

STUDIES OF MEDIUM-MEMBERED HETEROCYCLIC COMPOUNDS. I.
THE FORMATION OF 2,5-DIPHENYL-3,4-DIAZA-2,4-NORCARADIENE
FROM 4,6-DIHYDRO-3,7-DIPHENYL-1,2-DIAZEPINE

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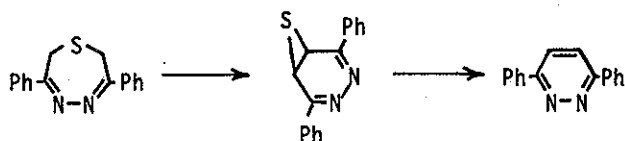
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Treatment of 4,6-dihydro-3,7-diphenyl-1,2-diazepine (**2**) with NBS or bromine afforded 4-methyl-3,6-diphenylpyridazine (**3**) which is formed from 2,5-diphenyl-3,4-diaza-2,4-norcaradiene (**1**) and hydrogen bromide. The dihydrodiazepine **2** reacted with chlorine or sulfuryl chloride, giving **1** and 4,5,5,6-tetrachloro-4,6-dihydro-3,7-diphenyl-1,2-diazepine (**4**).

Two methods have been available for the preparation of 2,5-diphenyl-3,4-diaza-2,4-norcaradiene (**1**): one is based on several reaction sequences starting from cis-cyclopropane-1,2-dicarboxylic anhydride¹ and the other, the Diels-Alder reaction of 3,6-diphenyl-1,2,4,5-tetrazine with cyclopropene.^{2,3} On the other hand, Loudon and Young⁴ reported that on treatment with N-bromosuccinimide(NBS)

2,7-dihydro-3,6-diphenyl-1,4,5-thiadiazepine was converted into 3,6-diphenylpyridazine with a ring contraction, and suggested that the pyridazine would be formed by a bromination-debromination process via the episulfide.

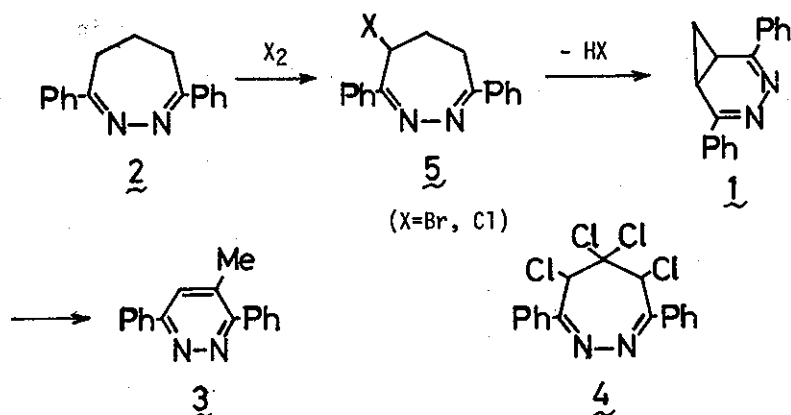


We have undertaken an investigation of the reaction of easily available 4,6-dihydro-3,7-diphenyl-1,2-diazepine (**2**)⁵ with halogenation-reagents, the diazanorcaradiene **1** being expected to form.

When a solution of **2** and three equivalents of NBS in carbon tetrachloride was refluxed over a lamp-heater for 1 h, 4-methyl-3,6-diphenylpyridazine (**3**) was obtained in 5.4% yield, accompanied with tarry material. The same change was effected with bromine in refluxing methylene dichloride, methanol or carbon tetrachloride: the yield of **3** was 8.0, 6.3 or 4.9%, respectively. The structure of **3**, mp 134.5–135.5°C [lit.¹ mp 135°C], was confirmed on the basis of the spectral data as well as of the microanalysis [$\delta_{\text{ppm}}^{\text{CDCl}_3}$: 2.43 (3H, s, CH_3), 7.3–7.8 (9H, m, aromatic protons), 8.0–8.3 (2H, m, aromatic protons); m/e 246 (M^+), 218 ($\text{M}^+ - \text{N}_2$), 203 ($218^+ - \text{Me}$), 103, 77]. As will be described below, it may be viewed that the pyridazine **3** was formed via the diazanorcaradiene **1**.⁶

On the other hand, treatment of the dihydrodiazepine **2** with chlorine gas in methylene dichloride at room temperature afforded the expected diazanorcaradiene **1** and tetrachloride **4** in 28.5 and 5.5% yields, respectively. Similarly, **2** was reacted with sulfuryl chloride in methylene dichloride at room temperature, giving **1** and **4** in 16.9 and 3.0% yields.

The structure of **1**, mp 198–199°C [lit.¹ mp 196°C], was confirmed on the basis of the spectral data as well as of the microanalysis. The nmr spectrum exhibited a typical AB_2X pattern for four aliphatic protons, besides aromatic



protons (10H): it was in agreement with that reported by Maier.¹ Its mass spectrum supports the structure of 1 [m/e (rel. intensity %): 246 (M^+ , 16), 218 ($M^+ - N_2$, 31), 217 (45), 216 (13), 215 (21), 117 (21), 116 ($218^+ - \text{PhC}\equiv\text{CH}$, 100), 102 ($\text{PhC}\equiv\text{CH}^+$, 21), 89 (C_7H_5^+ , 18), 77 (36)].

On the basis of the spectral data and microanalysis, 4, mp 155-156°C, was deduced to be 4,5,5,6-tetrachloro-4,6-dihydro-3,7-diphenyl-1,2-diazepine [$\nu_{\text{max}}^{\text{KBr}}$: 1555 cm^{-1} (C=N); $\delta_{\text{ppm}}^{\text{CDCl}_3}$: 4.46 (2H, s, $\geq\text{CH}$), 7.4-7.8 (10H, m, aromatic protons); m/e 384, 386, 388, 390, 392 (M^+ , rel. intensity ca 80:110:55:12:1), 349, 351, 353 ($M^+ - \text{Cl}$), 321, 323, 325 ($M^+ - \text{Cl} - N_2$), 286, 288, 290 ($M^+ - 2\text{Cl} - N_2$), 251, 253 ($M^+ - 3\text{Cl} - N_2$)].

Although the exact pathway for the formation of diazanorcaradiene 1 is not clear, we viewed the pathway via the formation of 4-halo-4,6-dihydro-3,7-diphenyl-1,2-diazepine (5), followed by dehydrohalogenation of 5 into 1. The formation of pyridazine 3 can be rationalized as arising from 1, because treatment of 1 with hydrogen bromide in methylene dichloride afforded 3 almost quantitatively.

Further investigation of the related reaction is in progress in our laboratory.

References

- 1 G. Maier, Angew. Chem., 1963, 75, 920; Chem. Ber., 1965, 98, 2438, 2446.
- 2 M. A. Battiste and T. J. Barton, Tetrahedron Letters, 1967, 1227.
- 3 J. Sauer and G. Heinrich, ibid., 1966, 4979.
- 4 J. D. Loudon and L. B. Young, J. Chem. Soc., 1963, 5496.
- 5 C. G. Overberger and J. J. Monagle, J. Amer. Chem. Soc., 1956, 78, 4470.
- 6 Although the reaction of 2 with bromine in methylene dichloride below room temperature afforded a crystalline compound, the compound could not be purified because of its decomposition.

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