Photolysis of 4,5-Diazatetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodeca-4,9-dienes: a Formal Homo-Cope Rearrangement

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The first example of a formal homo-Cope rearrangement in azoalkane chemistry is presented; a double bond in the proximity of a denitrogenation site participates in the rearrangement.

Azoalkane chemistry is a subject of continuing interest.[1] Chloro derivatives of diazatetra-cyclododecadiene (**1**) have been deazetised[2] to give the corresponding cyclopropane ring fused products; the authors commented on the passivity shown by the 'chloro-olefinic group' in any interaction with the 1,3-diradical (**2**) formed in the process.

The spatial proximity of two double bonds, isolated and non-conjugated, in the same molecule, such as in (**10**), is responsible for a facile Cope rearrangement.[3] Since (**2**) exhibits structural similarity with (**10**), in that the 1,3-diradical can be viewed as a homolysed σ-bond, we have re-examined the denitrogenation of this sytem. We report here a novel formal homo-Cope rearrangement, unprecedented in azoalkane chemistry.

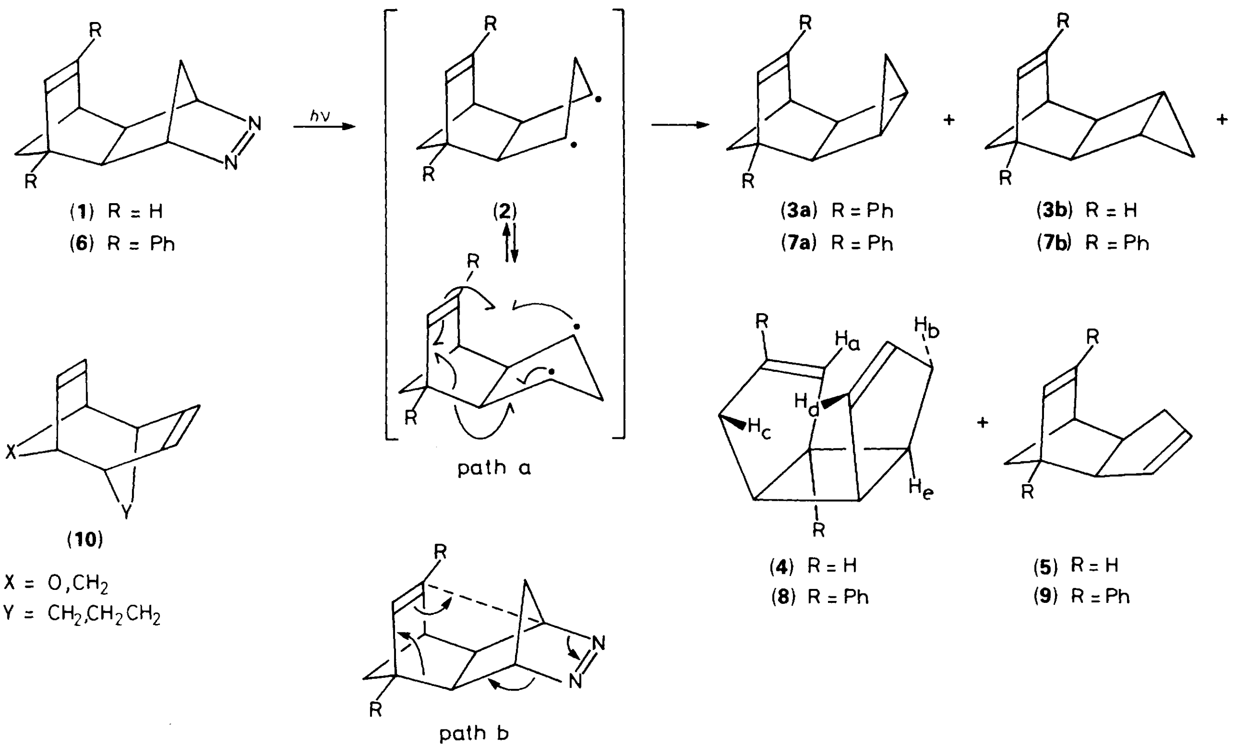
A n-hexane solution of (**1**) was irradiated for 2 h by a high pressure mercury lamp with a Pyrex filter. The photolysate was carefully concentrated[†] and the non-polar compounds (**3b**) and (**4**) were separated by silica gel column chromatography (hexane) in a combined yield of 72% [a 4 : 1 mixture of (**3b**) and (**4**), respectively, by g.l.c. analysis].[‡] In contrast to the photolysis, thermolysis of (**1**) in toluene or [^{2}H$_{6}$]benzene (in a sealed tube, 110 °C, 1 h) gave exclusive conversion to (**3b**). Lack of the formation of the *syn* isomer (**3a**) suggests that (**3a**) is thermally unstable, since a thermal *syn–anti* isomerization is precedented in this ring system.[2]

The ^{1}H n.m.r. spectrum (CDCl$_3$) of (**4**) showed four alkenic protons as two distinct multiplets centred at δ 5.79 and 5.68. The aliphatic region consisted of two sets of two protons, each at δ 3.45 and 3.10. Two sets of methylene signals appeared at δ 2.27. ^{13}C N.m.r. spectroscopy revealed five pairs of equivalent carbons, two of which were methines. The ^{1}H–^{1}H COSY spectrum supplemented the assignment for the structure as (**4**).[§]

[†] Owing to the high volatility of the hydrocarbons, yields were drastically reduced when the solvent was removed on a rotary evaporator.

[‡] A trace amount of (**5**) was also detected (10% SE-30 on Chromosorb GAW).

[§] The ring junction geometry was deduced from that established for (**8**). The regiochemistry of the double bonds was determined from spin decoupling experiments. The proton at the ring junction spin-coupled with two adjacent protons at the junctions.



Photolysis of the diphenyl derivative (**6**) gave four products (**7a**), (**7b**), (**8**), and (**9**) in a combined yield of 90% by silica gel column chromatography (benzene) as a 2:8:4:1 mixture, respectively, analysed by h.p.l.c. These compounds were purified by preparative h.p.l.c. (Si-60 Lichrosorb). Nuclear Overhauser enhancement (n.O.e.) experiments attested the *syn* stereochemistry of the rearrangement product (**8**). Irradiating H_a resulted in comparable enhancement of H_d (3.4%). Moreover, the H_e proton had a positive n.O.e. (3.2%) on the phenyl group. The *syn* stereochemistry of the cyclopropane ring to the double bond in (**7a**) was also confirmed from the n.O.e. relation between the alkenic proton and the *syn* proton of the methylene in the cyclpropane ring.

One possible mechanism for the formation of (4) and (**8**) involves 1,3-diradicals (**2**), assumed to be thermally equilibrated,[4] in a formal homo-Cope rearrangement (Scheme 1, path a); these diradicals are generated by both photolysis and thermolysis of the well studied 2,3-diazabicyclo[2.2.1]hept-2-ene ring system.[5] The second mechanism, in which bond reorganisation takes place (Scheme 1, path b),¶ similar to the retro-Diels–Alder reaction of 3,6-dihydropyridazines,[6] can also account for our observations and for the stepwise denitrogenation mechanism *via* diazenyl diradicals.[7]

Although further study is required to establish the reasons for the regioselectivity of the bond breaking in the rearrangement, the present results endorse the effective participation by the double bond in the spatial proximity of a denitrogenation site. Our findings also provide further impetus to unveil a new dimension in azoalkane chemistry as pioneered by Zimmerman[8] and Adam,[9] who demonstrated that deazetation of appropriate azoalkanes could be the source of an independent entry into the di-π-methane rearrangement.

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