

244. *Studies in Tar Hydrocarbons. Part II. Derivatives of 2 : 3-Dimethylnaphthalene.*

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When 2 : 3-dimethylnaphthalene is hydrogenated at 350° with an active charcoal-ammonium molybdate-sulphur catalyst the chief product is 1 : 2 : 3 : 4-tetrahydro-6 : 7-dimethylnaphthalene, but the *cis*- and the *trans*-form of 1 : 2 : 3 : 4-tetrahydro-2 : 3-dimethylnaphthalene are formed to a lesser degree, as well as decahydro-derivatives of 2 : 3-dimethylnaphthalene.

Sulphonation of 2 : 3-dimethylnaphthalene at low temperatures takes place with formation of 2 : 3-dimethylnaphthalene-5-sulphonic acid. The sodium salt furnishes on caustic fusion 6 : 7-dimethyl-1-naphthol of which the structure was proved by synthesis.

It was recently shown (J., 1935, 77) that good yields of 1 : 2 : 3 : 4-tetrahydro-2 : 6- and -2 : 7-dimethylnaphthalenes, required for the production of certain homologues of naphthacene, could be obtained by the hydrogenation of 2 : 6- and 2 : 7-dimethylnaphthalene. In continuation of these studies of naphthalene homologues, the hydrogenation with an ammonium molybdate-sulphur-active carbon catalyst of 2 : 3-dimethylnaphthalene was carried out under similar conditions, but the product was much less simple and merited fuller examination. The main constituent (50%) is 1 : 2 : 3 : 4-tetrahydro-6 : 7-dimethylnaphthalene (b. p. 248—256°), which has already been obtained synthetically (Barnett and Saunders, J., 1933, 434), but besides 6% of unchanged 2 : 3-dimethylnaphthalene there was about 44% of material, b. p. 210—246°, and this contained decahydro-derivatives and also the isomeric *cis*- and *trans*-forms of 1 : 2 : 3 : 4-tetrahydro-2 : 3-dimethylnaphthalene.

The separation of the two forms of this dimethyltetralin was effected by fractional distillation, three large fractions being obtained : (a) b. p. 222—224°, (b) b. p. 232—234°, and (c) b. p. > 250°. Fraction (a) consisted chiefly of dimethyldecalin. The dimethyltetralin present in this fraction, after removal as sulphonic acid, was recovered by desulphonation and shown by analysis and oxidation to consist of a *cis*- or *trans*-isomeride (A) of 1 : 2 : 3 : 4-tetrahydro-2 : 3-dimethylnaphthalene, b. p. 222—224°. Fraction (b) contained only a small proportion of decahydro-derivatives and consisted chiefly of the other *cis*- or *trans*-isomeride (B) of 1 : 2 : 3 : 4-tetrahydro-2 : 3-dimethylnaphthalene, b. p. 229—231°. The sodium dimethyltetralinsulphonates derived from both fractions (a) and (b) each gave the same two isomeric sulphonamides but in a different proportion; the main constituent of the mixture from (a) melted at 210—211° (A), and that from (b) at 143° (B).

It is unreasonable to suppose that in the sulphonation of *cis*- and *trans*-1 : 2 : 3 : 4-tetrahydro-2 : 3-dimethylnaphthalene any more than insignificant amounts of the 5-derivatives are formed, since only the 6 : 7-dimethyl-2-naphthol could be isolated after caustic fusion and dehydrogenation of the sulphonation products (cf. tetralin; Schroeter, *Annalen*, 1921, 426, 112). The two sulphonamides are not therefore merely position isomers, and the well-marked difference in m. p., coupled with the slight but quite definite differences in the b. p.'s of the hydrocarbons and of the corresponding tetralols, is sufficient to prove that the A and B forms are *cis*-*trans*-isomerides in each case. From the fact that both sulphonamides are obtained from each sodium sulphonate, although in very different proportions, it might appear that the two forms of the dimethyltetralin have not been completely separated, but it is suggested that to some extent interconversion occurs under the action of phosphorus pentachloride during the preparation of the sulphonamides. At present it is impossible to assign definitely to either form the *cis*- or the *trans*-structure.

Synthesis of 6 : 7-Dimethyl-1-naphthol.—It was not possible to get either 1 : 2 : 3 : 4-tetrahydro-6 : 7-dimethyl-5-naphthol or 2 : 3-dimethyl-1-naphthol, by caustic fusion of sodium 1 : 2 : 3 : 4-tetrahydro-6 : 7-dimethylnaphthalene-5-sulphonate. After fusion in an open pot there were isolated small amounts of 6 : 7-dimethyl-2-naphthol, m. p. 160° (identical with a specimen made by Kruber's method, *Ber.*, 1929, 62, 3044), and 6 : 7-dimethyl-1-naphthol, m. p. 140°. It is clear that these are products of secondary reactions.

At first it was not suspected that the 6 : 7-dimethyl-1-naphthol was other than the unknown 2 : 3-dimethyl-1-naphthol, and in order to complete the series of the three dimethylnaphthols derived from 2 : 3-dimethylnaphthalene the synthesis of 6 : 7-dimethyl-1-naphthol was effected from 1-keto-1 : 2 : 3 : 4-tetrahydro-6 : 7-dimethylnaphthalene, prepared by ring closure from γ -3 : 4-dimethylphenyl-*n*-butyric acid (Barnett and Saunders, *J.*, 1933, 436; Kröppfeiffer and Schäfer, *Ber.*, 1923, 56, 620). The 2 : 4-dinitrophenylhydrazone of the ketone is a stable substance formed slowly when an alcoholic solution of the components is boiled, rapidly in boiling acetic acid. Prepared from the cyclisation product, m. p. 49°, it is obtained in quantitative yield as a homogeneous individual substance; but if the ketone is boiled with phenylhydrazine in alcohol, the somewhat unstable phenylhydrazone first formed passes rapidly with loss of ammonia into 1 : 2-(4' : 5'-dimethylbenz)-3 : 4-dihydrocarbazole. By controlled bromination of the ketone there was obtained 2-bromo-1-keto-1 : 2 : 3 : 4-tetrahydro-6 : 7-dimethylnaphthalene, which lost hydrogen bromide and underwent rearrangement into the required 6 : 7-dimethyl-1-naphthol, m. p. 140°, when a solution in diethylaniline was boiled. Comparison of this synthetical specimen with that obtained by caustic fusion of sodium 1 : 2 : 3 : 4-tetrahydro-6 : 7-dimethylnaphthalene-5-sulphonate proved the identity of the two.

Sulphonation of 2 : 3-Dimethylnaphthalene.—When 2 : 3-dimethylnaphthalene is sulphonated at a high temperature, *viz.*, 160°, the sulphonic group is introduced in the 6-position (Kruber, *loc. cit.*). It is now found that the hydrocarbon is quite readily sulphonated at lower temperatures when dissolved in an inert solvent, *e.g.*, decalin or carbon tetrachloride. Either chlorosulphonic acid at 0—10° or concentrated sulphuric acid at 40—50° introduced a sulphonic group in the 5-position, and good yields of the pure homogeneous barium 2 : 3-dimethylnaphthalene-5-sulphonate were obtained by crystallisation of the crude barium salt of the sulphonation product from water. 6 : 7-Dimethyl-1-naphthol

is obtainable in good yield more conveniently by caustic fusion of *sodium 2 : 3-dimethylnaphthalene-5-sulphonate* than by the synthetic method.

EXPERIMENTAL (with ERIC C. HOLT).

Hydrogenation of 2 : 3-Dimethylnaphthalene.—500 G. of the hydrocarbon, when hydrogenated at 350—360° (J., 1935, 81), afforded 462 g. of liquid product. On fractionation in a 2' Dufton column, this boiled between 210° and 265°, but a large fraction, consisting essentially of 1 : 2 : 3 : 4-tetrahydro-6 : 7-dimethylnaphthalene (222.5 g.), boiled between 248° and 256°. Of the remainder, 25 g., b. p. 256—265°, crystallised as 2 : 3-dimethylnaphthalene; the rest, 200 g., b. p. 210—246°, was refractionated 6 times, and 3 relatively large sub-fractions were collected: (a) b. p. 222—224°, 19.6 g. (59.9 g. boiled between 218° and 226°); (b) b. p. 232—234°, 37.0 g. (63.0 g. boiled between 230° and 236°); (c) b. p. > 250°, 20.0 g.

If lower temperatures than 350—360° were used, other conditions being unchanged, relatively more dimethylnaphthalene escaped hydrogenation. When the reaction temperature was 390° and the time 2—3 hours, a relatively larger amount of the lower-boiling fraction (64 g., b. p. 214—220°, from 250 g. of dimethylnaphthalene) was obtained and less of the 1 : 2 : 3 : 4-tetrahydro-6 : 7-dimethylnaphthalene fraction (45 g., b. p. 248—256°), while 51 g. of the hydrocarbon escaped unhydrogenated.

1 : 2 : 3 : 4-Tetrahydro-6 : 7-dimethylnaphthalene.—When the crude dimethyltetralin, b. p. 248—256°, was shaken with 1½ times its weight of concentrated sulphuric acid with gentle heating below 60°, it was almost completely sulphonated in ½ hour. The deep red solution of sulphonic acid in excess of sulphuric acid was diluted, treated with barium carbonate, and the sparingly soluble *barium 1 : 2 : 3 : 4-tetrahydro-6 : 7-dimethylnaphthalene-5-sulphonate* purified by crystallisation from boiling water, from which it separates in minute colourless or pearly flakes [Found, after drying for 1 hour at 110°: S, 8.9. (C₁₂H₁₅SO₃)₂Ba, 6H₂O requires S, 9.0%]; yield 50% of theoretical. The *sodium* salt, obtained by treating this with sodium sulphate, is moderately soluble in water and crystallises in pearly flakes (Found, after drying for 1 hour at 110°: S, 8.3. C₁₂H₁₅SO₃Na, 7H₂O requires S, 8.3%).

The homogeneity and purity of the sodium salt and therefore of the barium salt was shown by conversion of the former into 1 : 2 : 3 : 4-tetrahydro-6 : 7-dimethylnaphthalene-5-sulphonamide in almost quantitative yield by fusion with an equal weight of phosphorus pentachloride and boiling the crude viscid sulphonyl chloride with concentrated ammonia solution. The sulphonamide crystallised from aqueous alcohol in minute colourless needles or plates, m. p. 135° (Found: C, 59.8, 60.23; H, 7.1, 7.3; N, 6.0. C₁₂H₁₇O₂NS requires C, 60.25; H, 7.1; N, 5.9%).

A pure specimen of 1 : 2 : 3 : 4-tetrahydro-6 : 7-dimethylnaphthalene, obtained by passing steam through a solution of the pure sodium salt in 50% sulphuric acid and extracting the aqueous distillate with petrol (b. p. 40—60°), and purified by distillation through an 8" Dufton column and over sodium, was a clear limpid oil (yield 81% of theor.), b. p. 244—246°. When cooled it set to a mass of colourless needles or prisms, m. p. 10° (Found: C, 90.3; H, 10.0. C₁₂H₁₈ requires C, 90.0; H, 10.0%). A boiling aqueous suspension of 1.5 g. of purified 1 : 2 : 3 : 4-tetrahydro-6 : 7-dimethylnaphthalene was treated with small portions of potassium permanganate until the latter was no longer decolorised after short boiling; sufficient alcohol was added to destroy the excess permanganate, and the filtered solution made acid, cooled, and thoroughly extracted with ether. Pyromellitic acid was recovered from the ethereal extract and purified by crystallisation from acetone-benzene; yield 0.5 g., m. p. 264° (decomp.).

Caustic Fusion of Sodium 1 : 2 : 3 : 4-Tetrahydro-6 : 7-dimethylnaphthalene-5-sulphonate.—The dry salt (20 g.) was added to a hot solution of 80 g. of potassium hydroxide in a few c.c. of water, and the temperature raised rapidly to 290°, below which no reaction occurs. After being kept at 300—330° for 10 minutes, the melt was cooled, diluted, made acid, and extracted with ether. The extract, after washing with sodium bicarbonate solution and water, was evaporated, affording a thick red phenolic oil. This was distilled in a vacuum, and the fraction of b. p. 140—148°/3 mm. (ca. 1.0 g.) set on cooling; when crystallised from benzene-petrol (b. p. 40—60°), it yielded 0.2 g. of pure 6 : 7-dimethyl-1-naphthol, identical in appearance and m. p. with an authentic sample (see below). The mother-liquor contained a second phenolic substance which crystallised in tufts of fine needles, m. p. 160°, and was shown by analysis and comparison with an authentic specimen to be 6 : 7-dimethyl-2-naphthol.

It was thought that carrying out the caustic fusion in a hydrogen atmosphere might prevent dehydrogenation. Accordingly, 88 g. of potassium hydroxide were dissolved in 200 c.c. of previously boiled water, 72 g. of the dry sodium sulphonate added, and the whole sealed in a

1-litre autoclave and the air displaced with hydrogen at 20 atm. After 3 hours' heating at 350°, the products consisted chiefly of a neutral oil and elementary sulphur. When the fusion was repeated in nitrogen for 1 hour at 350°, the products consisted of 2 : 3-dimethylnaphthalene and 6 : 7-dimethyl-2-naphthol. By using a lower temperature and a shorter time (320° for $\frac{1}{2}$ hour), even more 2 : 3-dimethylnaphthalene was formed.

1 : 2 : 3 : 4-Tetrahydro-6 : 7-dimethyl-5-aminonaphthalene.—1 : 2 : 3 : 4-Tetrahydro-6 : 7-dimethylnaphthalene (32 g., b. p. 244—246°) was cooled below 5°, and a nitration mixture (made by cooling 80 g. of acetic anhydride and gradually adding 20 g. of nitric acid, *d* 1.52) was added with stirring, the temperature being kept below 5°. The mixture was poured on crushed ice but the crude nitro-compound, which separated as a thick, golden-yellow, heavy oil (40 g.), could not be purified either by crystallisation (it did not set even when cooled to - 80°) or by distillation (appreciable decomposition took place during distillation at 1—2 mm., b. p. 128—132°, and became rapid at higher pressures and temperatures). It was suspended in 400 g. of concentrated hydrochloric acid, and zinc dust (80 g.) added in small portions. The solution containing zinc chloride and the hydrochloride of the base was separated, made alkaline, and the precipitated zinc hydroxide filtered off and washed with ether to remove any base absorbed therein; the bulk of the base was obtained by ethereal extraction of the filtrate. Purified by fractional distillation in a vacuum, 5-amino-1 : 2 : 3 : 4-tetrahydro-6 : 7-dimethylnaphthalene (7.0 g.) formed a slightly viscid oil, colourless at first but rapidly darkening on exposure to air, of piperidine-like odour and b. p. 126—128°/2 mm. or 154—156°/15 mm. (Found : C, 81.9; H, 9.8. $C_{12}H_{17}N$ requires C, 82.3; H, 9.7%). The sulphate and hydrochloride are slightly soluble in water. The acetyl derivative crystallised from aqueous alcohol in colourless needles or elongated plates, m. p. 125° (Found : C, 77.4; H, 8.7; N, 6.4. $C_{14}H_{19}ON$ requires C, 77.4; H, 8.8; N, 6.5%).

A solution of the base (4.0 g.) in dilute sulphuric acid (4.5 g. in 200 g. of water) was cooled to 0°, and sodium nitrite (2.0 g.) added; the solution was stirred and allowed to warm to room temperature very slowly, a colourless precipitate being formed, and finally brought to the boil, whereupon the precipitate passed into a thick dark red oil. Of the oil, only a small proportion was phenolic; the rest was neutral but more than half of the base remained undiazotised in the aqueous solution and was recovered. As a method of preparing 1 : 2 : 3 : 4-tetrahydro-6 : 7-dimethyl-5-naphthol this was worthless.

Derivatives of cis- and trans-1 : 2 : 3 : 4-Tetrahydro-2 : 3-dimethylnaphthalene.—The fraction (*b*), b. p. 232—234°, of the hydrogenation product (p. 1307) consisted chiefly of one of the two forms of 1 : 2 : 3 : 4-tetrahydro-2 : 3-dimethylnaphthalene, designated as the *B* form. Most of it boiled steadily at 233° but it contained at least 17.6% of decahydro-derivatives (Found : C, 89.4; H, 10.6%). When oxidised with potassium permanganate in boiling aqueous suspension, it gave only phthalic acid. It was sulphonated rapidly when shaken with 1½ times its weight of concentrated sulphuric acid, sufficient heat being evolved to raise the temperature to 40—50°. Barium 1 : 2 : 3 : 4-tetrahydro-2 : 3-dimethylnaphthalene-6-sulphonate (yield about 70%) is quite soluble in water and separates from a warm solution in colourless plastic needles which coalesce to a semi-solid mass, and on standing and cooling crystallise in pearly flakes. These still contain about 25% of water of crystallisation and melt on the steam-bath. After being heated for several hours at 110° in a vacuum, the barium salt formed a white micro-crystalline powder [Found : S, 10.3. $(C_{12}H_{15}SO_3)_2Ba$ requires S, 10.4%]. The sodium salt is even more soluble in water than the barium salt, and is very difficult to dehydrate (Found, after several hours' heating in a vacuum at 110° : S, 10.5. $C_{12}H_{15}SO_3Na$ requires S, 12.2%. $C_{12}H_{15}SO_3Na, 2H_2O$ requires S, 10.7%).

A pure specimen of the *B* form of 1 : 2 : 3 : 4-tetrahydro-2 : 3-dimethylnaphthalene was obtained by dissolving the steam-dried sodium sulphonate in 50% sulphuric acid, heating the solution to 140—160°, and then passing in steam. The dimethyltetralin was extracted from the aqueous distillate with petrol (b. p. 40—60°) and purified by fractional distillation. It was a clear colourless liquid, b. p. 229—231°, which set on cooling to a mass of fan-like tufts of needles, m. p. 4—8° (Found : C, 89.9; H, 10.2. $C_{12}H_{16}$ requires C, 90.0; H, 10.0%).

When 20 g. of the sodium sulphonate (dried on the steam-bath) had been heated for 10 minutes at 325—330° with 60 g. of potassium hydroxide, the product yielded, besides a very small and higher-boiling fraction which set on cooling and was recognised as the dehydrogenated 6 : 7-dimethyl-2-naphthol, 4 g. of a phenolic substance. This was purified by fractional distillation and obtained as a colourless or pale yellow oil, b. p. 130—132°/2 mm. It did not crystallise on cooling to - 80°, but when heated for 2 days at 310° with excess of selenium it was quantitatively dehydrogenated to 6 : 7-dimethyl-2-naphthol. There was no indication of

6 : 7-dimethyl-1-naphthol in the dehydrogenation product, although this crystallises in very characteristic and recognisable large needles even when mixed with the 2-isomeride. The dimethyltetralol is therefore homogeneous and is either the *cis*- or the *trans*-form (corresponding to the *B* dimethyltetralin above) of 1 : 2 : 3 : 4-tetrahydro-2 : 3-dimethyl-6-naphthol (Found : C, 81.6; H, 9.1. $C_{12}H_{16}O$ requires C, 81.8; H, 9.1%).

By fusion of 2 g. of sodium 1 : 2 : 3 : 4-tetrahydro-2 : 3-dimethylnaphthalene-6-sulphonate with 3 g. of phosphorus pentachloride there was obtained a sulphonyl chloride which was treated at once with concentrated ammonia solution (d 0.880). The crude sulphonamide (quantitative yield) contained two isomeric individuals. The predominant constituent was the more soluble and lower-melting; it separated from alcohol or aqueous alcohol in clusters of well-formed colourless needles, m. p. 143° (Found : C, 60.4; H, 7.1; N, 5.7. $C_{12}H_{17}O_2NS$ requires C, 60.25; H, 7.1; N, 5.9%). The other formed small colourless plates or needles, m. p. 210—211°, from alcohol (Found : C, 60.0; H, 7.2; N, 5.9%). These are considered to be the *cis*- and the *trans*-form of 1 : 2 : 3 : 4-tetrahydro-2 : 3-dimethylnaphthalene-6-sulphonamide, the lower-melting being assigned the *B* configuration.

The fractions of hydrogenation product, b. p. 218—226°, contained 75% of material which was not dissolved by concentrated sulphuric acid. This unattacked hydrocarbon boiled over a narrow range (68% at 218—220°) but is probably not an individual dimethyldecalin (6 stereoisomerides are possible) (Found : C, 86.5, 86.7; H, 13.5, 13.5. Calc. for $C_{12}H_{22}$: C, 86.8; H, 13.2%). The sulphonated material, although clearly a *cis*- or *trans*-form of 1 : 2 : 3 : 4-tetrahydro-2 : 3-dimethylnaphthalene, is sufficiently distinguishable from the *B* form to warrant the assignment to it of the alternative configuration (*A*). Barium 1 : 2 : 3 : 4-tetrahydro-2 : 3-dimethylnaphthalene-6-sulphonate (*A*) is similar to the *B* form in its solubility in and affinity for water and in its crystalline shape [Found, in material heated for several hours at 110° in a vacuum : S, 8.8. $(C_{12}H_{15}SO_3)_2Ba$ requires S, 10.4%. $(C_{12}H_{15}SO_3)_2Ba \cdot 6H_2O$ requires S, 8.9%]. The sodium sulphonate resembles that derived from the *B* dimethyltetralin in its solubility and affinity for water.

Pure *cis*- or *trans*-1 : 2 : 3 : 4-tetrahydro-2 : 3-dimethylnaphthalene (*A*) (3.5 g.) was obtained by desulphonating the corresponding sodium sulphonate (10 g., dried on the steam-bath) under the same conditions as the *B* derivative. It is a colourless oil which boils at a slightly lower temperature, 222—224°, than the *B* dimethyltetralin, crystallises in fine needles or plates when strongly cooled, and melts between -8° and -5° (Found : C, 89.8; H, 10.3. $C_{12}H_{16}$ requires C, 90.0; H, 10.0%). A mixture of the two forms melted over the range -8° to 3° . Upon oxidation with potassium permanganate in boiling aqueous suspension, the *A* dimethyltetralin furnished only phthalic acid.

Caustic fusion of sodium *cis*- or *trans*-1 : 2 : 3 : 4-tetrahydro-2 : 3-dimethylnaphthalene-6-sulphonate (*A*) was effected without marked dehydrogenation under conditions identical with those applied to the *B* isomeride. 1 : 2 : 3 : 4-Tetrahydro-2 : 3-dimethyl-6-naphthol (*A*) (3.0 g. from 10 g. of the sodium sulphonate) is a pale yellow liquid, b. p. 122—124°/2 mm., with a phenolic smell; it does not set on strong cooling (Found : C, 81.6; H, 9.2. $C_{12}H_{16}O$ requires C, 81.8; H, 9.1%). It was quantitatively dehydrogenated by 8 hours' heating with selenium at 310°, and the product contained only 6 : 7-dimethyl-2-naphthol.

The crude sulphonamide prepared from 2 g. of the sodium dimethyltetralinsulphonate (*A*) by fusion with phosphorus pentachloride (3 g.) and treatment of the melt with concentrated ammonia solution yielded on fractional crystallisation the same two individual sulphonamides as the *B* form but the relative proportions were reversed; the more plentiful (*A*) had m. p. 210—211°.

Synthesis of 2 : 3-Dimethyl-5-naphthol.—6 : 7-Dimethyl-1-keto-1 : 2 : 3 : 4-tetrahydro-naphthalene was purified by distillation in a vacuum, b. p. 138—140°/2 mm., 120—124°/1 mm., m. p. 49—51°. The *phenylhydrazone*, formed by boiling the ketone for 10 minutes in alcohol with phenylhydrazine, separated in cream needles, m. p. 120° (decomp.) (Found : C, 81.7; H, 7.9; N, 10.3. $C_{18}H_{20}N_2$ requires C, 81.8; H, 7.6; N, 10.6%). If a solution in acetic acid is boiled for $\frac{1}{4}$ hour, or if the ketone and phenylhydrazine are similarly heated in acetic acid, there results, by loss of ammonia and ring closure, 1 : 2-(4' : 5'-dimethylbenz)-3 : 4-dihydro-carbazole, which crystallises from alcohol in colourless flakes, m. p. 208° (Found : C, 88.0; H, 7.2; N, 5.8. $C_{18}H_{17}N$ requires C, 87.5; H, 6.9; N, 5.7%). The 2 : 4-dinitrophenylhydrazone is formed in boiling acetic acid solution and crystallises from this solvent in sparingly soluble scarlet flakes, m. p. 286° (decomp.) (Found : C, 60.98; H, 5.01; N, 15.6. $C_{18}H_{18}O_4N_4$ requires C, 61.02; H, 5.08; N, 15.82%).

When bromine (18.0 g.; 1 mol.) dissolved in carbon disulphide was added at room

temperature to a solution containing the ketone (20 g.), a yellow solid was first precipitated, but this gradually redissolved to a clear solution containing 2-bromo-1-keto-6 : 7-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene. This (29 g.) remained after evaporation of carbon disulphide, and was purified by crystallisation from benzene-petrol (b. p. 40—60°), being obtained in fine colourless needles, m. p. 102·5° (Found : C, 56·8; H, 5·3; Br, 31·6. $C_{12}H_{13}OBr$ requires C, 56·96; H, 5·14; Br, 31·6%). If more than 1 mol. of bromine was used, the product contained 2 : 2-dibromo-1-keto-6 : 7-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthalene, readily obtained in good yield by treating the monobromo-derivative with excess of bromine. Purified by crystallisation from benzene-petrol (b. p. 40—60°), it forms long colourless needles, m. p. 135° (Found : C, 43·4; H, 3·8; Br, 48·3. $C_{12}H_{12}OBr_2$ requires C, 43·4; H, 3·6; Br, 48·2%).

When the monobromo-compound (20 g.) was boiled for 1 hour with 100 g. of freshly distilled anhydrous diethylaniline, the product, after removal of basic substances, furnished 3 g. of 6 : 7-dimethyl-1-naphthol. This, when purified by distillation and by crystallisation from benzene-petrol (b. p. 40—60°), had m. p. 140°.

Sulphonation of 2 : 3-Dimethylnaphthalene.—(i) At 0—10°. To 19 g. of 2 : 3-dimethylnaphthalene, dissolved in 150 c.c. of carbon tetrachloride and cooled to 0°, were slowly added 14·5 g. of chlorosulphonic acid, and the whole was then poured on crushed ice. 6 G. of hydrocarbon escaped sulphonation, and from the aqueous solution of sulphonic acids there were obtained by treatment with barium carbonate 25 g. of crude barium sulphonates. This was fractionally crystallised from water and separated into (a) a very sparingly soluble fraction (2·0 g.), (b) the main bulk of homogeneous barium 2 : 3-dimethylnaphthalene-5-sulphonate (17·0 g.; 68%), and (c) the most soluble portion (6·0 g.). The principal salt crystallises from water in compact cream flakes [Found, after drying for 1 hour at 110° in a vacuum : S, 10·5. ($C_{12}H_{11}SO_3$)₂Ba requires S, 10·5%]. The sodium sulphonate is much more soluble in water and forms minute colourless pearly flakes (Found, after similar drying : S, 11·3. $C_{12}H_{11}SO_3Na \cdot 2H_2O$ requires S, 11·6%). By gently warming 2 g. of the dry sodium sulphonate with 3 g. of phosphorus pentachloride till all was liquid, then adding the melt to 20 c.c. of ammonia solution (*d* 0·880), 2 : 3-dimethylnaphthalene-5-sulphonamide was obtained in almost quantitative yield. After recrystallisation from acetic acid, from which it separates in cream flakes, it melted at 208° (Found : C, 60·9; H, 5·6; N, 6·0. $C_{12}H_{13}O_2NS$ requires C, 61·27; H, 5·53; N, 5·96%). The 2·0 g. of barium salt in fraction (a) were converted through the sodium salt into the corresponding sulphonamide, which melted at 227° and gave no depression when admixed with authentic 2 : 3-dimethylnaphthalene-6-sulphonamide.

(ii) At 40—50°. To the hydrocarbon (29 g.) dissolved in 500 c.c. of carbon tetrachloride were added 50 g. of concentrated sulphuric acid, and the whole was warmed to 40—50° and shaken. After 1 hour, the lower layer of sulphuric acid and sulphonation product was removed, and the warming and shaking repeated after addition of a further 25 g. of concentrated sulphuric acid. After a final treatment with another 25 g. of concentrated sulphuric acid, the sulphonation product was worked up as before, and the crude barium sulphonate (51 g.) was fractionally crystallised from water. The less soluble barium 2 : 3-dimethylnaphthalene-5-sulphonate (28 g.; 55%) did not appear to be contaminated with any of the sparingly soluble β -sulphonate.

Caustic Fusion of Sodium 2 : 3-Dimethylnaphthalene-5-sulphonate.—25 G. of the salt were added to 67 g. of fused potassium hydroxide containing 5 g. of water, the temperature raised to 290—310°, and maintained thereat for 10 minutes. After being cooled, diluted, and acidified, the solution was thoroughly extracted by ether, and the crude naphthol (14 g.), obtained after evaporation of ether, purified by distillation. 6 : 7-Dimethyl-1-naphthol boiled at 240—244°/22 mm., set on cooling, and melted at 140°. It is soluble in benzene, sparingly soluble in petrol (b. p. 40—60°), and crystallises from mixtures of the two solvents in well-formed colourless or cream needles (Found : C, 83·8; H, 7·2. $C_{12}H_{12}O$ requires C, 83·7; H, 7·0%).

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