Reversible Isomerisation of Alkyl Aromatics

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The isomerisation of α- and β-benzyl- and substituted-benzyl-naphthalenes catalysed by anhydrous aluminium chloride or toluene-*p*-sulphonic acid has been studied.

Halogen-substituted-benzylnaphthalenes failed to isomerise whilst *p*-methyl- and *p*-methoxy-benzylnaphthalenes, isomerise more readily than benzylnaphthalene. The isomerisation is reversible, and aluminium chloride is more effective than toluene-*p*-sulphonic acid.

THE mechanism of the Friedel–Crafts alkylation of aromatic compounds came to be considered, recently, as a typical electrophilic aromatic substitution.[1]

Several alkylations were reported, however, in which the proportion of *meta*-substituted product, was anomalously high for an electrophilic reaction,[2] and this was explained,[3] by postulating a high degree of reactivity to the attacking alkyl group, a condition which is accompanied by low selectivity.

Recently, a hypothesis was advanced,[4] which relates the higher proportion of *meta*-isomers, to the relatively high stability of the intermediate ion.

Since the intermediate σ-complex postulated for alkylation is identical to that postulated for isomerisation,[5] it is questionable whether alkylation exclusive of isomerisation would be possible. Consequently, an isomer distribution obtained by alkylation can change due to positional isomerisation under the Friedel–Crafts reaction conditions.

The early literature on the alkylation of naphthalene is often contradictory and misleading. Pure α- or β-isomers, or more often mixtures, are reported as products of alkylation with alcohols and aluminium chloride, boron trifluoride, or phosphorus pentoxide as condensing agents.[6]

In order to study the possibility that reversible isomerisation of the isomers may be responsible, the behaviour of some α- and β-substituted-benzylnaphthalenes has been studied with toluene-*p*-sulphonic acid as catalyst: the results are compared with those using aluminium chloride.

The α- and β-isomers were each isomerised when heated with catalysts to give mixtures containing both monoalkyl isomers. Aluminium chloride was a better catalyst than the sulphonic acid which required a higher temperature to be effective.

It was noted that the isomerisation was less ready when the basicity of the alkyl substitution was reduced, as in bromo- and chloro-benzylnaphthalenes. α- and β-*p*-Bromobenzylnaphthalene and the corresponding *p*-chloro-compounds were unaffected by toluene-*p*-sulphonic acid at 130°, or by aluminium chloride in boiling carbon disulphide; this agrees with a similar observation for the *p*-nitro-compound.[6]

Results for the isomerisation of substituted naphthalenes are given in Tables 1 and 2.

TABLE 1

Isomerisation products of 1-benzylnaphthalenes

	1-Benzyl [a]		1-*p*-Methyl-benzyl [a]		1-*p*-Methoxy-benzyl [b]	
Catalyst	1	2	1	2	1	2
Toluene-*p*-sulphonic acid at 125—130°	57	43	45	55	45	55
$AlCl_3$–CS_2–reflux	12	88	37	63	9	91

TABLE 2

Isomerisation products of 2-benzylnaphthalenes

	2-Benzyl [a]		2-*p*-Methyl-benzyl [a]		2-*p*-Methoxy-benzyl [b]	
Catalyst	1	2	1	2	1	2
Toluene-*p*-sulphonic acid at 125—130°	11	89	15	85	34	66
$AlCl_3$–CS_2–reflux	20	80			8	92

[a] G.l.c., column, 10% polyethylene glycol adipate on Chromosorb W (35—80 mesh) at 210°. [b] G.l.c., column, 20% SE 30 on Chromosorb W.A.W. (35—80 mesh) at 250°.

From Table 1 it is evident that α-isomers of monoalkyl naphthalenes have isomerised mainly to the β-isomers with aluminium chloride as a catalyst, whilst toluene-*p*-sulphonic acid gives no more than 55% of the β-isomers. In contrast isomerisation of β-isomers with either catalyst (Table 2) gave a relatively low percentage of the α-isomer.

Hickinbottom *et al.*[6] have deduced that in absence of any isomerisation reaction and with boron trifluoride, concentrated sulphuric acid or concentrated phosphoric acid as catalysts, mono-substitution occurs mainly at the α-position of naphthalene.

However more drastic conditions would increase the rate of alkylation–dealkylation. Although addition would be fast at positions of high electron availability (α-), substitution would be greater at positions giving the thermodynamically more stable β-isomer. The re-

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[1] J. H. Simons and H. Hart, *J. Amer. Chem. Soc.*, 1944, **66**, 1309; 1947, **69**, 979; T. M. Berry and E. E. Reid, *ibid.*, 1927, **49**, 3142; B. W. Malishiv, *ibid.*, 1935, **57**, 883; N. M. Cullinane and D. M. Leyson, *J. Chem. Soc.*, 1954, 2942.

[2] C. C. Price, 'Organic Reactions,' John Wiley, New York, N.Y., 1949, vol. III; C. C. Price, *Chem. Rev.*, 1941, **29**, 37; F. E. Condon, *J. Amer. Chem. Soc.*, 1949, **71**, 3544.

[3] H. C. Brown and C. R. Smoot, *J. Amer. Chem. Soc.*, 1956, **78**, 6246; H. C. Brown and C. R. Smoot, *ibid.*, 1956, **78**, 6256; H. C. Brown and K. L. Nelson, *ibid.*, 1953, **75**, 6292; H. C. Brown and C. W. McCary, *ibid.*, 1955, **77**, 2300.

[4] W. J. Hickinbottom, *Rev. Chim. Roumania*, 1962, **7**, No. 2, 907.

[5] K. L. Nelson and H. C. Brown in 'The Chemistry of Petroleum Hydrocarbons,' ed. B. T. Brooks, S. S. Kurtz, C. E. Boord, and L. Schmerling, Reinhold, New York, 1955, vol. III.

[6] M. Z. A. Badr and W. J. Hickinbottom, *J. Chem. Soc.*, 1965, 4101.

versibility of alkylation had been deduced by many workers.[7,8]

The observation that isomerisation is retarded or even prevented by a halogen or nitro-substituent in the benzyl provides evidence that the change depends on the capacity to accept protons: this is supported by the observation that a methyl or methoxy-group in the benzyl group facilitates the change.

EXPERIMENTAL

Isomerisation.—(a) *With toluene*-p-*sulphonic acid*. The substituted-benzylnaphthalene was added to a dehydrated mixture of toluene-*p*-sulphonic acid (1 mol.) and naphthalene (4 mol.) and the mixture was stirred and heated at 125—130° for *ca*. 5 hr. The product was fractionally distilled under vacuum from the excess of naphthalene. From each of these products, the α-isomer or β-isomer was isolated as the picrate by crystallisation from ethanol.

(b) *With aluminium chloride*. Aluminium chloride (9 g.) was added to a mixture of substituted-benzylnaphthalenes (1 mol.) and naphthalene (10 mol.), in dry carbon disulphide. The reaction mixture was stirred and heated under reflux for *ca*. 3 hr. The isomerisation product was fractionally distilled under reduced pressure to remove excess of naphthalene.

Analysis.—The isomerisation products were analysed by high-temperature gas chromatography, Model 1709, flame ionisation attachment of F. and M. Scientific corporation Model 500, with copper columns, 6 ft. × 4 mm. The columns used were, (*a*) 10% polyethylene glycol adipate on Chromosorb W (35—80 mesh) at 210° C, (*b*) 20% SE 30 on Chromosorb W (35—80 mesh) at 250°, then at 275° for some isomers. The experimental errors, estimated from comparative determinations, are about ±1%.

Preparation of Reference Compounds.—α- and β-Benzylnaphthalenes and the *p*-methyl-, *p*-methoxy-, *p*-chloro-, and *p*-bromo-benzylnaphthalenes were prepared by reduction of the corresponding arylnaphthylmethanols in dry ether by lithium aluminium hydride and aluminium chloride.[9] The purity of each compound was established by v.p.c. Light petroleum refers to fraction of b.p. 80—100°.

The following compounds are new:

p-Methoxyphenyl-α-naphthylmethanol; needles from light petroleum, m.p. 87—88° (Found: C, 81·9; H, 6·3. $C_{18}H_{16}O_2$ requires C, 81·8; H, 6·1%); α-(*p*-methoxy)benzylnaphthalene; microneedles from light petroleum, m.p. 87—88° (Found: C, 86·9; H, 6·8. $C_{18}H_{16}O$ requires C, 87·1; H, 6·5%), picrate, crystals from ethanol, m.p. 106°; *p*-methoxyphenyl-β-naphthylmethanol; crystals from light petroleum, m.p. 72—73° (Found: C, 81·6; H, 6·5. $C_{18}H_{16}O_2$ requires C, 81·8; H, 6·1%); β-(*p*-methoxy)-benzylnaphthalene; b.p. 245—250°/15 mm. white plates from ethanol, m.p. 57—58° (Found: C, 87·3; H, 6·5. $C_{18}H_{16}O$ requires C, 87·1; H, 6·5%), picrate, m.p. 89°; *p*-bromophenyl-α-naphthylmethanol; crystals from light petroleum, m.p. 95—96° (Found: C, 65·5; H, 4·2; Br, 25·2. $C_{17}H_{13}OBr$ requires C, 65·5; H, 4·1; Br, 25·6%); α-*p*-bromobenzylnaphthalene; needles from methanol, m.p. 65—66° (Found: C, 68·8; H, 4·5; Br, 26·5. $C_{17}H_{13}Br$ requires C, 68·7; H, 4·4; Br, 26·9%), picrate, crystals from ethanol, m.p. 132°; *p*-bromophenyl-β-naphthyl carbinol; crystallised from light petroleum (b.p. 40—60°), m.p. 95—96° (Found: C, 65·3; H, 4·4; Br, 25·3. $C_{17}H_{13}Br$ requires C, 65·5; H, 4·1; Br, 25·6%); β-*p*-bromobenzylnaphthalene, needles from ethanol, m.p. 60—61° (Found: C, 68·5; H, 4·1; Br, 26·6. $C_{17}H_{13}Br$ requires C, 68·7; H, 4·4; Br, 26·9%), picrate, crystals from ethanol, m.p. 110°.

[0/895 *Received, May* 29*th*, 1970]

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[9] J. Blackwell and W. J. Hickinbottom, *J. Chem. Soc.*, 1961, 1405.