NOTES.

*Preparation of Diphenyl-*p*-tolylamine and Phenyldi-*p*-tolylamine.* By RALPH J. B. MARSDEN.

*Diphenyl-*p*-tolylamine.*—Diphenylamine (8 g.), *p*-iodotoluene (13 g.), potassium carbonate (8 g.), and copper-bronze powder (2 g.) were heated in boiling nitrobenzene (50 c.c.) for 9 hours (cf. Wieland, *Ber.*, 1907, **40**, 4279; " Organic Syntheses," 1928, **8**, 186). The brown viscous residue left after removal of the nitrobenzene by steam distillation was extracted with ether. The oily residue obtained from the dried extract was treated while still hot with boiling alcohol (2 vols.). The crystallised product was filtered off and dissolved in benzene, and the solution dried by partial distillation of the benzene, saturated when cold with hydrogen chloride gas, and kept for 3 hours. After filtration, the benzene was removed, and the residue distilled under reduced pressure; the fraction, b. p. 230—244°/40 mm., crystallised, and after repeated crystallisation from alcohol was obtained in very pale yellowish-white needles (1·5 g.), m. p. 68·75° (corr.) (Found : C, 88·5; H, 6·7; N, 5·1. $C_{19}H_{17}N$ requires C, 88·0; H, 6·6; N, 5·4%).

*Phenyldi-*p*-tolylamine.*—Di-*p*-tolylamine (10 g.), iodobenzene (10·3 g.), potassium carbonate (7 g.), and copper-bronze powder (2 g.) were heated in boiling nitrobenzene (50 c.c.) for 11 hours, the nitrobenzene removed by steam distillation, and the residue extracted with benzene. After removal of the benzene the product was distilled under reduced pressure; the fraction, b. p. 210—250°/20—40 mm., solidified in orange-yellow crystals (8·5 g.), which were recrystallised once from ethyl acetate and twice from alcohol, giving pale yellow needles (4 g.), m. p. 109° (corr.) (Found : C, 87·6; H, 7·0; N, 5·1. $C_{20}H_{19}N$ requires C, 87·9; H, 7·0; N, 5·1%).

There is a continuous increase in colour on proceeding from the dead white of triphenylamine to the bright pale yellow of tritolylamine with the addition of successive methyl groups.

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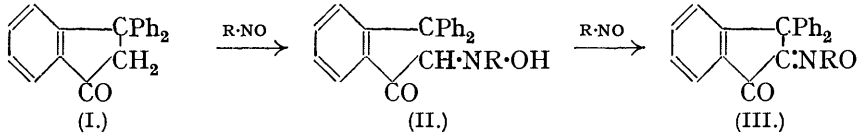
Formation of Nitrones by the Action of Aromatic Nitroso-compounds on Methylene Ketones. By ALEXANDER SCHÖNBERG and ROBERT MICHAELIS.

MANY cases have been described of the reaction between 1 : 2-methylene ketones, in alcoholic solution in the presence of alkali or piperidine, and nitrosobenzene (or its derivatives) producing the anils of 1 : 2-diketones (cf., *e.g.*, Skraup and Böhm, *Ber.*, 1926, **59**, 1015) :

$$Ph{\cdot}CO{\cdot}CH_2Ph + NMe_2{\cdot}C_6H_4{\cdot}NO \longrightarrow Ph{\cdot}CO{\cdot}CPh{:}N{\cdot}C_6H_4{\cdot}NMe_2$$

It was therefore expected that 3 : 3-diphenyl-1-hydrindone (I) would thus react with nitrosobenzene or *p*-dimethylaminonitrosobenzene to form the 2-anil. The reddish-orange product obtained, however, is not this anil but the corresponding *anil oxide* (III, R = Ph or $C_6H_4{\cdot}NMe_2$). The formation of a nitrone of a 1 : 2-diketone in this way has not hitherto been described, so far as we know. It may be explained by assuming that the primarily formed hydroxylamine derivative (II) is dehydrogenated by nitrosobenzene, somewhat in the same way that the



(I.) (II.) (III.)

hydroxylamine derivative (IV) is dehydrogenated to the nitrone (V) by benzaldehyde in the presence of air (Angeli, Alessandri, and Aiazzi-Mancini, *Atti R. Accad. Lincei*, 1911, **20**, i, 546; Staudinger, *Helv. Chim. Acta*, 1919, **2**, 559).

$$\text{(IV.)}\quad CHPh_2{\cdot}NPh{\cdot}OH \longrightarrow CPh_2{:}NPhO \quad \text{(V.)}$$

The properties of the compounds (III) are in agreement with the suggested formula, *e.g.*, the colour [compare also the colour of (V) and (VIII)]. Their reaction with sulphuric acid, forming 3 : 3-*diphenylindanedione*, is analogous to the formation of benzophenone from the

nitrone (V). The hitherto unexplained formation of the dinitrone (VIII) by the action of diazomethane on nitrosobenzene (Pechmann, *Ber.*, 1897, **30**, 2461, 2870; Staudinger and Miescher, *Helv. Chim. Acta*, 1919, **2**, 560) may be the result of a reaction similar to the formation of (III) from (II). We consider that the diazomethane and nitrosobenzene first produce (VI); this changes to the dimeric form (VII), which then reacts with nitrosobenzene to form the dinitrone (VIII) and phenylhydroxylamine :

$$CH_2N_2 + Ph{\cdot}NO \xrightarrow{-N_2} \underset{(VI.)}{CH_2{:}NPhO} \longrightarrow \underset{(VII.)}{[{:}CH{\cdot}NPh{\cdot}OH]_2} \xrightarrow{Ph{\cdot}NO} \underset{(VIII.)}{[{\cdot}CH{:}NPhO]_2} + NHPh{\cdot}OH$$

The phenylhydroxylamine has not been isolated, but azoxybenzene has been obtained, which is formed from phenylhydroxylamine and nitrosobenzene (Bamberger and Renaud, *Ber.*, 1897, **30**, 2278). In support of the scheme it may be mentioned that diphenyldiazomethane reacts with nitrosobenzene, forming triphenylnitrone, $CPh_2{:}NPhO$ (Staudinger, *Helv. Chim. Acta*, 1919, **2**, 568).

Experimental.

Action of Nitrosobenzene or its p-*Dimethylamino-derivative on* 3 : 3-*Diphenyl*-1-*hydrindone* (I). —1·5 G. of nitrosobenzene (2 mols.) are dissolved in a warm alcoholic solution (70 c.c.) of 2 g. of the ketone, and 0·5 c.c. of 10% aqueous sodium hydroxide added; the solution immediately becomes red. After 24 hours at room temperature, the red crystalline precipitate is filtered off (more may be obtained from the mother-liquor on evaporation), washed with cold alcohol, and recrystallised from absolute alcohol; m. p. 204°. 3 : 3-*Diphenylindanedione*-2-*anil oxide* (III, R = Ph) is sparingly soluble in cold chloroform and warm benzene. It forms an orange-yellow solution in concentrated sulphuric acid (Found : C, 83·3; H, 5·1; N, 3·8. $C_{27}H_{19}O_2N$ requires C, 83·3; H, 4·9; N, 3·6%). An active-hydrogen determination by Zerewitinoff's method gives a negative result.

Under the same conditions, nitrosobenzene being replaced by its *p*-dimethylamino-derivative, 3 : 3-*diphenylindanedione*-2-p-*dimethylaminoanil oxide* (III, R = $C_6H_4{\cdot}NMe_2$) is obtained in deep red crystals, m. p. 233—234°, after recrystallisation from alcohol. A solution in concentrated sulphuric acid is orange-yellow (Found : C, 80·3; H, 5·9; N, 7·0. $C_{29}H_{24}O_2N_2$ requires C, 80·5; H, 5·6; N, 6·5%).

3 : 3-*Diphenylindanedione*.—A mixture of the anil oxide (0·28 g.) or its *p*-dimethylamino-derivative and 45% sulphuric acid (10 c.c.) is rapidly heated to the boiling point, sufficient glacial acetic acid added to dissolve the anil oxide, and the mixture refluxed for 25 minutes. The cooled orange-yellow solution is poured into 100 c.c. of ice-water, and the orange precipitate filtered off and washed with water after 12 hours. After recrystallisation (twice) from ligroin 3 : 3-*diphenylindanedione* has m. p. 152—153°. It is soluble in benzene and easily soluble in pyridine. A solution in concentrated sulphuric acid is yellowish-green (Found : C, 84·3; H, 4·8. $C_{21}H_{14}O_2$ requires C, 84·5; H, 4·7%). The indophenin reaction gives a deep blue-green colour.

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