

**347.** *Some Catalysed Gas-phase Reactions of Aromatic Hydrocarbons.*  
*Part III. The Methylation of Naphthalene by Means of Dimethyl Ether.*

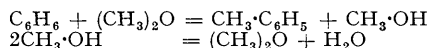
By G. P. ARMSTRONG, (MISS) D. H. GROVE, D. LL. HAMMICK, and H. W. THOMPSON.

Naphthalene has been methylated by the action of dimethyl ether on the hydrocarbon in the presence of bauxite. Flow methods at 450° gave yields of about 2% of monomethylnaphthalenes; at about 200—300° and 50—70 atmospheres in an autoclave, yields of monomethylnaphthalenes of about 7% were obtained, from a product containing 30% of methylated naphthalene. The ratio of 1-methyl- to 2-methyl-naphthalene was about 4 : 1.

Pure 1-methylnaphthalene passed over bauxite at 450° gave a mixture (*ca.* 2 : 1) of 1-methyl- and 2-methyl-naphthalene.

Extinction coefficients for naphthalene and the two monomethylnaphthalenes were determined at three wave-lengths in the ultra-violet and used for the identification and determination of methylated products.

It has been shown in Part I (*J.*, 1947, 928) that at 450° in the presence of catalysts of aluminium silicate type dimethyl ether interacts with benzene in accordance with the scheme :



It was pointed out that the small quantities of toluene obtained when methyl alcohol is substituted for dimethyl ether might have been derived from the interaction of the latter which is formed extremely rapidly from methyl alcohol in the presence of the type of catalyst employed. It was in any case to be expected that naphthalene could be methylated by dimethyl ether under similar conditions, and this has in fact proved to be the case.

Naphthalene vapour and dimethyl ether, together with a carrier gas (nitrogen), were led over bauxite at 450° with a contact time of 15—30 seconds. The condensates from a number of runs were collected, and the methylated products separated by fractional distillation. A fraction [sample F(2)β] containing 70% of monomethylnaphthalenes was obtained, corresponding to a minimum yield of 2—3% on the naphthalene. The presence of both monomethyl isomers was established from their ultra-violet absorption spectra, the ratio of 1-methyl to 2-methyl being found to be very nearly 2 : 1. Analysis of the highest-boiling fractions and their picrates indicated the presence of polymethylated naphthalenes.

Interaction of dimethyl ether and naphthalene in an autoclave at 250—300° in the presence of bauxite at pressures between 50 and 70 atmospheres gave much better yields of methylated product; estimated yields of mono- and di-methylnaphthalenes (in a representative run) were 7.5% and 3.5% respectively out of a total yield of 30% of methylated product.

In one run optically pure 1-methylnaphthalene was passed over the bauxite catalyst; the

product was shown spectroscopically to contain 2-methylnaphthalene, the ratio of the isomers being about 4 : 1 of 1-methyl to 2-methyl.

EXPERIMENTAL.

*Materials.—Dimethyl ether.* The ether was prepared by catalytic dehydrogenation of methyl alcohol over bauxite at 375°. Water and unchanged alcohol were condensed, and the ether absorbed in concentrated sulphuric acid, from which it was liberated by running the solution into water. The ether was passed successively through a double-surface condenser, an ice-cooled trap, and a column of anhydrous calcium chloride. It was finally condensed in an alcohol-solid carbon dioxide freezing mixture and stored in an iron cylinder; b. p. — 26° to — 27°.

*Naphthalene.* This was twice sublimed and recrystallised from ethyl alcohol, m. p. 80.5°.

*1-Methylnaphthalene.* A sample supplied as "pure" boiled at 233—234°/756 mm. (corr.). It was twice redistilled, and recrystallised by cooling a solution in ethyl alcohol in an alcohol-solid carbon dioxide freezing mixture to about — 70°. The crystals that separated were sucked into and pressed free from liquid on a sintered glass filter immersed in the solution. The solid was removed and allowed to melt. After two recrystallisations the liquid 1-methylnaphthalene was shaken with successive amounts of water, calcium chloride solution, and anhydrous calcium chloride to remove any remaining alcohol. The product was finally distilled [b. p. 242.5—243.0/763 mm. (corr.)]; its ultra-violet absorption spectrum showed no sign of naphthalene or of 2-methylnaphthalene.

*2-Methylnaphthalene.* A "pure" sample was recrystallised thrice from alcohol (to constant m. p.); m. p. 34.4° (corr.).

The monomethylnaphthalenes were required pure as standards in the spectroscopic detection and determination of the isomers in the products of methylation.

*Catalyst.* The catalyst used was a specimen of bauxite, ground and sieved to 2/5 mesh. Before use it was heated to 500° in a stream of nitrogen for 5 hours (Found : SiO<sub>2</sub>, 30.9; Al<sub>2</sub>O<sub>3</sub>, 35.6; Fe<sub>2</sub>O<sub>3</sub>, 6.9; TiO<sub>2</sub>, 4.3; loss on ignition, 22.7%).

After each run (1—2 hours) the catalyst was always found to be "carbonised"; this is almost certainly due to decomposition of dimethyl ether, as naphthalene could be passed over the catalyst at 450° and recovered practically unchanged in m. p. The carbonised catalyst was reactivated by heating it in a current of oxygen.

*Apparatus.*—A horizontal "Pyrex" reaction tube was used, 35 mm. in diameter and 85 cm. long, the average charge of catalyst being 450 g. Free space was about 28 c.c. as measured by water displacement. The tube was heated electrically, temperature being measured by means of thermocouples. The nitrogen and dimethyl ether were supplied from cylinders, and their rate of flow measured by flow-meters. The naphthalene was vapourised electrically from a tared "Pyrex" test tube, the mixed vapours being preheated to 300° before entering the catalyst tube, which was kept at ca. 450—460°. Molecular ratios of ether to naphthalene lay between 1 : 1 and 1 : 2. The crude product was separated from water, broken up, and dried over concentrated sulphuric acid. Experiments were also carried out under pressure in a gas-heated steel autoclave at 250—300° and about 50—60 atmospheres, under which conditions the reagents were partially liquid.

*Separation and Analysis of Products.*—Owing to the material collected from both flow and autoclave experiments being solid and the yields of methylated products being comparatively small, rapid analysis was not possible. For this reason no attempt was made in the present series of experiments to vary temperatures, rates, and reagent ratios in a search for optimum conditions; conditions were chosen as nearly analogous as possible to those found most suitable in the methylation of benzene (Given and Hammick, *loc. cit.*). The crude products from 10 runs in the flow apparatus and from the autoclave melted 4—5° below the m. p. of naphthalene, which was removed by distillation through a fractionating column\* delivering into a wide upright condenser and receiver.

As an example of the method of separation and determination we quote the following results obtained with the autoclave :

Catalyst (bauxite).	Naphthalene. (x)	Dimethyl ether. (y)	Mol. ratio. (x : y)	Temp.	Press.	Time.
100 G.	120 G.	50 G.	1 : 1.2	270—300°	53 atm.	4.5 hrs.

116 G. of oily solid product were recovered, and some naphthalene removed by ordinary distillation. The residue was fractionated and 13 fractions collected between 228° and 315°, totalling 44.2 g.; residual tar weighed 8.9 g. The lower fractions were combined in batches and refractionated; a further 17 g. boiling below 230° were rejected from these fractions. The following fractions were obtained and analysed :

Fraction.	B. p.	Wt., g.	Found, %.		Calc, %.		
			C.	H.	C.	H.	
I	235—242°	4.7	—	—	—	—	
II	244—249	6.0	93.01	7.29	—	—	
III	250—255	2.0	92.76	7.28	92.9	7.1	(1)
					(monomethyl)		
IV	257—262	2.6	92.3	7.92	92.3	7.7	(2)
V	262—266	0.6			(dimethyl)		
VI	269—278	1.0	91.5	7.99	91.77	8.23	(3)
VII	279—280	1.4			(trimethyl)		

\* The packing of the column consisted of a glass rod carrying discs, with lips round the edges to prevent hold-up of the refluxing liquid. The column was heavily lagged with asbestos and was heated by a coil wound in the the outer layers. Flow of current was adjusted in the coil during distillation so as to keep the column temperature 20° below the boiling point of the fraction to be distilled.

Total weight of methylated product was about 36 g., representing 31% on the initial charge of naphthalene, minimum yields of methyl-naphthalenes being: monomethyl-naphthalenes, 7.5%, dimethyl-naphthalenes, 3.5%, trimethyl-naphthalenes, 2.0%. From the high-boiling residue a picrate, m. p. 128—130°, was obtained, corresponding to a methylated naphthalene between penta- and hexa-methyl [Found: C, 59.46; H, 5.07. Calc. for  $C_{21}H_{21}O_7N_3$  (pentamethyl): C, 59.0; H, 4.92. Calc. for  $C_{22}H_{23}O_7N_3$  (hexamethyl): C, 59.9; H, 5.22%].

*Spectroscopic Examination and Analysis.*—In order to analyse the products, and in particular the fraction containing monomethyl-naphthalenes, differences in the ultra-violet absorption spectra of naphthalene, and 1- and 2-methyl-naphthalenes, were used. The spectra of these substances have been measured previously, the most relevant determinations being those of Morton and de Gouveia (*J.*, 1934, 916), using solutions in hexane. Since there was some divergence in the measured extinction coefficients, probably because of differences in instrumental resolving power, these were redetermined using a Spekker photometer with Hilger E 315 spectrograph. Since for each of the substances the extinction coefficient alters very steeply with wave-length, it was necessary to use a series of concentrations in hexane in each case.

The absorption of these substances extends from about 3200 Å. towards shorter wave-lengths. The bands in the region 3200—2950 Å. are the most characteristic and suitable for analysis of mixtures since at shorter wave-lengths there are broader and severely overlapping bands. The most convenient characteristic bands are as follows: naphthalene 3110 Å., 1-methyl-naphthalene 3140 Å., 2-methyl-naphthalene 3190 Å. The extinction coefficients at each of these wave-lengths were determined for the pure substances with the following results.

	3190 Å.	3140 Å.	3110 Å.
Naphthalene .....	18	60	260
1-Methyl-naphthalene.....	75	330	230
2-Methyl-naphthalene.....	540	175	260

Determination of the optical densities of a mixture at each of the 3 wave-lengths, followed by solution of the 3 linear equations, will then give the required analysis. It was known, however, that the samples to be analysed would contain only small percentages of naphthalene, and since high accuracy was not required a simpler method was devised for the analysis. A curve was constructed showing the ratio of optical densities at 3190/3140 Å. as a function of percentage of 2-methyl-naphthalene in a mixture with the 1-methyl isomer. For pure 1-methyl-naphthalene this ratio is 0.23, and for pure 2-methyl-naphthalene it is 3.09. A series of test mixtures of different composition showed that this calibration chart was satisfactory. The total amounts of the individual isomers could then be calculated from the optical density at either wave-length. Inexact agreement implies the possible presence of other compounds.

The dimethyl-naphthalenes have absorption bands which lie close to those of the monomethyl derivatives, and if much of these were present the whole analysis would be invalid. It was known, however, from the fractionation already described that this would not occur.

The results of 3 typical analyses are given.

I. Sample G (1) $\alpha$ ; collected after passage of 1-methyl-naphthalene over the catalyst at 450°. This was found to contain 1- and 2-methyl isomers and no detectable naphthalene or other methylated product. The ratio of optical densities at 3190/3140 was 0.575, which corresponds to about 20% of 2-methyl-naphthalene.

II. Sample F(2) $\alpha$ ; concentrate from a number of flow reactions. The ratio of optical densities was 0.76, corresponding to 30% of 2-methyl-naphthalene; only about 70% of the sample would be attributed to monomethyl-naphthalenes.

III. Sample F(2) $\beta$ ; similar concentrate to F(2) $\alpha$ . This contained about 30% of the 2-isomer, but the optical densities at a series of wave-lengths suggested that small amounts of the dimethyl-naphthalenes were also present.

THE DYSON PERRINS LABORATORY, UNIVERSITY OF OXFORD.  
THE PHYSICAL CHEMISTRY LABORATORY, UNIVERSITY OF OXFORD.

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