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Carbenes in polycyclic systems. Generation and fate of pentacyclo[5.4.0.0^{2,6}.0^{3,10}.5^{5,9}]undecanylidene species

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Abstract—Pyrolysis of lithium or sodium salts of pentacyclo[5.4.0.0^{2,6}.0^{3,5}.0^{5,9}]undec-8,11-dione ditosylhydrazone **1** gave two products, 4,5-diazahexacyclo[6.4.1.0^{2,7}.0^{3,11}.0^{6,10}.0^{9,12}]tridec-4-ene **2** and tetracyclo[6.3.0.0^{4,11}.0^{5,9}]undeca-2,6-diene **3** in a 9:1 ratio. Azoalkane **2** proved to be extremely thermally and photochemically stable. This result supports the proposed mechanism of formation of **3**, which includes the generation of dicarbene species **6a**. © 2002 Elsevier Science Ltd. All rights reserved.

Carbenes are highly reactive intermediates that can undergo electronic rearrangements either by the conversion to a stable product or by formation of a secondary intermediate of lower energy content. Carbene reactions have been used extensively for the synthesis of various strained polycyclic compounds.[1] Intramolecular carbene cycloaddition to the olefinic bond was used as a very good method for the preparation of [4.1.1]-,[2] [3.1.1]-,[3] and [2.2.1]propellanes.[4] Similarly, bridgehead olefins can be formed from carbene intermediates,[5] although the bridgehead olefins with sufficient torsional strain are also capable of undergoing reversion to carbenes.[6]

Our current study in this area[7] has prompted our interest in investigating the possibility of the existence of two carbene centers in the same polycyclic molecule. In this communication we report the evidence for the formation of polycyclic cage mono- and dialkylidene species **4** and **6a**, respectively. Also we report the first synthesis and characterization of 4,5-diazahexacyclo [6.4.1.0^{2,7}.0^{3,11}.0^{6,10}.0^{9,12}]tridec-4-ene **2**.

Mono- **4** and dicarbene **6a** were generated by pyrolyses of the corresponding lithium or sodium salts **1**[8] (Scheme 1). Pyrolysis of the dry salts **1** was performed at 200°C and 10^{-4} Torr and the volatile products (60 mg) were collected in a liquid nitrogen cooled trap. GC-analysis of the crude product showed the presence of two compounds in a ratio of 1:9. Separation by column chromatography led to a 3% yield (4.5 mg) of a colorless highly volatile solid which was identified as tetracyclo[6.3.0.0$^{4.11}$.0^{5,9}]undeca-2,6-diene **3** by comparison of its ^{1}H and ^{13}C NMR spectra with the spectral data reported for this hydrocarbon.[10] The major component was isolated in 25% yield (42.0 mg) and identified as 4,5-diazahexacyclo[6.4.1.0^{2,7}.0^{3,11}.0^{6,10}.0^{9,12}]-tridec-4-ene **2**. The structural proof for **2** is based on its spectral data.[11] The ^{1}H NMR spectrum displayed two doublets at 0.86 and 1.22, and five broad singlets at 1.58, 1.81, 1.97, 2.22 and 5.35 ppm. The ^{13}C NMR spectrum unambiguously established the structure of **2**. The off-resonance decoupled spectrum showed one triplet at 37.4 and five doublets at 37.1, 43.2, 43.9, 44.1 and 71.9 ppm.

We assume that azoalkane **2** is formed by thermal decomposition of **1** and formation of diazo-carbene **4** followed by intramolecular azine formation as in **5b**. Polycyclic azine **5b** may easily dissociate to the respective diradical **5c** and/or form diaza[2.2.2]propellane **5a**, which then reacts further by abstraction of two hydrogen atoms from its environment, yielding the stable 4,5-diazahexacyclo[6.4.1.0^{2,7}.0^{3,11}.0^{6,10}.0^{9,12}]tridec-4-ene **2**. To our knowledge this is the first reported synthesis of **2**.

There are two possible reaction paths leading to olefin **3** as shown in Scheme 1. One path involves a concerted loss of nitrogen from the diaza compound **2** and the second path involves simultaneous formation of dicarbene species **6a** during the pyrolyses of lithium or sodium salt **1**.

Keywords: cage compounds; azoalkane; carbene; dicarbene.

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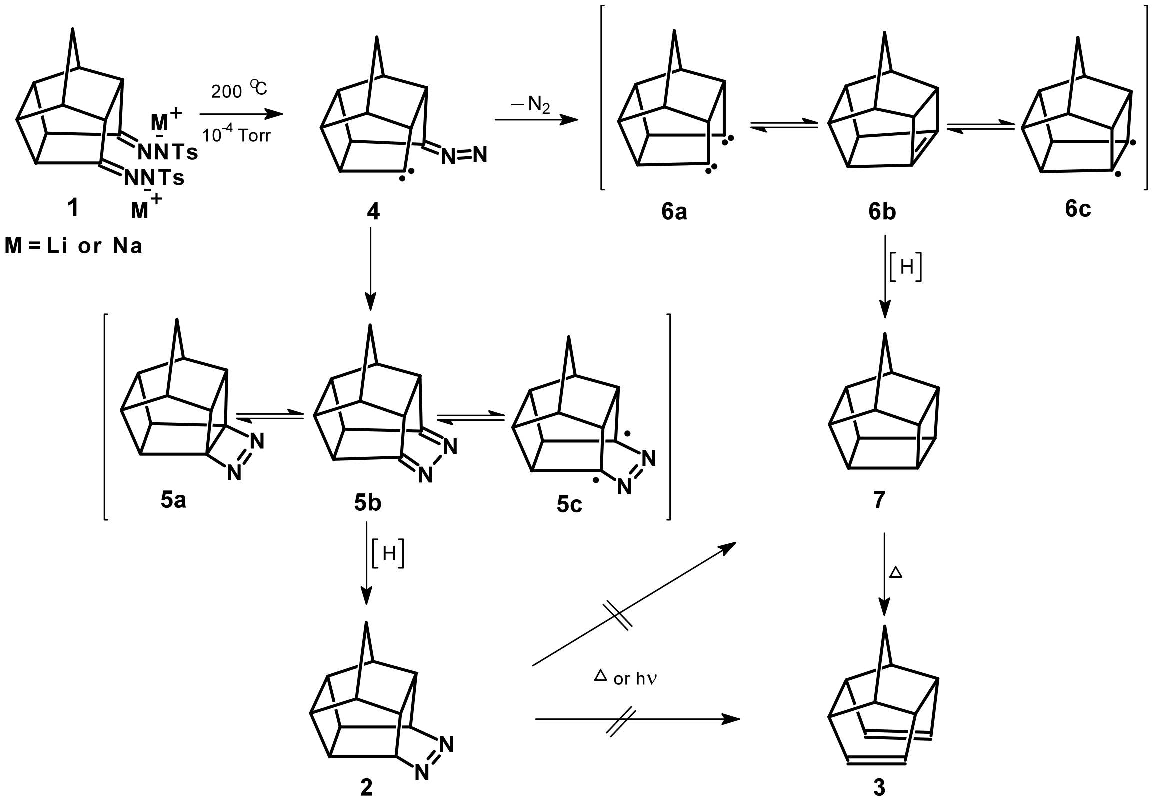

Scheme 1.

Thermal and photochemical eliminations of nitrogen are considered to be general reactions of cyclic azo compounds.[12,13] However, there are a number of examples in which the loss of nitrogen failed.[14] The extrusion of nitrogen failed also in the case of azoalkane **2** probably because **2** has a 2,3-diazabicyclo[2.2.2]oct-2-ene (DBO) unit, which is the most stable azoalkane,[15] incorporated in the polycyclic frame.

Azoalkane **2** was stable toward thermolysis in solution at 110°C. Also, it could be recovered, essentially unchanged, after (a) heating at 200°C and 10^{-4} Torr and (b) sublimation through a quartz tube at 320°C and 0.2 Torr. In addition, 4,5-diazahexacyclo[6.4.1.$0^{2,7}$.$0^{3,11}$.$0^{6,10}$.$0^{9,12}$]tridec-4-ene **2** is photostable. It was unchanged after irradiation in organic solvents (C_6D_6 or CD_3OD) at room temperature.[16]

The fact that azoalkane **2** is thermally stable even at much higher temperatures than the temperature at which pyrolysis of **1** was performed, suggests that the mechanism for formation of **3** involves generation of dicarbene **6a** which further reacts through H-abstraction followed by thermal [2+2] cycloreversion to give the observed product **3**.

One can raise the question whether **6** is electronically best described as the carbene **6a**. We are continuing to investigate the chemistry of **2** as well as the possibility of trapping the intermediate species **5** and **6**. Also, high-level quantum chemical calculations of carbene and transition state energies and geometries will be performed.

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8. (a) Pentacyclo[5.4.0.0^{2,6}.0^{3,5}.0^{5,9}]undec-8,11-dione[9] was converted into the corresponding ditosylhydrazone according to the our previously published procedure in 59% yield and then to the lithium or sodium salt **1** by reaction with Na[3c] or with LiOMe.[3a] (b) Spectral data of pentacyclo-[5.4.0.0^{2,6}.0^{3,5}.0^{5,9}]undec-8,11-dione tosylhydrazone: IR (KBr) 3293 (s), 2990 (m), 1330 (s), 1160 (s), 1092 (m), 816 (m), 550 (m) cm^{-1}; ^{1}H NMR (DMSO) δ: 1.11 (AB, $J_{AB}=10.31$ Hz, 1H), 1.42 (AB, $J_{AB}=10.31$ Hz, 1H), 1.96 (br s, 2H), 2.10 (br s, 2H), 2.37 (s, 6H), 2.45 (br s, 2H), 2.60 (br s, 2H), 7.38 (d, $J=7.65$ Hz, 4H), 7.73 (d, $J=7.65$ Hz, 4H), 9.41 (s, 2H); ^{13}C NMR (DMSO) δ: 21.2 (q, 2C), 36.5 (t, 1C), 40,0 (d, 2C), 41.5 (d, 2C), 44.2 (d, 2C), 46.4 (d, 2C), 95.2 (s, 2C), 127.9 (d, 4C), 129.4 (d, 4C), 136.6 (s, 2C), 142.8 (s, 2C); HRMS for $C_{25}H_{26}N_4S_2O_4$ calcd $[M_r+2H]^+$ 512.154651, found 512.154284.
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11. Spectral data of **2**: UV (CH_3OH) $\lambda_{max}=352.1$ nm ($\varepsilon=263$); IR (KBr) 2964 (s), 2868 (w), 1523 (m), 1302 (m) cm^{-1}; ^{1}H NMR (C_6D_6) δ: 0.86 (AB, $J_{AB}=10.4$ Hz, 1H), 1.22 (AB, $J_{AB}=10.4$ Hz, 1H), 1.58 (br s, 2H), 1.81 (br s, 2H), 1.97 (br s, 2H) 2.22 (br s, 2H), 5.35 (br s, 2H); ^{13}C NMR (C_6D_6) δ: 37.1 (d, 2C), 37.4 (t, 1C), 43.2 (d, 2C), 43.9 (d, 2C), 44.1 (d, 2C), 71.9 (d, 2C); HRMS for $C_{11}H_{12}N_2$ calcd $[M_r]^+$ 172.099499, found 172.099938.
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16. A benzene solution of azoalkane **2** was irradiated for 4 h at room temperature through a Pyrex filter with a 450 W mercury lamp. A solution of **2** in methanol was irradiated in a Ryonet reactor equipped with 350 nm lamps (16×24 W).