

A Study of the Sulphonation of 2-Methylnaphthalene

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All seven monosulphonic acids are formed in the sulphonation of 2-methylnaphthalene with 93% sulphuric acid. A rise in temperature results in a decrease in the proportion of the 1- and the 3-sulphonic acids, and (in the range 40—160°) of the 4- and the 8-acids, with a corresponding increase in the proportion of the 6- and 7-acids.

THE behaviour of 2-methylnaphthalene (Ia) in electrophilic substitution reactions has recently been discussed.¹ In contrast to the 'normal' behaviour of the hydrocarbon (Ia), whose positional reactivities generally follow the sequence 1 > 8 > 4 > 5 ~ 6 > 3 > 7, the literature reveals a confused picture for the sulphonation reaction. Previous reports on the sulphonation of 2-methylnaphthalene (Ia) are summarised in Table I.

TABLE I

Literature data on the sulphonation of 2-methylnaphthalene

Ref.	Conditions	Position of substitution (% yield)
a	H ₂ SO ₄ , 20°	?
b	H ₂ SO ₄ (d 1.84), 90—100°	6-
c	ClSO ₃ H, PhNO ₂ , 30—40°	8-
d	H ₂ SO ₄ , 40°	8-
e	ClSO ₃ H, CCl ₄ , -5°	8- (25%), 1- (7%)
f	93% H ₂ SO ₄ , 40°	8- (74—77%) + 6- (some)*
	93% H ₂ SO ₄ , 95°	6- (89—96%) †
	93% H ₂ SO ₄ , 160°	7- (79—90%) ‡
g	96% H ₂ SO ₄ , 95—100°	6- (80%)
	96% H ₂ SO ₄ , 160—165°	6- (mainly) §

* Sulphones (0.8—1.4%) were also formed. † Sulphones (0.9—4.2%) were also formed. ‡ No other isomers were found at 160°; sulphones (5.0—9.1%) were also formed. § Yield of sulphones < 3%.

^a G. Wendt, *J. prakt. Chem.*, 1892, [2] **46**, 317. ^b Ref. 4. ^c K. Dziejowski and A. Wulffsohn, *Ann. Chim.*, 1929, [1] **9**, 78. ^d Ref. 2. ^e V. Vesely and J. Pac, *Coll. Czech. Chem. Comm.*, 1930, **2**, 471. ^f Ref. 3. ^g Ref. 5.

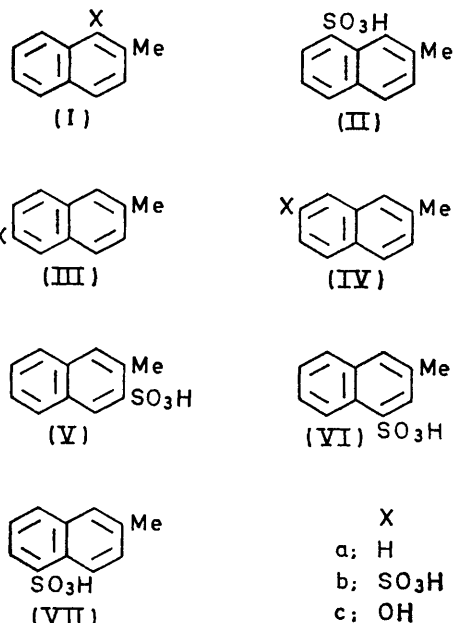
Reports suggest that with concentrated sulphuric acid the 8-isomer (II) is the main product at 40°^{2,3} and the 6-isomer (IIIb) at 95°.³⁻⁵ The exclusive formation of another isomer is reported for sulphonations carried out at 160°.³ The product, readily isolated because of the low solubility of its barium salt, could be degraded (by oxidation, followed by fusion with alkali) to 4-hydroxyphthalic acid. Since the acid was different from the known 2-methylnaphthalene-6-sulphonic acid † (IIIb), it was inferred that it was the 7-isomer (IVb).³ This conclusion has been challenged.⁶ On fusion with alkali of the sodium salts of the sulphonic acids formed in a sulphonation at 160—170°, a mixture of naphthols was formed. After several crystallisations a naphthol melting at 105—107° was obtained which was not identical with authentic 7-methyl-2-naphthol (IVc), m.p. 118°, obtained by an independent route.⁷

† In order to facilitate comparisons, the methylnaphthalene-sulphonic acids are numbered throughout with the methyl group in the 2-position.

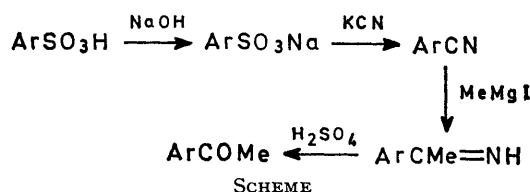
¹ P. H. Gore, A. S. Siddiquei, and S. Thorburn, *J.C.S. Perkin I*, 1972, 1781.

² G. T. Morgan and E. A. Coulson, *J. Soc. Chem. Ind.*, 1934, **53**, 73.

We have re-examined the action of 93% sulphuric acid on 2-methylnaphthalene (Ia) at 0, 40, 95, and 160°,



using the general reaction conditions recommended by Shreve and Lux.³ The analysis procedure employed was an indirect method of estimation (Scheme), which



should be regarded as only semi-quantitative. After the sulphonation reaction unchanged 2-methylnaphthalene and any sulphone (ArSO₂Ar) were removed. No attempt was made to examine the sulphones, since 28 isomers could have been formed. The sulphonic acid mixture was converted into the sodium salts, which on heating with potassium cyanide were converted into the corresponding carbonitriles. Addition of an excess of

³ R. N. Shreve and J. H. Lux, *Ind. Eng. Chem.*, 1943, **35**, 306.

⁴ K. Dziejowski, J. Schoenowna, and E. Waldmann, *Ber.*, 1925, **58**, 1211.

⁵ J. Reichel, A. Balint, A. Demian, and W. Schmidt, *Rev. Roumaine Chim.*, 1964, **9**, 751.

⁶ T. G. Halsall and D. B. Thomas, *J. Chem. Soc.*, 1956, 2564.

⁷ P. C. Mitter and S. De, *J. Indian Chem. Soc.*, 1939, **16**, 199.

methylmagnesium iodide, and acidic hydrolysis of the intermediate imines, afforded a mixture of methyl ketones. These acetyl derivatives of the hydrocarbon (Ia) could then be estimated by the g.l.c. procedure recently devised.¹ The method depends for its quantitative success on each step proceeding in the same yield for each isomer, on the absence of any isomerisation, and on the formation of disulphonic acids and of sulphones being unimportant. The last assumption appears to be justified.⁸ Disulphonation has been reported⁵ to become important especially for sulphonations carried out at 160° for longer reaction periods. Care was taken to allow the conversion stages to proceed for a sufficiently long period to ensure that the more slowly reacting isomers reacted substantially. For example, acidic hydrolysis of the mixture of imines was performed for 72 h, since it was known that certain hindered ketimines react very slowly.⁹ Even if the absolute values of the percentages of the isomers are in error, the results obtained for the different temperatures should be valid for comparison. The data obtained are summarised in Table 2. All seven isomers appear to be

TABLE 2
Sulphonation of 2-methylnaphthalene with 93% sulphuric acid for 8 h

Temp. (°C)	Yield (%) for substitution at position							Ratio $\alpha : \beta$ ^a
	1	3	4	5	6	7	8	
0	6.5	11	11	5.3	13	30	23	0.65
40	2.5	4.0	17	1.0	4.0	28	44	1.34
95	2.1	3.7	17	1.8	19	32	25	0.63
160	0.5	1.3	0.6	5.6	48	41	2.4	0.068

^a Normalised ($\times \frac{1}{2}$) to indicate mean relative reactivities.

formed with 93% sulphuric acid throughout the temperature range 0–160°. This contrasts with the reported formation only of the 6- (IIIb), 7- (IVb), and 8- (II) isomers.

The data obtained for sulphonations at 40, 95, and 160° appear to follow a regular pattern. With rise in temperature there is a decrease in the percentage of the 8- (II) and 4-isomers (VI) (α -naphthyl type), of the 1-isomer (Ib) (hindered α -naphthyl) and of the 3-isomer (V) (hindered β -naphthyl), accompanied by an increase in the percentage of the 6- (IIIb) and 7- (IVb) isomers (β -naphthyl). Such results were expected for a system where kinetic control initially favours the α -isomers, and thermodynamic control (operating for long reaction times or at higher temperatures) favours the β -isomers.¹⁰ The 3-isomer (V) is destabilised by the *ortho*-methyl group, which prevents full conjugation of the sulphonyl group with the naphthalene system; in this respect compound (V) behaves in this reaction more like an α -isomer. The 1-position of hydrocarbon (Ia), though electronically the most favoured position,^{1,11} is subject

⁸ A. Ito, *Kogyo Kagaku Zasshi*, 1959, **62**, 402 (*Chem. Abs.*, 1962, **57**, 8512).

⁹ W. E. Bachmann and M. C. Kloetzel, *J. Org. Chem.*, 1938, **3**, 55; W. E. Bachmann and L. J. Pence, *J. Amer. Chem. Soc.*, 1935, **55**, 1131; P. H. Gore, C. K. Thadani, and S. Thorburn, *J. Chem. Soc. (C)*, 1968, 2502.

to steric hindrance to attack by bulky electrophilic reagents, such as acylating reagents.¹ In the present system also, the low percentage of this isomer, even at 0°, is apparently due to steric hindrance.

The results obtained at 0° appear to be anomalous. An unexpectedly low ratio of α - to β -isomers is observed (Table 2), resulting from small proportions of the 4- (VI) and 8-isomers (II), and large proportions of the 6- (IIIb) and 7-isomers (IVb). The total yield of ketones in the reaction at 0° is less than half of that obtained at 40°, owing in part to the low solubility of the hydrocarbon (Ia) at 0°. At higher temperatures the sulphonation reaction becomes increasingly homogeneous, but at 0° is almost wholly heterogeneous, and thus diffusion-controlled. The small quantity of the hydrocarbon which is sulphonated remains in the acid phase, and rearrangement of the α -isomers to the β -isomers can proceed. The ratios of isomers observed at 0°, after an 8 h reaction, are therefore far from those in a mixture of isomers formed under kinetic control. It is noteworthy, however, that for other (less reactive) systems sulphonation is considered to be practically irreversible at low temperatures.¹²

At 160° the yields of both the 6- (IIIb) and 7-isomers (IVb) are at their maximum, as expected for reversible sulphonation.

Our results show that the claim³ of the formation in high yield of different isomers at 40, 95, and 160°, can be discounted. Similarly, the reported predominant formation of the 6-isomer (IIIb) with sulphuric acid at 90–100°,^{3,5} is now shown to be incorrect. The validity of the isolation procedure of the 6-acid (IIIb) *via* its barium salt, must therefore be brought into question. The earlier claim^{2,3} of the predominant formation of the 8-isomer (II) by sulphuric acid at 40° is shown to be qualitatively correct. The results obtained at 160° point to substantial and nearly equal formation of the 6- (IIIb) and 7-isomers (IVb). The earlier confusion (see before) of interpretation can now be resolved. It appears that purification *via* the barium salts resulted in the isolation of the relatively insoluble barium salt of 2-methylnaphthalene-7-sulphonic acid (IVb).³ Addition of sulphuric acid to the mixed sulphonic acids caused 'salting out' of the less soluble 6-acid (IIIb),⁵ and when the mixed sodium salts were converted into the corresponding naphthols, the most abundant 2-methyl-6-naphthol (IIIc) was obtained pure by recrystallisation.⁶

EXPERIMENTAL

*Sulphonations.*³—Equal weights of 2-methylnaphthalene and 93% sulphuric acid were stirred for 8 h at the chosen

¹⁰ H. E. Fierz-David and P. W. Weissenbach, *Helv. Chim. Acta*, 1920, **3**, 312; O. N. Witt, *Ber.*, 1915, **48**, 743; F. M. Vainshtein and E. A. Shilov, *Zhur. obshchei Khim.*, 1957, **27**, 2559; N. N. Vorozhtsov, jun., V. A. Koptyug, and A. M. Komagorov, *Zhur. Vsesoyuz. Khim. obshch. im. D.I. Mendeleeva*, 1960, **5**, 232; A. A. Spryskov and N. A. Ovsyankina, *J. Gen. Chem. (U.S.S.R.)*, 1946, **16**, 1057; A. A. Spryskov, *ibid.*, p. 2126.

¹¹ C. Eaborn, P. Golborn, R. E. Spillett, and R. Taylor, *J. Chem. Soc. (B)*, 1968, 1112.

¹² A. A. Spryskov, *Zhur. obshchei Khim.*, 1960, **30**, 2449.

temperature. The mixture was cooled, then poured on crushed ice and set aside for 12 h. The solid precipitate was filtered off, and to the filtrate (at *ca.* 70 °C) a slight excess of barium oxide was added. The precipitate was filtered off, and washed with several portions of boiling water. To the combined filtrate and washings a slight excess of sodium carbonate solution was then added. The precipitate was filtered off and washed with several portions of hot water. The filtrate and washings were combined and evaporated to *ca.* 100 ml. On cooling a precipitate of sodium salts formed; this was filtered off. Evaporation of the mother liquors to dryness gave a second fraction of sodium salts. The combined solids were dried at 140–150 °C for 4 h, and used directly for the next stage.

Conversion into Carbonitriles.—The mixture of the sodium salts of 2-methylnaphthalene-sulphonic acids and half their weight of potassium cyanide was heated gently over a direct flame, and the vapours were condensed (benzene trap). The benzene extracts were combined, washed with 3*N*-hydrochloric acid and water, dried, and evaporated to leave the mixed carbonitriles.

Conversion into Methyl Ketones.—A solution of the mixed nitriles in benzene was added rapidly to a ten-fold excess

of methylmagnesium iodide in dry ether, and the mixture was boiled under reflux for 24 h. 3*N*-Sulphuric acid was then added, most of the solvent was distilled off, and the acid layer was boiled under reflux for 72 h. The cooled mixture was extracted with chloroform. The extract was

TABLE 3

Conversion of 2-methylnaphthalene (10 g) *via* the sulphonic acids and the carbonitriles into acetyl-2-methylnaphthalenes

Temp. (°C) of sulphonation	Sodium salts	Yields (g) Carbonitriles	Ketones
0	5.0	0.65	0.32
40	12	1.4	0.70
95	8	1.0	0.53
160	10	1.2	0.60

washed with water, dried, and evaporated to dryness. The yields obtained in the separate stages of these conversions are recorded in Table 3. G.l.c. analyses were then carried out on the mixed ketones.¹

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