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The Reaction of [1.1.1]Propellane with Methylene

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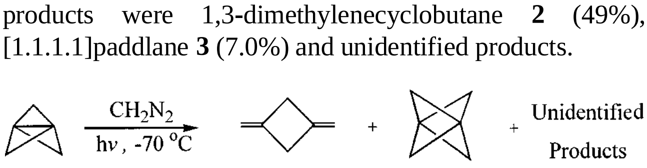
The chemistry of [1.1.1]propellane has received significant attention during the last few years.[1-4] [1.1.1]Propellane has an unusual structure with inverted geometry of the bridgehead carbon atom,[5,6(a)] and mainly reacts with electrophiles.[6-9] Especially, the reactions with carbenes are of considerable interest. In recent communications,[10,11] we have reported the reaction of [1.1.1]propellane with carbenoid and singlet dihalocarbenes. Here we wish to report our results on the addition of methylene to [1.1.1]propellane.

We have examined the direct photolysis of [1.1.1]propellane with diazomethane. [1.1.1]Propellane was prepared from 1,1-dihalo-2,2-bis(cyclomethyl)cyclopropane and methyllithium as described previously.[8] A solution of [1.1.1]propellane **1** (1.59 g, 24.0 mmol) and diazomethane[9] (1.26 g, 30.0 mmol) in dry diethyl ether was purged with nitrogen and irradiated through Pyrex filter for 20 minutes with a medium pressure mercury lamp at -70 °C. The solvent was removed and the residue was purified by preparative GC and characterized by GC/MS and NMR spectra. The observed products were 1,3-dimethylenecyclobutane **2** (49%), [1.1.1.1]paddlane **3** (7.0%) and unidentified products.



1 **2** **3**

[1.1.1.1]Paddlane is a new compound and a truly remarkable carbocyclic four-membered ring compound that has a highly symmetrical structure with D_4h point group. In 1874, Le Bel and Van't Hoff proposed that the carbon atom was at the center of regular tetrahedron, the bonds being directed towards the corners. The intervalency angles thus defined are 109.28°, which is comparable to those measured in saturated hydrocarbons (*Le Bel model*).[12] [1.1.1.1]Paddlane is an unusual model of distortion at the bridgehead carbons by a pyramid folding operation, which is a good example of *anti Le Bel model*. All four groups attached to the bridgehead carbon atoms of [1.1.1.1]paddlane are placed on one side of a plane. It shows a perfect inverted tetrahedral geometry. The carbocyclic compounds with four-membered rings are in any case highly strained and are often unstable, whereas [1.1.1.1]paddlane is a slightly stable compound. In this work, we found that [1.1.1.1]paddlane is a stable compound that could be stored in a refrigerator for several months if shielded from light. The structure of **3** has four carbon atoms of CH_2 group that are equivalent in symmetry and two central carbon atoms that are equivalent in symmetry. The detailed properties of [1.1.1.1]paddlane are currently under investigation.

In a recent paper,[11] we have suggested that [1.1.1.1]paddlane derivatives would be formed as the intermediate from the reaction of [1.1.1]propellane with singlet dihalocarbenes.[14] It is expected that [1.1.1.1]paddlane is thermally far more stable than [1.1.1.1]paddlane derivatives. This might be attributable to the higher strain energy of [1.1.1.1]paddlane derivatives due to the steric effect by bulky halogen atoms. In our work, we found that [1.1.1.1]paddlane derivatives were quickly converted into other products, whereas decomposition of [1.1.1.1]paddlane was slow.

Formation of [1.1.1.1]paddlane was identified by GC/MS spectrum and various NMR spectra; GC/MS m/e (rel. intensity) 80 (M^+, 100), 79 (64), 76 (26), 73 (8), 66 (3), 53 (6); ^1H NMR (600 MHz, C_6D_6) δ 1.79 (s, 8H); ^{13}C NMR (150.9 MHz, C_6D_6, rel. intensity) δ 66.6 (CH_2, 2.0), -3.16 (quaternary carbon, 1.0); DEPT-NMR (150.9 MHz, C_6D_6) δ 66.6 (CH_2). We have also identified by the HMBC spectrum as shown in Figure 1. The ^{13}C NMR spectrum without ^1H decoupling of **3** showed a triplet at δ 66.6 ppm corresponding to the direct coupling between ^{13}C and ^1H with J_{CH} = 152.6 Hz. This spectrum showed also a multiplet at δ -3.14

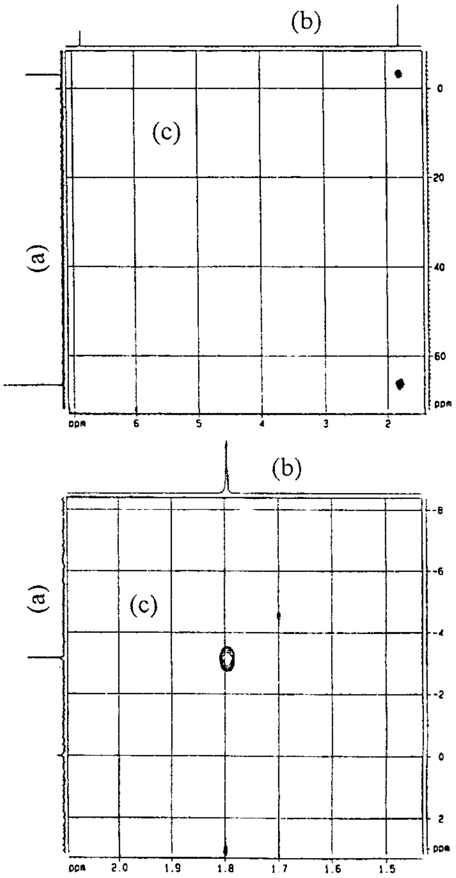


Figure 1. HMBC spectrum of [1.1.1.1]paddlane **3** in C_6D_6. (a) ^{13}C spectrum, (b) ^1H spectrum, (c) ^{13}C-^1H 2D-Correlated spectrum.

ppm corresponding to the geminal coupling between the central carbon atom and the adjacent CH_2 group with J_{CH} = 4.39 Hz. In addition, this spectrum showed a septet at δ 67.7, 66.6, 65.59, respectively. These peaks correspond to the long range coupling between the carbon atom of CH_2 group and protons of the adjacent CH_2 group with J_{CH} = 6.76 Hz. The quantitative analysis of ^{13}C NMR spectrum showed also an exact ratio (rel. intensity = 2 : 1) between four carbon atoms of the equivalent CH_2 group and the equivalent two central carbon atoms.

We found that under proper conditions, 1,3-dimethylenecyclobutane **2** can be obtained in a synthetically useful way by the reaction of [1.1.1]propellane with diazomethane. 1,3-Dimethylenecyclobutane **2** had been synthesized previously by F. F. Caserio and co-workers.[13] The early method was complex and used too many reagents and took a longer time. However, our method takes short reaction time and is simple. Although yield (three steps, 37% overall yield) has not significantly increased, it is more simple and efficient than the earlier synthesis (six steps, 35% overall yield). This product was separated by preparative GC and characterized by GC/MS, ^1H NMR, and ^{13}C NMR; GC/MS m/e (rel. intensity) 80 (M^+, 32), 79 (100), 76 (30), 52 (17), 39 (55); ^1H NMR ($CDCl_3$) δ 3.46 (quintet, 4H), 5.03 (quintet, 4H); ^{13}C NMR ($CDCl_3$) δ 40.95 (CH_2), 106.6 (CH_2), 143.9.

In summary, we have obtained the highly symmetrical [1.1.1.1]paddlane by the reaction of [1.1.1]propellane with singlet methylene that were prepared from photolysis of diazomethane. We have also developed a more simple and efficient method than the earlier synthesis for preparation of 1,3-dimethylenecyclobutane **2**.

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