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Ring Contraction of a Two-Carbon Bridged Spiropentane

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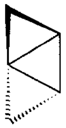
Abstract: The diazoketone derived from tricyclo[4.1.0.0^{1,3}]heptan-4-one on photolysis in dimethylamine leads to a novel product that appears to be formed via a cyclopropylcarbene rearrangement followed by dimethylamine addition and the cleavage of one of the cyclobutane rings. In a matrix at 15K, photolysis led to the loss of the 2085 cm^{-1} diazo band and the formation of a new band at 2117 cm^{-1} which is characteristic of a small ring ketene such as cyclopropylketene.

We have been interested in the structures and properties of spiropentanes bridged by 0, 1, 2 and 3 carbons (**1-4**). These compounds lead to marked distortions of the spiropentane unit, with the smaller bridges tending to bend the two rings toward each other and to twist the three membered rings toward planarity.[2] Compounds with two carbon bridges (**3**) are readily obtained by the intramolecular carbene addition developed by Skattebøl.[3] We have reported the synthesis of **1**, and have found it to exist for only a short time at -55° C before it is transformed into cyclopentadiene.[4] Compounds with three carbon bridges (**4**) may be obtained via the facile ring expansion of the two carbon bridged ketone (**5**).[5] There has, however, not been a report of the formation of the one-carbon bridged system, **2**.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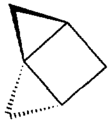
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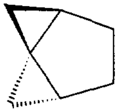
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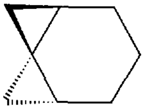
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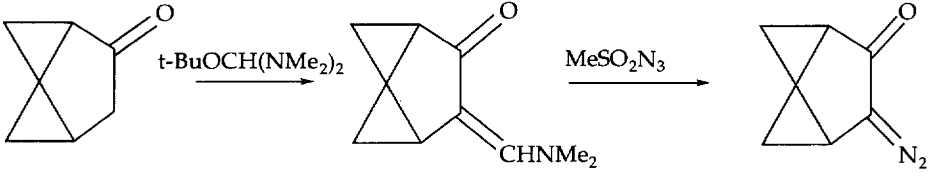
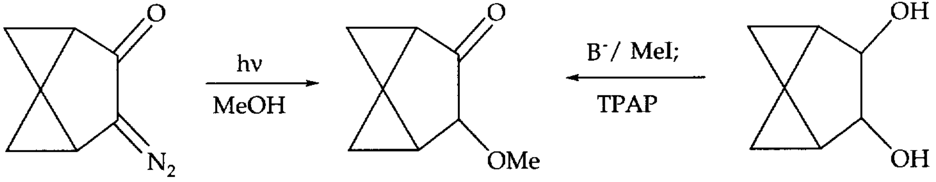
The most common method for ring contraction is the photochemical Wolff rearrangement of α-diazoketones.[6] It is known that the reaction is successful for cases where the ring strain increases by 35 kcal/mol or less. The strain energies of **1-4** have been estimated using MP2/6-31G* calculations,[7] and they are 137, 116, 79, and 66 kcal/mol respectively. The increase in strain on going from **3** to **2** is then 37 kcal/mol, at the upper end of the range of applicability.

It is possible to convert the ketone, **5**, into its enaminoketone (**6**) via its reaction with Bredereck's reagent.[8] The reaction of **6** with tosyl azide gave only a small yield of the diazoketone, **7**. However, the use of methanesulfonyl azide[9] led to a more satisfactory reaction, and gave **7** in a 35% yield. The diazoketone was quite stable, and could be purified via chromatography over silica gel using 1:1 pentane-ether containing 1.5% triethylamine.



5 **6** **7**

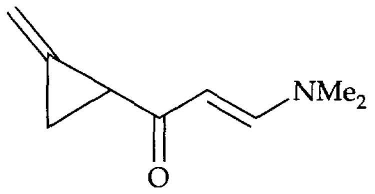
Photolysis of the diazoketone in methanol gave only the methoxyketone, **8**. It was identified by comparison with an authentic sample prepared from the diol, **9**, by methylation using sodium bis(trimethylsilyl)amide and methyl iodide and oxidation with TPAP.[10]



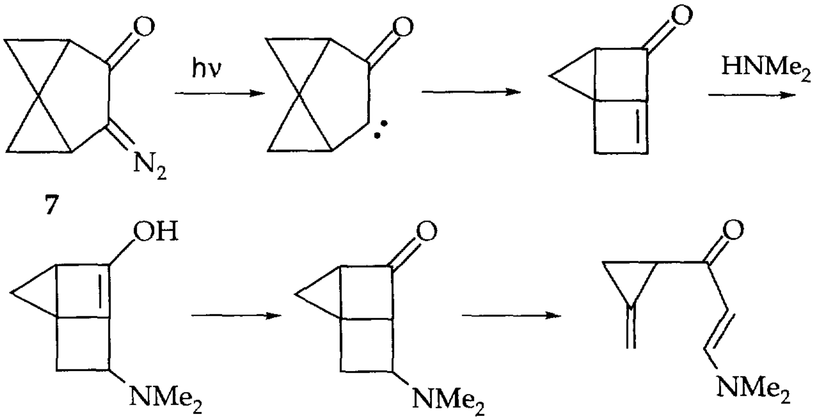
7 **8** **9**

The diazoketone is quite stable in methanol, and it is likely that the excited state of the diazoketone is sufficiently basic to abstract a proton from methanol, leading to a diazonium ion which can form the observed product.[11] A similar observation was made by Eaton and Temme in their studies leading to a [2.2.2]propellane derivative.[12]

In order to minimize proton transfer, the photolysis was carried out in dimethylamine at 0°C. After the excess amine had been allowed to evaporate, the remaining product had a mass (151) corresponding to the loss of nitrogen from **7** and the addition of the elements of dimethylamine. The ^{1}H NMR spectrum had bands at δ 1.55 (1H, t of t), 1.80 (1H, m), 2.43 (1H, m), 2.83 (N-Me, broad), 3.05 (N-Me, broad), 5.05 (1H, d, J=12.6 Hz), 5.45 (2H, d of t), 7.58 (1H, d, J=12.6 Hz) and the ^{13}C NMR spectrum had bands at δ 11.7 (t), 25.7 (d), 38 (N-Me), 45 (N-Me), 94.1 (d), 103.2 (t), 133.7 (s), 152.5 (d), 194.5(s). The IR spectrum had a carbonyl band at 1658 cm^{-1} and another strong band at 1579 cm^{-1}. These data are not compatible with the expected ring contracted N,N-dimethylamide. Decoupling studies indicated that the product had the structure:



It might be formed as follows: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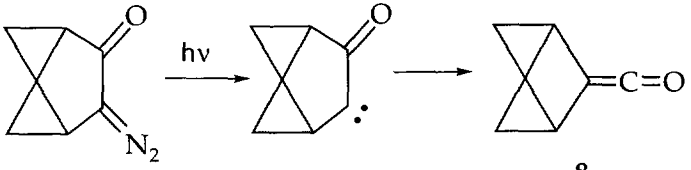
where the rearrangement of the intermediate carbene corresponds to the well known rearrangement of a cyclopropylcarbene to a cyclobutene.[13]

In order to gain further information on the reaction, the photolysis was carried out in a nujol matrix at 15 K using a 1000 w xenon arc lamp. As a test of the photolysis conditions, the diazoketone derived from bicyclo[3.1.0]hexan-2-one was first examined. This diazoketone undergoes the Wolff rearrangement in methanol to give the expected methyl ester, indicating that the ketene is an intermediate. In the matrix photolysis, the diazo band at 2140 cm^{-1} decreased in intensity and a new band at 2050 cm^{-1} appeared. The latter is at the normal position for a cyclopropylketene.[14] The photolysis of 7 under the same conditions gave the corresponding result: a decrease in the diazo band at 2085 cm^{-1}, with the formation of a new band at 2117 cm^{-1}. The latter agrees with a HF/6-31G* frequency calculation which predicted the ketene band of 8 to be at 2103 cm^{-1}. Thus, it appears that under matrix isolation conditions, 7 does undergo the normal Wolff rearrangement.


7 8

The difference in behavior of 7 between solution and low temperature matrix photolysis is interesting and will receive continued study. One of several possibilities is that the ketocarbene forms an ylid with dimethylamine and this changes the course of the reaction. It is known that carbenes react with amines such a pyridine to form relatively stable ylides.[15]

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