164. *Alkylation of the Aromatic Nucleus. Part VII.* Acenaphthene.*

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Alkylation of acenaphthene by thermal decomposition of alkyl benzenesulphonates in an excess of hydrocarbon gives a mixture of 3-, 4-, and 5-alkylacenaphthenes. The relative proportions of the isomers have been estimated and compared with those obtained by other methods of alkylation.

Electrophilic substitution in acenaphthene takes place in the 3- and the 5-position, *e.g.*, nitration,[1] halogenation,[2] acylation,[3] formylation,[4] and sulphonation.[5] Information on alkylation is less precise: 5-ethylacenaphthene has been reported to be obtained by

* Part VI, preceding paper.

[1] (*a*) Garascia, Batzis, and Kroeger, *J. Org. Chem.*, 1960, **25**, 1271; (*b*) Morgan and Harrison, *J. Soc. Chem. Ind.*, 1930, **49**, 413.

[2] (*a*) Crompton and Walker, *J.*, 1912, **101**, 958; Crompton and Smyth, *J.*, 1913, **103**, 1302; (*b*) Paillard and Favarger, *Helv. Chim. Acta*, 1933, **16**, 614.

[3] (*a*) Sachs and Mosebach, *Ber.*, 1910, **43**, 2473; (*b*) Fieser and Peters, *J. Amer. Chem. Soc.*, 1932, **54**, 4347; (*c*) Fieser and Hershberg, *ibid.*, 1940, **62**, 51.

[4] Hinkel, Ayling, and Beynon, *J.*, 1936, 344.

[5] Dziewonski and Stolyhwo, *Ber.*, 1924, **57**, 1531.

Friedel–Crafts alkylation [6] although it is certain that 4-ethylacenaphthene is also formed; [7a] t-butyl chloride gives either the 4-isomer or a mixture of 3- and 5-isomers depending on the alkylation promoter.[7] Benzylation gives 5-benzylacenaphthene.[8]

Alkylation of acenaphthene by thermal decomposition of sulphonate esters has been examined to obtain more precise information. Also this method of alkylation has the advantage that there is no noticeable migration of alkyl groups during the reaction. It was expected that the pattern of substitution would follow that of fluorene and of the alkylbenzenes in approximating to random distribution. The results are summarised in the Table.

Alkylation of acenaphthene.

		Composition (%)		
Reagent	Temp.	3	4	5
1. $Ph{\cdot}SO_3Et$	240°	45	33	22
2. $Ph{\cdot}SO_3Pr^i$	160	34	55	11
3. $Ph{\cdot}SO_3Bu^s$	125	28	39	33
4. $Ph{\cdot}SO_3{\cdot}C_6H_{11}$	120	34	53	13
5. $EtBr{-}AlCl_3{-}CS_2$	46	22	58	20
6. $Pr^iBr{-}AlCl_3{-}CS_2$	20	22	63	15
7. $Bu^sCl{-}AlCl_3{-}CS_2$	20	17	46	37
8. Cyclohexene$-AlCl_3-CS_2$	10	22	8	70
9. $Bu^sBr{-}AlCl_3{-}PhNO_2$	20	19	6	75
10. $Bu^sBr{-}AlCl_3{-}PhNO_2$	20	18	5	77
11. $Pr^iBr{-}FeCl_3{-}CS_2$	46	21	6	73
12. $Bu^sBr{-}FeCl_3{-}CS_2$	46	24	3	73

A significant feature of the thermal alkylation (Experiments 1—4) is the high proportion of the 4-isomer, despite the reaction being an electrophilic substitution. Indeed this method has been used for obtaining pure specimens of 4-isopropyl- and 4-cyclohexyl-acenaphthene. The contrast with alkylation on use of ferric or aluminium chloride in nitrobenzene is striking since these compounds, in which there is also no appreciable isomerisation, conform to the expected pattern of electrophilic substitution. It is noteworthy that Illingworth and Peters [7b] observed that ferric chloride brought about t-butylation mainly in the 5-position, with some in the 3-position. We found that the use of aluminium chloride in carbon disulphide favoured substitution in the 4-position and that the 5-isomer can be converted into the 4-isomer by heating it with aluminium chloride in carbon disulphide.

Experimental

Alkylation of Acenaphthene by Thermal Decomposition of Alkyl Benzenesulphonates.—The general procedure was the same as that described previously for the reaction with fluorene.

Ethylacenaphthenes. Ethyl benzenesulphonate (58 g.) and acenaphthene (100 g.) when heated together at 240° for 1 hr. gave a mixture of ethylacenaphthenes (9 g.), b. p. 172—178°/18 mm., n_D^{19} 1·6178 (Found: C, 92·3; H, 7·9. Calc. for $C_{14}H_{14}$: C, 92·3; H, 7·7%).

Isopropylacenaphthenes. Isopropyl benzenesulphonate (50 g.) and acenaphthene (80 g.) were heated together at 165°; there was a vigorous reaction and the evolution of a considerable volume of gas. More ester (23 g.) was added and the heating continued at 160° for 30 min. Isopropylacenaphthenes were obtained (8·6 g.), having b. p. 167—181°/14 mm. (Found: C, 92·0; H, 8·3. Calc. for $C_{15}H_{16}$: C, 91·8; H, 8·2%). The mixture solidified and, from some of it, 4-isopropylacenaphthene, m. p. 71—72°, was isolated by several crystallisations from methanol (Found: C, 91·4; H, 8·3%). The infrared spectrum had a very strong absorption peak at 11·55 μ and showed that 3- and 5-isopropylacenaphthene were absent.

s-Butylacenaphthenes. s-Butyl ester (86 g.) and acenaphthene (100 g.) were heated at 125° for 1 hr. to give a mixture of s-butylacenaphthenes (23 g.), b. p. 182—185°/15 mm., n_D^{19} 1·6016 (Found: C, 91·7; H, 8·4. Calc. for $C_{16}H_{18}$: C, 91·4; H, 8·6%).

[6] Mayer and Kaufmann, *Ber.*, 1921, **53**, 289.
[7] (*a*) Nürsten and Peters, *J.*, 1950, 2389; (*b*) Illingworth and Peters, *J.*, 1951, 2508; (*c*) Illingworth and Peters, *J.*, 1952, 2730.
[8] Dziewonski and Rychlik, *Ber.*, 1925, **58**, 2239.

Cyclohexylacenaphthenes. Acenaphthene (80 g.), when heated with the cyclohexyl ester (74·5 g.) at 120° for 4 hr., gave a mixture of cyclohexylacenaphthenes (12 g.), b. p. 134—146°/0·08 mm. (Found: C, 91·3; H, 8·4. Calc. for $C_{18}H_{20}$: C, 91·5; H, 8·5%). The product solidified and from it, by repeated crystallisation from methanol, 4-cyclohexylacenaphthene was isolated in white flakes, m. p. 69—70° (Found: C, 91·4; H, 8·4%), $\lambda_{max.}$ 11·65 μ. Hickinbottom and Rule [9] isolated from a similar product 5-cyclohexylacenaphthene, m. p. 88—89°, identical with a specimen from another source and characterised by absorption bands at 11·3w and 12·15s μ.

Alkylation of Acenaphthene by the Friedel–Crafts Reaction.—To ethyl bromide (50 g.) and acenaphthene (90 g.) in carbon disulphide (200 c.c.) was added aluminium chloride (35 g.); the reaction was completed by 5 hours' refluxing. A mixture of ethylacenaphthenes (12·5 g.), b. p. 158—160°/15 mm., n_D^{19} 1·6132, was obtained (Found: C, 92·3; H, 8·0%).

Isopropylacenaphthenes (6·2 g.), b. p. 178—186°/20 mm. (Found: C, 91·8; H, 8·1%), were similarly obtained from isopropyl bromide (12 g.), acenaphthene (30 g.), and aluminium chloride (10 g.) in carbon disulphide. This product solidified and, from it, 4-isopropylacenaphthene was isolated.

s-Butylacenaphthenes, b. p. 180—190°/14 mm., $n_D^{20·5}$ 1·5980 (Found: C, 91·3; H, 8·8%), were obtained from acenaphthene (30 g.), s-butyl chloride (9·3 g.), and aluminium chloride (10 g.) in carbon disulphide.

Cyclohexylacenaphthenes. A stirred solution of acenaphthene (150 g.) and cyclohexene (60 g.) in carbon disulphide (400 c.c.) was cooled in ice-water while aluminium chloride (30 g.) was slowly added. Stirring was then continued for 4 hr. and thereafter the mixture was kept at 10° for 12 hr. This gave a mixture of cyclohexylacenaphthenes (62 g.), b. p. 155—163°/0·1 mm. (Found: C, 91·5; H, 8·5%), which solidified; 5-cyclohexylacenaphthene, m. p. 88°, was isolated from it. Buu-Hoï [10] describes a product of m. p. 84°.

Alkylations in nitrobenzene instead of carbon disulphide gave with isopropyl and s-butyl bromide poor yields of products, mostly the 5-alkylacenaphthene. With ferric chloride in carbon disulphide only poor yields of isopropyl- and s-butyl-acenaphthene were obtained, consisting mostly of the 5-isomer.

Isomerisation of Cyclohexylacenaphthene.—A mixture of cyclohexylacenaphthenes (12 g.) (22%, 8%, and 70% of the 3-, 4-, and 5-isomers, respectively) was heated with acenaphthene (20 g.) and aluminium chloride (8 g.) in carbon disulphide (100 g.) for 5 hr. The product had the composition: 23%, 53%, and 24%, respectively. (Compare Experiments 5, 6, and 7 in the Table.) The original mixture was unchanged after it had been heated at 125° for 3 hr. with acenaphthene and benzenesulphonic acid.

Analysis of Alkylacenaphthene Mixtures.—The composition of the product of each alkylation was determined from its infrared spectrum by base-line technique. The following were used in the identification and estimation of the isomeric alkylacenaphthenes: 3-ethyl-, 3-isopropyl-, and 3-s-butyl-acenaphthene, 12·3vs; 4-isopropylacenaphthene, 11·55vs; 4-cyclohexylacenaphthene, 11·65vs; 5-ethyl-, 5-isopropyl-, 5-cyclohexyl-acenaphthene 11·3w, 12·15s; 5-s-butylacenaphthene, 11·3w, 12·1s μ.

Preparation of Reference Samples.—(*a*) 3-Alkylacenaphthenes were obtained from the corresponding 2-alkylnaphthalenes through chloromethylation to the corresponding 2-alkyl-1-naphthylacetic acids. Cyclisation and reduction of the resulting 3-alkylacenaphen-1-ones completed the synthesis.

3-Ethylacenaphthene, m. p. 30—30·5° (from methanol), b. p. 97—106°/0·13 mm. (Found: C, 92·4; H, 7·6%) (picrate, orange-red needles, m. p. 104—105°). Illingworth and Peters [7b] give m. p. 29—30° (picrate, m. p. 104—105°); Cook *et al.*[11] give m. p. 30° (picrate, m. p. 102—102·5°).

3-Isopropylacenaphthene had b. p. 105—110°/0·25 mm., n_D^{18} 1·6067 (Found: C, 91·6; H, 8·3%). In this preparation 2-isopropylnaphthylacetic acid was obtained with m. p. 158—160° (Found: C, 78·8; H, 7·0. Calc. for $C_{15}H_{16}O_2$: C, 78·9; H, 7·1%). Buu-Hoï and Cagniant [12] describe this acid as a liquid.

3-s-Butylacenaphthene had b. p. 108°/0·07 mm., n_D^{19} 1·5985 (Found: C, 91·3; H, 8·3%) (1,3,5-trinitrobenzene adduct, orange, m. p. 94—96°). In this preparation the following compounds were obtained—they appear not to have been described previously:

[9] Hickinbottom and Rule, *J.*, 1959, 2509.
[10] Buu-Hoï and Cagniant, *Compt. rend.*, 1945, **220**, 326.
[11] Cook, Haslewood, and Robinson, *J.*, 1935, 667.
[12] Buu-Hoï and Cagniant, *Rev. Sci.*, 1942, **80**, 176.

1-Chloromethyl-2-s-butylnaphthalene, b. p. 137—140°/0·09 mm., n_D^{19} 1·5890 (Found: C, 77·1; H, 7·5; Cl, 15·0. $C_{15}H_{17}Cl$ requires C, 77·4; H, 7·4; Cl, 15·2%).

2-s-Butyl-1-naphthylacetic acid, b. p. 176—182°/0·08 mm. (Found: C, 79·0; H, 7·4. $C_{16}H_{18}O_2$ requires C, 79·3; H, 7·4%).

3-s-Butylacenaphthen-1-one, yellow, b. p. 132°/0·06 mm., n_D^{16} 1·6160 (Found: C, 85·7; H, 7·1. $C_{16}H_{16}O$ requires C, 85·7; H, 7·2%) [2,4-dinitrophenylhydrazone, scarlet (from pyridine), m. p. 253—255°].

(*b*) 5-Alkylacenaphthenes were prepared from 5-acenaphthenyl methyl ketone [13] by standard methods, as follows:

5-Ethylacenaphthene, m. p. 42·5—43·5° (Found: C, 92·3; H, 7·7%), purified through its picrate, orange needles, m. p. 96—97°. Fleischer and Wolff [14] give 5-ethylacenaphthene, m. p. 42·5—43°.

5-Isopropylacenaphthene, m. p. 23—24° (from methanol), b. p. 93—95°/0·13 mm., n_D^{20} 1·6081 (Found: C, 92·0; H, 8·1%) [1,3,5-trinitrobenzene adduct, orange (from ethanol), m. p. 89—90°].

5-s-Butylacenaphthene, m. p. 46—47°, from methanol, identical with that described by Hickinbottom and Rule.[9]

5-Cyclohexylacenaphthene, m. p. 87—88° (Found: C, 91·3; H, 8·6%) [picrate, orange needles (from ethanol), m. p. 95—97°], is identical with that isolated by Hickinbottom and Rule [9] from acenaphthene and cyclohexyl benzenesulphonate. It was prepared conveniently by reaction of the Grignard reagent from 5-bromoacenaphthene with cyclohexanone and subsequent hydrogenation of the resulting *5-cyclohexenylacenaphthene*, m. p. 49—50° (Found: C, 91·9; H, 7·8. $C_{18}H_{18}$ requires C, 92·3; H, 7·7%).

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[13] Fieser and Hershberg, *J. Amer. Chem. Soc.*, 1939, **61**, 1279.
[14] Fleischer and Wolff, *Ber.*, 1921, **53**, 925.