Studies of the synthesis and chemistry of polycarbocyclic cage hydrocarbons and polynitropolycyclic compounds are described. These compounds constitute a new class of energetic materials; the former are of interest as high energy/high density fuels, and the latter have potential application as relatively insensitive high energy explosives. As part of this program, alkene dimers were prepared via low valent titanium-promoted reductive coupling of $D_3$-trishomocubanone and of homocubanone. The mechanism of addition of electrophiles to the $C=C$ double bond of each of the resulting alkene dimers (i.e., meso- and $d_1$-trishomocubylidene-trishomocubane and homocubylidenehomocubane, respectively) was investigated. In addition, the structures of several new cage intermediates were elucidated via single crystal X-ray crystallographic methods. Finally, ring homologations of substituted pentacycloundecanediones were studied.
FINAL REPORT

"SYNTHESIS OF NOVEL, SUBSTITUTED POLYCYCLIC CAGE SYSTEMS"

AFOSR-88-0132

Principal Investigator: Dr. Alan P. Marchand

Department of Chemistry, University of North Texas, Denton, TX 76203-0068

Date Submitted: July 22, 1991

The views, opinion, and/or findings contained in this report are those of the authors and should not be construed as an official Department of the Air Force position, policy, or decision, unless so designated by other documentation.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>COVER PAGE AND DISCLAIMER.</td>
<td>1</td>
</tr>
<tr>
<td>TABLE OF CONTENTS.</td>
<td>2</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>3</td>
</tr>
<tr>
<td>INTRODUCTION</td>
<td>4</td>
</tr>
<tr>
<td>SUMMARY OF PROGRESS, FY88-91</td>
<td></td>
</tr>
<tr>
<td>I. Polynitropolycyclic Compounds</td>
<td>5</td>
</tr>
<tr>
<td>II. Polycyclic Cage Dimers.</td>
<td>13</td>
</tr>
<tr>
<td>III. Ring Homologations of Substituted PCUD-8,11-diones.</td>
<td>28</td>
</tr>
<tr>
<td>REFERENCES &amp; FOOTNOTES</td>
<td>33</td>
</tr>
<tr>
<td>LIST OF PUBLICATIONS</td>
<td>37</td>
</tr>
</tbody>
</table>
ABSTRACT

Studies of the synthesis and chemistry of polycarbocyclic cage hydrocarbons and polynitropolycyclic compounds are described. These compounds constitute a new class of energetic materials; the former are of interest as high energy/high density fuels, and the latter have potential application as relatively insensitive high energy explosives. As part of this program, alkene dimers were prepared via low valent titanium-promoted reductive coupling of D$_3$-trishomocubanone and of homocubanone. The mechanism of addition of electrophiles to the C=C double bond of each of the resulting alkene dimers (i.e., meso- and d,l-trishomocubylidene-trishomocubane and homocubylidenehomocubane, respectively) was investigated. In addition, the structures of several new cage intermediates were elucidated via single crystal X-ray crystallographic methods. Finally, ring homologations of substituted pentacycloundecanediones were studied.
INTRODUCTION

A significant part of our AFOSR-sponsored research effort has been concerned with the synthesis and chemistry of strained, saturated polycyclic "cage" compounds. Much of our work in this area has been summarized in recent reviews.\textsuperscript{1-3} Compounds of this general type are of intense current interest to U. S. military agencies as a new class of energetic materials. As a consequence of their highly compact, rigid carbocyclic frameworks, polycarbocyclic cage hydrocarbons generally possess high densities. In addition, compounds of this type frequently contain considerable strain energy that can express itself in terms of unusually high net volumetric heats of combustion. Thus, there is considerable interest in cage hydrocarbons as potential fuels for volume-limited applications (e.g., as solid fuels and as fuel additives for use in air-breathing missiles). In addition, polynitro derivatives of cage hydrocarbon systems are of interest as a potential new class of high energy density explosives and propellants.\textsuperscript{2}

An important objective of our AFOSR-sponsored research program has been to unify our conceptually independent fuels and explosives projects, both of which utilize polycyclic cage molecules as synthetic intermediates. Here, our overriding concern has been to develop a cohesive program of research that is designed to explore the synthesis and chemistry of novel, functionalized cage molecules in systematic fashion. To this end, we have focused our attention upon a number of approaches to the synthesis of new, functionalized polycyclic cage systems, some of which have served as suitable precursors to new polynitropolycyclic systems.
SUMMARY OF PROGRESS, FY88-91

1. Polynitropolycyclic Compounds. As part of our research efforts to synthesize new polynitropolycyclic compounds, we have identified four target molecular systems, 1–4, whose structures are shown in Figure 1. Typical synthetic methodology that has been utilized in our laboratory in pursuit of these target molecules is shown in Figure 2. Here, the substituted polycyclic framework is first constructed via a combination of thermal and photochemical cycloadditions. The substituent groups (generally cage ketone carbonyl groups or pendant carboxylic ester, acid or phenyl functionalities) are converted subsequently into nitro groups.

By utilizing the general approach shown in Figure 2, we have completed the syntheses of a trinitro-4 and of a tetranitro-1,3-bishomocubane5 in thirteen and in ten stereocontrolled steps, respectively (i.e., target molecule 1, n = 3 and 4, see see Figure 3). In addition, the synthesis of D3-trishomocubanetrione has been completed.6 This cage trione was converted subsequently into the corresponding D3-hexanitrotrishomocubane (i.e., target molecule 3, see Figure 4).7 Also, syntheses of trinitro- and tetranitrotetraphenyl-1,3-bishomocubanes (Figure 5)7 and of 8,8,11,11-tetranitropentacyclo[5.4.0.02,6.03,10.05,9]undecane (i.e., 8,8,11,11-tetranitro-PCUD, target molecule 2, n = 4, see Figure 6)8 have been performed successfully.

The foregoing syntheses were completed under an Air Force-sponsored program during FY84-87 (i.e., Grant no. AFOSR-84-0085). More recently, we have extended the approach shown in Figures 3–6 to permit the successful synthesis of 4,4,8,8,11,11-hexanitro-PCUD (i.e., target molecule 2, n = 6, see Figure 7).9

Progress has accrued toward achieving the synthesis of our final target molecular system, 4. We recently reported our synthesis of the corresponding heptacyclotetradecanedione.10 Conversion of each ketone functionality into geminal dinitro
FIGURE 1. TARGET MOLECULES

1 (n = 3-8)

2 (n = 4-8)

3

(\text{NO}_2)^n

(\text{O}_2\text{N})^n

(\text{NO}_2)^n

(\text{O}_2\text{N})^n
A partial retrosynthetic perspective leading to I is shown below.

Introduction of the three nitro groups could occur either in an early stage of the synthesis, or, alternatively, the X, Y, and Z substituents could be converted to NO₂ substituents at a later stage, (e.g., after construction of the bishomocubane ring system). Of these two approaches, the latter was preferred. Once the appropriately substituted cage system had been constructed (i.e., 5), we relied on published procedures to effect conversion of the ketone functionality first to a nitro group and then to geminal dinitro groups. Subsequent conversion of the carbomethoxyl group in 8 to NO₂ via the sequence shown in Scheme II completed the synthesis.

The retrosynthesis of I is completed below.

\[ 4 (X, Y = \text{carbonyl oxygen}; Z = \text{CO₃Me}) \]
Synthesis of 3,5,5-Trinitropentacyle[6.3.0.0^{3,4}.0^{3,4}]decane

Alan P. Marchand* and Suresh Chander Suri
Department of Chemistry, North Texas State University, Box 5068, Denton, Texas 76203
Org. Chem. 1984, 49, 2041-2043

Scheme I

[Chemical structures and reactions]

(n = 3)

Synthesis of 5,5,9,9-Tetranitropentacyclo[6.3.0.0^{3,4}.0^{3,4}].0^{3,4}]decane

Alan P. Marchand* and D. Sivakumar Reddy
Department of Chemistry, North Texas State University, NTSU Station, Denton, Texas 76203
J. Org. Chem. 1984, 49, 4078-4080

Scheme I

[Chemical structures and reactions]

(n = 4)
Syntheses of Pentacyclo[5.4.0.02,0.0.03]undecane-4,8,11-trione, Pentacyclo[6.3.0.02,0.0.03]undecane-4,7,11-trione (D$_3$-Trishomocubanetrione), and 4,4,7,7,11,11-Hexanitro[6.3.0.02,0.0.03]undecane (D$_2$-Hexanitrotishomocubane)

Alan P. Marchand,* G. V. Madhava Sharma, G. S. Annapurna, and P. R. Pednekar

Department of Chemistry, North Texas State University, Denton, Texas 76203-5068

Scheme I

Scheme II

Target Molecule 3

* (a) EtCO$_2$H, concentrated H$_2$SO$_4$, 160 °C, 72 h, N$_2$ (51%); (b) Na, dry MeOH, room temperature, 1 h (100%); (c) PCC, CH$_2$Cl$_2$, room temperature, 2 h (46%); (d) NH$_2$OH-HCl, NaOAc, aqueous MeOH, 0 °C → room temperature, overnight (70%); (e) (CF$_3$CO$_2$)$_2$O, 90% H$_2$O$_2$, NaHCO$_3$, urea, CH$_3$CN, 70-75 °C, overnight (85%); (f) NaOH, aqueous MeOH, 2 h; then K$_2$Fe(CN)$_5$N$_2$, aqueous NaNO$_2$, Et$_2$O, 1 h (65%); (g) NaOH, aqueous MeOH, 2 h; then K$_2$Fe(CN)$_5$N$_2$, aqueous NaNO$_2$, Et$_2$O, 12 h (62%). Stereoc hemical assignments for 14 and 15 were made on the basis of (i) simple mechanistic considerations and (ii) analysis of the $^1$H and $^{13}$C NMR spectra of these compounds.
Synthesis of Nitro-Substituted 1,4,8-Tetraphenypentacyclo[5.3.0.0^2,0^3,0^5,0^7]decanes

Ian P. Marchand,* G. S. Annapurna, and V. Vidyasagar
Department of Chemistry, North Texas State University, Denton, Texas 76203-5068

Judith L. Flippen-Anderson,* Richard Gilardi, and Clifford George
Laboratory for the Structure of Matter, Naval Research Laboratory, Washington, D.C. 20375

Herman L. Ammon
Department of Chemistry, University of Maryland, College Park, Maryland 20742

Scheme I

\[
\text{NH}_2\text{OH-HCl, NaOAc, MeOH} \quad \text{room temp, 24 h} \quad (94\%) \\
\text{NOH}
\]

\[
\text{(CF}_3\text{CO})\text{NO}_2, \text{CH}_3\text{CN} \quad \text{reflux 12 h} \quad (77\%) \\
\text{fractionally recrystallize from MeOH}
\]

\[
\text{K}_2\text{Fe(CN)}_6, \text{NaNO}_2, \text{MeOH} \quad \text{MeOH-H}_2\text{O, EtO} \quad \text{N}_2, \text{stir at room temp 6 h} \quad (65\%) \\
\text{K}_2\text{Fe(CN)}_6, \text{NaNO}_2, \text{MeOH} \quad \text{MeOH-H}_2\text{O, EtO} \quad \text{N}_2, \text{stir at room temp 24 h} \quad (50\%)
\]

Figure 1. Results of the X-ray study on 3. For clarity, the phenyl groups on C-2, C-3, C-4, and C-8 are represented as single atoms (C-2a, C-3a, C-4a, and C-8a).

Figure 2. Results of the X-ray study on 4. For clarity, the phenyl groups on C-2, C-3, C-4, and C-8 are represented as single atoms (C-2a, C-3a, C-4a, and C-8a).
Synthesis of 8,8,11,11-Tetranitropentacyclo[5.4.0.0\(^2,8\).0\(^3,10\).0\(^4,1\)]undecane

Alan P. Marchand, Benny E. Arney, Jr., and Paritosh R. Dave

Department of Chemistry, North Texas State University, Denton, Texas 76203-5068

Scheme I

\[\text{Target Molecule} \quad 2 (n = 4)\]

\[\text{* (a) } \text{H}_{2}\text{O}_{2}, \text{CH}_{2}\text{OH}, \text{TsOH, benzene, Dean-Stark tube (92%);} \]
\[\text{(b) } \text{NH}_{2}\text{OH-HCl, NaOAc, EtOH, room temperature, overnight (79%);} \]
\[\text{(c) } \text{Br}_{2}, \text{NaHCO}_{3}, \text{DMF, } 0 ^\circ \text{C,} \text{and then } \text{O}_{3}, \text{CH}_{2}\text{Cl}_{2}, \text{0 } ^\circ \text{C (80%);} \]
\[\text{(d) } \text{NaBH}_{4}, \text{60\% aqueous EtOH, room temperature, 0.5 h (97%);} \]
\[\text{(e) } \text{K}_{2}\text{Fe(CN)}_{6}, \text{NaNO}_{2}, \text{aqueous MeOH, NaOH, room temperature, 0.5 h (3%);} \]
\[\text{(f) } \text{concentrated } \text{H}_{2}\text{SO}_{4}, \text{CH}_{2}\text{Cl}_{2}, \text{room temperature, overnight (73%);} \]
\[\text{(g) } \text{NH}_{2}\text{OH-HCl, NaOAc, EtOH, room temperature, overnight (89%);} \]
\[\text{(h) } \text{NBS, NaHCO}_{3}, \text{5\% aqueous dioxane, room temperature, 72 h (65.7%);} \]
\[\text{(i) } 98\% \text{ red HNO}_{3}, \text{NH}_{4}\text{NO}_{3}, \text{CH}_{2}\text{Cl}_{2}, \text{reflux 1 h, then 30\% } \text{H}_{2}\text{O}_{2}, \text{reflux 1 h (31\%,) \text{64\% based on recovered 11).} \]
Synthesis of $4,4,8,8,11,11$-Hexanitropentacyclo$[5.4.0.0^{2,4}.0^{3,6}.0^{8,11}]$-undecane

Alan P. Marchand,* Paritosh R. Dave, D. Rajapaksa, and Benny E. Arney, Jr.

Department of Chemistry, University of North Texas, Denton, Texas 76203-5068

Judith L. Flippen-Anderson,* Richard Gilardi, and Clifford George

Laboratory for the Structure of Matter, Naval Research Laboratory, Washington, D.C. 20375-5000

FIGURE 7

*Figure 7. X-ray structure drawing of 1.

*(a) NH$_2$OH-HCl, K$_2$CO$_3$, EtOH, reflux 24 h (79%); (b) NBS, dioxane, room temperature, overnight (62%); (c) NaBH$_4$, 60% aqueous EtOH, 0 °C → room temperature, 1 h (84%); (d) K$_3$Fe(CN)$_6$, NaNO$_2$, aqueous MeOH, room temperature, 2 h (83%); (e) concentrated H$_2$SO$_4$, CH$_2$Cl$_2$ room temperature, 24 h (50%); (f) NH$_2$OH-HCl, NaOAc, MeOH, reflux 2 h (75%); (g) 98% red nitric acid, NH$_4$NO$_3$, urea, dry CH$_3$Cl$_2$, reflux 0.5 h, then 30% aqueous H$_2$O$_2$, reflux 15 min (19%).

Target Molecule

2 (n = 6)
groups should be straightforward. In addition, we have made progress toward the synthesis of more highly substituted heptacyclo[6.6.0.0²,6.0³,13.0⁴,11.0⁵,9.0¹⁰,14]tetradecanes (see Figure 8).

II. Polycyclic Cage Dimers. We have had a long-standing interest in the synthesis and chemistry of PCUD-8,11-dione (5) and related compounds. The parent hydrocarbon, pentacyclo[5.4.0.0⁶.0³.0⁹]undecane (PCUD, 6), can be synthesized readily via a simple three-step synthesis by starting with two inexpensive and readily available materials, i.e., cyclopentadiene and p-benzoquinone (Figure 9). PCUD is a relatively strained hydrocarbon system; its calculated standard heat of formation is +27.42 kcal/mol, and its calculated strain energy content is on the order of 54 kcal/mol. Accordingly, PCUD holds considerable interest as a potential new solid fuel for airbreathing missiles.

Several years ago, we synthesized one pound of PCUD as part of a project that received funding from the Naval Air Systems Command. This material was submitted subsequently to personnel at the Naval Weapons Center, China Lake, CA for evaluation as a potential new solid ramjet fuel. In some respects, PCUD proved to be an excellent candidate fuel. It is an unusually dense hydrocarbon (1.23 g/cc), and its heat of combustion (10.00 kcal/g, 12.30 kcal/cc) is fully 30% above that of binder (hydroxy-terminated polybutadiene, HTPB) alone.

However, PCUD is relatively volatile; despite the fact that it is a high melting solid (mp 204 °C), it nevertheless sublimes readily under ambient conditions, thereby escaping from the binder. The volatility of PCUD was viewed as a serious limitation to its potential usefulness as a ramjet fuel. Accordingly, we have sought ways to reduce the volatility of PCUD without sacrificing its other desirable fuel properties, (e.g., high density, excellent thermal stability, and high net volumetric heat of combustion). In this regard, our search has led us recently to consider dimeric species that are derived from high density cage hydrocarbon monomers.

Structure of a Cage Dimer (I) and a Dimer Ketone (II) Formed via Thermal Reaction of Ethyl 3-Phenyl-2-norbornadienecarboxylate with Pentacarbonylferron

BY JUDITH L. FLIPPEN-ANDERSON,* RICHARD GILARDI AND CLIFFORD GEORGE

Laboratory for the Structure of Matter, Naval Research Laboratory, Washington, DC 20375-5000, USA

AND ALAN P. MARCHAND* AND PARITOSH R. DAVE

Department of Chemistry, North Texas State University, Denton, Texas 76203, USA

(Received 20 August 1988; accepted 4 January 1989)

Fig. 1. Diagram of (I) as determined by X-ray diffraction. The two positions for the disordered methyl groups on C(29) are shown [C(30a) and C(30b)].
An Improved Synthesis of Pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane

Alan P. Marchand* and Robert W. Allen

Department of Chemistry, University of Oklahoma, Norman, Oklahoma 73069

Received December 27, 1973

Scheme I

\[
\begin{align*}
\text{Furanc} + \text{Cyclobutane} & \xrightarrow{93\%} \text{Interproduct} & \xrightarrow{86\%} \text{Product} \\
\text{Product} & \xrightarrow{59\%} \text{Pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane} 
\end{align*}
\]
The calculated values that appear in Table I suggest that PCUD dimers indeed should possess unusually high, positive standard heats of formation and unusually high densities. Accordingly, we have investigated the Ti(0)-promoted dimerization of PCUD-8-one (7) as part of a project that has received financial support from the U. S. Air Force. The results of this reaction are summarized in Figure 10. All four possible dimers, 8a-8d, were obtained from the reaction of 7 with titanium trichloride-lithium aluminum hydride (or, more recently, via reaction of 7 with titanium tetrachloride in the presence of zinc). We have separated the mixture of isomeric products, and each of the individual dimers has been characterized spectrally and via C,H elemental microanalyses. In addition, we have obtained the X-ray crystal structure of one of the dimers, 8a (see Figure 10). The crystal density of 8a calculated by using data from the X-ray crystallographic study is 1.284 g/cc. This value stands in close agreement with the predicted value of 1.29 g/cc (Table I).

The C=C double bond in dimers 8a-8d appears to be highly congested and, therefore, relatively inaccessible. Probably for this reason, we have been unable to saturate this double bond via catalytic hydrogenation with a variety of catalysts and at hydrogen pressures ranging from 1 to 3 atmospheres (i.e., up to 45 psig). We are investigating alternative methods for synthesizing saturated D_3-trishomocubane dimers and related C_{22}H_{26} hydrocarbons.

The mixture of dimers 8a-8d, when treated with trifluoroacetic acid in chloroform solution at room temperature, affords a mixture of two products that result via addition of HX across the C=C double bond along with a mixture of two unreacted dimers. The mixture of the two HX adducts was isolated and subsequently was subjected to hydrolysis with aqueous base. Oxidation of the mixture of alcohols thereby obtained with pyridinium chlorochromate in chloroform afforded a mixture of two isomeric ketones, 9a and 9b (Figure 11). We have isolated and fully characterized these ketones, and their respective
Table I. Calculated standard heats of formation and densities of cage hydrocarbons and cage ketones

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>$\Delta H^\circ_f$ (kcal/mol)$^a$</th>
<th>Density (g-cm$^{-3}$)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$C_{11}H_{10}O_2$</td>
<td>-24.40</td>
<td>1.44 (observed, 1.38)</td>
</tr>
<tr>
<td></td>
<td>$C_{11}H_{12}O$</td>
<td>+1.51</td>
<td>1.34</td>
</tr>
<tr>
<td></td>
<td>$C_{11}H_{14}$</td>
<td>+27.42</td>
<td>1.23</td>
</tr>
<tr>
<td></td>
<td>$C_{22}H_{24}$</td>
<td>+97.54</td>
<td>1.29</td>
</tr>
<tr>
<td></td>
<td>$C_{22}H_{26}$</td>
<td>+67.76</td>
<td>1.26</td>
</tr>
</tbody>
</table>


Structure of a Novel $\text{C}_{22}\text{H}_{24}$ Cage Dimer

BY JUDITH L. FLIPPEN-ANDERSON, RICHARD GILARDI AND CLIFFORD GEORGE

Laboratory for the Structure of Matter, Naval Research Laboratory, Washington, DC 20375, USA

AND ALAN P. MARCHAND, PEI-WEN JIN AND MAHENDRA N. DESHPANDE

Department of Chemistry, North Texas State University, Box 5068, Denton, Texas 87203, USA

(Received 30 December 1987; accepted 25 April 1988)

Abstract. 8,11'-Bipentacyclo[5.4.0.0².6.0³.10.0⁵.9]undecanylidene, $\text{C}_{22}\text{H}_{24}$, $M_r = 288.43$, triclinic, $P\overline{1}$, $a = 6.613 (2)$, $b = 10.809 (3)$, $c = 10.883 (2)$ Å, $\alpha = 97.52 (2)$, $\beta = 99.85 (1)$, $\gamma = 99.32 (2)$°, $V = 746.2 (2)$ Å³, $Z = 2$, $D_x = 1.284 \text{ Mg} \text{ m}^{-3}$, $\lambda(\text{Mo K} \alpha) = 0.71073$ Å, $\mu = 0.07 \text{ mm}^{-1}$, $F(000) = 312$, $T = 295 \text{ K}$, final $R = 0.048$, $wR = 0.048$ for 1118 observed reflections. The molecule, which has an unusually high density for a hydrocarbon, consists of two cage moieties which are related by an approximate twofold axis along the C(11)—C(11') double bond. There are no intermolecular approaches less than van der Waals separations; the high density is probably due to compression of the cage C atoms ensuing from the small bond angles. For example, the internal ring angles at C(11) and C(11'), both $sp^2$ C atoms, are only 102.6 (2)° and 102.2 (2)°, respectively.

Fig. 1. Results of the X-ray study on 8a
Structures of Two Diastereoisomeric Saturated Polycyclic C_{12}H_{24}O Ketones

BY WILLIAM H. WATSON* AND ANTE NAGL†
Department of Chemistry, Texas Christian University, Fort Worth, Texas 76129, USA
AND ALAN P. MARCHAND* AND MAHENDRA N. DESHPANDE
Department of Chemistry, University of North Texas, PO Box 5068, Denton, Texas 76203, USA

(Received 9 September 1988; accepted 20 January 1989)

Abstract. 3-(Pentacyclo[5.4.0.0^2.6.0^3.10.0^5.8]undec-8-yl)pentacyclo[6.3.0.0^2.6.0^3.10.0^5.8]undecan-4-one.

\[ \text{(a)} \quad M_1 = 304.44, \text{triclinic, } P\overline{1}, \quad a = 6.3469 \text{ (6)}, \quad b = 11.425 \text{ (1)}, \quad c = 11.5724 \text{ (9)} \AA, \quad \alpha = 63.751 \text{ (7)}, \quad \beta = 82.039 \text{ (7)}, \quad \gamma = 88.534 \text{ (8)}^\circ
\]

\[ V = 744.7 \text{ (1)} \AA^3, \quad Z = 2, \quad D_\text{exp} = 1.358 \text{ g cm}^{-3}, \quad \lambda(\text{Mo } K\alpha) = 0.71073 \text{ Å}, \quad \mu = 0.75 \text{ cm}^{-1}, F(000) = 328, \quad T = 294 \text{ K}, \quad R = 0.0392 \text{ for 2372 independent reflections.}
\]

(b) \[ M_2 = 304.44, \text{triclinic, } P\overline{1}, \quad a = 6.4193 \text{ (6)}, \quad b = 10.812 \text{ (1)}, \quad c = 11.302 \text{ (1)} \AA, \quad \alpha = 90.180 \text{ (7)}, \quad \beta = 94.073 \text{ (7)}, \quad \gamma = 105.190 \text{ (7)}^\circ
\]

\[ V = 754.8 \text{ (1)} \AA^3, \quad Z = 2, \quad D_\text{exp} = 1.340 \text{ g cm}^{-3}, \quad \lambda(\text{Mo } K\alpha), \mu = 0.75 \text{ cm}^{-1}, F(000) = 328, \quad T = 300 \text{ K}, \quad R = 0.0362 \text{ for 1784 independent reflections.}
\]

The diastereoisomers consist of a cage composed of six fused five-membered rings containing a ketone moiety bonded to a cage composed of four fused five-membered rings and a four-membered ring. There are no short inter- or intramolecular interactions; however, \((5a)\) is more dense than \((5b)\) and it is calculated to be 5.2 kJ mol\(^{-1}\) less strained.

Fig. 1. Compound \(9a\) with thermal ellipsoids drawn at the 25\% probability level. H atoms are represented by spheres of arbitrary size.

Fig. 2. Compound \(9b\) with thermal ellipsoids drawn at the 25\% probability level. H atoms are represented by spheres of arbitrary size.

© 1989 International Union of Crystallography

structures have been determined via single crystal X-ray crystallographic analysis (Figure 11). We plan next to reduce each material to the corresponding hydrocarbon via Wolf-Kishner reduction.

In addition, we have studied the corresponding Ti(0)-promoted dimerization of trishomocubanone 10. In the case of 10, only two diastereoisomeric C_{22}H_{24} dimers are possible [meso (11a) and d,l (11b, Figure 12)]. Both 11a and 11b have been isolated and have been fully characterized. In addition, the structure of each compound has been determined via single crystal X-ray crystallographic analysis (Figure 12). Importantly, both of these compounds possess unusually high densities: i.e., 11a: mp 246 °C, density 1.302 g/cc; 11b: mp 186 °C, density 1.269 g/cc. (For comparison, the density of cubane is 1.29 g/cc).

In a separate study, we have obtained a mixture of pinacols (i.e., 12a and 12b) via dimerization of 10 with sodium in refluxing xylene (Figure 13). Recently we have successfully performed the acid-promoted pinacol rearrangement of each of these diols to the corresponding spiroketones (i.e., 13a and 13b, respectively). The X-ray structure of spiroketone 13b (which results from pinacol rearrangement of d,l diol 12b) is shown in Figure 13. Once both spiroketones 13a and 13b have been fully characterized and synthesized in multigram quantities, we plan to convert each of them to the corresponding hydrocarbons via Wolff-Kishner reduction.

Recently, we completed a study of the corresponding Ti(0)-promoted dimerization of homocubanone, 14. In our hands, reaction of 14 with TiCl_{4}-Zn afforded the corresponding pinacol (15, 21%) along with homocubanol (Figure 14). The structure of the pinacol was established via analysis of its 	extsuperscript{1}H and 	extsuperscript{13}C NMR spectra. The proton noise-decoupled 	extsuperscript{13}C NMR spectrum of 15 displayed only five resonances, consistent with the fact that 15 possesses two twofold symmetry elements.

Despite several attempts, we were unable to promote titanium-induced deoxygenation of
Synthesis and Reactions of meso- and dl-D₃-Trishomocubylidene-D₃-trishomocubane

Alan P. Marchand,*¹ G. Madhusudhan Reddy,¹ Mahendra N. Deshpande,¹
William H. Watson,*¹ Ante Nagl,¹ Oh Seuk Lee,¹ and Eiji Osawa*¹

Contribution from the Department of Chemistry, University of North Texas,
Denton, Texas 76203-3068, the Department of Chemistry, Texas Christian University,
Fort Worth, Texas 76129, and the Department of Chemistry, Faculty of Science, Hokkaido
University, Sapporo 060, Japan. Received April 26, 1989.
Revised Manuscript Received December 2, 1989

Scheme I

Scheme II

Scheme III

Figure 1. (Top) structure drawing of 11a (bottom) structure drawing of 11b
Formation of Diastereoisomeric Pinacols via Reductive Coupling of D₃-Trishomocubanone

BY WILLIAM H. WATSON* AND ANTE NAGL†

Materials Research Laboratory, Department of Chemistry, Texas Christian University, Fort Worth, Texas 76129, USA

AND ALAN P. MARCHAND* AND G. MADHUSUDHAN REDDY

Department of Chemistry, University of North Texas, Box 5068, Denton, Texas 76203, USA

(Received 24 February 1989; accepted 17 May 1989)

Abstract. Spiro[pentacyclo[7.3.0.0₄₁₈.0.0₁₂.0.0⁻⁴]decan-2-one-3,1₁'-pentacyclo[6.3.0.0₄₁₈.0.0₁₂.0.0⁻³]undecane] 13b, C₇₇H₁₂O, M, = 303.43, monoclinic, C2/c, a = 20.593 (3), b = 6.645 (1), c = 26.061 (4) Å, β = 121.78 (1)°, V = 3032.3 (9) Å³, Z = 8, D, = 1.13 g cm⁻³, µ = 0.74 cm⁻¹, F(000) = 1312, T = 298 K, R = 0.0439 for 1731 reflections. Compound 13b consists of two spiro-fused cage systems. One cage is composed of three fused norbornane (bicyclo[2.2.1]heptane) moieties, while the other contains two norbornane and one bicyclo[2.2.2]octane moiety. The spiro fusion involves the methano bridge of one norbornane and the ethano bridge of the bicyclo[2.2.2]octane group. The ideal envelope conformations of the five-membered rings comprising the norbornane moieties are significantly twisted by the ring fusions with the normal 0° torsion angles from 16.6 (2) to 28.5 (2)°. The bicyclooctane system also exhibits large twist distortions.
As an alternative, 15 was heated (165 °C) with triethyl orthoformate in the presence of benzoic acid, thereby affording the corresponding cyclic orthoformate, 16, in 95% yield. Excess triethyl formate was removed, and the residual orthoformate ester (16) was heated strongly with benzoic acid (200 °C). This procedure afforded homocubylidenehomocubane, 17 in good yield (90% from 15, ca. 18% overall from homocubanone; see Figure 14). The proton noise-decoupled $^{13}$C NMR spectrum of 17 contained only four absorption lines, consistent with the suggested structure.

Unequivocal confirmation of the structure of 17 was secured via single crystal X-ray structural analysis (Figure 15). A particularly noteworthy feature of 17 is the unusually high value of its crystal density as calculated from unit cell parameters, i.e., 1.38 g-cm$^{-3}$.

It was of interest to study the acid promoted pinacol rearrangement of 15. Thus, treatment of 15 with concentrated sulfuric acid at -10 °C afforded the corresponding pinacolone (i.e., spiroketone 18) in 61% yield (Figure 14). Compound 18 contains spirocyclic basketanone and homocubane moieties; its spirocyclic nature is confirmed by the presence of a quaternary carbon resonance at δ67.77 in its $^{13}$C NMR spectrum. The structure of 18 was established unequivocally by X-ray crystallographic methods (see Figure 16).

In addition, homocubane is known to undergo Ag(I)-promoted rearrangement to norsnoutane. It was of interest to determine whether a similar homocubane-norsnoutane rearrangement would occur in 17 or if Ag(I) would react preferentially with the C=C double bond in this substrate. In fact, the former process occurred when a benzene solution of 17 was treated with silver nitrate-impregnated silica gel at room temperature for 6 days. The structure of the rearranged product, 19 (Figure 14), was elucidated by single crystal X-ray structural analysis (see Figure 17).
**Figure 14**

14 → 15 (21%)

14 → 16 (95%)

16 → 17 (95%)

17 → 19 (30%)

18 (61%)

concd H₂SO₄
-10 °C, 1 h

TiCl₄, Zn
pyridine
THF, argon

HC(OEt)₃, PhCO₂H
165 °C, 3 h

AgNO₃
S₁₀₂
benzene

CF₃CO₂H, CHCl₃
reflux 6 h

Br₂, CHCl₃
25 ºC
6 h

(24%)
III. Ring Homologations of Substituted PCUD-8,11-diones. Ring expansion reactions of cage ketones have been utilized extensively as a method for synthesizing new polycyclic ring systems. In general, four basic methods have proved to be practical in this regard: (i) the use of diazo compounds (e.g., diazomethane or diazoesters, Method A), (ii) nitrous acid-promoted deamination reactions (i.e., Tieffenau-Demjanov ring expansions, Method B), (iii) Fe(III)-promoted ring opening of 1-trimethylsilyloxybicyclo[n.1.0]alkanes (i.e., the procedure developed by Saegusa and coworkers, Method C), and (iv) transition metal-promoted carbonyl insertion reactions (Method D). Representative examples of each type of ring expansion process are shown in Table II.

Diazomethane-promoted ring expansion processes often display very low regioselectivities, with the consequence that several products are formed, each in relatively low isolated yield. In the case of ring expansions that are promoted by ethyl diazoacetate (EDA) in the presence of boron trifluoride etherate, it is generally the less substituted of the two \( \alpha \)-carbon atoms that migrates preferentially, thereby affording at least some degree of regioselectivity in the ring homologation process. However, when \( \alpha \)-halo ketones are employed as substrates in reactions with EDA-F\(_3\)B.OEt\(_2\), regiospecific migration of the non-halogenated \( \alpha \)-carbon center occurs (e.g., \( 20 \to 21 \) and \( 22 \to 23 \), see Table II).

In addition, we have utilized formal intramolecular [\( \sigma^2 + \pi^2 \)] photocycloaddition of an enedione C=C double bond to a strained epoxide carbon-carbon \( \sigma \)-bond to prepare a new, ring-expanded heterocyclic cage system. Thus, irradiation of an acetonitrile solution of epoxide \( 24 \) with a 450 watt medium pressure mercury lamp (Vycor filter) at 30 °C for 2 h resulted in intramolecular alkene-oxirane photocyclization, thereby affording 5-oxapentacyclo[7.3.0.0\(^3\),0\(^7\),0\(^4\),12\(^6\),0\(^10\)]dodecane-2,8-dione (25, Figure 18) in 21% yield. Attempts to promote similar intramolecular [\( 2 + 2 \)] photocyclization of \( 26 \) to \( 27 \) (Figure 18) were unsuccessful.
Table II. Ring Homologations of Cage Ketones

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Method</th>
<th>Experimental Conditions</th>
<th>Product (% yield)</th>
<th>References</th>
</tr>
</thead>
</table>
| ![Substrate](image1.png) | A | CH$_2$N$_2$ (excess), Et$_2$O  
0 °C, 3 days | ![Product](image2.png) | 32 |
| ![Substrate](image3.png) | A | CH$_2$N$_2$ (excess), Et$_2$O  
0 °C, 3 days | ![Product](image4.png) | 32, 33 |
| ![Substrate](image5.png) | A | X = H: EDA (2 equiv.),  
F$_3$B.OEt$_2$, -78 °C + -40 °C  
X = OMe: EDA (excess),  
F$_3$B.OEt$_2$, -70 °C + +25 °C | ![Product](image6.png) | 34a (X = H)  
34b (X = OMe) |
| ![Substrate](image7.png) | A | EDA (1 equiv.), F$_3$B.OEt$_2$  
0 °C + +25 °C (X = Me, Ph)  
-20 °C + +25 °C (X = p-C$_6$H$_4$CN)  
-78 °C + -20 °C (X = p-C$_6$H$_4$OMe) | ![Product](image8.png) | 35 |
| ![Substrate](image9.png) | A | EDA (excess), F$_3$B.OEt$_2$  
0 °C + +25 °C | ![Product](image10.png) | 36 |

(X = H or OMe)
<table>
<thead>
<tr>
<th>Substrate</th>
<th>Method</th>
<th>Experimental Conditions</th>
<th>Product (% yield)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>EDA (1 equiv.), F$_3$B-OEt$_2$ -78 °C</td>
<td><img src="image" alt="Product A" /> + <img src="image" alt="Product B" /> (product ratio: 15 : 1)</td>
<td></td>
<td>37</td>
</tr>
<tr>
<td>B</td>
<td>(i) CH$_3$NO$_2$, NaOH, MeOH (ii) H$_2$, Pd/C (iii) NaNO$_2$, HOAc, 0 °C (iv) TsOH, CHCl$_3$, 50 °C, 1 h</td>
<td><img src="image" alt="Product C" /> (X = H: 14% 56%) (X = Me: 26% 39%)</td>
<td></td>
<td>36</td>
</tr>
<tr>
<td>C</td>
<td>(i) CH$_2$I$_2$, Et$_2$Zn, Et$_2$O, then dry O$_2$ (ii) anhydrous FeCl$_3$, DMF (iii) activated MnO$_2$ (6 equiv.), CH$_2$Cl$_2$, +25 °C, 6 h (iv) hv, Pyrex filter, EtOAc</td>
<td><img src="image" alt="Product D" /> (29% overall)</td>
<td></td>
<td>38b</td>
</tr>
<tr>
<td>D</td>
<td>(i) Rh$_2$(CO)$_4$Cl$_2$ (1 equiv.) (ii) Ph$_3$P (excess), CH$_2$Cl$_2$</td>
<td><img src="image" alt="Product E" /> (90%)</td>
<td></td>
<td>39</td>
</tr>
<tr>
<td>Substrate</td>
<td>Method</td>
<td>Experimental Conditions</td>
<td>Product (% Yield)</td>
<td>References</td>
</tr>
<tr>
<td>-----------</td>
<td>--------</td>
<td>--------------------------</td>
<td>------------------</td>
<td>------------</td>
</tr>
<tr>
<td><img src="image1.png" alt="Substrate" /></td>
<td>D</td>
<td>(1) Rh₂(CO)₄Cl₂, dry benzene (ii) Ph₃P (excess)</td>
<td><img src="image2.png" alt="Product" /></td>
<td>40</td>
</tr>
<tr>
<td>(X = H or OH)</td>
<td></td>
<td></td>
<td>(X = H, 99%) (X = OH, 92%)</td>
<td></td>
</tr>
<tr>
<td><img src="image3.png" alt="Substrate" /></td>
<td>D</td>
<td>Rh₂(CO)₄Cl₂, dry benzene 80 °C, 72 h</td>
<td><img src="image4.png" alt="Product" /></td>
<td>40</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(28%) (56%)</td>
<td></td>
</tr>
</tbody>
</table>
FIGURE 18

24 \xrightarrow{h\nu, \text{ Vycor filter}} 25 (21%)  
$\text{CH}_3\text{CN}, 30 ^\circ \text{C}$

26 \xrightarrow{(\text{as above})} 27 (0%)

\text{CO}_2\text{Me}
References & Footnotes


2. For a review of the synthesis of polynitropolycyclic cage compounds, see: Marchand, A. P. Tetrahedron 1988, 44, 2377.

3. For a review of the synthesis and chemistry of homo-, bishomo- and trishomocubanes, see: Marchand, A. P. Chem. Rev. 1989, 89, 1027.


13. Calculations were performed by Dr. Oscar Sandus, U. S. Army Research, Development and
Engineering Center, Picatinny Arsenal, NJ.


15. G. W. Burdette and K. Schadow, personal communication.


23. Note that the densities of 11a and 11b differ markedly despite the fact that these hydrocarbons are diastereoisomers. Such configurational dependence of density has been noted by other investigators. See: Paquette, L. A.: Nakamura, K.; Engel, P. Chem. Ber. 1986, 119, 3782.


35


LIST OF PUBLICATIONS (1988-1991) THAT ACKNOWLEDGE SUPPORT
UNDER GRANT NO. APOS8-88-0132


8. Watson, W. H.; Nagl, A.; Marchand, A. P.; Reddy, G. M. "Structure of the Product Formed via Regiospecific Cyclopropanation of


“Tiekenau-Demjanov Ring Homologations of Two Pentacyclo-

25. Marchand, A. P.; Annapurna, P. “A Convenient Synthesis of 1,7-Dibromo- and
1,7-Dichloropentacyclo[5.4.0.0^2,6.0^3,10.0^5,9]undecane-8,11-diones”, Synth. Commun. 1989,
19, 3477-3483.

26. Watson, W. H.; Nagl, A.; Kashyap, R. P.; Marchand, A. P.; Dave, P. R. “Two Iron(0)


Deshpande, M. N. “Ab Initio Studies of Structural Features Not Easily Amenable to
Experiment: 67. The 4-21G Optimized Structure of a Novel Cage Dimer, C_{22}H_{24}, and

Osawa, E. “Synthesis and Reactions of meso- and d,l-D_3-Trishomocubylidene-

31. Marchand, A. P.; Reddy, G. M. “Enantioselective Microbial Asymmetric Reduction of
Pentacyclo[5.4.0.0^2,6.0^3,10.0^5,9]undecane-8,11-dione”, Tetrahedron Lett. 1990, 31,
1811-1814.


