NOVEL $C_{22}H_{24}$ ALKENE DIMERS FORMED VIA TITANTIUM-PROMOTED REDUCTIVE DIMERIZATION OF POLYCYCLIC CAGE KETONES. POTENTIAL NEW FUELS FOR AIRBREATHING MISSILES

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INTRODUCTION

The development of new high-energy hydrocarbon fuels for use in air-breathing missiles has been the objective of a number of investigations which have received support during the past decade through programs sponsored by the Air Force Systems Command[1,2] and/or the Naval Air Systems Command.[3-5] The key characterstics which must be met by potential cruise missile fuels have been described by Burdette and coworkers.[6] A primary requirement in this regard is that candidate fuels must possess high net volumetric heat of combustion (preferably greater than 160,000 BTU/gallon).[2] In order to meet the primary requirement of high net volumetric heat of combustion, hydrocarbon systems, C_nH_m, have been sought that maximize the ratio n/m. Bridged ring (polycyclic) hydrocarbon systems, by virtue of their high densities (concomitant with their compact structures), are particularly promising candidate fuels. Compounds of this type already have been utilized extensively as fuels for air-breathing missiles.

In the early stages of our study, one-pound samples of two particularly promising fuel candidates, **1** (heptacyclo[6.6.0.0^{2,6}.0^{3,13}.0^{4,11}.0^{5,9}.0^{10,14}]tetradecane, HCTD) and **2** (pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane, PCUD, structures shown in Scheme 1) were synthesized. Both **1** and **2** display high densities (1.26 and 1.23 g-cm^{-3}, respectively). The performance of each compound as a ramjet fuel has been evaluated by personnel at the Naval Weapons Center.[7] In addition, several derivatives of **1**[8] and of **2**[9-11] have been synthesized

in our laboratory.

Scheme 1

1 (HCTD)

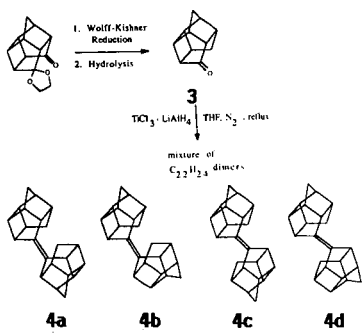
2 (PCUD)

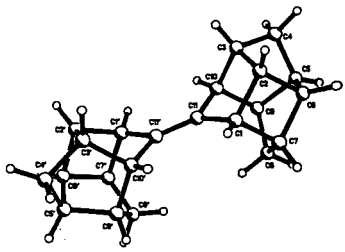
One difficulty attendant with the use of both HCTD and PCUD as fuels is their volatility. Although they are both high-melting solids, both hydrocarbons sublime readily and can escape from the binder (e.g., hydroxy-terminated polybutadiene, HTPB) on long standing at ambient temperature. In an effort to minimize the volatility of these systems (and thereby to improve their combustion and storage characteristics) without sacrificing other desirable fuel properties, we have undertaken the synthesis of HCTD and PCUD oligomers. We now report on the synthesis of some isomeric $C_{22}H_{24}$ alkenes obtained via titanium-promoted reductive dimerization[12] of polycyclic cage $C_{11}H_{20}O$ ketones and some aspects of the chemistry of the alkene dimers thereby obtained.

RESULTS & DISCUSSION

$C_{22}H_{24}$ Alkene Dimers Derived from PCUD-8-one. Our synthesis of PCUD alkene dimers, obtained via reaction of low-valent titanium with PCUD-8-one (**3**), is shown in Scheme 2. Four dimers potentially can result from this reaction, each of which possesses a twofold symmetry element (e.g., mirror plane, C_2 axis, or center of symmetry). In our hands, titanium-promoted reductive dimerization of **3** afforded a mixture of dimers, **4a-4d**, as expected. Careful fractional recrystallization of this mixture from hexane afforded a single isomer, **4a**, mp 214-215 ^{o}C, whose structure was determined via single crystal X-ray structural analysis.[13] Particularly noteworthy is the unusually high crystal density of **4a**, i.e., 1.284 g-cm^{-3} (calculated from the X-ray data).[13]

Scheme 2





Structure drawing of **4a**

Subsequently, the remaining three isomers (i.e, **4b-4d**) were isolated by a combination of column chromatographic techniques and fractional recrystallization. Ultimately, we hope to obtain X-ray data that will permit unequivocal characterization of each of the three remaining PCUD dimers.

Recently, a study was undertaken of electrophilic additions to these PCUD dimers (individually and in the gross mixture of four dimers that results via titanium-promoted dimerization of PCUD-8-one). This was done for several reasons: First, it was of interest to determine whether structural differences among the various dimers would lead to differences in reactivity toward the electrophilic reagent, HX. If this is indeed the case, then it may be possible to separate one or possibly two of the dimers from the mixture by taking advantage of these differential reactivities. Secondly, we anticipated that Wagner-Meerwein rearrangements might occur in carbonium ion intermediates, thereby leading to the formation of interesting new C_{22} compounds that are not easily accessed via direct, titanium-promoted dimerization reactions. Finally, we are interested in determining whether or not structural differences among the various PCUD dimers might

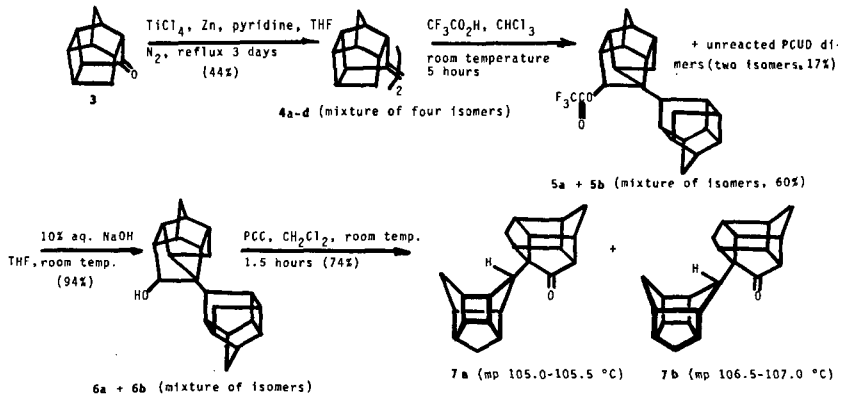
affect the mode of addition (syn vs. anti) of HX across the C=C double bond of each dimer.

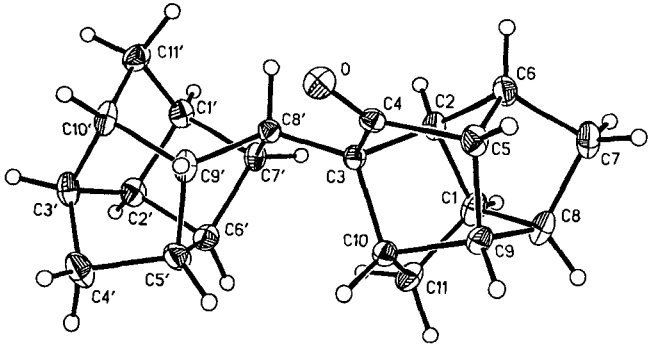
The results of electrophilic addition of trifluoroacetic acid to a mixture of the four PCUD dimers (Scheme 2) are shown in Scheme 3. When the reaction with CF_3CO_2H was performed at room temperature in chloroform solvent, a mixture of two trifluoroacetate adducts (**5a** and **5b**) was formed (60%) along with a mixture of two unreacted PCUD dimers (16.7%). The mixture of **5a** and **5b** was then subjected to hydrolysis with aqueous base, thereby affording a mixture of alcohols, **6a** and **6b**. The resulting mixture of alcohols was oxidized subsequently by using pyridinium chlorochromate (PCC) in methylene chloride solvent. The product was found to be a mixture of two isomeric ketones, **7a** and **7b**, which could be separated by flash column chromatography. The structures of **7a** and **7b** each have been established unequivocally by single crystal X-ray structural analysis.[14]

Subsequently, the unreacted dimer (recovered from the above reaction; mixture of two isomers) was treated with trifluoroacetic acid in refluxing chloroform. Addition of trifluoroacetic acid to the C=C double bond in the mixture of dimers occurred under these conditions. Basic hydrolysis of the trifluoroacetate adduct followed by oxidation with PCC again afforded a mixture of **7a** and **7b**.

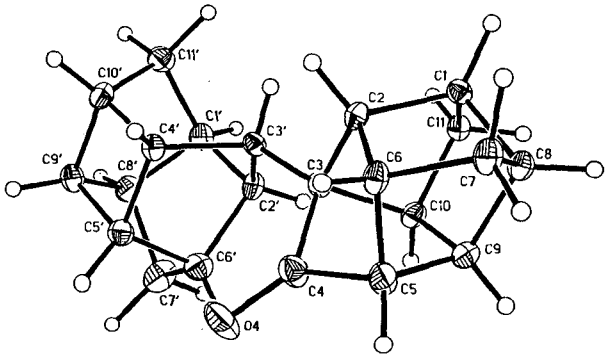
Recently, we have studied the Wolff-Kishner reduction of isomerically pure ketones **7a** and **7b**. Of particular interest is the fact that the hydrocarbons thereby obtained differ substantially in melting point. The product of Wolff-Kishner reduction of **7a** (i.e., **8a**) displays mp 114-115 ^{o}C, whereas the corresponding product obtained by Wolff-Kishner reduction of **7b** (i.e., **8b**) displays mp 74-75 ^{o}C. The structure of **8a** has been determined by X-ray crystallographic methods (Scheme 4); the calulated crystal density of **8a** was found to be 1.290 g-cm^{-3}.[15]

Scheme 3



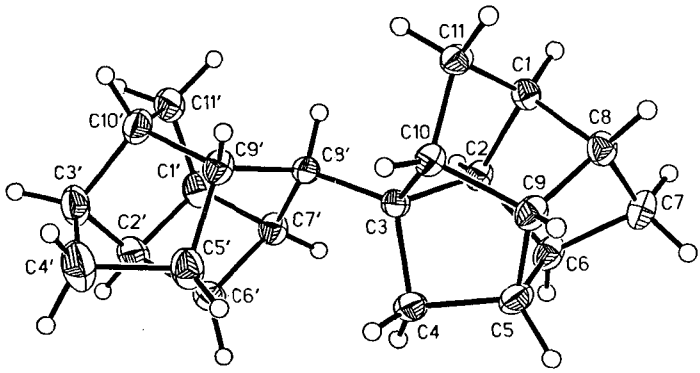


Structure drawing of **7a**



Structure drawing of **7b**

Scheme 4



Structure drawing of **8a**

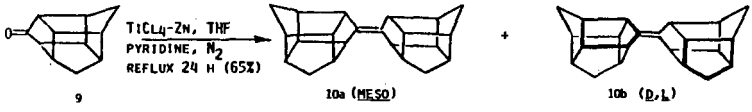
$C_{22}H_{24}$ Alkene Dimers Derived from D_3-Trishomocubanone. As an extension of the foregoing study, alkene dimers have been synthesized via titanium-promoted reductive dimerization of the D_3-trishomocubanone (**9**). In this case, only two dimers [i.e., **10a** (meso) and **10b** (d,l)] can result from this reaction (Scheme 5). Indeed, a 1:1 mixture of **10a** and **10b** was obtained from this reaction. Careful fractional recrystallization of the mixture of dimers thereby obtained from ligroin afforded a single isomer, mp 246 ^{o}C. This dimer was shown to possess the meso configuration (i.e., **10a**) by single crystal X-ray structral analysis.[16] Of particular significance is the unusually high calculated crystal density of **10a**, i.e., 1.302 g-cm^{-3}.

More recently, the corresponding d,l dimer, **10b**, mp 186 ^{o}C, has been isolated, and its structure has been determined by X-ray crystallographic methods (Scheme 5). Interestingly, the calculated crystal density of **10b** (1.269 g-cm^{-3}) is significantly lower than that of **10a**.[16]

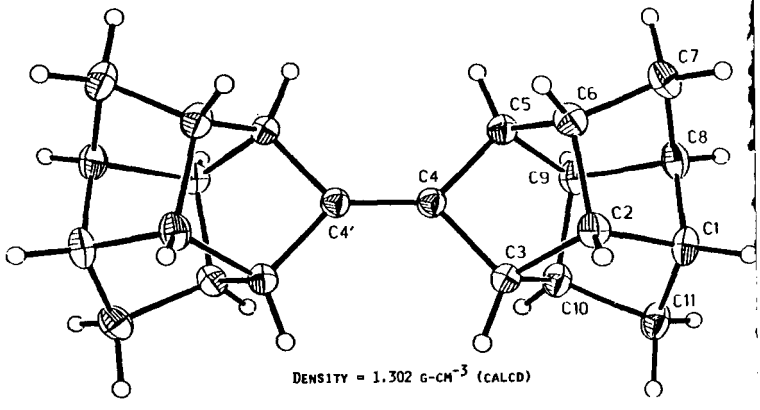
Two important results of that have emerged from the studies described above are

Scheme 5

DIMERS DERIVED FROM D_3-TRISHOMOCUBANONE

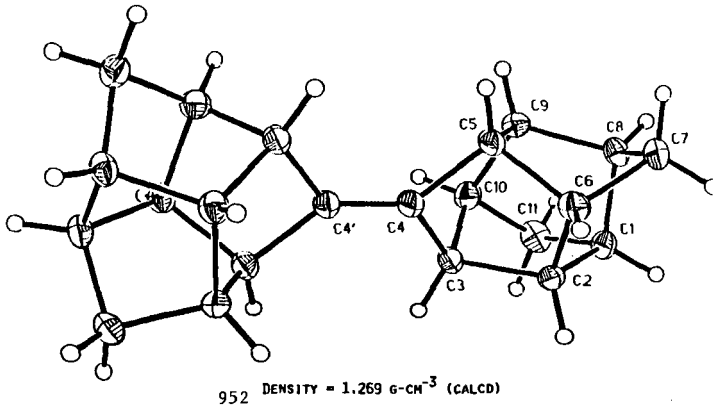


Structure drawing of **10a**



DENSITY = 1.302 G-CM^{-3} (CALCD)

Structure drawing of **10b**



DENSITY = 1.269 G-CM^{-3} (CALCD)

noteworthy. First, the calculated crystal densities of PCUD dimer **4a**, of the rearranged cage hydrocarbon **8a**, and of **10a** and **10b** (i.e., 1.284, 1.290, 1.302, and 1.269 g-cm^{-3}, respectively) rank among the highest known hydrocarbon densities; [compare these values with the densities of cubane (1.29 g-cm^{-3}),[17] 1,16-dimethyldodecahedrane (1.412 g-cm^{-3})[18] and dodecahedrane (1.448 g-cm^{-3})[19]].

Second, it is important to note that all of the three dimeric alkenes, i.e., **4a**, **10a**, and **10b**, whose X-ray crystal structures have been determined thus far in our study, are all $C_{22}H_{24}$ isomers that possess distinctly different crystal densities. Any of the existing calculational methods that are used to estimate crystal densities are based upon molecular formula and functional group additivity and therefore are incapable of predicting variations in densities among geometric isomers.[20] Hence, contrary to the X-ray crystallographic results cited above, all of our $C_{22}H_{24}$ isomers are predicted by any of these methods to possess the same density.

SUMMARY & CONCLUSIONS

Our efforts to synthesize oligomers of strained polcyclic cage monomers have resulted in the synthesis of novel cage alkene dimers **4a-4d**, **10a** and **10b**, along with derivatives of these systems. These dimers possess unusually high crystal densities and are relatively nonvolatile; both properties are considered to be desirable for new candidate fuel systems. The electrophilic addition of trifluoroacetic acid to a mixture of PCUD alkene dimers, **4a-4d**, has been studied, and several reaction products have been characterized by single crystal X-ray structural analysis. Future studies will be directed toward: (i) the synthesis of oligomers of HCTD (**1**) and (ii) studies of reactions of **10a** and **10b** with a variety of electrophiles.

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