NOTES.

Elimination of the Nitroso-group from Nitrosoamines. By WILLIAM GEORGE MACMILLAN and THOMAS HAROLD READE.

THE usual method of eliminating the nitroso-group of a nitrosoamine by dissolution in concentrated hydrochloric acid often leads to mixtures from which the secondary amine is obtainable only with difficulty, particularly when there is hydrogen in the para-position with respect to the nitrosoamine group. To facilitate elimination of the nitroso-group, different substances capable of decomposing nitrous acid have been used with varying degrees of success. In sulphuric acid, glycine, acetamide, and potassium cyanate or thiocyanate are useless, but urea and thiourea work admirably and this method of elimination can be recommended for its rapidity and simplicity. For example, on addition of 20 g. of *m*-nitrophenylmethylnitrosoamine to 15 g. of urea in 75 c.c. of water and 75 c.c. of sulphuric acid at 50°, instantaneous evolution of gas (nitrogen, carbon dioxide, and nitric oxide) took place. This was completed by heating for 15 minutes at 100°.

After cooling, precipitation by ammonia, and crystallisation from ligroin, the *m*-nitromonomethylaniline obtained (15·5 g.), m. p. 67·5° (Ullmann, *Annalen*, 1903, **327**, 112, gives m. p. 65—66°) (Found: C, 54·9; H, 5·9; N, 18·0. Calc.: C, 55·2; H, 5·3; N, 18·4%), failed to give Liebermann's nitrosoamine reaction and was reconverted by nitrous acid into the nitrosoamine (1·8 g. from 2·0 g. of base). The yields of secondary amine obtained varied from 90 to 95% from the *m*-compound and from 80 to 90% from *p*-nitrophenylmethylnitrosoamine. With thiourea a similar procedure gave equally satisfactory results, no experiment giving less than 80% or more than 95% of recrystallised secondary amine.

Nuclear nitroso-compounds, *e.g.*, *p*-nitrosodimethylaniline and α-nitroso-β-naphthylamine, were recovered unchanged.—UNIVERSITY OF ABERDEEN. [*Received, February 9th*, 1929.]

The Preparation of p-*Azoxyanisole and Derivatives.* By WILLIAM DAVIES and RALPH ALEXANDER RODGER DOWN.

THE two-fold action of sodium methoxide in the production of azoxyanisoles from *p*- and *o*-halogenonitrobenzenes has been recorded by Jackson and Fiske (*Ber.*, 1902, **35**, 1131) and Brand (*J. pr. Chem.*, 1903, **67**, 150).

In the preparation of *p*-azoxyanisole from *p*-chloronitrobenzene and sodium methoxide the conditions should be such that substitution as far as possible precedes reduction, because *pp'*-dichloroazoxybenzene cannot easily be converted into *p*-azoxyanisole. Under the following conditions a yield of 64% of pure azoxyanisole is readily obtained.

69 C.c. of a methyl-alcoholic solution of sodium methoxide (containing 100 g. Na per litre) are boiled for 12 hours with *p*-chloronitrobenzene (31·5 g.), 51 c.c. of the methoxide solution are then added (total quantity, 50% in excess of the theoretical amount required to produce the azoxyanisole), methyl alcohol (50 c.c.) is distilled off, and the residue is boiled for a further 12 hours and then treated with hot water to dissolve the inorganic matter. The

crude dry *p*-azoxyanisole obtained (23·5 g.) is recrystallised from boiling benzene (200 c.c.)–petroleum (130 c.c.; b. p. 80—100°), 14 g. of pure material being obtained directly and 2·5 g. from the mother-liquor by concentration to 150 c.c., dilution with petroleum (250 c.c.), and recrystallisation. The m. p. (118·5°) and the clearing point (134—135°) are unchanged by admixture of an authentic specimen of *p*-azoxyanisole.

Preparation of 3 : 3′-*Dichloro*-p-*azoxyanisole*.—1 : 2-Dichloro-4-nitrobenzene (m. p. 42°) is obtained in excellent yield after D.R.-P. 167297, but a chlorinating temperature of 95—105° and the presence of antimony trichloride (5% by weight of the *p*-chloronitrobenzene) are advantageous. It is converted into 3 : 3′-*dichloro*-p-*azoxyanisole* by using exactly the same molecular proportions of sodium methoxide and the other conditions recorded above. After crystallisation from benzene and from petroleum (b. p. 100—120°), the azoxyanisole is obtained in yellow prisms, m. p. 182° (yield, 10·5 g. from 19·2 g. of 1 : 2-dichloro-4-nitrobenzene). It does not form liquid crystals (Found: C, 51·3; H, 3·2. $C_{14}H_{12}O_3N_2Cl_2$ requires C, 51·4; H, 3·65%).—THE UNIVERSITY OF MELBOURNE. [*Received, February 1st*, 1929.]

The Action of Aromatic Acid Chlorides on Vinyldiacetoneamine.

By JOHN GRAYMORE.

IT has been shown by Kipping and Greasley (J., 1924, **125**, 2611) that vinyldiacetoneamine [2 : 2 : 6-trimethyl-4-piperidone] cannot be benzoylated by the Schotten–Baumann method: the only benzoyl derivative which is obtained is a trace of benzoic anhydride.

By heating vinyldiacetoneamine (2 mols.) with benzoyl chloride (1 mol.), however, they obtained a normal *N*-benzoyl derivative, $C_{15}H_{19}O_2N$, m. p. 156°, and when more benzoyl chloride was used an oil was produced from which ill-defined crystals of a structural isomeride, m. p. 110°, separated. Since further investigation was required in order to explain these observations, the author, at Professor Kipping's suggestion, has examined the behaviour of vinyldiacetoneamine towards various benzoylating agents.

Under the conditions of Schotten and Baumann acylation did not occur in any case, the results confirming those of Kipping and Greasley save that no anhydride formation took place. As this could be attributed to the presence either of water or of sodium hydroxide, experiments were made in aqueous solution in the absence of sodium hydroxide, but again no benzoyl derivative was formed, the benzoylating agent reacting to form a salt with the base, as the acid was precipitated on acidification.

With pure dry vinyldiacetoneamine (2 mols.) freshly distilled under reduced pressure, *m*- and *p*-nitrobenzoyl chlorides, *o*-nitro-*p*-toluoyl chloride, and *p*-toluenesulphonyl chloride (1 mol.) condensed in the cold in the expected manner to give normal *N*-acyl derivatives. The formation of isomerides was not observed and experiments with a larger proportion of the acid chloride were not made.

The yield in the case of *p*-nitrobenzoyl chloride was theoretical, but in all others not more than 75% of the calculated yield could be obtained. *N*-*m*-Nitrobenzoylvinyldiacetoneamine crystallises from hot acetone in long needles, m. p. 159—160°; it is insoluble in water and ether, very soluble in acetone, less so in chloroform, and fairly readily soluble in alcohol. The *p*-derivative crystallises from acetone in short needles, m. p. 170°. *N*-*o*-Nitro-*p*-toluoylvinyldiacetoneamine, m. p. 150—151°, and *N*-*p*-toluenesulphonylvinyldiacetoneamine, m. p. 184°, crystallise from alcohol.

A concentrated aqueous solution of ammonia and ethylamine react with benzoyl chloride in the expected manner; but in very dilute solution (less than 5%), where free ammonia and ethylamine molecules are few, the formation of benzoyl compounds takes place either not at all or on a greatly reduced scale. It seems probable, therefore, that vinyldiacetoneamine in aqueous solution combines with water to form the ammonium hydroxide, and that a hydrogen atom in such a quinquevalent ammonium group is not displaceable as is the case with certain hydrochlorides.—UNIVERSITY COLLEGE, NOTTINGHAM. [*Received, November 6th*, 1928.]

Salicylaldehyde and its Methyl Ether. By MAURICE COPISAROW.

o-TOLYL carbonate, which is mentioned by Einhorn and Hollandt (*Annalen*, 1898, **301**, 115) and serves for the preparation of salicylaldehyde by chlorination and subsequent hydrolysis (Raschig, D.R.-P. 233631; Friedländer, "Fortschritte der Teerfarbenfabrikation," vol. X, p. 163), was prepared by passing carbonyl chloride into a solution of 108 g. of *o*-cresol and 42 g. of sodium hydroxide in 300 c.c. of water at 70—75° until the gas ceased to be absorbed. The oily liquid that separated was triturated with cold dilute sodium hydroxide solution, washed, and dried. The white odourless product (yield, 100 g., *i.e.*, 83%) was chlorinated by Raschig's method (*loc. cit.*): the reaction was accelerated by sunlight and was accompanied by the evolution of carbonyl chloride in addition to hydrogen chloride. ωω-Dichloro-*o*-tolyl carbonate was obtained as a thick brownish-yellow liquid which set to a translucent resin and could not readily be purified.

The chlorination product (380 g.) from 1 g.-mol. of *o*-tolyl carbonate was suspended in 1200 c.c. of methyl alcohol, a solution of 260 g. of sodium hydroxide in 500 c.c. of water gradually added, and the mixture heated for 1 hour at 100°. The alcohol was then removed, and the residue acidified and steam-distilled. The pale yellow oil in the distillate was identified as salicylaldehyde (yield, 107 g.; 44%). The distillate contained 15 g. of dissolved salicylaldehyde (contaminated with salicylic acid), making the total yield of aldehyde 50%. Less satisfactory results were obtained by acid hydrolysis.

o-Anisaldehyde was prepared directly by the combined hydrolysis and methylation of the chlorination product. 120 G. of anhydrous sodium carbonate and 250 g. of methyl sulphate were gradually added to the hydrolysed chlorination product (before removal of the alcohol and acidification), the mixture was heated for 4 hours at 100°, the alcohol removed, and the residue acidified and distilled in steam. The product consisted of 103 g. (2% in solution) of anisaldehyde (yield, 38%) and 32 g. (6% in solution) of salicylaldehyde (yield, 13%). The anisaldehyde was ultimately obtained in small colourless crystals, m. p. 39—40°.

This method of preparing *o*-anisaldehyde is much more satisfactory than those already recorded (Perkin, *Annalen*, 1868, **145**, 302; J., 1889, **55**, 550; Voswinckel, *Ber.*, 1882, **15**, 2024; Irvine, J., 1901, **79**, 669; Katschalowsky and Kostanecki, *Ber.*, 1904, **37**, 2347).

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