Ring Contraction of Some Dihydrodiazepines

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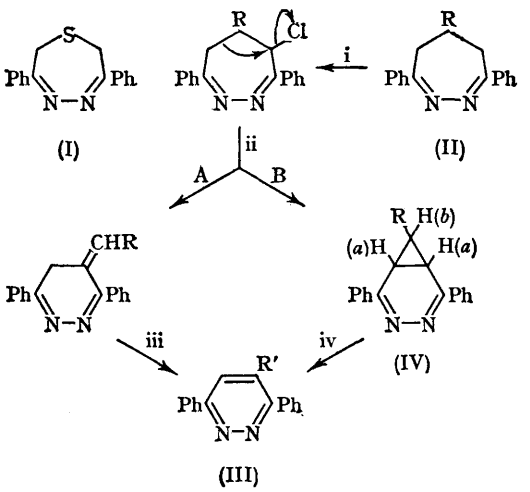
RING contraction is a distinguishing feature of tropolone chemistry where the carbonyl group, providing both a centre for attack and for activation of the α-positions, is itself extruded in the reaction. It has recently been shown that contraction in the azepine[1] series and of a diazepinone[2] may occur, and contractions of cycloheptatrienes, especially as tropylium derivatives,[3] are well known. A thiadiazepine (I) has been converted into a diphenylpyridazine *via* a postulated episulphide,[4] but as with the carbocyclic examples where caradiene-type intermediates are presumed,[3] no real evidence for the intermediate was adduced. We report here the contraction of three dihydrodiazepines to pyridazines and the isolation of the bicyclic intermediate (IV; R=Ph) in the favourable case of (II; R=Ph).

3,7-Diphenyl-1,2-diazacyclohepta-2,7-diene[5] (II;

[1] M. Anderson and A. W. Johnson, *Proc. Chem. Soc.*, 1964, 263.
[2] R. K. Bly, E. C. Zoll, and J. A. Moore, *J. Org. Chem.*, 1964, **29**, 2124.
[3] T. Mukai and H. Tsuruta, *Bull. Chem. Soc. Japan*, 1964, **37**, 1018.
[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.

R=H) reacts with *N*-bromosuccinimide or, more cleanly, with *N*-chlorosuccinimide to give 4-methyl-3,6-diphenylpyridazine (III; R′=Me), whose structure was supported by n.m.r. data. Two mechanisms may be envisaged to lead to (III) but both imply that carbon 5 is extruded in the contraction. This was confirmed by treating compound (II; R=Me) with *N*-chlorosuccinimide, when (III; R′=Et) and (III; R′=CHMeCl) were obtained. When one equivalent of *N*-chlorosuccinimide was used, these two products plus unchanged starting material were isolated in about equal proportions. If two equivalents of *N*-chlorosuccinimide were used (III; R′=CHMeCl) was isolated in about 60% yield. (III; R′=Et) is recovered unchanged from treatment with *N*-chlorosuccinimide under similar reaction conditions. Hence it can be concluded that chlorination occurs before rearrangement and that one equivalent only of *N*-chlorosuccinimide is necessary in the overall reaction.



i, *N*-chlorosuccinimide in carbon tetrachloride

ii, −HCl iii, H⁺ iv, −H⁺ , +H⁺

When (II; R=Ph) was treated in the usual way the major product was the expected pyridazine (III; R′=CH_2Ph), together with (III; R′=CHPhCl), and in small yield (III; R′=$CPhCl_2$). If the reaction was stopped when the solution was at its maximal yellow colour, the compound (IV; R=Ph) was isolated in fair yield (32%) together with unchanged material and ring-contracted products (33%). The structure follows from: the similarity of its infrared spectrum to that of (II; R=Ph); the ultraviolet spectrum is bathochromically shifted to 277—330 mμ (broad) from that found for (II; R=Ph) at 258—298 mμ, indicating conjugation of the cyclopropane ring with the π-electrons of the azine group and the phenyl substituent; the n.m.r. spectrum. Proton (*b*) appears as a triplet at τ 8·15 (J = 4·5 c./sec.) and the equivalent protons at (*a*) as a doublet at τ 6·99. The coupling constant is consistent with a *trans*-arrangement, and the shift in τ value for protons at (*a*) is to be expected from the nature of the substituents on the cyclopropane ring (*cf.* ref. 6). Compound (IV) is converted into (III; R′=CH_2Ph) by hydrogen chloride in ethanol and is a true intermediate in the reaction. Path B, therefore, represents the course of the reaction when R is phenyl.

In these three examples, activation of the methylene groups at positions 4 and 6 to chlorination is provided by the azine grouping. Halogenated intermediates have not been isolated, suggesting that internal nucleophilic displacement follows rapidly upon the halogenation step. This may be understood sterically, because of the proximity of carbons 4 and 6, and thermodynamically, because of the driving force for the overall contraction provided by the relative stability of the final aromatic structures. Although not proved, it is likely that all three ring contractions proceed through path B and the isolation of (IV; R=Ph) represents a favourable case because of the stability conferred upon it by the extended π-electron conjugation. The isolation of any chlorinated end product occurs only when (R) is not hydrogen and then a tertiary proton is in competition, even though less effectively, with the methylene groups as sites for initial attack.

Compound (IV; R=Ph) is the valency tautomer of the as yet undescribed 3,7-diphenyl-1,2-diazacyclohepta-2,4,7-triene. Any equilibrium in solution at 28° between such tautomers is ruled out by the n.m.r. spectrum. Formula (IV; R=Ph) therefore represents, not only an identified intermediate in the ring contractions described, but also the stable[6] caradiene-like isomer of the unknown 1,2-diazepine ring system.

Satisfactory spectral and analytical data were obtained for the new compounds described.

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[6] E. Ciganek, *J. Amer. Chem. Soc.*, 1965, **87**, 652.