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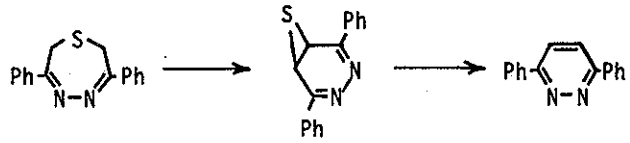
Treatment of 4,6-dihydro-3,7-diphenyl-1,2-diazepine (2) with NBS or bromine afforded 4-methyl-3,6-diphenylpyridazine (3) which is formed from 2,5-diphenyl-3,4-diaza-2,4-norcaradiene (1) and hydrogen bromide. The dihydrodiazepine 2 reacted with chlorine or sulfuryl chloride, giving 1 and 4,5,5,6-tetrachloro-4,6-dihydro-3,7-diphenyl-1,2-diazepine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

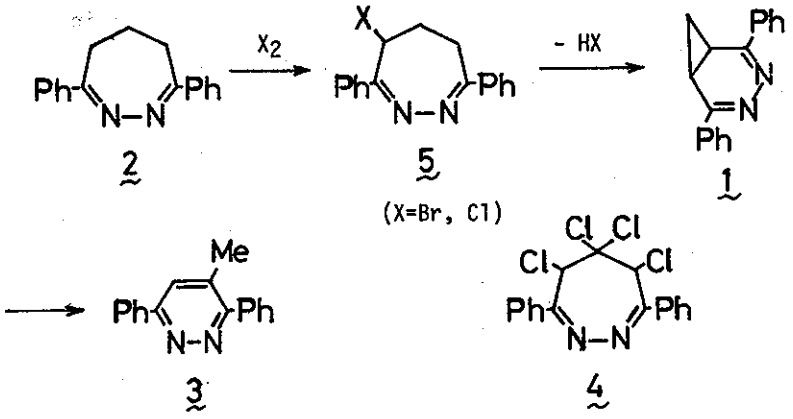


We have undertaken an investigation of the reaction of easily available 4,6-dihydro-3,7-diphenyl-1,2-diazepine (**2**)[5] with halogenation-reagents, the diazanorcaradiene **1** being expected to form.

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 [$\delta_{ppm}^{CDCl_3}$: 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 ($M^+ - N_2$), 203 (218^+ - 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^+ - PhC≡CH, 100), 102 ($PhC{\equiv}CH^+$, 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 [ν_{max}^{KBr}: 1555 cm^{-1} (C=N); $\delta_{ppm}^{CDCl_3}$: 4.46 (2H, s, ≥C<u>H</u>), 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^+ - Cl), 321, 323, 325 (M^+ - Cl - N_2), 286, 288, 290 (M^+ - 2Cl - N_2), 251, 253 (M^+ - 3Cl - N_2)].

Although the exact pathway for the formation of diazanorcaradiene 1 is not clear, we viewed the pathway <u>via</u> 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

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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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