76. *Nitrosoacylarylamines. Part II. The Action of Nitrous Fumes on Acylarylamines.*

By J. W. Haworth and D. H. Hey.

A study of the action of nitrous fumes on a variety of acylarylamines in acetic acid solution shows that they may be classified broadly into four groups: (i) those which, like acetanilide, yield *N*-nitroso-derivatives which react with benzene,

$$R{\cdot}N(NO){\cdot}COR' + C_6H_6 \longrightarrow R{\cdot}C_6H_5 + N_2 + R'{\cdot}CO_2H,$$

(ii) those which yield *N*-nitroso-derivatives which do not react with benzene, (iii) those which react with nitrous fumes but do not give *N*-nitroso-derivatives, and (iv) those which do not react with nitrous fumes. The results obtained and the properties of nitrosoacylarylamines in general are summarised. Certain nitroso-compounds, *e.g.*, dinitrososuccindianilide and nitrosocarbanilide, are shown to be far more stable than nitrosoacetanilide. The action of nitrous fumes on diacetyl-1 : 3-phenylenediamine gives *m*-acetamidobenzenediazonium nitrate, in contradistinction to diacetyl-1 : 4-phenylenediamine, which, on similar treatment, gives dinitrosodiacetyl-1 : 4-phenylenediamine. Nitrosation of *p*-benzamidoacetanilide yields a mononitroso-derivative, in which the acetamido-group only is nitrosated and which, with benzene, gives 4-benzamidodiphenyl.

It was shown by Fischer (*Ber.*, 1876, **9**, 463) that the action of nitrous fumes on a solution of acetanilide in glacial acetic acid gave rise to nitrosoacetanilide, and similar *N*-nitroso-derivatives prepared in like manner from aceto-*p*-toluidide, formanilide, and oxanilide were later described (*Ber.*, 1877, **10**, 959). It was subsequently shown by Bamberger (*Ber.*, 1897, **30**, 366) that nitrosoacetanilide gave diphenyl and its derivatives when dissolved in an aromatic compound such as benzene or toluene, nitrogen and acetic acid being liberated :

$$\mathrm{Ph{\cdot}N(NO){\cdot}CO{\cdot}CH_3 + R{\cdot}C_6H_5 \longrightarrow Ph{\cdot}C_6H_4R + N_2 + CH_3{\cdot}CO_2H}$$

A similar reaction was used by Kliegl and Huber (*Ber.*, 1920, **53**, 1655) for the preparation of 4-methyldiphenyl from nitrosoaceto-*p*-toluidide and benzene. The general applicability and utility of this reaction for effecting the union of aryl nuclei has been clearly demonstrated by its employment for the synthesis of many new derivatives of *p*- and *m*-terphenyl (France, Heilbron, and Hey, J., 1938, 1364; 1939, 1283, 1288).

The use of nitrosoacylarylamines for effecting the union of aryl nuclei was shown by Grieve and Hey (J., 1934, 1797) to belong to a class of reaction which does not conform to the normal laws of aromatic substitution, but gives rise, in general, to substitution at the *o*- and *p*-positions in the aromatic nucleus irrespective of the nature of any substituent group which may be present (see Hey and Waters, *Chem. Reviews*, 1937, **21**, 169). These observations, coupled with the results of a quantitative investigation of the decomposition of nitrosoacetanilide in a variety of aromatic and non-aromatic solvents (Grieve and Hey, J., 1934, 1797; Butterworth and Hey, J., 1938, 116), led to the hypothesis of a free-radical mechanism, which is supported by the observations of Waters (J., 1937, 113) that, when nitrosoacetanilide decomposes in many solvents, (a) some carbon dioxide is evolved in addition to nitrogen, and (b) certain metallic elements may be attacked (see also Hey, J., 1934, 1966).

During the preparation of a variety of nitrosoacylarylamines for the synthesis of members of the terphenyl series (France, Heilbron, and Hey, *locc. cit.*) a number of novel features were brought to light. (1) It was possible to prepare a dinitroso-derivative of diacetyl-1 : 4-phenylenediamine, and also of the corresponding diformyl and dipropionyl derivatives. The resulting dinitroso-compounds, the first examples of this type, were considerably more stable than nitrosoacetanilide but underwent reaction with benzene in the normal manner. (2) It appeared that a nitro-group situated in an *o*-position with respect to the acetamido-group effectively hindered the formation of a nitroso-derivative; *e.g.*, both 3-nitro-4-acetamidodiphenyl and 2 : 3-dinitrodiacetyl-1 : 4-phenylenediamine failed to form nitroso-compounds on treatment with nitrous fumes in the normal manner, and 2-nitrodiacetyl-1 : 4-phenylenediamine yielded only a mononitroso-compound, the acetamido-group at the 1-position remaining unattacked. (3) In reaction with chlorobenzene, bromobenzene, and toluene, 4-nitrosoacetamidodiphenyl gave *p*-terphenyl derivatives substituted in the 2-, 3-, and 4-positions. The simultaneous production of all three isomerides may be regarded as further evidence that the reaction is non-ionic in type and not affected by the normal polar directive influences.

Hitherto no comprehensive attempt has been made to see if the formation of *N*-nitroso-derivatives is characteristic of acylarylamines of all kinds, and the present communication deals with an examination of the action of nitrous fumes on a representative selection of acylarylamines of various types. Bamberger and his co-workers prepared nitroso-*p*-chloroacetanilide, nitroso-*p*-bromoacetanilide, and nitrosocarbanilide (*Ber.*, 1897, **30**, 368; 1909, **42**, 3589), but they, as well as v. Pechmann and Frobenius (*Ber.*, 1894, **27**, 653) and Hantzsch and Wechsler (*Annalen*, 1902, **325**, 226), were interested mainly in the constitution of the nitrosoacylarylamines and the relationship to the diazo-compounds rather than in their use for the preparation of biaryl derivatives. Unsuccessful attempts have been already recorded (Grieve and Hey, J., 1935, 691) for the preparation of nitroso-derivatives from *p*-nitroacetanilide, aceto-*m*-toluidide, aceto-*o*-chloroanilide, aceto-*p*-anisidide, aceto-*p*-phenetidide, aceto-α-naphthalide, and aceto-β-naphthalide. In some of these cases (*e.g.*, *p*-nitroacetanilide) the acylarylamine was recovered unchanged, in others very unstable oily nitroso-compounds appeared to be formed. With aceto-*p*-phenetidide nuclear nitration took place. By giving more careful attention to the conditions of nitrosation, and in particular to the avoidance of an excess of nitrous fumes or nitric acid most of the above acetyl derivatives have now been nitrosated, together with a large number of other acylarylamines. The reactions of the resulting nitroso-compounds with benzene have been studied. Some of the new nitroso-compounds were far more stable than nitrosoacetanilide and could be readily purified, but others decomposed on attempted crystallisation. In benzene solution they readily evolved nitrogen and an examination of the products served to establish the existence of the nitroso-compounds. Further, aqueous alkali converted the nitroso-compounds into salts of the corresponding *syn*- or *anti*-diazoates (cf. Bamberger, *Ber.*, 1894, **27**, 915), which on addition of acid yielded diazonium salts, detected by addition to alkaline β-naphthol. Those nitroso-compounds, such as dinitrosodiacetyl-1 : 4-phenylenediamine (France, Heilbron, and Hey, J., 1938, 1370), dinitrososuccindianilide, and nitrosocarbanilide, which are far more stable than nitrosoacetanilide, may be used as stable sources for the quick production of a diazonium salt in solution by successive addition of alkali and acid. Again, in almost all cases the existence of a nitrosoacylarylamine can be confirmed by the characteristic explosive " flash " which is produced when a small quantity of the compound is heated gently over a flame.

The action of nitrous fumes on an acylarylamine in acetic acid solution, however, does not necessarily produce a nitrosoacylarylamine. The results now described may be classified into four groups, but it must be emphasised that this subdivision is in a sense arbitrary and not necessarily sharply defined; *e.g.*, the nitroso-derivative of ω-bromoacetanilide possesses to a certain extent the properties of both class A and class B (see below).

Class A. Acylarylamines which yield *N*-nitroso-derivatives of the normal type, *e.g.*, acetanilide.

To this group belong formanilide, propionanilide, ω-chloroacetanilide, ω-bromoacetanilide, aceto-*p*-anisidide, aceto-*p*-phenetidide, aceto-α-naphthalide, aceto-β-naphthalide, diacetyl-1 : 4-phenylenediamine, diacetylbenzidine, succindianilide, 3 : 3′-*dichlorosuccindianilide*, carbanilide, 4 : 4′-dimethylcarbanilide, 3 : 3′- and 4 : 4′-dichlorocarbanilide. In each case a nitroso-derivative was formed which reacted with benzene in the normal manner to give a compound in which the nitrosoacylamino-group is replaced by a phenyl group.

In the case of the succinic acid derivatives the *dinitroso*-compounds, like that derived from diacetyl-1 : 4-phenylenediamine, are much more stable than nitrosoacetanilide. In contradistinction to the formation of dinitroso-compounds in the succinic acid series, carbanilide (and its derivatives) forms a comparatively stable *mononitroso*-compound, which reacts with benzene to give diphenyl and phenyl *iso*cyanate :

$$\mathrm{Ph{\cdot}N(NO){\cdot}CO{\cdot}NHPh + C_6H_6 \longrightarrow Ph_2 + N_2 + PhNCO + H_2O}$$

Some carbanilide is then regenerated by the interaction of the phenyl *iso*cyanate with water. Hantzsch and Wechsler (*loc. cit.*, p. 244) prepared a mononitroso-derivative of carbanilide, m. p. 82°, but the compound now described melts at 105° (decomp.). On the other hand, Ryan and O'Toole (*Proc. Roy. Soc. Dublin*, 1923, **17**, 139) state, on analytical evidence, that the action of nitrous fumes on an acetic acid solution of carbanilide gives a dinitroso-compound, m. p. 103° (decomp.). The analysis and chemical reactions of the compound now described indicate clearly that it is a mononitroso-derivative. Nitrosocarbanilide is also formed by the action of nitrous fumes on an acetic acid solution of *s*-diphenylguanidine. The primary action of the nitrous fumes probably results in the formation of carbanilide, which subsequently undergoes nitrosation.

Class B. Acylarylamines which yield abnormal *N*-nitroso-compounds.

To this class belong *o*-chloroacetanilide, 2 : 6-dichloro-4-nitroacetanilide, phenylurethane, and 1-acetamido-2-methylanthraquinone. The nitroso-derivatives of the first three liberate, not nitrogen, but oxides of nitrogen in benzene solution with resulting regeneration of the acylarylamine. The nitroso-derivative of 1-acetamido-2-methylanthraquinone yields 6 : 7-phthalylindazole when warmed in benzene solution. A similar compound, described in D.R.-P. 269,842 (*Chem. Zentr.*, 1914, I, 717), was obtained from diazotised 1-amino-2-methylanthraquinone. This recalls the similar reaction of nitrosoaceto-*o*-toluidide and nitrosobenzo-*o*-toluidide recorded by Jacobson and Huber (*Ber.*, 1908, **41**, 660; cf. Auwers, *Ber.*, 1919, **52**, 1335), both of which yield indazole.

Class C. Acylarylamines which react with nitrous fumes, but do not give *N*-nitroso-derivatives.

To this class belong 4-dimethylamino-4′-acetamidoazobenzene, which gives *p*-nitrodimethylaniline, and benzanilide and benzo-*p*-toluidide, which give diazonium nitrates. To this class also belongs diacetyl-1 : 3-phenylenediamine; this, unlike diacetyl-1 : 4-phenylenediamine, which yields the dinitroso-compound in the normal manner, gives rise to *m*-acetamidobenzenediazonium nitrate. The product, which in this case is precipitated from the reaction mixture by the addition of ether, is explosive and reacts with warm water to give *m*-acetamidophenol, with ethyl alcohol to give *m*-acetamidophenetole, and with aqueous cuprous cyanide to give *m*-cyanoacetanilide; in addition it is soluble in water and couples immediately with alkaline β-naphthol. Bamberger and Baudisch (*Ber.*, 1909, **42**, 3590) observed that, if an ethereal solution of nitrosoacetanilide was kept, some benzenediazonium nitrate was formed. This may be due to liberation of nitrous fumes and subsequent production of nitric acid, since it is now shown that both (a) prolonged action of nitrous fumes and (b) addition of concentrated nitric acid to an acetic acid solution of nitrosoacetanilide give rise to the formation of benzenediazonium nitrate. On the other hand Wohl (*Ber.*, 1892, **25**, 3632) has prepared nitrosobenzanilide by the action of benzoyl chloride on an aqueous solution of sodium benzenediazoate.

Class D. Acylarylamines which are recovered unchanged on treatment with nitrous fumes in the normal manner.

To this class belong *p*-nitroacetanilide, α- and β-acetamidoanthraquinone, benzenesulphonanilide, oxanilide (cf. Fischer, *loc. cit.*), oxanilic acid, 3 : 3′-dichloro-oxanilide, 3-chloro-oxanilic acid, *p*-nitrobenzanilide, *m*-nitrobenzanilide, *p*-toluenesulphonanilide, 3 : 3′-dinitrocarbanilide, and 4 : 4′-dinitrocarbanilide.

The fact that the acetamido-group normally submits to nitrosation with nitrous fumes whereas the benzamido-group remains unaffected, leads to the possibility of the preparation of a mononitroso-compound from a suitable acetylbenzoyldiamine. This has now been realised in the case of p-*benzamidoacetanilide*, which with nitrous fumes gives p-*benzamidonitrosoacetanilide*. The latter reacts with benzene to give 4-benzamidodiphenyl.

Summary of Results.—From the results described in this and previous communications the following conclusions may be deduced :

(a) The number of acylarylamines which will yield *N*-nitroso-compounds on treatment with nitrous fumes is strictly limited. In particular, acylarylamines containing a nitro-group in the *o*- or *p*-position in the aromatic nucleus (*m*-nitroacetanilide yields an unstable oily nitroso-compound; France, Heilbron, and Hey, J., 1939, 1291) and those in which the acyl group is benzoyl, or benzene- or toluene-sulphonyl, are generally resistant to nitrosation with nitrous fumes.

(b) Nitrosoacetylarylamines may react in one or more of three ways :

$$\mathrm{Ar{\cdot}N(NO){\cdot}CO{\cdot}CH_3 + RH \longrightarrow ArR + N_2 + CH_3{\cdot}CO_2H} \quad . \quad . \quad (A)$$

$$\mathrm{Ar{\cdot}N(NO){\cdot}CO{\cdot}CH_3 + RH \longrightarrow ArH + N_2 + [CH_3{\cdot}CO_2R]} \quad . \quad . \quad (B)$$

$$\mathrm{Ar{\cdot}N(NO){\cdot}CO{\cdot}CH_3 + H_2O \longrightarrow Ar{\cdot}NH{\cdot}CO{\cdot}CH_3 + HNO_2} \quad . \quad . \quad (C)$$

When R = aryl, the normal reaction (biaryl formation) is represented by (A). Reaction (B) is rarely prominent when R = aryl, but is illustrated in the following examples : (i) in the preparation of *p*-terphenyl from dinitrosodiacetyl-1 : 4-phenylenediamine and benzene some diphenyl is also formed, and (ii) in the preparation of *p*-quaterphenyl from dinitrosodiacetylbenzidine and benzene some *p*-terphenyl is also formed. In both of these cases one nitrosoacetamido-group acts according to reaction (A) and the second nitrosoacetamido-group according to reaction (B). No indication has yet been obtained of the formation of an ester, as in equation (B), but the two reactions (A) and (B) are an exact counterpart of the " RH scheme " of Gelissen and Hermans (*Ber.*, 1925, **58**, 984), which applies to certain reactions of diacyl peroxides and diazonium salts, reactions which have many features in common with those of the nitrosoacylarylamines (cf. Hey and Waters, *loc. cit.*). Reaction (B) becomes predominant when a non-aromatic hydrogen-containing solvent is used (cf. Waters, *loc. cit.*), *i.e.*, R = alphyl.

With certain nitrosoacylarylamines reaction (C), which requires the presence of water, predominates. The reaction is not one of normal hydrolysis, since the nitroso-compounds are isolated by addition of water to the reaction mixture, and the reaction proceeds even when no water is added to the system, thus showing that very little is required. Stoicheiometrically 10 g. of nitrosoacetanilide would require only just over 0·5 g. of water for complete decomposition according to reaction (C) owing to the instability of the nitrous acid with liberation of oxides of nitrogen and regeneration of water :

$$2HNO_2 \longrightarrow NO_2 + NO + H_2O$$

The manner in which a nitrosoacylarylamine reacts is probably bound up with the equilibrium $Ar{\cdot}N(NO){\cdot}CO{\cdot}CH_3 \rightleftharpoons Ar{\cdot}N{:}N{\cdot}O{\cdot}CO{\cdot}CH_3$, reactions (A) and (B) requiring the diazo-form and reaction (C) the nitroso-form.

EXPERIMENTAL.

The general procedure for the preparation of nitrosoacylarylamines consists in the passage of nitrous fumes into a solution of the acylarylamine in glacial acetic acid at about 10° until a clear deep green solution is obtained. The nitrosoacylarylamine, which is precipitated when the solution is poured into a large volume of water, is washed with water and dried on a porous tile. It was found advantageous to prepare the nitrous fumes from solid sodium nitrite and dilute sulphuric acid rather than from arsenious oxide and concentrated nitric acid. If the passage of the gases is continued until a very dark green solution is obtained, the yield of nitrosoacylarylamine is considerably reduced and the addition of water results largely in the formation of a solution of a diazonium salt together with some tarry matter. This observation accounts in part for the failures recorded by Grieve and Hey (J., 1935, 689). In some cases a mixture of glacial acetic acid and acetic anhydride is used as solvent in place of acetic acid alone. The use of acetic anhydride lowers the freezing point of the reaction mixture and thus prevents the solidification of the glacial acetic acid. In some cases the yield of the nitroso-compound may be slightly increased and the time for reaction reduced by the addition of a small quantity of phosphoric oxide to the reaction mixture. Completion of the reaction can usually be ascertained by pouring a small test portion into water and isolating the precipitate, which when dry should give a characteristic " flash " when gently heated over a flame. Most of the nitrosoacylarylamines now described resemble nitrosoacetanilide in stability and cannot be kept at room temperature for longer than a day without decomposition, but dinitrososuccindianilide, dinitroso-3 : 3′-dichlorosuccindianilide, nitrosocarbanilide, nitroso-3 : 3′- and 4 : 4′-dichlorocarbanilide are far more stable and can be kept when pure for many weeks or even months.

Class A.—Formanilide (cf. Fischer, *loc. cit.*). Nitrous fumes were passed for 3½ hours into a cold solution of formanilide (5 g.) in glacial acetic acid (70 c.c.), which was then poured into ice-water. The nitrosoformanilide [4·2 g., m. p. 45—46° (decomp.)] which separated was dissolved in benzene (100 c.c.) and kept over-night. Removal of the benzene on the water-bath and distillation of the residue gave diphenyl (1·9 g., m. p. and mixed m. p. 69—70° after crystallisation from alcohol).

Propionanilide. Addition of nitrous fumes to a solution of propionanilide (3 g.) in glacial acetic acid (50 c.c.), as above, yielded nitrosopropionanilide [1·9 g., m. p. 52° (decomp.)]. Reaction with benzene, as described above for nitrosoformanilide, yielded diphenyl (0·9 g.).

ω-Chloroacetanilide. Nitrous fumes were passed for 3 hours into a solution of ω-chloroacetanilide (5 g.) in glacial acetic acid (100 c.c.) at 10—15°. The nitroso-compound [4·3 g., m. p. 65° (decomp.)] separated as a yellow solid on pouring into excess of water. A solution of the nitroso-compound (3·2 g.) in benzene (200 c.c.) was kept at room temperature for 24 hours. Aqueous sodium carbonate extracted chloroacetic acid (m. p. and mixed m. p. 58—61°) from the solution. After removal of benzene further distillation gave diphenyl (1·1 g., m. p. and mixed m. p. 68—69° after crystallisation from alcohol).

ω-Bromoacetanilide. Nitrous fumes were passed for 4—5 hours into a solution of ω-bromoacetanilide (18 g.) in glacial acetic acid (500 c.c.) at 10—15°. The nitroso-compound [15 g., m. p. 54—55° (decomp.)] separated as a yellow precipitate when the dark green solution was poured into water (2 l.). A solution of the nitroso-compound (6 g.) in benzene (100 c.c.) was kept for 24 hours. Nitrogen and carbon dioxide were evolved. Some regenerated ω-bromoacetanilide (2·8 g., m. p. and mixed m. p. 130—131°) separated from the solution and was filtered off. Sodium carbonate solution extracted bromoacetic acid (m. p. 50°) from the benzene filtrate. After removal of benzene under reduced pressure diphenyl (0·8 g.) was collected at 130—140°/20 mm. (m. p. and mixed m. p. 68—70° after crystallisation from alcohol).

Aceto-p-*anisidide* (With E. C. BUTTERWORTH). Nitrous fumes were passed for 3 hours into a cold solution of aceto-*p*-anisidide (5 g.) in glacial acetic acid (100 c.c.). Water precipitated the nitroso-compound, m. p. 83—84° (decomp.). In benzene solution nitrogen was evolved. After removal of benzene hot alcohol extracted 4-methoxydiphenyl, m. p. and mixed m. p. 89°, in 55% yield from the residue.

Aceto-p-*phenetidide* (With E. C. BUTTERWORTH). Prepared as described for nitrosoaceto-*p*-anisidide, nitrosoaceto-*p*-phenetidide melted at 60° (decomp.). In benzene solution nitrogen was evolved. After removal of benzene the residue gave a distillate at 280—290° which solidified. It was crystallised from alcohol (charcoal); on cooling, 4-ethoxydiphenyl separated in plates, m. p. 72—73° (yield, 50%) (Found: C, 84·4; H, 7·3. Calc. for $C_{14}H_{14}O$: C, 84·7; H, 7·1%). Musser and Adkins (*J. Amer. Chem. Soc.*, 1938, **60**, 667) give m. p. 73—74°.

Aceto-α-naphthalide (With E. C. BUTTERWORTH). Nitrous fumes were passed into a cold solution of aceto-α-naphthalide (5 g.) in glacial acetic acid (50 c.c.). Addition of water precipitated the nitroso-compound as a viscous oil, which solidified with difficulty [m. p. 57° (decomp.)]. In benzene solution nitrogen was evolved. After removal of benzene, further distillation gave α-phenylnaphthalene, b. p. 320—330°, identified by oxidation to *o*-benzoylbenzoic acid.

Aceto-β-naphthalide (With E. C. BUTTERWORTH). The nitroso-compound, prepared as described above for nitrosoaceto-α-naphthalide, melted at 80° (decomp.). A solution of the nitroso-compound (9 g.) in benzene (250 c.c.) became deep red and evolved nitrogen. After removal of benzene the residue was sublimed in a vacuum, and the sublimate crystallised from alcohol. β-Phenylnaphthalene (2 g.) separated in flakes, m. p. and mixed m. p. 100—101°.

Diacetyl-1 : 4-*phenylenediamine*. Nitrosation and subsequent reaction with benzene were carried out as previously described by France, Heilbron, and Hey (J., 1938, 1370). In the high-vacuum sublimation of the crude *p*-terphenyl a small quantity of diphenyl was first collected, m. p. and mixed m. p. 69—70° after crystallisation from alcohol.

Diacetylbenzidine. Nitrous fumes were passed for 10 hours into a stirred suspension of diacetylbenzidine (10 g.) in a mixture of glacial acetic acid (200 c.c.) and acetic anhydride (100 c.c.). After filtration from unchanged diacetylbenzidine (6·2 g.), addition of water precipitated the dinitroso-compound (3 g.), which was added to benzene (200 c.c.). At 60° nitrogen was evolved and after 3 hours the excess of benzene was removed. Sublimation of the residue in a high vacuum gave at 100° a small quantity of *p*-terphenyl (m. p. and mixed m. p. 200—205°), and finally at 200° *p*-quaterphenyl (0·35 g.), which after several crystallisations from boiling benzene melted at 312°, not depressed by an authentic specimen kindly supplied by Dr. S. T. Bowden.

Succindianilide. Nitrous fumes were passed for 4½ hours into a solution of succindianilide (5 g.) in glacial acetic acid (400 c.c.) at 15°. The stable *dinitroso*-compound, which separated as a yellow precipitate without addition of water, was filtered off and dried (5·25 g., detonates at 111°) (Found: N, 16·9. $C_{16}H_{14}O_4N_4$ requires N, 17·1%). Addition of the dinitroso-compound (5 g.) to benzene (250 c.c.) at 65° produced a brisk effervescence and reaction was complete in 15 minutes. The benzene solution was shaken with water, which extracted succinic acid (m. p. and mixed m. p. 179—182°). After removal of benzene further distillation gave diphenyl (3·2 g., m. p. and mixed m. p. 69—70° after crystallisation from alcohol). The dinitroso-compound dissolved in aqueous sodium hydroxide. Acidification, followed by addition to alkaline β-naphthol, gave a red precipitate.

3 : 3'-*Dichlorosuccindianilide.* A mixture of *m*-chloroaniline (20 g.) and methyl succinate (10 g.) was boiled under reflux for 8 hours. When cold, 3 : 3'-*dichlorosuccindianilide* (1 g., m. p. 225—226°) separated, which was filtered off and washed with alcohol (Found: N, 8·4. $C_{16}H_{14}O_2N_2Cl_2$ requires N, 8·3%). Addition of alcohol to the filtrate precipitated *succino*-m-*chlorophenylimide* (2·5 g.), which crystallised from alcohol in needles, m. p. 119—120° (Found: N, 6·6. $C_{10}H_8O_2NCl$ requires N, 6·7%). Nitrous fumes were passed for 4 hours into a solution

of 3 : 3′-dichlorosuccindianilide (0·5 g.) in a mixture of glacial acetic acid (80 c.c.) and acetic anhydride (20 c.c.) at 10°. Addition of water precipitated the stable dinitroso-compound [0·4 g., m. p. 105—106° (decomp.)]. Like dinitrososuccindianilide, it dissolved in warm benzene with brisk effervescence and in aqueous sodium hydroxide to give a solution which, after acidification, coupled with alkaline β-naphthol.

Carbanilide (cf. Hantzsch and Wechsler, *loc. cit.*; Ryan and O'Toole, *loc. cit.*). Nitrous fumes were passed for 5 hours into a cold solution of carbanilide (5 g.) in glacial acetic acid (500 c.c.). The stable *nitroso*-compound, which separated as a cream-coloured precipitate (5·3 g.) when the mixture was poured into water, melted at 105° after crystallisation from ether (Found: N, 17·5. $C_{13}H_{11}O_2N_3$ requires N, 17·4%). A solution of nitrosocarbanilide (5 g.) in benzene (300 c.c.) was kept at room temperature for 3 days. Nitrogen was evolved and regenerated carbanilide (1 g., m. p. and mixed m. p. 234—236°) separated. After removal of benzene on the water-bath further distillation yielded (i) a fraction (2 g.), b. p. 100—200°, containing phenyl *iso*cyanate, identified by its lachrymatory action and the formation of carbanilide with water, and (ii) a fraction (1·5 g.), b. p. 250—255°, which solidified when cold and on crystallisation from alcohol gave diphenyl (m. p. and mixed m. p. 69—70°). The nitroso-compound dissolved in aqueous alkali, which solution, after acidification, coupled with alkaline β-naphthol.

Action of nitrous fumes on s-*diphenylguanidine.* Nitrous fumes were passed for 3½ hours into a solution of *s*-diphenylguanidine (5 g.) in a mixture of glacial acetic acid (80 c.c.) and acetic anhydride (20 c.c.) at 10°. Addition of water precipitated nitrosocarbanilide (5·2 g.), m. p. and mixed m. p. 101—102°, which reacted with benzene, as above, to give carbanilide, phenyl *iso*cyanate, and diphenyl.

The following substituted carbanilides were prepared in toluene solution by the action of carbonyl chloride on the appropriate aniline, the product being washed with water to remove amine hydrochloride. The carbanilides were finally crystallised from alcohol. The nitroso-compounds, prepared in each case by passing nitrous fumes for 4 hours into a solution of the carbanilide (0·5 g.) in a mixture of glacial acetic acid (80 c.c.) and acetic anhydride (15 c.c.) at 10°, were precipitated with water in quantitative yield as pale yellow solids and reacted with aqueous alkali, giving solutions which, after acidification, coupled with alkaline β-naphthol.

4 : 4′-Dimethylcarbanilide gave a *nitroso*-compound, m. p. 92° (decomp.) (Found: N, 15·7. $C_{15}H_{15}O_2N_3$ requires N, 15·6%).

3 : 3′-Dichlorocarbanilide gave a *nitroso*-compound, m. p. 106° (decomp.), which was stable for several weeks (Found: N, 13·5. $C_{13}H_9O_2N_3Cl_2$ requires N, 13·55%).

4 : 4′-Dichlorocarbanilide gave a stable *nitroso*-compound, m. p. 118° (decomp.) (Found: N, 13·4. $C_{13}H_9O_2N_3Cl_2$ requires N, 13·55%). A solution of the nitroso-compound (2 g.) in benzene (150 c.c.) was kept at room temperature for 24 hours. Nitrogen was evolved. After removal of benzene the residue was distilled, a fraction (0·7 g.), b. p. 200—270°, being collected, which solidified. Crystallisation from alcohol gave 4-chlorodiphenyl in colourless plates, m. p. and mixed m. p. 79—80°.

Class B.—o-*Chloroacetanilide.* Nitrous fumes were passed for 2 hours into a cold solution of *o*-chloroacetanilide (5 g.) in glacial acetic acid (50 c.c.). Addition of water precipitated the *nitroso*-compound, m. p. 59° (decomp.) (Found: N, 13·8. $C_8H_7O_2N_2Cl$ requires N, 14·1%). A solution of the nitroso-compound (2 g.) in benzene (100 c.c.) evolved oxides of nitrogen. After 3 days the benzene was removed by distillation and from the residue light petroleum (b. p. 60—80°) extracted *o*-chloroacetanilide, m. p. and mixed m. p. 87° after recrystallisation from light petroleum.

2 : 6-*Dichloro*-4-*nitroacetanilide.* Nitrous fumes were passed for 3 hours into a solution of 2 : 6-dichloro-4-nitroacetanilide (1 g.) in a mixture of glacial acetic acid (40 c.c.) and acetic anhydride (10 c.c.) at 10°. A yellow nitroso-compound [1 g., m. p. 100° (decomp.)] was precipitated on pouring into water. On standing or warming with benzene, 2 : 6-dichloro-4-nitroacetanilide was regenerated. The nitroso-compound was too unstable for analysis, but dissolved slowly in aqueous alkali to give a solution which, after acidification, coupled with alkaline β-naphthol.

1-*Acetamido*-2-*methylanthraquinone.* Nitrous fumes were passed for 4 hours into a solution of 1-acetamido-2-methylanthraquinone (10 g.) in glacial acetic acid (120 c.c.) at 15°. The nitroso-compound, which separated as a yellow solid [10 g., m. p. 106° (decomp.)] on pouring into water, was warmed with benzene (400 c.c.) for 4 hours. On evaporation to small bulk 6 : 7-phthalylindazole separated as an orange-brown solid (8 g., m. p. 240—245°), which, after purification by vacuum sublimation and crystallisation from glacial acetic acid, melted at 255—256° (cf.

D.R.-P. 269,842; *Chem. Zentr.*, 1914, I, 717) (Found: C, 72·2; H, 3·8. Calc. for $C_{15}H_8O_2N_2$: C, 72·5; H, 3·3%).

Phenylurethane (cf. Willstätter and Stoll, *Ber.*, 1909, **42**, 4876). Nitrous fumes were passed for 3 hours into a cold solution of phenylurethane (5 g.) in glacial acetic acid (100 c.c.). Addition of water precipitated the nitroso-compound as a pale yellow solid, m. p. 60—61° (decomp.). Treatment with aqueous alkali and subsequent acidification gave a solution which coupled with β-naphthol. On standing alone at room temperature, or on warming with benzene, oxides of nitrogen were evolved and phenylurethane (m. p. and mixed m. p. 51° after crystallisation from hot water) was regenerated.

Class C.—*4-Dimethylamino-4′-acetamidoazobenzene.* Nitrous fumes were passed for 3 hours into a solution of 4-dimethylamino-4′-acetamidoazobenzene (5 g.) in glacial acetic acid (60 c.c.) cooled in ice-water. The brown solid (4·3 g.), which separated on pouring into water, was sublimed at 120° in a high vacuum and gave *p*-nitrodimethylaniline (1 g.), which separated from alcohol in golden needles, m. p. and mixed m. p. 161—162° (Found: C, 58·1; H, 6·0. Calc. for $C_8H_{10}O_2N_2$: C, 57·8; H, 6·0%).

Benzanilide. Nitrous fumes were passed for 4½ hours into a solution of benzanilide (1 g.) in glacial acetic acid (70 c.c.). Addition of ether deposited benzenediazonium nitrate (0·4 g.), which detonated violently at about 90°. In aqueous solution it coupled with alkaline β-naphthol and gave a positive " brown ring " test for nitrate.

*Benzo-*p*-toluidide.* Nitrous fumes were passed for 4½ hours into a cold solution of benzo-*p*-toluidide (5 g.) in glacial acetic acid (150 c.c.). Addition of ether precipitated *p*-toluenediazonium nitrate, which detonated on heating, coupled with alkaline β-naphthol, and gave a positive " brown ring " test.

*Diacetyl-*1 : 3*-phenylenediamine.* Nitrous fumes were passed for 5 hours into a cold solution of diacetyl-1 : 3-phenylenediamine (5 g.) in glacial acetic acid (100 c.c.). Addition of water caused no separation of solid, but addition of ether precipitated *m*-acetamidobenzenediazonium nitrate (3·1 g.) as a light brown powder, which was filtered off and washed with ether. It detonated violently when warmed to about 95° or when scratched with a spatula, was soluble in water, and gave the " brown ring " test for a nitrate. *Reaction with water:* A solution of the diazonium nitrate (2·5 g.) in water (100 c.c.) was kept overnight at room temperature. Nitrogen was slowly evolved and evaporation of the solution to small bulk deposited *m*-acetamidophenol (0·7 g.), which was redissolved in water, boiled with charcoal, and filtered. Pure *m*-acetamidophenol, m. p. and mixed m. p. 146—147°, separated. *Reaction with ethyl alcohol:* The diazonium nitrate (0·5 g.) was boiled under reflux for 6 hours with ethyl alcohol (20 c.c.). Removal of the alcohol left a residue, which was extracted with hot water, boiled with charcoal, and filtered. *m*-Acetamidophenetole (m. p. 96—97°) separated from the filtrate. Wagner (*J. pr. Chem.*, 1885, **32**, 75) records m. p. 96—97°. *Reaction with cuprous cyanide:* A solution of the diazonium nitrate (2·5 g.) in ice-cold water (50 c.c.) was added to a warm solution of copper sulphate (8 g.) and potassium cyanide (7 g.) in water (50 c.c.), and the mixture heated on the water-bath for ½ hour. The cold reaction mixture was filtered, and the filtrate extracted with ether. Evaporation of the ether from the dried extract left a residue, which after three crystallisations from alcohol gave *m*-cyanoacetanilide, m. p. 129—130°. Bogert and Beans (*J. Amer. Chem. Soc.*, 1904, **26**, 473) record m. p. 130·5—131°.

Class D.—Nitrous fumes were passed for periods up to several hours into cold solutions of the substances already named (p. 364) in glacial acetic acid. When the solutions were poured into water, the original acylarylamines were recovered unchanged in every case.

Prolonged Action of Nitrous Fumes on Nitrosoacetanilide.—Nitrous fumes were passed for 4 hours into a cold solution of nitrosoacetanilide (5 g.) in glacial acetic acid (70 c.c.). Addition of ether precipitated benzenediazonium nitrate (4·5 g.), identified as described above for the product from benzanilide (Found: N, 24·55. Calc. for $C_6H_5O_3N_3$: N, 25·15%).

Action of Nitric Acid on Nitrosoacetanilide.—Concentrated nitric acid (*d* 1·42, 2 c.c.) was added to a cold solution of nitrosoacetanilide (5 g.) in glacial acetic acid (40 c.c.). After 4 hours addition of ether precipitated benzenediazonium nitrate (1 g.), identified as described above.

Nitrosation of p*-Benzamidoacetanilide.*— Benzoyl chloride (9 g.) was added slowly with shaking to a cold mixture of *p*-aminoacetanilide (10 g.), acetone (200 c.c.), and powdered sodium hydroxide (10 g.). Addition of water precipitated in quantitative yield, p*-benzamidoacetanilide*, which separated from alcohol in a microcrystalline form, m. p. 230° (Found: C, 71·2; H, 5·2. $C_{15}H_{14}O_2N_2$ requires C, 70·9; H, 5·5%). Nitrous fumes were passed for 4 hours into an ice-cold solution of *p*-benzamidoacetanilide (10 g.) in a mixture of glacial acetic acid (400 c.c.) and acetic anhydride (100 c.c.). The *nitroso*-compound slowly separated as a yellow precipitate

(10 g.), which was filtered off, pressed on a porous tile, and dried in a vacuum; m. p. 116° (decomp.) (Found: N, 14·2. $C_{15}H_{13}O_3N_3$ requires N, 14·8%). A portion of the nitroso-compound (1·5 g.) was added to benzene (100 c.c.) and warmed to 70°. Nitrogen was evolved and the reaction was completed by boiling under reflux for an hour. Evaporation to small bulk precipitated a brown solid, which was crystallised from alcohol after boiling with charcoal. On cooling, 4-benzamidodiphenyl separated, m. p. 229—230°, both alone and on admixture with an authentic specimen.

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