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PHOTOLYSIS OF THE AZOALKANE 2,3-DIAZATRICYCLO[4.3.0.$0^{4,9}$]NON-2-ENE: DIRECT OBSERVATION OF 4-CYCLOHEXENYLDIAZOMETHANE

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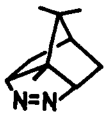
SUMMARY: Besides denitrogenation to the tricycloalkane 8, the photolysis of azoalkane 3 affords the diazoalkane 4, which serves as precursor to the minor hydrocarbon products 9, 10 and 11; irradiation of azoalkane 3 with the 333.6 nm line of an 18-W argon ion laser was essential to obtain preparative quantities of diazoalkane 4 for its detection and identification.

In a recent communication[1] we showed that some of the minor hydrocarbon products in the photolysis of azoalkane 1 were derived from the diazoalkane 2. Preparative laser photolysis was particularly helpful in the direct observation of diazoalkane 2 by means of IR and UV-VIS detection. It was, therefore, important to reinvestigate[2] the photolysis of the azoalkane 3 under laser irradiation in the specific interest of clarifying the origin of the minor hydrocarbon products. Indeed, during laser photolysis of azoalkane 3 the diazoalkane 4 is directly observed and on subsequent denitrogenation shown to afford the minor hydrocarbon products.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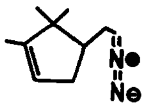
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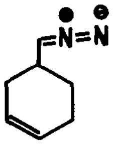
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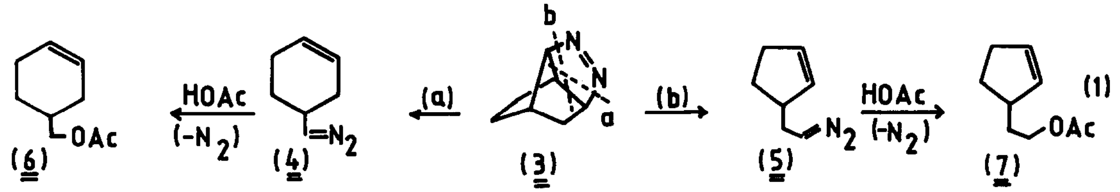
When a 0.14 M solution of azoalkane 3 in benzene was irradiated with the 333.6 nm-line of a COHERENT CS-18 argon ion laser for 15 min, a clear yellow solution resulted. Immediate recording of the IR spectrum revealed a strong band at 2060 cm^{-1} and of the UV-VIS spectrum an absorption at 465 nm. Both spectral observations are characteristic for diazoalkanes.

In view of the unsymmetrical structure of azoalkane 3, in principle two diazoalkanes are possible, namely 4 and 5 (Eq.1). To ascertain which of these two photo-fragmentations, i.e. via path (a) to give 4 or via path (b) to give 5 (Eq.1), was taking place, the photolysis



of azoalkane 3 was performed in the presence of acetic acid. The respective acetates 6 and 7 (Eq.1) should clear up the ambiguity of which of the diazoalkanes 4 and 5 is produced.

Photolysis of a 0.05 M solution of azoalkane 3 in benzene/acetic acid (10:1) at 350 nm in a Rayonet photoreactor gave only acetate 6 (6.3%), in addition to the tricycloalkane 8 (87.8%), diene 9 (3.9%) and the bicycloalkenes 10 (1.0%) and 11 (1.0%).[3] Product identification was achieved by comparison of retention times with the authentic materials using capillary GC.[4] For this purpose acetate 6 and diene 9 were prepared by the sequence shown in Eq.2.[5,6]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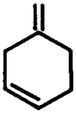
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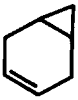
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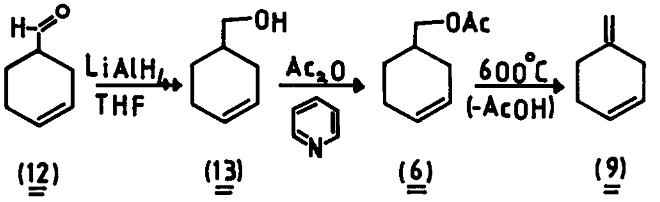
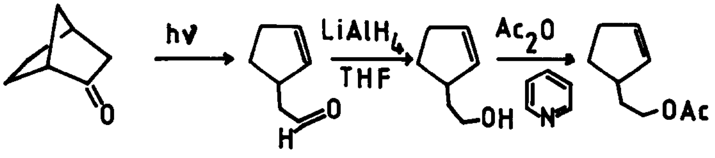


(2)

Authentic samples of bicycloalkenes 10 and 11 were obtained in the Bamford-Stevens decomposition of the tosylhydrazone of aldehyde 12.[6] In fact, a solution of authentic diazoalkane 4 in dimethoxyethane could be generated by thermolysis of the dry sodium salt of the tosylhydrazone of 12 at 80°C for 1 h under nitrogen. Photolysis of the authentic diazoalkane 4 at 350 nm in the Rayonet photoreactor gave the mixture of hydrocarbons 9 - 11 in the reported proportions.[6] Furthermore, except for the tricycloalkane 8 (major product), the photolysis mixture of azoalkane 3 matched well in composition that obtained from the photolysis of authentic diazoalkane 4.

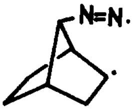
This data convincingly demonstrate that the photo-reversion of azoalkane 3 proceeds exclusively along path (a) to give diazoalkane 4 (Eq.1). To rule out rigorously photo-reversion to diazoalkane 5 via path (b), authentic acetate 7 was prepared via the sequence shown in Eq.3.[6,7] GC co-injection of the authentic acetate 7 established beyond doubt that not even traces of acetate 7 were formed.



(3)

(14) (15) (16) (7)

This regioselectivity on the photo-cycloreversion of azoalkane 3 is remarkable. Since this (4+2)-retrocyclic process is photochemically forbidden by the Woodward-Hoffmann rules, presumably the cycloreversion takes place stepwise via diradical intermediates. Of the possible diradicals 17 - 20 that can be formed by α- and β-cleavages of the n,π*-excited azoalkane 3, 17 and 19 can lead to diazoalkane 4, but 18 and 20 to diazoalkane 5. It is difficult to rationalize at this point which pair of these diradicals is preferred, except to note that in 17 and 19 the carbon-centered radical sites are contained in carbocyclic six-membered rings, but in 18 and 20 in five-membered rings. It is of interest to mention that triplet sensitization of azoalkane 1 with benzophenone gives only the tricycloalkane 8.



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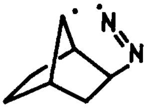

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(19)

(20)

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3. The percentages refer to relative yields, normalizing total volatile products to 100%, determined by capillary GC, using a 50-m column packed with OV-101 and operated at injector and detector temperatures of 170 and 175°C and a column temperature range of 70 - 150°C.

4. The diene **9** was previously[2] mistakenly assigned as bicyclo[3.2.0]hept-2-ene in view of their similar retention times. Capillary GC-MS provided the definitive proof that diene **9** rather than bicyclo[3.2.0]hept-2-ene was produced. In the 70 eV mass spectrum of the authentic diene **9** the base peak is m/e=79, while in that of bicyclo[3.2.0]hept-2-ene it is m/e=66.

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