, and Indian bauxite were also much less efficient.

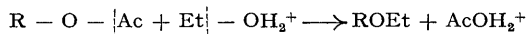
Some methylation of the benzene used to effect solution of the reactants was also noted, but this was not further studied as it has already been investigated elsewhere (Given and Hammick, *J.*, 1947, 928).

The catalysts were found to lose their activity rapidly, but their effectiveness was readily restored by passing a current of oxygen or air over them at a suitable temperature.

Substitution in the naphthalene molecule appears to occur initially at the 1-position, this tendency in alkylation being noted by Roux (*Ann. Chim. Phys.*, 1887, **12**, 289), Tzukervanik and Terentieva (*J. Gen. Chem. Russia*, 1937, **7**, 637), and Mayer and Schiffner (*Ber.*, 1934, **67**, 67). However, under the conditions described in the present work no 1-substitution product was isolated.

When 1-methylnaphthalene was passed over the alumina-silica catalyst at 450°, the initial material was completely transformed, yielding 2-methylnaphthalene as main product, some naphthalene with small amounts of dimethylnaphthalenes being also formed.†

\* It might be suggested that ethanolysis involves the attack of the neutral ester molecule by an ethoxonium ion, with acyl-oxygen fission in the former and alkyl-oxygen fission in the latter :



Since the concentration of ethoxonium ions  $\text{EtOH}_2^+$  is very much smaller than that of hydroxonium ions  $\text{H}_3\text{O}^+$  under the conditions chosen (Part II, *loc. cit.*), the amount of ethanolysis as compared with that of hydrolysis would then be very small. In any case, this mechanism is eliminated since it would also involve subsequent re-esterification of the acetic acid by the solvent, whereas, as was shown earlier, hydrolysis and ethanolysis occur simultaneously.

† A discussion of the theoretical problems involved in these reactions is being published elsewhere.

## EXPERIMENTAL.

A considerable number of experiments were carried out at varying temperatures and with different proportions of the reactants. Below 350° the amount of methylation was very small; also much better yields of 2-methylnaphthalene were obtained with the silicates than with type C alumina. In all cases a preliminary run-through was performed when fresh catalysts were employed, the products being discarded. Much ammonia was evolved, especially with the silicates, and the products were not examined until the evolution of the gas had ceased. Some typical experiments are described below.

All the catalysts were supplied by Messrs. Peter Spence and Sons, Ltd., and were of 4/8-inch mesh.

The apparatus was similar to that already described (Cullinane and Chard, *loc. cit.*), except that the mixture was dropped directly on the catalyst through an ordinary "Pyrex" glass tube; there was thus less tendency to clogging. The recovered benzene and naphthalene were used again in later experiments.

**Reaction with Alumina-Silica (1 : 2).**—Naphthalene (100 g.) and methanol (commercial 98%; 77 g.; 3 mols.), dissolved in benzene (200 c.c.), were dropped at a uniform rate on the catalyst (about 300 g.) at 450° during 6½ hours. The products consisted of an aqueous (49 g.) and a benzene layer (248 g.), which were separated and the latter partly distilled, yielding benzene (103 g.) and its homologues (b. p. 103—136°; 24 g.). The rest of the product was cooled to 30—40° and the resulting oily solid well pressed on a filter and washed with the recovered benzene (50 c.c.), the residue (32 g.) being composed almost entirely of naphthalene. After removal of benzene from the filtrate, the remaining oil was fractionally distilled with a column (Cullinane and Chard, *loc. cit.*), yielding (a) naphthalene (28 g.), b. p. 218°, picrate, m. p. 151°; (b) 2-methylnaphthalene (24.5 g.; 52% yield, based on the naphthalene consumed), b. p. 241°, m. p. 34°, picrate, orange needles, m. p. 115°, compound with *s*-trinitrobenzene, bright yellow needles, m. p. 123° (the identity of these compounds was confirmed by admixture with authentic specimens); (c) dimethylnaphthalenes (10.5 g.), b. p. 256—265°, which were not further separated (Found: *M*, 152. Calc. for C<sub>12</sub>H<sub>12</sub>: *M*, 156); (d) a brownish residue, b. p. > 265° (3 g.), of higher methylated products. No 1-methylnaphthalene was isolated.

Similar results were obtained with alumina-silica (1 : 4), but much smaller yields were obtained (and more naphthalene recovered) when the catalysts used were (a) Langside stone, (b) British Guiana bauxite, and (c) Indian bauxite.

**Action of Alumina-Silica (1 : 2) on 1-Methylnaphthalene.**—This compound was obtained from Messrs. Powell Duffryn, Ltd., and redistilled; it had b. p. 245°, picrate, lemon-yellow needles, m. p. 140°, compound with *s*-trinitrobenzene, bright yellow needles, m. p. 152.5° (Found: N, 11.8. Calc. for C<sub>17</sub>H<sub>18</sub>O<sub>6</sub>N<sub>3</sub>: N, 11.8%). Analysis by Drs. Weiler and Strauss, Oxford. Triandaf (*Ann. Sci. Univ. Jassy*, 1940, 26, 155) gives m. p. 147°. 1-Methylnaphthalene (40 g.) was dropped on the catalyst (about 300 g.) at 450° during 100 minutes. It was noticed that some solid mixed with liquid formed in the condenser. The product (31 g.) was fractionally distilled in the usual way yielding naphthalene (7 g.), 2-methylnaphthalene (18 g.), and dimethylnaphthalene (3 g.), all identified as already described.

**Gaseous products.** A sample of the gases formed in the above experiment was found to contain in addition to nitrogen: methane (with some ethane) 31.5%, hydrogen 9.1%, oxygen 7.6%, carbon dioxide 3.0%, carbon monoxide 2.4%, ethylene 2.0%.

**Reactivation of the Catalysts.**—After being in use in 3 or 4 operations, the alumina-silicas were found to have lost much of their activity, with considerable deposition of carbon. Their effectiveness was restored by passing a fairly rapid current of oxygen or air over them at 450° for 12 hours, by which time nearly all the carbon had been removed. For instance, the alumina-silica (1 : 2) catalyst treated in this way furnished, from the same weights of materials as above, 2-methylnaphthalene [29 g.; 48% yield calculated on the naphthalene consumed (64 g.)], dimethylnaphthalene (11 g.), and higher homologues (*ca.* 2 g.).

It was observed that mixtures of (a) the picrates and (b) the *s*-trinitrobenzene additive compounds of naphthalene and 2-methylnaphthalene all melted at intermediate temperatures between the m. p.s of the pure molecular compounds, and similar results were obtained with mixtures of the *s*-trinitrobenzene addition compounds of 1- and 2-methylnaphthalene.

**System Naphthalene-2-Methylnaphthalene.**—A temperature-concentration diagram for mixtures of these substances was plotted, thaw points (*T*<sub>1</sub>) and melting temperatures (*T*<sub>2</sub>) being determined (compare Cullinane and Plummer, *J.*, 1938, 63). The results are shown graphically in the figure, and the complete data are tabulated below:

|                       |       |       |       |       |       |       |       |       |       |       |       |
|-----------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Naphthalene, mols. %  | 0     | 8.52  | 11.49 | 16.02 | 19.98 | 26.78 | 33.65 | 63.16 | 90.2  | 95.54 | 100   |
| <i>T</i> <sub>1</sub> | 33.0° | 26.8° | 27.0° | 27.0° | 26.8° | 26.5° | 26.6° | 26.8° | 27.0° | 27.0° | 81.0° |
| <i>T</i> <sub>2</sub> | 34.0° | 31.6° | 30.6° | 30.1° | 28.4° | 29.0° | 37.9° | 60.0° | 74.8° | 78.2° | 80.0° |

The curve exhibits a eutectic at 27°, corresponding to about 25 mols. % of naphthalene.

The authors are greatly indebted to Messrs. Peter Spence and Sons, Ltd., for the loan of apparatus and for the gift of chemicals, and to Dr. J. Chatt for his continued interest.

