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2-Azanorbornadiene

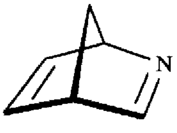
Michele Maggini, Maurizio Prato,* and Gianfranco Scorrano

Centro CNR Meccanismi di Reazioni Organiche, Dipartimento di Chimica Organica, Via
Marzolo 1, I-35131 Padova (Italy)

Abstract: *The unstable and hitherto unknown 2-azanorbornadiene 1, interesting example of imine-olefin homoconjugation, has been generated and spectroscopically characterized. Its instability is due to a retro-Diels-Alder reaction which generates cyclopentadiene and hydrogen cyanide.*

2-Azanorbornadiene **1** is the only aza-substituted norbornadiene where the nitrogen atom is fundamental part of the unsaturated system.[1,2] This structural modification results in a series of features which make this molecule of high interest for many reasons, first of all as a comparison with the parent norbornadiene **2**, an archetype of homoconjugative interactions.[3-5]

The transannular conjugation of the two π-bonds in norbornadiene has been the object of several theoretical calculations and has been experimentally supported by chemical,[6] photochemical[7] and UV spectroscopic[8] properties. On the other hand, the interaction between the C-C double bond and the carbonyl group in norbornenones has resulted in not readily predictable consequences.[3]



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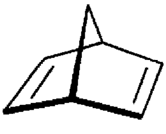

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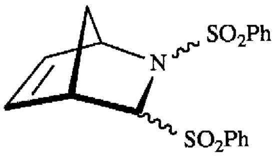
In this context, the unsubstituted 2-azanorbornadiene represents a unique example of imine-olefin homoconjugation. However, the synthesis of **1** has never been approached, although the preparation of few

3-substituted derivatives has been reported.[9,10] In this paper we wish to show that 2-azanorbornadiene **1** is an unstable species which can be generated in solution and characterized through spectroscopic and chemical means.

During our continuing studies on cycloaddition reactions of imines activated by strong electron-withdrawing groups,[11] we envisioned that the cyclopentadiene adduct **3** of the corresponding 1,2-disulfonyl imine[12] could be, by analogy with the full-carbon system,[13] a suitable precursor of **1**. However, treatment of **3** with 6% sodium amalgam in MeOH/aq NaH_2PO_4 buffer afforded only the C-desulfonylated material **4**. This unexpected result prompted us to investigate the reactivity of 3-tosyl-2-azanorbornadiene[9] **5**



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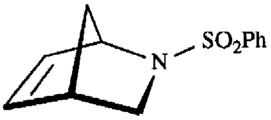

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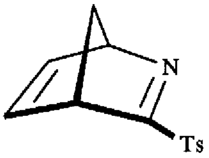

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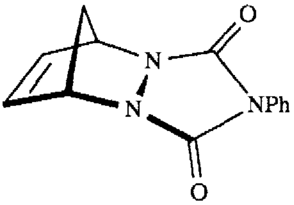
with Na/Hg (4%). The reaction was carried out under sonication at 0°C in perdeuterauted tetrahydrofuran (other solvents gave much poorer results). After 15 minutes the mixture was filtered through celite. The ^1H-NMR of the filtrate showed a set of signals which could clearly be assigned to structure **1** as the main component (200 MHz, TMS): azomethine proton as a doublet at δ 8.48 (J = 1.20 Hz), vinylic protons at δ 6.77 (ddd, J = 4.97, 2.84, and 0.71 Hz) and 6.60 (ddd, J = 4.97, 3.19, and 1.42 Hz), bridgehead protons as multiplets at δ 5.10 (H-1) and 3.93 (H-4) and methano-bridged protons as doublets of triplets at δ 1.89 (J = 6.74 and 1.77 Hz) and 1.75 (J = 6.74 and 1.06 Hz). ^{13}C-NMR (THF-d_8) exhibited the correct number of carbon atoms with signals at δ 177.70 (C=N), 142.81 and 139.74 (C-5 and C-6), 75.13 (C-7), 72.69 (C-1) and 56.34 (C-4). IR (THF-d_8) showed C=N stretching at 1647 cm^{-1}. A UV band at 232 nm in THF-d_8 could be detected although a calculation of ϵ was not possible. When the desulfonylation reaction was carried out in THF-d_8 in the presence of excess D_2O, the intensity of the azomethine proton signal in the ^1H-NMR spectrum of the mixture sharply decreased, with no change in the other patterns.

All attempts to isolate any product from this reaction failed. Evaporation of THF in the cold and take up of the residue with a solvent ($CDCl_3$, benzene-d_6, etc) resulted in the formation of intractable tars.

2-Azanorbornadiene is in fact a rather unstable compound which decomposes in THF-d_8 at 25 °C with a half-life of about 30 minutes.[14] A retro-Diels-Alder reaction occurs, with formation of cyclopentadiene (observable by ^{1}H-NMR spectroscopy) and hydrogen cyanide. Once formed, the latter probably causes polymerization of the remaining **1**. Addition of a strong dienophile (4-phenyl-1,2,4-triazolin-3,5-dione, PTAD) accelerates the retro Diels-Alder process with instantaneous quantitative formation of the cycloadduct **6**.[15] On the other hand, hydrogen cyanide could be trapped as silver cyanide by bubbling nitrogen through the solution containing **1** and collecting the stream into a 4M aqueous nitric acid solution of $AgNO_3$. The white solid which precipitated was filtered and analyzed by IR (KBr, 2137 cm^{-1}, lit[16], aq. soln., 2135).



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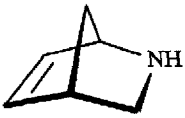

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Treatment of the THF solution of **1** with $LiAlH_4$ at 0°C afforded the 2-azanorbornene **7** in 48% yield (from 3-tosyl derivative), which was identical with an authentic sample prepared according to the reported procedure.[10] Irradiation of the THF-d_8 solution of **1** at 0°C with a 100 W high-pressure mercury lamp with pyrex filter gave only insoluble polymeric materials. No stable metal complex could be obtained by adding Pt or Rh complexes to a THF solution of **1**. No reaction but only decomposition was observed on addition of 1,3-dienes or 1,3-dipolar reagents.

The spectroscopic investigations on **1** do not allow, so far, any speculation on possible interactions between the C=C and C=N bonds. In fact, whereas the UV band is typical of isolated C=N bonds,[17] the IR measurement might be indicative of some conjugation[18] (although IR and UV of these systems have not previously been reported; moreover, THF-d_8 is not a common solvent for comparing data). Further studies on the extent of homoconjugation between the two double bonds are underway.

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