

### 501. Alkylation of the Aromatic Nucleus. Part II.<sup>1</sup> The Scope of the Reaction.

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It is shown that thermal decomposition of alkyl and cycloalkyl esters of sulphonic acids can be used to alkylate biphenyl, diphenylmethane, bibenzyl, naphthalene, fluorene, acenaphthene, and phenanthrene. This method is unsuccessful with anthracene and pyrene.

The temperature of decomposition of esters of arenesulphonic acids can be related to the nature of the substituents in the aromatic ring.

In Part I<sup>1</sup> it is shown that cyclohexyl, butyl, and isopropyl toluene-*p*-sulphonates decompose thermally in toluene and its homologues to introduce an alkyl or cyclohexyl group into the benzene ring. This reaction provides another method of alkylating the aromatic nucleus, and it is obviously desirable to determine the limits of its usefulness and application.

Esters of primary alcohols can be used for alkylation although at the expense of largely isomerising the alkyl group. The temperatures required for satisfactory alkylation by use of sulphonic esters of primary alcohols, except benzyl and substituted benzyl, are higher than for the isomeric secondary alcohols; this reflects the greater general thermal stability of the esters of primary than of those of secondary alcohols.<sup>2</sup> Indeed, the temperature of decomposition of alkyl esters of sulphonic acids has a direct relation to the facility of alkylation; the lower the decomposition temperature, the easier the alkylation. The temperature of decomposition of arenesulphonates is also determined by the nature of the *Bz*-substituents, and in the accompanying table the m. p. and decomposition temperatures of a number of cyclohexyl esters are given.

#### Cyclohexyl esters.

	M. p.	Decomp.	Found (%)		
			C	H	S
2,5-Dichlorobenzenesulphonic acid .....	106°	106°	46.2	4.4	10.5
2,5-Dibromobenzenesulphonic acid .....	115	115	36.6	3.5	8.1
<i>p</i> -Chlorobenzenesulphonic acid .....	35—36	116	52.2	5.1	11.8
<i>p</i> -Bromobenzenesulphonic acid .....	47—48	118	45.1	4.2	9.9
Benzenesulphonic acid .....	41—42	136			
Toluene- <i>p</i> -sulphonic acid .....	45—46	139			
2,4,6-Trimethylbenzenesulphonic acid .....	62—63	155	64.1	7.7	11.2

All these esters decompose in boiling mesitylene to give good yields of cyclohexyl-mesitylene; similarly cyclohexylbenzene was prepared by thermal decomposition in

<sup>1</sup> Part I, Hickinbottom and Rogers, *J.*, 1957, 4124.

<sup>2</sup> Drahowzal and Klamann, *Monatsh.*, 1951, **82**, 467.

benzene of these esters with the exception 2,4,6-trimethylbenzenesulphonate. This ester was largely unchanged after refluxing for 3 days; longer heating gave a mixture containing mesitylene and probably some cyclohexylbenzene and other products.

The direct introduction of alkyl groups into polycyclic aromatic hydrocarbons such as fluorene, acenaphthene, or phenanthrene has not yet been systematically or frequently studied. Adequate summaries are available for naphthalene.<sup>3</sup> Friedel-Crafts reaction of naphthalene with alkyl halides is not invariably a good or even useful method, although there are some exceptions.<sup>4</sup> Some success has been reported in using olefins and aluminium chloride; alcohols and boron trifluoride also give alkyl naphthalenes,<sup>5</sup> although our result does not agree with that of the authors who described the method.

We find that when the cyclohexyl group is introduced into naphthalene a high proportion of the  $\beta$ -isomer is formed (40%) together with the  $\alpha$ -isomer; with benzyl, the product is mainly the  $\alpha$ -isomer; with *s*-butyl the product consists of a mixture of 20% of  $\beta$ - and 80% of  $\alpha$ -isomer; isopropyl gives mainly  $\alpha$ .<sup>1</sup> The nature of the alkyl group thus seems to have a marked influence on the extent of  $\beta$ -substitution in naphthalene.

In the alkylation of fluorene by this method substitution in the 2-position has been established for *s*-butyl and by analogy also for cyclohexyl groups; it is reasonably certain that other isomers, not yet characterised, are also present. It is noteworthy that monochlorination, -bromination, and -nitration and -acylation are reported to occur only in the 2-position;<sup>6</sup> the introduction of benzyl by reaction of fluorene with benzyl chloride and a suitable condensing agent also occurs in the 2-position.

Alkylation of acenaphthene by thermal decomposition of cyclohexyl and *s*-butyl esters occurs mainly in the 5-position, and here also there is good reason for presuming the presence of other isomers in smaller amount. Mayer and Kaufmann<sup>8</sup> report the formation of 5-ethylacenaphthene from acenaphthene and ethyl bromide in carbon disulphide with aluminium chloride. On the other hand, Dziewonski *et al.*<sup>9</sup> find that 5-benzyl-acenaphthene with the 3- or the 4-isomer is formed from benzyl chloride, acenaphthene, and zinc chloride. In contrast, halogenation is reported to give 5-halogeno-substituted acenaphthenes; and nitration to give 3- and 5-mononitro-compounds.

The alkylation of biphenyl, diphenylmethane, and bibenzyl was also examined; substitution occurs mainly in the *para*-position. If cyclohexyl esters are used for alkylation, the products, since they can be dehydrogenated smoothly, furnish useful starting points for the preparation of linear polyphenyls and polyphenylalkanes.

#### EXPERIMENTAL

*Alkylation of Polycyclic Hydrocarbons.*—The general method of alkylation was to stir the sulphonic ester with an excess of the fused hydrocarbon at a suitable temperature. The onset of reaction was generally indicated by a darkening, but heating and stirring were continued for some hours in order to complete the reaction.

A solvent, generally ether, was added to the cooled reaction mixture, the free sulphonic acid was removed by alkali, and then the dried solution was distilled to remove solvent and excess of hydrocarbon. The alkylated hydrocarbon was then distilled over and purified by a suitable method.

*Reactions of Cyclohexyl Benzenesulphonate.*—(a) *Biphenyl.* Cyclohexyl benzenesulphonate (120 g.) and biphenyl (154 g.) at 90° for 3 hr. gave a product which was roughly separated: (i) b. p. 192—236°/16 mm., 55 g.; (ii) b. p. 186—258°/0.8 mm., 16.1 g.; (iii) a stiff gum not

<sup>3</sup> (a) Elsevier's "Encyclopaedia of Organic Chemistry," Vol. 12B, pp. 31, 32; (b) Price, "Organic Reactions," **3**, 53.

<sup>4</sup> (a) Bromby, Peters, and Rowe, *J.*, 1943, 144; (b) Whitmore and James, *J. Amer. Chem. Soc.*, 1943, **65**, 2088.

<sup>5</sup> (a) Price and Ciskowski, *ibid.*, 1938, **60**, 2499; (b) Price and Tomisek, *ibid.*, 1943, **65**, 439.

<sup>6</sup> (a) Buffle, *Helv. Chim. Acta*, 1932, **15**, 1483; (b) Courtot, *Ann. Chim.*, 1930, **14**, 5; (c) Thurston and Shriner, *J. Amer. Chem. Soc.*, 1935, **57**, 2163.

<sup>7</sup> Dziewonski and Reicher, *Chem. Abs.*, 1933, **27**, 283.

<sup>8</sup> Mayer and Kaufmann, *Ber.*, 1920, **53**, 289.

<sup>9</sup> Dziewonski and Leonhard, *Chem. Abs.*, 1930, **24**, 2126.

distilled or further examined. Fraction (i) consisted of cyclohexylbiphenyls, from which 4-cyclohexylbiphenyl was obtained by crystallisation from alcohol; it had m. p. 77—77·5° (Found: C, 91·7; H, 8·5. Calc. for  $C_{18}H_{20}$ : C, 91·5; H, 8·5%). Fraction (ii) was recrystallised from alcohol-benzene to give 4:4'-dicyclohexylbiphenyl, m. p. 201—202° (Found: C, 90·1; H, 9·4. Calc. for  $C_{24}H_{30}$ : C, 90·5; H, 9·5%) (Basford<sup>10</sup> gives for 4-cyclohexylbiphenyl, m. p. 74·5°; for 4:4'-dicyclohexylbiphenyl, m. p. 205°).

(b) *Diphenylmethane*. Cyclohexyl benzenesulphonate (80 g.) and diphenylmethane (336 g.) at 110° for 4 hr. gave a product, b. p. 229—238°/25 mm.,  $n_D^{20}$  1·5735—1·5728 (33 g.), which slowly deposited crystals. They were purified by crystallisation from methyl alcohol to give 4-cyclohexyldiphenylmethane, m. p. 48—49° (Found: C, 91·0; H, 8·8.  $C_{18}H_{22}$  requires C, 91·1; H, 8·9%). This was dehydrogenated with selenium at 320° for 6 days; sublimation of the product after removal of unchanged selenium gave 4-phenyldiphenylmethane, m. p. 86—87° after crystallisation from alcohol (Found: C, 93·6; H, 6·4. Calc. for  $C_{18}H_{16}$ : C, 93·4; H, 6·6%). Bodroux<sup>11</sup> records b. p. 252—257°/35 mm.,  $n_D^{20}$  1·587, for cyclohexyldiphenylmethanes prepared by the interaction of cyclohexene with diphenylmethane in presence of aluminium chloride. Goldschmidt<sup>12</sup> gives m. p. 85° for 4-phenyldiphenylmethane.

(c) *Bibenzyl*. Cyclohexyl benzenesulphonate (60 g.) and bibenzyl (95 g.) at 120° for 4 hr. gave 1-cyclohexylphenyl-2-phenylethane, b. p. 236—254°/14 mm. (30·6 g.). This solidified almost completely; it was freed from adherent oil by draining and was then crystallised from alcohol to give pure 1-p'-cyclohexylphenyl-2-phenylethane, m. p. 69—69·5° (Found: C, 91·0; H, 9·1.  $C_{20}H_{24}$  requires C, 90·9; H, 9·1%). This was dehydrogenated with selenium at 320° for 4 days; 1-p-biphenyl-2-phenylethane was obtained, m. p. 109·5—110° after sublimation under reduced pressure and crystallisation from alcohol (Found: C, 92·6; H, 7·1. Calc. for  $C_{20}H_{18}$ : C, 93·0; H, 7·0%). Bergmann<sup>13</sup> records m. p. 109°; Bodroux<sup>11</sup> describes a cyclohexylbibenzyl, m. p. 68—69°, which is probably identical with our preparation.

(d) *Naphthalene*. From cyclohexyl benzenesulphonate (120 g.) and naphthalene (192 g.) at 100° for 2 hr., there were obtained cyclohexylnaphthalenes, b. p. 176—200°/13 mm.,  $n_D^{20}$  1·6020—1·6016 (55·7 g.); a fraction, b. p. 230—266°/13 mm. (11·8 g.), was a viscid intractable oil, not further examined. Further fractionation of the main product concentrated it within the range 180—185°/13 mm.,  $n_D^{20}$  1·6020 (Found: C, 91·4; H, 8·6. Calc. for  $C_{16}H_{18}$ : C, 91·4; H, 8·6%). This is a mixture of 1- and 2-cyclohexylnaphthalene. From its infrared spectrum and that of the pure components, it is estimated to contain 60% of the 1- and 40% of the 2-isomer. The former was isolated as its picrate, orange crystals, m. p. 122—123·5° after crystallisation; this was identical with that from another source. Dehydrogenation of another portion of the mixture by selenium at 310° for 7 days gave 2-phenylnaphthalene, m. p. 101—102·5° (Found: C, 93·7; H, 5·8. Calc. for  $C_{16}H_{12}$ : C, 94·1; H, 5·9%).

*Preparation of 1-Cyclohexylnaphthalene*.—Boron trifluoride was passed into a suspension of naphthalene (50 g.) in cyclohexanol (38 g.), Price and Ciskowski's procedure being used.<sup>5a</sup> There was obtained a mixture (28·5 g.) of cyclohexylnaphthalenes, b. p. 182—194°/14 mm.,  $n_D^{20.5}$  1·5969. Price and Ciskowski claimed that this is essentially 2-cyclohexylnaphthalene; picrate m. p. 100°. Instead it proved to be a convenient source of 1-cyclohexylnaphthalene. For this purpose, the mixed cyclohexylnaphthalenes were distilled over sodium, and the fraction of b. p. 194—201°/23 mm. converted in alcohol into picrate. The crude picrate thus obtained had m. p. 114—119°, raised to 127—128° after several crystallisations from alcohol containing some picric acid. 1-Cyclohexylnaphthalene liberated from the picrate had b. p. 178—183°/12 mm.,  $n_D^{19.3}$  1·6040 (Found: C, 91·3; H, 8·6. Calc. for  $C_{16}H_{18}$ : C, 91·4; H, 8·6%) (Cook and Lawrence<sup>14</sup> give b. p. 118—120°/0·3 mm.,  $n_D^{11}$  1·6000; picrate, m. p. 122—123·5°). Its infrared spectrum gave no indication of any 2-cyclohexylnaphthalene.

*Preparation of 2-Cyclohexylnaphthalene*.—This was prepared by adding powdered aluminium chloride (20·5 g.) to a warm and stirred homogeneous mixture of naphthalene (200 g.) and cyclohexene (41 g.). After being kept overnight, it was worked up in the usual way to give crude 2-cyclohexylnaphthalene, b. p. 290—315°, which solidified. It was purified through its picrate, m. p. 99—100°; the pure hydrocarbon, crystallised from chilled methyl alcohol, had

<sup>10</sup> Basford, *J.*, 1936, 1593.

<sup>11</sup> Bodroux, *Ann. Chim.*, 1929, **11**, 511.

<sup>12</sup> Goldschmidt, *Monatsh.*, 1881, **2**, 433.

<sup>13</sup> Bergmann and Weizmann, *J. Org. Chem.*, 1944, **9**, 408.

<sup>14</sup> Cook and Lawrence, *J.*, 1936, 1431.

m. p. 31—32° (Found: C, 91.7; H, 8.5%). From its infrared spectrum, it contained no detectable amount of the 1-isomer (Bodroux<sup>11</sup> records for 2-cyclohexylnaphthalene, m. p. 31°; picrate m. p. 100—101°).

2-Phenylnaphthalene was obtained by dehydrogenation of 7-cyclohexyl-1,2,3,4-tetrahydronaphthalene with selenium at 315° for 3 days. It melted at 103—103.5° (Found: C, 94.0; H, 6.0. Calc. for C<sub>16</sub>H<sub>12</sub>: C, 94.1; H, 5.9%). The substituted tetralin, b. p. 112—117°/0.2 mm.,  $n_D^{19.3}$  1.5500 (Found: C, 89.9; H, 10.2. Calc. for C<sub>16</sub>H<sub>22</sub>: C, 89.6; H, 10.4%), from the reduction of 7-cyclohexyl-1-tetralone by hydrazine hydrate (100%) and potassium hydroxide in ethylene glycol, is probably identical with that described by Bodroux<sup>11</sup> as cyclohexyltetralin from cyclohexene, tetralin, and aluminium chloride.

7-Cyclohexyltetralone was obtained by cyclisation of  $\gamma$ -*p*-cyclohexylphenylbutyryl chloride (Buu-Hoï,<sup>15</sup> Fieser<sup>16</sup>).

*Reaction with Benzyl Benzenesulphonate.*—Naphthalene (150 g.) and benzyl benzenesulphonate (90 g.) when heated reacted even before the mixture had become homogeneous. The reaction was completed by keeping the mixture at 120° for 3 hr. Benzyl-naphthalene (18.2 g.) was collected at 223—232°/27 mm.; it solidified to a brown solid. Pure 1-benzyl-naphthalene, obtained by crystallisation from alcohol, melted at 59—60.5° (Found: C, 93.3; H, 6.4. Calc. for C<sub>17</sub>H<sub>14</sub>: C, 93.5; H, 6.5%), and was characterised by its picrate, yellow crystals, m. p. 104—105°, from alcohol (Roux<sup>17</sup> gives for 1-benzyl-naphthalene, m. p. 59°; for the picrate, m. p. 103—104°).

*Reactions of Fluorene.*—(i) *With cyclohexyl benzenesulphonate.* Fluorene (166 g.) and the sulphonic ester (60 g.) at 140° for 1 hr. gave nearly pure cyclohexylfluorene (40 g.), b. p. 180—215°/1.5 mm. 2-Cyclohexylfluorene, m. p. 130—132°, was obtained by crystallisation from alcohol (Found: C, 91.9; H, 8.1. C<sub>19</sub>H<sub>20</sub> requires C, 91.9; H, 8.1%). A picrate could not be prepared.

(ii) *With s-butyl benzenesulphonate.* Fluorene (83 g.) and s-butyl benzenesulphonate (53 g.) were heated to 120°; a vigorous reaction occurred with evolution of butene and the temperature of the mixture rose to 160°. The reaction was completed by cooling to 120° and keeping the mixture at this temperature for 1 hr. The product was concentrated by a number of distillations into fractions, b. p. 190—200°/14 mm.,  $n_D^{20}$  1.6060—1.6015, which were essentially butylfluorenes (Found: C, 91.9; H, 8.2. Calc. for C<sub>17</sub>H<sub>18</sub>: C, 91.8; H, 8.2%). These liquid fractions deposited crystals when kept in a refrigerator for some days. These were 2-*s*-butylfluorene, m. p. 47.5—48.5°, from methyl alcohol (Found: C, 91.8; H, 8.3%). A picrate could not be prepared. Nitration of the butylfluorene mixture in acetic acid by nitric and sulphuric acids gave a pale brown solid, m. p. 301.5°, which is probably a dinitro-compound although a satisfactory analysis was not obtained (Found: N, 9.4. C<sub>17</sub>H<sub>16</sub>O<sub>4</sub>N<sub>2</sub> requires N, 9.0%).

*Preparation of 2-s-Butylfluorene.*—Hydrogenation of 2-*s*-butenylfluorene (Pd-C, ethyl alcohol, 3 atm.) gave a semisolid from which 2-*s*-butylfluorene was obtained by sublimation and crystallisation from alcohol; it had m. p. 47—48°, unchanged by admixture with a sample from the alkylation (Found: C, 91.6; H, 8.3%). Use of Raney nickel (W.4) for the hydrogenation in ethyl alcohol at 3 atm. gave a solid, m. p. 176—177°, from alcohol. It decolorises bromine in carbon tetrachloride and is presumably an unsaturated dimer (Found: C, 92.8; H, 7.1%; M, 383. C<sub>34</sub>H<sub>32</sub> requires C, 92.7; H, 7.3%; M, 440). From the more soluble portion of the hydrogenation product, 2-*s*-butylfluorene was isolated by sublimation.

2-*s*-Butenylfluorene was prepared by reaction of 2-acetylfluorene with ethylmagnesium bromide and boiling the product with acetic anhydride. The solid thus obtained melted over a range of 105—118° even after several crystallisations, and is probably a mixture of stereoisomers (Found: C, 92.5; H, 7.2. C<sub>17</sub>H<sub>16</sub> requires C, 92.7; H, 7.3%).

*Reactions of Acenaphthene.*—(i) *With cyclohexyl benzenesulphonate.* From acenaphthene (154 g.) and the sulphonic ester (80 g.) at 120° for 8 hr., a product was collected between 185° and 210°/2 mm. (yield 42 g.); the greater part boiled at 194—196°/2 mm. and from it 5-cyclohexylacenaphthene, m. p. 88—88.5°, was isolated (Found: C, 91.6; H, 8.3. Calc. for C<sub>18</sub>H<sub>20</sub>: C, 91.5; H, 8.5%); its picrate formed bright orange spikes, m. p. 95—96° (Buu-Hoï<sup>18</sup> gives m. p. 84°; picrate, orange, m. p. 98°, for 5-cyclohexylacenaphthene from cyclohexene,

<sup>15</sup> Buu-Hoï, *Bull. Soc. chim. France*, 1944, **11**, 127.

<sup>16</sup> Fieser, *J. Amer. Chem. Soc.*, 1948, **70**, 3200.

<sup>17</sup> Roux, *Ann. Chim.*, 1887, **12**, 289.

<sup>18</sup> Buu-Hoï, *Compt. rend.*, 1945, **220**, 236.

acenaphthene, and aluminium chloride). It was not possible to isolate any other isomer from the more fusible parts of this product.

(ii) *With s-butyl benzenesulphonate.* From acenaphthene (154 g.) and s-butyl benzenesulphonate (160 g.) at 110° for 5 hr., there were obtained but-2-ene (5 c.c.) and a mixture of butylacenaphthenes, b. p. 142—163°/1.5 mm.,  $n_D^{20}$  1.5870 (42 g.). Further distillation gave a fraction, b. p. 132—134°/1 mm.,  $n_D^{20}$  1.5987 (Found: C, 91.2; H, 8.6. Calc. for  $C_{16}H_{18}$ : C, 91.4; H, 8.6%). The infrared spectrum indicated that this contained 5-s-butylacenaphthene with probably a small amount of the 3-isomer and other isomers not identified.

*Preparation of 3-s-Butylacenaphthene.*—To ethylmagnesium bromide [from magnesium (2.5 g.)] was added a solution of 3-acetylacenaphthene (6 g.) (Fieser and Herschberg<sup>19</sup>) in ether (100 c.c.) The resulting alcohol was dehydrated by boiling acetic anhydride for 10 hr. 3-s-Butenylacenaphthene (4.7 g.) thus obtained boiled at 152—156°/1 mm.,  $n_D^{19}$  1.6349—1.6370 (Found: C, 92.6; H, 7.6.  $C_{16}H_{16}$  requires C, 92.3; H, 7.7%). It was hydrogenated in ethanol (Pd-C, 3 atm.) to give 3-s-butylacenaphthene, b. p. 141—146°/1 mm.,  $n_D^{15}$  1.6010 (Found: C, 91.3; H, 8.9.  $C_{16}H_{18}$  requires C, 91.4; H, 8.6%).

*Preparation of 5-s-Butylacenaphthene.*—This was prepared from 5-acetylacenaphthene (Graebe<sup>20</sup>) by the same procedure as for the 3-isomer. It is a solid, m. p. 44—46° (Found: C, 91.3; H, 8.6%).

5-s-Butenylacenaphthene had b. p. 132—134°/1 mm.,  $n_D^{20}$  1.6233—1.6244.

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<sup>19</sup> Fieser and Herschberg, *J. Amer. Chem. Soc.*, 1939, **61**, 1272.

<sup>20</sup> Graebe, *Annalen*, 1903, **327**, 77.