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REACTION OF 3,6-DIPHENYL-1,2,4,5-TETRAZINE WITH *cis,cis*-1,5-CYCLOOCTADIENE

AN ATTEMPT AT PREPARING SOME DIHYDROPYRIDAZINE DERIVATIVES

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Abstract—The reaction of 3,6-diphenyl-1,2,4,5-tetrazine (**1**) with *cis,cis*-cycloocta-1,5-diene (**7**) has been studied with a view to preparing some interesting dihydropyridazine derivatives. Refluxing a mixture of **1** with excess of **7** in benzene solution for 8 hr resulted in the formation of a mixture of products consisting of 1,4-diphenyl-10a-hydroperoxy-4a,5,6,9,10,10a-hexahydrocycloocta[d]pyridazine (**8**, 27%) and 2,4a,5,6,8,10a,11,12-octahydro-1,4,7,10-tetraphenyldipyridazo[4,5-a:4',5'-e]cyclooctene (**9**, 14%). However, when the reaction of **1** with **7** was carried out in refluxing benzene for nearly 40 hr, the products formed were a 14% yield of **8**, a 17% yield of **9** and a 37% yield of 1,4-diphenyl-5,6,9,10-tetrahydrocycloocta[d]pyridazine (**10**). Neat heating of **1** with **7** around 150° for 10 hr, on the other hand, gave a 20% yield of **9**, as the only isolable product. Thermolysis of **8** around 155° gave a mixture of products consisting of 2-oxocyclooct-5-enyl phenyl ketone N-benzoylhydrazone (**15**, 30%) and 1H-3-phenyl-4,5,8,9-tetrahydrocycloocta[d]pyrazole (**16**, 22%). Nickel peroxide-oxidation of the adduct **9** gave a 67% yield of 1,4,7,10-tetraphenyldipyridazo[4,5-a:4',5'-e]cyclooctene (**27**). Acetylation of **9**, on the other hand, gave a 70% yield of 2,3,8,9-tetraacetyl-2,3,5,6,8,9,11,12-octahydro-1,4,7,10-tetraphenyldipyridazo[4,5-a:4',5'-e]cyclooctene (**28**).

1,2,4,5-Tetrazines are known to undergo facile $[\pi^4s+\pi^2s]$ type of additions with electron-rich dienophiles, giving rise to pyridazine and dihydropyridazine derivatives, depending on the nature of the dienophiles.[1] Thus, it has been shown that the reaction of 3,6-diphenyl-1,2,4,5-tetrazine (**1**) with acetylene, for example, is reported to give 3,6-diphenylpyridazine (**3**), presumably formed through the initial addition product, **2** (Scheme 1).[1a] The reaction of 3,6-diphenyl-1,2,4,5-tetrazine (**1**) with an olefinic dienophile like styrene, on the other hand, gives rise to 1,4-dihydro-3,4,6-triphenylpyridazine (**6**), presumably arising through the initially formed, 4,5-dihydro-3,5,6-triphenylpyridazine (**5**) (Scheme 1).[1a] Detailed studies by Carboni and Lindsey, Jr. and other workers have shown that both electronic and steric factors play dominant roles in these addition reactions.[1]

In view of our general interest in the thermal and photochemical transformations of potential heterotriene systems, we have explored the reaction of 3,6-diphenyl-1,2,4,5-tetrazine (**1**) with an olefinic dienophile like *cis,cis*-cycloocta-1,5-diene (**7**), as a possible route to preparing some interesting dihydropyridazine systems.[2]

RESULTS AND DISCUSSION

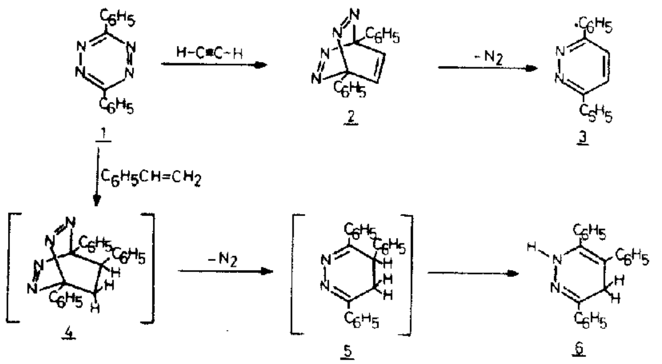
The reaction of 3,6-diphenyl-1,2,4,5-tetrazine (**1**) with excess of *cis,cis*-cycloocta-1,5-diene (**7**) in refluxing benzene gave a mixture of products consisting of a 27% yield of **8**, m.p. 154–155° (d) and analysing for $C_{22}H_{22}N_2O_2$ and a 14% yield of **9**, m.p. 201–202° and analysing for $C_{36}H_{32}N_4$ (Scheme 2). The reaction of **1** with **7**, when carried out by refluxing equimolar amounts of these substances in benzene for 40 hr, a 14% yield of **8** and a 17% yield of **9** were obtained. In addition, a 37% yield of a product **10**, m.p. 119–120° and analysing for $C_{22}H_{20}N_2$ could also be isolated from this run. When the reaction of **1** with **7** was carried out in the absence of any solvent and by heating around 150° for 10 hr, under N_2 atmosphere, a 20% yield of **9** could be obtained as the only isolable product (Scheme 2). The structures of these different products have been elucidated on the basis of analytical results, spectral data and chemical evidences.

The structure of **8**, for example, has been deduced as 1,4-diphenyl-10a-hydroperoxy-4a,5,6,9,10,10a-hexahydrocycloocta[d]pyridazine. The UV spectrum of **8** was characterized by the presence of an absorption band at 263 nm (ε, 7000). It is interesting to note that the UV spectrum of **8** in presence of a trace of HCl showed marked variation from the original spectrum in that three absorption maxima now were observed at 231 nm (ε, 17,500), 244 nm (sh) (ε, 15,600) and 288 nm (sh) (ε, 6500), respectively. Further, it has been observed that the spectral features of **8** in presence of HCl were quite similar to the spectrum of **10** in presence of a drop of HCl, indicating thereby that the acid-catalysed transformation of **8** leads to the formation of **10**.

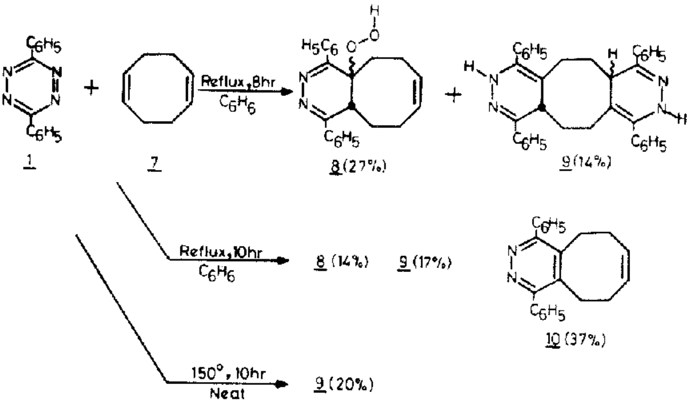
The IR spectrum of **8** was characterized by the presence of two bands at 3360 and 3340 cm^{-1}, respectively, which could be assigned to a hydroperoxy group. In this connection, it might be mentioned that hydroperoxides like cumene hydroperoxide, for example, are reported to exhibit a doublet in the hydroxy region of the spectrum, presumably due to intramolecular hydrogen bonding with the π-cloud of the benzene ring.[3]

The NMR spectrum of **8** showed several signals at 2.15δ (m, 8H), 2.96δ (m, 1H), 5.62δ (m, 2H), 6.70δ (s, 1H) and 7.62δ (m, 10H). Of these, the multiplet at 2.15δ is assigned to the methylene protons, whereas, the multiplet (doublet of a doublet) at 2.96δ is attributed to the methine proton in **8**, adjacent to the methylene protons. The multiplet centered around 5.63δ can be assigned to the two vinylic protons, whereas the broad singlet at 6.70δ, which was exchangeable with D_2O is assigned to the OH proton of the hydroperoxide group. The aromatic protons in **8** appears as a complex multiplet centered around 7.62δ.

Further support for the structure of **8** was derived from its mass spectral fragmentation studies. The mass spectrum of **8** showed the molecular ion peak at *m/e* 346



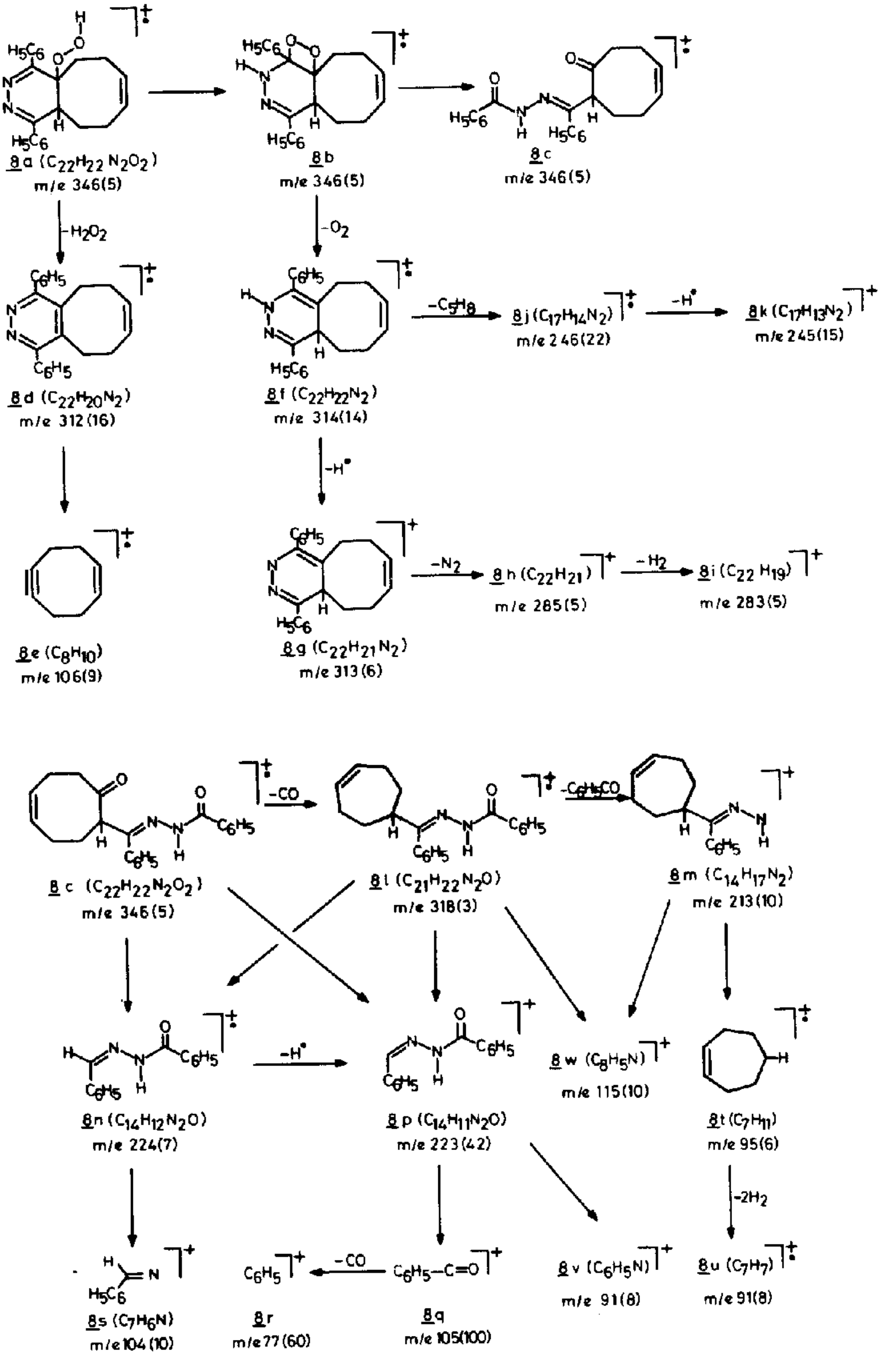
Scheme 1.



Scheme 2.

(5). Other peaks in the spectrum were observed at *m/e* 318(3), 315(4), 314(15), 313(6), 312(16), 311(8), 285(5), 283(5), 247(4), 246(22), 245(15), 224(7), 223(42), 213(10), 115(10), 106(9), 105(100), 104(10), 95(6), 91(8), 79(5), 78(7), 77(60), 67(8), 55(9), 51(12) and 41(9). Some of the probable modes of fragmentations are shown in Scheme 3. The molecular ion **8a** could lose H_2O_2, under electron impact to give the fragment **8d** at *m/e* 312, which in turn, can further fragment to give the species **8e** at *m/e* 106. The molecular ion **8a**, on the other hand, can also undergo rearrangements, under electron impact to give the isomeric fragments **8b** (*m/e* 346) and **8c** (*m/e* 346), respectively. Loss of an O_2 molecule from **8b**, for example, can result in the fragment **8f** at *m/e* 314, which in turn can lose an H atom to give the fragment **8g** at *m/e* 313. Further loss of nitrogen from the pyridiazine species **8g** would result in the fragment **8h** at *m/e* 285. It might be mentioned in this connection that such a loss of nitrogen molecule from pyridazine derivatives, under electron-impact is known to occur quite readily.[4] Further loss of two H atoms from **8h** will result in the fragment **8i** at *m/e* 283. The loss of a C_5H_8 fragment from **8f**, on the other hand, will result in the formation of **8j** at *m/e* 246, which in turn can lose an H atom to give the fragment **8k** at *m/e* 245. A probable mode of fragmentation of the species **8c** is through the loss of CO to give the fragment **8l** at *m/e* 318, which can subsequently lose a benzoyl fragment to give **8m** at *m/e* 213. Further fragmentation of **8m** will result in the fragment **8t** at *m/e* 95, which can then lead to **8u** at *m/e* 91, with the loss of four H atoms. An alternative mode of fragmentation of **8l** will give rise to the fragment **8p** at *m/e* 223, which can also result from the fragment **8n**, with the loss of an H atom. The fragment **8n** itself can be assumed to be formed from either **8c** or **8l**, through a hydrogen transfer reaction, followed by rearrangement. The peak at *m/e* 104 can be assigned to the fragment, **8s**, formed from **8n**. The base peak at *m/e* 105 can be attributed to the benzoyl fragment, **8q**, whereas the peak at *m/e* 77 is attributed to the phenyl fragment, **8r**. The peak at *m/e* 115 can be attributed to the fragment **8w** (C_8H_5N), formed from the fragmentation of either **8l** or **8m**. It is also likely, that the peak at *m/e* 91 may be due to the phenylnitrene fragment **8v**, which can arise through an aroylnitrene intermediate, formed from **8p**.

Evidence in support of the presence of a hydroperoxy group in **8** was derived from the fact that it liberated iodine on treatment with acidified potassium iodide solution.[5] Further confirmation of the structure of **8** and its relationship to the product **10**, isolated from the reaction of 3,6-diphenyl-1,2,4,5-tetrazine with *cis,cis*-cycloocta-1,5-diene, was derived from hydrogenation studies. Catalytic hydrogenation of **8**, using platinum gave a 80% yield of a product identified as 1,4-diphenyl-5,6,9,10-tetrahydrocycloocta[d]pyridazine (**13**). The same pyridazine derivative **13** was obtained in a 80% yield, on hydrogenation, of **10**, under similar conditions. The structure of **13** was established on the basis of analytical data and spectral evidences. The UV spectrum of **13**, for example, showed several absorption maxima at 231 (sh) (13,200), 242 (13,800) and 305 nm (sh) (ϵ, 400), respectively, characteristic of pyridazine derivatives.[6] The UV spectrum of **13** in presence of a trace of HCl, however,

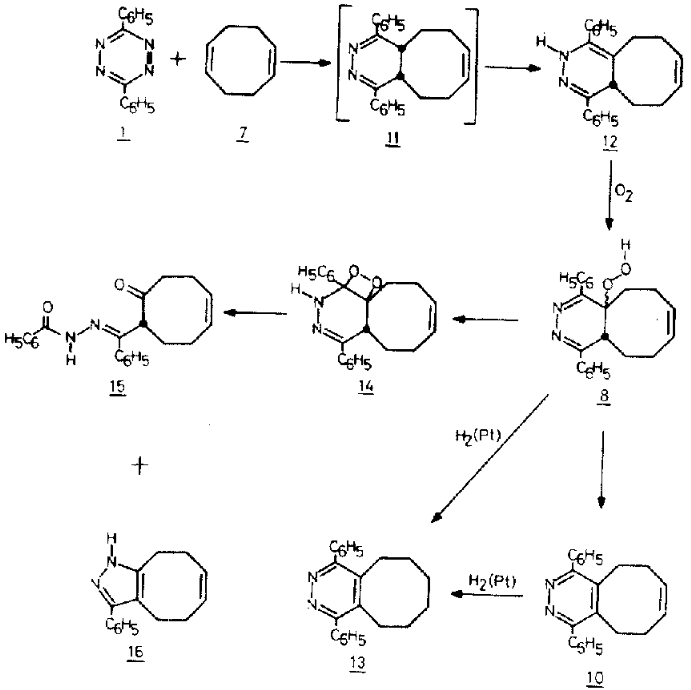


Scheme 3.

showed absorption maxima at 243 (15,100), 252 (sh) (14,100) and 294 nm (sh) (ε, 4600), respectively. It might be pointed out in this connection that the UV spectrum of **13** in presence of a trace of HCl resembles closely the spectrum of **8** in presence of HCl, indicating thereby that the same chromophore is formed from **8**, under acid-catalyzed conditions.

The NMR spectrum of **13** showed several multiplets centered around 1.50δ (8H), 2.80δ (4H) and 7.20δ (10H). Of these, the complex multiplet around 1.50δ is assigned to the methylene protons away from the pyridazine ring, whereas the multiplet around 2.80δ is attributed to the methylene protons, adjacent to the pyridazine ring in **13**. The multiplet around 7.20δ is assigned to the aromatic protons of the two phenyl groups.

Additional confirmation of the structure of **8** was derived through its thermal transformation studies. Neat heating of **8** around 155° for 15 minutes, under nitrogen atmosphere, resulted in the formation of the products, identified as 2-oxocyclooct-5-enyl phenyl ketone N-benzoylhydrazone (**15**, 30%) and 1H-3-phenyl-4,5,8,9-tetrahydracycloocta[d]pyrazole (**16**, 22%) (Scheme 4). The



Scheme 4.

structures of both **15** and **16** have been established on the basis of analytical data and spectral evidences.

Analytical results have shown that compound **15**, for example, can be represented by the molecular formula, $C_{22}H_{22}N_2O_2$ and that it is isomeric with the starting material, **8**. The UV spectrum of **15** was characterized by the presence of two absorption maxima at 232 (14,000) and 282 nm (ε, 17,000), respectively. The IR spectrum of **15** showed the presence of an NH band at 3349 cm^{-1} and a keto carbonyl band at 1692 cm^{-1}. In addition, the spectrum showed two absorption bands at 1672 and 1496 cm^{-1} characteristic of the amide I and amide II bands, respectively.

The NMR spectrum of **15** showed several signals at 2.06δ (m, 8H), 3.95δ (m, 1H), 5.87δ (m, 2H), 7.65δ (m, 10H) and 9.20δ (s, broad, 1H). Of these, the broad singlet at 9.20δ, which disappeared on D_2O-shake is assigned to the NH proton, whereas the complex multiplet centered around 2.06δ is assigned to the methylene protons. The multiplet around 3.95δ appeared as the doublet of a doublet and is assigned to the methine proton, whose signal will be split by the presence of the adjacent methylene protons. The multiplet around 5.87δ is assigned to the two vinylic protons, whereas the complex multiplet centered around 7.65δ is assigned to the aromatic protons of the phenyl groups.

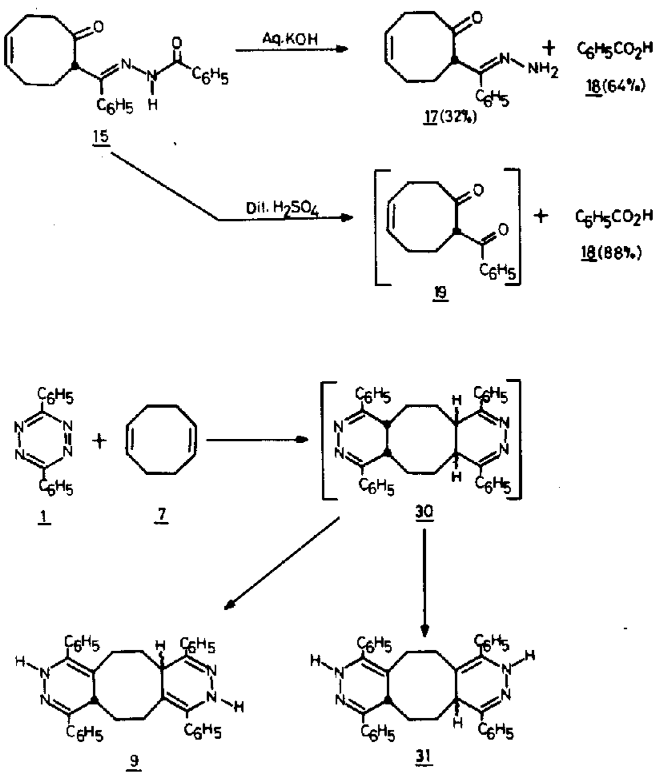
Further confirmation of the structure of **15** was derived from its mass spectrum. The mass spectrum of **15** showed the molecular ion peak at *m/e* 346 (2). In addition, the spectrum showed several peaks at *m/e* 318(1), 278(3), 251(2), 224(16), 223(100), 184(3), 180(11), 122(8), 119(4), 105(90), 104(14), 95(26), 91(9), 77(93) and 67(22). It is interesting to note that the mass spectral fragmentations of **15** bear a close resemblance to the fragmentation pattern of the species **8c**, presumed to be formed from **8**, under electron impact (Scheme 3).

Additional evidence for the structure of **15** was derived from its hydrolytic cleavage. Thus, the treatment of **15** with aqueous alkali, under reflux gave a 32% yield of a product, identified as 2-oxocyclooct-5-enyl phenyl ketone hydrazone (**17**), and a 64% yield of benzoic acid (Scheme 5). The structure of **17** was established on the basis of analytical results and spectral data. The IR spectrum of **17**, for example, showed absorption bands at 3450 and 3330 cm^{-1}, characteristic of NH_2 stretching frequencies. In addition, the spectrum showed a keto carbonyl absorption band at 1650 cm^{-1}. The NMR spectrum of **17** showed several signals at 2.05δ (m, 8H), 5.80δ (m, 2H), 6.10δ (s, broad, 2H) and 7.35δ (m, 5H), respectively. Of these, the complex multiplet at 2.05δ has been assigned to the methylene protons, whereas the multiplet at 5.80δ is assigned to the vinylic protons. The signal at 6.10δ appeared as a broad singlet, which disappeared on D_2O-shake and hence is assigned to the NH_2 protons. The multiplet centered around 7.35δ has been attributed to the phenyl protons.

Further confirmation of the structure of **17** was derived from its mass spectrum. The mass spectrum of **17** showed a molecular ion peak at *m/e* 242(16). Other peaks in the spectrum were observed at *m/e* 226(1), 224(2), 183(13), 175(25), 173(12), 159(1), 156(1), 146(3), 130(1), 120(9), 119(100), 105(10), 104(15), 103(10), 95(20), 93(2), 91(2) and 77(58).

Acid-hydrolysis of **15** by refluxing it with dilute sulphuric acid for 45 min gave a 88% yield of benzoic acid (Scheme 5). In addition, the product mixture showed the presence of a 1,3-diketo derivative, which could not be isolated in a pure form. This diketo derivative could be **19**, as it showed the presence of two CO peaks at 1750 and 1690 cm^{-1}, respectively, characteristic of 1,3-dicarbonyl compounds. In addition, it gave an impure chelate compound, on treatment with cupric acetate, again confirming the presence of a 1,3-diketo group.

The second product obtained in the thermal transformation of **8** has been identified as 1H-3-phenyl-4,5,8,9-tetrahydrocycloocta[d]pyrazole (**16**).[7] The structure of **16**



Scheme 5.

was arrived at on the basis of analytical results and spectral information. The UV spectrum of **16**, for example, was characterized by the presence of an absorption maximum at 242 nm (ϵ, 13,000). The IR spectrum of **16** showed the presence of an NH band at 3184 cm^{-1}.

The NMR spectrum of **16** showed several signals at 2.60δ (m, 8H), 5.46δ (m, 2H), 7.38δ (m, 5H) and 10.30δ (s, broad, 1H). Of these, the broad singlet at 10.30δ is assigned to the NH proton as it disappeared on D$_2$O-shake. The complex multiplet centered around 2.60δ has been assigned to the methylene protons, whereas the multiplet centered around 5.46δ is assigned to the vinylic protons. The multiplet around 7.38δ has been assigned to the aromatic protons of the phenyl group.

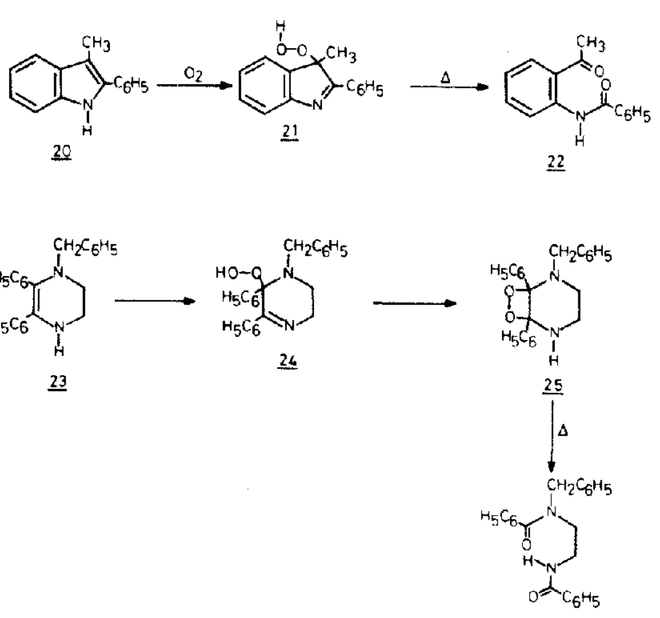
Further evidence for the structure of **16** was derived from its mass spectrum. The mass spectrum of **16** showed a molecular ion peak at *m/e* 224 (94). Other peaks in the spectrum were observed at *m/e* 223(8), 220(9), 209(6), 196(5), 195(12), 171(17), 170(100), 169(27), 157(5), 142(4), 141(6), 140(10), 130(5), 129(10), 128(5), 122(5), 121(52), 120(7), 119(4), 116(4), 115(12), 107(4), 105(13), 104(9), 103(4), 94(4), 91(5), 78(10), 77(22), 51(8), 41(5) and 39(6), most of which can be explained in terms of the fragmentations of **16**.

It might be pointed out here that although we have represented the pyrazole **16** as the 1H-isomer, it can also be represented as the 2H-isomer. Further, it is also likely that this compound may be existing as a tautomeric mixture of both the 1H- and 2H-isomers. It is known that similar pyrazole derivatives exist as a mixture of the two possible tautomeric forms, from which individual isomers have not been isolated.[7]

A reasonable pathway for the formation of the hydroperoxide, **8** in the reaction of 3,6-diphenyl-1,2,4,5-tetrazine with *cis,cis*-cycloocta-1,5-diene is shown in Scheme 4. In this scheme we assume that the initial reaction of the tetrazine **1** with **7** results in the formation of the 1,2-dihydropyridazine intermediate **11**, which may exist as the more stable 1,4-dihydro derivative, **12**. The dihydropyridazine **12** can subsequently undergo air-oxidation, under the reaction conditions to give **8**. It might be mentioned in this connection that numerous examples of hydroperoxide formation through the oxidation of enamine substrates are reported in the literature.[8] Witkop and Patrick,[8c] for example, have shown that 2-phenylskatole (**20**), on allowing to stand in air for a couple of days is converted to 2-phenyl-3-methyl-3-hydroperoxyindolenine (**21**), which could be further transformed to *o*-benzoylaminoacetophenone (**22**), either on heating or by treatment with acid (Scheme 6). Similarly, Lunsford *et al.*[8f] have shown that in the attempted preparation of the pyrazine derivative, **23**, the hydroperoxide **24** is invariably formed. This hydroperoxide has been found to undergo further transformation, on heating to the amide **26** and the reaction may be proceeding through the cyclic peroxy intermediate, **25** as shown in Scheme 6.

The thermal transformation of the hydroperoxy derivative **8** leading to the formation of **15** can be rationalized in terms of the cyclic peroxide **14** (Scheme 4) and this reaction is analogous to the transformation of **24** to **26** (Scheme 6). The formation of the pyrazole derivative **16**, on the other hand, can be rationalized in terms of the cyclization of **15**, under thermolytic conditions.

In the reaction of 3,6-diphenyl-1,2,4,5-tetrazine with *cis,cis*-cycloocta-1,5-diene, besides the hydroperoxide **8**, two other products (**9** and **10**) could also be isolated in varying yields, under different experimental conditions (Scheme 2). The structure of **10** has been established as



Scheme 6.

1,4 - diphenyl - 5,6,9,10 - tetrahydrocycloocta[d] pyridazine on the basis of analytical data and spectral evidences. The UV spectrum of **10** was characterized by the presence of several absorption maxima at 225 (15,000), 243 (13,000) and 301 nm (sh) (ε, 500), characteristic of pyridazine chromophores.[6] The UV spectrum of **10** in presence of a trace of HCl showed slight changes in the absorption maxima and these were observed at 244 (13,800), 253 (sh) (12,600) and 295 nm (sh) (ε, 4000), respectively. It is pertinent to observe that the spectrum of **10** in presence of a trace of HCl was very similar to the spectra of both **8** and the hydrogenated product, **13**, in presence of acid, strongly supporting the pyridazine structure for **10**.

The NMR spectrum of **10** showed several multiplets centered around 2.40δ (4H), 3.05δ (4H), 5.68δ (2H) and 7.63δ (10H), respectively. Of these, the multiplet around 2.40δ is assigned to the methylene protons, adjacent to the olefinic double bond, whereas the multiplet around 3.05δ has been assigned to the methylene protons adjacent to the pyridazine ring. The multiplet centered around 5.68δ has been assigned to the vinylic protons, whereas the multiplet around 7.63δ is assigned to the aromatic protons.

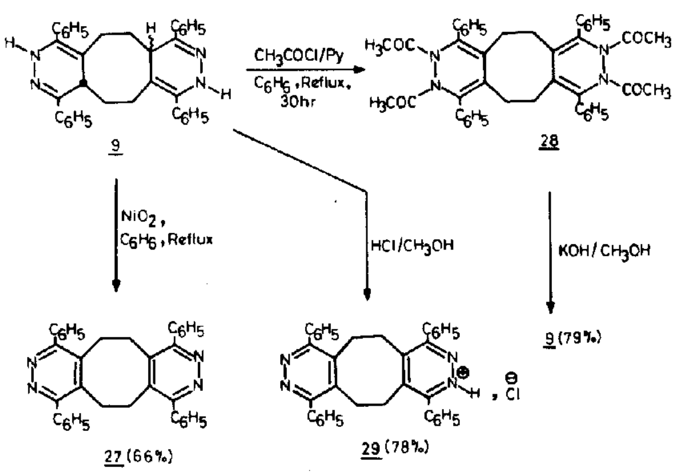
Further confirmation of the structure of **10** was derived through its hydrogenation studies. As it has been stated earlier, catalytic hydrogenation of **10** using platinum gave an excellent yield of the pyridazine derivative **13**, identical to the product obtained in the catalytic hydrogenation of **8** (Scheme 4).

A reasonable pathway for the formation of **10** in the reaction of **1** with **7** would be through the air-oxidation of the initially formed dihydropyridazine derivative **12**, as shown in Scheme 4. It is also quite likely that the hydroperoxide, **8** is involved as an intermediate in the transformation of **12** to **10**. It is pertinent to observe that the mass spectrum of **8** shows a peak corresponding to the species, **10**, indicating thereby that the hydroperoxide can undergo elimination of H_2O_2, leading to the formation of **10** (see Scheme 3).

The structure of the third product, **9**, obtained in the reaction of 3,6 - diphenyl - 1,2,4,5 - tetrazine with *cis,cis* - cycloocta - 1,5 - diene, has been tentatively assigned as 2,4a,5,6,8,10a,11,12 - octahydro - 1,4,7,10 - tetraphenyldipyridazo[4,5-a:4'5'-e]cyclooctene, on the basis of analytical results, spectral data and chemical evidences. Analytical results, for example, have shown that compound **9** is best represented by the molecular formula $C_{36}H_{32}N_4$. The UV spectrum of **9** was characterized by the presence of an absorption maximum at 325 nm (ε, 11,500), whereas its IR spectrum showed the presence of two absorption bands at 3416 cm^{-1} and 3276 cm^{-1}, due to a free NH and H-bonded NH groups, respectively. The NMR spectrum of **9** showed two complex multiplets centered around 2.80δ (10H) and 7.52δ (22H), respectively. Of these, the multiplet around 2.80δ, has been attributed to both the methylene and methine protons present in **9**, whereas the multiplet around 7.52δ accounts for both the aromatic and NH protons.

Further confirmation of the structure of **9** was derived from its mass spectrum. The mass spectrum of **9** showed the presence of a molecular ion peak at *m/e* 520(6). Other peaks in the spectrum were observed at *m/e* 519(31), 518(100), 517(97), 516(10), 515(7), 503(3), 502(2), 501(3), 490(2), 489(38), 441(3), 427(2), 285(4), 274(7), 273(37), 272(26), 271(19), 270(2), 260(4), 259.5(10), 259(43), 258.5(2), 258(6), 257(3), 249(2), 247(12), 246(11), 245(28), 244(3), 233(3), 207.5(2), 128(2), 122(1), 116(3), 115(4), 105(3), 103(3), 102(3) and 77(7). Most of these peaks can be accounted for, in terms of several fragments that could arise from **9**, under electron impact.

Further confirmation of the structure **9** was derived from its chemical transformations. Oxidation of **9** with nickel peroxide,[9] for example, gave a 67% yield of a product, identified as 1,4,7,10 - tetraphenyldipyridazo[4,5-a:4',5'-e]cyclooctene (**27**) (Scheme 7). The structure of **27** has been arrived at, on the basis of analytical results and spectral information. Analytical results have shown that compound **27** is best represented by the molecular formula $C_{36}H_{28}N_4$. The IR spectrum of **27** did not show the presence of any NH absorption band. On the other hand, the spectrum showed several



Scheme 7.

bands of 1550, 1440, 1385, 1070 and 770 cm^{-1}, characteristic of pyridazine ring systems.[10] The NMR spectrum of **27** showed two separate multiplets, centered around 2.80δ (8H) and 7.38δ (2H), corresponding to the methylene protons and aromatic protons, respectively.

Additional support for the structure of **27** was obtained through its acetylation, using acetyl chloride and pyridine. Refluxing a benzene-solution of **27** with a mixture of acetyl chloride and pyridine for 30 hr resulted in the formation of a 70% yield of a product identified as 2,3,8,9 - tetraacetyl - 2,3,5,6,8,9,11,12 - octahydro - 1,4,7,10 - tetraphenyldipyridazo[4,5-a:4',5'-e]cyclooctene (**28**) (Scheme 7). The IR spectrum of **28** showed an absorption band at 1690 cm^{-1}, characteristic of CO groups. The NMR spectrum of **28** showed several signals at 2.29δ (s, 12H), 2.60δ (m, 8H) and 7.20δ (m, 20H). Of these, the singlet at 2.29δ has been assigned to the Me protons, whereas the multiplet around 2.60δ was assigned to the methylene protons. The multiplet around 7.20δ has been assigned to the aromatic protons. Additional confirmation of the structure of **28** was derived from the fact that it could be converted back to **9** in a 79% yield, on treatment with methanolic potassium hydroxide.

It is interesting to note that the dihydropyridazine adduct **9**, on treatment with methanolic HCl gave a 78% yield of a product melting over the range of 252–254°, with decomposition and analyzing for $C_{36}H_{29}N_4Cl$. The structure of this product has been tentatively assigned as the hydrochloride **29**, shown in Scheme 7. However, further studies have to be carried out to confirm the structure **29**, for this product. The formation of **29**, from **9** may be assumed to involve the initial oxidation of **9**, followed by salt formation.

A reasonable pathway for the formation of **9** in the reaction of 3,6-diphenyltetrazine (**1**) with *cis,cis* - cycloocta - 1,5 - diene (**7**) is shown in Scheme **8**. In this scheme, we assume that two moles of the tetrazine **1** react with one mole of **7** to give the dihydropyridazine derivative **30**, after the loss of nitrogen molecules from the initially formed adduct. The dihydropyridazine **30**, can subsequently tautomerize to give either **9** or **31**, one of the more stable forms. Although we have assumed structure **9**, for the dihydropyridazine formed in the reaction of **1** with **7**, we have no definitive evidences in support of this assumption. It is equally likely that the compound in question may be correctly represented by structure **31** or perhaps it may even be a mixture of both the isomers **9** and **31**.

EXPERIMENTAL

All m.ps are uncorrected. The IR spectra were recorded on a Perkin-Elmer, Model 521 Infrared Spectrophotometer and electronic spectra on either a Cary-14 or a Beckman DB spectrophotometer. NMR traces were recorded on either a Varian A-60 or a HA-100 spectrometer. Mass spectra were recorded on a Hitachi RMU-6F, single focussing, mass spectrometer.

Starting materials. Benzonitrile, b.p. 40–41° (1 mm) and *cis,cis*-cycloocta-1,5-diene, b.p. 61–62° (20 mm) were freshly distilled before use. 1,4 - Dihydro - 3,6 - diphenyl - 1,2,4,5 - tetrazine (m.p. 191°) was prepared by a reported procedure.[11,12] Petroleum ether used was of b.p. 60–80°.

Oxidation of 1,4 - *dihydro* - 3,6 - *diphenyl* - 1,2,4,5 - *tetrazine*

To a suspension of 1,4 - dihydro - 3,6 - diphenyl - 1,2,4,5 - tetrazine (4.0 g, 17.0 mmol) and $NaNO_2$ (9.3 g, 0.13 mol) in EtOH (200 ml), maintained around 55°, was added dil H_2SO_4 (2N, 70 ml), over a period of 1/2 hr. After stirring the mixture for a further period of 1 hr, an equal volume of the acid was added, and the mixture was subsequently allowed to stand for 2 hr. The mixture was then cooled and poured into ice-water (700 ml). The ppt gave 3.2 g (82%) of violet-red crystals of **1**, which was recrystallized from EtOH to give a pure sample melting at 195° (lit.[12] m.p. 195°).

Reaction of 3,6 - *diphenyl* - 1,2,4,5 - *tetrazine* (**1**) *with* cis,cis - *cycloocta* - 1,5 - *diene* (**7**)

(a) ***Refluxing in benzene for*** **8 *hr*.** A mixture of **1** (4.0 g, 17 mmol) and **7** (13.0 g, 120 mmol) in 40 ml benzene, was refluxed for 8 hr, during which period the deep violet colour of the tetrazine disappeared completely. Removal of the solvent from the mixture gave a product which was chromatographed over alumina. Elution with petroleum ether gave a pale yellow solid, which on recrystallization from a mixture (1:2) of petroleum ether and benzene gave 1.6 g (27%) of **8**, m.p. 154–155° (d). (Found: C, 76.66; H, 6.22; N, 7.72; Mol. wt., 346 (Mass spect.). $C_{22}H_{22}N_2O_2$ requires: C, 76.30; H, 6.35; N, 8.09%; mol. wt., 346). IR spectrum (KBr) ν_{max}: 3360 and 3340 cm^{-1} (ν_{O-H}), 3070, 3020, 2990 and 2950 cm^{-1} (ν_{C-H}, tertiary, vinylic and aromatic), 2930, 2900 and 2800 cm^{-1} ($\nu_{s\text{-}CH_2}$ and $\nu_{as\text{-}CH_2}$), 1495 and 1475 cm^{-1} (ν_{O-H} and ν_{C-H}), 830 cm^{-1} (ν_{O-OH}). IR spectrum (CCl_4) ν_{max}: 3395 cm^{-1} (ν_{O-H}).

Further elution of the column with a mixture (1:1) of petroleum ether and benzene gave a white solid, which on recrystallization from benzene yielded 1.2 g (14%) of a product, m.p. 206–207° and identified as **9**. (Found: C, 83.25; H, 6.23; N, 10.40; Mol.wt., 520 (Mass spect.). $C_{36}H_{32}N_4$ requires: C, 82.95; H, 6.12; N, 10.70%; Mol. wt., 520). IR spectrum (KBr) ν_{max}: 3416 cm^{-1} (ν_{N-H} free), 3276 cm^{-1} (ν_{N-H} H-bonded), 3060 and 3020

cm^{-1} ($\nu_{C\text{-}H}$), 2930, 2890 and 2850 cm^{-1} ($\nu_{s\text{-}CH_2}$ and $\nu_{as\text{-}CH_2}$). UV spectrum (CH_3OH) λ_{max}: 325 nm (ϵ, 11,500). UV spectrum ($CH_3OH + HCl$) λ_{max}: 230 nm (ϵ, 33,900) and 290 (sh) (13,100). NMR spectrum ($CDCl_3$): 2.80δ (multiplet, 10H, methylene and methine protons) and 7.52δ (multiplet, 22H, aromatic and NH protons).

(b) *Refluxing in benzene for* 40 *hr.* A mixture of **1** (2.0 g, 8.5 mmol) and **7** (1.0 g, 9 mmol) was refluxed in benzene (40 ml) for 40 hr. Removal of the solvent under vacuum gave a viscous material, which was chromatographed over alumina. Elution of the column with petroleum ether, gave 500 mg (25%) of the unchanged starting material, **1**, m.p. 195° (m.m.p.).

Further elution with petroleum ether gave 300 mg (14%) of **8**, m.p. 154–155° (d) (m.m.p.).

Subsequent elution of the column with a mixture (3:1) of petroleum ether and benzene gave a white solid, which on recrystallization from a mixture (1:2) of petroleum ether and benzene gave 750 mg (37%) of **10**, m.p. 119–120°. (Found: C, 84.60; H, 6.58; N, 8.59. $C_{22}H_{20}N_2$ requires: C, 84.61; H, 6.41; N, 8.90%). IR spectrum (KBr) ν_{max}: 3060, 3030 and 2960 cm^{-1} ($\nu_{C\text{-}H}$, vinylic and aromatic), 2935, 2900 and 2850 cm^{-1} ($\nu_{as\text{-}CH_2}$ and $\nu_{s\text{-}CH_2}$), 1550, 1446, 1386, 1066 and 770 cm^{-1} (pyridazine ring vibration).

Further elution of the column with a mixture (1:1) of benzene and petroleum ether gave 280 mg (17%) of **9**, m.p. 206–207° (m.m.p.), after recrystallization from benzene.

(c) *Neat heating under nitrogen atmosphere in a sealed tube.* A mixture of **1** (0.25 g, 1 mmol) and **7** (0.20 g, 1.8 mmol) was heated in a sealed tube under N_2, around 150° for 10 hr. The mixture, after cooling, was chromatographed over alumina. Elution of the column with a mixture (2:1) of benzene and chloroform gave a white solid, which on recrystallization from a mixture (1:3) of benzene and petroleum–ether yielded 55 mg (20%) of **9**, m.p. 206–207° (m.m.p.).

Hydrogenation of 1,4 - *diphenyl* - 10a - *hydroperoxy* - 4a,5,6,9,10,10a - *hexahydrocycloocta*[d]*pyridazine* (**8**)

Platinum dioxide (50 mg) was taken in 35 ml EtOH and activated for 20 min by shaking it under H_2, at atmospheric pressure. To this mixture was added 120 mg (0.3 mmol) of **8**, and hydrogenation was carried out at atmospheric pressure for 10 hr, during which period, approximately 2 moles of H_2 were absorbed. From the mixture, the catalyst was filtered off and the solvent was removed under vacuum to give a residue, which was chromatographed over alumina. Elution of the column with benzene gave 90 mg (80%) of **13**, m.p. 167°, after recrystallization from a mixture (2:1) of petroleum ether and benzene (Found: C, 83.88; H, 6.99; N, 9.08. $C_{22}H_{22}N_2$ requires: C, 84.0δ H, 7.00; N, 8.91%). IR spectrum (KBr) ν_{max}: 3060 and 3030 cm^{-1} ($\nu_{C\text{-}H}$), 2920 cm^{-1} ($\nu_{as\text{-}CH_2}$), 2850 cm^{-1} ($\nu_{s\text{-}CH_2}$); 1550, 1440, 1385, 1070 and 770 cm^{-1} (pyridazine ring vibration).

Hydrogenation of 1,4 - *diphenyl* - 5,6,9,10 - *tetrahydrocycloocta*[d]*pyridazine* (**10**)

A soln of **10** (150 mg, 0.4 mmol), in EtOAc was hydrogenated in presence of Pt (generated from 50 mg of PtO_2) for 9 hr, during which period, approximately 1 mole of H_2 was absorbed. From the mixture, the catalyst was filtered off, and afterwards the solvent was removed under vacuum to give a viscous solid, which was subsequently chromatographed over alumina. Elution of the column with benzene gave 120 mg (80%) of a product identified as **13**, m.p. 167° (m.m.p.), after recrystallization from a mixture (2:1) of petroleum ether and benzene.

Thermolysis of 1,4 - *diphenyl* - 10a - *hydroperoxy* - 4a,5,6,9,10,10a - *hexahydrocycloocta*[d]*pyridazine* (**8**)

A sample of **8** (600 mg, 1.7 mmol) was heated around 155°, for 15 min. The melt, on cooling was chromatographed over alumina. Elution of the column with a mixture (2:1) of petroleum ether and benzene gave a solid residue, which on recrystallization from a mixture (2:1) of petroleum ether and benzene yielded 180 mg (30%) of a crystalline product, identified as **15**, m.p. 171–172°. (Found: C, 76.14; H, 6.56; N, 7.86; Mol. wt., 346 (Mass spect.). $C_{22}H_{22}N_2O_2$ requires: C, 76.30; H, 6.35; N, 8.09%; Mol. wt., 346). IR spectrum (KBr) ν_{max}: 3349 cm^{-1} ($\nu_{N\text{-}H}$, amide), 3020 cm^{-1} ($\nu_{C\text{-}H}$), 2944 cm^{-1} ($\nu_{as\text{-}CH_2}$), 2850 cm^{-1} ($\nu_{s\text{-}CH_2}$), 1692 cm^{-1} ($\nu_{C=O}$), 1672 cm^{-1} (amide I band), 1496 cm^{-1} (amide II band), and 1232 cm^{-1} ($\nu_{C\text{-}N}$ of amide).

Further elution of the column with EtOAc gave a viscous mass, which was subsequently chromatographed over alumina. Elution with a mixture (9:1) of benzene and chloroform gave a product, which was crystallized from a mixture (1:1) of petroleum ether and benzene to give 85 mg (22%) of **16**, m.p. 148–149°. (Found: C, 80.13; H, 6.77; N, 12.72; Mol. wt., 224 (Mass spect.). $C_{15}H_{10}N_2$ requires: C, 80.31; H, 7.14; N, 12.50%; Mol. wt., 224). IR spectrum (KBr) ν_{max}: 3184 cm^{-1} ($\nu_{N\text{-}H}$), 3060 cm^{-1} ($\nu_{C\text{-}H}$).

Alkaline-hydrolysis of 2 - *oxocyclooct* - 5 - *enyl phenyl ketone* N - *benzoylhydrazone* (**15**)

A mixture of 200 mg (0.58 mmol) of **15**, and 7 ml of 8N KOH was refluxed for 5 hr. The mixture, on cooling, was diluted with water and extracted with ether. The ether-extract was washed with water, dried over Na_2SO_4. Removal of the solvent under vacuum gave a viscous mass, which was chromatographed over alumina. Elution with a mixture (1:1) of petroleum ether and benzene, gave 45 mg (32%) of a product, m.p. 117–118°, after recrystallization from a mixture (1:1) of petroleum ether and benzene, and was identified as **17**. (Found: C, 74.42; H, 7.36; N, 11.32; Mol. wt., 242 (Mass spect.). $C_{15}H_{18}N_2O$ requires: C, 74.38; H, 7.43; N, 11.50%; Mol. wt., 242). IR spectrum (KBr) ν_{max}: 3450 cm^{-1} ($\nu_{as\text{-}NH_2}$), 3330 cm^{-1} ($\nu_{s\text{-}NH_2}$), 3230 cm^{-1} ($\nu_{N\text{-}H}$ H-bonded), 3040 cm^{-1} ($\nu_{C\text{-}H}$), 2940 cm^{-1} ($\nu_{as\text{-}CH_2}$), 2850 cm^{-1} ($\nu_{s\text{-}CH_2}$) and 1650 cm^{-1} ($\nu_{C=O}$). UV spectrum (MeOH) λ_{max}: 224 nm (ϵ, 7500) and 280 (12,500). NMR spectrum ($CDCl_3$): 2.05δ (multiplet, 8H, methylene protons), 5.80δ (multiplet, 2H, vinylic protons), 6.10δ (broad singlet, 2H, exchangeable with D_2O) and 7.35δ (multiplet, 5H, aromatic protons).

The aqueous-alkaline layer, after removal of the ether soluble fractions from the hydrolysed mixture of **15**, was acidified with dil HCl. Extraction with ether and work-up in the usual manner gave 55 mg (64%) of a product, m.p. 120–121° (mixture m.p.), after recrystallization from hot water, and identified as benzoic acid.

Acid-hydrolysis of 2 - *oxocyclooct* - 5 - *enyl phenylketone* N - *benzoylhydrazone* (**15**)

A mixture of 200 mg (0.58 mmol) of **15**, and 8 ml of 70% HSO_4 was refluxed for 45 min. The mixture was allowed to cool and was subsequently extracted with benzene. The benzene-layer was washed with $NaHCO_3$ aq to remove any organic acids and was subsequently dried over $NaSO_4$. Removal of the solvent under vacuum gave a residual mass, which was chromatographed over alumina. Elution with benzene gave a product, which was found to be homogeneous on tlc. Qualitative tests revealed the absence of N in this product. IR spectrum (CCl_4) ν_{max}: 1750 cm^{-1} and 1690 cm^{-1} ($\nu_{C=O}$).

Treatment of this material with an AcOH solution of cupric acetate resulted in the formation of an impure copper chelate complex, indicating the presence of a 1,3-diketofunctionality in this material. Our attempts, to purify this copper complex, however, were unsuccessful.

The Na_2CO_3 extract was acidified with dil HCl and was subsequently extracted with ether. The ether-extract was washed with water and dried over Na_2SO_4. Removal of the solvent under vacuum gave 62 mg (88%) of benzoic acid, m.p. 120–121° (m.m.p.), after recrystallization from hot water.

Nickel peroxide oxidation of 2,4a,5,6,8,10a,11,12 - *octahydro* - 1,4,7,10 - *tetraphenyldipyridazo*[4,5-a:4'5'-e]*cyclooctene* (**9**)

A mixture of 150 mg (0.29 mmol) of **9** and 60 mg of nickel peroxide[13] was stirred in refluxing benzene for 10 hr. The inorganic residue was filtered off and the solvent was removed under vacuum to give a viscous mass, which was chromatographed over alumina. Elution with benzene gave 96 mg (67%) of a product, m.p. 324° (d), after recrystallization from a mixture (3:1) of chloroform and methanol, and was identified as **27**. (Found: C, 83.56; H, 5.22; N, 10.65. $C_{36}H_{28}N_4$ requires: C, 83.72;

H, 5.42; N, 10.85%). IR spectrum (KBr) ν_{max}: 3080 cm^{-1} (ν_{C-H}), 2960 cm^{-1} ($\nu_{as\text{-}CH_2}$), 2850 cm^{-1} ($\nu_{s\text{-}CH_2}$), 1550, 1440, 1385, 1070 and 770 cm^{-1} (pyridazine ring vibrations). NMR spectrum ($CDCl_3$): 2.80δ (multiplet, 8H, methylene protons) and 7.38δ (multiplet, 20H, aromatic protons).

Acetylation of 2,4a,5,6,8,10a,11,12 - *octahydrotetraphenyl - pyridazo*[4,5-a:4′,5′-e]*cyclooctene* (9)

A mixture of **9**, (0.2 g, 0.39 mmol), acetyl chloride (0.1 g, 2 mmol) and pyridine (3 drops) was refluxed in dry benzene for 30 hr. On removal of the solvent from the mixture, a viscous mass was obtained, which was chromatographed over alumina. Elution with a mixture (3:1) of petroleum ether and benzene gave a solid, which was recrystallized from alcohol to give 188 mg (70%) of a product, m.p. 298–299° (d) and identified as **28**. (Found: C, 77.90; H, 6.20; N, 8.50. $C_{44}H_{40}O_4N_4$ requires: C, 77.59; H, 5.90; N, 8.20). IR spectrum (KBr) ν_{max}: 3060 cm^{-1} (ν_{C-H}), 2960 cm^{-1} ($\nu_{as\text{-}CH_2}$), 2850 cm^{-1} ($\nu_{s\text{-}CH_2}$), 1690 cm^{-1} ($\nu_{C=O}$). UV spectrum (CH_3OH) λ_{max}: 217 nm (ϵ, 44,940) and 290 (34,100). NMR spectrum ($CDCl_3$): 2.29δ (singlet, 12H, CH_3 protons), 2.60δ (multiplet, 8H, methylene protons), 7.20δ (multiplet, 20H, aromatic protons).

Alkaline-hydrolysis of 2,3,8,9 - *tetraacetyl* - 2,3,5,6,8,9,11,12 - *octahydro* - 1,4,7,10 - *tetraphenyldipyridazo*[4,5-a:4′,5′-e]*cyclo - octene* (**28**)

A mixture of 100 mg (0.2 mmol) of **28** and 4N-methanolic KOH was refluxed for 4 hr. Removal of all MeOH under vacuum, gave a viscous mass, which was treated with water. The aqueous soln was extracted with ether, and the ether-extract was dried over Na_2SO_4. Removal of the solvent under vacuum gave a product, which was crystallized from a mixture (1:1) of benzene and petroleum ether to give 60 mg (79%) of **9**, m.p. 206–207° (m.m.p.).

Treatment of 2,4a,5,6,8,10a,11,12 - *octahydro* - 1,4,7,10 - *tetraphenyldipyridazo*[4,5-a:4′,5′-e]*cyclooctene* (**9**) *with methanolic-hydrogen chloride*

The adduct **9** (100 mg, 0.2 mmol) was treated with methanolic HCl. Removal of the solvent yielded a viscous product, which on crystallization from MeOH, gave 82 mg (78%) of a white compound, m.p. 252–254° (d), tentatively identified as the hydrochloride of **27**. (Found: C, 78.25; H, 5.05; N, 9.70. $C_{36}H_{29}N_4Cl$ requires: C, 78.55; H, 5.24; N, 10.13%). IR spectrum (KBr) ν_{max}: 2550, 2000, 1480, 1380, 1020, 810, 760, 725 and 695 cm^{-1}. UV spectrum (C_2H_5OH) λ_{max}: 218 nm (ϵ, 17,950) and 324 (7900).

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