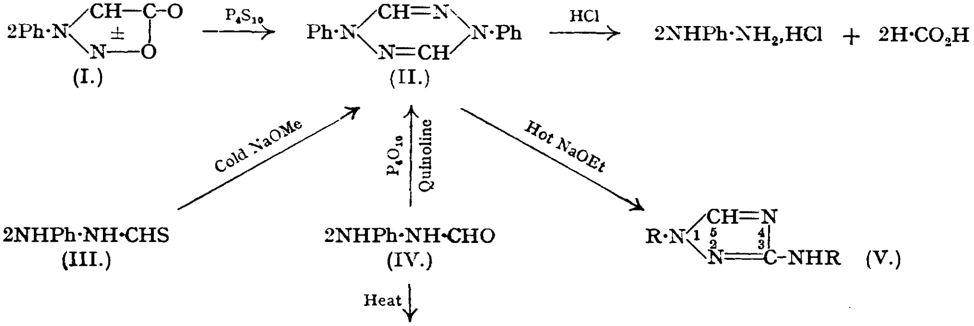
663. 1 : 4-*Diaryl*-1 : 4-*dihydro*-1 : 2 : 4 : 5-*tetrazines and Derived Substances.*

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

N-Phenylsydnone (I) reacts with phosphorus pentasulphide to give 1 : 4-dihydro-1 : 4-diphenyl-1 : 2 : 4 : 5-tetrazine (II), but compounds of this type are best prepared from *N*-aryl-*N'*-thioformylhydrazines (III) by treatment with cold sodium methoxide. Reaction of diaryldihydrotetrazines (II) with hot sodium ethoxide yields basic isomerides which are regarded as 1 : 2 : 4-triazole derivatives (V), the rational synthesis of which has been attempted. Examples in the literature of alleged 1 : 4-diaryl-1 : 4-dihydro-1 : 2 : 4 : 5-tetrazines are discussed.

In continuation of our studies on the sydnones (*J.*, 1949, 307; 1950, 1542), which belong to the class of cyclic meso-ionic compounds, an attempt was made to prepare mono- or di-thio-analogues by heating *N*-phenylsydnone (I) with phosphorus pentasulphide in toluene. The reaction resulted, however, in the production in 27% yield of a bright yellow compound, $C_{14}H_{12}N_4$, m. p. 189°, which may formally be derived from two molecules of *N*-phenylsydnone (I) by loss of two molecules of carbon dioxide. The properties of this substance show that it is 1 : 4-dihydro-1 : 4-diphenyl-1 : 2 : 4 : 5-tetrazine (II), a conclusion which is supported by alternative syntheses.



Ruhemann's compound, $C_{14}H_{12}N_4$

The reasons for assigning the tetrazine structure (II) to the yellow compound, $C_{14}H_{12}N_4$, are the following. (*a*) Hydrolysis with aqueous alcoholic hydrochloric acid gives two molecules each of phenylhydrazine and formic acid. (*b*) It shows no basic properties and is unaltered by being boiled with acetic anhydride, and hence it is unlikely to contain an NH group or groups. (*c*) Its very low dipole moment, as well as those of the corresponding 1 : 4-dihydro-1 : 4-di-*p*-tolyl- and 1 : 4-di-*p*-chlorophenyl-1 : 4-dihydro-1 : 2 : 4 : 5-tetrazine, is in agreement with structure (II). (*d*) The substance is very similar to the 1 : 4-dihydro-1 : 3 : 4 : 6-tetraphenyl-1 : 2 : 4 : 5-tetrazine prepared by Bamberger and Grob (*Ber.*, 1901, **34**, 523), and to the 1 : 4-di-*p*-bromophenyl-1 : 4-dihydro-3 : 6-diphenyl-1 : 2 : 4 : 5-tetrazine prepared by Chattaway and Walker (*J.*, 1925, **127**, 975) which are both yellow; all three compounds give a blue colour when treated with an oxidising agent in concentrated sulphuric acid.

A more rational synthesis of (II) has been found in the reaction of equimolecular quantities of *N*-phenyl-*N'*-thioformylhydrazine (III) (prepared from phenylhydrazine and sodium dithioformate) and sodium methoxide in methanol at room temperature, which gives the same tetrazine in 43% yield [cf. the cyclisation of thioformamidopyrimidines (Kenner and Todd, *J.*, 1946, 852 and later papers)]. The dehydration of *N'*-formyl-*N*-phenylhydrazine with phosphoric anhydride in quinoline also gives the tetrazine (II), but in only 5% yield. The interaction of sodium methoxide with *N*-aryl-*N'*-thioformylhydrazines, prepared from arylhydrazines and sodium dithioformate, is a general method for the production of 1 : 4-diaryl-1 : 4-dihydro-1 : 2 : 4 : 5-tetrazines. Thus *N*′-thioformyl-*N*-*p*-tolylhydrazine gives 1 : 4-dihydro-1 : 4-di-*p*-tolyl-1 : 2 : 4 : 5-tetrazine, and *N*-*p*-chlorophenyl-*N*′-thioformylhydrazine gives 1 : 4-di-*p*-chlorophenyl-1 : 4-dihydro-1 : 2 : 4 : 5-tetrazine. The method, however, does not succeed with *N*-benzyl-*N*′-thioformylhydrazine, $CH_2Ph{\cdot}NH{\cdot}NH{\cdot}CHS$, nor does this compound yield a tetrazine on being heated in quinoline (cf. Baddiley, Lythgoe, McNeil, and Todd, *J.*, 1943, 383), or on being heated with potassium acetate in methyl cyanide (cf. Kenner, Rodda, and Todd, *J.*, 1949, 1613).

Ultra-violet absorption measurements show that the 1 : 4-diaryl-1 : 4-dihydro-1 : 2 : 4 : 5-tetrazines are characterised by an absorption band at 290—300 $m\mu$. (see Fig. 1, curves 1 and 2), and this suggests considerable interaction between the phenyl groups and the heterocyclic ring. In addition, all the 1 : 4-diaryl-1 : 4-dihydro-1 : 2 : 4 : 5-tetrazines are bright yellow, and these facts suggest that forms such as that shown inset make important contributions to their hybrid structure. It follows that 1 : 4-diaryl-1 : 4-dihydro-1 : 2 : 4 : 5-tetrazines probably possess an almost planar structure, and the remote possibility that *cis* and *trans* forms might exist is thereby excluded.

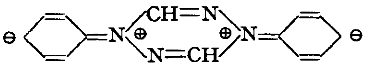
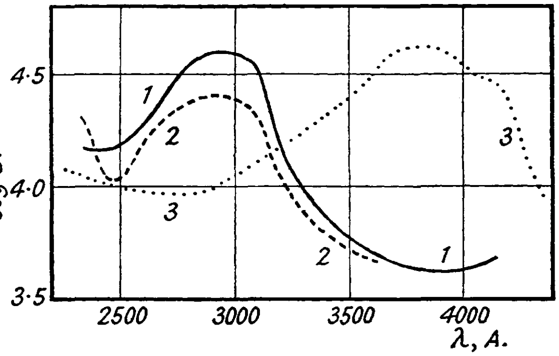
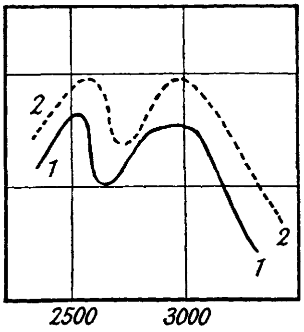


FIG. 1.



1. 1 : 4-*Dihydro*-1 : 4-*diphenyl*-1 : 2 : 4 : 5-*tetrazine.*
2. 1 : 4-*Dihydro*-1 : 4-*di*-p-*tolyl*-1 : 2 : 4 : 5-*tetrazine.*
3. *Compound* $C_{20}H_{20}O_4N_4$ (*Bowack and Lapworth*).

FIG. 2.

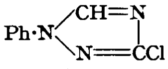


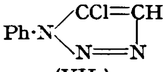
1. *Ruhemann's compound,* $C_{14}H_{12}N_4$.
2. *Derivative of above compound,* $C_{14}H_{10}N_4Cl_2$.

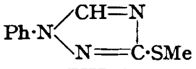
Isomerisation of 1 : 4-*Diaryl*-1 : 4-*dihydro*-1 : 2 : 4 : 5-*tetrazines in the presence of Sodium Ethoxide.* 1-*Aryl*-3-*arylamino*-1 : 2 : 4-*triazoles* (V).—The yellow 1 : 4-dihydro-1 : 4-diphenyl-1 : 2 : 4 : 5-tetrazine (II), when heated in alcoholic solution with a trace of sodium ethoxide, is rapidly converted into a colourless isomeride which is basic, yields a monoacetyl derivative, and is unaltered by concentrated hydrochloric acid at 150°. These facts and consideration of the most probable course of the isomerisation lead to the conclusion that this base is 3-anilino-1-phenyl-1 : 2 : 4-triazole (V; R = Ph). The structure (V) is preferred to the tautomeride with the NH-group in position 2 because it is more fully aromatic, and if the NH-group were in position 4 the substance would of necessity be meso-ionic and closely allied to " nitron " (see Baker, Ollis, and Poole, *loc. cit.*); as such it would be expected to have a large dipole moment (nitron, 7·2 D.), whereas its moment is only *ca.* 3·5 D. Exactly similar isomerisations are undergone by 1 : 4-dihydro-1 : 4-di-*p*-tolyltetrazine and 1 : 4-di-*p*-chlorophenyl-1 : 4-dihydro-1 : 2 : 4 : 5-tetrazine which yield 3-*p*-toluidino-1-*p*-tolyl-1 : 2 : 4-triazole (V; R = p-C_6H_4Me) and 3-*p*-chloroanilino-1-*p*-chlorophenyl-1 : 2 : 4-triazole (V; R = p-C_6H_4Cl) respectively. The latter triazole was also obtained as a by-product in the preparation of 1 : 4-di-*p*-chlorophenyl-1 : 4-dihydro-1 : 2 : 4 : 5-tetrazine by the action of sodium methoxide upon *N*-*p*-chlorophenyl-*N*′-thioformylhydrazine. These triazoles were basic and gave mono-acetyl derivatives.

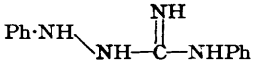
Attempts have been made to synthesise 1-aryl-3-arylamino-1 : 2 : 4-triazoles by unambiguous methods. (i) 3-Chloro-1-phenyl-1 : 2 : 4-triazole (VI) did not react with aniline, a fact which contrasts with the ready conversion of the isomeric 5-chloro-1-phenyl-1 : 2 : 3-triazole (VII) into the related anilino-triazole (Dimroth, *Annalen*, 1909, **364**, 225). (ii) 3-Methylthio-1-phenyl-

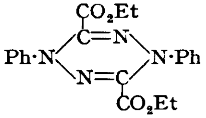
1 : 2 : 4-triazole (VIII) failed to react with aniline (see Johnson and Hahn, *Chem. Reviews*, 1933, **13**, 225—227). (iii) The guanidine (IX), which might be converted into (V) by reaction with formic acid [cf. the similar conversion of *N''*-amino-*NN'*-diphenylguanidine into 3-anilino-4-phenyl-1 : 2 : 4-triazole (Busch and Bauer, *Ber.*, 1900, **33**, 1067)], could not be prepared from either (*a*) phenylhydrazine hydrochloride and phenylcyanamide (cf. Ainley, Curd, and Rose, *J.*, 1949, 101; Pellizzari *et al.*, *Gazzetta*, 1891, **21** (i), 333; 1894, **24** (i), 455), or (*b*) phenylhydrazine and *N*-phenylthiourea (cf. Busch and Bauer, *loc. cit.*); the latter reaction resulted in loss of ammonia to give 1 : 4-diphenylthiosemicarbazide, NHPh·CS·NH·NHPh.


(VI.)


(VII.)


(VIII.)

(IX.)



(X.)

Examples of Alleged 1 : 4-*Diaryl*-1 : 4-*dihydro*-1 : 2 : 4 : 5-*tetrazines*.—(1) Compounds claimed to be 1 : 4-diaryl-1 : 4-dihydro-1 : 2 : 4 : 5-tetrazines, *e.g.* (II), were prepared in 2—5% yield by Ruhemann (Ruhemann and Elliott, *J.*, 1888, **53**, 850; Ruhemann, *J.*, 1889, **55**, 242; 1890, **57**, 50) by heating arylhydrazines, chloroform, and alcoholic potassium hydroxide. The reactions were supposed to proceed *via* the intermediate *iso*cyanamides, NHAr·NC. Phenylhydrazine gave a colourless product, $C_{14}H_{12}N_4$, m. p. 180°, for which the structure (II) was suggested, and the same compound was obtained by Bamberger (*Ber.*, 1897, **30**, 1263) by strongly heating *N'*-formyl-*N*-phenylhydrazine. The difficulty of preparing Ruhemann's compounds has prevented their close examination, but in the case of the phenylhydrazine derivative the molecular formula, $C_{14}H_{12}N_4$, has been confirmed. It gives an unstable hydrochloride, does not acetylate, and is unaltered by prolonged heating with either acids or alkalis, and its dipole moment of 2·1 D. almost certainly excludes a symmetrical structure. The pale yellow compound prepared by Ruhemann's method from *p*-tolylhydrazine has m. p. 185—186°, and differs markedly from the true, bright yellow 1 : 4-dihydro-1 : 4-di-*p*-tolyl-1 : 2 : 4 : 5-tetrazine, m. p. 182—183°.

Hewitt (*J.*, 1891, **59**, 213) was unable to prepare the corresponding *p*-chlorophenyl compound from chloroform, *p*-chlorophenylhydrazine, and alcoholic potassium hydroxide; the product, m. p. 152°, was described as *N*-*p*-chlorophenyl-*N'*-formylhydrazine, but the calculated analytical figure is incorrect. We find that this reaction does, in fact, give a very small amount of the *p*-chlorophenyl analogue of Ruhemann's compound (0·22% yield), and the similarity of structure is shown by comparison of the ultra-violet light extinction curves (Fig. 2). The phenyl compound shows absorption bands with maxima at 253 and 296 mμ.; the *p*-chlorophenyl compound shows maxima at 257 and 299 mμ., the slight shifts being due to the bathochromic effect of the chlorine atoms. From the reaction described above, the true *N*-*p*-chlorophenyl-*N'*-formylhydrazine, m. p. 186—187°, was also isolated; it was identical with the material prepared by formylation of *p*-chlorophenylhydrazine with formamide. All the compounds of the type described by Ruhemann show a strong white fluorescence in ultra-violet light.

(2) Ethyl " phenylhydrizinobromomethylenecarboxylate " (α-bromo-α-phenylhydrazonoacetate), $NHPh{\cdot}N{:}CBr{\cdot}CO_2Et$, was prepared by Bowack and Lapworth from benzenediazonium sulphate and ethyl α-bromoacetoacetate, and this compound reacted with aqueous alcoholic sodium carbonate in the cold to give a compound, $C_{20}H_{20}O_4N_4$, forming deep-red crystals with a blue metallic lustre, regarded as 3 : 6-dicarbethoxy-1 : 4-dihydro-1 : 4-diphenyl-1 : 2 : 4 : 5-tetrazine (X) (*J.*, 1905, **87**, 1867). The preparation of this intensely coloured compound has been repeated, but in view of the fact that (X) is simply the dicarbethoxy-derivative of the genuine, yellow 1 : 4-dihydro-1 : 4-diphenyl-1 : 2 : 4 : 5-tetrazine (II), it is clear that Bowack and Lapworth's compound must possess a very different structure. This is supported by comparing the ultra-violet light extinction curve of this compound (Fig. 1, curve 3) with the curves (1 and 2) of the true tetrazines. These authors also made the related *p*-tolyl compound, which likewise differs greatly from our 1 : 4-dihydro-1 : 4-di-*p*-tolyl-1 : 2 : 4 : 5-tetrazine.

We are indebted to Dr. L. E. Sutton and Mr. P. G. Edgerley for the determination of the dipole moments, which are discussed in the following communication.

EXPERIMENTAL.

Preparation of 1 : 4-*Dihydro*-1 : 4-*diphenyl*-1 : 2 : 4 : 5-*tetrazine* (II).—(a) *Reaction of phosphorus pentasulphide with* N-*phenylsydnone*. *N*-Phenylsydnone (2 g.) in dry toluene (20 c.c.) was heated with phosphorus pentasulphide (0·6 g.) in a sealed tube at 120° for six hours. The toluene solution was decanted and the residue repeatedly extracted with hot benzene. The combined solutions were evaporated and the yellow residue crystallised, first from ethanol and then from chloroform–light petroleum (b. p. 60—80°). 1 : 4-*Dihydro*-1 : 4-*diphenyl*-1 : 2 : 4 : 5-*tetrazine* (II) (0·4 g.; 27%) separated as small, yellow plates, melting sharply at 189—189·5° (Found: C, 70·7; H, 5·2; N, 23·6. $C_{14}H_{12}N_4$ requires C, 71·2; H, 5·1; N, 23·7%).

(b) *Dehydration of* N′-*formyl*-N-*phenylhydrazine*. *N*′-Formyl-*N*-phenylhydrazine (5 g.; see below) was mixed with quinoline (30 c.c.) and phosphoric anhydride (*ca.* 5 g.) and kept at 200° for one hour. The mixture was then cautiously diluted with water and neutralised with sodium carbonate. The quinoline was removed by steam-distillation, and the residual solid collected, washed with a little ethanol, and then crystallised from ethanol, giving 1 : 4-dihydro-1 : 4-diphenyl-1 : 2 : 4 : 5-tetrazine (II) (5% yield) as tiny, yellow plates, m. p. and mixed m. p. 190° (Found: C, 70·7; H, 5·1; N, 23·7%).

(c) *From* N-*phenyl*-N′-*thioformylhydrazine*.—Dry, powdered sodium methoxide (4 g.) was slowly added to crude *N*-phenyl-*N*′-thioformylhydrazine (11 g.; see below) dissolved in dry methanol (40 c.c.). The solution became warm, developed a red colour, and slowly deposited a yellow-green solid which, after 1 hour, was collected, washed with methanol and ether, and then crystallised from chloroform–light petroleum (b. p. 60—80°). 1 : 4-Dihydro-1 : 4-diphenyl-1 : 2 : 4 : 5-tetrazine (3·3 g.) separated as yellow plates, m. p. 194—194·5° (Found: C, 70·9; H, 5·6; N, 23·5%; *M*, ebullioscopic in benzene, 247, 245, 242. Calc. for $C_{14}H_{12}N_4$: *M*, 236). The higher melting point of this material is due to the fact that this method of preparation yields a more easily purified product.

N′-*Formyl*-N-*phenylhydrazine* (cf. Hirst and Cohen, *J.*, 1895, **67**, 829).—Phenylhydrazine (50 g.; freshly distilled; b. p. 128°/15 mm.) was slowly added to acetic acid (140 g.) with shaking and cooling, and formamide (21 g.) was then added. After three hours the mixture was diluted with water (150 c.c.) and the solid collected, washed with very dilute acetic acid and then with water, dried, and crystallised from ethanol, giving *N*′-formyl-*N*-phenylhydrazine (44 g.; 70%) as colourless plates, m. p. 143—144° (lit. m. p. 140°).

N-*Phenyl*-N′-*thioformylhydrazine* (III).—Phenylhydrazine (10 g.; freshly distilled) was dissolved in warm water (50 c.c.) and a solution of sodium dithioformate (20 g.) in water (50 c.c.) added. After three hours the mixture had deposited a dark oil which was extracted into ether. The dried extract was evaporated, leaving the crude N-*phenyl*-N′-*thioformylhydrazine* (11 g.) as a dark oil. A small portion separated from light petroleum (b. p. 60—80°) as colourless crystals, m. p. 39—41° (Found: C, 55·6; H, 5·0; N, 18·4; S, 20·8. $C_7H_8N_2S$ requires C, 55·3; H, 5·3; N, 18·4; S, 21·1%). It dissolves in hydrochloric acid with decomposition, does not give a condensation product with *p*-nitrobenzaldehyde, but forms a somewhat unstable picrate, which crystallises from ethanol in bright yellow-green needles, m. p. 177—178° (decomp.).

Acid Hydrolysis of 1 : 4-*Dihydro*-1 : 4-*diphenyl*-1 : 2 : 4 : 5-*tetrazine* (II).—1 : 4-Dihydro-1 : 4-diphenyl-1 : 2 : 4 : 5-tetrazine (0·35 g.) was boiled under reflux for two hours with a mixture of concentrated hydrochloric acid (6 c.c.), water (6 c.c.), and ethanol (4 c.c.). The clear liquid was cooled and evaporated to dryness under diminished pressure; the distillate gave a positive result for formic acid in the Krauss and Tampke test (*Chem. Ztg.*, 1921, **45**, 521). The residue was dried to constant weight under diminished pressure (0·42 g.; 98% of that theoretically obtainable, calculated as $NHPh{\cdot}NH_2,HCl$). The phenylhydrazine hydrochloride was identified by conversion into the *p*-nitrobenzylidene derivative (0·58 g.; 81%), m. p. and mixed m. p. with an authentic specimen, 159°.

For the quantitative estimation of the formic acid, 1 : 4-dihydro-1 : 4-diphenyl-1 : 2 : 4 : 5-tetrazine (0·30 g.) was boiled under reflux with concentrated sulphuric acid (2 c.c.), water (5 c.c.), and ethanol (5 c.c.). The mixture was extracted continuously with ether (30 c.c.) for six hours, and the extract diluted with water (100 c.c.) and ethanol (50 c.c.) and titrated with aqueous sodium hydroxide (0·213N.), methyl red being used as indicator (Required, 10·7 c.c.; 89% of that calculated for 2 mols. of $H{\cdot}CO_2H$).

N′-*Thioformyl*-N-p-*tolylhydrazine*.—*p*-Tolylhydrazine (4 g.) was dissolved in ethanol (40 c.c.) and sodium dithioformate (7 g.) in water (100 c.c.) added. After two hours, the solid which had separated was collected, dried, and recrystallised from aqueous ethanol, giving N′-*thioformyl*-N-p-*tolylhydrazine* (4·18 g.; 78%) as colourless needles, m. p. 59—60° (Found: C, 58·0; H, 6·2; N, 17·0; S, 19·5. $C_8H_{10}N_2S$ requires C, 57·8; H, 6·0; N, 16·9; S, 19·3%). The material is insoluble in dilute hydrochloric acid and does not react with *p*-nitrobenzaldehyde.

N-p-*Chlorophenyl*-N′-*thioformylhydrazine*.—*p*-Chlorophenylhydrazine (8·2 g.) was dissolved in warm ethanol (50 c.c.) and sodium dithioformate (12 g.) in water (80 c.c.) added. The mixture was warmed to 50° and then left for two hours. The solid was collected, dried, and then crystallised from aqueous ethanol, giving N-p-*chlorophenyl*-N′-*thioformylhydrazine* (8 g.; 75%) as colourless needles, m. p. 86—86·5° (Found: C, 45·6; H, 3·8; N, 15·0. $C_7H_7N_2ClS$ requires C, 45·1; H, 3·8; N, 15·0%).

1 : 4-*Dihydro*-1 : 4-*di*-p-*tolyl*-1 : 2 : 4 : 5-*tetrazine*.—*N*′-Thioformyl-*N*-*p*-tolylhydrazine (1·2 g.) was dissolved in methanol (10 c.c.) and dry sodium methoxide (0·8 g.) added slowly. The solution became red and deposited a yellow solid. After two hours the solid was collected, washed with a little methanol, and crystallised from chloroform–light petroleum (b. p. 60—80°), giving 1 : 4-*dihydro*-1 : 4-*di*-p-*tolyl*-1 : 2 : 4 : 5-*tetrazine* (0·6 g.; 63%) as yellow plates, m. p. 182—183° (Found: C, 72·7; H, 5·9; N, 21·3. $C_{16}H_{16}N_4$ requires C, 72·7; H, 6·1; N, 21·2%).

1 : 4-*Di*-p-*chlorophenyl*-1 : 4-*dihydro*-1 : 2 : 4 : 5-*tetrazine*.—To *N*-*p*-chlorophenyl-*N*′-thioformylhydrazine (4·5 g.) in warm methanol (40 c.c.) sodium methoxide (1·3 g.) was slowly added. The mixture

was warmed until the red colour changed to yellow, and then left for four hours. The solid was collected and recrystallised several times from chloroform–light petroleum (b. p. 40—60°), giving 1 : 4-*di*-p-*chlorophenyl*-1 : 4-*dihydro*-1 : 2 : 4 : 5-*tetrazine* (0·6 g.; 16%) as yellow plates, m. p. 185·5—186·5° (Found : C, 55·4; H, 3·5; N, 18·3. $C_{14}H_{10}N_4Cl_2$ requires C, 55·1; H, 3·3; N, 18·4%). Evaporation of the mother-liquors yielded a solid, m. p. 140°, from aqueous ethanol, which was identical with that obtained by the action of sodium ethoxide on 1 : 4-di-*p*-chlorophenyl-1 : 4-dihydro-1 : 2 : 4 : 5-tetrazine (see below).

N-*Benzyl*-N′-*thioformylhydrazine*.—Benzylhydrazine (8·6 g.) (Wohl and Oesterlin, *Ber.*, 1900, **33**, 2736) was mixed with water (50 c.c.), and sodium dithioformate (15 g.) in water (50 c.c.) added. After being warmed to 30° and left for two hours the solid was collected, washed with water, dried, and recrystallised from aqueous ethanol, giving N-*benzyl*-N′-*thioformylhydrazine* (6·6 g.; 56%) as colourless plates, m. p. 114—114·5° (Found : C, 57·9; H, 6·2; N, 16·9; S, 19·2. $C_8H_{10}N_2S$ requires C, 57·8; H, 6·1; N, 16·9; S, 19·3%). It did not react with *p*-nitrobenzaldehyde.

Reaction of Sodium Ethoxide with 1 : 4-*Dihydro*-1 : 4-*diphenyl*-1 : 2 : 4 : 5-*tetrazine* (II). 3-*Anilino*-1-*phenyl*-1 : 2 : 4-*triazole* (V; R = Ph).—A small piece of sodium was dissolved in ethanol (10 c.c.), and then 1 : 4-dihydro-1 : 4-diphenyl-1 : 2 : 4 : 5-tetrazine (0·3 g.) added. The mixture was refluxed until a colourless solution was obtained (10 minutes), then cooled and water (40 c.c.) added. The precipitate was collected, dried, and recrystallised from aqueous ethanol, giving colourless needles (0·27 g.), m. p. 114·5—115° [Found : C, 71·5; H, 5·2; N, 23·5%; *M* (ebullioscopic in benzene), 238, 239. $C_{14}H_{12}N_4$ requires C, 71·2; H, 5·1; N, 23·7%; *M*, 236]. 3-*Anilino*-1-*phenyl*-1 : 2 : 4-*triazole* is soluble in dilute acids and forms a *monoacetyl* derivative, m. p. 113·5—114·5°; colourless needles from benzene–light petroleum (b. p. 60—80°) (Found : C, 69·3; H, 5·3; N, 20·1. $C_{16}H_{14}ON_4$ requires C, 69·0; H, 5·1; N, 20·2%). Hydrolysis of the acetyl derivative by heating it with concentrated hydrochloric acid regenerated the parent triazole in 96% yield.

Reaction of Sodium Ethoxide with 1 : 4-*Di*-p-*chlorophenyl*-1 : 4-*dihydro*-1 : 2 : 4 : 5-*tetrazine*. 3-p-*Chloroanilino*-1-p-*chlorophenyl*-1 : 2 : 4-*triazole* (V; R = *p*-C_6H_4Cl).—The reaction was carried out with 1 : 4-di-*p*-chlorophenyl-1 : 4-dihydro-1 : 2 : 4 : 5-tetrazine (0·2 g.) as in the previous case. The product separated from aqueous ethanol as colourless needles (0·18 g.), m. p. 140° (Found : C, 55·3; H, 3·2; N, 18·4; Cl, 23·9. $C_{14}H_{10}N_4Cl_2$ requires C, 55·1; H, 3·3; N, 18·4; Cl, 23·2%). 3-p-*Chloroanilino*-1-p-*chlorophenyl*-1 : 2 : 4-*triazole* is soluble in dilute acids; the *monoacetyl* derivative forms colourless needles, m. p. 183—184·5°, from aqueous ethanol (Found : C, 55·3; H, 3·4; N, 15·8; Cl, 20·1. $C_{16}H_{12}ON_4Cl_2$ requires C, 55·3; H, 3·5; N, 16·1; Cl, 20·4%).

Reaction of Sodium Ethoxide with 1 : 4-*Dihydro*-1 : 4-*di*-p-*tolyl*-1 : 2 : 4 : 5-*tetrazine*. 3-p-*Toluidino*-1-p-*tolyl*-1 : 2 : 4-*triazole* (V; R = *p*-C_6H_4·Me).—1 : 4-Dihydro-1 : 4-di-*p*-tolyl-1 : 2 : 4 : 5-tetrazine (1·80 g.) gave, as in the previous cases, 3-p-*toluidino*-1-p-*tolyl*-1 : 2 : 4-*triazole* (1·78 g.), colourless needles, m. p. 118—118·5°, from aqueous ethanol (Found : C, 72·7; H, 5·9; N, 21·0. $C_{16}H_{16}N_4$ requires C, 72·7; H, 6·1; N, 21·2%). *Acetyl* derivative, needles, m. p. 147—148°, from benzene–light petroleum (b. p. 60—80°) (Found : C, 70·8; H, 5·9; N, 18·1. $C_{18}H_{18}ON_4$ requires C, 70·6; H, 5·9; N, 18·3%).

3-*Chloro*-1-*phenyl*-1 : 2 : 4-*triazole*.—1-Phenyl-1 : 2 : 4-triazol-3-one (2·5 g.) (Widman, *Ber.*, 1893, **26**, 2613) was heated with phosphorus oxychloride (4·5 c.c.) in a sealed tube at 200° for two hours. The mixture was cooled, poured on ice, and made faintly alkaline with sodium hydroxide solution. The solid was collected and recrystallised from aqueous ethanol, giving 3-chloro-1-phenyl-1 : 2 : 4-triazole (2·1 g.; 75%) as colourless needles, m. p. 76—78° (Andreocci, *R. Atti Accad. Lincei*, 1855, **6**, 225, gives m. p. 76°).

3-*Methylthio*-1-*phenyl*-1 : 2 : 4-*triazole* (VIII).—To potassium hydroxide (4·5 g.) dissolved in dry methanol (150 c.c.) was added 3-mercapto-1-phenyl-1 : 2 : 4-triazole (14 g.) (Pellizzari and Ferro, *Gazzetta*, 1898, **28**, (ii), 552). Methyl iodide (4·5 c.c.) was then added slowly to the yellow solution. After ¼ hour, the solution was concentrated (to 80 c.c.), water (300 c.c.) added, and the oil extracted into ether. The extract yielded a pale-yellow oil (13·5 g.) which solidified on being kept; the solid has m. p. 47—48°. 3-*Methylthio*-1-*phenyl*-1 : 2 : 4-*triazole* (VIII) crystallises from light petroleum (b. p. 60—80°) in colourless plates, m. p. 50° (Found : C, 57·3; H, 4·7; N, 22·0. $C_9H_9N_3S$ requires C, 56·5; H, 4·7; N, 22·0%).

Ruhemann's Compound, $C_{14}H_{12}N_4$.—(*a*) The method described by Ruhemann and Elliott (*loc. cit.*) yielded in our hands only *N*′-formyl-*N*-phenylhydrazine. The following method is based on that described by Hammick, New, Sidgwick, and Sutton (*J.*, 1930, 1876) for the preparation of *iso*cyanides.

Phenylhydrazine (25 g.), chloroform (13 c.c.), and methanol (50 c.c.) were heated to 60° with stirring. Solid potassium hydroxide (6 g.) was then added; a vigorous reaction occurred and the liquid became deep red. As the reaction subsided, potassium hydroxide (6 g.) and a mixture of chloroform and methanol (5 c.c. of a mixture composed of 26 c.c. chloroform and 34 c.c. methanol) were added, and these additions were repeated 12 times until the whole of the chloroform–methanol mixture and potassium hydroxide (72 g.) had been used. The mixture was then boiled under reflux for one hour, cooled, diluted with water (500 c.c.), and extracted with ether (500 c.c.). The extract yielded a red oil, which was steam-distilled and the residue extracted with ether (200 c.c.) [the solid insoluble in ether (0·8 g.) was identified by m. p. and mixed m. p. as *N*′-formyl-*N*-phenylhydrazine]. The extract was concentrated under reduced pressure and the residual dark oil was triturated with ethanol (10 c.c.). The solid which separated overnight was collected, dried, and recrystallised from ethanol, giving silky white needles (0·54 g.; 2%), m. p. 180°, identical with the product prepared by the following method.

(*b*) We were unable to obtain any of the compound, m. p. 180°, by the method described by Bamberger (*Ber.*, 1897, **30**, 1263). *N*′-Formyl-*N*-phenylhydrazine (10 g.) was kept at 250—260° for one hour, and the mixture then steam-distilled. The residue was extracted with ether (200 c.c.), the thick oil left after removal of the solvent triturated with a little ethanol, and the solid collected, dried, and crystallised from ethanol, giving fine white needles (0·42 g.; 5%), m. p. 180° [Found: C, 71·3; H, 4·9; N, 23·6%; *M*(ebullioscopic in benzene), 248, 241. Calc. for $C_{14}H_{12}N_4$: C, 71·2; H, 5·1; N, 23·7%; *M*, 236]. The substance shows a strong white fluorescence in ultra-violet light.

Analogue of Ruhemann's Compound derived from p-*Tolylhydrazine*.—(*a*) This substance was prepared from *p*-tolylhydrazine (15 g.) in the manner described above (method *a*) for the preparation of Ruhemann's compound, $C_{14}H_{12}N_4$. The product after crystallisation from ethanol, formed faintly yellow plates, m. p. 185—186° (0·25 g.; 1·5% yield). Ruhemann records m. p. 185°. (*b*) *N'*-Formyl-*N*-*p*-tolylhydrazine (5 g.) was heated at 250° for one hour, and the product isolated as in the manner previously given (method *b*) for the preparation of Ruhemann's compound, $C_{14}H_{12}N_4$. The product (0·35 g.; 8%) had m. p. and mixed m. p. 185—186° (Found: C, 72·8; H, 6·4; N, 21·4. Calc. for $C_{16}H_{16}N_4$: C, 72·7; H, 6·1; N, 21·2%). The substance shows a strong white fluorescence in ultra-violet light.

N-p-*Chlorophenyl*-N'-*formylhydrazine*.—*p*-Chlorophenylhydrazine (10 g.), glacial acetic acid (100 c.c.), and formamide (3·5 g.) were heated to 70° and after ½ hour the mixture was diluted with water (100 c.c.) and the precipitate collected. After crystallisation from ethanol (yield 9·7 g.; 81%) and then from water, the N-p-*chlorophenyl*-N'-*formylhydrazine* formed colourless needles, m. p. 186—187° (Found: C, 49·8; H, 4·3; N, 16·8; Cl, 20·4. $C_7H_7ON_2Cl$ requires C, 49·3; H, 4·3; N, 16·5; Cl, 20·8%) (Hewitt, *loc. cit.*, gives m. p. 152°).

Analogue of Ruhemann's Compound derived from p-*Chlorophenylhydrazine*.—*p*-Chlorophenylhydrazine (13 g.) was treated with chloroform and potassium hydroxide as in the preceding cases. The residue, after steam distillation, was shaken with ether (350 c.c.), and the insoluble material collected and dried (0·03 g.). Crystallisation from ethanol gave the *compound* as faintly yellow needles, m. p. 254° (Found: C, 55·2; H, 3·4; N, 17·5. $C_{14}H_{10}N_4Cl_2$ requires C, 55·1; H, 3·3; N, 18·3%). This compound showed a very strong white fluorescence in ultra-violet light. Evaporation of the ethereal extract left a thick red oil from which *N*-*p*-chlorophenyl-*N'*-formylhydrazine (1·0 g.), m. p. and mixed m. p. 185—187°, was isolated.

The authors thank the Department of Scientific and Industrial Research for a maintenance allowance (to V. D. P.), Monsanto Chemicals, Ltd., for a Fellowship (to V. D. P.), and Imperial Chemical Industries, Ltd., for a grant. Microanalyses are by Drs. Weiler and Strauss, Oxford, and Mr. W. M. Eno, Bristol.

THE UNIVERSITY, BRISTOL.

[*Received, July 27th,* 1950.]