# CCCCXIV.—*The Alleged Nitration of* S-*Methylthioguaiacol. A Criticism.*

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HOLMES, INGOLD, and INGOLD (this vol., p. 1684) have described the mononitration of *S*-methylthioguaiacol by means of a mixture of nitric acid and acetic anhydride and state that the liquid product, $SMe{\cdot}C_6H_3(OMe){\cdot}NO_2$, may be oxidised by cold fuming nitric acid to a related sulphone, $C_8H_9O_5NS$, m. p. 144—145°. This substance was found to differ from the 3-, 4-, and 5- nitro-2-methoxyphenylmethylsulphones, which were synthesised for comparison, and was by exclusion regarded as 6-nitro-2-methoxyphenylmethylsulphone. The conclusion was drawn that the nitroxyl entered the *o*-position to the methylthiol group and the authors, far from expressing surprise at so remarkable a result, proceeded to develop a theory which accommodated it. This hypothesis, which we consider to be an unsound development of the theory of crotenoid systems, cannot be discussed here because we do not understand it. We especially fail to comprehend the meaning of the phrase " externally neutralised " on p. 1686 (*loc. cit.*).

In short, we were disposed to doubt the correctness of Holmes, Ingold, and Ingold's conclusion as to the *o*-substitution both on theoretical grounds and from analogies. The logical but dangerous method of exclusion of alternatives, relied upon by these authors, as mentioned above, was not supplemented either by the synthesis of the remaining possibility or by the close examination of the supposed 6-nitro-2-methoxyphenylmethylsulphone. Confirmatory evidence was all the more to be sought in view of the well-known fact that nitric acid is usually employed to oxidise a sulphide to a sulphoxide rather than to a sulphone.

We have had no difficulty in obtaining the substance, m. p. 144—145°, by following the instructions of Holmes, Ingold, and Ingold, but find that it is a sulphoxide in that it may be further oxidised by potassium permanganate to a sulphone. The latter was identified as 5-nitro-2-methoxyphenylmethylsulphone, m. p. 149—150° (Holmes, Ingold, and Ingold, *loc. cit.*). In the combined nitration and oxidation of *S*-methylthioguaiacol, therefore, the substituent enters chiefly the *p*-position to the methoxyl group.

It occurred to us that the explanation of the ultimate production of 5-nitro-2-methoxyphenylmethylsulphone might be that oxidation precedes nitration and that actually 2-methoxyphenyl methyl sulphoxide is the substance that is nitrated. If so, the position taken up by the substituent would be the normal one *p*- to the methoxyl group. This view cannot be reconciled with the results of Holmes, Ingold, and Ingold on the mononitration of *S*-methylthioguaiacol, which are very positive and described in the most precise manner; consequently we did not at first entertain the possibility. Nevertheless, on repetition of the experiment we obtained 2-methoxyphenyl methyl sulphoxide instead of the nitro-*S*-methylthioguaiacol which Holmes, Ingold, and Ingold state to be the product.

The nitration of *S*-methylthioguaiacol has not yet been accomplished and further work is necessary in order to establish the order of the directive efficiencies of sulphur and oxygen atoms directly attached to the aromatic nucleus.

## EXPERIMENTAL.

*2-Methoxyphenyl Methyl Sulphoxide.*—*S*-Methylthioguaiacol crystallises on standing and melts at about 19°. When it is treated as described by Holmes, Ingold, and Ingold (*loc. cit.*, p. 1687) under the heading *Mononitration*, the chief product is a yellow oil which crystallises after distillation (Found : C, 55·7 ;* H, 6·6. $C_8H_{10}O_2S$ requires C, 56·9 ; H, 5·9%). (For a pale yellow oil, prepared in this way but not found to crystallise, Holmes, Ingold, and Ingold gave C, 47·8; H, 4·4. $C_8H_9O_3NS$ requires C, 48·0; H, 4·5%.) On vigorous reduction with zinc dust and boiling dilute hydrochloric acid an oil, volatile in steam and having the odour of *S*-methylthioguaiacol, is produced. Oxidation with potassium permanganate gives a good yield of 2-methoxyphenylmethylsulphone, identified by comparison and by the m. p.† (91°) of a mixture with an authentic specimen. The sulphoxide is difficult to recrystallise, but separates from light petroleum in colourless prisms, m. p. 44° (Found : C, 56·6 ; H, 6·0%).

*5-Nitro-2-methoxyphenyl methyl sulphoxide* was prepared by the action of cold fuming nitric acid on *S*-methylthioguaiacol as described by Holmes, Ingold, and Ingold (*loc. cit.*) under the heading : *6-Nitro-2-methoxyphenylmethylsulphone.* We did not succeed in obtaining the 80% yield claimed by these authors, but the substance crystallised from methyl alcohol in very pale yellow needles, m. p. 144—145°, in agreement with their description (Found in air-dried

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* By microanalysis; a combustion on the ordinary scale gave a lower result for the carbon content.

† Troeger and Budde (*J. pr. Chem.*, 1902, **66**, 130) describe this sulphone as crystals, m. p. 84°, from alcohol. We have obtained it in colourless laminæ, m. p. 91°, from benzene–light petroleum.

material: C, 44·8; H, 4·2. $C_8H_9O_4NS$ requires C, 44·6; H, 4·2%). Holmes, Ingold, and Ingold gave C, 41·2; H, 3·9. $C_8H_9O_5NS$ requires C, 41·5; H, 3·9%.

The sulphoxide (0·85 g.) was dissolved in hot water (40 c.c.), and aqueous potassium permanganate (30 c.c. of 2%) added. After a few minutes, the small excess of the latter was reduced by alcohol, and the manganese dioxide converted into dithionate. The colourless precipitate (0·75 g.) crystallised from alcohol in colourless leaflets, which melted at 149—150° and at the same temperature when mixed with an authentic specimen of 5-nitro-2-methoxyphenylmethylsulphone (Holmes, Ingold, and Ingold, *loc. cit.*, describe pale yellow needles, m. p. 149°).

5-*Nitro*-2-*hydroxyphenylmethylsulphone*, $NO_2{\cdot}C_6H_3(OH){\cdot}SO_2Me$.—The sulphoxide, m. p. 144—145°, and the sulphone, m. p. 149—150°, are each readily hydrolysed by boiling dilute aqueous sodium hydroxide, yielding bright yellow alkaline solutions from which colourless compounds are precipitated on acidification. The reaction, strongly suggestive of the hydrolysis of *p*-nitroanisole derivatives, confirms our view of the nature of these substances. 5-Nitro-2-hydroxyphenylmethylsulphone dissolves in hot water to a yellow solution, from which flat, transparent needles are deposited on cooling; these change in contact with the solvent into an opaque, prismatic form, m. p. 167° (Found in material dried at 100°: N, 6·4, 6·4; S, 14·5. $C_7H_7O_5NS$ requires N, 6·5; S, 14·7%). The substance is readily soluble in aqueous sodium carbonate to a lemon-yellow solution. On the addition of bromine water to an aqueous solution a bromo-derivative is rapidly formed and soon separates in colourless, slender needles, m. p. 173°. This derivative dissolves in hot water to a bright yellow solution and is probably 3-bromo-5-nitro-2-hydroxyphenylmethylsulphone.

3 : 5-*Dinitro*-2-*hydroxyphenylmethylsulphone*.—A solution of 5-nitro-2-hydroxyphenylmethylsulphone in nitric acid (*d* 1·42) was boiled and then poured into water. The solid was collected and crystallised from water; a small amount of picric acid was isolated from the original acid liquor after concentration and removal of a further quantity of dinitrohydroxyphenylmethylsulphone. The latter crystallises from water or alcohol in brittle, sulphur-yellow needles, m. p. 166° (Found in material dried at 100°: N, 10·6; S, 12·1. $C_7H_6O_6N_2S$ requires N, 10·7; S, 12·2%). This substance resembles picric acid in its properties, dyes silk yellow, and develops a brownish-red coloration with aqueous potassium cyanide on heating.

The carbon, hydrogen, and nitrogen determinations (micromethods) recorded in this paper were made by Mr. A. Bennett.

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