

AZIRIDINES XVII. REACTIONS OF

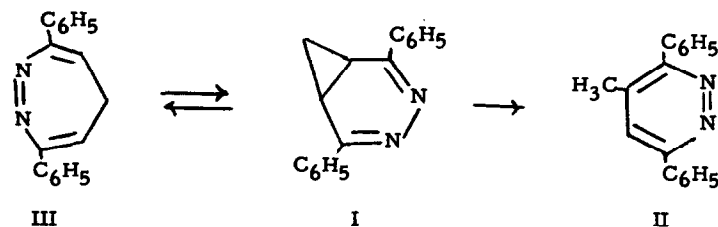
7-BENZYL-2,5-DIPHENYL-3,4,7-TRIAZA-2,4-NORCARADIENE

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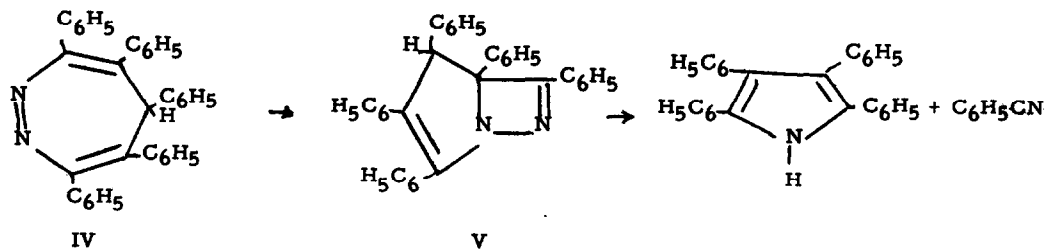
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Several recent communications have been concerned with the syntheses and isomerizations of diazanorcaradiene derivatives. Maier¹ prepared 2,5-diphenyl-3,4-diazanorcaradiene (I) which rearranged in acetic acid containing hydrochloric acid into 4-methyl-3,6-diphenylpyridazine (II). Battiste and Barton² have demonstrated the reversible conversion of I into the diazacycloheptatriene III at high temperatures. Furthermore, the latter investigators have shown that the pentaphenyldiazepine IV in refluxing xylene is converted,

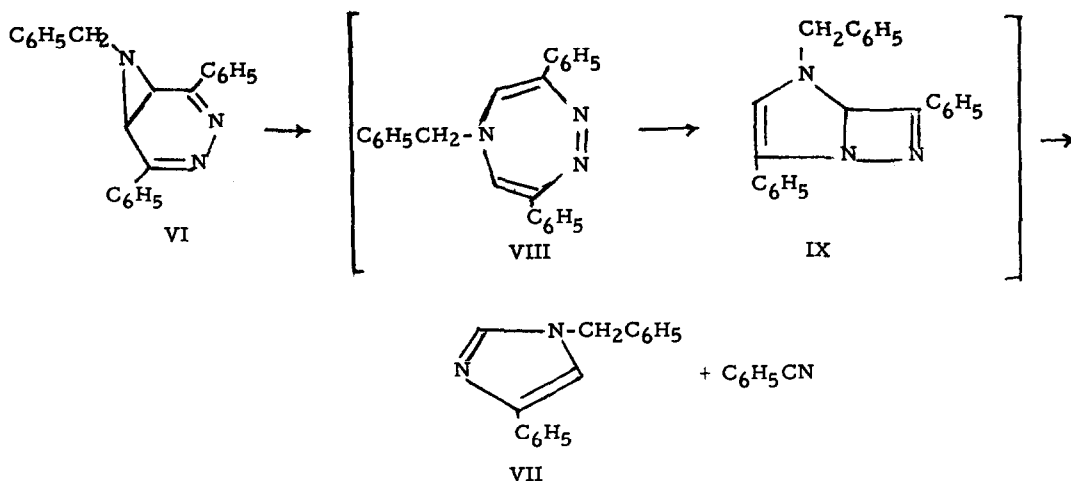


presumably, into the diazabicyclo[3.2.0]heptadiene V. Heating of V at 235° for 15 minutes gave tetraphenylpyrrole and benzonitrile.



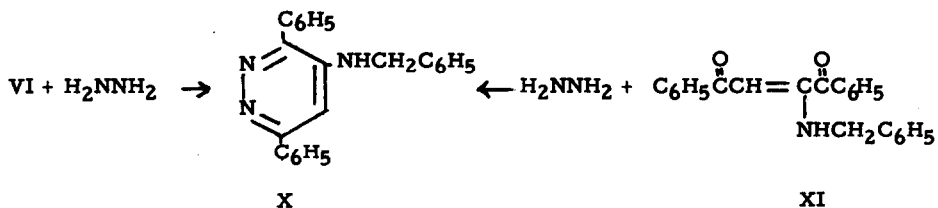
We have been engaged in an investigation of the 3, 4, 7-triazanorcaradiene system and now wish to report our observations. Brief heating of 7-benzyl-2, 5-diphenyl-3, 4, 7-triaza-2, 4-norcaradiene(VI)³ in benzene or ethanol formed benzonitrile and 1-benzyl-4-phenyl-imidazole(VII) in 73% yield. The reaction also occurs slowly at room temperature in chloroform and methanol. An authentic sample⁴ of VII prepared by reaction of 4(5)phenylimidazole with benzyl chloride was identical in all respects to the material obtained from heating VI.

The products can be accounted for by the valence tautomerization of VI into the triazacycloheptatriene VIII, conversion of VIII into IX, followed by fragmentation of IX into benzonitrile and VII.



The conversion of VI to VII and benzonitrile in chloroform at 41° was followed by nmr spectroscopy over the entire reaction range. The only absorption peaks observed were those of VI, VII and benzonitrile. At no time did signals appear that could be attributed to the suggested intermediates VIII and IX. Thus VIII and IX, if formed, are too reactive to be isolated under the experimental conditions employed.

Compound VI in refluxing hydrazine for several minutes isomerized in 50% yield into 3, 6-diphenyl-4-benzylaminopyridazine(X). Anal. Calcd. for C₂₃H₁₉N₃: C, 81.87; H, 5.68; N, 12.45. Found: C, 82.21; H, 5.71; N, 12.70.



A mass spectrometric analysis of X indicated a molecular weight of 337. The structure of X was supported by nmr and ir data. The nmr spectrum in CDCl_3 showed a broad signal for the N-H proton at 5.2 ppm(1 H) downfield from tetramethylsilane, a doublet for the methylene protons at 4.40 ppm(2 H), a singlet at 6.88 ppm(1 H) for the pyridazine proton and a complex pattern of bands from 7.25-8.10 ppm characteristic of the aromatic protons. After D_2O exchange the broad peak at 5.52 ppm is removed and the doublet at 4.40 ppm now appears as a singlet. Finally, an alternate synthesis of X was achieved by reaction of hydrazine with 1-benzylamino-1,2-dibenzoyl ethene(XI)³.

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References

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