#### NOTES.

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## Rây's Supposed Triethylene Trisulphide. By George Macdonald Bennett and William Ambler Berry.

MORE than two years ago one of us made the suggestion (J., 1922, 121, 2144, footnote) that the substance described by Rây (J., 1920, 117, 1090) as triethylene trisulphide was probably identical with the well-known diethylene disulphide (1:4-dithian).  $\mathbf{As}$ this suggestion was not accepted (J., 1923, 123, 2178, footnote), and as further reactions of "triethylene trisulphide" have been described (J. Indian Chem. Soc., 1924, 1, 63), the question has now been tested by direct experiment. The preparation was repeated as described by Rây, and 1.2 g. of the crystalline substance were obtained, of m. p. 113° (corr.) (Found : C, 39.9; H, 6.5. Calc., C. 40.0; H. 6.7%). The molecular weight of the substance in nitrobenzene solution agrees with the formula C<sub>4</sub>H<sub>8</sub>S<sub>2</sub> (Found : M, 128, 126. Calc., M, 120).\* The substance was compared directly with a specimen of dithian prepared as described by V. Meyer (Ber., 1886, 19, 3260): this melted at 113°, and its mixture with the supposed triethylene trisulphide melted equally sharply at the same temperature. The two substances had the same characteristic odour, the same remarkable volatility at laboratory temperature, and the same boiling point (200°). Their identity was finally confirmed by examination under the microscope, the crystals being clearly identical both in form and in optical properties.

It is unnecessary to discuss in detail the reactions which have been attributed to this "triethylene trisulphide," but it may be mentioned that among the substances prepared from it the "trisulphone" (J., 1923, 123, 2174) was evidently identical with Baumann and Walter's disulphone (*Ber.*, 1893, 26, 1132), and the "disulphone" was presumably an impure specimen of the same substance, and that the case of a nine-membered ring compound yielding a six-membered ring compound under the influence of ethyl iodide in alcoholic solution (J., 1922, 121, 1279) no longer requires any explanation.

It is evident that in some cases the derivatives described were not homogeneous substances, and this appears all the more probable where they were not purified by recrystallisation. The substance formulated as  $(C_2H_4)_3S_3PtCl_4$ , for instance (*loc. cit.*, p. 1283), was taken from a succession of crops of material giving analytical figures agreeing approximately with the formula stated. It is

<sup>\*</sup> Sir P. C. Rây is mistaken in supposing that a molecular-weight determination had previously been made by us with the substance; this method of testing the formula was left open to him in the first instance.

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now doubtful whether this crop was more homogeneous than those that preceded it.

Our thanks are due to the Department of Scientific and Industrial Research for a grant which has enabled one of us (W. A. B.) to take part in this work.—UNIVERSITY OF SHEFFIELD. [Received, March 6th, 1925.]

The Physiological Action of certain Benzothiazoles and Mercaptan Derivatives. By ROBERT FERGUS HUNTER.

4'-AMINO-1-PHENYL-5-METHYLBENZOTHIAZOLE (J. Soc. Chem. Ind., 1923, 42, 302) and certain related compounds have been found to have a peculiar action on the skin of the face and hands.

Hot solutions of dehydrothiotoluidine in contact with the skin develop an unpleasant form of eczema. The effect is worst between the fingers, and the irritation is intense during the first few days. The skin rises in peculiar, practically colourless blisters, which break, liberating a colourless infectious liquid which spreads the trouble.

Observations of this nature have been made by other investigators with regard to related sulphur compounds. Thus Hofmann (Ber., 1887, 20, 2251) states that the vapour of o-aminophenyl mercaptan has a most detrimental effect on the skin, producing intense irritation and swelling. The author has observed a similar effect produced by the higher homologue of this compound, namely, the thiocresol which results on the alkali fusion of dehydrothiotoluidine.

Bathing the infected skin in hot water relieves the irritation to a certain extent, and treatment with 2% aqueous phenol also has a beneficial action.—The IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY, S.W. 7. [Received, February 28th, 1925.]

# Preparation of 1-p-Sulphophenyl-3-methyl-5-pyrazolone. By George Reeves.

INGOLD (J., 1921, 119, 329) has put forward evidence in favour of the view that in condensations between tautomeric substances of the keto-enol type and substances which have active hydrogen the tautomeric substance reacts in the enolic form, the unsaturated linking being responsible for the initial condensation and the elimination of water being a subsequent effect. The methods employed to effect condensation between ethyl acetoacetate and phenylhydrazine-*p*-sulphonic acid (Cain, "Manufacture of Intermediate Products for Dyes," 1918 edition, p. 162; Fierz-David, "Grundlegende Operationen der Farbenchemie," 1924 edition, p.

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144) do not favour preliminary enolisation of the ester, which is apparently considered to react in the keto-form, and it occurred to the author to attempt the preparation of 1-p-sulphophenyl-3-methyl-5-pyrazolone under conditions which would tend to the preliminary enolisation of the ester, this being accomplished by using sodium phenylhydrazine-p-sulphonate in somewhat alkaline solution.

A solution of sodium phenylhydrazine-*p*-sulphonate (from 94 g. of the acid) in 750 c.c. of water was made strongly alkaline to litmus and treated quickly at 28° with 65 g. of redistilled ethyl acetoacetate. This dissolved at once and the temperature rose to 36°. After 15 minutes, the solution was heated at 90° for 2 hours, and then acidified with 100 c.c. of hydrochloric acid (28%), a copious precipitate forming rapidly. After 12 hours, the crystalline cake was collected and washed very quickly with a little water. The moist product weighed 226 g. and contained 123 g. of 1-*p*-sulphophenyl-3-methyl-5-pyrazolone (analysis by titration with N/10-benzenediazonium chloride). It was very clean and quite pure enough for use as an intermediate for dyes.—The ORCHARD, CHADDESDEN, DERBY. [Received, February 11th, 1925.]

## The Micro-estimation of Methoxyl. By JOHN CHARLES SMITH.

In using the method of Pregl (micro-Zeisel) for the estimation of methoxyl, very low results were obtained until it was noticed that the filtrate from the silver iodide gave a further precipitate on dilution with large quantities of alcohol and water. The silver nitrate stock solution had been made by dissolving 20 g. of silver nitrate in 200 g. of 95% alcohol as recommended in the English translation of Pregl's " Die Quantitative Organische Mikroanalyse " (Springer, Berlin, 1923). Reference to the German edition, however, showed that the concentration of the solution should be 20 g. of silver nitrate in 500 g. of 95% alcohol, and this was found to give good results.

The analyses were carried out on a very pure specimen of quinol monomethyl ether, m. p. 56° (OMe, 25.0%).

<i>a</i> . AgNO <sub>3</sub> soln., 20 g. in 200 g. of 95% EtOH.		b. $AgNO_3$ soln., 20 g. in 500 g. of 95% EtOH.		
Mg. of subs. Mg. of	AgI. OMe %.	Mg. of subs.	Mg. of AgI.	ОМе %.
3.263 5.504	4 22.3	3.335	6.178	24.5
3.841 4.50	0 15.5	$3 \cdot 828$	7.218	$24 \cdot 9$
3.110 4.43	1 18.8	4.396	8.304	24.9

THE UNIVERSITY, MANCHESTER. [Received, March 20th, 1925.]