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Supplementary Material Available. Tables of bond distances and bond angles, anisotropic thermal parameters, positional parameters for hydrogen atoms, and listings of observed and calculated structure factors. Supplementary materials are available from one of the authors (S. O. Kang) upon request.

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[1.1.1]Propellane : Reaction with Singlet Dihalocarbene

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The [1.1.1]propellane has been extensively investigated in recent years and has provided important information on the very small ring hydrocarbon chemistry.[1,2] The smallest propellane, [1.1.1]propellane, was first prepared by Wiberg in 1982.[3] This compound has an inverted structure at the two bridgehead carbon atoms[4,5] and the central C-C bond has sp^2 character, as well as the charge distribution has the high local charge density near the bridgehead carbon.[5,6] This would suggest the possibility of relatively facile carbene addition across the bridgehead bond of [1.1.1]propellane. In a recent communication,[7] we have reported the reaction of [1.1.1]propellane with carbenoid. The reaction of [1.1.1]propellane with phenylchlorocarbene had been studied previously by other workers.[8,9] However, no example has been reported of the addition of singlet dihalocarbenes to [1.1.1]propellane.

In this paper, we have described the addition of singlet dihalocarbenes to [1.1.1]propellane and the reaction mechanism was discussed.

Experimental

General. Manipulations were performed under an inert atmosphere of nitrogen. Dry, oxygen-free solvents were employed throughout the reaction.

^1H and ^{13}C NMR spectra were recorded at 300 MHz on a Varian unity plux spectrometer, GC-Mass were 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.

Reaction of [1.1.1]Propellane with dihalocarbene. [1.1.1]Propellane was prepared from 1,1-dibromo-2.2-bis-(chloromethyl)cyclopropane and methyllithium as described,[10] and characterized by ^1H NMR (δ=2.04, s, 6H). Dihalocarbenes were generated from chloroform, bromoform and potassium-tert-butoxide at $-30\,^{\circ}C$.

The reactions of [1.1.1]propellane with carbenes were carried out in nitrogen atmosphere at −30 °C. Haloform was added dropwise over a period of 50 minutes to a stirred solution of [1.1.1]propellane in ether and potassium-tert-butoxide at −30 °C under nitrogen. The mixture was stirred for another 90 minute at −30 °C before the temperature was allowed to rise above 0 °C and the resulting solution was extracted by water and ether. Solvent was removed from the dried ($MgSO_4$) organic solution by evaporation under reduced pressure. Isolation was performed by preparative GC and characterized by several spectroscopies for the products **2** and **3**.

Data for (2,2-dichloromethylene)methylenecyclobutylidene (2a). GC/MS m/e (rel. intensity) 152 (M+4, 2), 150 (M+2, 14), 148 (M^+, 20), 113 (40), 77 (100), 39 (22); ^1H NMR ($CDCl_3$) δ 3.58 (t, 4H, J=2.4 Hz), 5.27 (quintet, 2H, J=2.4 Hz); ^{13}C NMR ($CDCl_3$) δ 39.7 (CH_2), 109 (=CH_2), 12.3 (C), 136 (C), 139 (C); Dept-NMR ($CDCl_3$) δ 39.7 (CH_2), 109 (=CH_2).

Data for (2,2-dibromomethylene)methylenecyclobutylidene (2b). GC/MS m/e (rel. intensity) 240 (M+4, 19), 238 (M+2, 38), 236 (M^+, 19), 159 (68), 157 (68), 78 (100), 51 (45), 38 (30); ^1H NMR ($CDCl_3$) δ 3.22 (t, 4H, J= 2.5 Hz), 5.05 (quintet, 2H, J=2.5 Hz).

Data for 1-methyl-3,3-dichloromethylenecyclobutene (3a). GC/MS m/e (rel. intensity) 152 (M+4, 2), 150 (M+2, 14), 148 (M^+, 20), 113 (40), 77 (100), 39 (24); ^1H NMR ($CDCl_3$) δ 2.00 (s, 3H), 3.00 (s, 2H), 6.00 (s,1H); ^{13}C NMR ($CDCl_3$)/Dept-NMR δ17.2 (CH_3), 39.6 (CH_2), 107 (C), 129 (CH), 136 (C), 152 (C).

Data for 1-methyl-3,3-dibromomethylenecyclobutene (3b). GC/MS m/e (rel. intensity) 240 (M+4, 6), 238 (M+2, 12), 236 (M, 6), 159 (20), 157 (20), 78 (100), 51 (39), 38 (39); ^1H NMR ($CDCl_3$) δ1.90 (s, 3H), 2.80 (s, 2H), 5.95 (s, 1H); ^{13}C NMR ($CDCl_3$)/Dept-NMR δ 16.8 (CH_3), 41.4 (CH_2), 110 (C), 130 (CH), 142 (C), 152 (C).

Data for 1,1-dichloromethyl-3-methylenecyclobutene (4a). GC/MS m/e (rel. intensity) 152 (M+4, 4), 150 (M+2, 28), 148 (M^+, 40), 113 (42), 77 (100), 39 (20).

Data for 1,1-dibromomethyl-3-methylenecyclobutene (4b). GC/MS m/e (rel. intensity) 240 (M+4, 13), 238 (M+2, 26), 236 (M^+, 13), 159 (78), 157 (78), 78 (100), 51 (40), 38 (34).

Data for 1-chlorobicyclo[1.1.1]pentane (5a). GC/MS m/e (rel. intensity) 104 (M+2, 11), 102 (M^+, 33), 67 (100).

Data for 1-chlorobicyclo[1.1.1]pentane (5a). GC/MS m/e (rel. intensity) 148 (M+2, 17), 146 (M^+, 17), 78 (20), 67 (100), 39 (30).

Result and Discussion

[1.1.1]Propellane **1** acting as a substrate can be easily prepared from 1,1-dibromo-2,2-bis(chloromethyl)cyclopropane in good yield (70%).[10] Dihalocarbene can be easily prepared from the reaction of haloform with potassium-*tert*-butoxide. Dihalocarbene are known to have singlet ground states and the triplets have never even been postulated as intermediates.[11]

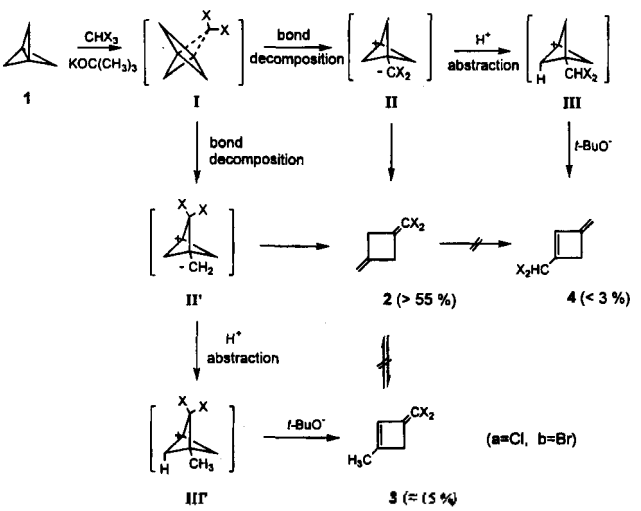
The reaction of [1.1.1]propellane with dihalocarbenes led to (2,2-dihalomethylene)methylenecyclobutylidene **2** as the major product and 1-methyl-3,3-dihalomethylenecyclobutene **3** and 1,1-dihalomethyl-3-methylenecyclobutene **4** as the minor products (Scheme 1). Small amount of unisolated product, 1-halobicyclo[1.1.1]pentane **5**, was also produced.

5 (a: Cl, b: Br)

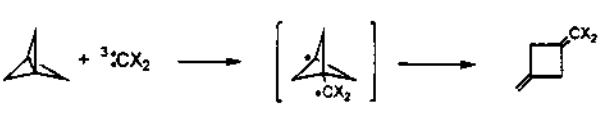
The reaction of [1.1.1]propellane with dihalocarbenes was expected to occur by one of two possible pathways; (I) addition of singlet dihalocarbenes to form a [1.1.1.]paddlane intermediate **I** followed by ring cleavage to form three isomeric compounds (Scheme 1), or (II) addition of triplet dihalocarbenes to form a diradical intermediate **IV** which subsequently cleaves to produce the only product **2** (Scheme 2).

The reaction of [1.1.1]propellane with dihalocarbenes is believed to proceed via intermediate **I**. It is predicted from product analysis. The addition of triplet carbene to [1.1.1] propellane cannot produce the isomeric products **3** and **4**. This reaction was proceed through a diradical intermediate as shown in Scheme 2. The addition of singlet carbene, on the other hand, produced **3** and **4**. This result strongly indicates that the reaction pathway for the addition of singlet dihalocarbene is different from that of triplet carbene. As shown in Scheme 1, the mechanism for the reaction of [1.1.1]propellane with singlet dihalocarbenes involved [1.1.1.1] paddlane intermediate **I**, which was expected on the basis of the insertion reaction by dihalocarbene. This intermediate has much higher strain energy. Therefore, ring opening takes place and that leads to dipole intermediates **II** and **II'** which then convert into isomeric products **2**, **3** and **4**.

Isomerization of **2**, **3** and **4** may also take place. Isomerization of compounds **2** and **3** derivatives was reported by



Scheme 1. The reaction of [1.1.1]propellane with singlet carbenes.



Scheme 2. The reaction of [1.1.1]propellane with triplet carbenes.

Frederick F. Caserio and co-workers.[12] In this work, to seek the evidence of isomerization **2**, **3** and **4**, the following studies were performed. The reaction of the reaction mixture (**2**, **3** and **4**) with strong base (potassium-*tert*-butoxide) at room temperature as well as high temperature was carried out in ether. The reaction of **2** with strong base was also carried out in ether. However, the evidence of isomerization was not observed. This result indicates that the products **3** and **4** were not produced from **2**.

Formation of products **3** and **4** involves abstraction of a hydrogen from tert-butanol to form dipole intermediates **III** and **III'** which lose hydrogen by the base (potassium-*tert*-butoxide) to give products **3** and **4**.

Major product **2** (**2a**: 60%, **2b**: 55%) was obtained from dipole intermediates **II** and **II'**. This product was separated by preparative GC and characterized by GC-Mass, ^{1}H NMR, ^{13}C NMR and Dept-NMR.

The ^{1}H NMR spectrum of **2a** showed a quintet of two protons at δ 5.27 corresponding to the vinyl hydrogen and a triplet at δ3.58 (4H) corresponding to the ring hydrogen. The ^{1}H NMR spectrum of **2b** has a triplet at δ 3.22 (4H) and quintet (2H) at δ 5.05. This spin-spin resonance splitting was ascribed to the long range coupling between vinyl hydrogens (2H) and ring hydrogens (4H).

Minor products **3a** (15%) and **3b** (18%) were characterized by GC-Mass, ^{1}H NMR, ^{13}C NMR and Dept-NMR. The spectral data was in agreement with the proposed structure.

A minor products **4a**, **4b** and **5** were also present. The amount of these products was too small to be isolated (<3%); only identified by GC-Mass. The mass spectrum of these minor products exhibited the correct isotopic ratio for halogen atom and a fragmentation pattern for a proposed structure. We propose that **5** may came from the reaction of [1.1.1]propellane with potassium halide generated from KOC$(CH_3)_3$ and CHX_3.

In summary, we have obtained compounds **2**, **3** and **4** through the reaction of [1.1.1]propellane with singlet dihalocarbene. In addition, we have examined isomerization of **2**, **3** and **4** in strong base (potassium-*tert*-butoxide) at room temperature as well as high temperature. No isomerization was observed. Formation of compounds **3** and **4** in the reaction of [1.1.1]propellane with dihalocarbene strongly indicates that reaction intermediate for the products is [1.1.1.1]paddlane **I**. The detailed mechanistic study is currently under investigation and the results of these studies will be reported in due course.

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Eu(III) Luminescence Probe into the Cation Binding Sites of Subtilisin Carlsberg

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Static and time-resolved Eu^{3+} luminescence spectra are investigated to understand the environments and functions of metal cation binding sites of subtilisin Carlsberg (sC). Our results show that Eu^{3+} luminescence spectroscopy is a good probe to the structures and roles of the Ca^{2+} binding sites in sC,[1-3] which is one of subtilisin family.[4] Only the Ca^{2+} ion in the weak binding site[1,2] is replaced by Eu^{3+} ion. Eu^{3+} luminescence indicates that the weak binding site has a significantly lower symmetry than an octahedral group. The Eu^{3+} ion in the weak binding site is coordinated to four wat-