PHOTOLYSIS OF [1.1.1]PROPELLANE : SYNTHESIS OF NEW COMPOUNDS AND MECHANISTIC STUDY

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Abstract – The reaction of [1.1.1]propellane with singlet methylene afforded 1,3-dimethylenecyclobutane and [1.1.1.1]paddlane (**3**). Various minor products were also produced. The reaction of [1.1.1]propellane with triplet methylene afforded 1,3-dimethylenecyclobutane (**2**) and various minor products. But even trace of [1.1.1.1]paddlane was not detected. The mechanism for the addition of singlet methylene involved [1.1.1.1]paddlane intermediate. The addition of triplet methylene led to diradical intermediate. In order to reveal the reaction pathway for generation of various minor products, various studies were carried out under the same condition.

INTRODUCTION

While carbene transfer reactions to hydrocarbons, such as cyclopropanation and insertion, have been widely investigated,[1] carbene transfer reactions to strained cycloalkane compounds have not been extensively investigated.[2,3] Recently we have reported the reaction of [1.1.1]propellane with various carbenes.[4,5,6] [1.1.1]Propellane has been of great concern as an example of a highly strained symmetric compound.[7,8,9] Also in a bicyclo[1.1.0]butane[2,9,11] and [1.1.1]-propellane are found that central bonds are formed from orbital with high *p* character. The nature of the central bond in **1** has been extensively investigated.[9] The charge density at the middle point of the bond is more spread out than the normal C-C bond of hydrocarbon. The charge distribution was also a high charge density near the bridgehead carbons. The central bridgehead bond distance was reported to be about 1.602 Å with hybridization of $sp^{4.1}$. The bridgehead carbon atoms of **1** have an inverted tetrahedral structure, which is an example of the *anti* Le Bel model. In a previous paper, we have reported the synthesis of a novel product, [1.1.1.1]paddlane **3**, from the reaction of [1.1.1]propellane with diazomethane.[6] This product **3** is a new compound and an usual model of distortion at the bridgehead carbons that shows a perfect inverted tetrahedral geometry. It is a good example of the *anti* Le Bel model. The aim of the current work was to attempt a novel approach for a mechanistic study of products.

In this paper, we have described the addition of methylene to [1.1.1]propellane, and the reaction pathway for generation of various products is discussed.

MATERIALS AND METHODS

General This reaction was carried out in dilute solution at a low temperature (-70°C) in order to avoid polymerization of [1.1.1]propellane. Benzophenone was employed as the sensitizing agent. [1.1.1]Propellane was prepared from 1,1-dihalo-2,2-bis(cyclo-methyl)cyclopropane and methyllithium as described.[8] Diazomethane was prepared from N,N'-nitrosomethylurea and potassium hydroxide in ether as described.[10] ^1H and ^{13}C-NMR spectra were recorded at 300 and 500 MHz on a Varian unity plux spectrometer, GC-Mass were obtained on a HP 5890 series II spectrometer and preparative GC separation was carried out in a Gow-Mac instrument with TCD detector and provided with a 5 ft packed column of 15 % OV101. Product yields were determined by analytical GC with bromoform as an internal standard and predetermined response factor for the products.

Direct photolysis of [1.1.1]propellane with diazomethane A solution of [1.1.1]propellane **1** (1.59g, 24.0mmol) and diazomethane (1.26g, 30.0mmol) in a dry diethyl ether were purged with nitrogen and irradiated through Pyrex filter with a medium pressure mercury lamp at -70°C. After 20 minutes, the photolysis was stopped and the solvent was removed under reduced pressure. The residue was purified by preparative GC and characterized by GC/MS and various NMR spectra. The observed products were 1,3-dimethylenecyclobutane **2**,

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[1.1.1.1]paddlane **3**, 1-bromo-3-methylbicyclo-[1.1.1]pentane **4**, 1-iodo-3-methylbicyclo[1.1.1]pentane **5**, 1,3-dimethylbicyclo[1.1.1]pentane **6**, 1-methylbicyclo[1.1.1]pentane **7**, and 1-iodo-1-methyl-3-methylenecyclobutane **8**.

Benzophenone-sensitized photolysis of [1.1.1]propellane with diazomethane A mixture of [1.1.1]propellane **1** (1.59 g, 24.0 mmol), diazomethane (1.26g, 30.0 mmol) and benzophenone in a dry diethyl ether were placed in an immersion well and degassed by nitrogen bubbling through it for 0.1 h. The solution was photolyzed with a medium pressure mercury arc lamp, using a Pyrex filter at -70°C. After 20 minutes, the photolysis was stopped and the solvent was removed under reduced pressure. The residue was purified by preparative GC and characterized by GC/MS and various NMR spectra. The observed products were 1,3-dimethylenecyclobutane **2**, 1-bromo-3-methylbicyclo[1.1.1]pentane **4**, 1-iodo-3-methylbicyclo[1.1.1] pentane **5**, 1,3-dimethylbicyclo[1.1.1]pentane **6**, methylbicyclo[1.1.1]pentane **7** and 1-iodo-1-methyl-3-methylenecyclo-butane **8**.

Photolysis of solvent-free [1.1.1]propellane with diazomethane Solvent-free [1.1.1]propellane was prepared by the reaction of 1,3-diiodobicyclo[1.1.1]pentane with sodium cyanide in DMSO.[13] A solution of [1.1.1]propellane (0.80 g, 12.0mmol) and diazomethane (0.63 g, 15.0 mmol) in a dry diethyl ether were purged with nitrogen and irradiated through Pyrex filter with a medium pressure mercury lamp at -70°C. After 20 minutes, the photolysis was stopped and the solvent was removed under reduced pressure. The products were identified by GC/MS. The observed products were 1,3-dimethylenecyclobutane **2** and [1.1.1.1]paddlane **3**.

Photolysis of [1.1.1]propellane with iodomethane A solution of [1.1.1]propellane **1** (1.59 g, 24.0 mmol) and 4.26 g (30.0 mmol) of iodomethane in a dry diethyl ether were purged with nitrogen and irradiated through Pyrex filter with a medium pressure mercury lamp at -70°C. After 20 minutes, the photolysis was stopped and the solvent was removed under reduced pressure. The products were identified by GC/MS. The observed products were 1-iodo-3-methylbicyclo[1.1.1]pentane **5**, 1,3-dimethylbicyclo[1.1.1]pentane **6**, 1-methylbicyclo[1.1.1]pentane **7** and 1-iodo-1-methyl-3-methylenecyclobutane **8**.

Data for 1,3-dimethylenecyclobutane 2 GC/MS m/e (rel. intensity) 80 (M⁺, 32), 79 (100), 76 (30), 52 (17), 39 (55); ¹H-NMR (CDCl₃) δ 3.46 (quintet, 4H), 5.03 (quintet, 4H); ¹³C-NMR (CDCl₃) δ 40.95 (CH₂), 106.6 (CH₂), 143.9 (C)

Data for [1.1.1.1]paddlane 3 GC/MS m/e (rel. intensity) 80 (M⁺, 100), 79 (64), 76 (26), 73 (8), 66 (3), 53 (6) ; ¹H-NMR (C6D6) δ1.79 (s, 8H); DEPT-NMR (C₆D₆) δ 66.6 (CH₂) ; ¹³C-NMR11 (C₆D₆, rel. intensity) δ 66.6 (CH₂, 2.07), -3.16 (quaternary carbon, 1.0)

Data for 1-bromo-3-methylbicyclo[1.1.1]pentane 4 GC/MS m/e (rel. intensity) 162 (M⁺², 20), 160 (M⁺, 20), 81 (100), 66 (15), 53 (55)

Data for 1-iodo-3-methylbicyclo[1.1.1]pentane 5 GC/MS m/e (rel. intensity) 208 (M⁺, 17), 193 (M-CH₃, 4), 168 (9), 127 (35),

81 (M-I, 100), 79 (80), 66 (9), 53 (39); ¹H-NMR (CDCl₃) δ1.19 (s, 3H), 2.17 (s, 6H); ¹³C-NMR (CDCl₃) δ6.70, 18.76 (CH₃), 44.76, 62.19 (CH₂)

Data for 1,3-dimethylbicyclo[1.1.1]pentane 6 GC/MS m/e (rel. intensity) 96 (M⁺, 13), 95 (20), 81 (M-CH3, 100), 67 (53), 55 (88); ¹H-NMR (CDCl₃) δ 1.10 (s, 6H), 2.10 (s, 6H)

*Data for 1-methylbicyclo[1.1.1]pentane 7* GC/MS m/e (rel. intensity) 82 (8), 81 (100), 79 (52), 67 (5), 53 (28), 39 (28), 27 (4); ¹H-NMR (CDCl₃) δ 1.2 (s, 3H), 2.2 (s, 6H), 2.7 (s, 1H)

Data for 1-iodo-1-methyl-3-methylenecyclobutane 8 ¹H-NMR (CDCl₃) δ 2.15 (m, 1H), 2.20 (d, 3H), 3.1 (m, 2H), 3.6 (m, 2H), 5.0 (quintet, 2H); ¹³C-NMR (CDCl₃) δ 29.71, 36.97 (CH₃), 54.95 (CH₂), 108.4 (CH₂), 144.0

RESULTS AND DISCUSSION

The reaction of [1.1.1]propellane with singlet methylene generated by direct irradiation using medium pressure mercury arc lamp afforded 1,3-dimethylenecyclobutane **2** (49%) as the major product and [1.1.1.1]paddlane **3** (7.0%) as the minor product. Various other products were also produced: 1-bromo-3-methylbicyclo-[1.1.1]pentane **4** (<1%), 1-iodo-3-methylbicyclo[1.1.1]pentane **5** (9%), 1,3-dimethylbi-cyclo [1.1.1]pentane **6** (<2%), 1-methylbicyclo[1.1.1]pentane **7** (3%), and 1-iodo-1-methyl-3-methylenecyclobutane **8** (4.5%).

The reaction of [1.1.1]propellane with triplet methylene which is generated by the sensitized reaction afforded 1,3-dimethylenecyclo-butane **2** (55%) as the major product and various other products were also produced: 1-bromo-3-methylbicyclo[1.1.1]pentane **4** (<1%), 1-iodo-3-methylbicyclo[1.1.1]pentane **5** (10%), 1,3-dimethylbicyclo[1.1.1]-pentane **6** (<2%), 1-methylbicyclo[1.1.1]pentane **7** (5%), and 1-iodo-1-methylmethylenecyclobutane 8 (4%). However, no trace of [1.1.1.1]paddlane was detected in this reaction. As illustrated in Scheme 1, two different reaction pathways can explain this result. Scheme 1 suggests that the mechanism for the addition of singlet methylene involved [1.1.1.1]paddlane intermediate followed by ring opening leading to 1,3-dimethylenecyclobutane **2**. The formation of [1.1.1.1]paddlane strongly indicates that the concerted addi-
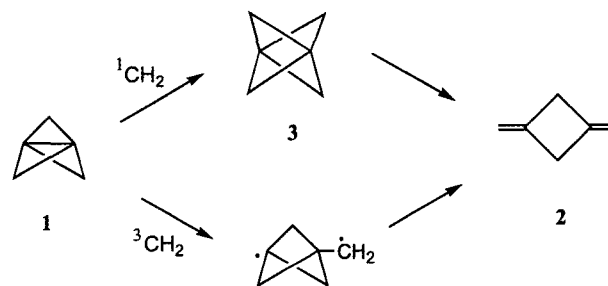
Scheme 1. Proposed mechanism for the reaction of [1.1.1]propellane with methylene.

tion of the methylene across the central bond of [1.1.1]propellane. [1.1.1.1]paddlane has a high strain energy. Therefore, ring opening takes place and that leads to **2**.

The same product **2** also formed by the triplet methylene addition. However, [1.1.1.1]paddlane was not obtained. This result can be explained by the diradical intermediate. The addition of triplet methylene lead to diradical intermediate that has a faster rearrangement followed by **2** through ring opening. Support for a diradical intermediate was provided in an elegant paper by previous workers.[2]

In order to reveal the reaction pathway for generation of various minor products, the following studies were carried out. The photolysis of diazomethane with solvent free [1.1.1]propellane was carried out under the same reaction condition. Solvent free [1.1.1]propellane was prepared from 1,3-diiodobicyclic[1.1.1]pentane and sodium cyanide in DMSO.[10] This compound did not involve methyl iodide and methyl bromide that is generated during the preparation of [1.1.1]propellane. This reaction lead to 1,3-dimethylenecyclobutane **2** (60 %) as the major product and [1.1.1.1]paddlane **3** (10 %) as the minor product with no other minor products. However, when the reaction of [1.1.1]propellane with methyl iodide was carried out under the same reaction condition, various minor products were detected by GC and GC/MS. These results show that these minor products were generated from the reaction of [1.1.1]propellane with methyl halide that is generated during the preparation of [1.1.1]propellane.

As suggested in Scheme 2, the reaction pathway for generation of various minor products is believed to proceed via radical intermediate. [1.1.1]Propellane is converted by methyl radical into radical intermediate **I**, which is then allowed to react with a free radical such as iodine, methyl, hydrogen to form 1-iodo-3-methylbicyclo- [1.1.1]pentane **5**, 1,3-dimethyl-bicyclo[1.1.1]pentane **6** and 1-methylbicyclo[1.1.1]pentane **7**, respectively.

Also ring opening of radical intermediate **I** takes place and that leads to intermediate **II** which is converted by hydrogen into 1-iodo-1-methyl-3-methylenecyclobutane **8**. Products **5**, **7** and **8** were separated by preparative GC and characterized by GC-Mass, ^{1}H NMR and ^{13}C NMR spectra. A minor product **4** was also present. The amount of this product was too small to be isolated; it was identified only by GC/MS.

The mass spectrum of compound **4** exhibited a molecular ion peak at m/e 160 and base ion peak at m/e 81 (for 1-methylbicyclo[1.1.1]pentane cation) with the correct isotopic ratio for one halogen atom and a fragmentation pattern for an expected structure.

In summary, we have obtained various compounds through the reaction of [1.1.1]propellane with methylene. In order to reveal the reaction pathway for generation of various products, studies were also carried out. While the photolysis of
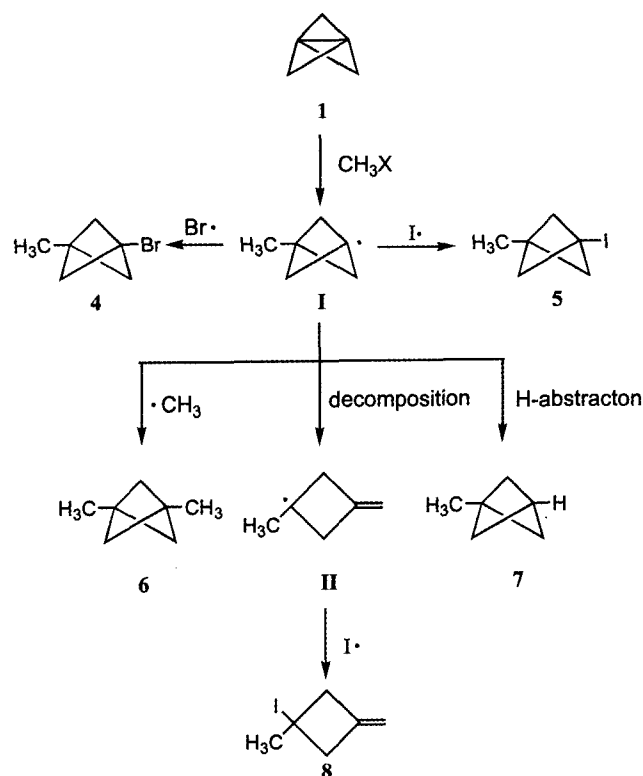
Scheme 2. Proposed mechanism for generation of minor products.

[1.1.1]propellane with singlet methylene afforded [1.1.1.1]paddlane **3**, the reaction of [1.1.1]propellane with triplet methylene did not lead to [1.1.1.1]paddlane. This result strongly indicates that the reaction pathway for the addition of singlet dihalocarbene is different from that of triplet carbene. The mechanism for the addition of singlet methylene involved [1.1.1.1]paddlane intermediate. The addition of triplet methylene led to diradical intermediate. It is expected that various minor products were generated from the reaction of [1.1.1]propellane with methyl halide via radical intermediate.

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12. The ^{13}C NMR spectrum without ^{1}H decoupling of 3 showed a triplet at δ66.6 ppm corresponding to the direct coupling between ^{13}C and ^{1}H with J_{CH} = 152.6 Hz. This spectrum showed also a multiplet at δ3.14 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 δ67.7, 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.