320. *Cyclic Meso-ionic Compounds. Part III. Further Properties of the Sydnones and the Mechanism of their Formation.*

By Wilson Baker, W. D. Ollis, and V. D. Poole.

Some substituted *NC*-diarylsydnones have been prepared for dipole-moment investigation, and the direct nitration of *N*-phenylsydnone in the heterocyclic nucleus has been achieved.

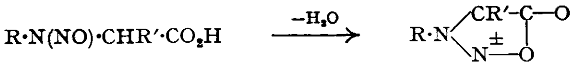
When heated with benzylamine the sydnones are smoothly converted into the benzylamides of *N*-substituted *N*-nitrosoglycines (IV); reaction does not occur with aniline.

The usual method of preparation of a sydnone, *e.g.*, *N*-phenylsydnone, by heating *N*-nitroso-*N*-phenylglycine (I; R = Ph, R′ = H) with acetic anhydride has been shown to proceed *via* the mixed anhydride (VIII) of acetic acid and *N*-nitroso-*N*-phenylglycine. This anhydride (VIII) has been prepared from acetyl chloride and the potassium salt of *N*-nitroso-*N*-phenylglycine; it passes slowly into *N*-phenylsydnone with loss of acetic acid when kept at room temperature, but rapidly when heated. The acid chloride of *N*-nitroso-*N*-phenylglycine is even more reactive and cannot be isolated, since it passes immediately into *N*-phenylsydnone with loss of hydrogen chloride. The mechanisms of these reactions and their significance in connection with the formation of oxazolones from α-acylamido-acids is discussed. Reaction of trifluoroacetic anhydride with *N*-nitroso-*N*-phenylglycine results in the immediate formation of *N*-phenylsydnone in 93% yield.

Suggestions governing the use of the term meso-ionic are made, and a note on the resonance energy of meso-ionic compounds is given. Unsuccessful attempts have been made to prepare meso-ionic compounds of the type (XXIV).

The properties of the sydnones, prepared by dehydration of *N*-nitroso-*N*-aryl(or -alkyl)-glycines (I), were interpreted in Part I of this series (Baker, Ollis, and Poole, *J.*, 1949, 307) on the basis of a five-membered cyclic structure (II) which could not be represented, even approximately, by any conventional covalent formula. It was shown that the sydnones must be regarded as possessing a single hybrid structure of aromatic type, derived from a number of contributing forms all of dipolar (zwitterionic) or polypolar nature. Such compounds were termed meso-ionic, and the symbol ± was used, as in (II), to indicate this hybrid character. This view of the structure of the sydnones was strongly supported in Part II (Hill and Sutton, *J.*, 1949, 746) by a study of their dipole moments.

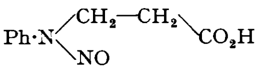
(I.)

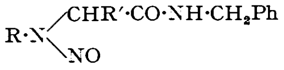


(II.)

Several new *NC*-diarylsydnones have been prepared for further dipole-moment investigation. α-Halogeno-phenylacetyl chlorides, prepared either by the action of phosphorus pentachloride on a mandelic acid or by bromination of a phenylacetyl chloride, were converted *via* the methyl α-halogeno-phenylacetates into the methyl α-arylamino-phenylacetates by reaction with aniline, *p*-toluidine, or *p*-chloroaniline, and then hydrolysed to the α-arylamino-phenylacetic acids. Nitrosation then yielded the *N*-nitroso-*N*-arylamino-phenylacetic acids (I; R and R′ = aryl groups), which were then dehydrated with acetic anhydride to the *NC*-diarylsydnones (II; R and R′ = aryl groups). The following sydnones were prepared in this way: *N*-phenyl-*C*-*p*-chlorophenylsydnone (II; R = Ph, R′ = *p*-C_6H_4Cl); *NC*-di-*p*-chlorophenylsydnone (II; R = R′ = *p*-C_6H_4Cl); *N*-phenyl-*C*-*p*-tolylsydnone (II; R = Ph, R′ = *p*-C_6H_4Me); *NC*-di-*p*-tolylsydnone (II; R = R′ = *p*-C_6H_4Me). These *NC*-diarylsydnones fluoresce in ultra-violet light, which indicates a certain degree of conjugation throughout the whole molecule.

Of interest to the general question of the structure of the sydnones is the observation that *N*-nitroso-β-anilinopropionic acid (III) is not dehydrated by acetic anhydride. If the

(III.)

$\mathrm{Ph{\cdot}N(NO){\cdot}CH_2{-}CH_2{\cdot}CO_2H}$

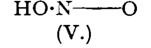

$\mathrm{R{\cdot}N(NO){\cdot}CHR'{\cdot}CO{\cdot}NH{\cdot}CH_2Ph}$
(IV.)

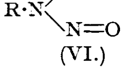
sydnones were correctly represented by the bicyclic structure originally proposed (Earl and Mackney, *J.*, 1935, 899; Earl and Eade, *J.*, 1946, 591), then *N*-nitroso-β-anilinopropionic acid (III) should, when dehydrated, give a bicyclic structure containing a bridged 6-membered heterocyclic ring. . On the basis of a meso-ionic structure for the sydnones, (III) is incapable of dehydration to such a compound, as the presence of the methylene group in the 6-membered ring would prevent the possession of a similar cyclic, electronic system.

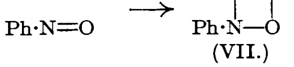
The direct chlorination of *N*-phenylsydnone in acetic acid to give *C*-chloro-*N*-phenylsydnone has been described by Eade and Earl, but we find that the reaction proceeds more smoothly in acetic anhydride at 0°. *N*-*p*-Chlorophenylsydnone is similarly halogenated to *C*-chloro-*N*-*p*-chlorophenylsydnone. It has also been found possible to nitrate *N*-phenylsydnone in concentrated sulphuric acid at −10° to give *C*-nitro-*N*-phenylsydnone, but attempts to reduce this to the amine have not succeeded. The position of the nitro-group follows from the fact that the substance differs from the known *N*-*o*-, *N*-*m*-, and *N*-*p*-nitrophenylsydnones (Eade and Earl, *loc. cit.*). *C*-Bromo-*N*-phenylsydnone could not be made to yield a Grignard reagent, and it was unaffected by refluxing with sodium in benzene or dioxan. The persistent non-reactivity of the benzene nucleus in *N*-arylsydnones is further proof of the fact, already discussed in Part I, that the nitrogen atom to which it is attached bears a large fractional positive charge and is certainly not tervalent and neutral.

Reaction of the Sydnones with Benzylamine.—When sydnones are heated with benzylamine at 120—130° they yield the benzylamides of *N*-nitroso-*N*-aryl(or -alkyl)glycines (IV). Thus *N*-phenylsydnone, *N*-benzylsydnone, *N*-*cyclo*hexylsydnone, and *NC*-diphenylsydnone yield the benzylamides (IV; R′ = H, R = Ph, CH_2Ph, and *cyclo*hexyl, respectively). The benzylamide (IV; R′ = H, R = Ph) of *N*-nitroso-*N*-phenylglycine was also prepared by the nitrosation of the benzylamide of *N*-phenylglycine. This reaction of sydnones with benzylamine does not occur when the reactants are refluxed in benzene solution, and no reaction occurs when a sydnone is heated with aniline at 125°. The " lactone " group in the sydnone molecule is therefore much less reactive than a normal lactone, and this is consistent with the meso-ionic structure which does not permit the normal cationoid properties to be exhibited by the lactonic carbonyl group (see the contributors to the hybrid structure set out in Part I).

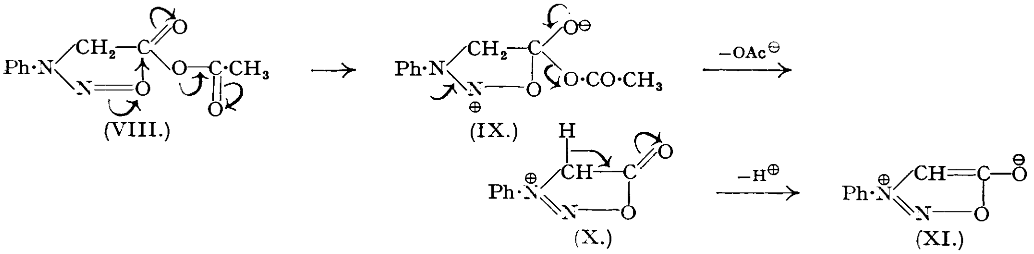
Mechanism of Sydnone Formation.—No satisfactory explanation has yet been given of the mechanism of the formation of sydnones from *N*-nitroso-*N*-aryl- or -alkyl-glycines (I). By analogy with the formally related γ-keto-acids, the reaction might proceed *via* a hydroxy-lactone-like intermediate (V) (cf. Earl and Mackney, *J.*, 1935, 899). The γ-keto-acids are, however, converted by acetic anhydride into the γ-acetoxy-lactones, and (V), if formed, might therefore be expected to yield its *O*-acetyl derivative rather than to undergo dehydration to a sydnone. A second possibility discussed by Earl (*Nature*, 1946, **158**, 909) is that the nitroso-acid (I) might undergo dehydration to a nitroso-keten (VI) with subsequent addition of the nitroso-oxygen atom to the carbonyl-carbon atom, by analogy with one mode of addition of a nitroso-compound to a keten to give a 4-membered lactone as, for example, in the case of the formation of the compound (VII) (Staudinger and Jelagin, *Ber.*, 1911, **44**, 365). There is, however, no evidence of the formation of ketens by the dehydration of carboxylic acids with acetic anhydride, and the fact that the sydnones may be prepared from the *N*-nitrosoglycines (I) by reaction with acetic anhydride in the cold makes it extremely unlikely that the keten (VI) is an intermediate.


(V.)


$\mathrm{R{\cdot}N(N{=}O){\cdot}CR'{=}CO}$
(VI.)


(VII.)

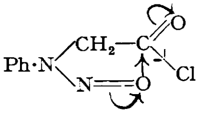
Some light was thrown on the mechanism of sydnone formation by the observation that *N*-phenylsydnone may be prepared by the action of acetic anhydride on the potassium salt of *N*-nitroso-*N*-phenylglycine. Owing to the insolubility of the potassium salt the reaction proceeds more slowly than with the free acid, but dissolution and sydnone formation take place rapidly if one equivalent of acetyl chloride is added. The reaction of the potassium salt with acetyl chloride could scarcely proceed otherwise than by formation of the mixed anhydride (VIII) of *N*-nitroso-*N*-phenylglycine and acetic acid, and this will almost certainly be formed also by the action of acetic anhydride on the free nitroso-acid. In (VIII), as in other anhydrides, one or other of the carbonyl groups may behave like a normal ketonic group rather than like a carboxylic-carbonyl group, because the bridge oxygen atom cannot effectively neutralise the cationoid character of both carbonyl groups simultaneously (cf. the reactivity of a methyl group in acetic anhydride in the Perkin reaction, the carbonyl reactivity in phthalic anhydride, etc.). The glycine carbonyl group may, therefore, in the mixed anhydride (VIII) develop much stronger cationoid properties than in the free acid (or in the salt) so that attack by the anionoid nitroso-oxygen atom becomes possible (see VIII). These changes lead to (IX) which by a natural process loses an acetate anion, and probably undergoes shift of the positive charge to give the cation (X). This, in turn, by the normal electronic movements shown, passes by loss of a proton (a process analogous to enolisation) into one of the more important contributors (XI) (see dipole moment evidence in Part II; Hill and Sutton, *J.*, 1949, 746) to the hybrid sydnone structure. The overall change involves loss of acetic acid from (VIII), and the final distribution of the electrons to give the single hybrid sydnone molecule will follow the formation of (XI) or of any structure containing the same heterocyclic ring. The alternative cyclisation involving the other carbonyl group is much less likely as it would lead to the formation of a seven-membered ring, and this could not in any case yield a sydnone by loss of acetic acid.

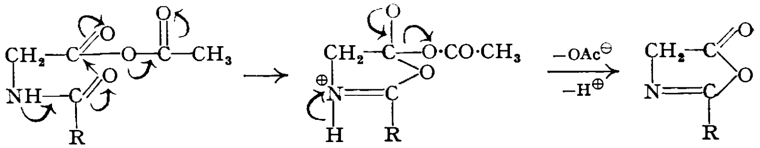

(VIII.) (IX.) (X.) (XI.)

Evidence that the usual method of sydnone formation proceeds as just described is provided by the properties of the mixed anhydride (VIII). This substance was obtained by treating a suspension of the potassium salt of *N*-nitroso-*N*-phenylglycine in benzene with rather less than one equivalent of acetyl chloride, and was isolated from the filtrate as a low-melting unstable solid. At room temperature the anhydride (VIII) loses acetic acid and passes into the much higher-melting sydnone during the course of five days; the change also occurs, giving very high yields, in hot benzene, and is almost quantitative when the solid is kept under diminished pressure over potassium hydroxide at room temperature. The anhydride (VIII) clearly behaves as a true intermediate.

These experiments and considerations suggested a new method by which sydnones might be prepared. The very great chemical activity exhibited by the acid chlorides may be ascribed to the abnormally high degree of cationoid character possessed by the carbon atom, which may exceed even that in an aldehyde or ketone owing to the strong inductive effect of the chlorine atom, $\overset{\curvearrowleft}{O{=}\overset{|}{C}}{\rightarrow}Cl$. Hence the acid chloride (XII) of *N*-nitroso-*N*-phenylglycine should undergo even more ready transformation into *N*-phenylsydnone than the mixed anhydride (VIII); the same series of changes as (VIII) to (XI) would occur, but in this case the reaction would proceed with loss of hydrogen chloride. There is, however, one complicating factor, namely, that *N*-phenylsydnone readily reacts with hydrogen chloride in a variety of solvents to give coloured decomposition products. Nevertheless, reaction of *N*-nitroso-*N*-phenylglycine in cold ethereal solution with thionyl chloride gave extremely rapidly, if not immediately, a 28% yield of *N*-phenylsydnone, and in dioxan, in presence of three equivalents of pyridine to react with the hydrogen chloride, a 75% yield of the sydnone was obtained. It seems likely that the acid chloride (XII) passes spontaneously at room temperature into *N*-phenylsydnone. This new method of sydnone formation possesses advantages over the usual much slower dehydration of the *N*-nitroso-*N*-arylglycines with acetic anhydride.

A very close parallel may be drawn between the formation of sydnones and the preparation of 2-substituted oxazol-5-ones (XV) by the action of acetic anhydride on α-acylamido-acids. The latter must now be regarded as occurring *via* the mixed anhydride (XIII), in which the electronic changes shown in (XIII) and (XIV) lead to the loss of acetic acid and the formation of the oxazolone (XV). The parallel extends also to the spontaneous conversion of the chloride of *N*-nitroso-*N*-phenylglycine (XII) into *N*-phenylsydnone, since it was found by Barber, Gregory, Slack, Stickings, and Woolman (*CPS* 234; " The Chemistry of Penicillin," Princeton Univ. Press, 1949, p. 731, 746) that the acid chlorides of the α-acylamido-acids pass directly into the oxazolone hydrochlorides; the mechanism is doubtless similar to that given above.


(XII.)

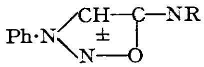


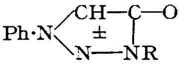
(XIII.) (XIV.) (XV.)

One further novel method for the preparation of sydnones from *N*-nitroso-*N*-arylglycines has resulted from the foregoing experiments. It has been found by Bourne, Stacey, Tatlow, and Tedder (*J.*, 1949, 2976) that trifluoroacetic anhydride rapidly brings about the complete formation of esters from alcohols or phenols and acids at room temperature, and it was suggested that the reaction proceeded *via* the mixed anhydride of the carboxylic acid and trifluoroacetic acid, $R\cdot CO\cdot O\cdot CO\cdot CF_3$. If this is indeed the case, then trifluoroacetic anhydride should react with *N*-nitroso-*N*-arylglycines to give, for example, the mixed anhydride $Ph\cdot N(NO)\cdot CH_2\cdot CO\cdot O\cdot CO\cdot CF_3$, which, in view of the very powerful electrophilic properties of the CF_3 group, should lose trifluoroacetic acid and pass into *N*-phenylsydnone even more easily than the related acetyl derivative (VIII). This expectation was fully realised as it was found that addition of trifluoroacetic anhydride to an ethereal solution of *N*-nitroso-*N*-phenylglycine at −5° caused immediate separation of *N*-phenylsydnone in 93% yield.

Support of a negative character for the preceding views on the mechanism of sydnone formation was afforded by the facts that the ethyl ester, the anilide, and the benzylamide of *N*-nitroso-*N*-phenylglycine are unaffected by hot acetic anhydride. This is to be expected, since in all three cases the cationoid properties of the carbonyl carbon atoms are largely neutralised by direct linkage with the electron-donating ethoxy-, anilino-, and benzylamino-groups respectively. It is of interest that formally the anilide and benzylamide of *N*-nitroso-*N*-phenylglycine might give rise on dehydration to cyclic meso-ionic compounds of the types (XVI) and (XVII) ($R = Ph$ or CH_2Ph), but these modes of dehydration are excluded by the mechanism now proposed for sydnone formation, and require that, even should cyclisations occur under more drastic conditions, they should yield *N*-phenylsydnone by loss of either aniline or benzylamine.

(XVI.)



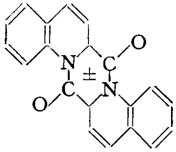


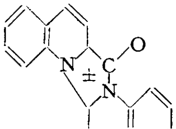
(XVII.)

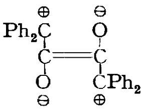
Note on the Use of the Term Meso-ionic and the Symbol ±.—In Part I (*loc. cit.*, p. 311) the meaning of the term meso-ionic was applied primarily to compounds which cannot be represented even approximately by any one covalent formula, or as a hybrid of a number of covalent formulæ, but which can be depicted as a hybrid of a number of ionic (dipolar, tetrapolar, etc.) forms. Purely meso-ionic compounds already known in the cyclic series are the sydnones, the " *endo*thiodihydrothiodiazoles " and a number of closely related " *endo* " compounds (see Part I, p. 311), and probably the complex quinaldic acid derivative (XVIII) (Brown and Hammick, *Nature*, 1949, **164**, 831) and Besthorn's Red (XIX) (Krollpfeiffer and Schneider, *Annalen*, 1937, **530**, 34; see Brown and Hammick, *loc. cit.*). In the open-chain series an example of a meso-ionic compound is provided by the " dimeric diphenylketen " derived from benzilic acid, which is regarded by Schönberg and Sina (*J.*, 1947, 175) as a molecule which has possibilities of resonance and to which di- and tetra-polar forms such as (XX) contribute.

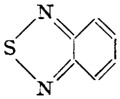
A strict application of the above definition of a meso-ionic compound would include the aliphatic diazo-compounds, the organic azides, and a number of inorganic compounds, for example, nitrous oxide, which is usually represented as a hybrid of ionic forms. It seems desirable, however, that the term " meso-ionic " and the ± symbol should not be applied to compounds unless their use obviously conveys a better understanding of the actual structure of the molecule than may be given by the more commonly used methods of description and representation. No advantage appears to be gained by classifying these compounds as " meso-ionic," although they are very simple examples of the type.

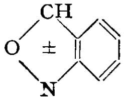
In the cyclic series the meso-ionic structure was previously represented by a single formula with the symbol ± placed within the ring, and the conversion of a bridged formula into a meso-ionic representation merely involved the replacement of the bridge bond by ±. In view of the fact that in some cases alternative hypothetical bridged structures may be drawn, it is now considered more satisfactory to represent all the atoms actually concerned in the meso-ionic part of the molecule as being united by single bonds (consisting of localised electron pairs) and then to add the symbol ± indicating the presence of mobile (π) electrons. We now prefer to represent, for example, the sydnones as in (II), and the "*endo*thiodihydrothiodiazoles" by (XXV). An advantage gained by the use of single bonds is that the resulting structure is probably as simple and satisfactory a representation of the actual molecule as may be obtained within the limits of a single, simple formula.

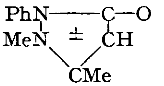

(XVIII.)


(XIX.)


(XX.)


(XXI.)


(XXII.)


(XXIII.)

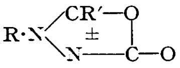
Cyclic compounds such a piazthiole, benzfurazan, anthranil, etc., may be described as partially meso-ionic because they can be regarded as hybrids of both covalent (*o*-quinonoid) and ionic forms (see Part I). The expression "partially meso-ionic" is permissible just as is the term "partially aromatic"; indeed, a compound such as pyrrole may be said to be both partially meso-ionic and partially aromatic, but the former emphasises the polar, ionic nature of some of the contributing forms. It does not seem desirable to extend the idea of partially meso-ionic compounds to simple open-chain substances, for example, the amides, and in the case of the cyclic compounds mentioned above they may be represented either by *o*-quinonoid formulæ (*e.g.*, XXI, piazthiole) or by meso-ionic formulæ using the ± symbol (*e.g.*, XXII, anthranil) as seems to agree more closely with their chemical properties. The ± sign is used with single bonds in the heterocyclic rings, and can be conveniently applied to such compounds as antipyrin (see Brown, Hukins, Le Fèvre, Northcott, and Wilson, *J.*, 1949, 2812) which, if it is wished to emphasise its meso-ionic character, may be written as (XXIII).

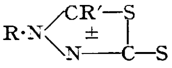
The Resonance Energy of Meso-ionic Compounds.—It has been suggested that meso-ionic compounds possess considerable resonance energy. The resonance energy of a molecule is calculated with respect to an arbitrarily chosen covalent structure, but in the case of meso-ionic compounds there is no covalent structure with which comparison can reasonably be made For example, the resonance energy of a sydnone molecule calculated with reference to the original bicyclic structure would be unsatisfactory, and it would be equally so to attempt to use any one of the ionic contributors to the hybrid as the reference state. The stability of a meso-ionic compound cannot, therefore, be readily expressed in terms of a resonance energy.

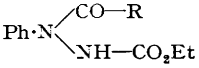
According to the molecular-orbital treatment (see Coulson, *Quart. Reviews*, 1947, **1**, 165) the stability of the sydnones and of aromatic compounds, in general, is explicable by the fact that the non-localised electrons in the molecular orbitals have higher binding energy than when paired in localised bonds, and this energy will clearly be greater in cyclic than in open-chain structures. Thus, the stability of the sydnones is due to their cyclic structure and the possession of a number of mobile (π) electrons. Calculations of the charges on the atoms composing the ring structure have been made (Longuet-Higgins, quoted by Hill and Sutton, *J.*, 1949, 752; *J. Chim. physique*, 1949, **46**, 247), and it is possible that a more accurate picture of the actual state of the molecule may thus be obtained than is possible by assessing the relative probabilities of the canonical forms contributing to the hybrid and arriving at a weighted mean value for the charge distribution. The latter method has, however, much to commend it to the organic chemist, and applied with proper knowledge and caution may lead to a moderately accurate picture of the charge distribution, and hence to a rough idea of the magnitude and direction of the dipole moment of the molecule. It may be pointed out here that a meso-ionic structure is not necessarily associated with a high dipole moment, as is the case with the sydnones and many closely related compounds; the moment may even be zero, as should be the case with the quinaldic acid derivative (XVIII). Professor H. D. Springall and Mr. C. B. Knowles have determined the heats of combustion of certain sydnones at the University of Manchester, and the results of their work will be published shortly.

Attempts to prepare Cyclic Meso-ionic Compounds of Type (XXIV).—A possible cyclic meso-ionic system is shown in formula (XXIV), which differs from the sydnones in the reversal of the ‒CO‒O‒ grouping. The dithio-analogues (XXV) are known (see Schönberg, *J.*, 1938, 824; Jensen and Friediger, *Kgl. Danske Videnskab. Selskab*, 1943, **20**, 1; Earl, Leake, and Le Fèvre, *J.*, 1948, 2273; this series, Part I, *loc. cit.*). Our attempted syntheses of (XXIV) are mainly based on methods by which the dithio-analogues have been prepared, and failure is due in several cases to the instability of carbamic acids.

(1) Compounds of type (XXV) are formed from acid chlorides and salts of *N*′-dithiocarboxy-*N*-arylhydrazines (Busch *et al.*, *J. pr. Chem.*, 1899, **60**, 218, 228, 231; 1903, **67**, 201, 202, 250, 257). The potassium salt of *N*′-carboxy-*N*-phenylhydrazine reacted with acid chlorides to give only mixtures of *N*- and *N*′-acyl- and *NN*′-diacyl-*N*-phenylhydrazines. In attempts to prepare the *N*′-carboxy-*N*-acyl-*N*-phenylhydrazines, the *N*-formyl-, *N*-acetyl- (Heller, *Annalen*, 1891, **263**, 281), and *N*′-carbethoxy-*N*-benzoyl-*N*-phenylhydrazines (XXVI; R = H, Me, and Ph) were subjected to cold alkaline hydrolysis, but *N*-acylhydrazines resulted through loss of carbon dioxide. Again, *N*-benzoyl-*N*-phenylhydrazine did not undergo carboxylation with carbon dioxide in ethereal solution (cf. the carboxylation of phenylhydrazine; E. Fischer, *Annalen*, 1878, **190**, 123; Busch and Stern, *J. pr. Chem.*, 1899, **60**, 236). (2) *iso*Cyanates (XXVII) might cyclise to compounds (XXIV), but *N*-benzoyl-*N*′-carbethoxy-*N*-phenylhydrazine (XXVI; R = Ph) did not yield an *iso*cyanate by reaction with phosphoric anhydride, and the hydrochloride of *N*-benzoyl-*N*-phenylhydrazine reacted with carbonyl chloride giving the urea derivative (Ph·CO·NPh·NH)$_2$CO. (3) Benzimino ethyl ether hydrochloride and the potassium salt of *N*′-carboxy-*N*-phenylhydrazine gave carbon dioxide and *N*-anilinobenzamidine, Ph·C(:NH)·NH·NHPh, isolated as its picrate [cf. the corresponding synthesis of (XXV), Busch and Schneider, *J. pr. Chem.*, 1903, **67**, 246]. (4) The dithio-compounds (XXV; R = H) are formed from sodium dithioformate and the potassium salts of *N*′-dithiocarboxy-*N*-arylhydrazines (unpublished observation), but the reaction of sodium dithioformate with the potassium salt of *N*′-carboxy-*N*-phenylhydrazine gave only *N*′-thioformyl-*N*-phenylhydrazine, Ph·NH·NH·CHS.


(XXIV.)


(XXV.)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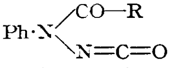
(XXVII.)

EXPERIMENTAL.

Methyl α-*Chloro*-p-*chlorophenylacetate*.—Phosphorus pentachloride (42 g.) and *p*-chloromandelic acid (18·5 g.; Jenkins, *J. Amer. Chem. Soc.*, 1931, **53**, 2341) were heated on the steam-bath for ½ hour, and then refluxed (oil-bath) for 3 hours. After cooling, the mixture was treated with methanol (400 c.c.), diluted with water, and extracted with ether. The extract was washed with aqueous sodium hydrogen carbonate, dried (MgSO$_4$), and distilled, giving *methyl* α-*chloro*-p-*chlorophenylacetate* (17 g., 79%), b. p. 140—143°/16 mm. (Found: C, 49·7; H, 3·8. $C_9H_8O_2Cl_2$ requires C, 49·4; H, 3·7%).

α-*Anilino*-p-*chlorophenylacetic Acid*.—Methyl α-chloro-*p*-chlorophenylacetate (20 g.), aniline (5·5 c.c.), hydrated sodium acetate (12·5 g.), and methanol (20 c.c.) were refluxed at 125—130° for 5 hours, cooled, poured into water (500 c.c.), and extracted with ether. The extract yielded methyl α-anilino-*p*-chlorophenylacetate, b. p. 165°/1 mm. (slight decomp.), which was characterised as the *toluene*-p-*sulphonyl* derivative, colourless tablets (from methanol), m. p. 137° (Found: C, 61·3; H, 4·8. $C_{22}H_{20}O_4NClS$ requires C, 61·4; H, 4·7%). The α-anilino-ester was hydrolysed by boiling it with excess of 10% aqueous sodium hydroxide for ½ hour, and the filtered solution yielded on acidification α-*anilino*-p-*chlorophenylacetic acid* which separated from aqueous ethanol as small needles, m. p. 178° (decomp.) (14 g., 59%) (Found: C, 64·0; H, 4·5; N, 4·8; Cl, 13·8. $C_{14}H_{12}O_2NCl$ requires C, 64·3; H, 4·6; N, 5·4; Cl, 13·6%).

N-*Phenyl*-C-p-*chlorophenylsydnone*.—Sodium nitrite (1·75 g.) was added with stirring to a solution of α-anilino-*p*-chlorophenylacetic acid (6 g.) in concentrated sulphuric acid (90 c.c.) at 0°, and after 1½ hours the mixture was poured on to ice. The crude nitroso-acid was extracted into ether, acetic anhydride (20 c.c.) added to the dried (MgSO$_4$) extract, and the solution heated on the water-bath for ½ hour after removal of the ether by distillation. The solid precipitated by the addition of water was washed with sodium carbonate solution, and crystallised from aqueous ethanol, giving N-*phenyl*-C-p-*chlorophenylsydnone* (4·4 g., 71%) as fine, faintly yellow needles, m. p. 129° (decomp.) (Found: C, 61·5; H, 3·3; N, 10·2; Cl, 13·4. $C_{14}H_9O_2N_2Cl$ requires C, 61·7; H, 3·3; N, 10·3; Cl, 13·0%). It shows a weak greenish-white fluorescence in ultra-violet light.

Methyl α-*Bromo*-p-*chlorophenylacetate*.—*p*-Chlorobenzyl cyanide (95 g.; Jackson and Field, *Amer.*

Chem. J., 1880, **2**, 88) was hydrolysed by boiling it for 2½ hours with acetic acid, water, and concentrated sulphuric acid (75 c.c. each). The isolated *p*-chlorophenylacetic acid (101 g.; m. p. 103—104°; lit., m. p. 103·5—104°) was converted into *p*-chlorophenylacetyl chloride (35 g.; b. p. 115°/16 mm.) by refluxing it with thionyl chloride (100 g.) and pyridine (1 c.c.) for 5 hours and fractionating the product. To this acid chloride was added anhydrous bromine (10 c.c.), whilst stirring and irradiating the mixture with ultra-violet light during ½ hour, the temperature then being slowly raised to 60°, where it was maintained for 3 hours. The resulting crude bromo-acid chloride was cautiously added to absolute methanol, the excess of which was then removed. The residual oil was dissolved in ether, washed with aqueous sodium carbonate, dried, and distilled, giving *methyl α-bromo-*p*-chlorophenylacetate* (36·4 g., 75%), b. p. 149—152°/16 mm., 128—129°/3 mm. (Found: C, 41·5; H, 3·5. $C_9H_8O_2BrCl$ requires C, 41·0; H, 3·1%).

*Methyl α-*p*-Chloroanilino-*p*-chlorophenylacetate.*—Methyl α-bromo-*p*-chlorophenylacetate (20 g.), *p*-chloroaniline (9·7 g.), hydrated sodium acetate (10·3 g.), and absolute ethanol (20 c.c.) were heated at 135—140° for 5 hours, and the product isolated as in the previous case. *Methyl α-*p*-chloroanilino-*p*-chlorophenylacetate* (19·0 g., 81%) was obtained as colourless needles, m. p. 129°, from benzene–light petroleum (b. p. 60—80°) (Found: C, 58·1; H, 4·2; N, 4·6; Cl, 22·9. $C_{15}H_{13}O_2NCl$ requires C, 58·1; H, 4·2; N, 4·5; Cl, 22·9%). This compound was also obtained in a similar manner from methyl α-chloro-*p*-chlorophenylacetate.

*α-*p*-Chloroanilino-*p*-chlorophenylacetic Acid.*—Hydrolysis of the preceding ester with 10% aqueous sodium hydroxide for ½ hour gave the *acid* (98% yield) as colourless needles (from ethanol), m. p. 164° (decomp.) (Found: C, 57·2; H, 3·7; N, 4·6; Cl, 23·4. $C_{14}H_{11}O_2NCl_2$ requires C, 56·8; H, 3·7; N, 4·7; Cl, 24·0%). When dried for analysis at 80° under diminished pressure the crystals became opaque.

NC-*Di-*p*-chlorophenylsydnone.*—Nitrosation of the preceding acid (9 g.) was effected in concentrated sulphuric acid (100 c.c.) by the addition of sodium nitrite (2·3 g.) at 0°, addition of the mixture to ice after 1½ hours, and extraction into ether. The extract was dried ($MgSO_4$), acetic anhydride (60 c.c.) added, and after 48 hours at room temperature the solvent was removed, the residue heated on the steam-bath for 5 minutes (longer heating results in the formation of dark material), water added, and the solid collected, washed with sodium carbonate solution, and crystallised from ethanol. NC-*Di-*p*-chlorophenylsydnone* (4·8 g., 51%) was obtained as almost colourless plates, m. p. 144° (Found: C, 54·6; H, 2·7; N, 9·5; Cl, 23·3. $C_{14}H_8O_2N_2Cl_2$ requires C, 54·7; H, 2·6; N, 9·1; Cl, 23·1%), which exhibit a marked greenish-white fluorescence in ultra-violet light.

*Methyl α-Chloro-*p*-tolylacetate.*—*p*-Methylmandelic acid (62 g.), prepared from *p*-tolualdehyde (99 g.) by the method given by Jenkins (*loc. cit.*) for the preparation of *p*-chloromandelic acid, was added to phosphorus pentachloride (160 g.), and after the vigorous reaction had subsided the mixture was refluxed for 3 hours, cooled, and added to methanol (1 l.). The solution was then diluted with water and extracted with ether, the extract shaken with sodium hydrogen carbonate solution, dried, and distilled, giving *methyl α-chloro-*p*-tolylacetate* (45 g., 61%), b. p. 139—140°/13 mm. (Found: C, 60·5; H, 5·3; Cl, 17·2. $C_{10}H_{11}O_2Cl$ requires C, 60·5; H, 5·6; Cl, 17·8%).

*α-Anilino-*p*-tolylacetic Acid.*—The preceding ester (20 g.), aniline (9·4 g.), hydrated sodium acetate (14 g.), and methanol (20 c.c.) were refluxed for 5 hours and poured into water (100 c.c.). Extraction with ether gave impure methyl α-anilino-*p*-tolylacetate (24 g.), which could not be distilled without decomposition but gave a *toluene-*p*-sulphonyl* derivative separating from aqueous methanol in colourless bipyramids, m. p. 109—110° (Found: C, 67·6; H, 5·0. $C_{23}H_{23}O_4NS$ requires C, 67·5; H, 5·6%). Alkaline hydrolysis of the crude ester (20 g.) as in the previous cases gave *α-anilino-*p*-tolylacetic acid* (14 g.), small, colourless needles (from aqueous methanol), m. p. 151—152° (Found: C, 73·9; H, 5·9; N, 5·8. $C_{15}H_{15}O_2N$ requires C, 74·7; H, 6·3; N, 5·8%).

N-*Phenyl*-C-*p*-*tolylsydnone.*—Nitrosation of the preceding acid (7·5 g.) in concentrated sulphuric acid (80 c.c.) with sodium nitrite (2·25 g.), and treatment of the nitroso-acid in ether with acetic anhydride (50 c.c.), as in the case of *N*-phenyl-*C*-*p*-chlorophenylsydnone, gave N-*phenyl*-C-*p*-*tolylsydnone* (5·1 g., 65%), light yellow needles (from ethanol), m. p. 144·5—146° (Found: C, 71·0; H, 4·6; N, 10·9. $C_{15}H_{12}O_2N_2$ requires C, 71·4; H, 4·8; N, 11·1%). It shows a weak greenish-white fluorescence in ultra-violet light.

*Methyl α-*p*-Toluidino-*p*-tolylacetate.*—Reaction of methyl α-chloro-*p*-tolylacetate (20 g.) with *p*-toluidine (10·8 g.), as in the preparation of methyl α-anilino-*p*-tolylacetate, gave *methyl α-*p*-toluidino-*p*-tolylacetate* (14·5 g., 43%), as tablets, m. p. 60—60·5°, from aqueous methanol (Found: C, 76·1; H, 6·8; N, 5·2. $C_{17}H_{19}O_2N$ requires C, 75·8; H, 7·1; N, 5·2%).

*α-*p*-Toluidino-*p*-tolylacetic Acid.*—Alkaline hydrolysis of the preceding ester (12·2 g.) gave the *acid* (9 g., 78%) as small needles, m. p. 153°, from aqueous ethanol (Found: C, 75·0; H, 6·2; N, 5·6. $C_{16}H_{17}O_2N$ requires C, 75·3; H, 6·7; N, 5·5%).

NC-*Di-*p*-tolylsydnone.*—The nitroso-acid obtained from the preceding acid (6·7 g.), concentrated sulphuric acid (100 c.c.), and sodium nitrite (2 g.), as in previous cases, was extracted into ether, the extract dried, and acetic anhydride (40 c.c.) added. The ether was removed by distillation, the residue heated on the steam-bath for 5 minutes, cooled rapidly, and poured into water, and the solid collected, washed with water and aqueous sodium carbonate, triturated with ether, and finally crystallised from ethanol. The *NC*-di-*p*-tolylsydnone formed colourless needles (5·2 g., 74%), m. p. 156—157·5° (decomp.) (Found: C, 72·0; H, 5·1; N, 10·7. $C_{16}H_{14}O_2N_2$ requires C, 72·1; H, 5·3; N, 10·5%). It exhibits a marked greenish-white fluorescence in ultra-violet light.

Ethyl β-Anilinopropionate.—Ethyl β-chloropropionate (36 g.), aniline (50 c.c.), hydrated sodium acetate (36 g.), and ethanol (10 c.c.) were heated at 125—130° for 12 hours. Water (100 c.c.) was added, and the oil taken up in ether, washed with 2N-sodium hydroxide (100 c.c.), dried ($MgSO_4$), and distilled, giving ethyl β-anilinopropionate (38 g., 75%) as a colourless oil, b. p. 125°/2 mm. (this ester, b. p. 175°/18 mm., was previously prepared by de Mouilpied, *J.*, 1905, **87**, 441, from β-iodopropionic ester and aniline).

β-Anilinopropionic Acid.—Ethyl β-anilinopropionate (40 g.), sodium hydroxide (12·5 g.), water (125 c.c.), and ethanol (10 c.c.) were refluxed for ½ hour, cooled, acidified to pH 4 with concentrated hydrochloric acid, and kept overnight at 0°. The β-anilinopropionic acid (24·2 g., 70%) was used directly for the nitrosation. Crystallisation from benzene–light petroleum (b. p. 60—80°) gave the pure acid as plates, m. p. 59° (Bischoff and Mintz, *Ber.*, 1892, **25**, 2351, prepared the acid from β-iodopropionic acid and aniline and give m. p. 59—60°).

N-*Nitroso-β-anilinopropionic Acid* (III).—A solution of sodium nitrite (13·5 g.) in water (100 c.c.) was slowly added at 0° to β-anilinopropionic acid (32 g.) suspended in water (400 c.c.). After 1½ hours the mixture was stirred with charcoal, filtered, and acidified with hydrochloric acid, and the crystalline precipitate was collected after being kept overnight at 0°, washed, and dried (yield : 33·7 g., 90%). Crystallisation from aqueous ethanol gave N-*nitroso-β-anilinopropionic acid* as almost colourless needles, m. p. 77° (Found : C, 55·9; H, 5·2; N, 14·7. $C_9H_{10}O_3N_2$ requires C, 55·7; H, 5·2; N, 14·4%).

C-*Chloro*-N-*phenylsydnone*.—Chlorine (4·4 g.) was passed into a solution of *N*-phenylsydnone (10 g.) in pure acetic anhydride (100 c.c.) at 0°, the solvent removed under diminished pressure, and the residue washed with ethanol and crystallised from 50 c.c. of ethanol. *C*-Chloro-*N*-phenylsydnone (4 g.) was obtained as colourless needles, m. p. 128·5° (Found : C, 49·1; H, 2·7; N, 14·0; Cl, 18·3. Calc. for $C_8H_5O_2N_2Cl$: C, 48·9; H, 2·5; N, 14·3; Cl, 18·1%). Eade and Earl chlorinated the sydnone in acetic acid in presence of sodium acetate, and obtained the chloro-compound, m. p. 127°, which was incompletely analysed.

C-*Chloro*-N-p-*chlorophenylsydnone*.—Reaction of chlorine (2·6 g.) with *N*-p-chlorophenylsydnone (7 g.) in acetic anhydride (120 c.c.) gave, by the previous procedure, C-*chloro*-N-p-*chlorophenylsydnone* (4·2 g., 51%) as faintly yellow needles, m. p. 108° (decomp.) from ethyl alcohol (Found : C, 41·6; H, 1·7; N, 12·2; Cl, 30·4. $C_8H_4O_2N_2Cl_2$ requires C, 41·6; H, 1·8; N, 12·1; Cl, 30·7%).

C-*Nitro*-N-*phenylsydnone*.—*N*-Phenylsydnone (3·6 g.) in concentrated sulphuric acid (15 c.c.) was stirred at −10° during the dropwise addition of a mixture of concentrated nitric acid (2 c.c.) and sulphuric acid (3 c.c.). The mixture was then stirred for ½ hour and poured on ice, and the solid collected, washed with aqueous sodium hydrogen carbonate and water, and crystallised from aqueous dioxan. C-*Nitro*-N-*phenylsydnone* (1·1 g., 24%) separated as light yellow plates, m. p. 142° (Found : C, 46·4; H, 2·4. $C_8H_5O_4N_3$ requires C, 46·4; H, 2·4%). This compound is rather unstable, cannot be crystallised from alcohol, and undergoes general decomposition when heated with dilute acids. In comparison, the N-*o*-, -*m*-, and -*p*-nitrophenylsydnones may be readily recrystallised, and yield the nitrophenylhydrazines on acid hydrolysis.

Benzylamide of N-*Nitroso*-N-*phenylglycine* (IV; R = Ph, R′ = H).—(a) *From* N-*phenylsydnone*. A mixture of *N*-phenylsydnone (5 g.) and benzylamine (7·5 c.c.) was heated at 120° for 8 hours and then poured into water. The precipitate (8 g., 96%) was collected, dried, washed with a little ether, and recrystallised several times from ethanol. The *benzylamide* of *N*-nitroso-*N*-phenylglycine separated in almost colourless needles, m. p. 109—110° (Found : C, 66·6; H, 5·5; N, 15·8. $C_{15}H_{15}O_2N_3$ requires C, 66·9; H, 5·6; N, 15·6%). It gave a positive Liebermann nitroso-reaction.

(b) *By nitrosation of the benzylamide of* N-*phenylglycine*. Sodium nitrite (6·33 g.) was slowly added to a stirred solution of the benzylamide of *N*-phenylglycine (see below) (20 g.) in concentrated sulphuric acid (200 c.c.) at 0—5°. After 2 hours it was poured on crushed ice (500 g.) and water (250 c.c.), and the precipitate was collected, washed and dried (19·0 g., 85%). Crystallisation from ethanol (50 c.c.) gave the benzylamide of *N*-nitroso-*N*-phenylglycine as colourless needles, m. p. and mixed m. p. 110·5° (Found : C, 67·0; H, 5·8; N, 15·3%).

Benzylamide of N-*Phenylglycine*.—*N*-Phenylglycine ethyl ester (15 g.) and benzylamine (25 c.c.) were kept at 140° for 8 hours and then poured into water, and the solid was collected, washed with dilute hydrochloric acid, and dried. The benzylamide of *N*-phenylglycine (18·8 g., 94%) separated from ethanol or benzene as colourless plates, m. p. 114° (Found : C, 74·8; H, 6·7; N, 11·8. Calc. for $C_{15}H_{16}ON_2$: C, 75·0; H, 6·7; N, 11·7%) (Dermer and King, *J. Org. Chem.*, 1943, **8**, 169, prepared this compound from *N*-phenylglycine and gave m. p. 113—114°). The *toluene*-p-*sulphonyl* derivative forms colourless needles, m. p. 138°, from ethanol (Found : C, 67·3; H, 5·6; N, 7·4; S, 8·4. $C_{22}H_{22}O_3N_2S$ requires C, 67·0; H, 5·6; N, 7·1; S, 8·1%).

Benzylamide of N-*Nitroso*-N-*benzylglycine* (IV; R = CH₂Ph, R′ = H).—Reaction of *N*-benzylsydnone (3 g.) with benzylamine (5 c.c.) was carried out as with *N*-phenylsydnone (above), and yielded the *benzylamide* of *N*-nitroso-*N*-benzylglycine as colourless needles (2·7 g., 56%), m. p. 110·5°, from ethanol (Found : C, 67·9; H, 6·1; N, 14·8. $C_{16}H_{17}O_2N_3$ requires C, 67·8; H, 6·0; N, 14·8%).

Benzylamide of N-*Nitroso*-N-cyclo*hexylglycine* (IV; R = C_6H_{11}, R′ = H).—*N*-*cyclo*Hexylsydnone (3 g.) and benzylamine (9 c.c.) gave, as in the previous cases, the *benzylamide* of *N*-nitroso-*N*-*cyclo*hexylglycine as colourless needles (1·4 g., 29%), m. p. 130·5—131°, from ethanol (Found : C, 65·5; H, 7·6; N, 14·9. $C_{15}H_{21}O_2N_3$ requires C, 65·5; H, 7·7; N, 15·3%).

Benzylamide of N-*Nitroso-α-anilinophenylacetic Acid* (IV; R = R′ = Ph).—A mixture of *NC*-diphenylsydnone (3 g.) and benzylamine (10 c.c.) was heated at 125° for 14 hours and then poured into water. The solid (3·85 g., 89%) was collected, washed with light petroleum, and crystallised from benzene–light petroleum (b. p. 60—80°) (50 c.c.) and then from ethanol, giving the *benzylamide* (2·1 g.) of *N*-nitroso-α-anilinophenylacetic acid as almost colourless needles, m. p. 142·5° (Found : C, 72·8; H, 5·6; N, 12·4. $C_{21}H_{19}O_2N_3$ requires C, 73·1; H, 5·5; N, 12·2%).

Preparation of N-*Phenylsydnone from the Potassium Salt of* N-*Nitroso*-N-*phenylglycine*.—The potassium salt of *N*-nitroso-*N*-phenylglycine (0·5 g.), prepared by the addition of alcoholic potassium hydroxide to *N*-nitroso-*N*-phenylglycine dissolved in the minimum quantity of ethyl alcohol, and acetic anhydride (15 c.c.) were heated on a steam-bath till complete dissolution occurred. The cooled, filtered solution was evaporated under diminished pressure, and the residue washed with water and crystallised from water, giving *N*-phenylsydnone, m. p. and mixed m. p. 134° (0·34 g., 91%). A similar result was obtained when 1 equivalent of acetyl chloride was added to the mixture, but dissolution occurred immediately and the reaction time was reduced to 1 hour.

Mixed Anhydride of N-*Nitroso*-N-*phenylglycine and Acetic Acid* (VIII).—Pure acetyl chloride (0·33 c.c.) in dry benzene (2 c.c.) was added to the finely powdered potassium salt of *N*-nitroso-*N*-phenylglycine (1·01 g.) in dry benzene (10 c.c.) with vigorous stirring at 10°. After 1 hour the filtered solution was evaporated under diminished pressure, leaving a thick oil (0·75 g.) which slowly solidified at 0° to a crystalline mass, m. p. 40—42°. Recrystallisation of a portion was effected by adding light petroleum (b. p. 40—60°) to its solution in benzene and cooling to 0°, the ***mixed anhydride*** of *N*-nitroso-*N*-phenylglycine and acetic acid separating as long, colourless needles, m. p. 45·5—46·0° (Found, in material analysed within 1 hour of collection : N, 12·7. $C_{10}H_{10}O_4N_2$ requires N, 12·6%).

When kept at 5° this compound developed a strong smell of acetic acid (Found, after 12 hours : N, 13·4%), and the m. p. rose to *ca.* 120° after 5 days. Yields of 75—80% of *N*-phenylsydnone were thus obtained, but slight decomposition of the sydnone occurs by long storage in contact with acetic acid, and the best conversion occurred by keeping the substance under diminished pressure over potassium hydroxide. After 5—6 days the solid (m. p. 131°) was washed with a little ether and dried, and then had m. p. and mixed m. p. with *N*-phenylsydnone 135°.

N-Phenylsydnone (0·20 g., 85%; m. p. 131—134°) was also obtained by refluxing the mixed anhydride (0·32 g.) in dry benzene (5 c.c.) for 6 hours.

Reaction of Thionyl Chloride with N-*Nitroso*-N-*phenylglycine*.—(*a*) To *N*-nitroso-*N*-phenylglycine (2 g.) in dry ether (20 c.c.) was added pure thionyl chloride (1·32 g.) in dry ether (5 c.c.). After a few minutes *N*-phenylsydnone began to separate in colourless needles. When this material showed signs of discoloration the ethereal layer was decanted, the solid washed with a little ether and then dilute sodium hydrogen carbonate solution, collected, and dried (0·5 g., 28%; m. p. 132—135°, undepressed when mixed with *N*-phenylsydnone).

(*b*) Pure thionyl chloride (1·32 g.) in dry dioxan (2 c.c.) was added slowly, with occasional cooling in ice, to a solution of *N*-nitroso-*N*-phenylglycine (2 g.) in a mixture of dioxan (5 c.c.) and pyridine (2·7 c.c.). After 0·25 hour at room temperature the solution was poured into water (150 c.c.), the solid collected, washed with dilute sodium hydrogen carbonate solution and then water, and dried (yield: 1·35 g., 75%); it had m. p. and mixed m. p. with *N*-phenylsydnone, 134—135°.

Reaction of Trifluoroacetic Anhydride with N-*Nitroso*-N-*phenylglycine*.—*N*-Nitroso-*N*-phenylglycine (1·0 g.) was dissolved in dry ether (10 c.c.), and trifluoroacetic anhydride (1·0 c.c.) added at −5°. *N*-Phenylsydnone separated immediately and, after removal of volatile compounds under reduced pressure, was washed with dilute aqueous sodium hydrogen carbonate and then with water, and dried (yield : 0·84 g., 93%); it had m. p. and mixed m. p. 135—136°.

Anilide of N-*Phenylglycine*.—When chloroacetyl chloride (50 g.) in ether (100 c.c.) was added to a solution of aniline (182 c.c.) in ether (500 c.c.) (cf. Meyer, *Ber.*, 1875, **8**, 1153) it yielded both the chloroacetyl derivative of aniline (53 g.; m. p. 133°, from ethanol) and the anilide of *N*-phenylglycine (37 g.; m. p. 111°, from water). The former was converted into the latter (92% yield) by reaction with aniline and sodium acetate in ethanol (Meyer, *loc. cit.*).

Anilide of N-*Nitroso*-N-*phenylglycine*.—Sodium nitrite (6·7 g.) was added with stirring to a solution of the preceding anilide (20 g.) in concentrated sulphuric acid (200 c.c.) at 0°. After 1½ hours the mixture was poured into crushed ice (500 g.) and water (200 c.c.), the precipitate collected, washed, and crystallised from dilute ethanol (yield 18·4 g.) and then from ethanol (charcoal), giving the *anilide* of *N*-nitroso-*N*-phenylglycine as straw-coloured needles, m. p. 144° (Found : C, 65·9; H, 5·0; N, 16·4. $C_{14}H_{13}O_2N_3$ requires C, 65·9; H, 5·1; N, 16·5%).

N-*Benzylsydnone*.—The yield of *N*-benzylsydnone from *N*-nitroso-*N*-benzylglycine (40 g.), inadvertently omitted in Part I, was 33·9 g. (94%).

N′-*Carbethoxy*-N-*benzoyl*-N-*phenylhydrazine* (XXVI; R = Ph).—*N*′-Carbethoxy-*N*-phenylhydrazine (10 g.; Heller, *Annalen*, 1891, **263**, 278), benzoyl chloride (7·8 g.), and pyridine (30 c.c.) were heated on the steam-bath for 2 hours, water was added, and the solid was collected. Recrystallisation from benzene–light petroleum (b. p. 60—80°) gave N′-*carbethoxy*-N-*benzoyl*-N-*phenylhydrazine* as needles, m. p. 128° (5·2 g., 33%) (Found : C, 67·6; H, 5·6; N, 10·4. $C_{16}H_{16}O_3N_2$ requires C, 67·6; H, 5·7; N, 9·9%).

N′-*Carbethoxy*-N-*formyl*-N-*phenylhydrazine* (XXVI; R = H).—A mixture of *N*′-carbethoxy-*N*-phenylhydrazine (10 g.) and 70% formic acid (80 c.c.) was heated on the steam-bath for 1½ hours, poured into water (200 c.c.), neutralised with sodium hydroxide solution, and extracted with ether. The extract was dried ($MgSO_4$) and evaporated, giving N′-*carbethoxy*-N-*formyl*-N-*phenylhydrazine* as needles [from benzene–light petroleum (b. p. 60—80°)], m. p. 85° (9·6 g., 83%) (Found : C, 57·8; H, 5·9; N, 13·5. $C_{10}H_{12}O_3N_2$ requires C, 57·7; H, 5·8; N, 13·5%).

Reaction between N-*Benzoyl*-N-*phenylhydrazine Hydrochloride and Carbonyl Chloride*.—*N*-Benzoyl-*N*-phenylhydrazine hydrochloride (4·9 g.) was prepared by hydrolysis of *N*-benzoyl-*N*′-acetyl-*N*-phenylhydrazine (5 g.; Widman, *Ber.*, 1893, **26**, 947) with concentrated hydrochloric acid (7·5 c.c.), water (30 c.c.), and ethanol (15 c.c.) on the steam-bath for 3 hours and evaporation to dryness. The hydrochloride (5 g.) and a 12·5% w/w solution (40 c.c.) of carbonyl chloride in toluene were refluxed with vigorous stirring until evolution of hydrogen chloride ceased (*ca.* 5 hours). The solid which separated on cooling (3·7 g.) was crystallised from nitrobenzene, giving needles of NN′-*di*(*benzanilido*)*urea*, $(Ph{\cdot}CO{\cdot}NPh{\cdot}NH)_2CO$, m. p. 274° (decomp.) (Found : C, 72·0; H, 4·9; N, 12·6. $C_{27}H_{22}O_3N_4$ requires C, 72·0; H, 4·9; N, 12·4%).

Reaction of Benzimino Ethyl Ether Hydrochloride with the Potassium Salt of N′-*Carboxy*-N-*phenylhydrazine*.—The potassium salt of *N*′-carboxy-*N*-phenylhydrazine (5 g.; Fischer, *Annalen*, 1878, **190**, 123; Busch and Stern, *J. pr. Chem.*, 1899, **60**, 236) was vigorously stirred in ethanol (100 c.c.) at −10°, and benziminoethyl ether hydrochloride added slowly. After 2 hours the mixture was allowed to warm to room temperature and then evaporated to dryness under reduced pressure in an atmosphere of nitrogen. Ether (100 c.c.) was now added, the extract evaporated, and the residual oil which solidified on trituration with light petroleum (b. p. 60—80°) was washed with light petroleum and dried [yield, 3·8 g.; m. p. 90—94° (decomp.)]. This basic material was unstable and could not be recrystallised; it gave a bright yellow *picrate*, m. p. 199° (decomp.), as needles from ethanol (Found : C, 51·8; H, 3·7; N, 19·1. $C_{19}H_{16}O_7N_6$ requires C, 51·8; H, 3·7; N, 19·1%). The free base, $C_{13}H_{13}N_3$, is presumably *N*-anilinobenzamidine, previously described by Voswinckel (*Ber.*, 1903, **36**, 2484) as an unstable oil.

Reaction of Sodium Dithioformate with the Potassium Salt of N′-*Carboxy*-N-*phenylhydrazine*.—To a solution of the potassium salt of *N'*-carboxy-*N*-phenylhydrazine (10 g.) in water (50 c.c.) was added a solution of sodium dithioformate (11 g.) in water (50 c.c.). After 48 hours the purple oil which later solidified was collected and dried (5·1 g.). It crystallised from light petroleum (b. p. 60—80°), giving *N'*-thioformyl-*N*-phenylhydrazine as thick colourless needles, m. p. 39·5—41°, undepressed on admixture with *N'*-thioformyl-*N*-phenylhydrazine, m. p. 39·5—41°, prepared similarly from phenylhydrazine and sodium dithioformate (Baker, Ollis, and Poole, forthcoming publication).

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