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91-07414



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

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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-trishomocubylidenetrishomocubane 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.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.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

I. 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).⁶ Also, syntheses of trinitro- and tetranitrotetraphenyl-1,3-bishomocubanes (Figure 5)⁷ and of 8,8,11,11-tetranitropentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]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

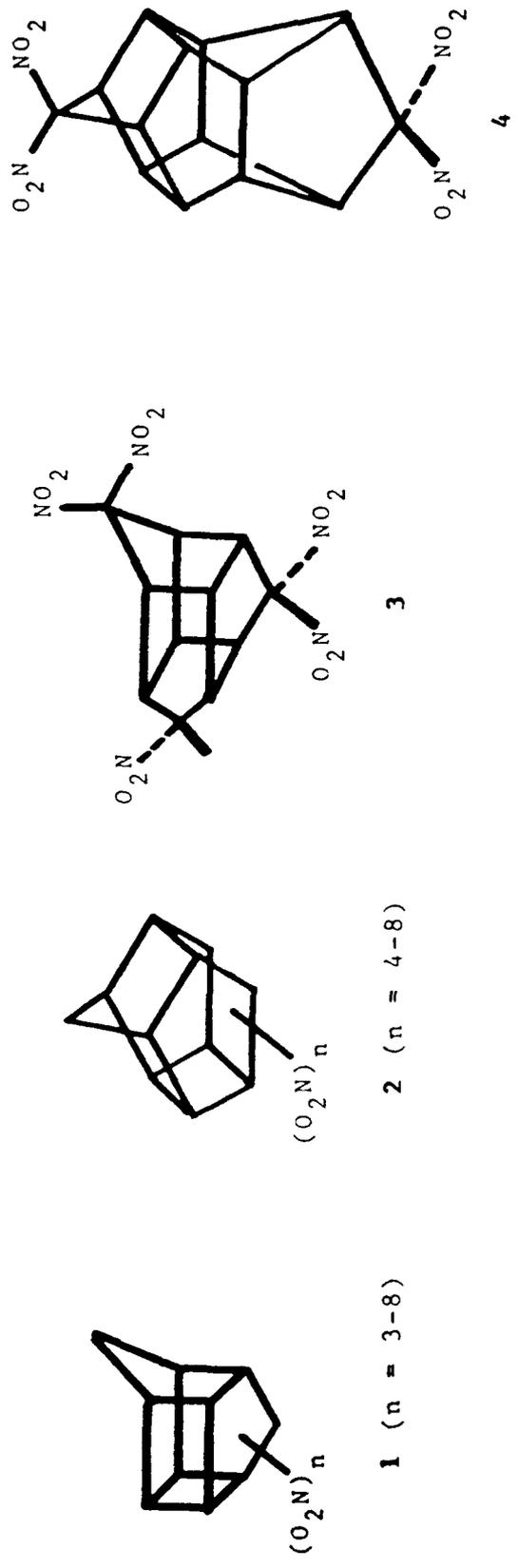
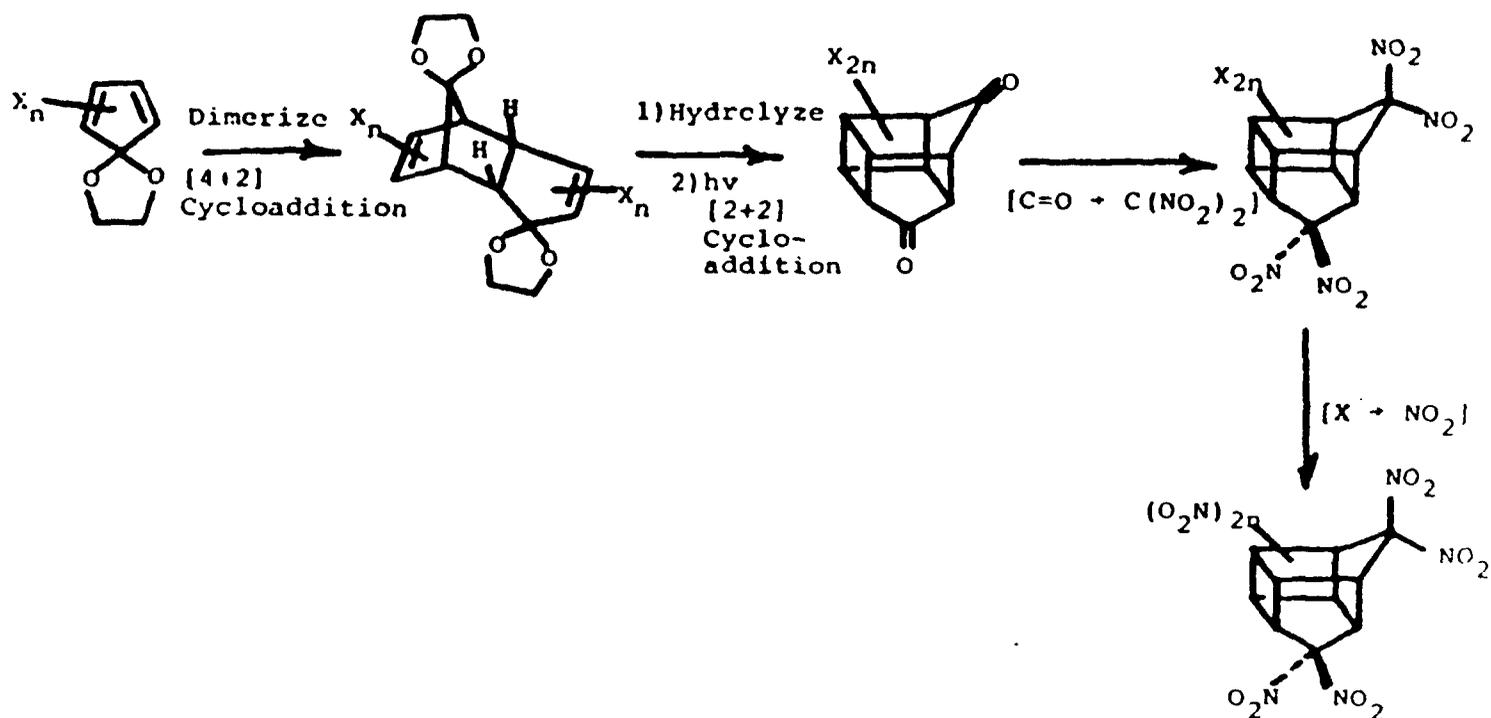
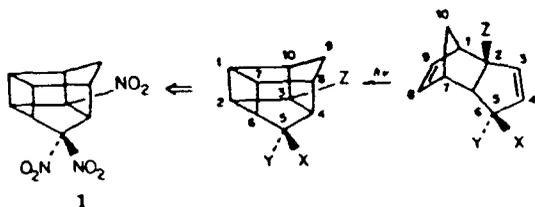


FIGURE 2

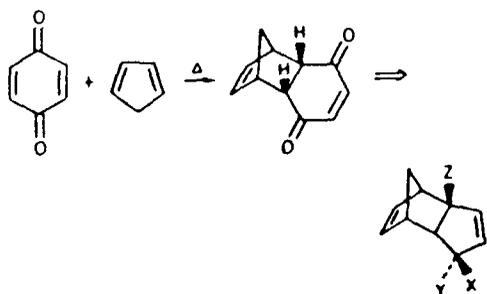


A partial retrosynthetic perspective leading to 1 is shown below.



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^{4,5} and then to geminal dinitro groups.⁶ Subsequent conversion of the carbomethoxyl group in 8 to NO₂ via the sequence shown in Scheme 1^{7,8} completed the synthesis.

The retrosynthesis of 1 is completed below.



Marchand, A. P.; Suri, S. C.

J. Org. Chem. **1984**, *49*, 2041-2043

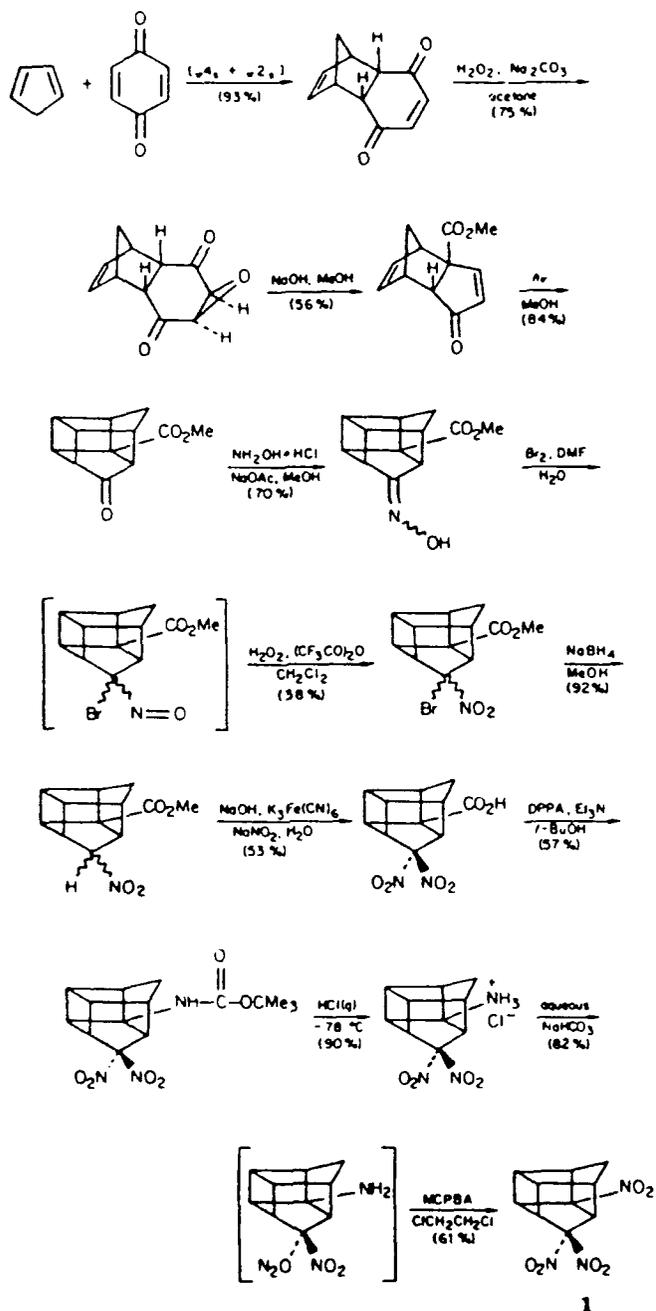
Synthesis of 3,5,5-Trinitropentacyclo[5.3.0.0^{2,4}.0^{3,10}.0^{4,8}]decane

Alan P. Marchand* and Suresh Chander Suri

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

J. Org. Chem. 1984, 49, 2041-2043

Scheme 1



(n = 3)

Synthesis of 5,5,9,9-Tetranitropentacyclo[5.3.0.0^{2,6}.0^{3,10}.0^{4,8}]de- cane

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

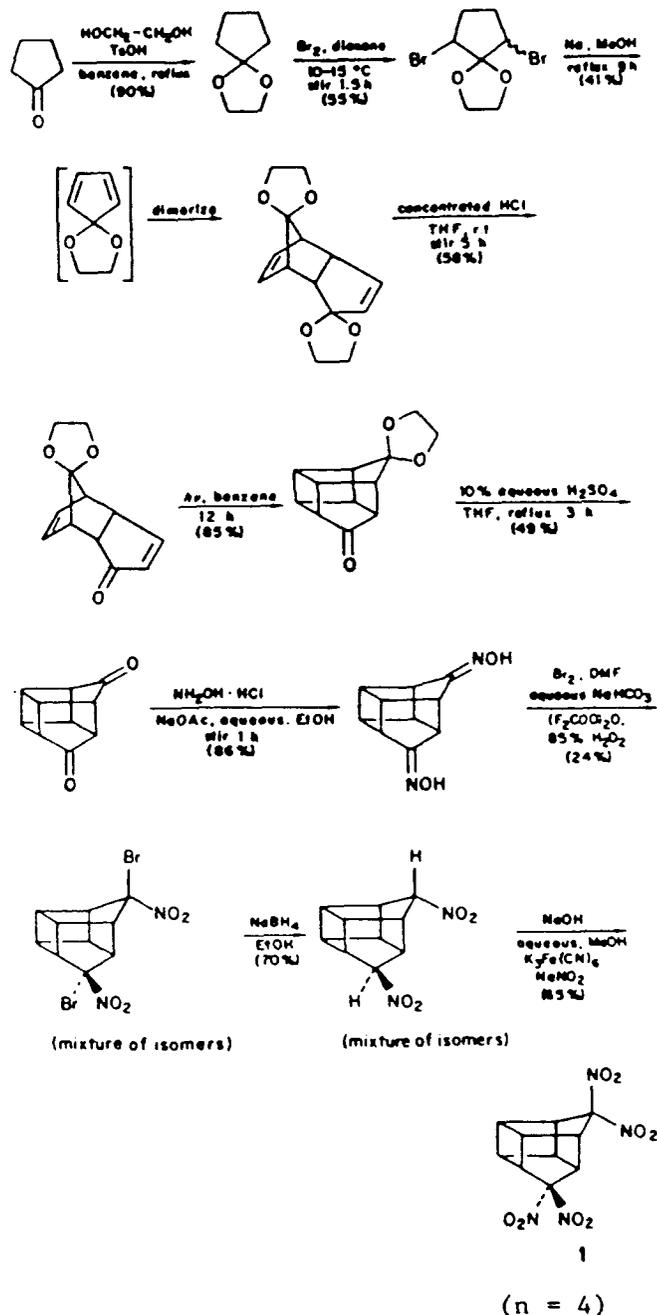
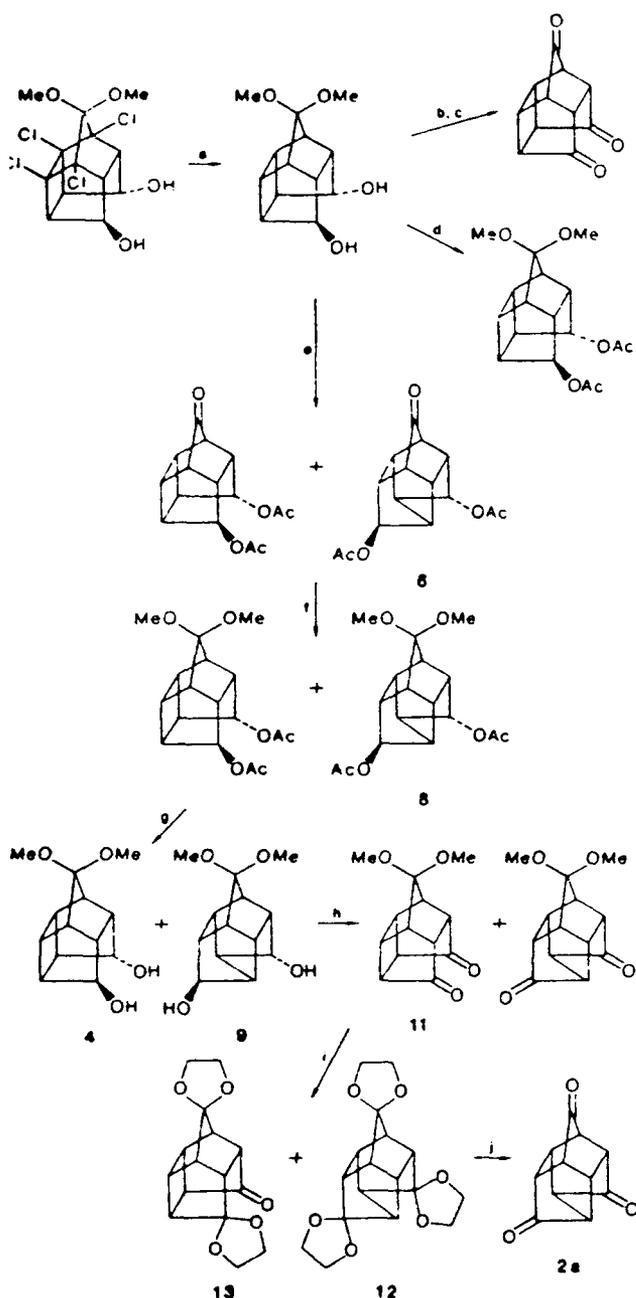


FIGURE 4

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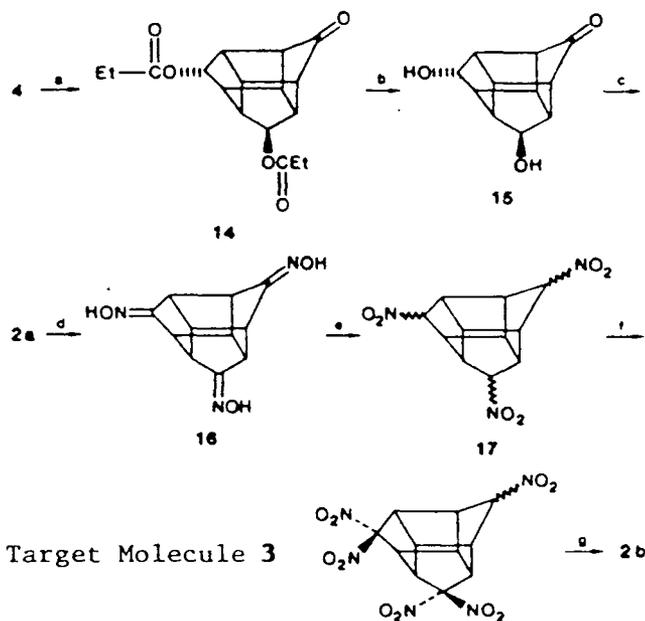
Scheme I^{a,b}

^a (a) Li, *t*-BuOH, THF, liquid NH₃, -33 °C (92%); (b) excess 10% aqueous HCl, reflux 4 h (100%); (c) PCC, CH₂Cl₂ (100%); (d) Ac₂O, pyridine, room temperature, 10 h (87%); (e) glacial HOAc, concentrated H₂SO₄, 150 °C (sealed tube), 42 h (55%); (f) HC(OAc)₂, TsOH (catalytic amount), overnight at room temperature (91%); (g) LiAlH₄, THF-Et₂O, room temperature, 6 h (95%); (h) PDC, CH₂Cl₂, room temperature, 4 days (90%); (i) HOCH₂CH₂O-H, TsOH (catalytic amount), benzene, reflux 48 h [12 (29%) + 13 (27%)]; (j) concentrated H₂SO₄, CH₂Cl₂, room temperature, 2 days (69%). ^b Stereochemical assignments for, e.g., 6, 8, and 9 were made on the basis of (i) simple mechanistic considerations and (ii) analysis of the ¹H and ¹³C NMR spectra of these compounds.

Syntheses of
 Pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-4,8,11-trione.
 Pentacyclo[6.3.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-4,7,11-trione
 (*D*₃-Trishomocubanetrione), and
 4,4,7,7,11,11-Hexanitro[6.3.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane
 (*D*₃-Hexanitrotrishomocubane)

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 II^{a,b}

Target Molecule 3

^a (a) EtCO₂H, concentrated H₂SO₄, 160 °C, 72 h, N₂ (51%); (b) Na, dry MeOH, room temperature, 1 h (100%); (c) PCC, CH₂Cl₂, room temperature, 2 h (46%); (d) NH₂OH-HCl, NaOAc, aqueous MeOH, 0 °C → room temperature, overnight (70%); (e) (CF₃C-O)₂O, 90% H₂O₂, NaHCO₃, urea, CH₃CN, 70–75 °C, overnight (35%); (f) NaOH, aqueous MeOH, 3 h; then K₃Fe(CN)₆, aqueous NaNO₂, Et₂O, 1 h (65%); (g) NaOH, aqueous MeOH, 24 h; then K₃Fe(CN)₆, aqueous NaNO₂, Et₂O, 12 h (62%). ^b Stereochemical assignments for 14 and 15 were made on the basis of (i) simple mechanistic considerations and (ii) analysis of the ¹H and ¹³C NMR spectra of these compounds.

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**Synthesis of Nitro-Substituted
1,4,8-Tetraphenylpentacyclo[5.3.0.0^{2,6}.0^{4,8}.0^{4,6}]de-
canes**

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

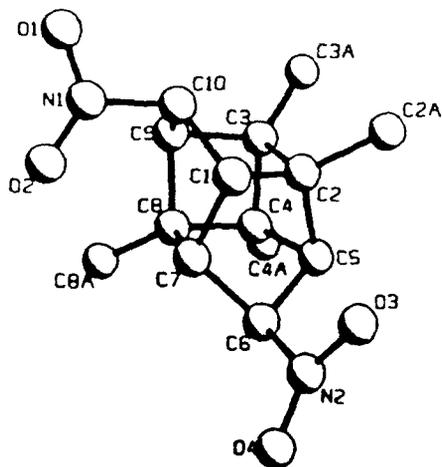
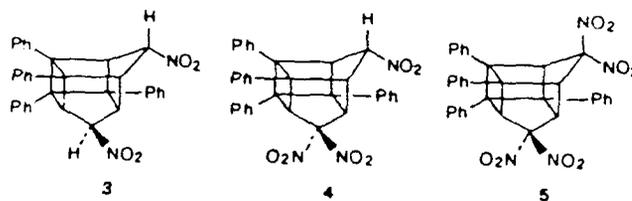
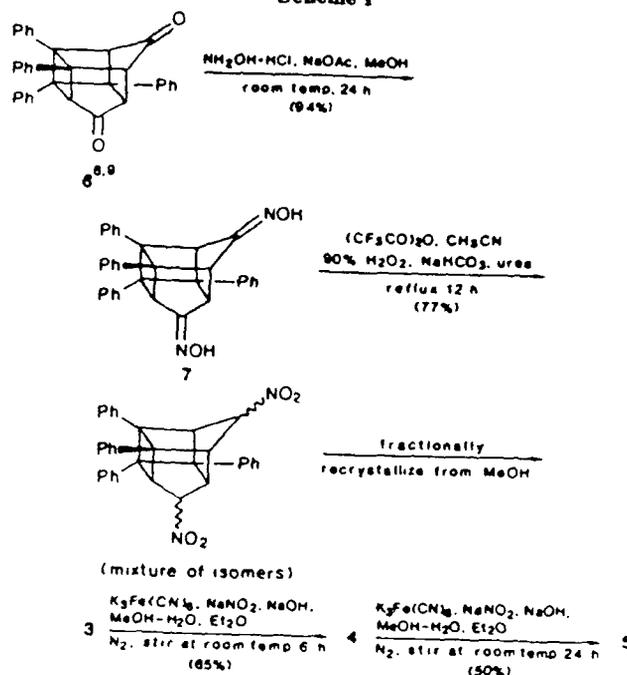


Figure 1. Results of the X-ray study on 3. For clarity, the phenyl groups on C-2, C-3, C-4, and C-8 are represented as single atoms (C-2a, C-3a, C-4a, and C-8a).

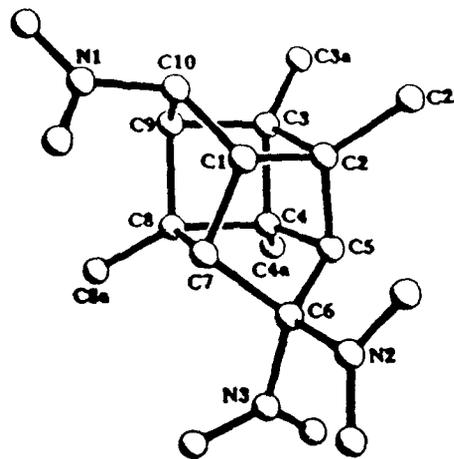


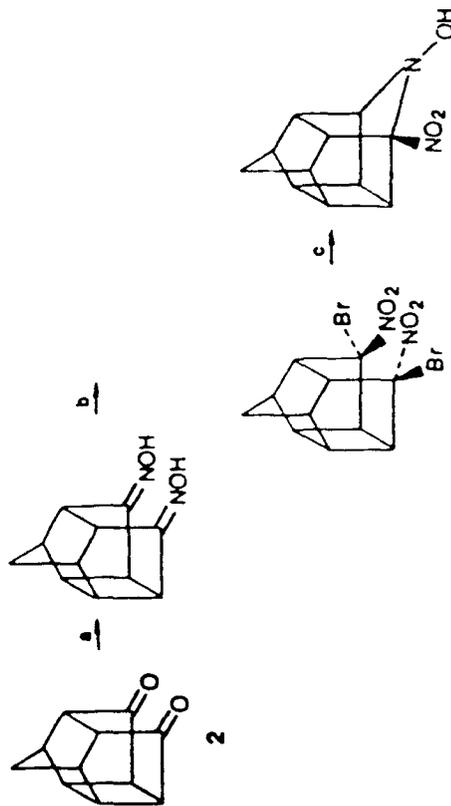
Figure 2. Results of the X-ray study on 4. For clarity, the phenyl groups on C-2, C-3, C-4, and C-8 are represented as single atoms (C-2a, C-3a, C-4a, and C-8a).

Synthesis of 8,8,11,11-Tetranitropentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{6,9}]un- decane

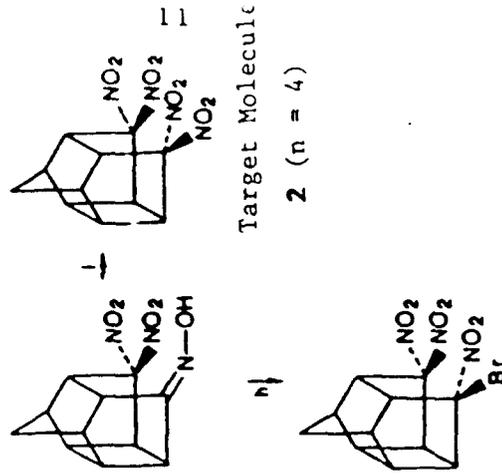
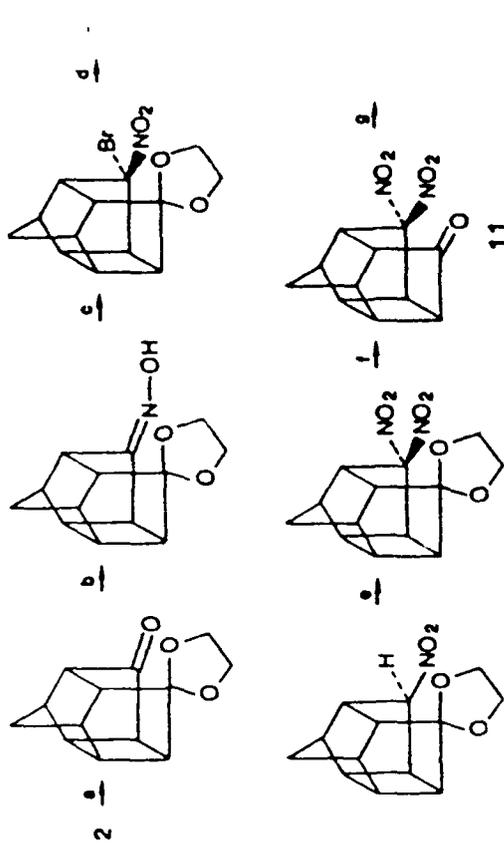
Alan P. Marchand,* Benny E. Arney, Jr., and
Paritosh R. Dave

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

Scheme I^a



* (a) $\text{NH}_2\text{OH}\cdot\text{HCl}$, NaOAc , EtOH (87%); (b) NBS, NaHCO_3 , dioxane, room temperature, 48 h (49%); (c) NaBH_4 , 60% aqueous EtOH , room temperature, 45 min (28%).



Target Molecule

2 (n = 4)

* (a) $\text{HOCH}_2\text{CH}_2\text{OH}$, TsOH , benzene, Dean-Stark tube (92%); (b) $\text{NH}_2\text{OH}\cdot\text{HCl}$, NaOAc , EtOH , room temperature, overnight (79%); (c) Br_2 , NaHCO_3 , DMF , 0°C , and then O_3 , CH_2Cl_2 , 0°C (80%); (d) NaBH_4 , 60% aqueous EtOH , room temperature, 0.5 h (97%); (e) $\text{K}_3\text{Fe}(\text{CN})_6$, NaNO_2 , aqueous MeOH , NaOH , room temperature, 0.5 h (3%); (f) concentrated H_2SO_4 , CH_2Cl_2 , room temperature, overnight (73%); (g) $\text{NH}_2\text{OH}\cdot\text{HCl}$, NaOAc , EtOH , room temperature, overnight (89%); (h) NBS, NaHCO_3 , 5% aqueous dioxane, room temperature, 72 h (65.7%); (i) 98% red HNO_3 , NH_4NO_3 , CH_2Cl_2 , reflux 1 h, then 30% H_2O_2 , reflux 1 h (31%, 64% based on recovered 11).

FIGURE 6

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**Synthesis of
 4,4,8,8,11,11-Hexanitropentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{4,9}]-
 undecane**

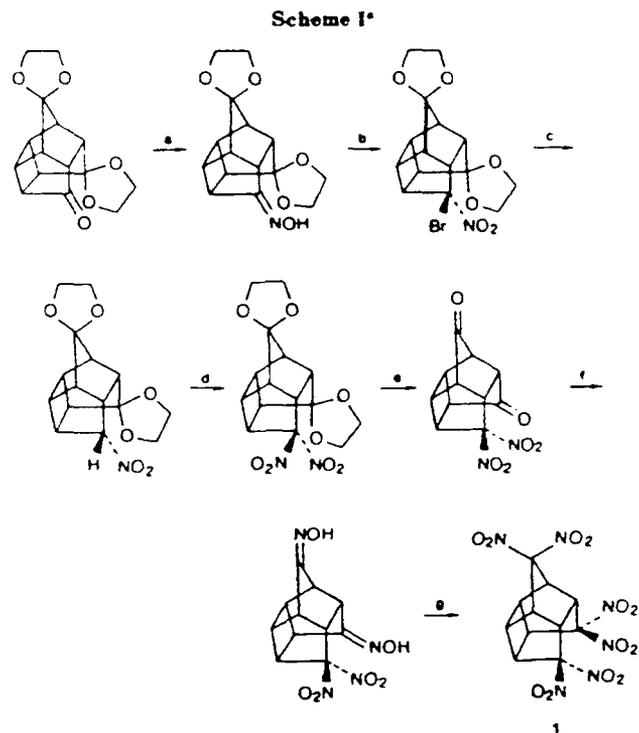
Alan P. Marchand,* Paritosh R. Dave, D. Rajapaksa, and
 Benny E. Arney, Jr.

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

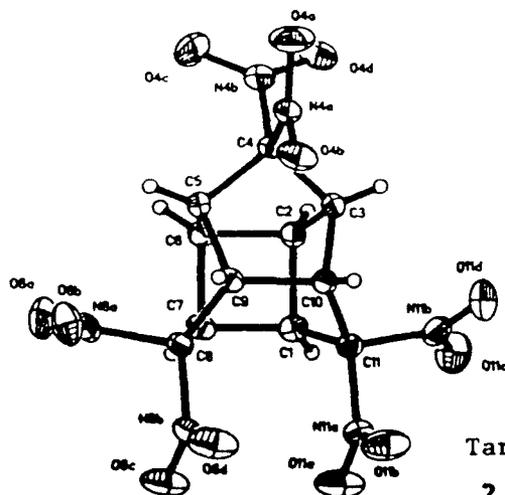
Judith L. Flippen-Anderson,* Richard Gilardi, and
 Clifford George

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

FIGURE 7



* (a) $\text{NH}_2\text{OH}\cdot\text{HCl}$, K_2CO_3 , EtOH, reflux 24 h (79%); (b) NBS, dioxane, room temperature, overnight (62%); (c) NaBH_4 , 60% aqueous EtOH, 0 °C \rightarrow room temperature, 1 h (84%); (d) $\text{K}_3\text{Fe}(\text{CN})_6$, NaNO_2 , aqueous MeOH, room temperature, 2 h (83%); (e) concentrated H_2SO_4 , CH_2Cl_2 , room temperature, 24 h (50%); (f) $\text{NH}_2\text{OH}\cdot\text{HCl}$, NaOAc, MeOH, reflux 2 h (75%); (g) 98% red nitric acid, NH_4NO_3 , urea, dry CH_2Cl_2 , reflux 0.5 h, then 30% aqueous H_2O_2 , reflux 15 min (19%).



Target Molecule
 2 (n = 6)

Figure 1. X-ray structure drawing of 1.

groups should be straightforward. In addition, we have made progress toward the synthesis of more highly substituted heptacyclo[6.6.0.0^{2,6}.0^{3,13}.0^{4,11}.0^{5,9}.0^{10,14}]tetradecanes (see Figure 8).¹¹

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.¹ The parent hydrocarbon, pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]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).¹² 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.¹³ 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.¹⁴ 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.¹⁵

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.

Acta Cryst. (1989). C45, 1171-1174

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

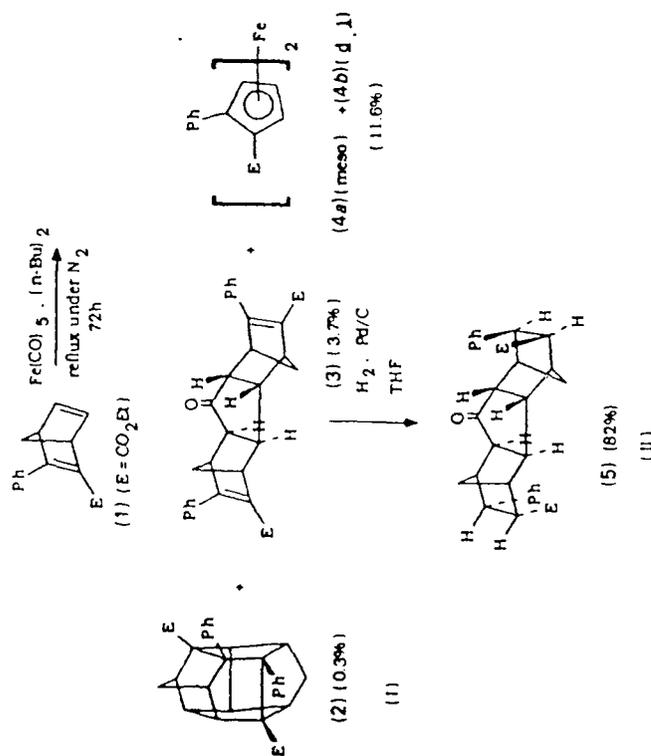
BY JUDITH L. FLIPPEN-ANDERSON,* RICHARD GILARDI AND CLIFFORD GEORGE

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)



Scheme 1

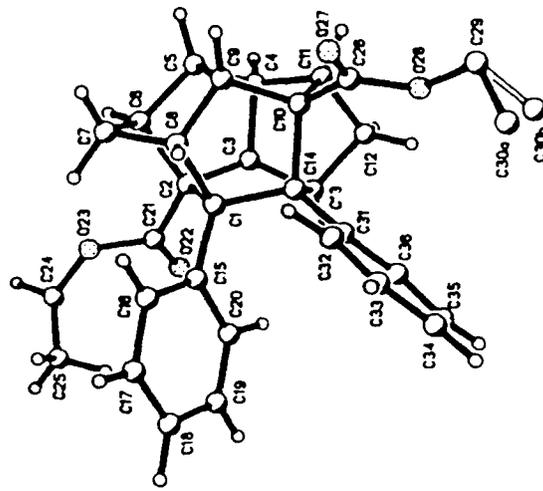


Fig. 1. Diagram of (I) as determined by X-ray diffraction. The two positions for the disordered methyl groups on C(29) are shown [C(30a) and C(30b)].

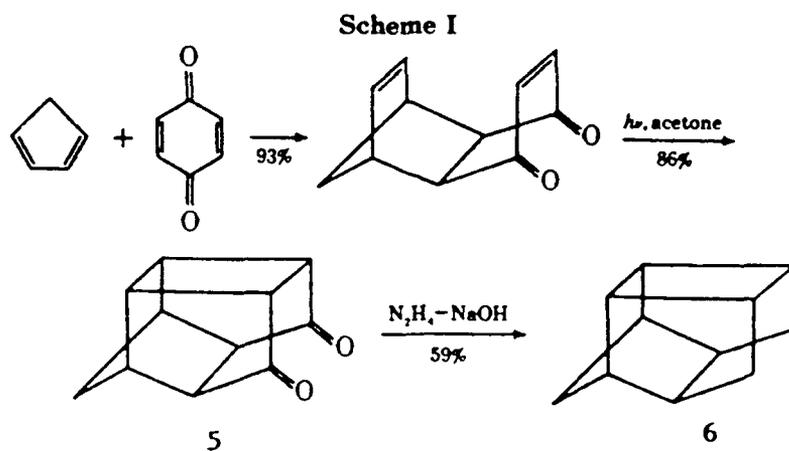
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An Improved Synthesis of Pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane

Alan P. Marchand* and Robert W. Allen

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

Received December 27, 1973

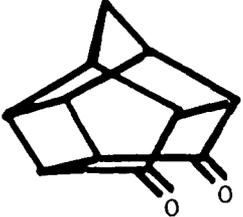
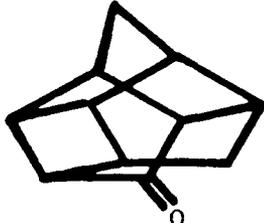
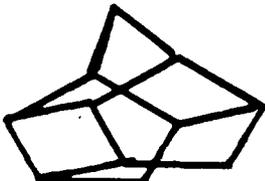
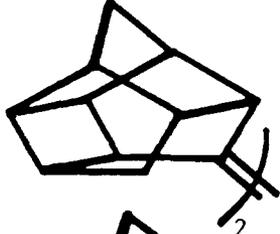
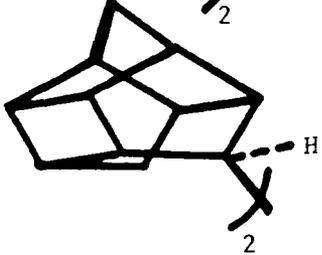


The calculated values that appear in Table I suggest that PCUD dimers indeed should possess unusually high, positive standard heats of formation and unusually high densities.¹³ Accordingly, we have investigated the Ti(O)-promoted dimerization¹⁶ of PCUD-8-one (7) as part of a project that has received financial support from the U. S. Air Force.¹⁷ The results of this reaction are summarized in Figure 10.¹⁸ All four possible C₂₂H₂₄ 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).¹⁹ 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 predicted¹³ 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 D₃-trishomocubane dimers and related C₂₂H₂₆ 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,^{18a} and their respective

Table I. Calculated standard heats of formation and densities of cage hydrocarbons and cage ketones

Compound	Formula	ΔH_f° (kcal/mol) ^a	Density (g-cm ⁻³) ^b
	C ₁₁ H ₁₀ O ₂	-24.40	1.44 (observed, 1.38)
	C ₁₁ H ₁₂ O	+ 1.51	1.34
	C ₁₁ H ₁₄	+27.42	1.23
	C ₂₂ H ₂₄	+97.54	1.29
	C ₂₂ H ₂₆	+67.76	1.26

^aCalculated values. Method used for calculation of ΔH_f° values: Report on "Study of Pure Explosive Compounds. Part II. Correlation of Thermal Quantities with Explosive Properties"; Office of the Chief of Ordnance, Contract No. W-19-020-6436, Report No. C-57625, 2 April 1947.

^bCalculated values. Method used for calculation of densities: J. R. Stine, "Prediction of Crystal Densities of Organic Explosives by Group Additivity", Los Alamos National Laboratory, Report No. LA-8920, August, 1981.

Acta Cryst. (1988). C44, 1617–1619

Structure of a Novel $C_{22}H_{24}$ 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

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Abstract. 8,11'-Bipentacyclo[5.4.0.^{2.6}.0^{3.10}.0^{5.9}]-undecanylidene, $C_{22}H_{24}$, $M_r = 288.43$, triclinic, $P\bar{1}$, $a = 6.613$ (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, $Z = 2$, $D_x = 1.284$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 0.07$ mm⁻¹, $F(000) = 312$, $T = 295$ 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.

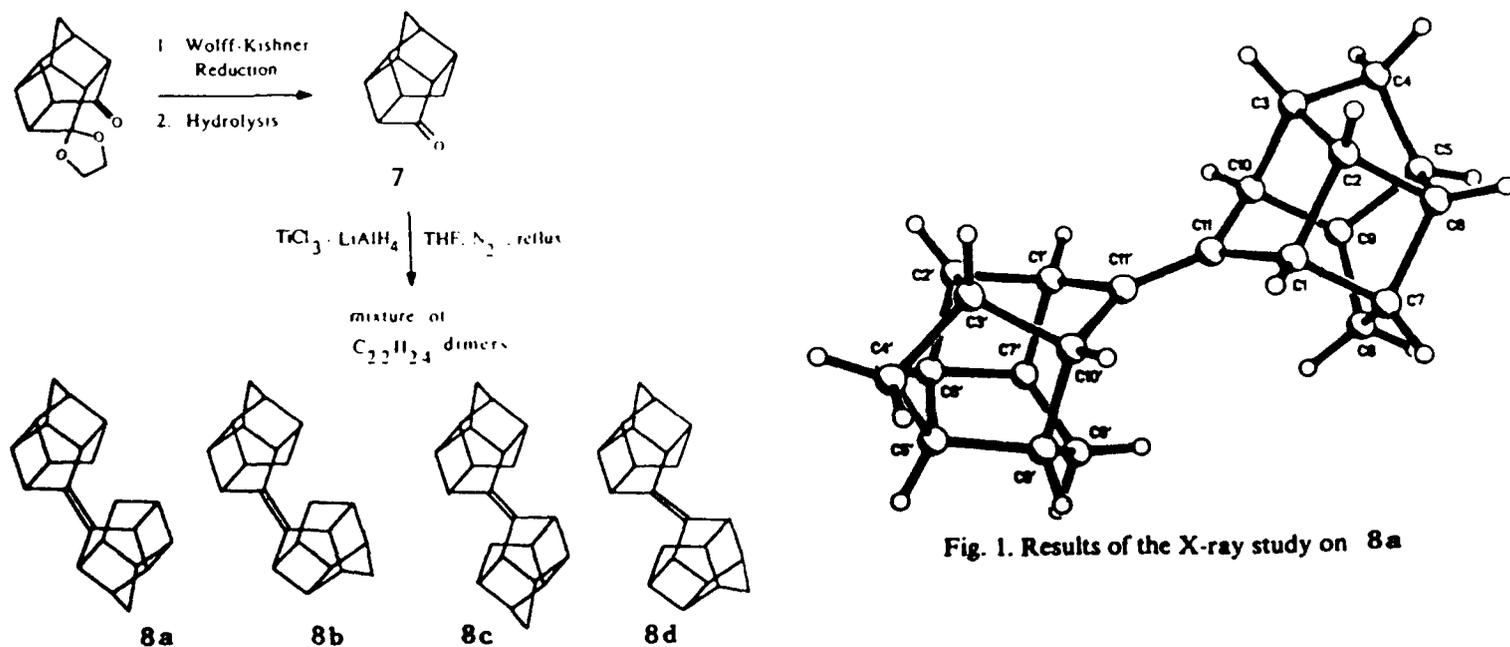


Fig. 1. Results of the X-ray study on 8a

Structures of Two Diastereoisomeric Saturated Polycyclic C₂₂H₂₄O 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^{5.9}]undec-8-yl)pentacyclo[6.3.0.0^{2.6}.0^{3.10}.0^{5.9}]undecan-4-one. (a), $M_r = 304.44$, triclinic, $P\bar{1}$, $a = 6.3469$ (6), $b = 11.425$ (1), $c = 11.5724$ (9) Å, $\alpha = 63.751$ (7), $\beta = 82.039$ (7), $\gamma = 88.534$ (8)°, $V = 744.7$ (1) Å³, $Z = 2$, $D_x = 1.358$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 0.75$ cm⁻¹, $F(000) = 328$, $T = 294$ K, $R = 0.0392$ for 2372 independent reflections. (b), $M_r = 304.44$, triclinic, $P\bar{1}$, $a = 6.4193$ (6), $b = 10.812$ (1), $c = 11.302$ (1) Å, $\alpha = 90.180$ (7), $\beta = 94.073$ (7), $\gamma = 105.190$ (7)°, $V = 754.8$ (1) Å³, $Z = 2$, $D_x = 1.340$ g cm⁻³, $\lambda(\text{Mo } K\alpha)$, $\mu = 0.75$ cm⁻¹, $F(000) = 328$, $T = 300$ K, $R = 0.0362$ 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.

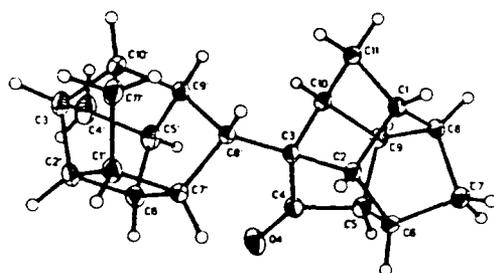


Fig. 1. Compound **9a** with thermal ellipsoids drawn at the 25% probability level. H atoms are represented by spheres of arbitrary size.

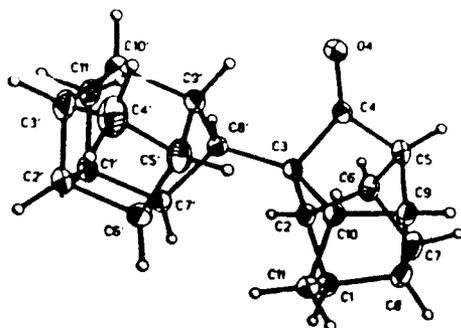
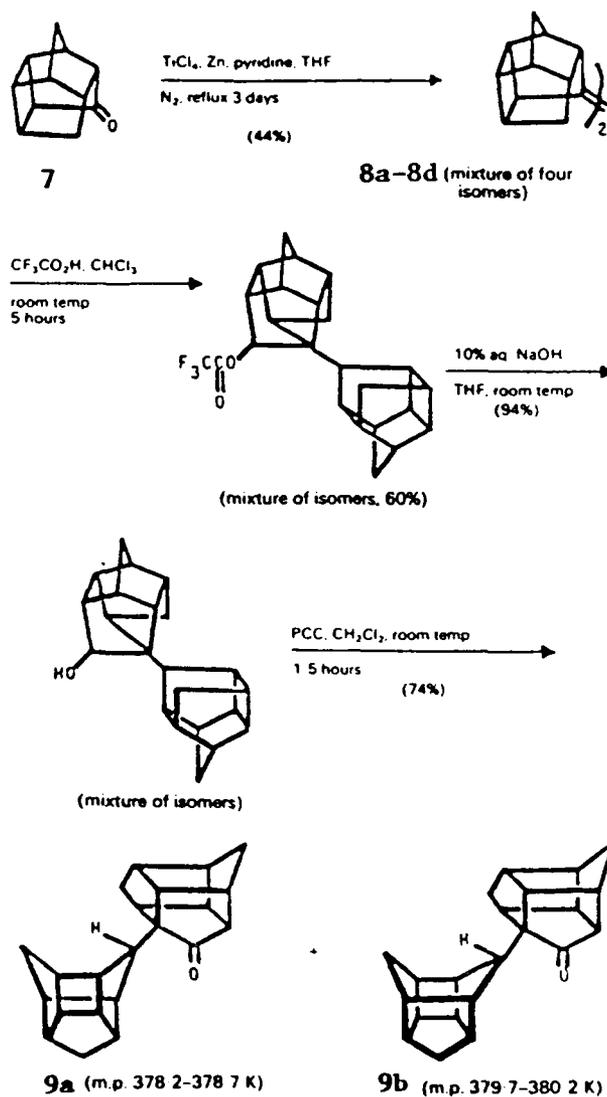


Fig. 2. Compound **9b** with thermal ellipsoids drawn at the 25% probability level. H atoms are represented by spheres of arbitrary size.



Scheme 1

structures have been determined via single crystal X-ray crystallographic analysis (Figure 11).²⁰ 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**.²¹ In the case of **10**, only two diastereoisomeric C₂₂H₂₄ dimers are possible [meso (**11a**) and d,l (**11b**, Figure 12)]. Both **11a** and **11b** have been isolated and have been fully characterized.²² In addition, the structure of each compound has been determined via single crystal X-ray crystallographic analysis (Figure 12).²² 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.^{22,23} (For comparison, the density of cubane is 1.29 g/cc).²⁴

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).²⁵ 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).²⁵ The X-ray structure of spiroketone **13b** (which results from pinacol rearrangement of d,l diol **12b**) is shown in Figure 13.²⁵ 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**.^{26,27} In our hands, reaction of **14** with TiCl₄-Zn²⁸ afforded the corresponding pinacol (**15**, 21%) along with homocubanol (Figure 14). The structure of the pinacol was established via analysis of its ¹H and ¹³C NMR spectra. The proton noise-decoupled ¹³C 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

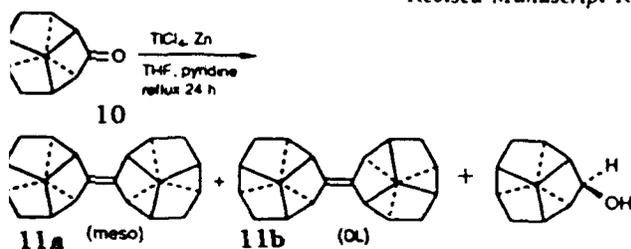
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Synthesis and Reactions of *meso*- and *dl*-*D*₃-Trishomocubylidene-*D*₃-trishomocubane

Alan P. Marchand,^{*,†} G. Madhusudhan Reddy,[†] Mahendra N. Deshpande,[†]
William H. Watson,^{*,‡} Ante Nagl,[†] Oh Seuk Lee,[‡] and Eiji Ōsawa^{*,§}

Contribution from the Department of Chemistry, University of North Texas,
Denton, Texas 76203-5068, 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

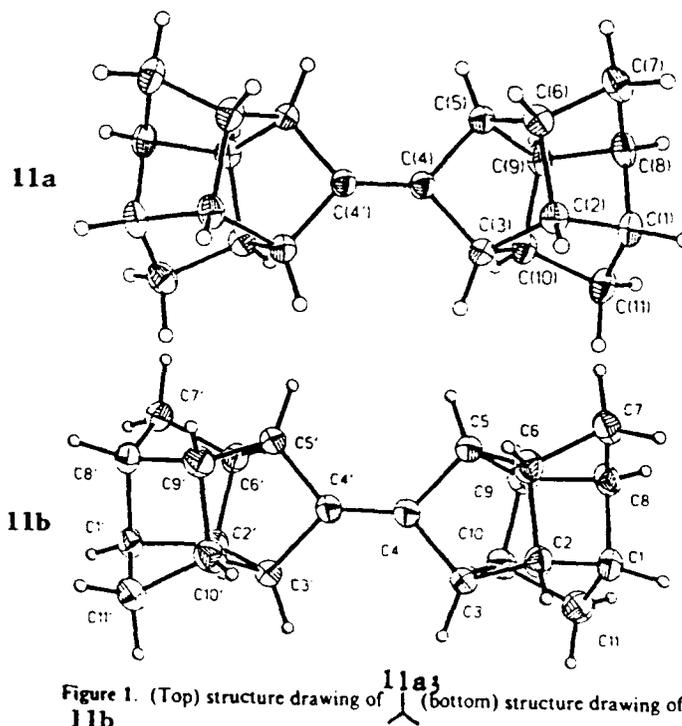
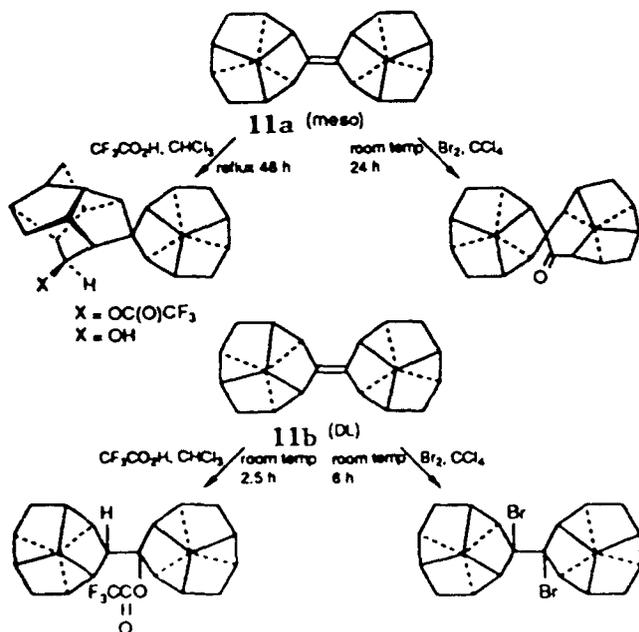
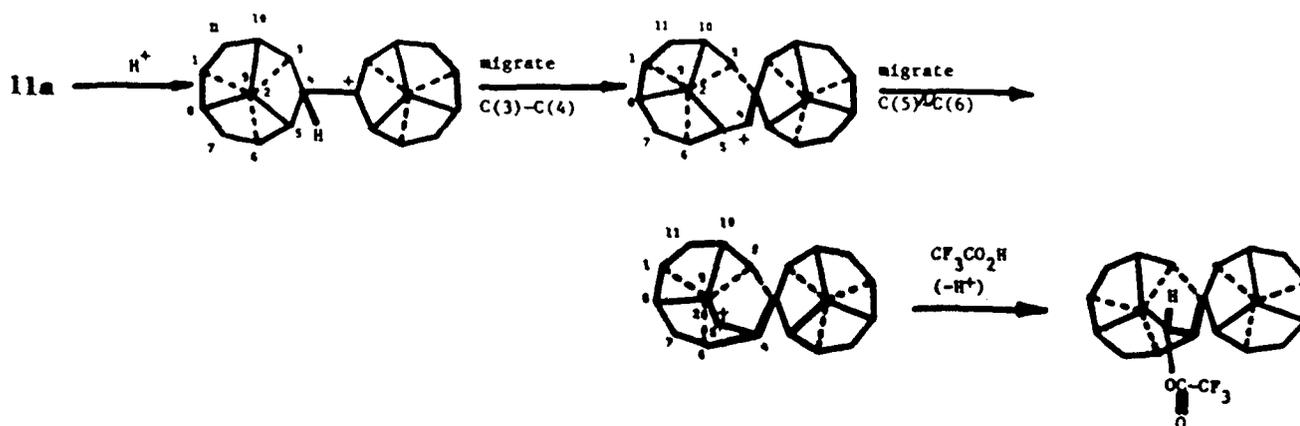


Figure 1. (Top) structure drawing of 11a; (bottom) structure drawing of 11b

Scheme III



Acta Cryst. (1990). C46, 253-256

Formation of Diastereoisomeric Pinacols *via* Reductive Coupling of D_3 -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[7.3.0.0^{4,8}.0^{5,12}.0^{7,11}]dodecan-2-one-3,11'-pentacyclo[6.3.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane] **13b**, C₂₂H₂₄O, *M_r* = 303.43, monoclinic, *C*2/*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_x* = 1.133 g cm⁻³, λ (Mo *K*α) = 0.71073 Å, 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]octanone 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.

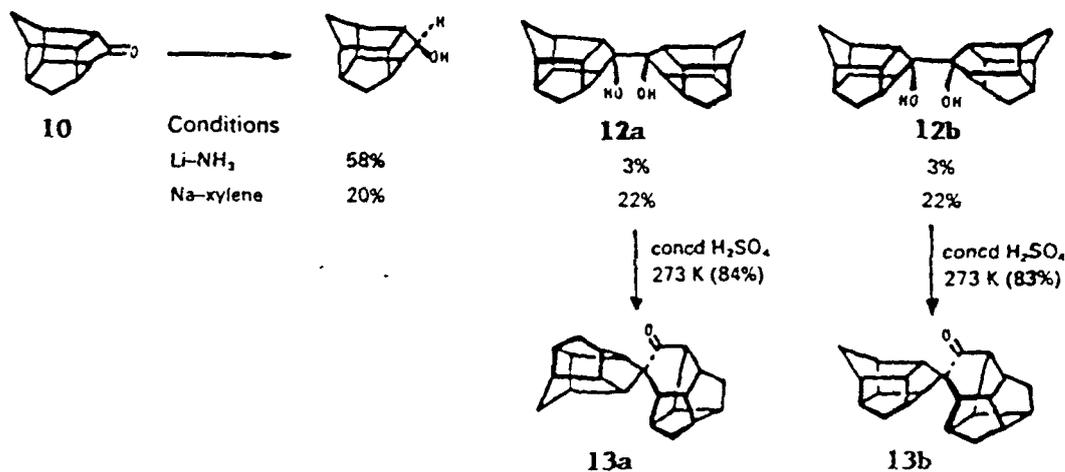


Fig. 1. Synthetic scheme.

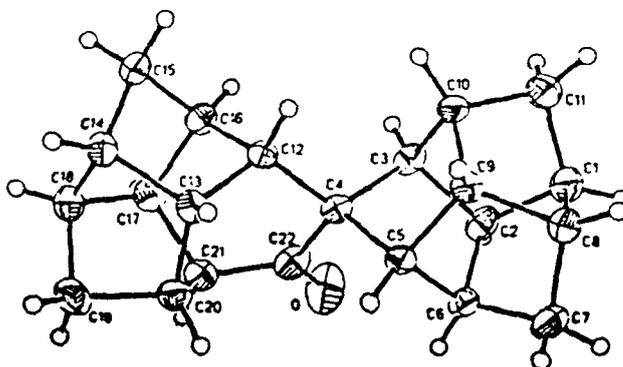


Fig. 2. Drawing of compound **13b**. Thermal ellipsoids are drawn at the 35% probability level while H atoms are represented by spheres of arbitrary size.

15. 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.²⁹ 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 ¹³C 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 δ 67.77 in its ¹³C 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.³⁰ 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

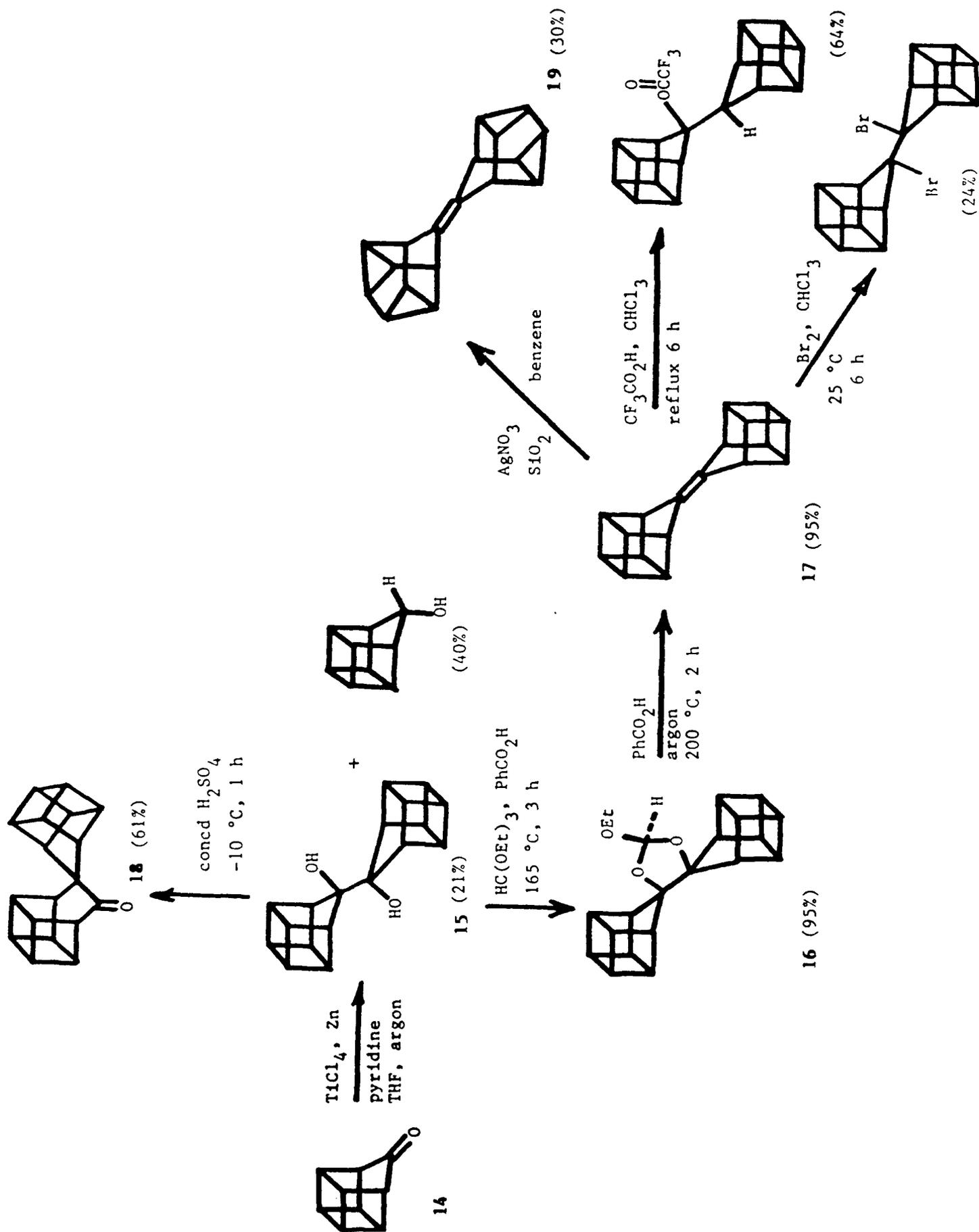
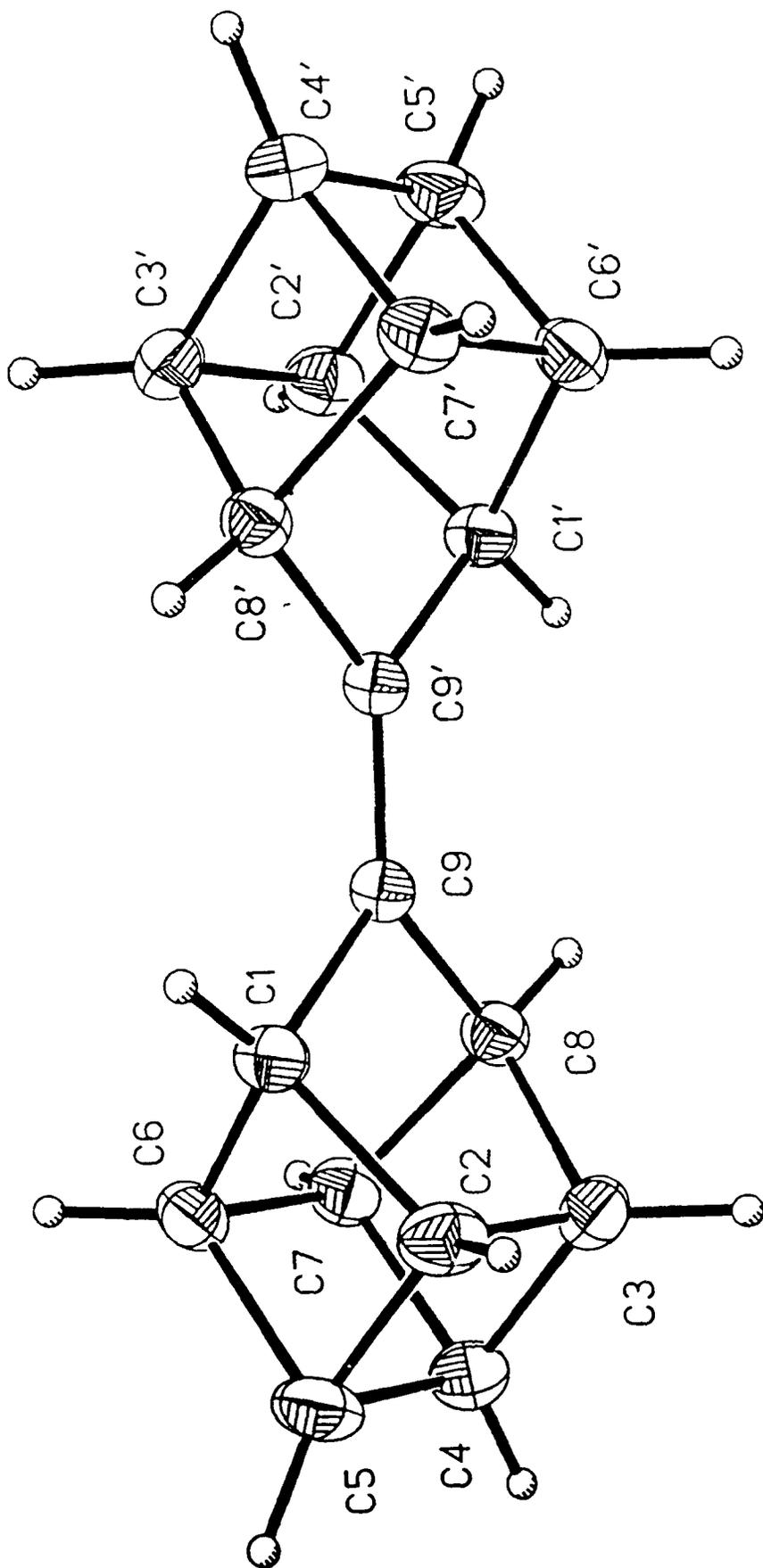
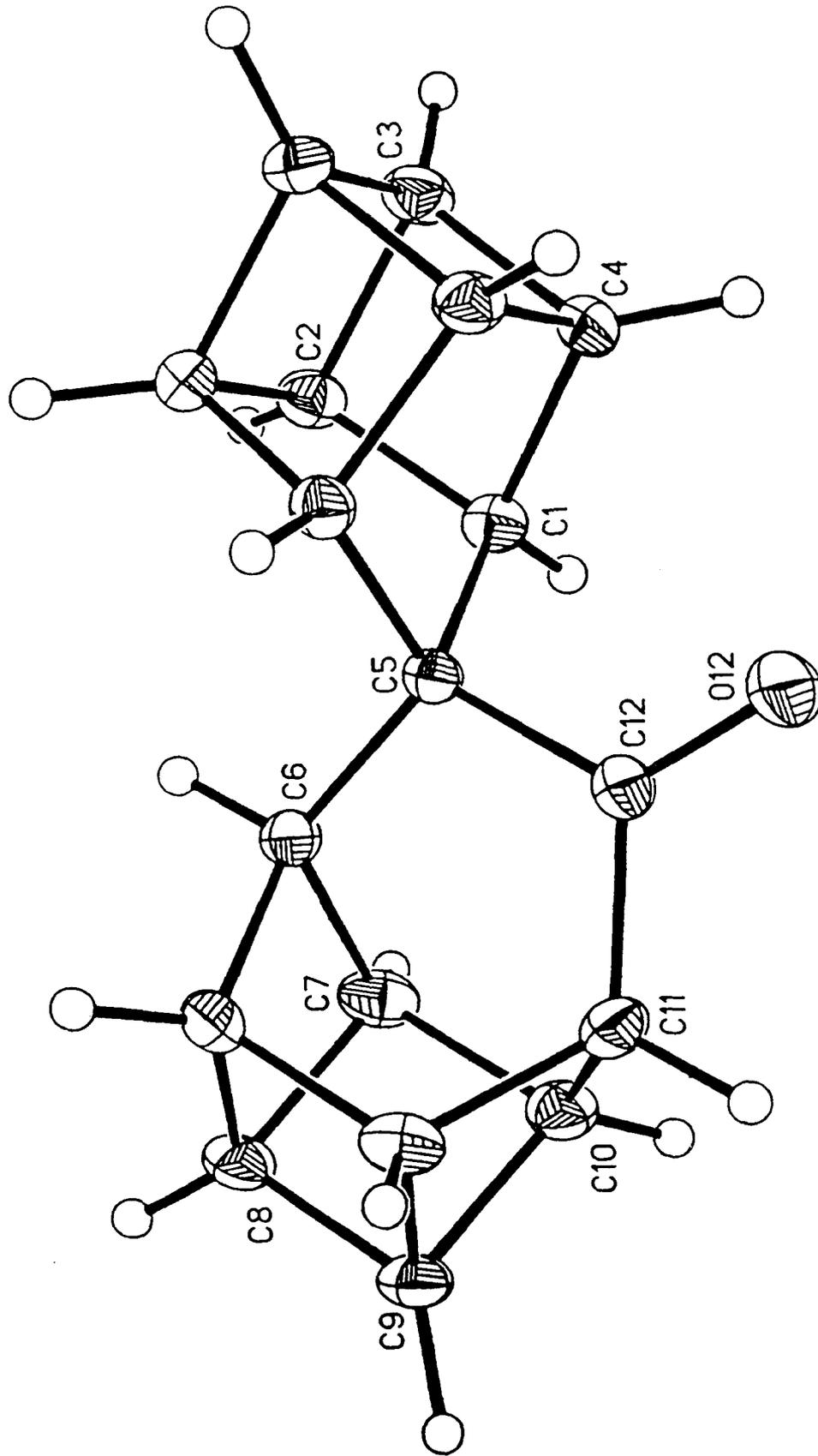


FIGURE 15



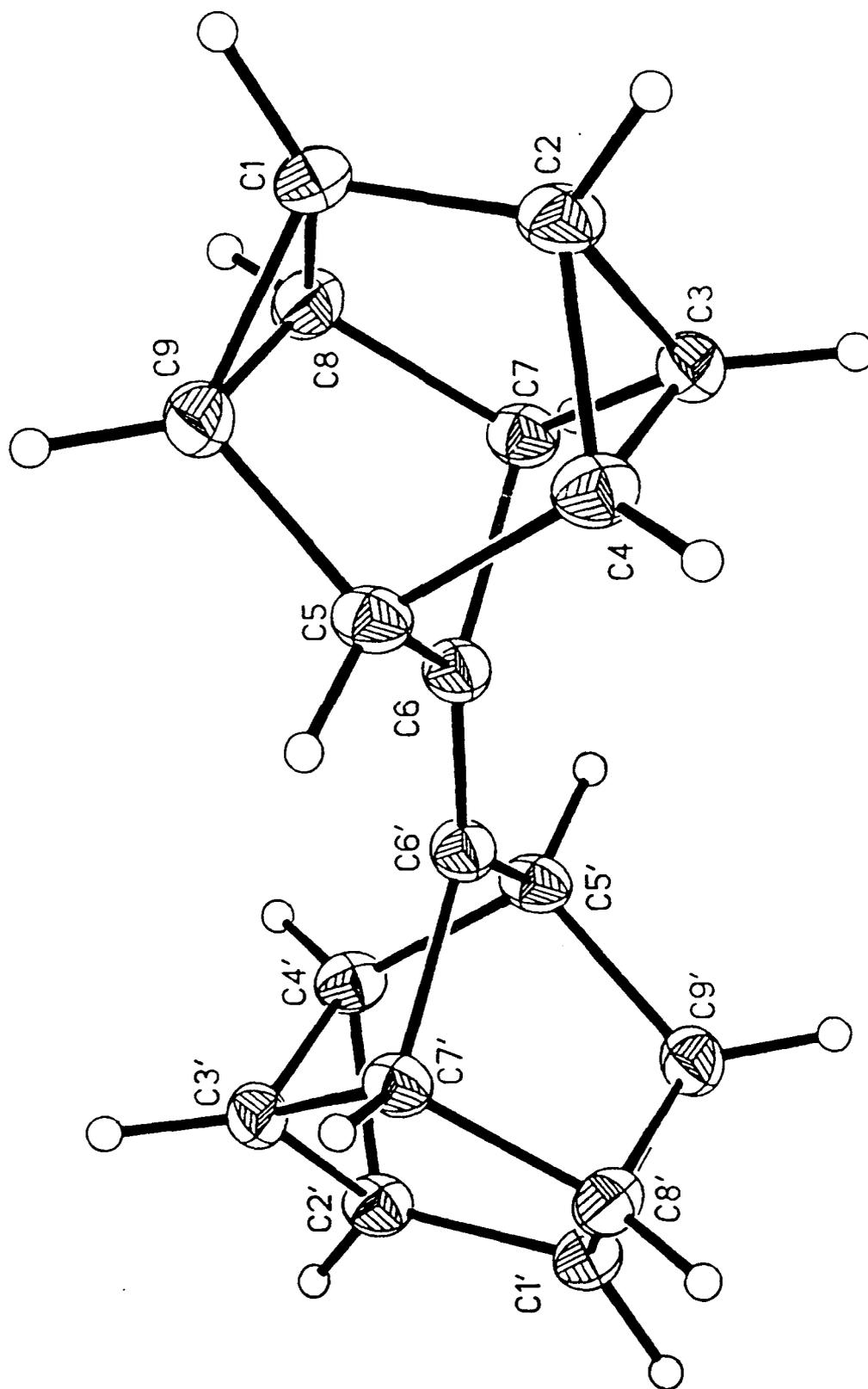
X-ray structure drawing of homocubylidenehomocubane (17)

FIGURE 16



X-ray structure drawing of 18

FIGURE 17



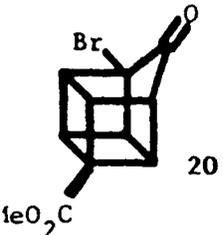
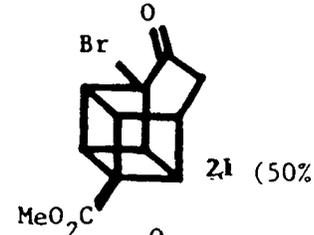
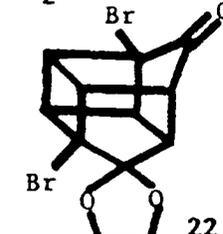
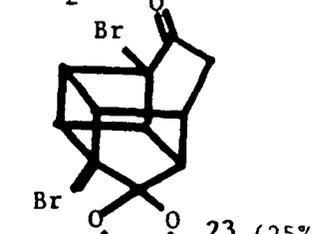
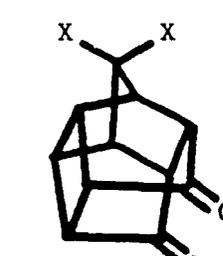
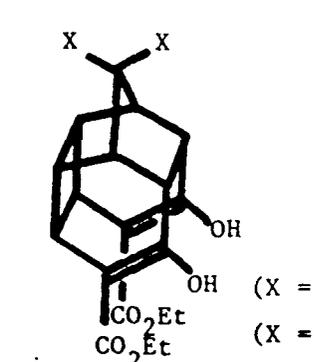
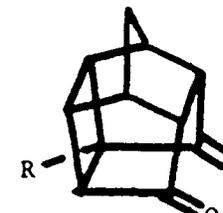
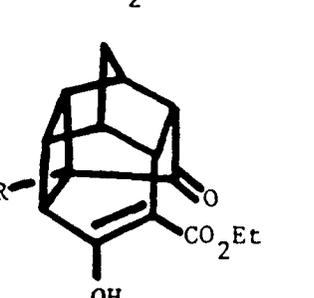
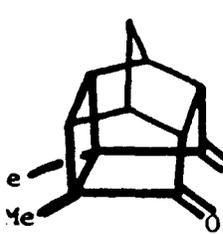
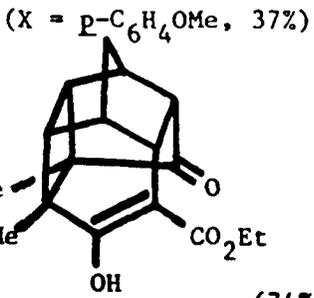
X-ray structure drawing of 19

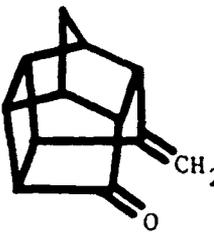
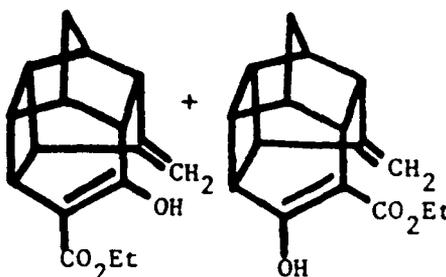
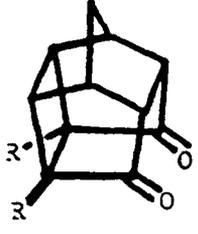
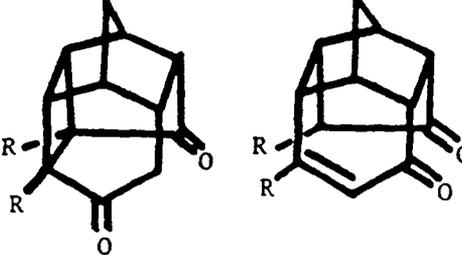
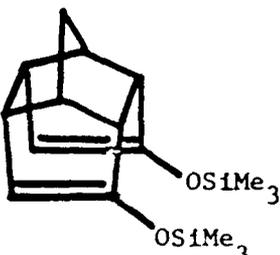
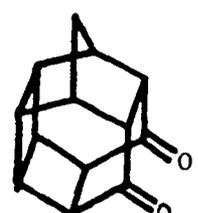
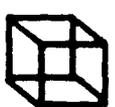
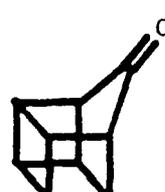
III. Ring Homologations of Substituted PCUD-8,11-diones. Ring expansion reactions of cage ketones have been utilized extensively as a method for synthesizing new polycyclic ring systems.³¹ In general, four basic methods have proved to be practical in this regard: (i) the use of diazo compounds (e.g., diazomethane or diazoesters, Method A),³²⁻³⁷ (ii) nitrous acid-promoted deamination reactions (i.e., Tieffenau-Demjanov ring expansions, Method B),³⁶ (iii) Fe(III)-promoted ring opening of 1-trimethylsilyloxybicyclo[n.1.0]alkanes (i.e., the procedure developed by Saegusa and coworkers,^{38a} Method C),^{38b} and (iv) transition metal-promoted carbonyl insertion reactions (Method D).^{39,40} 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.^{31,33} 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 α -carbon atoms that migrates preferentially, thereby affording at least some degree of regioselectivity in the ring homologation process.⁴¹ However, when α -halo ketones are employed as substrates in reactions with EDA-F₃B·OEt₂, regiospecific migration of the non-halogenated α -carbon center occurs⁴² (e.g., **20** + **21**³² and **22** + **23**,^{32,33} see Table II)

In addition, we have utilized formal intramolecular [σ 2 + π 2] photocycloaddition of an enedione C=C double bond to a strained epoxide carbon-carbon σ -bond to prepare a new, ring-expanded heterocyclic cage system.⁴³ 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^{3,7}.0^{4,12}.0^{6,10}]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.^{43a}

Table II. Ring Homologations of Cage Ketones

Substrate	Method	Experimental Conditions	Product (% yield)	References
	A	CH ₂ N ₂ (excess), Et ₂ O 0 °C, 3 days	 21 (50%)	32
	A	CH ₂ N ₂ (excess), Et ₂ O 0 °C, 3 days	 23 (25%)	32,33
	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	 (X = H, 45%) (X = OMe, 22%)	34a (X = H) 34b (X = OMe)
	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)	 (X = Me, 25%) (X = Ph, 25%) (X = p-C ₆ H ₄ CN, 61%) (X = p-C ₆ H ₄ OMe, 37%)	35
	A	EDA (excess), F ₃ B·OEt ₂ 0 °C + +25 °C	 (74%)	36

Substrate	Method	Experimental Conditions	Product (% yield)	References
	A	EDA (1 equiv.), $F_3B \cdot OEt_2$ -78 °C	 (product ratio: 15 : 1)	37
 (R = H or Me)	B	(i) CH_3NO_2 , NaOH, MeOH (ii) H_2 , Pd/C (iii) $NaNO_2$, HOAc, 0 °C (iv) TsOH, $CHCl_3$, 50 °C, 1 h	 (X = H: 14% 56%) (X = Me: 26% 39%)	36
	C	(i) CH_2I_2 , Et_2Zn , Et_2O , then dry O_2 (ii) anhydrous $FeCl_3$, DMF (iii) activated MnO_2 (6 equiv.), CH_2Cl_2 , +25 °C, 6 h (iv) hν, Pyrex filter, EtOAc	 (29% overall)	38b
	D	(i) $Rh_2(CO)_4Cl_2$ (1 equiv.) (ii) Ph_3P (excess), CH_2Cl_2	 (90%)	39

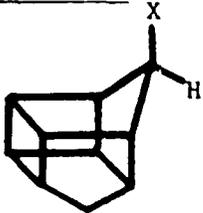
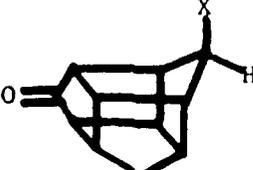
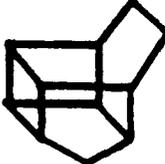
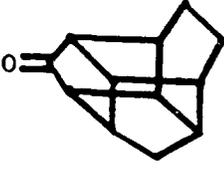
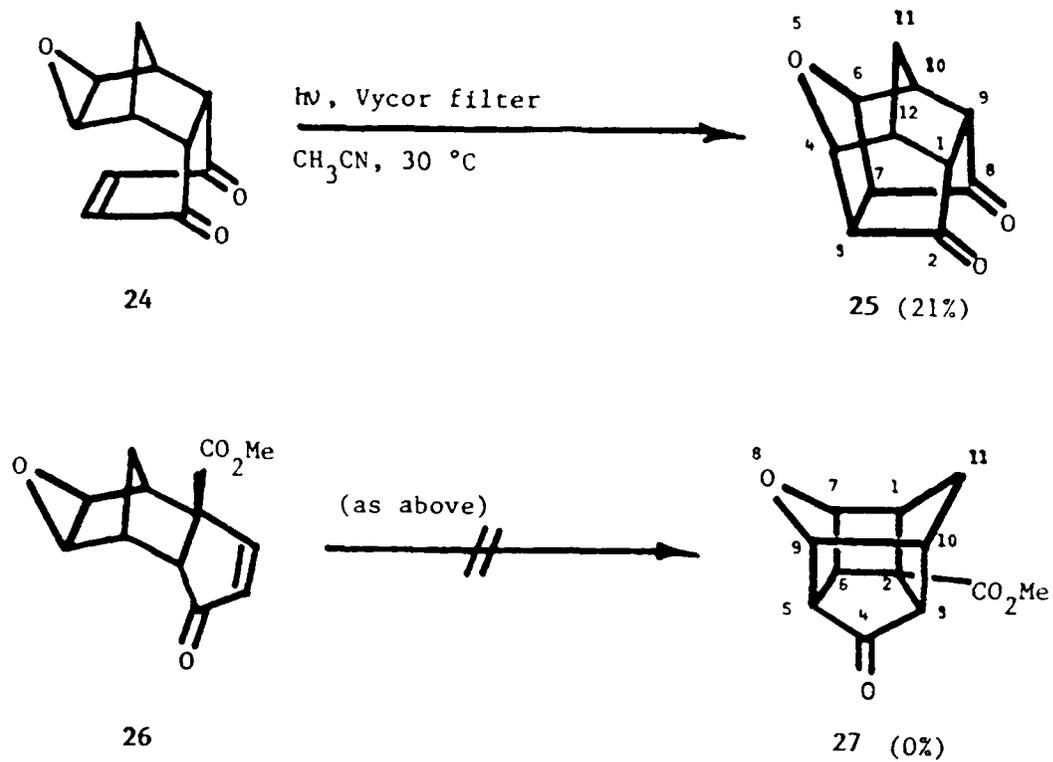
Substrate	Method	Experimental Conditions	Product (% Yield)	References
 <p data-bbox="104 506 299 534">(X = H or OH)</p>	D	(i) $\text{Rh}_2(\text{CO})_4\text{Cl}_2$, dry benzene (ii) Ph_3P (excess)	 <p data-bbox="1014 491 1196 519">(X = H, 99%) (X = OH, 92%)</p>	40
	D	$\text{Rh}_2(\text{CO})_4\text{Cl}_2$, dry benzene 80 °C, 72 h	 <p data-bbox="1014 838 1080 866">(28%)</p>  <p data-bbox="1212 838 1278 866">(56%)</p>	40

FIGURE 18



References & Footnotes

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