Synthesis of 1,2-Diphenylazaspiro[2,2]pentane

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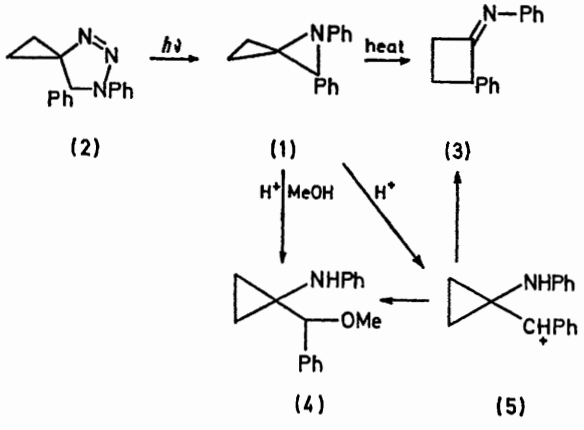
Summary The novel heterocycle 1,2-diphenylazaspiro-[2,2]pentane (**1**) has been synthesized, thermally rearranged to cyclobutanimine (**3**), and solvolysed in methanol to give the adduct (**4**) of unrearranged carbon skeleton.

SUBSTANTIAL recent interest has centred on the synthesis and characterization of oxaspiropentanes,[1] heterocyclic analogues of the well known, highly strained, spiropentane system.[2] We now report on an example of the nitrogen analogue.



1,2-Diphenylazaspiro[2,2]pentane (**1**) was obtained cleanly by irradiation (3100 Å) of (**2**), the thermal adduct of phenyl azide and benzylidenecyclopropane, in methylene chloride at 0° until the cessation of nitrogen evolution. The identification of (**1**) rests on its correct elemental analysis and characteristic 220 MHz n.m.r. spectrum [δ 0·82 (m, 1) 0·91 (m, 1), 1·14 (m, 1), 1·38 (m, 1), 3·57 (s, 1), and 7·0—7·3 (m, 10)]. Although a sample of (**1**) was kept without decomposition for more than a year at 0°, heating a chloroform solution of (**1**) to 100° in a sealed tube resulted in rapid conversion into isomer (**3**) [ν 5·9; δ (220 MHz) 2·1 (m, 1), 2·65 (m, 1), 2·86 (m, 2), 4·45 (t, 1, *J* 7 Hz), and 6·8—7·2 (m, 10)]. As expected, hydrolysis of imine (**3**) gave 2-phenylcyclobutanone [ν 5·62; δ 2·2 (m, 1), 2·5 (m, 1), 3·0 (m, 1), 3·1 (m,1), 4·44 (t, 1, *J* 7 Hz), and 7·2 (m, 5)] and aniline in good yield. The same conversion of (**1**) into (**3**) could be effected by prolonged irradiation under the conditions described above. On the other hand, (**1**) reacted completely with methanol in 2 h at 25° to give solvent adduct (**4**) [ν 2·95, δ 0·64 (m, 1) 0·73 (m, 2), 1·00 (m, 1), 3·16 (s, 3), 4·20 (br s, 1), 4·53 (s, 1), 6·7 (m, 3), and 7·2 (m, 7)] which clearly retains the cyclopropyl ring of the starting material. This transformation was followed in CD_3OD solution by n.m.r. and shown to be markedly accelerated by the incorporation of minute amounts of acetic acid and retarded slightly by pretreatment of the solvent with solid $NaHCO_3$.

The ready rearrangement of this new heterocyclic skeleton into the cyclobutane compound (**3**) is formally analogous to both the oxaspiropentane–cyclobutanone[1] and spiropentane–methylenecyclobutane[2] isomerizations. However, although the latter is almost certainly a unimolecular thermal process,[2] it appears likely that the heteroatomic compounds utilize an acid-catalysed heterolytic mechanism for their isomerization, perhaps *via* an intermediate cation such as (**5**). This would account for the much more ready rearrangement of these species relative to

the parent hydrocarbon. In methanol, nucleophilic substitution at the C–N bond becomes the predominant reaction. Solvent trapping of cation (**5**) readily explains the formation of (**4**), although S_N2 attack on protonated (**1**) is an alternate possible route to (**4**).

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