NOTES.

Some Derivatives of m-*Phenylenediamine.* By F. BELL and R. COHEN.

Bromination of 1 : 3-*Di*-p-*toluenesulphonamidobenzene.*—10 G. of the powdered material were introduced into pyridine and bromine (7·7 g.) was added drop by drop to the thick mass of the pyridine salt. After 12 hours, the mixture was agitated with hydrochloric acid, and the solid collected and boiled with alcohol. The residue (7 g.), recrystallised from acetic acid, furnished 4 : 6-*dibromo*-1 : 3-*di*-p-*toluenesulphonamidobenzene* as stout needles, m. p. 209° (Found : N, 5·0. $C_{20}H_{18}O_4N_2Br_2S_2$ requires N, 5·0%). Hydrolysis with cold sulphuric acid gave the corresponding base, m. p. 134° (acetyl derivative, m. p. 257—260°). The alcoholic mother-liquor gave a further small yield of the same compound and some of the 2 : 4 : 6-tribromo-derivative (below).

Bromination of 4 : 6-*Dibromo*-1 : 3-*di*-p-*toluenesulphonamidobenzene.*—With excess of bromine in pyridine, this gave 2 : 4 : 6-*tribromo*-1 : 3-*di*-p-*toluenesulphonamidobenzene*, which formed needles, m. p. 223°, from acetic acid (Found : N, 4·4. $C_{20}H_{17}O_4N_2Br_3S_2$ requires N, 4·3%). This constitution was confirmed by hydrolysis to 2 : 4 : 6-tribromo-1 : 3-phenylenediamine, m. p. 162° (acetyl derivative, m. p. $>$300°).

1 : 3-*Di*-m-*nitrobenzenesulphonamidobenzene.*—The product of interaction of *m*-phenylenediamine and *m*-nitrobenzenesulphonyl chloride in pyridine was an oil. This was warmed with dilute aqueous sodium hydroxide, and the filtered solution introduced slowly into dilute hydrochloric acid. The resultant solid crystallised from acetic acid in plates, m. p. 195° (Found : N, 11·9. $C_{18}H_{14}O_8N_4S_2$ requires N, 11·7%).

Nitration. (a) To 10 g. in acetic acid (100 c.c.) at 70° was added fuming nitric acid (10 c.c.) in acetic acid (10 c.c.). On cooling, 4 : 6-*dinitro*-1 : 3-*di*-m-*nitrobenzenesulphonamidobenzene* separated; it formed needles (4 g.), m. p. 235°, after recrystallisation from acetic acid (Found : N, 15·0. $C_{18}H_{12}O_{12}N_6S_2$ requires N, 14·8%). On solution in sulphuric acid this gave 4 : 6-dinitro-1 : 3-phenylenediamine, m. p. 303° (acetyl derivative, m. p. 228°). No other pure product could be isolated from the mother-liquor. (b) The dinitro-compound (2 g.) was dissolved in fuming nitric acid (4 c.c.), and the solution diluted with acetic acid. The precipitate after recrystallisation from acetic acid gave 2 : 4 : 6-*trinitro*-1 : 3-*di*-m-*nitrobenzenesulphonamidobenzene* as stout prisms, m. p. 218° (Found : N, 15·6. $C_{18}H_{11}O_{14}N_7S_2$ requires N, 16·0%). On solution in sulphuric acid this compound furnished 2 : 4 : 6-trinitro-1 : 3-phenylenediamine, m. p. 285° (acetyl derivative, m. p. $>$300°).

Nitration of 1 : 3-*Di*-p-*toluenesulphonamidobenzene.*—(a) 10 G. were heated on a steam-bath with a mixture of acetic acid (40 c.c.) and nitric acid (5 c.c., *d* 1·4) for 2 hours. On cooling, 4 : 6-*dinitro*-1 : 3-*di*-p-*toluenesulphonamidobenzene* separated; after recrystallisation from acetic acid it formed pale yellow plates (7 g.), m. p. 208—210° (Found : N, 11·4. $C_{20}H_{18}O_8N_4S_2$ requires N, 11·1%). Apart from a further small quantity of the 4 : 6-dinitro-compound no pure product could be isolated from the mother-liquor. (b) Fuming nitric acid converted the dinitro-compound into 2 : 4 : 6-*trinitro*-1 : 3-*di*-o-*nitro*-p-*toluenesulphonamidobenzene*, which formed rhombohedra, m. p. 223°, from acetic acid (Found : N, 15·2. $C_{20}H_{15}O_{14}N_7S_2$ requires N, 15·3%). This compound was hydrolysed by sulphuric acid to 2 : 4 : 6-trinitro-1 : 3-phenylenediamine.—BATTERSEA POLYTECHNIC, S.W.11. [*Received, December* 19*th*, 1933.]

The Rates of Formation of Some Quaternary Phosphonium Salts. By W. CULE DAVIES and SIDNEY U. EVANS.

A PRELIMINARY study of the interaction of equivalent quantities of tri-*n*-propyl- and tri-*n*-butyl-phosphine with a series of *n*-alkyl bromides in dilute solution in acetone at 25° has shown that the rate of formation of the quaternary salt diminishes with increase in weight of the alkyl group of the organic bromide, and that the former phosphine is more reactive than the latter. The reactivity towards alkyl halides of the phosphines is much greater than that of tri-*n*-propylamine.

In none of the reactions was complete formation of the -onium salt observed, but an equilibrium was reached; the reaction was more complete the faster the rate of interaction of the alkyl bromide with the tertiary base.

The following is a typical experiment. A mixture of 2·0350 g. (1 mol.) of tri-*n*-butylphosphine and 1·3784 g. (1 mol.) of *n*-butyl bromide was diluted to 53·28 c.c. with acetone and divided into a number of test-tubes, which were then sealed off and kept in a thermostat at 25°. After suitable intervals tubes were broken under water and the bromide ion was titrated with silver nitrate solution.

t (minutes)	3175	4182	6066	7495	8942	10,074	20,065	∞
$Bu^{a}Br$ in tube initially, g.	0·07814	0·07949	0·07952	0·07749	0·07900	0·07958	0·07877	0·08007
$Bu^{a}Br$ used after *t* minutes, g.	0·01462	0·01811	0·02263	0·02524	0·02681	0·02856	0·03552	0·03843

Velocity coefficients calculated on the assumption that the formation of an -onium salt is a reversible reaction, $R_3P + RBr \rightleftharpoons R_4P\}Br$, were satisfactorily constant.

Detailed examination of the effect of changes of the experimental conditions and of the base on the reaction velocity is in progress.—UNIVERSITY COLLEGE, CARDIFF. [*Received, January 1st,* 1934.]

The Anil of 2-*Hydroxy*-6-*methylbenzaldehyde.* By THOMAS LOVE.

THIS anil, described as a liquid by Anselmino (*Ber.*, 1917, **50**, 395), has now been obtained as a solid, m. p. 51·5°. *m*-Cresol was submitted to the Reimer–Tiemann reaction, and the mixture (5 g.) of *o*-hydroxy-aldehydes isolated by distillation in steam was heated on the water-bath with aniline (6 g.) and a crystal of iodine. On cooling, a semi-solid mass was obtained, from which, by filtration, the anil of 2-hydroxy-4-methylbenzaldehyde was separated; recrystallised from alcohol, it gave yellow needles (2·5 g.), m. p. 93°. The aniline solution, treated with dilute acetic acid, gave a solid, which crystallised from alcohol in yellow needles (5 g.), m. p. 51·5° (Found: N, 6·6. Calc. for $C_{14}H_{13}ON$: N, 6·7%).—ROYAL TECHNICAL COLLEGE, GLASGOW. [*Received, November 22nd,* 1933.]

The aci-*Form of Trinitromethane.* By LESLIE W. ANDREW and DALZIEL LL. HAMMICK.

BY a modification of the method of Hantzsch and Rinckenberger (*Ber.*, 1899, **32**, 635) for the preparation of nitroform, we have obtained a substance that is almost certainly the *aci*-form of trinitromethane. In the method of preparation referred to, the potassium salt of nitroform is dissolved in dilute sulphuric acid, whereupon nitroform separates. We have found, however, that when the damp salt is stirred into concentrated sulphuric acid at the ordinary temperature, an oil separates on the surface and solidifies after a few minutes. The colourless crystals, having been skimmed off the surface and pressed on porous tile to remove as much acid as possible, melt at about 50°, giving a liquid that solidifies entirely on cooling below 0°. The solid then melts completely at about 14°, the m. p. of pure nitroform being 15°. All attempts to purify the higher-melting solid by solution in organic solvents have failed, nitroform, m. p. 15°, being recovered in all cases.—THE DYSON PERRINS LABORATORY, OXFORD. [*Received, December 19th,* 1933.]