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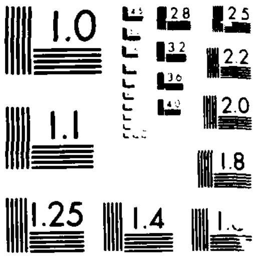

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POLYFUNCTIONALIZATION OF CAGE HYDROCARBONS

First Interim Report

by

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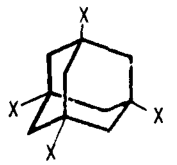
Summary

Investigations to introduce as many functional groups in the cage hydrocarbons, e.g. adamantane, diamantane, and norbornadiene dimer, as specifically as possible are being pursued. The procedures typically involve specific introduction of a limited number of halogens (bromines or chlorines) by ionic reactions, followed by photochemical chlorination. With adamantane, 13 chlorines have been introduced in this manner. A sample is being transmitted to Army contractors in the USA to explore conversion to high density energy materials.

Background and Introduction

This project is being carried out in close collaboration with personnel of the US Army Research Laboratory in Dover, New Jersey, and with Dr. G. Sollott, who formerly was also at that location, but now is employed by an independent contractor and is carrying out research at Villanova University. Since the present research proposal was submitted, there has been considerable success at both these laboratories in elucidating the nature of samples we have supplied. For more detailed background information, the readers are referred to the research proposal; a brief summary follows.

In earlier work at Erlangen it was shown that for photochlorination of 1,3,5,7,-terachloro (or tetrabromo) adamantane (1) could be controlled. After the eighth halogen was introduced, the reaction slowed down appreciably. Although a very large number of octachloroadamantanes (2) are possible, the product mixture contained three principal components. Analytical and preparative chromatographic separations of these components have now been achieved at Dover.



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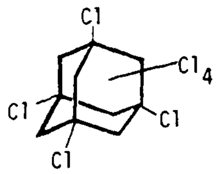

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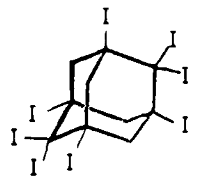

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In earlier work, Dr. Sollott was able to convert the octahaloadamantane mixture to a crystalline octaiodoadamantane, which exhibited unexpected chemical reactions. These reactions can now be understood on the basis of an X-ray structure, 3, which shows geminal diiodo units to be present. These units exhibit enhanced reactivity, e.g.

towards substitution, and provide potentially good sites for introduction of nitrogen-based functionalities.

However, 3 is produced only in around 15% yields from the octachloroadamantane mixture and thus evidently does not correspond to either of the major components. Accordingly, an immediate objective of the project at Erlangen is to explore ways to effect geminal halogenation as efficiently as possible.

A. Photobromination

A review of the literature indicates that photobromination proceeds much more specifically than photochlorination. Thus, photobromination of alkyl halides tends to occur at the site where the original halogen is already attached. In contrast, photochlorination prefers positions farther away.

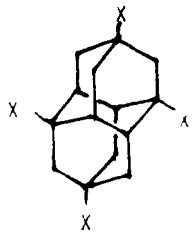
As a consequence, we reasoned that the photobromination of 1,3,5,7-tetrachloro (or tetrabromo) adamantane (1) should produce a much higher percentage of octahalo products realted to 3 than the photochlorination. Unfortunately, the first series of experiments have been unsuccessful; photobromination of the tetrahalo adamantanes did not proceed at all! This approach has not been abandoned, but appears unpromising at this stage.

B. Exhaustive Chlorination

As the major components of the octachloroadamantane mixture do not contain gem-dihalo groups (based on NMR analyses carried out in Dover), further chlorination of these materials should take place, at least in part, at monochlorinated sites. A larger number of halogen substituents would also be desirable since such materials produced might serve as precursors for conversion to high density energy materials with a very high degree of nitrogen functionalization. Indeed, exhaustive photohalogenation of adamantane proceeds quite well. Dr. Peter Gregory has now been able to produce a mixture containing 11, 12, and 13 chlorines. A sample is being sent to Dr. Sollott to explore further conversions, the first step into the corresponding polyiodo compound.

C. Polyhalogenation of Other Cage Hydrocarbons

Under ionic conditions, we have now been able to tetrahalogenate diamantane: the product is believed to be 4. This material is being subjected to photochlorination under varying conditions. The six methylene groups in diamantane are farther removed from one another than those in adamantane so that the percentage of geminal dihalogenation might be increased.



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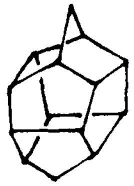

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Dr. Alan Marchand kindly provided a ca. 20g sample of bicycloheptadiene dimer, 5. Our earlier experiments on smaller quantities of this material indicated that it was inert to ionic substitution conditions, but that it could be photochlorinated to a rather massive stage of substitution. Unlike both adamantane and diamantane, the ratio of bridgehead to methylene hydrogens in 5 is much higher. This reduces the possibility of obtaining a higher degree of geminal derivatization, but compounds of this type have already been prepared chemically by Dr. Marchand. Hence, our experiments will provide a method for introducing functional groups into the other positions of 5.

Scientific personnel involved in this work:

Prof. Dr. P.v.R. Schleyer (principal investigator)
Dr. Peter Gregory, postdoctoral associate