537. *The Reduction of β-Alkylnaphthalenes.*

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Catalytic hydrogenation of four β-*n*-alkylnaphthalenes to the tetrahydro-stage gave, in all cases, an approximately 2 : 1 mixture of the 6- and the 2-*n*-alkyl-1 : 2 : 3 : 4-tetrahydronaphthalene.

Reduction of the naphthalene nucleus may yield dihydronaphthalenes, tetralins, or decalins, depending on the reagent used, and can occur in either the substituted or the unsubstituted ring. For example, with sodium and pentyl alcohol α-naphthylamine gives 5-aminotetralin [1] whilst β-naphthylamine affords 2-aminotetralin.[2] In many investigations only the major product of the reduction has been isolated. Several authors [3, 4, 5, 6, 7] have reported that hydrogenation of a 2-substituted naphthalene with nickel catalysts gives predominantly the 6-substituted tetralin. In the particular case of the 2-alkylnaphthalenes both chemical [6] and physical [7] analysis demonstrated the presence of only the 6-alkyltetralin. As pure specimens of 2- and 6-alkyltetralins [8] were available in this laboratory, it was decided to re-investigate the reduction of a series of 2-alkylnaphthalenes.

Hydrogenation of 1-alkylnaphthalenes gives a mixture of 1- and 5-alkyltetralins, separable by fractional distillation.[9, 10] This method of separation was not used for the mixtures of 2- and 6-alkyltetralins because of the smaller differences in boiling points.[8] (5-Ethyltetralin has b. p. 248·0°, 1-ethyl- has b. p. 239·4° : difference, 8·6°. 6-Ethyltetralin has b. p. 246·5°, 2-ethyl-, 242·6° : difference, 3·9°.) The physical properties of the alkyltetralins used for analysis were the infrared spectra and the refractive indices. Mixtures of 2- and 6-alkyltetralins of known composition gave smooth curves when their refractive indices were plotted against composition. The infrared spectra of the tetralins were measured; two characteristic absorption maxima for each tetralin were selected, and paired, and the spectra of the mixtures measured in a standard 0·1 mm. cell. The differences in optical density for each pair of maxima were plotted against composition, giving a smooth curve.

For these methods of analysis to be accurate the reduction product of the alkylnaphthalene must consist only of the two alkyltetralins and must contain no decalins or unreduced

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[1] Bamberger and Althausse, *Ber.*, 1888, **21**, 1786.
[2] Bamberger and Müller, *ibid.*, p. 847.
[3] Musser and Adkins, *J. Amer. Chem. Soc.*, 1938, **60**, 664.
[4] Fieser and Jones, *ibid.*, p. 1940.
[5] Adkins and Davis, *ibid.*, 1949, **71**, 2956.
[6] Schroeter, *Ber.*, 1921, **54**, 2242.
[7] Lévy, *Ann. Chim.* (*France*), 1938, **9**, 5,
[8] Staveley and Smith, *J. Inst. Petroleum*, 1956, **42**, 55; Bailey and Staveley, *ibid.*, p. 97.
[9] Hipsher and Wise, *J. Amer. Chem. Soc.*, 1954, **76**, 1747.
[10] Karo, McLaughlin, and Hipsher, *ibid.*, 1953, **75**, 3233.

alkylnaphthalene. Raney nickel is reported [3, 4, 5] to give mixtures of tetralin contaminated with naphthalene and decalin. The most satisfactory catalyst for hydrogenation of naphthalenes to tetralins is copper chromite since this is inactive to the benzene nucleus and decalins are not formed.[3, 9, 11] 1-Alkylnaphthalenes have been reduced with this catalyst,[9] and no tetralin or unchanged alkylnaphthalene was detected.

Measurements of refractive index of the hydrogenation product usually indicated a higher proportion of the less refractive component (the 2-alkyltetralin) than did the infrared spectra; this may have been due to lowering of the refractive index by traces of impurity in the mixture. The rate of change in refractive index of mixtures of 2- and 6-alkyltetralins with change in composition is small; for example a 10% difference in composition of the 2-*n*-propyltetralins corresponds to a change of 0·0006 unit in refraction. It is thought therefore that more reliance should be placed on the infrared spectra.

The results show that the products obtained by catalytic hydrogenation of four 2-alkylnaphthalenes consist of mixtures of the 2- and 6-alkyltetralins, the 6-isomer constituting 60—65%.

Reduction of naphthalene with sodium and ethanol gives 1 : 4-dihydronaphthalene, whilst reduction with sodium and pentyl alcohol yields tetralin; [12, 13] Veselý and Kapp [14] examined the sodium–ethanol reduction of 1- and 2-methylnaphthalene and found (by oxidative methods) that the unsubstituted ring was reduced. Lévy [7] observed that reduction of 2-ethylnaphthalene by sodium and pentyl alcohol gave a product containing 97% of ethyldihydronaphthalenes (by bromine titration), but did not examine the product further. We have repeated Lévy's work and confirmed the fact that this reduction proceeds only to the dihydro-stage; the product was then reduced to the tetrahydro-stage with palladium–strontium carbonate at room temperature (it was shown that 2-ethylnaphthalene itself was unaffected under these conditions). The product was a mixture of 2- and 6-ethyltetralin containing 52—58% of the 6-isomer; the product from copper chromite reduction of 2-ethylnaphthalene contained 61—66% of the 6-isomer.

These results show that, contrary to most statements in the literature, reduction of a 2-alkylnaphthalene gives rise to both the 2- and the 6-alkyltetralin, the proportion of the isomers being approximately 1 : 2.

EXPERIMENTAL

M. p.s and b. p.s were determined with short-stem Anschütz thermometers; infrared spectra were measured on a Perkin-Elmer spectrophotometer, on slit schedule 4, as liquids, in a 0·1 mm. cell.

2-Alkylnaphthalenes.—A pure specimen [15] of 2-methylnaphthalene, m. p. 34·2°, was available. The other alkylnaphthalenes were obtained by acylating naphthalene in nitrobenzene solution and reducing the pure products by Huang-Minlon's procedure. Methyl 2-naphthyl ketone, m. p. 53—54°, gave 2-ethylnaphthalene, b. p. 118°/13 mm., m. p. −7·3°, n_D^{20} 1·5999 (picrate, m. p. 77—77·5°) (lit.,[15] m. p. −7°, n_D^{20} 1·5999; picrate, m. p. 77°). Ethyl 2-naphthyl ketone, m. p. 60°, gave 2-*n*-propylnaphthalene, b. p. 127—128°/8 mm., m. p. −3·9°, n_D^{20} 1·5878 (lit.,[15] m. p. −3°, n_D^{20} 1·5872). 2-Naphthyl *n*-propyl ketone, m. p. 54·7—55°, gave 2-*n*-butylnaphthalene, b. p. 145°/9 mm., m. p. −6·1°, n_D^{20} 1·5776 (lit.,[16] m. p. −5°, n_D^{20} 1·5776).

The preparation of pure specimens of 2- and 6-alkyltetralins has been described previously.[8]

Methyltetralins.[8]—2-Methyltetralin, n_D^{20} 1·5267, had suitable infrared bands at 9·00 and 9·91 μ, and 6-methyltetralin, n_D^{20} 1·5352, at 10·16 and 11·63 μ. Properties of mixtures are tabulated (O.d. = optical density).

2-Methyltetralin (%)	n_D^{20}	$O.d._{11·6} - O.d._{9·91}$	$O.d._{9·0} - O.d._{10·16}$
29·4	1·5329	0·203	0·085
46·5	1·5312	0·096	0·257
64·0	1·5298	−0·008	0·403
Hydrogenation product	1·5310	0·160	0·186

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[11] Adkins and Reid, *J. Amer. Chem. Soc.*, 1941, **63**, 741.

[12] Bamberger and Lodter, *Ber.*, 1887, **20**, 3075; Bamberger and Kitschelt, *Ber.*, 1890, **23**, 1561.

[13] Straus and Lemmel, *Ber.*, 1913, **46**, 232; Strauss, *ibid.*, p. 1051.

[14] Veselý and Kapp, *Coll. Czech. Chem. Coll.*, 1931, **3**, 448.

[15] Morrell, Pickering, and Smith, *J. Inst. Petroleum*, 1948, **34**, 677.

[16] Bailey, Pickering, and Smith, *ibid.*, 1949, **35**, 103.

2-Methylnaphthalene (20 g.) in ethanol (100 c.c.) was hydrogenated in the presence of copper chromite catalyst (4 g.) at 220° for 6 hr.; the initial pressure of hydrogen at room temperature was 117 atm. After removal of the catalyst and solvent the residue distilled at 129—132°/16 mm. The absorption at 3200 Å was too small to be measured, showing the absence of 2-methylnaphthalene. The refractive index of the product, n_D^{20} 1·5310, indicates 52% of 6-methyltetralin; the infrared data show 61—64% of 6-methyltetralin.

Ethyltetralins.—2-Ethyltetralin, n_D^{20} 1·5252, had suitable infrared bands at 9·1 and 10·14 μ, and 6-ethyltetralin, n_D^{20} 1·5322, at 10·30 and 11·65 μ. Properties of mixtures are tabulated.

2-Ethyltetralin (%)	n_D^{20}	O.d.$_{9\cdot1}$ — O.d.$_{10\cdot30}$	O.d.$_{11\cdot65}$ — O.d.$_{10\cdot14}$
31·2	1·5309	−0·225	0·32
50·0	1·5297	−0·093	0·218
65·6	1·5283	0·036	0·119
Hydrogenation product	1·5294	−0·166	0·300

2-Ethylnaphthalene was hydrogenated at 190—199° as described for 2-methylnaphthalene; the product had b. p. 105—108°/13 mm. and the extinction at 3200 Å indicated less than 0·3% of 2-ethylnaphthalene. The content of 6-ethyltetralin was 48% (by refractive index), 61—65% (from the infrared spectra). A solution of 2-ethylnaphthalene (15 g.) in boiling *n*-pentyl alcohol (150 c.c.) was treated with sodium (15·5 g.). When all the metal had reacted the solution was poured into water, and the organic layer was separated, washed with water, dilute hydrochloric acid, and water, and distilled; the fraction of b. p. 116—118°/12 mm. had n_D^{20} 1·556 (Lévy[7] reports n_D^{13} 1·5551). It was unsaturated to permanganate. A sample (13 g.) in ethanol (30 c.c.) was hydrogenated in the presence of palladised strontium carbonate at room temperature and 4 atm. (1 mol. absorbed). The solution was filtered, the solvent removed, and the residue distilled; the distillate was stirred with sodium and redistilled. The product had O.d.$_{9\cdot1}$ − O.d.$_{10\cdot30}$ = −0·099 and O.d.$_{11\cdot65}$ − O.d.$_{10\cdot14}$ = 0·262. The infrared data thus indicate 52—58% of 6-ethyltetralin.

n-*Propyltetralins.*—2-*n*-Propyltetralin, n_D^{20} 1·5202, had suitable infrared bands at 9·63 and 10·60 μ, and 6-*n*-propyltetralin, n_D^{20} 1·5263, at 10·1 and 11·0 μ. Properties of mixtures are tabulated.

2-*n*-Propyltetralin (%)	n_D^{20}	O.d.$_{10\cdot6}$ — O.d.$_{11\cdot0}$	O.d.$_{9\cdot63}$ — O.d.$_{10\cdot1}$
19·7	1·5255	−0·625	−0·192
51·5		−0·21	−0·067
53·3	1·5237	−0·19	0·068
72·4	1·5225	0·355	0·313
Hydrogenation product	1·5237	−0·441	−0·050

2-*n*-Propylnaphthalene was hydrogenated at 150° (initial pressure of hydrogen, 112 atm. at 20°). The product, b. p. 129—132°/16 mm., n_D^{20} 1·5245, had ε 7·93 at 3190 Å, indicating *ca.* 1·3% of unreduced *n*-propylnaphthalene. This will increase the refractive index by 0·0008; the corrected refractive index is therefore 1·5237, corresponding to 47% of 6-*n*-propyltetralin; the infrared spectra indicate 60—63% of the 6-isomer.

n-*Butyltetralins.*—2-*n*-Butyltetralin, n_D^{20} 1·5161, had suitable infrared bands at 9·65 and 10·60 μ, and 6-*n*-butyltetralin, n_D^{20} 1·5220, at 10·1 and 11·0 μ. Properties of mixtures are tabulated.

2-*n*-Butyl tetralin (%)	n_D^{20}	O.d.$_{10\cdot6}$ — O.d.$_{11\cdot0}$	O.d.$_{10\cdot1}$ — O.d.$_{9\cdot65}$
32·2	1·5202	−0·055	0·100
46·9	1·5195	0·060	−0·020
70·7	1·5181	0·232	−0·182
Hydrogenation product	1·5193	−0·012	0·068

2-*n*-Butylnaphthalene was reduced as described for 2-methylnaphthalene; the product had b. p. 150—152°/20 mm., and the extinction at 3200 Å was too small to be measured. The content of the 6-isomer was 52% by refractive index and 62—64% by infrared spectra.

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