

CCCCXV.—*Action of Nitric Acid on S-Methylthioguaiacol. A Correction.*

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IN the course of a systematic repetition, now nearly completed, of work described in certain previous communications from this laboratory, the following error has been detected. Holmes, Ingold, and Ingold (this vol., p. 1684) described a compound, m. p. 144—145°, which had been obtained as the main product of the action of excess of fuming nitric acid on *S*-methylthioguaiacol, and, owing (as it now appears) to the coincidence of an erroneous carbon and hydrogen determination,\* regarded it as 6-nitro-2-methoxyphenylmethylsulphone (*ibid.*, p. 1687), the orientation being deduced from its non-identity with 5-, 4-, or 3-nitro-2-methoxyphenylmethylsulphone, all of which had been synthesised by methods which placed their constitutions beyond doubt. We find, however, that the substance having m. p. 144—145° is really 5-nitro-2-methoxyphenyl methyl sulphoxide for the following reasons: (1) We have analysed it, with these results: Found: C, 44.9, 44.6, 44.7; H, 4.4, 4.2, 4.4.  $C_8H_9O_4NS$  requires C, 44.6, H, 4.2%. (A nitromethoxyphenylmethylsulphone would require C, 41.6; H, 3.9%). (2) We have also oxidised it (0.40 g.) by boiling for 8 minutes with 6 c.c. of dilute sulphuric acid (1:3 by volume) and potassium dichromate (0.30 g., previously dissolved in about 2 c.c. of water), and have thus obtained a sulphone (Found: C, 41.6; H, 4.0%), m. p. 147—148° (yield 0.27 g. after crystallisation from methyl alcohol; yield 0.40 g. and m. p. about 140° before crystallisation), which does not depress the m. p. of 5-nitro-2-methoxyphenylmethylsulphone prepared either from 4-nitro-*o*-anisidine or from 2-methoxyphenylmethylsulphone (*loc. cit.*).

The first action of nitric acid on *S*-methylthioguaiacol may be to convert it into the sulphoxide; alternatively,† the nitration may

\* This may possibly have been due to the escape of methane or ethane, an occurrence which we have experienced on several occasions recently with sulphur compounds containing the methoxyl and similar groups.

† Analyses which have been made of the crude product, b. p. 144—146°/2 mm. (*loc. cit.*), suggest both actions.

occur through the thionium nitrate, and the oxidation subsequently. In either case, it follows that the desired information regarding the relative directive powers of oxygen and sulphur probably cannot be obtained from the study of the nitration of *OS*-dialkyl derivatives of monothiopyrocatechol, and therefore we propose to examine the action of substituting agents on other sulphur derivatives. Also, the most extreme case hitherto recorded of the vicinal substitution of an *o*-disubstituted benzene containing two *op*-directing groups is furnished now, not by *S*-methylthioguaiacol, but by *o*-fluoroanisole (*ibid.*, pp. 1328, 1686).

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