

757. Alkylation of the Aromatic Nucleus. Part XIV.<sup>1</sup>  
Naphthalene

By M. Z. A. BADR and W. J. HICKINBOTTOM

The proportion of  $\alpha$ - and  $\beta$ -isomers has been determined in the products of the thermal decomposition, in naphthalene, of sulphonic esters of benzyl and some substituted benzyl alcohols and also of cyclopentanol, cyclohexanol, and cycloheptanol. The isomer ratio from any one sulphonic ester is of the same order as that from alkylation by using the alcohol and boron trifluoride, sulphuric acid, or phosphoric acid as condensing agents. Pentan-2-ol and pentan-3-ol give the same distribution of 2- and 3- $\alpha$ - and - $\beta$ -naphthylpentanes whatever method of alkylation is used; similarly for hexan-2-ol and hexan-3-ol. From pentan-1-ol, and also from hexan-1-ol, a notable proportion of the corresponding n-alkylnaphthalene is formed by the thermal decomposition of the sulphonic ester, or by reaction with the alcohol and boron trifluoride.

THE earlier literature on the alkylation of naphthalene refers mostly to qualitative studies, and is often contradictory and misleading. Price and Ciskowski<sup>2</sup> report that the  $\beta$ -isomer is formed when naphthalene is alkylated by propan-2-ol or t-butyl alcohol, or with cyclohexanol or cyclohexene by using boron trifluoride; benzyl alcohol gave almost entirely the  $\alpha$ -isomer. Romadane,<sup>3</sup> also using boron trifluoride as the condensing agent, reports that both  $\alpha$ - and  $\beta$ -isomers are formed from n-propyl, n-butyl, n-pentyl, and n-hexyl alcohols, whilst isobutyl and isopentyl alcohols gave both  $\alpha$ - and  $\beta$ -isomers with rearrangement of the alkyl group. Other observations are the formation of  $\alpha$ -n-butyl-naphthalene

TABLE 1  
Percentage of isomers in product from benzylation of naphthalene using  $\text{XC}_6\text{H}_4\cdot\text{CH}_2\text{OH}$

	H		<i>p</i> -Me		<i>p</i> -Cl		<i>p</i> -NO <sub>2</sub>	
	$\alpha$	$\beta$	$\alpha$	$\beta$	$\alpha$	$\beta$	$\alpha$	$\beta$
Toluene- <i>p</i> -sulphonate .....	77	23	81	19	71	29	35	65
Alcohol-BF <sub>3</sub> .....	74	26	72	28	62	38*	34	66
Alcohol-H <sub>2</sub> SO <sub>4</sub> .....	76	24	84	16	72	28*	32	68*
Alcohol-H <sub>3</sub> PO <sub>4</sub> .....	76	24	86	14	75	25	34	66

\* In CS<sub>2</sub>.

TABLE 2  
Percentage of isomers from cycloalkylation of naphthalene

	Cyclopentyl		Cyclohexyl		Cycloheptyl	
	$\alpha$	$\beta$	$\alpha$	$\beta$	$\alpha$	$\beta$
Toluene- <i>p</i> -sulphonate .....	69	31	55	45*	73	27¶
Alcohol-BF <sub>3</sub> .....	77	23	64	36†	78	22
Alcohol-H <sub>2</sub> SO <sub>4</sub> .....	78	22	68	32‡	79	21**
Alcohol-H <sub>3</sub> PO <sub>4</sub> .....	79	21	69	31§	78	22††

The values give only the ratio of  $\alpha$ - and  $\beta$ -isomers having an unrearranged cycloalkyl group. No estimate of the ratio of  $\alpha$ - and  $\beta$ -isomers in the rearranged product was possible. The percentage of rearrangement in the alkylation product is given by the following figures: methylcyclopentane: \* 1, † 5, ‡ 2, § 14; methylcyclohexane: ¶ 21, || 20, \*\* 26, †† 60.

from n-butanol and aluminium chloride, whilst the  $\beta$ -isomer is formed from isobutyl and isopentyl alcohols with rearrangement of the alkyl group.<sup>4</sup> Tsukervanik *et al.*<sup>5</sup> report the formation of  $\alpha$ -s-butyl-naphthalene from butan-2-ol and aluminium chloride, whilst the other alcohols give the  $\beta$ -isomer. Some uncertainty also exists about the benzylation of naphthalene. Against the statement that the  $\alpha$ -isomer is the product of the reaction between alcohol, naphthalene, and boron trifluoride, is the report that between 70 and 80%

<sup>1</sup> Part XIII, P. R. Adams and W. J. Hickinbottom, preceding Paper.

<sup>2</sup> C. C. Price and J. M. Ciskowski, *J. Amer. Chem. Soc.*, 1938, **60**, 2499.

<sup>3</sup> I. Romadane, *Zhur. obshchei Khim.*, 1957, **66**, 1833, 1939.

<sup>4</sup> A. E. Pavelkina and I. Terent'eva, *J. Gen. Chem. (U.S.S.R.)*, 1939, **12**, 1422.

<sup>5</sup> I. P. Tsukervanik and I. Terent'eva, *J. Gen. Chem. (U.S.S.R.)*, 1937, **7**, 637.

of the  $\alpha$ -isomer is present in the product from benzyl chloride when aluminium chloride, zinc chloride, ferric chloride, or phosphorus pentoxide are used as condensing agents.<sup>6</sup>

In this Paper, the alkylation of naphthalene by the thermal decomposition of some esters of toluene-*p*-sulphonic acid is compared with alkylations brought about by using the alcohols with boron trifluoride, sulphuric acid, or phosphoric acid as condensing agents. The results of benzylation and cyclohexylation are given in Tables 1 and 2.

No isomerisation of the pure alkyl- and cycloalkyl-naphthalenes has been observed when they are treated with boron trifluoride, sulphuric acid, or phosphoric acid under the conditions of alkylation. Consequently, the values given in Tables 1 and 2 are those for primary substitution. In alkylation by decomposition of cycloalkyl, benzyl, and *p*-methylbenzyl esters of toluene-*p*-sulphonic acid, the values for  $\alpha$ -substitution are somewhat too

TABLE 3  
Isomer distribution in the pentylation of naphthalene

Orientation of naphthyl group	Pentan-1-ol				Pentan-2-ol				Pentan-3-ol			
	(A)	(B) *	(C)	(D) †	(A)	(B) ‡	(C)	(D) §	(A)	(B) ¶	(C)	(D)
1- $\alpha$	6	3	2									
1- $\beta$	4	2	2									
2- $\alpha$	32	24	26	52	47	44	44	50	43	44	43	53
2- $\beta$	36	44	32	20	26	24	20	17	28	23	20	16
3- $\alpha$	11	9	16	19	19	24	27	25	20	24	28	23
3- $\beta$	11	17	12	8	8	8	9	8	9	9	9	8

(A) Decomposition of toluene-*p*-sulphonic ester. (B) Boron trifluoride and the alcohol. (C) Sulphuric acid and the alcohol. (D) Phosphoric acid and the alcohol.

The product also contains (i) *t*-butylnaphthalene: \* 1%, † 8%, ‡ 3%, § 7%, ¶ 4%, || 8%; (ii) *t*-pentylnaphthalene: † 6%, ‡ 2%, § 7%, ¶ 2%, || 5%.

Alkylation by pentan-3-ol with aluminium chloride in carbon disulphide at 46° gave 2- $\alpha$ -, 3%; 2- $\beta$ -, 66%; 3- $\alpha$ -, 22%; 3- $\beta$ -, 9%.

Alkylation by pentan-3-ol with aluminium chloride in carbon disulphide at 7° gave 2- $\alpha$ -, 39%; 2- $\beta$ -, 30%; 3- $\alpha$ -, 19%; 3- $\beta$ -, 12%.

TABLE 4  
Isomer distribution in the hexylation of naphthalene

Oxidation of naphthyl group	Hexan-1-ol				Hexan-2-ol				Hexan-3-ol			
	(A)	(B) <sup>a</sup>	(C) <sup>b</sup>	(D) <sup>c</sup>	(A) <sup>d</sup>	(B) <sup>e</sup>	(C) <sup>f</sup>	(D) <sup>g</sup>	(A)	(B) <sup>h</sup>	(C)	(D) <sup>i</sup>
1- $\alpha$	4	4	4	2								
1- $\beta$	7	2	2	1								
2- $\alpha$	21	27	30	40	41	42	38	45	39	42	40	43
2- $\beta$	38	38	25	22	25	22	18	24	26	21	16	21
3- $\alpha$	12	10	22	24	22	25	31	21	23	26	33	25
3- $\beta$	18	19	17	12	12	11	13	10	12	11	11	11

(A) Decomposition of toluene-*p*-sulphonic ester. (B) Boron trifluoride and the alcohol. (C) Sulphuric acid and the alcohol. (D) Phosphoric acid and the alcohol.

The product contains *t*-butylnaphthylene: <sup>c</sup> 1%, <sup>g</sup> 4%, <sup>h</sup> 2%, <sup>j</sup> 4%; *t*-pentylnaphthalene: <sup>a</sup> 1%, <sup>b</sup> 1%, <sup>c</sup> 4%, <sup>e</sup> 4%, <sup>f</sup> 4%, <sup>g</sup> 10%, <sup>h</sup> 3%, <sup>i</sup> 9%; *t*-heptylnaphthalene: <sup>c</sup> 2%, <sup>d</sup> 1%, <sup>e</sup> 3%, <sup>f</sup> 1%, <sup>g</sup> 5%, <sup>h</sup> 2%, <sup>i</sup> 3%.

low; the  $\alpha$ - and  $\beta$ -isomers are interconvertible by treatment with toluene-*p*-sulphonic acid at 130°, although the effect is not great. *p*-Chloro- and *p*-nitro-benzyl-naphthalenes are unchanged after being heated with toluene-*p*-sulphonic acid under the same conditions as for alkylation.

It is evident from Tables 1 and 2 that the proportion of isomers in any one product depends on the substituting group. Further, for any one alkylating group, the isomer ratio is approximately the same, however the alkylation is brought about. A more searching test is provided by comparing the products of alkylation with pentan-2-ol and pentan-3-ol. Here, the number of possible isomers is increased by the isomerisation of the alkyl group and also by the formation of  $\alpha$ - and  $\beta$ -isomers; similarly for hexan-2- and -3-ols. It is seen from Tables 3 and 4 that, within the permissible limits of experimental error, the

<sup>6</sup> E. Koike and M. Okawa, *J. Chem. Soc. Japan*, 1953, **74**, 971; N. K. Moshchinskaya and Z. E. Krukovskaya, *Ukrain. Chim. Zhur.*, 1957, **23**, 353.

proportion of 2- and 3- $\alpha$ - and - $\beta$ -naphthylalkanes is the same, whatever method of alkylation is used.

It may be concluded from the results in Tables 1—4, if we exclude pentan-1-ol and hexan-1-ol, that in any one group of alkylations there is a common substituting agent.

In benzylation with boron trifluoride, there is satisfactory evidence that the reaction proceeds through the formation of an ion-pair,  $R^+[HOBF_3]^-$ , in which the carbonium ion reacts with the aromatic nucleus to give an alkylarene, the negative ion acting as a proton acceptor.<sup>7</sup> In benzylations with sulphuric acid or phosphoric acid a similar course may be assumed on the evidence presented in this Paper. With the cycloalkanols and the pentanols and hexanols, the alkylation may be assumed to depend on the formation of a carbonium ion-pair with the additional complication that rearrangement and also olefin formation can occur. It is reasonably certain that olefins take only a minor part in alkylations by boron trifluoride or sulphuric acid, or in the decomposition of sulphonic esters. With phosphoric acid, however, the formation of olefin in the reaction is obvious, and that this is confirmed from the evidence of side-reactions in alkylations by pentanols and hexanols. Thus, t-pentyl- and t-heptyl-naphthalenes are formed in the hexylation of naphthalene, t-butyl- and t-hexyl-naphthalenes in pentylation, and these are formed to any serious extent only with the alcohol and phosphoric acid. The presence of olefin in such alkylations can be recognised without difficulty, and it is the determining factor in the disproportionation of the alkyl group. Support for this is provided by the results of the reaction of pent-1-ene and of pent-2-ene with naphthalene and phosphoric acid; a high proportion (23%) of the product is a mixture of t-butyl- and t-hexyl-naphthalenes; there is also present some dimerised olefin. The most probable explanation is based on that given by Friedman and Morritz<sup>8</sup> for the formation of t-butylbenzene from "isoamylenes" by reaction with aluminium chloride with some pentyl chloride or hydrogen chloride; dimerisation occurs to give  $C_{10}H_{20}$  and then fission, in part at least, to  $C_4H_8$  and  $C_6H_{12}$ , both of which react independently to give t-butyl- and t-hexyl-naphthalenes.

A similar course may be presumed to account for the formation of t-butyl-, t-hexyl-, and t-heptyl-naphthalenes from t-pentyl alcohol and boron trifluoride. 2-Methylpentan-2-ol and boron trifluoride give a product containing t-butyl-, t-pentyl-, and t-heptyl-naphthalenes with some 60% of the required t-hexyl-naphthalene. A mixture of t-alkyl-naphthalenes is similarly formed from 2-methylhexan-2-ol. Streitwieser *et al.*<sup>9</sup> have reported the formation of t-butyl- and t-pentyl-benzenes from 3-methylbutan-2-ol and boron trifluoride; from t-pentyl alcohol only polymerised olefin was obtained.

#### EXPERIMENTAL

*Alkylation.*—(a) *By esters of toluene-p-sulphonic acid.* This was carried out as described in previous Papers of this Series.<sup>10</sup> Each product was characterised by its b. p., refractive index, and elemental analysis. Table 5 summarises the results with esters of benzyl alcohols and cycloalkanols.

From each of these products, the  $\alpha$ -isomer was isolated as the picrate by crystallisation from alcohol. From the nitrobenzyl-naphthalenes, both the  $\alpha$ - and  $\beta$ -isomers were separated in a pure state by a fractional crystallisation of the picrates. The  $\alpha$ -isomer was identified by hydrogenation to the amine (acetyl derivative, m. p. 151—152°) and subsequent deamination by the diazo-reaction ( $H_3PO_2$ ) to  $\alpha$ -benzyl-naphthalene, m. p. and mixed m. p. 59—60°;  $\alpha$ -p-nitrobenzyl-naphthalene, m. p. 87° (Found: C, 77.4; H, 5.0; N, 5.6.  $C_{17}H_{13}NO_2$  requires C, 77.6; H, 5.0; N, 5.3%); picrate, m. p. 129—130°;  $\beta$ -p-nitrobenzyl-naphthalene, m. p. 80—81° (Found: C, 77.6; H, 5.1; N, 5.5%); picrate, m. p. 103—104°.

Table 6 gives the yields and constants of the products from the alkylations with the toluene-p-sulphonic esters of the n-pentanols and the n-hexanols.

In these alkylations olefins were collected. From the ester of pentan-1-ol a mixture of

<sup>7</sup> A. Streitwieser, W. D. Schaeffer, and S. Andreades, *J. Amer. Chem. Soc.*, 1959, **81**, 1113.

<sup>8</sup> B. S. Friedman and F. L. Morritz, *J. Amer. Chem. Soc.*, 1956, **78**, 3430.

<sup>9</sup> A. Streitwieser, D. P. Stevenson, and W. D. Schaeffer, *J. Amer. Chem. Soc.*, 1959, **81**, 1110.

<sup>10</sup> J. Blackwell and W. J. Hickinbottom, *J.*, 1963, 366.

TABLE 5  
Alkyl-naphthalenes from esters of toluene-*p*-sulphonic acid

Substituted naphthalene	Yield (%)	B. p./mm.	$n_D^{20}$	Found (%)		Calc. (%)	
				C	H	C	H
Cyclopentyl .....	33	92—95°/0.1	1.6120	91.8	8.1	91.8	8.2
Cyclohexyl .....	56	107—116°/0.1	1.6206	91.4	8.7	91.4	8.6
Cycloheptyl .....	36	111—117°/0.1	1.6000	90.9	8.9	91.0	9.0
Benzyl .....	66	117—130°/0.1	Solid	93.6	6.4	93.5	6.5
<i>p</i> -Methylbenzyl ...	73	145—150°/0.1	1.6336	93.3	6.9	93.1	6.9
<i>p</i> -Chlorobenzyl *	74	142—153°/0.1	1.6473	81.2	5.6	80.8	5.2
<i>p</i> -Nitrobenzyl † ...	56	193—198°/0.1	Solid	77.4	5.0	77.6	5.0

\* Found: Cl, 13.8. Calc., Cl, 14.0%. † Found: N, 5.6. Calc., N, 5.3%.

TABLE 6  
Alkylation of naphthalene with toluene-*p*-sulphonates

	Yield (%)	B. p./mm.	$n_D^{20}$	Found (%)		Calc. (%)	
				C	H	C	H
Pentan-1-ol * .....	28	166—173/19	1.5745	90.9	9.1	90.9	9.1
Pentan-2-ol .....	61	77—84°/0.2	1.5751	90.7	9.0	90.9	9.1
Pentan-3-ol .....	54	150—157/11	1.5760	90.6	9.0	90.9	9.1
Hexan-1-ol † .....	41	162—170/10	1.5677	90.4	9.6	90.5	9.5
Hexan-2-ol .....	70	164—174/13	1.5691	90.5	9.6	90.5	9.5
Hexan-3-ol .....	70	163—173/13	1.5694	90.2	9.6	90.5	9.5

\* Ester (0.28 mole) and naphthalene (1.56 mole) at 160—170° for 8 hr. † Ester (0.3 mole) and naphthalene (1.5 mole) at 160—170° for 9 hr. Other alkylations were carried out at 125° for 5 hr.

pent-1-ene and pent-2-ene was collected, b. p. 29—35°. The dibromide was separated into two fractions, b. p. 52—54°/11 mm.,  $n_D^{20}$  1.5063 and b. p. 60°/11 mm.,  $n_D^{20}$  1.5093 (Found: C, 26.6, 26.1; H, 4.5, 4.4; Br, 69.0, 69.6%, for the two fractions). The esters of pentan-2- and -3-ol similarly gave a mixture of pentenes.

The olefin from the ester of hexan-1-ol boiled at 60—65°,  $n_D^{20}$  1.3945; dibromide, b. p. 70—72°/8 mm.,  $n_D^{20}$  1.5040 (Found: C, 29.5; H, 4.9; Br, 66.6. Calc. for  $C_6H_{12}Br_2$ : C, 29.5; H, 4.9; Br, 65.6%).

Hexan-2-ol and hexan-3-ol similarly gave hexenes, recognised by their constants and their dibromides.

(b) *Boron trifluoride*. For all but the primary alcohols boron trifluoride was passed into a suspension of naphthalene in the alcohol at room temperature for  $\frac{1}{2}$ —2 hr. For the primary alcohols, the reaction was carried out at 80° for 2 hr.

(c) *Sulphuric acid*. A mixture of the alcohol and an excess of naphthalene was stirred with concentrated sulphuric acid at room temperature for 15 hr.

(d) *Phosphoric acid*. The alkylation was carried out as described in previous Papers.

*Alkylation by Olefins*. (a) *Pent-1-ene*. Boron trifluoride was passed into a suspension of naphthalene (0.6 mole) in pent-1-ene (0.4 mole) at 0° for  $\frac{1}{2}$  hr. The product boiled at 162—170°/15 mm.,  $n_D^{20}$  1.5598 (Found: C, 90.3; H, 9.7. Calc. for  $C_{15}H_{18}$ : C, 90.9; H, 9.2%).

Alkylation with sulphuric acid or phosphoric acid was effected as with the alcohols.

With phosphoric acid, an *olefin*, b. p. 148—153°,  $n_D^{20}$  1.4320, was also obtained (Found: C, 85.6; H, 14.2.  $C_{10}H_{20}$  requires C, 85.6; H, 14.4%).

(b) *Pent-2-ene*. With phosphoric acid a dimer was obtained, b. p. 55—56°/10 mm.,  $n_D^{20}$  1.4409, characterised at its *dibromide* (Found: C, 42.7; H, 6.5; Br, 50.4.  $C_{11}H_{22}Br_2$  requires 42.0; H, 7.0; Br, 50.9%).

The distribution of isomers in the products from the pentenes is given in Table 7.

TABLE 7  
Isomer distribution in the product from pentenes

	Pent-1-ene				Pent-2-ene					
	Yield (%)	2- $\alpha$	2- $\beta$	3- $\alpha$	3- $\beta$	Yield (%)	2- $\alpha$	2- $\beta$	3- $\alpha$	3- $\beta$
$BF_3$ .....	5	52	23	19	6	4	44	27	21	8
$H_2SO_4$ .....	4	33	38	12	17	9	31	37	14	18
$H_3PO_4$ .....	36 <sup>a</sup>	61	15	18	6	40 <sup>b</sup>	55	16	22	7

<sup>a</sup> Other products (calc. percentage of the total yield): *t*-butylnaphthalene, 15%; *t*-hexylnaphthalene, 8%. <sup>b</sup> Other products: *t*-butylnaphthalene, 13%; *t*-hexylnaphthalene, 10%.

(c) *Tri-isobutylene*. Concentrated phosphoric acid and tri-isobutylene at 130° for 20 hr. gave *t*-butylnaphthalene, b. p. 145—150°/14 mm.,  $n_D^{20}$  1.5825 (yield 15%) (Found: C, 91.2; H, 8.6. Calc. for  $C_{14}H_{16}$ : C, 91.3; H, 8.8%). Its infrared spectrum had strong absorption bands at 11.7 and 12.25  $\mu$ , characteristic of  $\beta$ -substitution in naphthalene.<sup>11</sup> There was no absorption at 12.45 and 12.9  $\mu$ , indicating the absence of any appreciable amount of the  $\alpha$ -isomer.

*Analyses*.—The alkylation products were analysed by vapour-phase chromatography with a Pye Argon unit provided with an ionisation detector and 10% Apiezon L on Celite (100—125 mesh) or on Silocel (60—72 mesh). The experimental error, estimated from comparative determinations, is about  $\pm 2\%$ .

*Preparation of Reference Compounds*.— $\alpha$ - and  $\beta$ -Benzylnaphthalenes and the *p*-methyl- and *p*-chloro-benzylnaphthalenes were prepared by reduction of the corresponding aryl naphthylcarbinols in ether by lithium aluminium hydride and aluminium chloride.<sup>12</sup> The purity of each compound was established by vapour-phase chromatography.

The following appear to be new:

$\beta$ -*p*-Methylbenzyl naphthalene, b. p. 146°/1 mm., m. p. 55—56° (Found: C, 93.0; H, 6.9.  $C_{18}H_{16}$  requires C, 93.1; H, 6.9%); picrate, lemon-yellow needles from ethanol, m. p. 88—89°;  $\alpha$ -*p*-chlorobenzyl naphthalene, m. p. 62° (Found: C, 80.9; H, 5.1; Cl, 13.8.  $C_{17}H_{13}Cl$  requires C, 80.8; H, 5.2; Cl, 14.0%); picrate, yellow-orange, m. p. 128—129°;  $\beta$ -*p*-chlorobenzyl naphthalene, m. p. 51—52° (Found: C, 80.4; H, 5.5; Cl, 14.0); picrate, yellow, m.p. 83—84°.

The pentyl- and hexyl-naphthalenes (Table 8) were prepared from the appropriate carbonyl compound through reaction with naphthylmagnesium bromides. The purity of each product was established by vapour-phase chromatography.

TABLE 8  
Naphthylalkanes

	B. p./mm.	$n_D^{20}$	Found (%)		Calc. (%)	
			C	H	C	H
1- $\alpha$ -Naphthylpentane *	163°/11	1.5700	90.9	9.0	90.9	9.2
1- $\beta$ -Naphthylpentane †	163/11	1.5670	90.5	9.4	90.9	9.2
2- $\alpha$ -Naphthylpentane	159/15	1.5736	90.7	9.1	90.9	9.2
2- $\beta$ -Naphthylpentane ‡	162/18	1.5645	90.8	9.4	90.9	9.2
3- $\alpha$ -Naphthylpentane	156/17	1.5710	90.8	9.3	90.9	9.2
3- $\beta$ -Naphthylpentane	156/17	1.5700	90.7	9.2	90.9	9.2
1- $\alpha$ -Naphthylhexane §	166/7	1.5616	90.5	9.5	90.5	9.5
1- $\beta$ -Naphthylhexane ¶	188/17	1.5516	90.2	9.7	90.5	9.5
2- $\alpha$ -Naphthylhexane	159/8	1.5669	90.5	9.5	90.5	9.5
2- $\beta$ -Naphthylhexane	163/9	1.5610	90.4	9.6	90.5	9.5
3- $\alpha$ -Naphthylhexane	165/13	1.5643	90.4	9.7	90.5	9.5
3- $\beta$ -Naphthylhexane	169/13	1.5620	90.4	9.6	90.5	9.5

\* Lit.,<sup>3</sup> b. p. 87.1°/0.2 mm.,  $n_D^{20}$  1.5731. † Lit.,<sup>3</sup> b. p. 99.9°/0.2 mm.,  $n_D^{20}$  1.5704. ‡ Lit.,<sup>13</sup> b. p. 292—293°/725 mm.,  $n_D^{20}$  1.5759. § Lit.,<sup>3</sup> b. p. 104.7°/0.1 mm.,  $n_D^{20}$  1.5650. ¶ Lit.,<sup>3</sup> b. p. 108.5°/0.1 mm.,  $n_D^{20}$  1.5622. || Lit.,<sup>14</sup> b. p. 154°/8 mm.,  $n_D^{20}$  1.5660.

The following cycloalkylnaphthalenes were similarly prepared:  $\beta$ -cyclopentyl, picrate, m. p. 107° (lit.,<sup>15</sup> 94—95°);  $\alpha$ -cyclohexyl,  $n_D^{20}$  1.6075; picrate, m. p. 127—128° (lit.,<sup>16</sup>  $n_D^{20}$  1.6000; picrate, m. p. 122—123.5°);  $\beta$ -cycloheptyl, b. p. 123—125°/0.25 mm.,  $n_D^{20}$  1.5907 (Found: C, 90.8; H, 9.2.  $C_{17}H_{20}$  requires C, 91.0; H, 9.0%); picrate, m. p. 104—105°.

The naphthylalkanols (Table 9) and naphthylalkenes (Table 10) were also prepared by standard methods.

*Reaction of Tertiary Alcohols and Boron Trifluoride with Naphthalene*.—(a) *t*-Butyl alcohol. Boron trifluoride, passed into a suspension of naphthalene (0.6 mole) in the molten alcohol (0.5 mole) for  $\frac{1}{2}$  hr., gave *t*-butylnaphthalene, b. p. 146—151°/17 mm.,  $n_D^{20}$  1.5834, in 27% yield.

<sup>11</sup> R. Huisgen and L. Zirngibl, *Ber.*, 1958, **91**, 1438.

<sup>12</sup> J. Blackwell and W. J. Hickinbottom, *J.*, 1961, 1405.

<sup>13</sup> A. N. Tatarenko and I. P. Tsukervanik, *J. Gen. Chem. (U.S.S.R.)*, 1948, **18**, 106.

<sup>14</sup> N. I. Shuilkin, L. A. Eriyskaya, N. L. Komissarova, and Ai H-si Yang, *Izvest. Akad. Nauk. S.S.S.R., Otdel. Khim. Nauk*, 1962, 327.

<sup>15</sup> F. Winternitz, M. J. Mousseron, and J. Vinas, *Bull. Soc. chim. France*, 1951, 570.

<sup>16</sup> J. W. Cook and C. A. Lawrence, *J.*, 1936, 1431.

TABLE 9  
 Naphthylalkanols

	M. p. or b. p./mm.	$n_D^{20}$	Found (%)		Calc. (%)	
			C	H	C	H
1- $\alpha$ -Naphthylpentan-1-ol .....	67°		84.5	8.5	84.1	8.5
1- $\beta$ -Naphthylpentan-1-ol .....	49		84.1	8.5	84.1	8.5
2- $\alpha$ -Naphthylpentan-2-ol .....	67					
2- $\beta$ -Naphthylpentan-2-ol .....	167—170/16	1.6062				
3- $\alpha$ -Naphthylpentan-3-ol .....	104—105/0.4	1.5944				
1- $\alpha$ -Naphthylhexan-1-ol .....	51—52		84.3	8.7	84.2	8.8
1- $\beta$ -Naphthylhexan-1-ol .....	73—74		84.2	8.7	84.2	8.8
2- $\alpha$ -Naphthylhexan-2-ol .....	121—123/0.5	1.5797				
2- $\beta$ -Naphthylhexan-2-ol .....	147—149/0.3	1.5863				
3- $\alpha$ -Naphthylhexan-3-ol .....	86					
3- $\beta$ -Naphthylhexan-3-ol .....	147—150/0.15	1.5887				

 TABLE 10  
 Naphthylalkenes

	M. p. or b. p./mm.	$n_D^{20}$	Found (%)		Calc. (%)	
			C	H	C	H
1- $\alpha$ -Naphthylpentene .....	165°/12	1.5775	91.8	8.2	91.8	8.2
1- $\beta$ -Naphthylpentene .....	44		92.1	8.1	91.8	8.2
2- $\alpha$ -Naphthylpentene .....	157/17	1.5896			91.8	8.2
2- $\beta$ -Naphthylpentene .....	161/18	1.5645			91.8	8.2
3- $\alpha$ -Naphthylpentene .....	154/14	1.5959	91.6	8.2	91.8	8.2
3- $\beta$ -Naphthylpentene .....	163/12	1.6073	91.6	8.2	91.8	8.2
1- $\alpha$ -Naphthylhexene .....	172/17	1.5834	91.1	9.0	91.4	8.6
1- $\beta$ -Naphthylhexene .....	186/13	1.5906	91.2	8.9	91.4	8.6
2- $\alpha$ -Naphthylhexene .....	154/7	1.5812	91.3	8.7	91.4	8.6
2- $\beta$ -Naphthylhexene .....	173/8	1.6013	91.4	8.7	91.4	8.6
3- $\alpha$ -Naphthylhexene .....	164/12	1.5842	91.2	8.8	91.4	8.6
3- $\beta$ -Naphthylhexene .....	177/14	1.5990	91.1	8.8	91.4	8.6

From its infrared spectrum it is  $\beta$ -*t*-butylnaphthalene and identical with that from other alkylations (Found: C, 91.3; H, 8.8.  $C_{14}H_{18}$  requires C, 91.3; H, 8.8%).

(b) *2-Methylbutan-2-ol*. A similar preparation from *t*-pentyl alcohol gave a product which, from vapour-phase chromatography, contained *t*-butylnaphthalene, 36%; *t*-pentylnaphthalene, 45%; *t*-hexylnaphthalene, 16%; *t*-heptylnaphthalene, 3%.

*t*-Pentylnaphthalene was obtained more satisfactorily from neopentyl alcohol and naphthalene saturated at 80° for  $\frac{1}{2}$  hr.; b. p. 163—168°/17 mm.,  $n_D^{20}$  1.5765; yield, 62%. It contained some *t*-butylnaphthalene, 8% and *t*-hexylnaphthalene, 3% (Found: C, 90.7; H, 9.3.  $C_{15}H_{18}$  requires C, 90.9; H, 9.2%).

(c) *2-Methylpentan-2-ol*, this gave a product in 35% yield, b. p. 176—182°/15 mm.,  $n_D^{20}$  1.5532, consisting of *t*-hexylnaphthalene, 63%; *t*-pentylnaphthalene, 15%; and *t*-heptylnaphthalene, 12%.

(d) *2-Methylhexan-2-ol*. This gave a product containing *t*-butyl- (9%), *t*-pentyl- (8%), *t*-hexyl- (14%), and *t*-heptyl-naphthalene (59%), with unidentified products (10%).

With sulphuric acid instead of boron trifluoride, the product contained *t*-heptyl- (75%), *t*-butyl- (3%), *t*-pentyl- (3%), and *t*-hexyl-naphthalene (10%), and other products.

(e) *1-Methylcyclohexanol*. Reaction with boron trifluoride and naphthalene at room temperature for 2 hr. gave a product, b. p. 115—120°/0.025 mm.,  $n_D^{20}$  1.5780 (yield 16%), containing 75% of 1-methylcyclohexylnaphthalene. Three other products were present, but were not identified.

Khromov and Balenkova<sup>17</sup> report 1- $\alpha$ -naphthylmethylcyclohexane, b. p. 142—143°/3 mm.,  $n_D^{20}$  1.5901.

(f) *1-Methylcyclopentanol*. This kept in carbon disulphide at room temperature for 2 hr. with naphthalene and aluminium chloride, gave a product, b. p. 114—120°/0.2 mm.,  $n_D^{20}$  1.5490 (yield 20%) (Found: C, 91.3; H, 8.6. Calc. for  $C_{16}H_{18}$ : C, 91.4; H, 8.6%). The main

<sup>17</sup> S. I. Khromov and E. S. Balenkova, *Vestnik Moscov. Univ.*, **10**, No. 12, Ser. Fiz. Mat. Estestven Nauk, 1955, No. 8, 121 (*Chem. Abs.*, 1956, **50**, 11,305).

product was identical (vapour-phase chromatography) with one of the products from the cyclohexylation of naphthalene, and is assumed to be 1-naphthyl-1-methylcyclopentane. The other products were not identified.

Attempts to make 1- $\alpha$ -naphthylmethylcyclopentane from  $\alpha$ -naphthylmercuric halides or  $\alpha$ -naphthylmagnesium bromide and 1-chloro-1-methylcyclopentane were unsuccessful.

The authors thank the Hydrocarbons Research Group of the Institute of Petroleum for support and the Education Mission of the United Republic for a scholarship (to M. Z. A. B.).

DEPARTMENT OF CHEMISTRY, QUEEN MARY COLLEGE, MILE END ROAD, LONDON E.1.

[Present address (W. J. H.): UNIVERSITY OF KHARTOUM,  
SUDAN.]

[Received, November 16th, 1964.]

---