Synthesis of Alkynes from Bi-3*H*-diazirin-3-yls: Trapping of Strained Cycloalkynes

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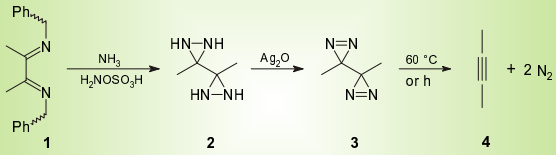
Diazirines are in general more difficult to synthesize than their diazo isomers.[1] The strain of the small ring along with the potential for splitting of molecular nitrogen make these heterocycles highly reactive toward loss of nitrogen on thermal or photoexcitation. In this study, alkynes are produced and trapped nearly quantitatively by a new method utilizing bidiazirinyls as precursors. This method can also be transferred to strained cycloalkynes. Their transient existence[2] and generation using different precursors and trapping reagents had been provided.[3,4]

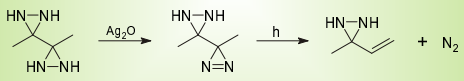
Compound **4** could be generated quantitatively by photolysis or thermolysis of bi-3*H*-diazirin-3-yl **3**. The precursor **3** was synthesized by oxidation of the corresponding diaziridine **2** which was prepared from diimine **1**.



1 **2** **3** **4**

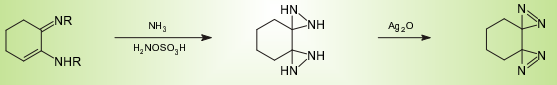
We assume, that **2** exists in solution in the *meso* and *racemic* forms because the protons on both nitrogen atoms of one ring are in *trans* position to each other, which is the normal result of nitrogen configuration in diaziridines.[5] Thus, compound **2** exhibits two sets of the NMR signals of the two diastereomers (ca. 10:1) whereas only one set is obtained for **3** (^{1}H, ^{13}C, ^{15}N NMR).

Diaziridine **2** can also be partially oxidized by silver oxide to give compound **5** in 36% yield. This partially oxidized compound undergoes photolysis to give **6** through 1,2-hydrogen migration after the formation of a carbene. The spectral data of **5** (four ^{13}C NMR signals) confirm the structure of **2** and exclude other possible structures.



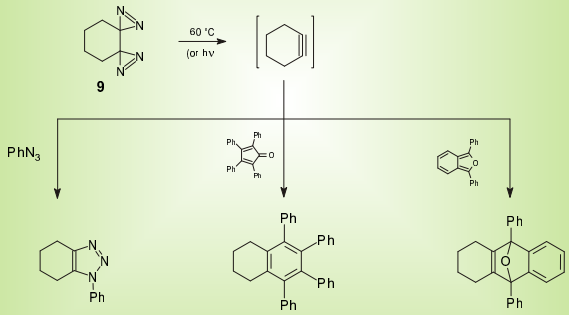
2 **5** **6**

Compound **9** was prepared by oxidation of the corresponding precursor **8**, which was generated from the diimine derivative **7**[6] existing mainly in the imine-enamine form.



7 **a** R=CHMe$_2$
b R=PhCH$_2$ **8** **9**

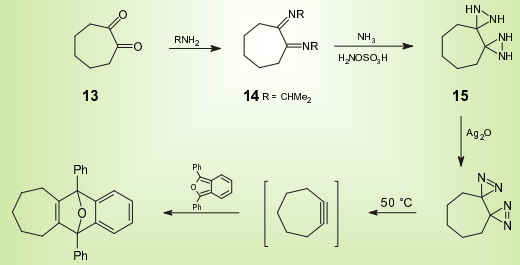
The heterocycle **9** undergoes thermolysis or photolysis to generate cyclohexyne. This strained cycloalkyne was trapped nearly quantitatively using different reagents such as phenyl azide, tetraphenylcyclopentadienone, and 1,3-diphenylisobenzofuran to give **10**, **11**, and **12**, respectively.



9 **10** **11** **12**

Compound **16** was prepared by oxidation of the corresponding precursor **15**, which was generated from the diimine derivative **14**. Compound **14** was synthesized from cycloheptan-1,2-dione **13**[7].

The heterocycle **16** undergoes thermolysis at 50 °C with splitting of molecular nitrogen to produce cycloheptyne **17**. The formation of this strained cycloalkyne is clearly demonstrated by a trapping experiment with 1,3-diphenylisobenzofuran to give the Diels-Alder product **18**.



13 **14** R = CHMe$_2$ **15**

18 **17** **16**

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