

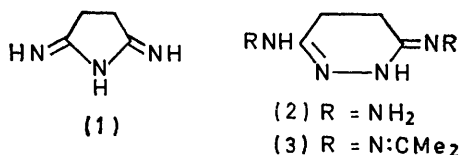
## Heterocyclic Imines and Amines. Part XIV.<sup>1</sup> Products from 2,5-Di-iminopyrrolidine (Succinimidine) and Hydrazine

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Hydrazine (in excess) reacts with 2,5-di-iminopyrrolidine (1) or succinonitrile to yield 6-hydrazino-3-hydrazono-2,3,4,5-tetrahydropyridazine (2). Treatment of this with acetone, glyoxylic acid, and butyl glyoxylate affords the expected di-condensation products: with glyoxal a polymeric hydrazone is obtained. Acylation of compound (2) with ethyl chloroformate was successful but attempts to oxidise the product to known pyridazines failed, as did attempts to dehydrogenate compound (2) to 3,6-dihydrazinopyridazine. 5-Imino-2-pyrrolidone (13) with hydrazine gave 6-hydrazino-4,5-dihydropyridazin-3(2*H*)-one (14).

In hot pyridine, succinonitrile reacts with an equimolar quantity of hydrazine to give a polymer, (C<sub>4</sub>H<sub>6</sub>N<sub>4</sub>)<sub>n</sub>: with 2 molecular proportions a dimeric condensation product, C<sub>8</sub>H<sub>10</sub>N<sub>10</sub>, results. Structures for these are proposed on the basis of spectral and other evidence. The behaviour of these compounds and related pyridazines on thermolysis is reported.

TREATMENT of 2,5-di-iminopyrrolidine (succinimidine)<sup>2</sup> (1) with hydrazine hydrate caused evolution of ammonia and separation of a product, C<sub>4</sub>H<sub>10</sub>N<sub>6</sub>. The molecular composition indicated that all three imino-functions in the starting material had been replaced, but the product



cannot have been a trihydrazino-compound because it gave only a di-isopropylidene derivative with acetone. Evidently ring expansion had occurred, as encountered with an imidine derivative before<sup>3</sup> (*cf.* the Ing-Manske reaction<sup>4</sup>).

The new compound, obtained also from succinonitrile and an excess of hydrazine, was identified as 3,6-dihydrazino-4,5-dihydropyridazine with the tautomeric form (2) in solution. It was best handled under nitrogen to obviate superficial oxidation to a red material, the colour of which however could be discharged with hydrazine. Attempts to dehydrogenate the compound (2) to 3,6-dihydrazinopyridazine<sup>1</sup> (10) with 1-chlorobenzotriazole<sup>5</sup> in dichloromethane and with aqueous potassium ferricyanide were not successful. The compound (2) formed a monohydrate below 65°, and was easily hydrolysed by acid or alkali to succinic acid, probably *via* succinohydrazide which, in contrast to maleohydrazide, is hydrolysed readily. The di-isopropylidene derivative (3) was converted back into compound (2) with hydrazine hydrate. The light

<sup>1</sup> Part XIII, J. A. Elvidge and J. A. Pickett, *J.C.S. Perkin I*, 1972, 1483.

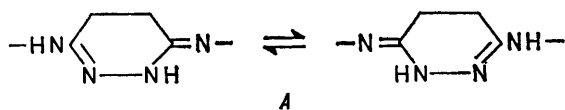
<sup>2</sup> J. A. Elvidge and R. P. Linstead *J. Chem. Soc.*, 1954, 442.

<sup>3</sup> L. K. Thompson, V. T. Chacko, J. A. Elvidge, A. B. P. Lever, and R. V. Parish, *Canad. J. Chem.*, 1969, **47**, 4141.

<sup>4</sup> H. R. Ing and R. H. F. Manske, *J. Chem. Soc.*, 1926, 2348.

<sup>5</sup> C. W. Rees and R. C. Storr, *J. Chem. Soc. (C)*, 1969, 1474.

absorption maximum of compound (2) (273 nm) was 66 nm below that of 3,6-dihydrazinopyridazine<sup>1</sup> (10), a hypsochromic shift similar in magnitude to that found for other 4,5-dihydropyridazines.<sup>6</sup> Evidence for the tautomeric form (2) in aqueous solution came from the <sup>1</sup>H n.m.r. spectrum, which showed 2 complex two-proton multiplets (an ABFG pattern) from the methylene groups, indicating that these were non-equivalent. When the solution was made alkaline, the signals collapsed to a singlet. Evidently, a tautomeric equilibrium (A) had been catalysed to the extent that on the



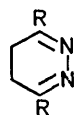
n.m.r. time scale the structure became effectively symmetrical. Similar observations were made with the di-isopropylidene derivative. This was considered to have the unsymmetrical structure (3) in neutral solution because there were four singlets in the <sup>1</sup>H n.m.r. spectrum from the methyl groups. The signal from the ring methylene protons in this case happened not to be diagnostic, being a centrosymmetric AA'BB' multiplet. When the solution was made alkaline, the latter signal collapsed to a singlet and the methyl lines to two six-proton singlets, again indicating a rapid equilibration (A). In agreement with these explanations based on rates of tautomerism, the u.v. spectra of compounds (2) and (3) remained virtually the same with change from neutral to alkaline solution, showing that the species involved did not alter.

The dihydrazino-compound (2) condensed with glyoxylic acid and with butyl glyoxylate, as expected, to give the di-condensation products (4) and (5), characterised in part by their spectra. With glyoxal, a hydrated polymeric hydrazone was formed, which was dehydrated at 100° under reduced pressure. The thermolysis behaviour of the anhydrous material (6) is recorded in the Table. Acylation of compound (2) with ethyl chloroformate gave the diacyl derivative (7), but attempts to oxidise<sup>7</sup> this with hydrogen peroxide, peracetic acid, oxygen, or nitric acid to the known pyridazines (8) and/or (9)<sup>1</sup> failed.

5-Imino-2-pyrrolidone<sup>2</sup> (13), the product of partial hydrolysis of the imidine (1), behaved with hydrazine hydrate analogously to the parent compound, undergoing substitution and ring expansion to give the hydrazinodihydropyridazone (14). This structure was supported by the light absorption, by hydrolysis to succinic acid, and by condensation with acetone to give a mono-isopropylidene derivative (15). Treatment of the latter with hydrazine hydrate regenerated the parent compound (14).

When succinonitrile was heated with one molecular proportion of hydrazine hydrate in boiling pyridine, a creamy sparingly soluble solid, C<sub>2</sub>H<sub>3</sub>N<sub>2</sub>, was formed

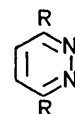
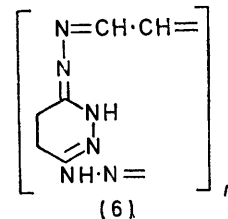
[m.p. 285° (decomp.)]. The i.r. spectrum showed that cyano-groups were absent. That it was a polymer based on a C<sub>4</sub>H<sub>6</sub>N<sub>4</sub> unit was indicated by the mass spectrum, which showed peaks at intervals of 110 mass



(4) R = NH·N:CH·CO<sub>2</sub>H

(5) R = NH·N:CH·CO<sub>2</sub>Bu<sup>n</sup>

(7) R = NH·NH·CO<sub>2</sub>Et



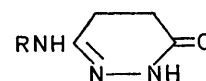
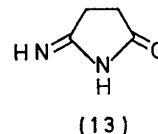
(8) R = NH·NH·CO<sub>2</sub>Et

(9) R = N:N·CO<sub>2</sub>Et

(10) R = NH·NH<sub>2</sub>

(11) R = NH·N:CMe<sub>2</sub>

(12) R = NH·N:CH·CO<sub>2</sub>H



(14) R = NH<sub>2</sub>

(15) R = N:CMe<sub>2</sub>

#### Thermolysis behaviour under nitrogen<sup>a</sup>

Compound	Thermolysis temp. (°C)	Weight loss (%)	Gas (ml per g at S.T.P.)	Residue
(2)	165	21	N <sub>2</sub> + 13% NH <sub>3</sub> (240)	Pale solid, softens > 200°
(3)	145	19 <sup>b</sup>	N <sub>2</sub> + 0.5% NH <sub>3</sub> (101)	Brown tar
(4)	170	49	N <sub>2</sub> + 30% CO <sub>2</sub> (270)	Pale brown solid
(6)	228	20	N <sub>2</sub> + 1% NH <sub>3</sub> (140)	Black solid
(18)	280	30	N <sub>2</sub> (210)	Colourless solid
(19)	188	32	N <sub>2</sub> + CO <sub>2</sub> (200)	Discoloured solid
(20)	200	28	N <sub>2</sub> H <sub>4</sub> + N <sub>2</sub> + 4% NH <sub>3</sub>	Pale brown solid
(10) <sup>c</sup>	190	22	N <sub>2</sub> + 8% NH <sub>3</sub> (220)	Brown solid
(11) <sup>c</sup>	240	29	Acrid vapour	Dark solid
(12) <sup>c</sup>	199	43	N <sub>2</sub> + 2CO <sub>2</sub> (270)	Dark solid
(21) <sup>c</sup>	240	7	N <sub>2</sub> + 3% NH <sub>3</sub> (70)	Colourless solid

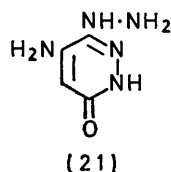
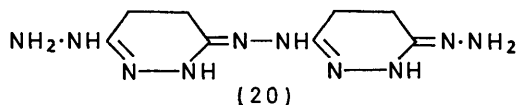
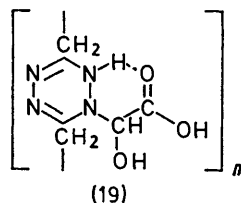
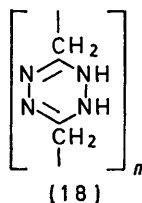
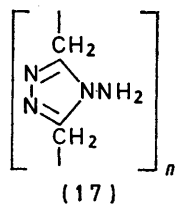
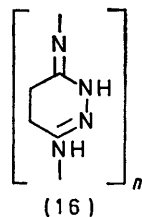
<sup>a</sup> A Stanton Thermobalance was used. <sup>b</sup> Including 6% by sublimation. <sup>c</sup> Ref. 1.

units, diminishing in intensity with increasing mass number. In the u.v. it showed maximum absorption at 248 nm, and so it was not the polymer (16) based on the reduced pyridazine unit which might have been provided by the compound (2). Other possibilities were structures (17) and (18). The aminotriazole structure (17) seemed unlikely in view of the i.r. spectrum (which lacked NH<sub>2</sub>

<sup>6</sup> G. Korshun and C. Roll, *Bull. soc. chim. France*, 1926, **39**, 1223.

<sup>7</sup> Cf. W. A. Schulze and H. L. Lochte, *J. Amer. Chem. Soc.*, 1926, **48**, 1030; U.S. Pat. 2,520,339/1950; T. Curtius and K. Heidenreich, *Ber.*, 1894, **27**, 773.

absorption) and because the compound was unchanged after treatment with nitrous acid. Moreover, condensation products were not obtained with acetone or benzaldehyde. However, glyoxylic acid did react with the



polymer, but only to give an addition product, stable at 150° under reduced pressure. This product was not a salt: it dissolved with effervescence in aqueous sodium carbonate and showed strong carbonyl absorption at 1700 cm<sup>-1</sup>. When the insoluble polymer itself was stirred with sodium carbonate solution in the air,<sup>8</sup> a deep red colour developed, and eventually a small amount of a purple solid was isolated. This absorbed light in the u.v. and in the 520–530 nm region of the visible spectrum, and so appeared to be a 1,2,4,5-tetrazine.<sup>9,10</sup> In agreement, the colour was discharged and nitrogen evolved when the purple solid was treated with hydrochloric acid.<sup>10</sup> Consequently it appeared that the polymer had the dihydrotetrazine structure (18), a conclusion strengthened by the fact that the single NH stretching frequency at 3250 cm<sup>-1</sup> was close to that (at 3270 cm<sup>-1</sup>) from a simple 1,2-dihydro-1,2,4,5-tetrazine.<sup>11</sup> The glyoxylic acid addition product showed broad OH absorption at 3500 cm<sup>-1</sup> and a peak at 3200 cm<sup>-1</sup> attributable to bonded NH, so it appeared to have the structure (19).

<sup>8</sup> Cf. K. Nakahara and M. Ohta, *Nippon Kagaku Zasshi*, 1956, **77**, 388.

<sup>9</sup> S. F. Mason, *J. Chem. Soc.*, 1959, 1247.

<sup>10</sup> E. Müller and L. Herrdegen, *J. prakt. Chem.*, 1921, **102**, 113.

<sup>11</sup> F. Dallacker, *Monatsh.*, 1960, **91**, 294.

Acetonitrile reacts with hydrazine to give 1,2-dihydro-3,6-dimethyl-1,2,4,5-tetrazine,<sup>12</sup> so it is hardly surprising that succinonitrile should yield the polymer (18). Other  $\alpha\omega$ -polymethylenedicarbonitriles have been treated with hydrazine, but only under relatively mild conditions, and these gave di-amidrazones.<sup>13</sup> However, amidrazones can be regarded as intermediates for dihydrotetrazines.<sup>14</sup>

It happened that, for the reaction which gave the polymer (18), equimolar proportions of succinonitrile and hydrazine had been used. In an attempt to improve the yield, the theoretically correct 1:2 ratio of the reagents in boiling pyridine was tried. This gave a product, C<sub>8</sub>H<sub>16</sub>N<sub>10</sub>, m.p. 200° ( $\lambda_{\max}$  303 nm), with molecular formula corresponding to a compound (20) formed by the self-condensation of the dihydropyridazine (2) with elimination of hydrazine. However, the new product (20) was not formed in boiling pyridine from compound (2): the latter was recovered. So evidently it arose from an earlier hydrazine-succinonitrile product.

A surprising finding was that the compound (20) lost hydrazine slowly at 140° with conversion into the polymer (18), as judged from the m.p., thermolysis behaviour, and light absorption properties. The same polymer (18) was also obtained by heating compound (20) in boiling pyridine. The conversion  $n(\text{C}_8\text{H}_{16}\text{N}_{10}) \rightarrow (\text{C}_4\text{H}_8\text{N}_4)_{2n} + n\text{N}_2\text{H}_4$  presumably occurs by a ring-opening and alternative reclosure process, as indicated in the Scheme.

The foregoing dihydropyridazines, some related pyridazines<sup>1</sup> (10)–(12), and the polymer (18) were subjected to thermogravimetric analysis. All of these compounds of high nitrogen content decomposed on heating, with a reasonable rate and extent of gas evolution, so they were of possible interest as 'blowing' agents. In each case the nature of the gas was investigated by appropriate qualitative tests and titrations. The 'blowing' characteristics are recorded in the Table.

#### EXPERIMENTAL

I.r. spectra were measured for mulls, with a Unicam SP 200 spectrophotometer. U.v. and <sup>1</sup>H n.m.r. spectra were recorded with a Unicam SP 800B and a Perkin-Elmer R10 (60 MHz) instrument, respectively.

*6-Hydrazino-3-hydrazono-2,3,4,5-tetrahydropyridazine* (2). —(a) *Preparation*. (i) A solution of 2,5-di-iminopyrrolidine<sup>2</sup> (5 g) in dry methanol (20 ml) was stirred under nitrogen and hydrazine hydrate (15 ml) was added. Ammonia was evolved and after 3 h crystallisation began; stirring was continued until it was complete. The product (7 g, 85%) was collected under nitrogen, washed with 7:3 methanol-ether, and recrystallised from hot water (charcoal) to give fine needles of the *hydrate*, m.p. 165–166° (decomp.) (Found: Wt. loss at 65° under N<sub>2</sub>, 11%. C<sub>4</sub>H<sub>10</sub>N<sub>6</sub>·H<sub>2</sub>O requires H<sub>2</sub>O, 11%),  $\nu_{\max}$  (hexachlorobutadiene) 3510 (H<sub>2</sub>O), 3310, 3210, and 3060 (NH<sub>2</sub>, NH),

<sup>12</sup> T. Curtius, A. Darapsky, and E. Müller, *Ber.*, 1915, **48**, 1614.

<sup>13</sup> T. Kaufmann and L. Bán, *Chem. Ber.*, 1966, **99**, 2600.

<sup>14</sup> Cf. A. Pinner, *Ber.*, 1894, **27**, 984 and 1897, **30**, 1871; H. Wuyts and A. Lacourt, *Bull. soc. chim. belges*, 1936, **45**, 685.

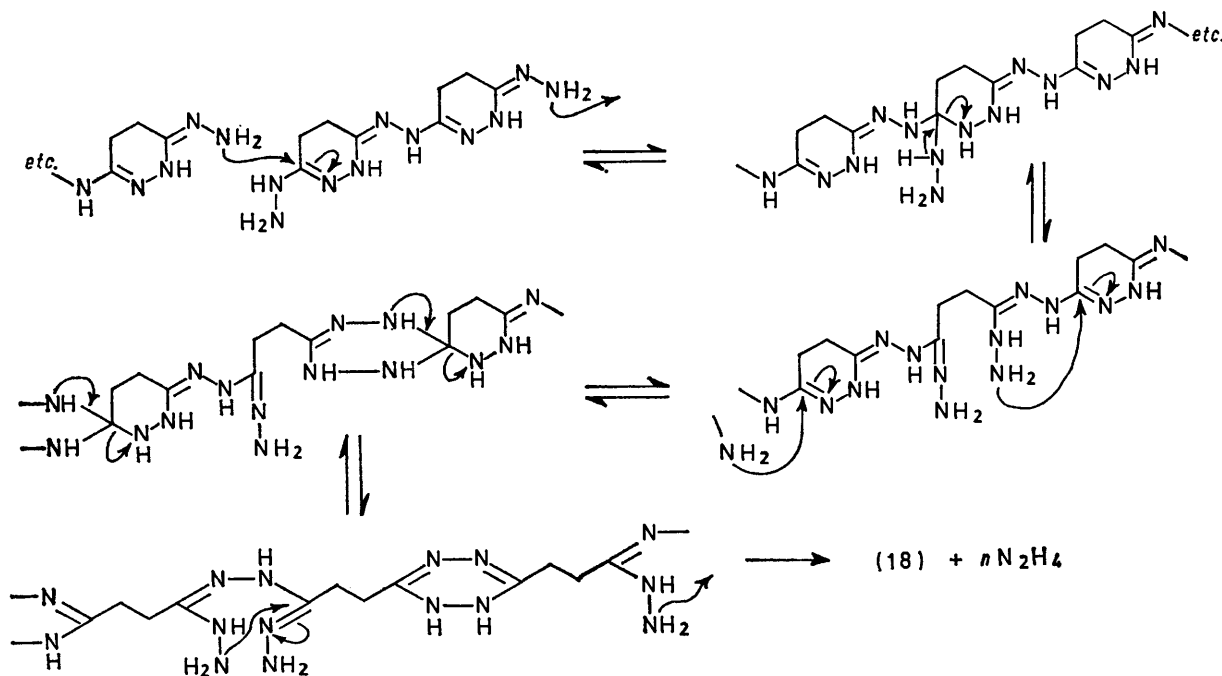
and 2940w,  $\nu_{\max}$  (Nujol) 1620s and 1610s (C=N, NH), 1540s, 1405w, 1365w, 1320w, 1300, 1120w, 1080, 960, 910, 850w, and 760w  $\text{cm}^{-1}$ . The *anhydrous compound*, m.p. unchanged, was obtained by drying at 65° and 10 mmHg (Found: C, 33.9; H, 7.2; N, 59.1.  $\text{C}_4\text{H}_{10}\text{N}_6$  requires C, 33.8; H, 7.0; N, 59.2%),  $m/e$  142,  $\lambda_{\max}$  ( $\text{H}_2\text{O}$ ) 273 nm ( $\epsilon$  11,000) (unchanged after addition of 1 drop of conc. ammonia),  $\nu_{\max}$  (hexachlorobutadiene) 3310, 3240, 3210, and 3060 ( $\text{NH}_2$ , NH), 2970, 2940, and 2850,  $\nu_{\max}$  (Nujol) 1640sh, 1630s, 1610s, 1580, 1550, 1425w, 1405w, 1365w, 1300, 1280w, 1160w, 1150w, 1120w, 1060, 1040, 1010w, 960, 900, 860w, 800w, and 760w  $\text{cm}^{-1}$ ,  $\tau$  ( $\text{D}_2\text{O}$ ) 7.32 (m,  $\text{CH}_2$ ), 6.92 (m,  $\text{CH}_2$ ),  $\tau$  ( $\text{D}_2\text{O}$  + 1 drop  $\text{NH}_4\text{OH}$ ) 7.5 (s,  $2 \times \text{CH}_2$ ).

continuous extraction with ether, the hydrazide was recovered.

(ii) Succinohydrazide<sup>16</sup> (200 mg) was heated with 2*N*-hydrochloric acid (2 ml) on a steam-bath for 15 min. Continuous extraction with ether and evaporation gave succinic acid (125 mg), m.p. and mixed m.p. as before.

(iii) Hydrolysis of succinohydrazide with alkali, as in (b) (ii), gave succinic acid (m.p. and mixed m.p.).

**2,3,4,5-Tetrahydro-6-isopropylidenehydrazino-3-isopropylidenehydrazonopyridazine (3).**—Compound (2) (3 g) was heated with acetone (20 ml) under reflux, under nitrogen, for 4 h. Concentration of the solution to 0.25 bulk under reduced pressure afforded the *product* (3 g, 64%) as pale



SCHEME

(ii) Hydrazine hydrate (20 ml) was added to a solution of redistilled succinonitrile (10 g) in methanol (30 ml) under nitrogen. After 18 h, the mixture was partially evaporated in a stream of nitrogen and the product was collected (12 g, 60%), washed, and dried as before; m.p. 165–166° (decomp.) (Found: C, 33.8; H, 7.2; N, 59.1%).

(b) *Hydrolysis.* (i) The compound (2) (600 mg) was heated in 6*N*-hydrochloric acid (10 ml) on a steam-bath for 40 min, the solution was extracted continuously with ether, and the ether was evaporated off to afford succinic acid (299 mg), m.p. 180–182° (183–184° in admixture with the authentic acid). Evaporation of the aqueous solution under reduced pressure left hydrazine dihydrochloride (mixed m.p.).

(ii) The compound (2) (200 mg) was dissolved in 2*N*-sodium hydroxide (2 ml). Next day, the solution was neutralised (HCl), and extracted as before to yield succinic acid (101 mg), m.p. 180–182°, mixed m.p. 183–184°.

(c) *Related hydrolyses.* (i) Maleohydrazide<sup>15</sup> (514 mg) was heated under reflux with concentrated hydrochloric acid (7 ml) and glacial acetic acid (7 ml) for 3 h. By

orange prisms, m.p. 149–150° (decomp.) (from acetone) (Found: C, 54.0; H, 8.2; N, 38.0.  $\text{C}_{10}\text{H}_{18}\text{N}_6$  requires C, 54.1; H, 8.1; N, 37.8%),  $\nu_{\max}$  (hexachlorobutadiene) 3260sh, 3210, and 3020w (NH), and 2940w,  $\nu_{\max}$  (Nujol) 1625s and 1600s (C=N, NH), 1360s, 1300w, 1250, 1200w, 1130, 1080w, and 960  $\text{cm}^{-1}$ ;  $\lambda_{\max}$  (MeOH) 310 nm ( $\epsilon$  19,300),  $\lambda_{\max}$  ( $\text{H}_2\text{O}$ ) 308 nm,  $\lambda_{\max}$  ( $\text{H}_2\text{O}-\text{NH}_4\text{OH}$ ) 306 nm;  $\tau$  ( $\text{CDCl}_3$ ) (100 MHz) 8.23, 8.06, 8.04, and 8.01 (each s,  $\text{CH}_3$ ), 7.55–7.20 (m,  $2 \times \text{CH}_2$ ), 2.52br (s, NH), and 1.52br (s, NH),  $\tau$  ( $\text{D}_2\text{O}$  + 1 drop  $\text{NH}_4\text{OH}$ ) 8.01 (s,  $2 \times \text{CH}_3$ ), 7.95 (s,  $2 \times \text{CH}_3$ ), and 7.41 (s,  $2 \times \text{CH}_2$ ).

This di-isopropylidene derivative (200 mg) in ethanol (0.5 ml) was kept under nitrogen with hydrazine hydrate (0.5 ml) for 16 h. The dihydrazino-compound (2) separated (124 mg); m.p. and mixed m.p. 163–165°,  $\lambda_{\max}$  (EtOH) 272 nm ( $\epsilon$  11,500).

**3,6-Biscarboxymethylenehydrazino-4,5-dihydropyridazine (4) (or Tautomer).**—Glyoxylic acid monohydrate (1.44 g) in water (2 ml) was added to a filtered solution of the pure dihydrazino-compound (2) (1.11 g) in air-free water (7 ml) under nitrogen, and the yellow microcrystalline product was

<sup>15</sup> R. H. Mizzoni and P. E. Spoerri, *J. Amer. Chem. Soc.*, 1951, **73**, 1873.

<sup>16</sup> H. Feuer, G. B. Bachman, and E. H. White, *J. Amer. Chem. Soc.*, 1951, **73**, 4716.

collected, washed with water, and dried (yield 1.8 g, 91%), m.p. 175—176° (decomp.) (Found: C, 37.7; H, 4.1; N, 32.9.  $C_8H_{10}N_6O_4$  requires C, 37.8; H, 3.9; N, 33.1%),  $\nu_{\max}$  (Nujol) 3500br (OH), 3195 and 3155 (NH), 1700 (C=O), 1635s, 1610s, 1570s, 1305w, 1290, 1175w, 1090s, 1000, 975, 950, and 880  $cm^{-1}$ ,  $\lambda_{\max}$  ( $H_2O$ ) 340 nm,  $\lambda_{\max}$  (Na salt in  $H_2O$ ) 354 nm ( $\epsilon$  17,000);  $\tau$  (Na salt in  $D_2O$ ) 7.0 (s,  $2 \times CH_2$ ) and 2.25 (s,  $2 \times CH$ ).

**3,6-Bis-*n*-butoxycarbonylmethylenehydrazino-4,5-dihydro-pyridazine (5) (or Tautomer).**—*n*-Butyl glyoxylate (2.8 g) in methanol was added to an aqueous solution of the dihydrazino-compound (2) (1.4 g), which was then kept under nitrogen at 0°. Overnight, the ester separated as a yellow solid (2.9 g), m.p. 145° (decomp.) (from dimethylformamide-ether) (Found: *m/e* 366.  $C_{16}H_{26}N_6O_4$  requires *M*, 366),  $\nu_{\max}$  (Nujol) 3300—3230 (NH), 1710s (C=O), 1650s (C=N), 1580s (NH), 1340, 1290, 1200, 1140, 1060, 1000, 970, and 900w  $cm^{-1}$ ,  $\lambda_{\max}$  (MeOH) 344 nm ( $\epsilon$  12,000).

**Polymeric Hydrazone from the Dihydrazino-compound (2) and Glyoxal.**—A solution of glyoxal monohydrate (0.35 g) in air-free water was filtered into a similar solution of freshly recrystallised compound (2) (0.65 g) under nitrogen. After 2 days at 0°, the precipitate (0.6 g) was collected, washed with water, and dried at 10 mmHg ( $CaCl_2$ ) to give the yellow hydrated product, m.p. 228° (decomp.) [Found: C, 41.3; H, 4.9.  $(C_6H_8N_6 \cdot 0.5H_2O)_n$  requires C, 41.6; H, 5.2%],  $\nu_{\max}$  (Nujol) 3300 and 3250 (bonded OH, NH), 1620s (C=N), 1520, 1280, 1200w, 1150, 1070w, and 920w  $cm^{-1}$ ,  $\lambda_{\max}$  ( $H_2O$ ) 386 nm ( $\epsilon$  15,000).

**3,6-Bisethoxycarbonylhydrazino-4,5-dihydropyridazine (7) (or Tautomer).**—To a stirred slurry of the dihydrazino-compound (2) (1.42 g) in dry pyridine (4 ml) and ethanol (4 ml) under nitrogen, ethyl chloroformate (2.17 g) in ethanol (2 ml) was slowly added. After 4 h, the solution was filtered into acetone (50 ml) and the pale pink gelatinous precipitate collected and dried (yield 1.8 g, 63%), m.p. 138° (decomp.). Two precipitations from ethanol with acetone afforded the diacyl derivative as a white powder, m.p. 145° (decomp.) (Found: C, 41.8; H, 6.2; N, 29.3.  $C_{10}H_{18}N_6O_4$  requires C, 42.0; H, 6.3; N, 29.4%), *m/e* 286,  $\nu_{\max}$  (Nujol) 3400w and 3200 (NH), 1740s (C=O), 1630w, 1600s (C=N), 1560 (NH), 1310w, 1260w, 1170w, 1100w, 1060, 970w, and 780  $cm^{-1}$ ,  $\tau$  ( $D_2O$ ) 8.73 and 5.75 (t, q, *J* 6.9 Hz,  $2 \times EtO \cdot CO$ ), and 7.15 (s,  $2 \times CH_2$  of ring).

**6-Hydrazino-4,5-dihydropyridazin-3(2H)-one (14).**—When hydrazine hydrate (5 ml) was added to 5-iminopyrrolidin-2-one<sup>2</sup> (1.3 g), the solid dissolved and ammonia was evolved. After being kept under nitrogen overnight, the solution was evaporated and the residue crystallised from hydrazine hydrate-ethanol (charcoal) to give the hydrazino-compound as prisms, m.p. 145—147° (Found: C, 37.8; H, 6.5; N, 44.0.  $C_4H_8N_4O$  requires C, 37.5; H, 6.3; N, 43.7%),  $\nu_{\max}$  (KBr) 3247s and 3030 (NH<sub>2</sub>, NH), 2985, 2928, and 2865 (CH), 1639s (C=O), 1619s (C=N), 1550, 1513, 1470, 1428, 1398, 1362s, 1304, 1290, 1219, 1166, 1130, 1115w, 1085w, 1006, 983, 957, 805, 796, and 763  $cm^{-1}$ ,  $\lambda_{\max}$  (EtOH) 267 nm ( $\epsilon$  7350).

**4,5-Dihydro-6-isopropylidenehydrazinopyridazin-3(2H)-one (15).**—The foregoing hydrazino-compound (14) (600 mg) was heated under reflux in acetone (3 ml) and methanol (3 ml), under nitrogen. Evaporation gave the isopropylidene derivative (705 mg), m.p. 197° (instantaneous decomp.) (from nitromethane) (Found: C, 49.7; H, 7.3; N, 33.5.  $C_7H_{12}N_4O$  requires C, 50.0; H, 7.2; N, 33.3%),  $\nu_{\max}$  (KBr) 3175 and 3053 (NH), 2976 and 2907 (CH), 1657s

(C=O), 1629s (C=N), 1504, 1466, 1432, 1419, 1380, 1368s, 1301, 1258, 1201w, 1140, 1104, 1075w, 1038w, 1024, 1000w, 970, 921w, 801, 769, and 759  $cm^{-1}$ ,  $\lambda_{\max}$  284 nm ( $\epsilon$  13,600).

The isopropylidene derivative (96 mg) was kept with hydrazine hydrate (0.5 ml) for 3 h. Evaporation of the solution to dryness under reduced pressure over sulphuric acid afforded a faintly pink solid (65 mg), crystallisation of which from hydrazine hydrate-ethanol provided the hydrazino-compound (14), m.p. and mixed m.p. 144—145°.

**Poly-[(1,2-dihydro-1,2,4,5-tetrazine-3,6-diyl)dimethylene] (18).**—To redistilled succinonitrile (16.5 g) dissolved in dry pyridine (100 ml), hydrazine (95%; 8 ml) was added, and the stirred solution was heated under reflux under nitrogen for 2 days. The bulk of the pyridine was decanted (P) and the creamy solid polymer was triturated with methanol and collected and dried (yield 4 g, 18%); m.p. 285° (decomp.) (from boiling water) [Found: C, 43.6; H, 5.5; N, 50.9.  $(C_4H_6N_4)_n$  requires C, 43.7; H, 5.5; N, 50.8%],  $\nu_{\max}$  (Nujol) 3250 (NH), 1650 (C=N), 1580, 1550s, 1520s, 1430, 1310w, 1260w, 1200w, 1160w, 1130w, 1070w, 1010w, 980w, 960w, 940w, 880, 780w, 740, and 720  $cm^{-1}$ ,  $\lambda_{\max}$  ( $H_2O$ ) 248 nm ( $\epsilon$  4500). The mass spectrum showed a series of large peaks at intervals of 110 mass units, diminishing in intensity to beyond *m/e* 770.

Addition of ether to the pyridine solution (P) caused separation of white solid (40 mg), m.p. 180° (decomp.) [190° (decomp.) when mixed with compound (20)].

To a hot filtered solution of the purified polydihydro-tetrazine (0.4 g) in water (20 ml), a filtered solution of glyoxylic acid monohydrate (1 g) in water (10 ml) was added. As the solution cooled, a granular precipitate formed of the addition product (19) (0.6 g, 90%), m.p. 188° (decomp.) [Found: C, 39.1; H, 4.6.  $(C_6H_8N_4O_3)_n$  requires C, 39.1; H, 4.4%],  $\nu_{\max}$  (Nujol) 3500br (OH, free and bonded), 3200 (NH bonded), 1700br (C=O), 1620w, 1580s, 1530w, 1300w, 1230w, 1200w, 1160w, 1150w, 1100, 1020w, 960w, 930, and 850w  $cm^{-1}$ . The compound was unaffected by drying at 150° and 20 mmHg.

When the polydihydro-tetrazine (100 mg) was stirred with sodium carbonate (0.2 g) in water (5 ml) for 2 days, a deep red colour developed. After evaporation, extraction with methanol ( $\times 3$ ), filtration of the extract, and evaporation again, a purple-red solid was obtained (10 mg), m.p. 110° (decomp.),  $\lambda_{\max}$  ( $H_2O$ ) 298 and 522 ( $\epsilon$  4300 and 212),  $\lambda_{\max}$  (EtOH) 294 and 528 nm. Treatment with 0.1*N*-hydrochloric acid discharged the colour of the solid and inert gas (nitrogen) was evolved.

**6-Hydrazino-3-(3-hydrazono-2,3,4,5-tetrahydropyridazin-6-yl)hydrazono-2,3,4,5-tetrahydropyridazine (20).**—Succinonitrile (5 g), pyridine (40 ml), and hydrazine (95%; 10 ml) were heated together under reflux under nitrogen for 30 h, and the solid (4 g, 52%) was triturated with methanol and crystallised from water and dried (70° at 2 mmHg) to afford the product, m.p. 200° (decomp.) (Found: C, 37.9; H, 6.3; N, 55.7.  $C_8H_{16}N_{10}$  requires C, 38.1; H, 6.4; N, 55.6%), *m/e* 252;  $\nu_{\max}$  (Nujol) 3300s and 3250s (NH<sub>2</sub>, NH), 1600s (C=N), 1530, 1420w, 1340s, 1300w, 1210w, 1170w, 1150w, 1120, 1010w, 990w, and 960  $cm^{-1}$ ,  $\lambda_{\max}$  ( $H_2O$ ) 303 nm ( $\epsilon$  15,300). Thermogravimetric analysis at 140° under nitrogen showed a weight loss of 15% during 21 h ( $C_8H_{16}N_{10}$  requires  $N_2H_4$  loss, 13%) after which the weight remained constant. The slightly pink product had m.p. 260° (decomp.) [270° (decomp.) in admixture with the polymeric dihydro-tetrazine (18)]. A further sample of compound (20) (100 mg) was stirred in boiling pyridine under nitrogen

for 2 days, after which the solid was collected, triturated with methanol, and dried. The recovered solid (60 mg) had m.p. 250° (decomp.) [264° (decomp.) in admixture with the polymer (18)].

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