pellane (bond path angle = 59.4°, conventional angle = 61.8°).[33] The origin of these differences continues to be studied.

Calculations. The vibrational frequencies were calculated using GAUSSIAN-86.[34] The transformation of the infrared intensities to atomic polar tensors was carried out using programs written by Dempsey.[35]

Acknowledgment. This investigation was supported by a grant from the National Science Foundation.

Supplementary Material Available: Tables of alternative symmetry coordinates for bicyclobutane and force constants for bicyclobutane and cyclopropane (4 pages). Ordering information is given on any current masthead page.

(33) Wiberg, K. B.; Bader, R. W. F.; Lau, C. D. H. *J. Am. Chem. Soc.* **1987**, *109*, 985.
(34) Frisch, M. J.; Binkley, J. S.; Schlegel, H. B.; Raghavachari, K.; Melius, C. F.; Martin, R. L.; Stewart, J. J. P.; Bobrowicz, F. W.; Rohlfing, C. M.; Kahn, L. R.; DeFrees, D. J.; Seeger, R.; Whiteside, R. A.; Fox, D. J.; Fleuder, E. M.; Pople, J. A. *Carnegie*-Mellon Quantum Chemistry Publishing Unit, Pittsburgh, PA, 1984.
(35) Dempsey, R. Ph.D. Thesis, Yale University, 1983.

Reactions of [1.1.1]Propellane

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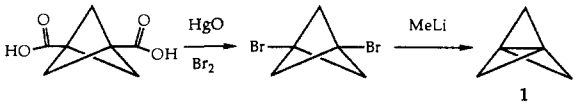
Received July 28, 1989

Abstract: The free radical addition reactions of [1.1.1]propellane (**1**) are described in some detail and allowed the preparation of a wide variety of 1,3-disubstituted bicyclo[1.1.1]pentanes. The reaction of **1** with free radicals was more rapid than that of bicyclo[1.1.0]butane (**2**), whereas bicyclo[2.1.0]pentane (**3**) was relatively inert. In some cases the free-radical additions led to oligomers, and in the case of tetrahydrofuran addition the chain-transfer constant was measured. The addition of thiophenol to **1** followed by reduction with the lithium radical anion from 4,4′-di-*tert*-butylbiphenyl gave 1-lithiobicyclo[1.1.1]petane, from which a variety of 1-substituted bicyclo[1.1.1]pentanes may be prepared. In the Baeyer–Villiger oxidation of 1-benzoylbicyclo[1.1.1]pentane, the *tert*-butyl group migrated in preference to the bicyclopentyl group. Conversion of the ketone to the tosylhydrazone followed by base treatment gave products of the type expected from the corresponding carbene. The reaction of **1** with NO in carbon disulfide gave a unique reaction in which nitro and thiocyano groups were introduced. The reactions of **1**, **2**, and **3** with NO_2 also were examined. Whereas **1** gave 1,3-dinitrobicyclo[1.1.1]pentane, the other hydrocarbons followed different reaction paths. The reaction of **1** with electron-deficient alkenes and alkynes are described in some detail and are compared with the corresponding reactions of **2** and **3**. Here, the relative reactivities of **1** and **2** were often comparable but varied considerably with the reagent used. Again, **3** was relatively unreactive. The reaction of **1** with Rh(I) gave a dimer, and evidence is presented for a metallocarbene intermediate.

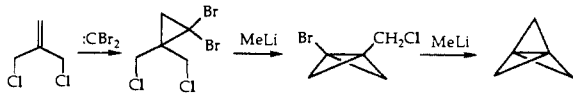
1. Introduction

The chemistry of [1.1.1]propellane (**1**) has undergone a remarkable evolution over a relatively short period. It was first predicted to be incapable of existence.[1] It was then theoretically predicted to be readily formed from a 1,3-disubstituted bicyclo[1.1.1]pentane and to be relatively stable, and this was followed by a successful preparation:[2]



1

Subsequently, Szeimies et al. described a remarkably simple preparation for **1**,[3] and it now is one of the most easily obtained of small ring compounds. The ready availability of **1** has made it possible to investigate a wide variety of its reactions which are described herein.

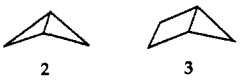


Before examining the reactions of **1**, it may be helpful to compare some of the properties of **1** with those of bicyclo[1.1.0]butane (**2**) and bicyclo[2.1.0]pentane (**3**) (Table I). All three compounds are fairly reactive and will add a variety of

Table I. Properties of Cycloalkanes

property	1	2	3
ionization potential (eV)	9.7	9.3	9.6
strain energy relief (kcal/mol)	30	37	49
local charge concn ($-\nabla^2\rho$, e/au^5)	0.33	0.23	0.19

substances across the central bond.[1] In addition, each of these compounds has one unique property that may lead to enhanced reactivity.[4]



2 **3**

In those reactions that involve a relatively late transition state, **3** should be the most reactive because fission of its central bond leads to the greatest strain relief.[5] Cleavage of the central bond in **3** eliminates both small rings, whereas with **1** and **2** small rings remain after the cleavage reaction. Another class of reactions, those involving donor–acceptor complexes, have rates of reaction that follow the energy of the highest occupied orbital of the donor.[6] In these cases, the rates are correlated with the ionization potentials, and so **2** should be the most reactive of the three because it has the lowest ionization potential.[7] Finally, all of the com-

(1) Greenberg, A.; Liebman, J. F. *Strained Organic Molecules*; Academic Press: New York, 1978; p 347.
(2) Wiberg, K. B.; Walker, F. H. *J. Am. Chem. Soc.* **1982**, *104*, 5239.
(3) Semmler, K.; Szeimies, G.; Belzner, J. *J. Am. Chem. Soc.* **1985**, *107*, 6410. Belzner, J.; Bunz, U.; Semmler, K.; Szeimies, G.; Opitz, K.; Schlüter, A. *Chem. Ber.* **1989**, *122*, 397.
(4) Wiberg, K. B.; Waddel, S. T.; Laidig, K. E. *Tetrahedron Lett.* **1986**, *27*, 1553.
(5) Wiberg, K. G. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 312.
(6) Albright, T. A.; Burdett, J. K.; Whangbo, M. H. *Orbital Interactions in Chemistry*; Wiley: New York, 1985.
(7) Honnegger, E.; Hanspeter, H.; Heilbronner, E.; Dailey, W. P.; Wiberg, K. B. *J. Am. Chem. Soc.* **1985**, *107*, 7172. Bombach, R.; Dannacher, J.; Stadelmann, J.-P.; Neier, R. *Helv. Chim. Acta* **1977**, *60*, 2213. Bieri, G.; Burger, F.; Heilbronner, E.; Maier, J. P. *Helv. Chim. Acta* **1977**, *60*, 2213.

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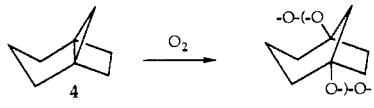
pounds have central bonds that are formed from orbitals with high p character. As a result, the back lobes of these orbitals will lead to significant charge density near the bridgehead carbons in a direction away from the bond. One of the better ways by which to characterize this local charge concentration[8] is to obtain values of the laplacian of the charge density ($\nabla^2\rho = \partial^2\rho/\partial x^2 + \partial^2\rho/\partial y^2 + \partial^2\rho/\partial z^2$) from the molecular wave functions at points near these carbons. A negative value corresponds to a region of local charge concentration. It can be seen that **1** has the most negative value, and thereby the highest local charge concentration outside the bridgehead. Local charge concentration has been related to nucleophilicity,[8] and **1** should be the most reactive of the three in reactions where concentration of charge plays a dominant role.

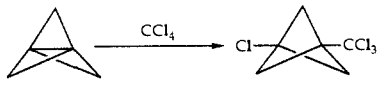
2. Free-Radical Additions[9]

Some small ring propellanes are known to undergo facile free radical addition reactions. For example, [3.2.1]propellane (**4**) reacted spontaneously with atmospheric oxygen to give a 1:1 copolymer[10] and also undergoes free-radical addition of carbon



4

tetrachloride. Both [2.2.1][11] and [2.1.1]propellanes[12] undergo facile polymerization reactions as low as 50 K, presumably because of the small bond energy for the central C–C bonds. In contrast to these compounds, **1** is quite stable thermally, and does not react with oxygen. The same is true with **2** and **3**. Both **1** and **2** undergo slow reactions with carbon tetrachloride[10] and much faster reactions with bromotrichloromethane:

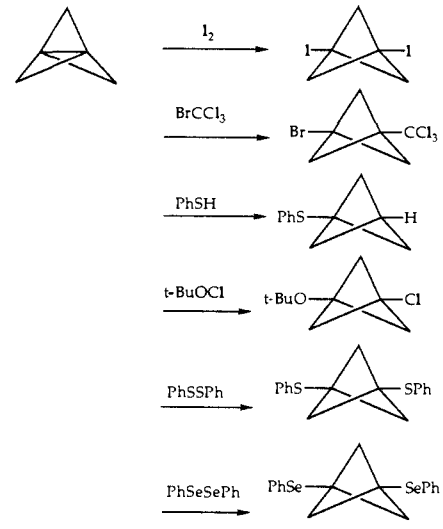


The relative rates of reaction of **1** and **2** with carbon tetrachloride were measured via competition, and **1** was found to be more reactive than **2** by a factor of about 7. On the other hand, solutions of **3** in carbon tetrachloride were stable for long periods, and **3** did not react with bromotrichloromethane. The low reactivity of **3** suggests a relatively early transition state for this reaction, and the lower reactivity of **2** compared to **1** indicates that the ionization potential is not a major factor in determining the rate of reaction. It can be seen that only $-\nabla^2\rho$ correlates with the rate of free-radical addition to these strained compounds.

The reactions of **1** with iodine, bromotrichloromethane, and thiophenol[13] occurred almost instantly and gave little or no oligomerization even when the reagent was slowly added to a solution of the propellane in ether (Scheme I). All of these reactions presumably involve free radical chain processes with large chain-transfer constants. It should be noted that reagents such as iodine, which do not normally react with unstrained alkenes, react rapidly with [1.1.1]propellane due to the driving force of strain relief.

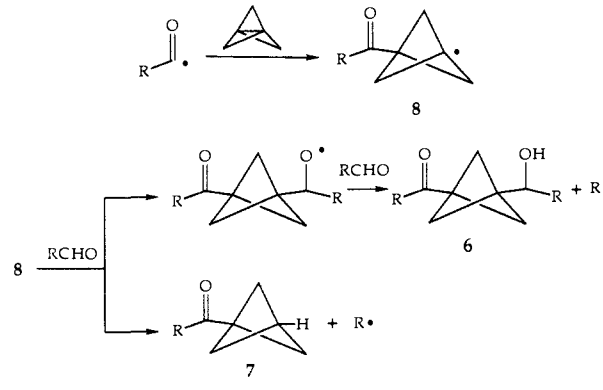
The reactions of **1** with carbon tetrachloride, diphenyl disulfide,[14] and diphenyl diselenide were spontaneous, but rather slow. A large concentration of the adding reagent was required for the chain to be efficient. *tert*-Butyl hypochlorite also added spontaneously, but if the conditions were not carefully controlled, a complex mixture of products was obtained. Clean formation of 1-*tert*-butoxy-3-chlorobicyclo[1.1.1]pentane could be obtained

Scheme I. Free Radical Addition Reactions



if a solution of **1** in *tert*-butyl hypochlorite was prepared at −78 °C and allowed to warm to room temperature while exposed to room light.

Aldehydes are known to add to alkenes via a free radical chain process to form 1:1 adducts.[15] The reaction of **1** with acetaldehyde using a peroxide catalyst gave a surprising result, the predominant formation of a 2:1 adduct (**6**) with only a minor amount of the 1:1 adduct **7**. This clearly indicates that the initially formed 3-acetylbicyclo[1.1.1]pentyl radical (**8**) prefers to add to the carbonyl of acetaldehyde rather than abstracting the aldehyde hydrogen.



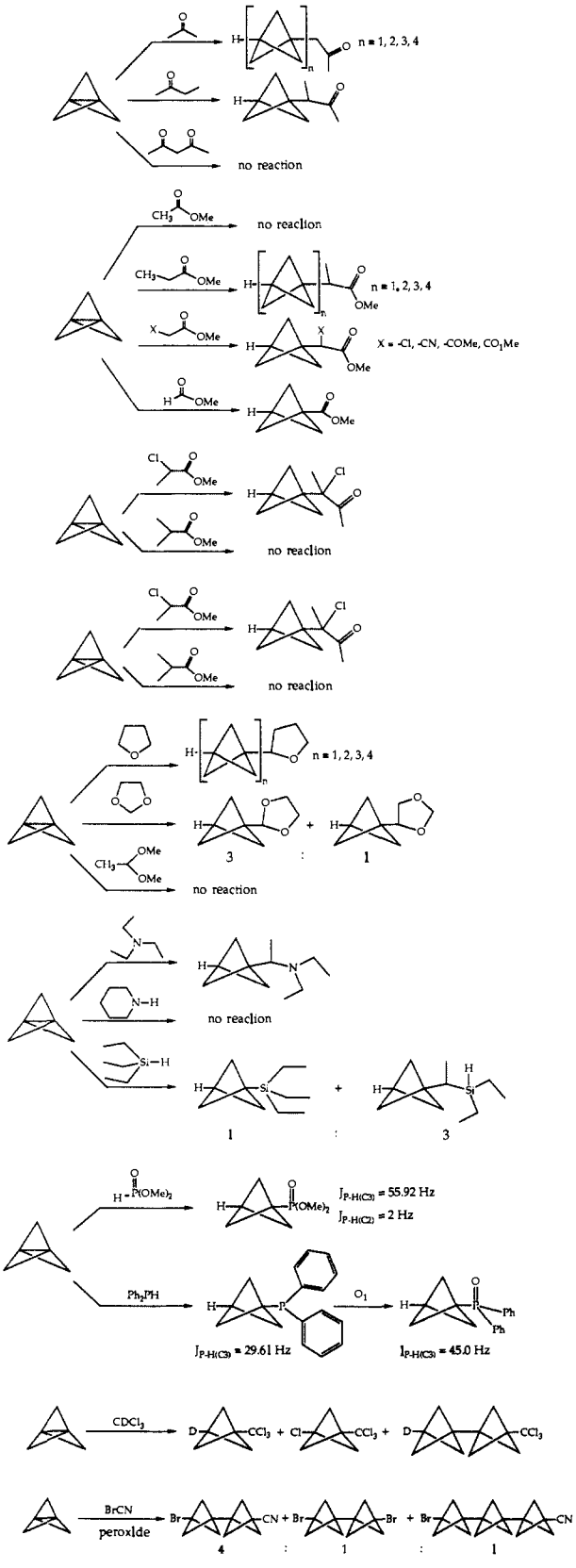
As far as we are aware, this apparently nucleophilic type of free-radical addition to a carbonyl has previously been found only in the addition of 1-hydroxyalkyl radicals to formaldehyde.[16] This may be a characteristic of the 1-bicyclo[1.1.1]pentyl radical, or in view of the strong interaction between the bridgehead carbons in bicyclo[1.1.1]pentane,[17] the bridgehead radical may be strongly affected by the acyl substituent leading to an altered reactivity. Further studies will be carried out in order to determine the origin of the unusual reactivity.

The ratio of 1:1 to 2:1 adducts was sensitive to the structure of the aldehyde. Whereas acetaldehyde and benzaldehyde gave essentially only the 2:1 adduct, with butyraldehyde the ratio decreased to approximately 2:1 favoring the 2:1 adduct, suggesting steric hindrance to addition at the carbonyl group.

Isobutyraldehyde has two hydrogens which may be removed to give stable radicals. In addition, the acyl radical may decarbonylate to form the stable 2-propyl radical. This leads to three chain carrying species, each of which may react to form both 1:1 and 2:1 adducts (Scheme III). Six products were expected, and

(8) Bader, R. F. W.; MacDougall, P. J.; Lau, C. D. H. *J. Am. Chem. Soc.* **1984**, *106*, 1594.
(9) For a preliminary account of the free radical addition reactions, see ref 4.
(10) Wiberg, K. B.; Burgmaier, G. J. *Tetrahedron Lett.* **1969**, 317.
(11) Walker, F. H.; Wiberg, K. B.; Michl, J. *J. Am. Chem. Soc.* **1982**, *104*, 2056.
(12) Wiberg, K. B.; Walker, F. H.; Pratt, W. E.; Michl, J. *J. Am. Chem. Soc.* **1983**, *105*, 3638.
(13) The reaction with thiophenol was first reported by Szeimies, ref 3.
(14) Bunz, U.; Polborn, K.; Wagner, H.-U.; Szeimies, G. *Chem. Ber.* **1988**, *121*, 1785.
(15) Kharasch, M. S.; Urry, W. H.; Kuderna, B. M. *J. Org. Chem.* **1949**, *14*, 248.
(16) Oyama, M. *J. Org. Chem.* **1965**, *30*, 2429.
(17) Maillard, B.; Walton, J. C. *J. Chem. Soc., Chem. Commun.* **1983**, 900.

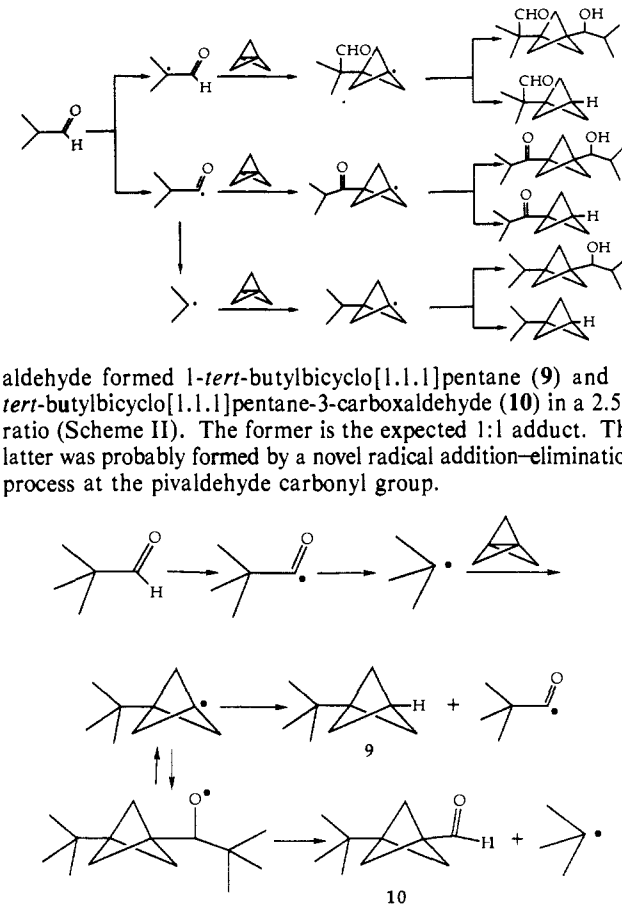
Scheme II. Catalyzed Free Radical Addition Reactions



all were isolated except 1-isopropylbicyclo[1.1.1]pentane which was probably lost on workup. For this more hindered aldehyde the overall ratio of 1:1 to 2:1 adduct was 1:1.3.

Pivaldehyde leads to an acyl radical that is known to decarbonylate readily to give the *tert*-butyl radical.[18] As a result, this radical became the chain carrier. The reaction of **1** with pivaldehyde formed 1-*tert*-butylbicyclo[1.1.1]pentane (**9**) and 1-*tert*-butylbicyclo[1.1.1]pentane-3-carboxaldehyde (**10**) in a 2.5:1 ratio (Scheme II). The former is the expected 1:1 adduct. The latter was probably formed by a novel radical addition–elimination process at the pivaldehyde carbonyl group.

Scheme III



It can be seen that the radical additions of aldehydes to [1.1.1]propellane form a variety of unusual bicyclo[1.1.1]pentane derivatives which are otherwise difficult to prepare. The reaction with acetaldehyde is of particular importance in that it leads to differentiated carbon functionality at both bridgehead positions. For example, the acetaldehyde 2:1 adduct was converted to bicyclo[1.1.1]pentane-1,3-dicarboxylic acid via the haloform reaction. It is amusing to note that this acid was a precursor in the original synthesis of **1**! The same transformation may be effected by adding diacetyl to **1**, followed by a haloform reaction.[19]

Some ketones proved to be effective addition reagents with peroxide initiation. Methyl ethyl ketone gave a high yield of 1:1 adduct without significant oligomerization. Acetone, on the other hand, gave extensive oligomerization. Only the 1:1 adduct was isolated, but the 2:1, 3:1, and 4:1 adducts were clearly visible by GC–MS analysis. These observations are in accord with the expectation that methyl ethyl ketone will have a greater chain-transfer constant than acetone. The extra methyl group helps to stabilize the radical and lowers the barrier to hydrogen abstraction. Conversely, pentane-2,4-dione formed neither low molecular weight products nor polymers. Its radical is probably too stable to support a chain reaction.

Radicals are less well stabilized by ester groups than by keto groups, and this is reflected in their behavior as adding reagents. When methyl acetate was used, a thick white gelatinous precipitate was formed, indicating that the chain-transfer constant was too low to permit formation of low molecular weight products. Methyl propionate gave a mixture of 1:1 adducts and oligomers, while the analogous ketone (methyl ethyl ketone) gave only 1:1 adduct. If a better radical stabilizing group than methyl is employed, good yields of 1:1 adducts without oligomerization can be obtained. Methyl chloroacetate, methyl cyanoacetate, methyl acetoacetate, and dimethyl malonate gave only 1:1 adducts (Scheme II). Methyl formate, although an ester, has an acyl radical as the chain-

(18) Ladd, E. C. U.S. Patent 2,552,980, 1951.

(19) Kaszynski, P.; Michl, J. *J. Org. Chem.* **1988**, *53*, 4593.

Table II. Oligomer Ratios for the Addition of Tetrahydrofuran to **1**

	1:1		2:1		3:1		4:1		5:1			
molarity	obsd	calcd	obsd	calcd	obsd	calcd	obsd	calcd	obsd	calcd	K_2/K_3	k_2/k_3
0.06	83	82	14	14	3	4	0	0.5	0	0.5	0.36	1.8×10^{-3}
0.13	68	68	23	20	7	7	2	2	0	2	0.18	1.8×10^{-3}
0.19	60	63	25	22	10	8	4	3	1	4	0.12	1.8×10^{-3}
0.57	36	41	31	20	18	13	12	8	3	18	0.04	1.8×10^{-3}

carrying species, and so it reacted as an aldehyde. Good yields of methyl bicyclo[1.1.1]pentane-1-carboxylate were obtained in this reaction. Peroxide initiation was necessary for all additions of ketones and esters. The results of the free-radical additions of ketones and esters illustrate the point that the chain-carrying radical must be neither too stable nor too unstable. If it is too stable, no reaction will occur; if too unstable, polymerization results.

Alcohols are known to add across carbon–carbon double bonds with α-hydroxy radicals as the chain-carrying species.[20] When either methanol or 2-propanol were used as adding reagents for **1** with peroxide initiation, only a thick white gelatinous precipitate resulted. The chain-transfer constants for these reagents were apparently too low to yield low molecular weight products. Methanol is probably the solvent of choice for the free-radical polymerization of **1**.

Some ethers and acetals have been found to be effective free radical addition reagents in reactions with **1**. Tetrahydrofuran formed a spectrum of oligomers from 1:1 through 5:1. 1,3-Dioxolane worked well as an adding reagent, but there were two chain-carrying species: the 2-dioxolanyl radical and the 4-dioxolanyl radical. The two corresponding 1:1 adducts were formed in 3:1 ratio (Scheme II). This reaction gave mainly 1:1 adducts along with a small amount of 2:1 and a trace of 3:1 adduct. The dimethyl acetal of acetaldehyde was found to be unreactive.

Tertiary amines, such as triethylamine, were found to undergo addition of **1** with peroxide initiation to give mainly 1:1 adducts, but the reactions gave poor yields. Secondary amines such as piperidine failed to react. Triethylsilane added to **1** to give mainly 1:1 adducts, but two chain-carrying species were present: [1-(1-bicyclo[1.1.1]pentyl)ethyl]diethylsilane and bicyclo[1.1.1]-pentyltriethylsilane were formed in 3:1 ratio (Scheme II).

Compounds containing phosphorus–hydrogen bonds have extremely large chain-transfer constants and add very efficiently to **1** even if not present in large excess. Uncatalyzed additions occurred, but they were more satisfactory with peroxide catalysis. Diphenylphosphine added efficiently to form bicyclo[1.1.1]-pentyldiphenylphosphine.[21] This compound oxidized at a moderate rate in air to form bicyclo[1.1.1]pentyldiphenylphosphine oxide. Dimethyl phosphite added to form dimethyl bicyclo-[1.1.1]pentylphosphonate (Scheme II). These derivatives of bicyclo[1.1.1]pentane with phosphorus attached to a bridgehead carbon are interesting because of the large NMR coupling with the proton on the opposite bridgehead. In bicyclo[1.1.1]pentyldiphenylphosphine the coupling constant was 29.6 Hz, in the phosphine oxide it was 45 Hz, and in dimethyl bicyclo[1.1.1]-pentylphosphonate it was 59.6 Hz. In the last compound even the methylene protons were split by about 2 Hz. This and 1-fluorobicyclo[1.1.1]pentane[22] appear to be the only bicyclo-[1.1.1]pentane derivatives for which a bridgehead substituent gives a measurable coupling constant to the methylene protons. The large bridgehead–bridgehead coupling constants are characteristic of the bicyclo[1.1.1]pentane ring system and were first observed with the parent hydrocarbon.[23] Subsequently, a number of other examples of 1,3-coupling have been reported.[22]

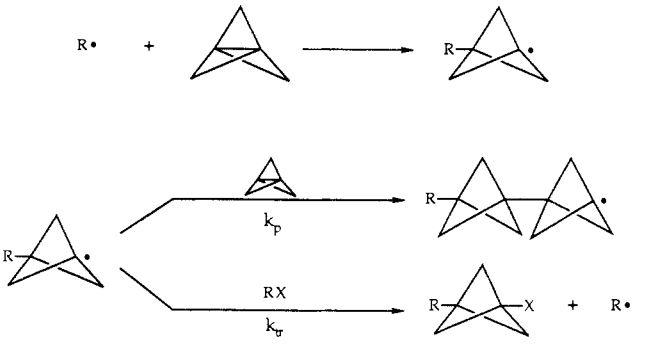
The addition of chloroform to **1** also required initiation by *tert*-butyl peroxide. In addition to the 1:1 adduct, the 2:1 oligomer and 1-chloro-3-(trichloromethyl)bicyclo[1.1.1]pentane were formed in a 10:3:1 ratio (Scheme II). The latter product presumably arises from abstraction of chlorine by the 3-(trichloromethyl)bicyclo[1.1.1]pentyl radical.

Cyanogen bromide also adds to **1**. Products were formed spontaneously, but peroxide initiation was desirable for reliable and clean formation of products in reproducible yields. The cyano radical was the main chain carrying species, although the bromine radical also seems to carry the chain to some extent as indicated by the formation of a dibromide. The reaction was unusual in that only oligomeric products were formed; little or no 1-bromo-3-cyanobicyclo[1.1.1]pentane (1:1 adduct) was formed. The main product was 3-cyano-3′-bromo-[1,1′-bibicyclo[1.1.1]-pentane], and significant amounts of trimeric product also were formed (Scheme II).

It should be noted that Szeimies and his co-workers have observed many examples of free-radical additions to bridged [1.1.1]propellanes.[24]

3. Oligomerization and Polymerizations of [1.1.1]Propellane

If the chain-transfer constant of a free-radical addition is low, oligomerization occurs. In the previous section, we have noted several examples of adding reagents which produce oligomers. These include cyanogen bromide, acetone, methyl propionate, tetrahydrofuran, and 1,3-dioxolane.



R• = chain carrying species

Chain transfer constant = k_{tr}/k_p

Increasing the concentration of **1** should give relatively more oligomeric products. This was studied for the addition of tetrahydrofuran since it was possible to observe 1:1 through 1:5 adducts by capillary gas chromatography. Several solutions of **1** in tetrahydrofuran covering a 10-fold concentration range were prepared, and after the reaction had been completed, the products were analyzed by GC. The results are shown in Table II. In accord with expectation, increasing propellane concentration led to increased amounts of oligomers.

We were able to model the reaction of **1** with tetrahydrofuran by using the MSIM4 stochastic mechanism simulation program.[25] The reaction scheme shown in Scheme IV was assumed to account to the formation of the products. The assumption was made that the chain-transfer constant would be the same for all of the

(20) Urry, W. H.; Stacey, F. W.; Juveland, O. O.; McDonnell, C. H. *J. Am. Chem. Soc.* **1953**, *75*, 250. Urry, W. H.; Stacey, F. W.; Huyser, E. S.; Junveland, O. O. *Ibid.* **1954**, *76*, 450.

(21) This reaction also has been observed by Kaszynski, P.; Michl, J. *J. Am. Chem. Soc.* **1988**, *110*, 5225.

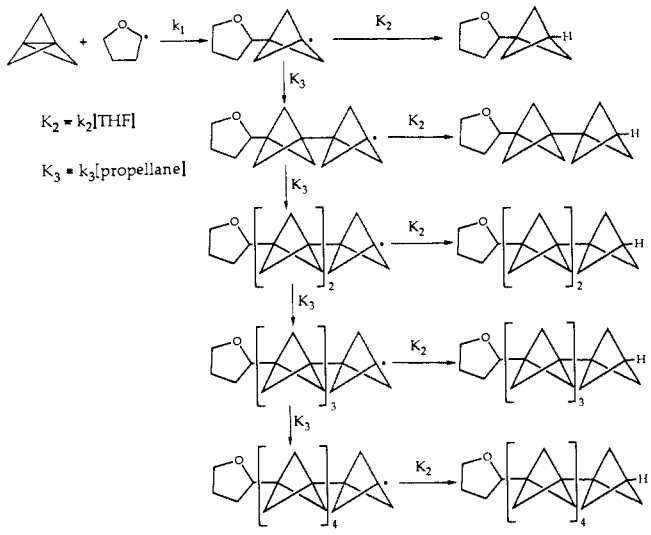
(22) Della, E. W.; Pigou, P. E. *J. Am. Chem. Soc.* **1984**, *106*, 1085. Barfield, M.; Della, E. W.; Pigou, P. E.; Walter, S. R. *Ibid.* **1982**, *104*, 3549.

(23) Wiberg, K. B.; Connor, D. S. *J. Am. Chem. Soc.* **1966**, *88*, 4437.

(24) Szeimies, G. In *Strain and Its Implications in Organic Chemistry*; deMeijere, A., Blechert, S., Eds.; Kluwer Academic Publishers: Dordrecht, the Netherlands, 1989.

(25) Bunker, D. L.; Houle, F. A. QCPE program 293, Quantum Chemistry Program Exchange, Indiana University, Bloomington, IN.

Scheme IV



oligomeric bicyclopentyl radicals. In this way, only three terms were required: k_1, for the rate of initiation, $K_2 = k_2[THF]$ for hydrogen abstraction and $K_3 = k_3[propellane]$. K_2 was a constant because the concentration of THF remained essentially constant during a run. K_3 decreased during a reaction as propellane was consumed (this is taken into account by the program), and the initial value of K was different from run to run because the starting concentration of **1** was different. It was further assumed that the rate of initiation was small compared to the other steps, and this was supported by the observation that most of the *tert*-butyl peroxide catalyst could be recovered unchanged.

It can be seen by reference to Table II that by assuming a chain transfer constant (k_2/k_3) of 1.8×10^{-3} all of the data were fit quite well except that for the highest concentration of propellane. The poor fit for this sample was undoubtedly related to the formation of higher oligomers and polymers, which were observed as a milky gelatinous precipitate, but are not allowed for in the model. Unfortunately, the chain-transfer constants for the addition of THF to olefins have not been measured, so a direct comparison is impossible at present. It seems qualitatively that chain-transfer constants for additions to **1** are smaller than for additions to simple olefins such as 1-octene. For example, methanol adds to 1-octene to give significant 1:1 adduct[20] under conditions which only polymerize **1**.

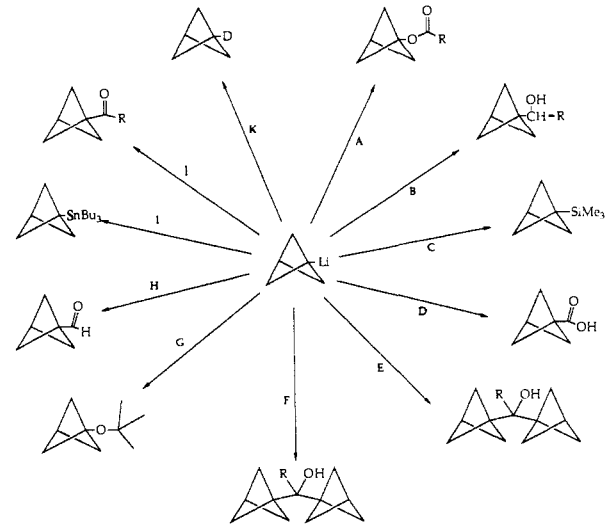
The oligomerization reactions have been examined in some detail by Michl et al. for the formation of rodlike molecular systems.[26]

4. 1-Bicyclo[1.1.1]pentyllithium

1-Substituted bicyclo[1.1.1]pentanes are relatively difficult to prepare. They were first obtained by free radical substitution reactions on the parent hydrocarbon.[27] Subsequently, some additional derivatives were obtained by photoextrusion of CO from bicyclo[2.1.1]hexan-2-ones.[28] Applequist and Wheeler found that dichlorocarbene could be added to methyl 3-phenylbicyclo[1.1.0]butane-1-carboxylate, which after reduction and oxidation gave bicyclo[1.1.1]pentane-1,3-dicarboxylic acid.[29] Decarboxylation gave the 1-acid that was transformed into other derivatives.

None of these methods are convenient for the preparation of 1-substituted bicyclo[1.1.1]pentanes. With **1** as the most conveniently prepared compound containing this ring system, it would be desirable to use it as the starting material. Thiophenol added

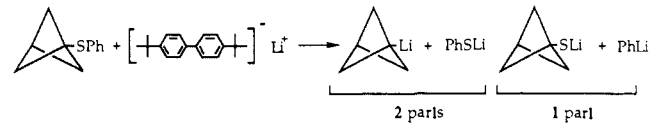
Scheme V



A = 1) O_2 2) RCOCl, R = tBu, Ph
B = RCHO, R = tBu, Ph
C = trimethylsilyl chloride
D = 1) CO_2 2) H^+
E = RCO_2Me, R = tBu, Ph
F = RCOCl, R = tBu, Ph
G = tBuOOtBu
H = methyl formate
I = tributyltin chloride
J = RCN, R = tBu, Ph
K = MeOD

to **1** in a convenient and essentially quantitative fashion.[13] Screttas and co-workers have shown that sulfides may be cleaved by reagents such as lithium naphthalide to give organolithium compounds.[30] Lithium di-*tert*-butylbiphenyl has been found to give higher yields and faster rates at lower temperatures than lithium naphthalide.[31]

The reaction of phenyl bicyclo[1.1.1]pentyl sulfide with lithium di-*tert*-butylbiphenyl in tetrahydrofuran proceeded satisfactorily at −60 °C. The desired 1-bicyclo[1.1.1]pentyllithium was the major product, but sulfur–phenyl bond cleavage also occurred to a smaller extent to yield phenyllithium and lithium 1-bicyclo[1.1.1]pentylthiolate.[32] The thiols were usually lost in the aqueous workup, but a reaction with an acid chloride allowed them to be easily isolated as thioesters.

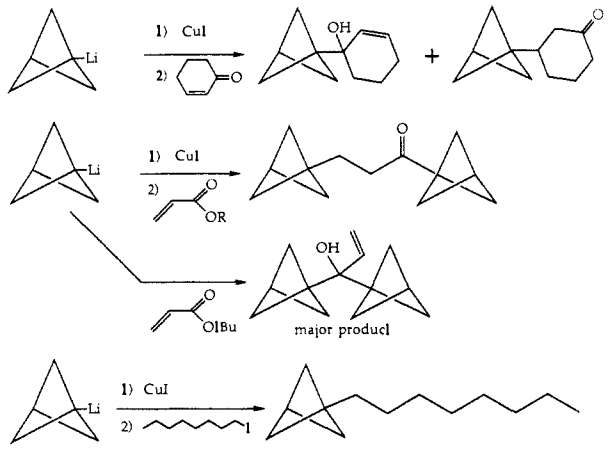


1-Bicyclo[1.1.1]pentyllithium reacted with the usual range of reagents as shown in Scheme V. The yields for these reactions were in the range of 30–60% with no effort at optimizing them. Quenching the anion solution with methanol-*d* gave bicyclo[1.1.1]pentane-*1-d*, but the difficulty of separating it from the solvent limited the usefulness of this procedure. The reaction with aldehydes and with nitriles gave the expected secondary alcohols and ketones, respectively. The reaction with esters gave tertiary alcohols containing two bicyclopentane groups. However, methyl formate gave bicyclo[1.1.1]pentane-1-carboxaldehyde rather than a secondary alcohol. Perhaps the tetrahedral intermediate from the first addition was stable at −78 °C because of the small groups, thus avoiding bis addition.

The reaction with carbon dioxide gave the bridgehead acid, and reaction with oxygen followed by treatment with benzoyl chloride gave 1-bicyclo[1.1.1]pentyl benzoate. The reaction with di-

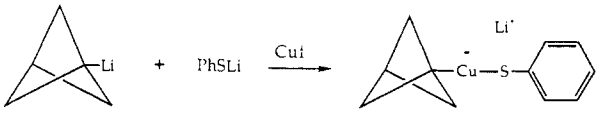
(26) Michl, J.; Kaszynski, P.; Friedli, A. C.; Murthy, G. S.; Yang, H.-C.; Robinson, R. E.; McMurdie, N. D.; Kim, T. In *Strain and its Implications in Organic Chemistry*; deMeijere, A., Blechert, S., Eds.; Kluwer Academic Publishers: Dordrecht, the Netherlands, 1989.
(27) Wiberg, K. B.; Williams, V. Z., Jr. *J. Org. Chem.* **1970**, *35*, 369.
(28) Meinwald, J.; Chapman, R. A. *J. Am. Chem. Soc.* **1968**, *90*, 3218. Della, E. W.; Cotsaris, E.; Hine, P. T. *Ibid.* **1981**, *103*, 4131.
(29) Applequist, D. E.; Renken, T. L.; Wheeler, J. W. *J. Org. Chem.* **1982**, *47*, 4985.
(30) Screttas, C. G.; Micha-Screttas, M. *J. Org. Chem.* **1978**, *43*, 1064.
(31) Rücker, C. *Tetrahedron Lett.* **1984**, 4349.
(32) For a preliminary report on the formation of 1-bicyclo[1.1.1]pentyllithium, see: Wiberg, K. B.; Waddell, S. T. *Tetrahedron Lett.* **1988**, *29*, 289.

Scheme VI



tert-butyl peroxide gave a modest yield of bicyclo[1.1.1]pentyl *tert*-butyl ether. When the bicyclopentyllithium solution was treated with chlorotrimethylsilane, the corresponding silyl compound was formed, and an analogous reaction occurred with tri-*n*-butyltin chloride. The latter product was interesting because coupling of the opposite bridgehead hydrogen to all three magnetic isotopes of tin was observed in the proton NMR spectrum, and the coupling constants were the largest yet observed for this long-range coupling: ^{119}SnH J = 179.5 Hz, ^{117}SnH J = 171.0 Hz, ^{115}SnH J = 156.1 Hz.

Although organolithium reagents exhibit a wide range of reactivity, they do not usually give conjugate addition to enones or react with alkyl halides. In these cases, the organocuprate reagents are more useful. Posner and co-workers studied heterocuprates and concluded that, for secondary and tertiary alkyl groups, PhS(R)CuLi gave the best results for the above reactions.[33] These cuprates are normally prepared by adding an organolithium compound to a mixture of lithium thiophenoxide and cuprous iodide. By a fortunate coincidence, the anion solution prepared by the reduction of bicyclo[1.1.1]pentyl phenyl sulfide contains equimolar amounts of bicyclopentyllithium and lithium thiophenoxide. Addition of cuprous iodide should then yield the desired cuprate.



Cuprates prepared in this fashion usually gave a mixture of cuprate and organolithium reaction products that suggests that in most cases cuprate formation was incomplete. It seems likely that conditions could be further optimized to improve cuprate formation.

The reactions of the cuprate prepared in this fashion are summarized in Scheme VI. Addition of cyclohexenone gave a 1:1 mixture of 1,2 and 1,4 addition products, whereas bicyclopentyllithium gave only 1,2 addition. Addition of ethyl acrylate to the cuprate solution did not give the conjugate addition product, but rather a bis addition product was formed from both conjugate addition and replacement of the alkoxy group by bicyclopentyl. Similar behavior was observed with *sec*-butyl and *tert*-butyl acrylate. The reaction of *tert*-butyl acrylate with bicyclopentyllithium (and no copper catalyst) gave mainly the expected bis 1,2-addition product, as well as a small amount of the product formed in the cuprate addition.

The reaction of the cuprate with benzoyl chloride gave ketone and tertiary alcohol in a 1.5:1 ratio. The ketone was, however, more easily prepared by reaction of bicyclopentyllithium with benzonitrile. The reaction of cuprate with 1-iodooctane gave 1-octylbicyclo[1.1.1]pentane.

(33) Posner, G. H.; Whitten, C. E.; Sterling, J. J. *J. Am. Chem. Soc.* **1973**, *95*, 7788.

Table III. Relative Migratory Aptitudes of Some Alkyl Groups

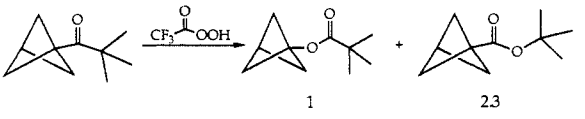
group	k_{rel}	group	k_{rel}
ethyl	0.07	isopropyl	1.9
neopentyl	0.11	cyclohexyl	3.0
phenyl	1.0	1-bicyclo[1.1.1]pentyl	17
cyclopentyl	1.1	*tert*-butyl	39
benzyl	1.3	1-apocamphyl	39

The addition of diphenyl disulfide to the propellane gave 1,3-bis(thiophenoxy)bicyclo[1.1.1]pentane as described in section 2. An attempt was made to reduce it with lithium di-*tert*-butylbiphenyl using a procedure similar to that for the monosulfide. The reaction did not produce the 1,3-dilithio derivative, but rather gave reduction to [1.1.1]propellane. The formation of the latter was demonstrated by addition of iodine and observation of the bridgehead diiodide.

5. Reactions of Bicyclo[1.1.1]pentane Derivatives

The increased availability of bicyclopentane derivatives makes it possible to explore their chemistry in greater detail than has previously been possible. Two examples of such studies follow.

In an effort to explore the differences in reactivity between the bicyclo[1.1.1]pentyl group and the *tert*-butyl group, we have determined their relative migratory aptitudes in the Baeyer–Villiger reaction. Hawthorne, Emmons, and McCallum have studied the Baeyer–Villiger oxidation of alkyl phenyl ketones with buffered trifluoroperacetic acid in methylene chloride, and in this way they have compiled data on the relative migratory aptitude of a wide range of alkyl groups.[34] The oxidation of bicyclo[1.1.1]pentyl *tert*-butyl ketone (prepared from 1-lithiobicyclopentane as described in section 4) was carried out under the same conditions and gave a 2.3:1 mixture of *tert*-butyl bicyclo[1.1.1]-pentanecarboxylate and bicyclo[1.1.1]pentyl pivalate. The latter



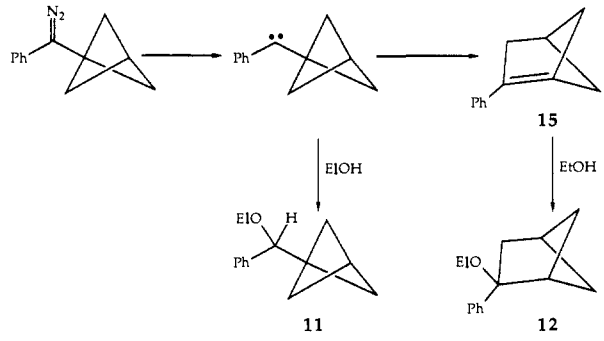
was identified by an independent preparation from bicyclo[1.1.1]pentyllithium and oxygen, followed by treatment with pivaloyl chloride. The reaction appeared to be clean by GC–MS, and no evidence for transesterification by trifluoroacetic acid was observed.

The relative reactivity observed in this study was converted to that relative to phenyl using the data for *tert*-butyl phenyl ketone, and the migratory aptitude thus obtained is compared with that for other groups in Table III. It should be noted that the relative values for bicyclo[1.1.1]pentyl and *tert*-butyl may have a steric component. The lowest energy rotamer of the Criegee intermediate usually favors migration of the bulkier substituent,[34] which in this case is *tert*-butyl.

There has been much interest in the formation and properties of anti-Bredt alkenes.[35] A number of alkenes of this type, such as bicyclo[2.2.2]oct-1-ene appear to have been formed by a ring expansion involving a carbene intermediate.[36] Eaton has recently presented the results of a study of the carbene derived from phenyl cubyl ketone.[37] The availability of bicyclo[1.1.1]pentyl phenyl ketone made it possible to carry out a similar study. Bicyclo[1.1.1]pentyl phenyl ketone (along with some benzophenone impurity) was converted to the tosylhydrazone, and treated with 1 M sodium ethoxide in ethanol. On heating to reflux, the solution turned red suggesting transient formation of the diazo compound. The crude product was analyzed by gas chromatography, showing the formation of four products in a 9:5:1:5 ratio. They were isolated by preparative gas chromatography and were identified

(34) Hawthorne, M. F.; Emmons, W. D.; McCallum, K. S. *J. Am. Chem. Soc.* **1958**, *80*, 6393.
(35) Keese, R. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 528. Kobrich, G. *Ibid.* **1973**, *12*, 464.
(36) Wolf, A. D.; Jones, M. *J. Am. Chem. Soc.* **1973**, *95*, 8209.
(37) Eaton, P. E.; Hoffmann, K.-L. *J. Am. Chem. Soc.* **1987**, *109*, 5285.

Scheme VII



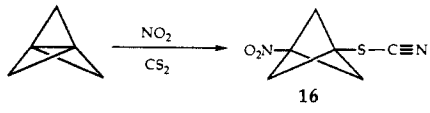
(in the order given in the ratio) as the ethyl ether of bicyclo-[1.1.1]pentylphenylcarbinol (**11**), 2-ethoxy-2-phenyl bicyclo-[2.1.1]hexane (**12**), an unidentified isomer of A (**13**), and the ethyl ether of diphenylcarbinol (**14**). The identity of **12** was confirmed by independent synthesis: phenyllithium was added to 2-bicyclo[2.1.1]hexanone, and the alcohol was alkylated with ethyl iodide in dimethyl sulfoxide. Compound **14** arose from the benzophenone contaminant in the ketone sample.

The products correspond in kind to those observed in the cubyl system, and may be formed as shown in Scheme VII. Decomposition of the diazo compound may give the carbene, which either reacts with ethanol to give **11** or undergoes ring expansion to give the bridgehead alkene, **15**, which adds ethanol to give the observed product, **14**. For the cubyl system, Eaton observed exclusive rearrangement of the carbene. For the bicyclopentyl system, rearrangement of the carbene before addition of ethanol occurs less than half the time. This is consistent with the formation of a more strained anti-Bredt alkene after rearrangement in the bicyclopentyl system.

It is also possible that the reaction may proceed by initial proton addition to the diazo compound, followed by cationic reactions. However, bridgehead cations in the bicyclo[2.1.1]hexyl system open readily to monocyclic cations,[38] and no products of this type were formed.

6. Reaction of [1.1.1]Propellane with Nitrogen Oxides

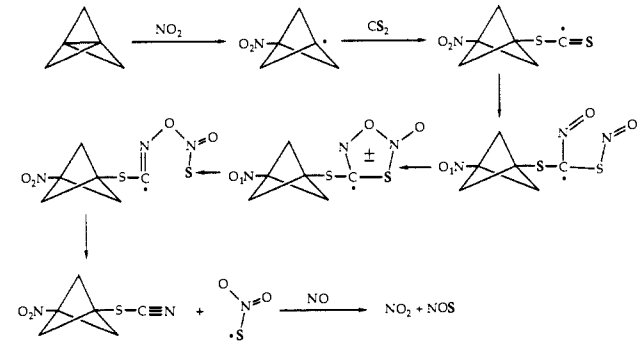
In an effort to prepare bicyclo[1.1.1]pentane derivatives with nitrogen containing groups at the bridgehead positions, the reaction of **1** with nitric oxide was investigated. A solution of **1** in ether was added to NO in carbon disulfide at −78 °C, and the solution was then slowly warmed to room temperature. Removal of the solvent gave a single compound (**16**) in good yield. The molecular weight was determined to be 170 by chemical-ionization mass spectroscopy, and the IR spectrum had bands at 2162 and 1548 cm^{-1}, indicating the presence of nitro and cyano groups. The proton NMR spectrum had a single band at δ 2.7 showing that the bicyclo[1.1.1]pentane ring was intact. These data clearly indicate the compound to be 1-nitro-3-(thiocyano)bicyclo-[1.1.1]pentane (**16**).



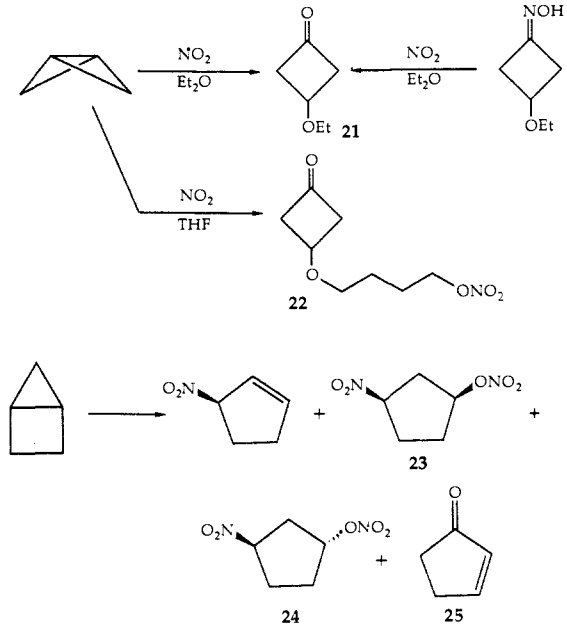
An examination of the literature dealing with the mechanism of the reaction of NO with alkenes[39] provides an explanation of this remarkable transformation. Here it has been found that the reaction is initiated by NO_2, which is invariably present in small concentration. The products are then formed by addition of NO to the initially formed carbon radical, and a series of oxygen transfer reactions occur that lead to the products (nitronitrites and similar compounds) and regenerate NO_2.

Addition of NO_2 to **1** leads to the bridgehead radical, which must then add to carbon disulfide, presumably at the sulfur.

Scheme VIII

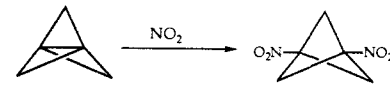


Scheme IX



Further reaction with NO as shown in Scheme VIII will then lead to the observed product, as well as NOS and NO_2.

Since the reaction appeared to involve initial addition of NO_2, the reaction of **1** with NO_2 in ether was examined. Here, the major product was found to be 1,3-dinitrobicyclo[1.1.1]pentane, formed in about 35–40% yield. The other products were not easily isolated or identified. The dinitro compound was identified by comparison with an authentic sample prepared from bicyclo-[1.1.1]pentane-1,3-dicarboxylic acid via a series of Hoffmann-type rearrangements and peroxy acid oxidations of the resultant amines.[40]

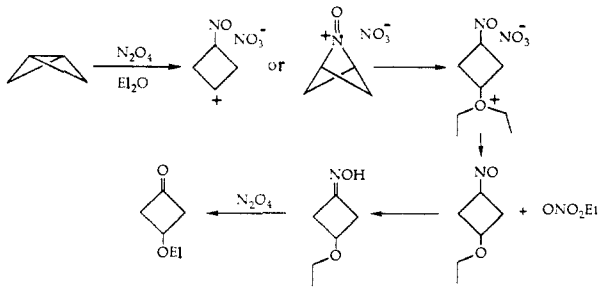


The reactions of **2** and **3** with NO_2 also were examined. The reaction of **2** in ether led to 3-ethoxycyclobutanone, **21** (Scheme IX). The carbonyl group probably arose from an oxime function, we have shown that the corresponding oxime reacts with NO_2 to form the ketone. When tetrahydrofuran was used as the solvent, a similar reaction occurred to form **22**. These reactions are almost certainly ionic processes and are readily derived by addition of NO^+ ($2NO_2 \rightarrow NO^+ + NO_3^-$), followed by capture of the cyclobutyl cation by the ether solvent.

The reaction of **3** with NO_2 proceeded in a different fashion than that of either **1** or **2**. The products are shown in Scheme IX. Compounds **23** and **24** were undoubtedly formed by further oxidation of the 1,3-nitro nitrites, which could arise from either ionic or free-radical addition of NO_2 across the central bond.

(38) Wiberg, K. B.; Lowry, B. R. *J. Am. Chem. Soc.* **1963**, *85*, 3188.
(39) Brown, J. F. *J. Am. Chem. Soc.* **1957**, *79*, 2480. Burkhard, C. A.; Brown, J. F., Jr. *J. Org. Chem.* **1964**, *29*, 2235.

(40) Wiberg, K. B.; Dailey, W. Unpublished results.



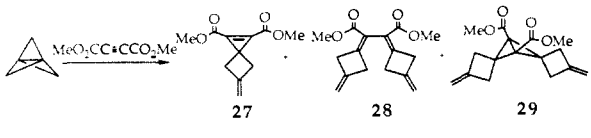
Conspicuously absent from the product mixture was any significant amount of 1,3-dinitrocyclopentane. Compound **25** was probably formed by an oxidative process similar to that which operates for bicyclobutane, but the larger ring size favors the enone over the β-keto ether.

7. Reaction with Electron-Deficient Alkenes and Alkynes

The reactions of various derivatives of **2** and **3** with electron-deficient alkenes and alkynes have been the subject of considerable study over the past two decades. In spite of their similar structures, the reactions of **2** and **3** appear to proceed by quite different mechanisms. The reactions of **3** with electron-deficient alkenes and alkynes are relatively simple.[41] A mechanism that involves initial attack of the alkene under the flap of the bicyclopentane to produce a biradical intermediate, which partitions to give a mixture of "cycloaddition" and "ene" style product, accounts fully for the experimental data. The reactions of **2** with electron-deficient alkenes and alkynes are somewhat more complicated and controversial. With very electron deficient alkenes and alkynes, derivatives of **2** react very rapidly at low temperatures to produce "ene" style product only.[42] By contrast, less electron deficient and even electron rich olefins react with derivatives of **2** at high temperature with almost exclusive formation of "cycloaddition" style product.[41] The orientation of addition of unsymmetrically substituted alkenes to unsymmetrically substituted bicyclobutanes in the high temperature cycloaddition reaction is consistent with the intermediacy of a biradical, but in the low temperature "ene" style reaction this is the opposite of what would be expected if a biradical were an intermediate. Pomerantz has suggested that this "ene" style reaction is either concerted or has a zwitterionic intermediate.[43]

In order to further illuminate this area of hydrocarbon chemistry, we have studied the reactions of **1** and **2** with a variety of electron deficient alkenes and alkynes. The reactions of **1** were of special interest because the additional structural constraint prohibits both "ene" and "cycloaddition" style products from being formed; the reaction must take some new course. We chose also to study the reactions of **2** because most previous studies have made use of the bicyclobutane derivative, 1-cyano-3-methylbicyclobutane. For purposes of comparison with **1** and **3**, it is of course the reactions of the parent which concern us, and these have received scant attention.[42]

The reaction between **1** and dimethyl acetylenedicarboxylate (**26**) proceeded at room temperature at a moderate pace. If **26** was in excess, a mixture of 1:1 adduct (**27**) and 2:1 adducts (**28** and **29**, formed in a 17:1 ratio) was present at the reactions end. If **1** was in excess, then only **28** and **29** were present when the reaction was finished, although **27** might be observed early in the reaction.



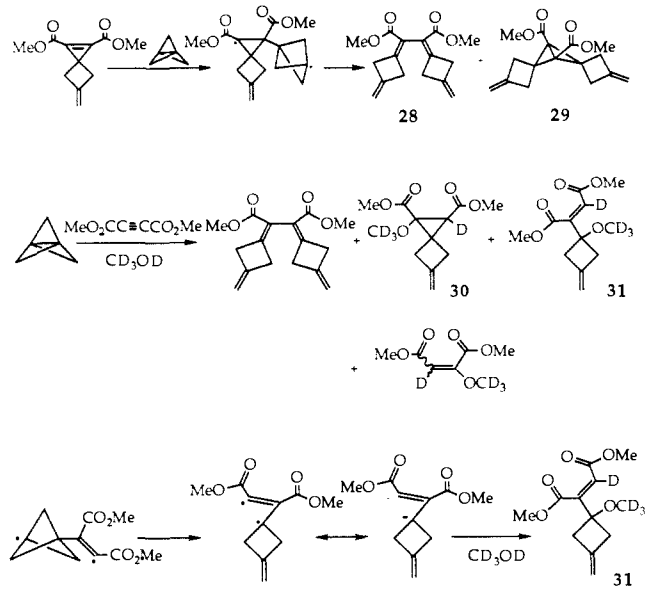
27 **28** **29**

(41) Gassman, P. G.; Mansfield, K. T. *J. Am. Chem. Soc.* **1968**, *90*, 1524. Gassman, P. G.; Mansfield, K. T.; Murphy, T. J. *Ibid.* **1968**, *90*, 4746; **1969**, *91*, 1684. Gassman, P. G. *Acc. Chem. Res.* **1971**, *4*, 128.

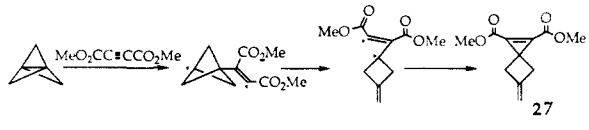
(42) Blanchard, E. P.; Cairncross, A. *J. Am. Chem. Soc.* **1966**, *88*, 487, 496.

(43) Pomerantz, M.; Wilke, R. N.; Gruber, G. W.; Roy, U. *J. Am. Chem. Soc.* **1972**, *94*, 2752.

Scheme X



This suggests that the 2:1 adducts are formed by reaction of **1** with **27**, and this is confirmed by the characteristic sigmoidal shape of the appearance curve for **27**. The mechanism for the reaction of **1** with **26** can be formulated as initial formation of a biradical or zwitterion followed by opening of the bicyclo[1.1.1]pentane skeleton, and finally closure to produce the cyclopropene **27**. The cyclopropene **27** is itself an electron-deficient olefin and can react with another molecule of **1** in a similar fashion, as outlined in Scheme X. The reaction proceeded as described above only in non-hydroxylic solvents. In methanol-d_4 two new products were formed (Scheme X). Compound **30** was obviously formed by methanol trapping of **27**, and compound **31** apparently arose from methanol trapping of an intermediate in the formation of **27** from **1** and **26**.

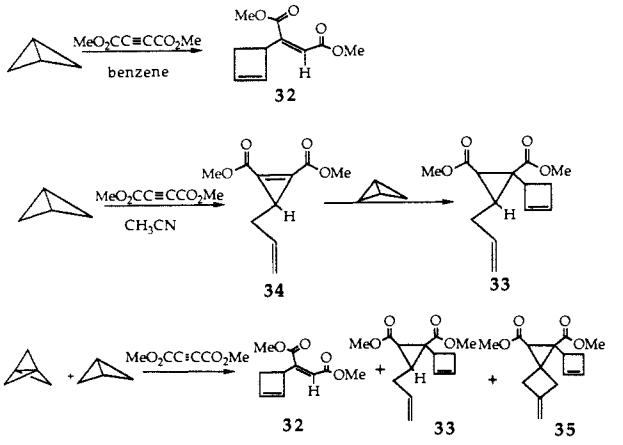


27

Although Pomerantz has reported that **2** does not react with **26**,[43] we have found that the reaction proceeded readily at room temperature at a moderate rate. If the reaction was conducted in a nonpolar solvent such as benzene or cyclohexane, exclusive formation of "ene" style product **32** was observed.

Greater solvent polarity favored formation of a new product which was a 2:1 adduct (**33**). In chloroform, the ratio of **32** to **33** was 4:1, and in acetonitrile or methanol it was 1.5:1. By analogy to the reaction of **1**, it appears that the electron-deficient cyclopropene **34** was formed initially and reacted further with **2** to form **33**. In contrast to the reaction of **26** with **1**, however, **34** was never observed in the NMR and can have only fleeting existence. In further contrast, the reaction of **2** with **26** in MeOH produced no new products; notably, no trapping of **34** with methanol is observed. The style of reactivity for **2** which produced **33** only in polar solvents (presumably via **34**) is unprecedented and along with the "ene" and "cycloaddition" pathways constitutes a third, previously unknown style of reactivity for bicyclobutane with electron-deficient alkenes and alkynes.

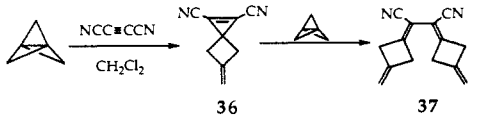
In an effort to conduct a competition experiment, a mixture of **1** and **2** was treated with **26**. The expected products from bicyclobutane (that is **32** and **33**) were formed normally, but none of the usual products incorporating **1** (that is **27**, **28** and **29**) were seen. Instead, a new product (**35**) was formed as the only product incorporating **1**. Additionally, none of compound **27** could be observed by NMR of any point in the reaction. It is clear that **2** reacts extraordinarily quickly with the electron-deficient cyclopropenes **27** and **34** which are formed in the first step of the reaction.



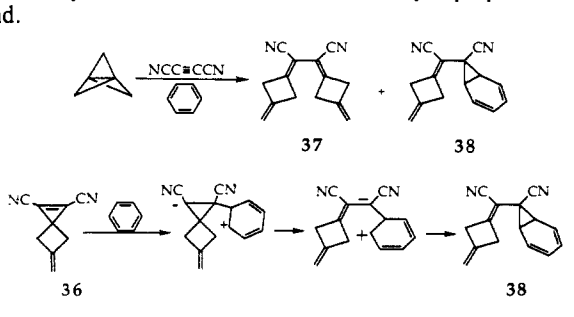
To better understand these reactions, kinetic measurements were performed by sealing the reactants into an NMR tube into which a glass rod had been inserted to eliminate the head space. Concentrations were determined over several days by integration of the proton NMR spectra against an internal standard. Then the data were fit by using the MSIM4 stochastic mechanism simulation program, assuming the mechanisms outlined in Scheme XI. Five reactions were studied: bicyclobutane and propellane individually in a polar and a nonpolar solvent, and the mixed reaction in a polar solvent. Reasonably good fits of the experimental concentrations were obtained (Figure 1), and the data are collected in Table IV.

The rate of the reaction of bicyclobutane with **27** could not be measured directly, but a lower limit was obtained by lowering the rate in the simulation until the calculated rate of formation of **28** exceeded the experimentally determined upper limit. (Only a trace of **28** was observed even at very long reaction times.) Discussion of the data will be postponed until the mechanistic analysis at the end of this section.

The reaction of **1** with the more powerfully electron deficient dicyanoacetylene in chloroform solvent produced products **36** and **37**, similar to those observed with **26**. This reaction was extremely rapid, and although no formal kinetic measurements were made, we estimate that it was at least 10^5 times as fast as the reaction of **1** with **26**.



If the reaction of **1** with dicyanoacetylene was conducted in benzene, **37** was formed along with a new product (**38**) which arose from benzene trapping of **36**. The reaction may proceed via the zwitterionic intermediate shown below, or it might involve initial cleavage of **36** to a vinylcarbene[44] followed by addition to benzene. This remarkable reaction dramatically illustrates the enhanced reactivity of cyclopropenes substituted with electron-withdrawing groups over the corresponding alkyne, which does not react with benzene. In this reaction the loss of aromaticity was apparently balanced by the strain relief on fission of the cyclopropene double bond.



(44) Barton, W. J.; DeCamp, M. R.; Hendrick, M. E.; Jones, M., Jr.; Levin, R. H.; Sohn, M. B. In *Carbenes*; Jones, M. R., Jr., Moss, R. A., Eds.; Wiley: New York, 1973; Vol. 1, p 132.

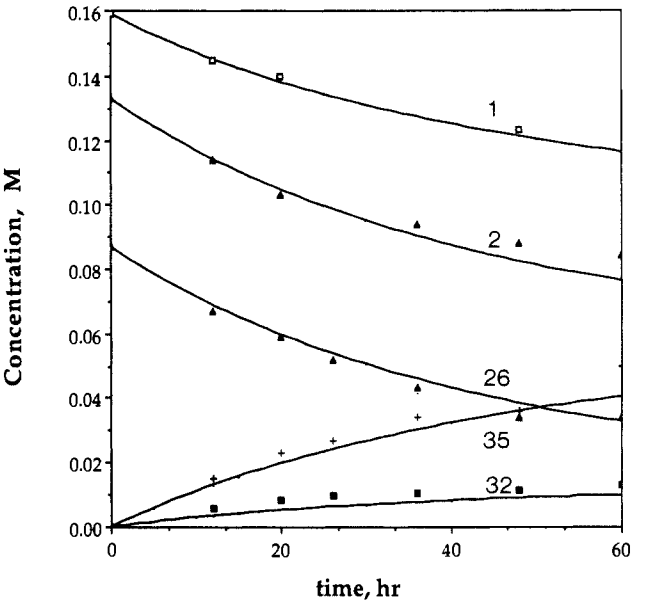


Figure 1. Changes in concentration with time for the reaction of [1.1.1]propellane (**1**) and bicyclo[1.1.0]butane (**2**) with dimethyl acetylenedicarboxylate (**26**), giving **32** and **35** as the principal products. The observed concentrations are given by the symbols, and the lines give the concentrations calculated with the rate constants given in Table IV.

Scheme XI

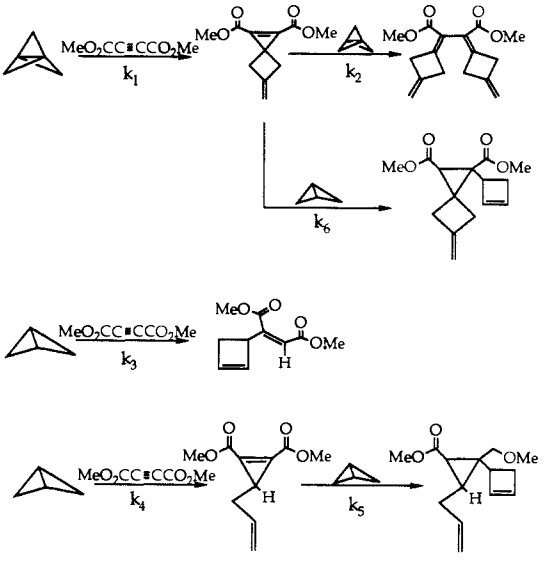


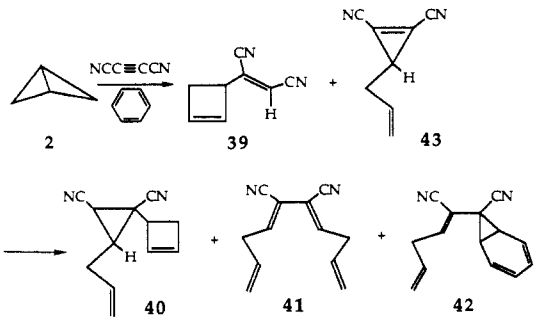
Table IV. Rates of Reaction, 25 °C

reaction	solvent	rate constants[a]
1 + 26	acetone	$k_1 = 0.088$, $k_2 = 3.0$
1 + 26	cyclohexane	$k_1 = 0.014$, $k_2 = 3$
2 + 26	acetone	$k_3 = 0.035$, $k_4 = 0.011$, $k_5 > 1$
2 + 26	cyclohexane	$k_3 = 0.011$, $k_4 = 0.000$
1 + 2 + 26	acetone	$k_1 = 0.09$, $k_2 = 2$, $k_3 = 0.03$ $k_4 = 0.01$, $k_5 > 1$, $k_6 \sim 50$

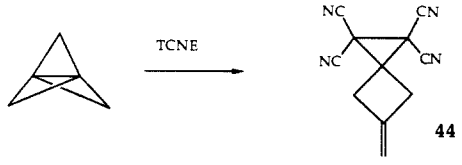
[a] Units: M^{-1} h^{-1}. Estimated uncertainty in rate constants is ±20%.

The reaction of **2** with dicyanoacetylene proceeded in an analogous fashion. In chloroform, **39**, **40**, and **41** were formed in a 10:18:1 ratio, and in benzene, **39**, **40**, **41**, and **42** were formed in a 10:10:1:10 ratio. It should be noted that this reaction produced a small amount of a new type of 1:1 adduct (**41**), which was presumably formed from reaction of **2** with the cyclopropene intermediate (**43**) and which is structurally reminiscent of **28**.

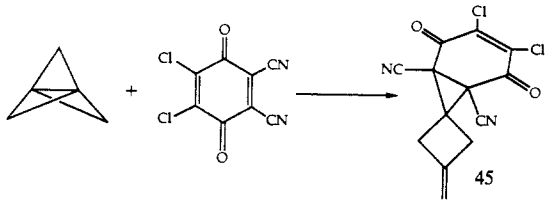
The reaction of **1** with tetracyanoethylene (TCNE) in acetone was rapid and gave the 1:1 adduct, **44**, as the only product. When the reaction was carried out in benzene solution, **44** was again



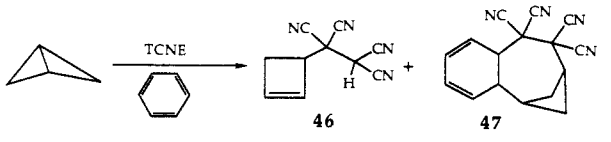
the major product, but a GC–MS analysis of the crude reaction mixture indicated small amounts of products incorporating benzene. It was not possible to isolate these compounds.



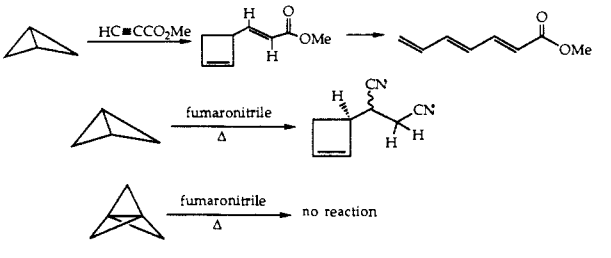
The reactions of **1** with quinones were studied briefly in order to probe for electron-transfer reactions. The reaction of **1** with tetrachloro-1,4-benzoquinone failed to occur at 80 °C, but a facile reaction with dicyanodichloroquinone occurred to give a product (**45**) similar to that encountered in the reaction of **1** with tetracyanoethylene. No evidence of charge transfer in this reaction was observed, and it is undoubtedly similar in mechanism to the TCNE reaction.



The reaction of **2** with tetracyanoethylene in benzene was rapid and produced the "ene" style adduct **46** and the novel tricycle **47** in a 4:1 ratio. The mechanism of formation of **47** probably involves a zwitterionic, instead of a biradical, intermediate. We are unable at present to distinguish between benzene trapping of an initially formed zwitterion and direct attack of bicyclobutane upon benzene complexed by TCNE.

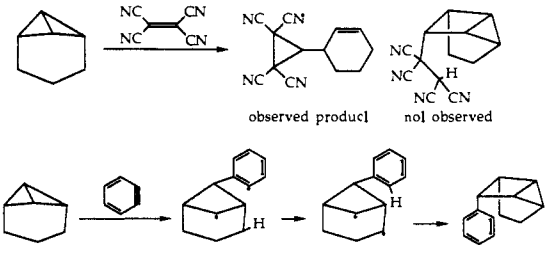


With the more modestly electron deficient methyl propiolate, fumaronitrile, or dimethyl maleate, neither **1** nor **2** reacts at a perceptible rate at room temperature. Upon heating to 80 °C, however, **2** undergoes facile "ene" style reaction with methyl propiolate and fumaronitrile but not with dimethyl maleate. Even at elevated temperatures, **1** does not undergo reaction with any of these compounds.



Prior to this work, virtually all reactions of bicyclobutane derivatives with olefins were observed to proceed by either the "ene" or "cycloaddition" style pathways. We have discovered a type of reactivity for bicyclobutane that is almost unprecedented. This style of reactivity which we shall call the "polar" style, can be formally dissected as a retrocarbene/carbene addition of bicyclobutane to an olefin or alkyne and leads to products such as **35**. In the reaction of **2** with dimethyl acetylenedicarboxylate, the "polar" process competes with "ene" process: in nonpolar solvents, no "polar" reaction at all is observed, and increasing solvent polarity gives increasing amounts of "polar" style reaction. Because of the dramatic differences in product ratio caused by change of solvent, we can exclude the partitioning of a common intermediate as a mechanistic possibility. We have shown that the rate constant for the "ene" reaction increases by only a factor of 4 in going from cyclohexane to acetone, and this is consistent with a concerted mechanism. Since the "polar" reaction does not occur in cyclohexane, it is almost certainly not concerted. In keeping with the orthodox thought on these reactions, a biradical mechanism can probably be excluded because "cycloaddition" should result. All we can say with assurance is that the transition state for the "polar" reaction has a greater dipole moment than the transition state for the "ene" reaction. Probably the most attractive mechanistic alternative involves formation of an intermediate with some charge separation; something between a biradical and a zwitterion.

Several lines of evidence link the "polar" pathway with a charge-separated intermediate or transition state. The first involves Christl's report of a "polar" style product in the reaction of Moore's hydrocarbon with TCNE.[45] This is, to the best of our knowledge, the only other reported instance of this style of reactivity. The reaction of Moore's hydrocarbon with benzyne has been shown to give "homoene" style reaction, which has been established as the alternative path for a biradical intermediate when "cycloaddition" is impossible.[46] Since TCNE is more powerfully electron withdrawing than benzyne, it is not unreasonable to expect that an intermediate with more charge separation than a biradical is formed, and so "polar" style reaction is observed instead of "homo-ene".



A comparison of the reactions of **2** with the series of increasingly electron deficient acetylenes, methyl propiolate, dimethyl acetylenedicarboxylate, and dicyanoacetylene, further establishes the connection between electron withdrawing ability (thus charge separation) in the transition state and "polar" style reaction. The reaction of **2** with methyl propiolate, the least electron deficient member of the series, gives only "ene" style product. With dimethyl acetylenedicarboxylate, which is of intermediate electron deficiency, **2** reacts to give only "ene" style product in nonpolar solvents but gives significant "polar" style product (2:1 adduct) in polar solvents. With the strongly electron deficient dicyanoacetylene, **2** gives mostly "polar" style product even in relatively nonpolar solvents. Clearly, the amount of "polar" style reaction is related to the ability of the electron-deficient acetylene to produce charge separation and in borderline cases also to the ability of the solvent to stabilize charge separation.

It should further be noted that **2** reacts with the electron-deficient cyclopropenes **27** and **34** exclusively in "ene" fashion to form the cyclobutene derivatives **35** and **33**. With the more electron deficient cyclopropene **43**, however, **2** reacts to give both "ene" style product **39** and "polar" style product **40**.

(45) Christl, M.; Lang, R.; Herzog, C.; Stangl, R.; Peters, K.; Peters, E. M.; von Schnering, H. G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 611.
(46) Gassman, P. G.; Richmond, G. D. *J. Am. Chem. Soc.* **1970**, *92*, 2090.

Although the reaction of **1** with dimethyl acetylenedicarboxylate (**26**) produces a compound (**28**) with a structure similar to that of **33**, which is the result of the "polar" style reaction of **2** with **26**, we must not necessarily conclude that the two reactions proceed by the same mechanism. Because of the extra structural constraint, **1** is able to form neither "cycloaddition" nor "ene" products. Since the reaction is only 6 times slower in cyclohexane than in acetone, we feel that its mechanism cannot be the same as for bicyclobutane's "polar" reaction. We are unable to distinguish with certainty between a concerted and a biradical mechanism, but because of the large number of bonding changes and the fact that **30** is formed in methanol solvent, we favor the latter.

Further examination of the rate data reveals that the reaction of **1** with **27** is about 30 times as fast as the reaction of **1** with **26**. We assume that both of these reactions proceed through a biradical intermediate, and so it is clear that the electron deficient cyclopropene is much more reactive than the corresponding electron deficient alkyne. It should be noted that an unstrained olefin bearing two ester groups (dimethyl maleate) is completely unreactive toward **1**.

A similar but still more remarkable rate acceleration is observed in the reactions of **2**. The rate of the "ene" style reaction of **2** with electron-deficient cyclopropene, **43**, is more than 500 times as fast as its reaction with **26**. A rate difference this large is especially curious considering the modest 30-fold acceleration observed for **1**. In light of the extremely facile "ene" style dimerization of cyclopropenes, it is possible that bicyclobutane behaves as a sort of "homologous" cyclopropene.

Now we must consider a few pieces of data which are difficult to reconcile with the mechanistic outline we have presented. The first is the fact that the "ene" style reaction of **2** with fumaronitrile gives a mixture of diastereomers and so is clearly not concerted. We favor a biradical intermediate for this reaction, and we are forced to conclude that the biradical pathway does not lead inevitably to cyclization but can also produce "ene" style product in certain cases.

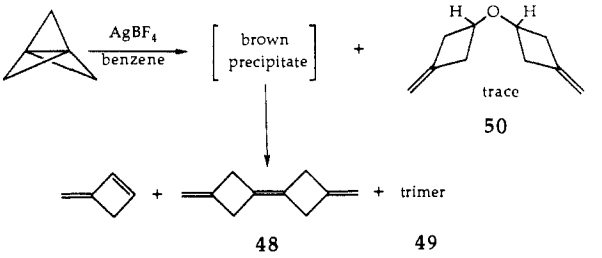
The second troublesome observation concerns the reaction of **1** and **2** with **26** in methanol. Bicyclobutane, which reacts in part by the "polar" pathway with some charge separation, does not form a product resulting from methanol trapping of an intermediate zwitterion. Propellane, on the other hand, does form such a product even though a biradical mechanism is favored. We have no satisfactory explanation for this result. Finally, one might wonder why **45** is formed in the reaction of **2** with TCNE instead of "polar" style product, considering that a charge separated intermediate is almost certainly involved.

We are clearly unable to present a comprehensive mechanistic picture of the reactions of small ring hydrocarbons with electron-deficient alkenes and alkynes. Nevertheless, we have obtained data which limit the mechanistic possibilities and will provide a starting point for more detailed examinations of the origin of the differences in reaction and reactivity between **1** and **2**.

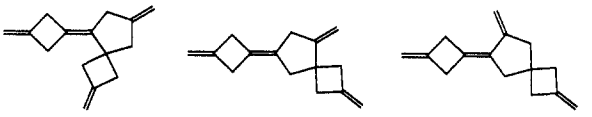
8. Reaction with Transition-Metal Ions

The reactions of bicyclo[1.1.0]butane (**2**) and bicyclo[2.1.0]-pentane (**3**) with transition-metal ions have received extensive study.[47] In the case of **2**, two different mechanisms have been established with silver reacting via an argentocarbocation,[48] and rhodium(I) reacting via a metallocarbene.[49] We were interested in comparing the reactions of **1** with those of **2**.

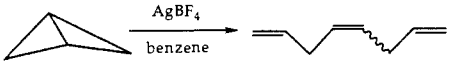
When **1** was added to a solution of silver tetrafluoroborate in benzene, an immediate formation of a flocculate brown precipitate was noted, and if excess silver was present, the NMR spectrum indicated that all of the propellane had been consumed. When the mixture was allowed to stand in the dark, the complex disappeared after several hours to give a clear solution. The products of the reaction were bis(3-methylenecyclobutylidene) (**48**) and a trimer (**49**). The NMR spectrum indicated the presence of a small amount of methylenecyclobutene. If some water is present, bis(3-methylenecyclobutyl) ether (**50**) also is formed. The amount of trimer increased with increasing concentration of **1**.



The NMR spectrum of the trimer showed three sets of *exo*-methylene protons (six protons), signals characteristic of one methylenecyclobutane with nonequivalent faces (four protons), and one with nonequivalent sides (four protons) along with two singlets (two protons each). The carbon NMR spectrum showed three *exo*-methylene carbons and five methylene carbons. The quaternary carbons were not observed. Three structures are consistent with these data:



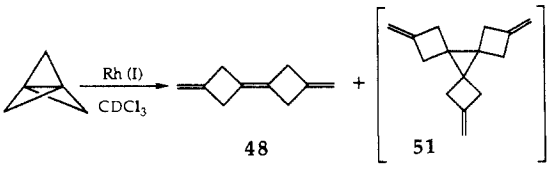
The reaction of bicyclobutane with silver fluoroborate in benzene was reported to give butadiene.[50] However, in our hands the reaction led to a slow formation of 1,4,7-octatriene. No precipitate was formed and essentially no butadiene was observed.



In a competition reaction a solution of **1** and **2** in benzene was treated with silver fluoroborate. The precipitate was formed immediately, and the NMR spectrum indicated a sharp drop in the concentration of **1** whereas that of **2** was unaffected. After 16 h, the precipitate was gone, no **1** remained, but at least 80% of **2** remained. Analysis by GC–MS showed the propellane dimer, a small amount of the bicyclobutane dimer, and small amounts of four different cross-dimers of **1** with **2**.

It might be noted that Majerski observed dimer formation in the silver catalyzed reaction of 9,10-dehydroadamantane[51] similar to that found with **1**.

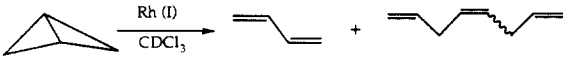
When a small amount of rhodium dicarbonyl chloride dimer was added to a solution of **1** in chloroform, an instantaneous reaction occurred leading to the formation of the propellane dimer. In addition to the signals of the dimer, the proton NMR spectrum showed a small triplet at δ 3.66 and a small quintet at δ 5.28. The GC–MS spectrum showed a large peak for the dimer and a very small peak for a trimer. We have not been able to isolate the trimer, but it is likely that it corresponds to the small bands in the NMR spectrum. If so, it suggests the symmetrical structure **51**.



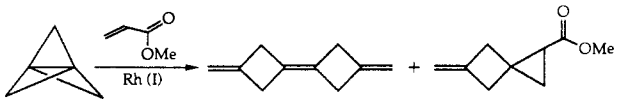
The reaction of bicyclobutane with rhodium dicarbonyl chloride also was rapid and led to butadiene and 1,4,7-octatriene in about a 2:1 ratio. This corresponds to the results presented by Gassman et al. for the rearrangement with norbornadiene rhodium chloride dimer.[52] In a competition experiment, rhodium dicarbonyl

(47) Bishop, K. C. *Chem. Rev.* **1976**, *76*, 461.
(48) Paquette, L. A. *Acc. Chem. Res.* **1971**, *4*, 280.
(49) Gassman, P. G.; Williams, F. J. *J. Am. Chem. Soc.* **1972**, *94*, 7733. Gassman, P. G.; Atkins, T. J. *Ibid* **1972**, *94*, 7748.
(50) Sakai, M.; Yamaguchi, H.; Westberg, H. H.; Masamune, S. *J. Am. Chem. Soc.* **1981**, *93*, 1043.
(51) Majerski, Z.; Mlinaric-Majerski, K. *J. Org. Chem.* **1986**, *51*, 3219.
(52) Gassman, P. G.; Reitz, R. R. *J. Organomet. Chem.* **1973**, *52*, C51.

chloride was added to an equimolar solution of **1** and **2** in chloroform, and a proton NMR spectrum was taken about 90 s after warming to room temperature. All of **1** had been consumed, but about one-third of **2** remained. Propellane dimer, butadiene, and 1,4,7-octatriene were found but no cross-dimers were observed. This indicates that **1** reacts much more rapidly than **2**.



The intermediate in the reaction of **1** is probably a metallocarbene. Evidence for its formation was obtained using a procedure similar to that which was successful with **2**.[52] The reaction was carried out in methyl acrylate as the solvent, and now the propellane dimer and 1-carbomethoxy-5-methylenespirohexane (**52**) were formed in a 1.5:1 ratio. The formation of the carbene addition product provides clear evidence for the metallocarbene intermediate.



48 52

In addition to Rh(I), we have investigated the rearrangement of **1** with complexes of Pd(II), Pt(0), Pt(II), and Ir(I). The reaction of **1** with palladium cyclooctadienyl dichloride and palladium bis(benzonitrile) dichloride proceeded in the same fashion as with rhodium dicarbonyl dimer or rhodium tris(triphenylphosphine) chloride, i.e. an almost instantaneous reaction leading to the propellane dimer.

The behavior of the complexes of the third row transition metals Pt(0), Pt(II), and Ir(I) was quite different. With these complexes, the rearrangement of **1** was quite slow, and large amounts of methylenecyclobutene was formed in addition to propellane dimer. The ratio of methylenecyclobutene to dimer appeared to be related to the oxidation state of the metal. Pt(0) (platinum tetrakis(triphenylphosphine) or platinum bis(triphenylphosphine) ethylenecomplex) gave 8–10 times as much methylenecyclobutene as dimer; Ir(I) (iridium bis(triphenylphosphine) carbonyl chloride) gave 3–4 times as much; and Pt(II) (platinum bis(triphenylphosphine) dichloride) gave about equal amounts.

It is often observed that reactions catalyzed by the second row transition metals are faster than those catalyzed by third row metals,[53] and this trend is dramatically manifested in the rearrangement of **1**.

It can be seen that the reactions of **1** and **2** with transition-metal species are quite similar, the main difference being found in the considerably higher reactivity of **1**. This may well be due to the increased local charge concentration near the bridgehead for **1**, which would make it more susceptible to attack by electrophilic reagents.

9. Experimental Section

General Procedures. Unless otherwise specified, ^{1}H NMR spectra were obtained at 250 MHz in $CDCl_3$ solution. The 1-substituted and 1,3-disubstituted bicyclo[1.1.1]pentane derivatives were usually readily identified by their 6 H sharp singlet for the methylene hydrogens between about δ 2–2.6, but it should be noted that a chiral center at the bridgehead can split the methylene hydrogens into a doublet of doublets. The ^{13}C NMR spectra were obtained at 62.5 MHz in the same solvent. The medium-resolution mass spectra were obtained by using a GC–MS system, and the high-resolution mass spectra were obtained using a Kratos spectrometer. In both cases, either electron impact (70 V) or chemical ionization (isobutane) was used. The more intense peak is indicated by an asterisk.

[1.1.1]Propellane (1). To a septum-capped 250-mL flask were added 5.5 g of 1,1-dibromo-2,2-bis(chloromethyl)cyclopropane[3] and a magnetic stir bar. The material was cooled to −78 °C under nitrogen, and over a period of 15 min there was added 44 mL of 1.2 M methyllithium in ether (low halide). The cooling bath was replaced with an ice–salt bath (−10 to −15 °C), and the mixture was stirred for 1 h. The septum was replaced with an adaptor for a vacuum line, and the volatile material was transferred under vacuum to a liquid nitrogen cooled flask. The propellane was purified by preparative GC equipped with an 18 in. × $^1/_4$ in. 15% Apiezon L on Chromosorb W column at 30 °C. Methyl bromide had a retention time of 5 min, ether of 6 min, and propellane of 10 min. The yield of pure propellane was 55%: ^{1}H NMR δ 2.06 (s, 6 H); ^{13}C NMR δ 74.3 (CH_2), 1.0 (C). The crude solution could be stored for several weeks at −78 °C without noticeable decomposition. In some cases, the reactions may be carried directly using the crude solution.

Reaction of [1.1.1]Propellane with Iodine: 1,3-Diiodobicyclo[1.1.1]pentane. To 2 mL of crude [1.1.1]propellane solution containing ~30 mg of propellane was added 110 mg (0.96 equiv) of I_2 crystals with stirring at room temperature. The iodine was consumed as quickly as it dissolved in solution. At the end of the reaction the solution was clear because of the slight excess of propellane. The solution was evaporated to yield a white solid which can be purified by sublimation (70 °C bath at 0.1 Torr). This gave 110 mg (88%) of white crystals that were determined by ^{1}H NMR and GC–MS to be pure 1,3-diiodobicyclo[1.1.1]pentane: ^{1}H NMR δ 2.66 (s, 6 H); ^{13}C NMR δ 68.2 (CH_2), 1.0 (bridgehead). GC–MS *m/e* 193 (M − I), 127, 66; high-resolution MS (HRMS) (EI) calcd = 319.8558, obsd = 319.8553.

Reaction of [1.1.1]Propellane with Carbon Tetrachloride: 1-Chloro-3-(trichloromethyl)bicyclo[1.1.1]pentane. Pure [1.1.1]propellane (10 mg) was sealed under vacuum in a glass tube containing 0.5 mL of CCl_4. After about 1 h at room temperature and after all propellane had been consumed, the reaction tube was broken open and the solution was purified by GC equipped with a 5 ft × $^1/_4$ in. 1.5% OV-101 on Chromosorb G column at 90 °C. There was only one peak after solvent, and it had a retention time of 8 min. The yield of 26 mg (79%) of pure 1-chloro-3-(trichloromethyl)bicyclo[1.1.1]pentane: ^{1}H NMR (acetone-d_6) δ 2.40 (s, 6 H); ^{13}C NMR (acetone-d_6) δ 97.1 (CCl_3), 56.7 (CH_2), 51.4, 49.1 (bridgeheads); GC–MS *m/e* 149, 147* (M − HCl − Cl), 111, 73, 65, 51; HRMS (CI) calcd = 82.9535 (M − Cl), obsd = 182.9539; IR (CCl_4) 1202 cm^{-1}.

Competition Experiment between [1.1.1]Propellane and Bicyclobutane in Carbon Tetrachloride. An NMR tube containing 0.5 mL of CCl_4 was freeze–pump–thaw cycled twice, frozen in liquid nitrogen, and then 8 mg (0.12 mmol) of propellane and 6.5 mg (0.12 mmol) of bicyclobutane was vacuum transferred into the tube. It was sealed by flame under vacuum and warmed carefully to room temperature. The reaction was monitored by 250-MHz NMR. The spectra were acquired using a 10-s delay between pulses for more accurate integration. Propellane's chemical shift was δ 2.15 and bicyclobutane had peaks at δ 1.70, 1.57, and 0.68. 1-Chloro-3-(trichloromethyl)bicyclo[1.1.1]pentane was observed growing in at δ 2.58. The relative rate of reaction of **1** and **2** was 7:1.

Reaction of [1.1.1]Propellane with Bromotrichloromethane: 1-Bromo-3-(trichloromethyl)bicyclo[1.1.1]pentane. Pure [1.1.1]propellane (5 mg) was isolated by gas chromatography and sealed under vacuum in an NMR tube containing 50 mg of $BrCCl_3$ (3.3 equiv) in 0.5 mL of $CDCl_3$. The reaction mixture was warmed to room temperature in room light. A proton NMR spectrum taken 1 h after warming showed that all propellane had been consumed. The only peak visible in the spectrum was a large singlet at δ 2.45. The yield was not determined but appeared to be quantitative by proton NMR. 1-Bromo-3-(trichloromethyl)bicyclo[1.1.1]pentane: ^{1}H NMR δ 2.45 (s, 6 H); ^{13}C NMR δ 96.3 (CCl_3), 56.9 (CH_2), 53.5 ($CCCl_3$), 35.6 (CBr); GC–MS *m/e* 149, 147 (M − HCl − Br), 111*, 77, 65, 51.

Reaction of [1.1.1]Propellane with Thiophenol: Bicyclo[1.1.1]pentyl Phenyl Sulfide. To a [1.1.1]propellane solution (7.3 mL containing ~110 mg of propellane) was added dropwise rapidly 165 μL (0.96 equiv, based on 110 mg of propellane) of thiophenol. The solution was stirred for 10 min in normal room light and was then evaporated to remove ether and MeBr, redissolved in ~5 mL of pentane, and eluted through a short plug of silica gel (1 in. × $^1/_4$ in.) with pentane. The eluent was periodically spotted on a TLC plate and visualized with UV light in order to tell when the product had come off the column. The pentane was then evaporated, giving 275 mg (98%) based on thiophenol) of a clear liquid which was determined by ^{1}H NMR and GC–MS to be pure bicyclo[1.1.1]pentyl sulfide: ^{1}H NMR δ 7.50–7.44 (m, 2 H), 7.35–7.25 (m, 4 H), 2.73 (s, 1 H), 1.96 (s, 6 H); GC–MS *m/e* 176 (M), 135, 110*, 91, 67, 65; HRMS (CI) calcd = 177.0739 (M + 1), obsd = 177.0744.

Reaction of [1.1.1]Propellane with *tert*-Butyl Hypochlorite: 1-Chloro-3-*tert*-Butoxybicyclo[1.1.1]pentane. Pure [1.1.1]propellane (10 mg) was isolated by gas chromatography and vacuum transferred into a reaction tube. About 4 mL of *tert*-butyl hypochlorite was then vacuum transferred onto the propellane, and the reaction mixturew as stirred at −78 °C for 3 h and then allowed to warm to room temperature. Flash chromatography on silica gel eluting with 5:1 pentane/ether allowed isolation of 15 mg (57%) of a pure 1-chloro-3-*tert*-butoxybicyclo-

(53) Collman, J. P.; Hegedus, L. S. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1980; p 49.

[1.1.1]pentane: ^{1}H NMR δ 2.36 (s, 6 H), 1.25 (s, 9 H); ^{13}C NMR δ 62.9 (CO *t*-Bu), 60.9 (CH_2), 45.7 (CCl), 28.9 (CH_3); GC–MS *m/e* 139 (M − Cl), 117 (M − *t*-Bu), 101 (M − *t*-BuO), 83.57* (*t*-Bu).

Reaction of [1.1.1]Propellane with Diphenyl Disulfide: 1,3-Bis(thiophenoxy)bicyclo[1.1.1]pentane. To 1 mL of a [1.1.1]propellane solution containing ~15 mg of propellane in a 10-mL reaction tube was added 90 mg of diphenyl disulfide. The reaction tube was septum-capped, magnetically stirred, and irradiated overnight with a 60 W electric light bulb placed ~12 in. away. The mixture was evaporated and chromatographed on silica gel. Pentane was used to elute until the diphenyl disulfide came off the column; then the column was eluted with ether until the product came off. The yield was 29 mg of 1,3-bis(thiophenoxy)bicyclo[1.1.1]pentane (45%): ^{1}H NMR δ 7.4 (m, 2 H), 7.3 (m, 4 H), 2.03 (s, 6 H); ^{13}C NMR δ 133.7, 128.9, 127.5, 127.0 (aromatic ring), 57.3 (methylenes), 15.2 (bridgehead); GC–MS *m/e* 283 (M − 1), 175*, 142, 109, 91, 77, 65; HRMS (EI) calcd = 284.0695, obsd = 284.0705.

Reaction of [1.1.1]Propellane with Diphenyl Diselenide: 1,3-Bis(selnophenoxy)bicyclo[1.1.1]pentane. To 1 mL of a solution containing ~15 mg of propellane in a 10-mL reaction tube were added 90 mg of diphenyl diselenide. The reaction tube was septum capped and magnetically stirred for 36 h under hood lights. Chromatography on silica gel used pentane to elute the diphenyl disulside then used ether to obtain the product. The yield was 33 mg of 1,3-bis(selenophenoxy)bicyclo[1.1.1]-pentane (38%): ^{1}H NMR δ 7.5 (m, 2 H), 7.3 (m, 4 H), 2.03 (s, 6 H); ^{13}C NMR δ 135.5, 131.6, 129.7, 129.2 (aromatic ring), 59.6 (methylenes), 29.7 (bridgehead); GC–MS *m/e* 222 (M − SePh), 156, 142, 129, 115, 102, 91, 77*, 65, 51; HRMS (EI) calcd = 379.9583, obsd = 379.9580.

Catalyzed Free-Radical Additions. A thin-walled glass tube containing 0.5 mL of the reagent and 3 μL of *tert*-butyl peroxide was degassed by two freeze–thaw cycles and frozen in liquid nitrogen. To this was vacuum transferred 6–7 mg of propellane. The tube was sealed under vacuum, warmed to room temperature, and photolyzed for 15 min in a Rayonet-style photolysis apparatus. The tube was opened, and the products were separated by use of a 2.8 ft × $^1/_4$ in. 5% OV-101 column.

Reaction of [1.1.1]Propellane with Deuterochloroform. The reaction with $CDCl_3$ was carried out as described above. The yield was 8.4 mg of 1-deutero-3-(trichloromethyl)bicyclo[1.1.1]pentane (43%): ^{1}H NMR δ 2.02 (s, 6 H); GC–MS (Cl isobutane) *m/e* 150 (M − Cl), 114, 80, 68.

3-Deutero-3′-(trichloromethyl)-1,1′-bibicyclo[1.1.1]pentane]: This compound was not isolated but was observed in the NMR and mass spectrum: ^{1}H NMR δ 1.82 (s, 6 H), 1.69 (s, 6 H); GC–MS (Cl isobutane) *m/e* 216 (M − Cl), 180, 144, 123, 80, 68.

Reaction of [1.1.1]Propellane with Acetaldehyde: 1-(1-Hydroxyethyl)-3-(1-oxoethyl)bicyclo[1.1.1]pentane. The reaction with acetaldehyde was carried out as described above. The tube was broken open, and the excess acetaldehyde was allowed to evaporate at room temperature, leaving solid material. The solid was chromatographed on silica gel eluting with 5:1 pentane/ether to yield 8.4 mg (52%) of 1-(1-hydroxyethyl)-3-(1-oxoethyl)bicyclo[1.1.1]pentane: ^{1}H NMR δ 3.82 (q, $J \approx 7.5$ Hz, 1 H), 2.12 (s, 3 H), 1.90 (d of d, $J \approx 7$ Hz, 6 H), 1.13 (d, $J \approx 7.5$ Hz, 3 H); GC–MS *m/e* 153 (M − 1), 139, 121, 93, 77*, 71, 55; HRMS (Cl) calcd = 155.1072 (M + 1), obsd = 155.1061.

Reaction of [1.1.1]Propellane with Butyraldehyde: 1-(1-Hydroxybutyl)-3-(1-oxobutyl)bicyclo[1.1.1]pentane and 1-Bicyclo[1.1.1]pentyl Propyl Ketone. The reaction with butyraldehyde was carried out as described above. The tube was broken open, and the solution was carefully evaporated. The crude material was chromatographed on silica gel eluting with 5:1 pentane/ether to yield 11.9 mg (50%) of 1-(1-hydroxybutyl)-3-(1-oxobutyl)bicyclo[1.1.1]pentane and 3.0 mg (19%) of 1-bicyclo[1.1.1]pentyl butyl ketone. Analysis of the reaction mixture by GC indicated that the products were formed in a 2:1 ratio.

1-(1-Hydroxybutyl)-3-(1-oxobutyl)bicyclo[1.1.1]pentane: ^{1}H NMR δ 3.60 (d of d, J = 3.3 and 8.4 Hz, 1 H), 2.43 (t, J = 7.3 Hz, 2 H), 1.93 (d of d, $J \approx 1.5$ Hz, 6 H), 1.70–1.25 (m, 7 H), 0.93 (apparent quartet, $J \approx 7.3$ Hz, 6 H); HRMS (Cl) calcd = 193.1593 (M + 1 − H_2O), obsd = 193.1589.

1-Bicyclo[1.1.1]pentyl butyl ketone: ^{1}H NMR δ 2.48 (s, 1 H), 2.40 (t, J = 7.31 Hz, 2 H), 2.06 (s, 6 H), 1.57 (m, 4 H), 0.91 (t, J = 7.67 Hz); GC–MS *m/e* 138 (M), 123, 109, 95, 67*; HRMS (CI) calcd = 139.1123 (M + 1), obsd = 139.1135.

Reaction of [1.1.1]Propellane with Isobutyraldehyde. The reaction with isobutyraldehyde was carried out as described above. The tube was broken open, and the solution was carefully evaporated. TLC in 1:1 pentane/ether and development with *p*-anisaldehyde stain showed four spots. The crude material was chromatographed on silica gel eluting with 10:1 pentane/ether until the two high R_f spots came off the column, then eluting with 1:1 pentane/ether to get off the two low R_f spots. Obtained in this manner was 3.3 mg of a ≈1:3.5 mixture of compounds [A] and [B] (21%), 1.9 mg of compound [C] (9%), 3.1 mg of compound [D] (13%), and 3.1 mg of compound [E] (13%).

Compound [A]: ^{1}H NMR δ 9.55 (s, 1 H), 2.56 (s, 1 H), 1.73 (s, 6 H), 1.01 (s, 6 H); GC–MS (70 eV) *m/e* 137 (M − 1), 123, 109, 95, 81, 67*, 55, 41 (Cl isobutane) 139 (M + 1), 121, 95; HRMS (Cl) of unseparated mixture of compounds [A] and [B]: calcd = 139.1123 (M + 1), obsd = 139.1135. It was identified as 1-bicyclo[1.1.1]pentyldimethylacetaldehyde.

Compound [B]: ^{1}H NMR δ 2.85 (apparent quintet, J = 6.94, 1 H), 2.49 (s, 1 H), 2.10 (s, 6 H), 1.57 (m, 4 H), 1.06 (d, J = 6.94 Hz); GC–MS (70 eV) *m/e* 138 (M), 123, 109, 95, 67*, 41 (Cl isobutane) 139 (M + 1), 121; HRMS (CI) of unseparated mixture of compounds [A] and [B] calcd = 139.1123 (M + 1), obsd = 139.1135. It was identified as 1-bicyclo[1.1.1]pentyl isopropyl ketone.

Compound [C]: ^{1}H NMR δ 3.32 (d, J = 5.5 Hz, 1 H), 1.80–1.55 (m, 2 H), 1.53 (d of d, $J \approx 3$ Hz, 6 H), 0.95 (d, J = 6.9 Hz, 3 H), 0.93 (d, J = 6.8 Hz, 3 H), 0.83 (d, J = 6.6 Hz, 6 H); GC–MS (70 eV) *m/e* 167 (M − Me), 149, 121*, 105, 93, 81, 69, 55, 43 (Cl isobutane) 165 (M + H^+ − H_2O), 109, 95. It was identified as 1-(1-hydroxy-2-methylpropyl)-3-isopropylbicyclo[1.1.1]pentane.

Compound [D]: ^{1}H NMR δ 9.56 (s, 1 H), 3.34 (d, J = 5.5 Hz, 1 H), 1.68 (d, of d, $J \approx 3$ Hz, 6 H), 1.03 (s, 6 H), 0.95 (d, J = 4 Hz, 3 H), 0.92 (d, J = 4 Hz, 3 H); GC–MS (70 eV) *m/e* 209 (M − 1), 195, 177, 163, 149, 121*, 107, 93, 79, 67, 55, 43 (CI isobutane) 193 (M + H^+ − H_2O), 165, 135, 121, 71; HRMS (CI) calcd = 193.1593 (M + 1 − H_2O), obsd = 193.1597. It was identified as 1-(1-hydroxy-2-methylpropyl)-3-(1-oxo-2-methyl-2-propyl)bicyclo[1.1.1]pentane.

Compound [E]: ^{1}H NMR δ 3.36 (d, J = 5.1 Hz, 1 H), 2.87 (apparent quintet, J = 6.95, 1 H), 2.04 (d of d, $J \approx 3$ Hz, 6 H), 1.84–1.61 (m, 1 H), 1.09 (s, 3 H), 1.06 (s, 3 H), 0.96 (d, $J \approx 6.6$ Hz, 3 H), 0.94 (d, $J \approx 6.9$ Hz, 3 H); GC–MS *m/e* (70 eV) 177 (M − Me − H_2O), 149, 121, 107, 93, 81, 71, 55, 43* (Cl isobutane) 193 (M + H^+ − H_2O), 167, 135, 121, 71; HRMS (CI) calcd = 193.1593 (M + 1 − H_2O), obsd = 193.1588. It was identified as 1-(1-hydroxy-2-methylpropyl)-3-(1-oxo-2-methylpropyl)bicyclo[1.1.1]pentane. Analysis of the reaction mixture by capillary GC showed that the reaction products were formed in the ratio of [A]:[B]:[C]:[D]:[E] = 1.0:1.4:1.1:1.0:2.1.

Reaction of [1.1.1]Propellane with Pivaldehyde: 1-*tert*-Butylbicyclo[1.1.1]pentane-3-carboxaldehyde (10) and 1-*tert*-Butylbicyclo[1.1.1]pentane (9). The reaction with pivaldehyde was carried out as described above. Five peaks were seen in the GC trace: pivaldehyde came off from 0 to 1 min, *tert*-butyl peroxide and 1-*tert*-butylbicyclo[1.1.1]pentane came off as two partially resolved peaks (collected together) from 1 to 2 min, an unidentified compound that has a singlet at δ 1.24 in the proton NMR came off from 3 to 4 min, and 3-*tert*-butylbicyclo[1.1.1]pentane-1-carboxaldehyde came off from 6 to 7 min.

3-*tert*-Butylbicyclo[1.1.1]pentane-1-carboxaldehyde: ^{1}H NMR δ 9.61 (s, 1 H), 1.83 (s, 6 H), 0.87 (s, 9 H); GC–MS *m/e* 151 (M − 1), 137 (M − Me), 119, 109, 95, 83, 67, 55*, 41.

1-*tert*-Butylbicyclo[1.1.1]pentane: ^{1}H NMR δ 2.44 (s, 1 H), 1.58 (s, 6 H), 0.82 (s, 9 H); GC–MS *m/e* 109 (M − Me), 83, 67, 55, 41*.

Integration of the proton NMR spectrum of the reaction mixture showed that 3-*tert*-butylbicyclo[1.1.1]pentane-1-carboxaldehyde and 1-*tert*-butylbicyclo[1.1.1]pentane were formed in a ratio of approximately 1:2.5.

Reaction of [1.1.1]Propellane with Benzaldehyde: 1-(1-Hydroxybenzyl)-3-(1-oxobenzyl)bicyclo[1.1.1]pentane. The reaction with benzaldehyde was carried out as described above. Most of the benzaldehyde was removed under high vacuum with gentle heating with a Kugelrohr apparatus. The remaining material was chromatographed on silica gel eluting with 3:1 pentane/ether to yield 14.4 mg (49%) of 1-(1-hydroxybenzyl)-3-(1-oxobenzyl)bicyclo[1.1.1]pentane: ^{1}H NMR δ 8.2–7.3 (m, 10 H), 4.80 (s, 1 H), 2.13 (d of d, $J \approx 4.5$ Hz, 6 H); HRMS (Cl) calcd = 261.1280 (M + 1 − H_2O), obsd = 261.1282.

Reaction of [1.1.1]Propellane with Cyanogen Bromide. The reaction with cyanogen bromide was carried out as described above with use of 0.5 mL of a saturated solution of cyanogen bromide in pentane and 15 mg of propellane. The pentane and excess cyanogen bromide were removed under aspirator vacuum in a fume hood, and the remaining material was chromatographed on silica gel eluting with 10:1 pentane/ether to yield 12 mg of 3-cyano-3′-bromo[1,1′-bibicyclo[1.1.1]pentane] (45%), 2.5 mg of 3-cyano-3′-bromo[1,1′:3′,1″-terbicyclo[1.1.1]pentane] (11%), and 2.6 mg of 3,3′-dibromo[1,1′-bibicyclo[1.1.1]pentane] (8%).

3,3′-Dibromo[1,1′-bibicyclo[1.1.1]pentane]: ^{1}H NMR δ 2.12 (s, 6 H); ^{13}C NMR δ 58.0 (CH_2), 57.7 (C-Br), 29.8 (quaternary); GC–MS (Cl isobutane) *m/e* 213, 211 (M − Br), 132, 131.

3-Cyano-3′-bromo[1,1′:3′,1″-terbicyclo[1.1.1]pentane: ^{1}H NMR δ 2.07 (s, 6 H), 2.06 (s, 6 H), 1.50 (s, 6 H); ^{13}C NMR δ 57.6, 53.2, 48.5 (methylenes); GC–MS (Cl isobutane) *m/e* 306, 304 (M + 1), 224, 123*.

3-Cyano-3′-bromo[1,1′-bibicyclo[1.1.1]pentane]: ^{1}H NMR δ 2.12 (s, 6 H), 2.11 (s, 6 H); ^{13}C NMR δ 57.5 (CH_2), 53.8 (CH_2), 42.8, 36.3, 25.3,

23.3 (bridgeheads: the last two are weak in the spectrum and a bit uncertain); GC–MS (Cl isobutane) *m/e* 240*, 238 (M + 1), 158, 131; HRMS (Cl) calcd = 238.0232 (M + 1), obsd = 238.0233.

Under these conditions 1-cyano-3-bromobicyclo[1.1.1]pentane was not formed in significant quantity. Photolysis was not always necessary to initiate this reaction but provides more reproducible results than simply allowing the reaction to stand in the light.

Reaction of [1.1.1]Propellane with Acetone. The reaction with acetone was carried out as described above. The mass spectrum of the reaction mixture showed clean formation of 1:1, 2:1, 3:1 and 4:1 adducts (propellane to ketone) in decreasing amounts. In the GC after the solvent, there was a single peak, with a retention time of 3 min, that was collected to yield 3.8 mg of 1-bicyclo[1.1.1]pentylacetone (33%): ^{1}H NMR δ 2.58 (s, 2 H), 2.51 (s, 1 H), 2.13 (s, 3 H), 1.81 (s, 6 H); GC–MS *m/e* 123 (M − 1), 109, 91, 81, 67, 53, 43*.

2:1 adduct: This compound was not isolated but was clearly seen in the GC–MS, *m/e* 175 (M − Me), 165, 149, 131, 121, 105, 91, 79, 65, 43*.

3:1 adduct: This compound was not isolated but was clearly seen in the GC–MS, *m/e* 197, 183, 171, 157, 143, 129, 117, 105, 91, 77, 67, 59, 43*.

4:1 adduct: This compound was not isolated but was clearly seen in the GC–MS, *m/e* 195, 185, 173, 149, 133, 123, 107, 91, 77, 67, 53, 43*.

Reaction of [1.1.1]Propellane with Methyl Ethyl Ketone: 3-(1-Bicyclo[1.1.1]pentyl)-2-butanone. The reaction with methyl ethyl ketone was carried out as described above. In the GC after the solvent, there was a single peak, with a retention time of 3 min, that was collected to yield 9 mg of 3-(1-bicyclo[1.1.1]pentyl)-2-butanone (72%): ^{1}H NMR δ 2.68 (q, J = 6.95 Hz, 1 H), 2.52 (s, 1 H), 2.12 (s, 3 H), 1.73 (s, 6 H), 1.02 (d, J = 6.95, 3 H); GC–MS *m/e* 123 (M − Me), 109, 95*, 81, 67, 55.

Reaction of [1.1.1]Propellane with Methyl Formate: Methyl Bicyclo[1.1.1]pentane-1-carboxylate. The reaction with methyl formate was carried out as described above. In the GC after the solvent there was one peak, with retention time of 1 min. The yield was 5.3 mg of methyl bicyclo[1.1.1]pentane-1-carboxylate (40%): ^{1}H NMR δ 3.67 (s, 3 H), 2.43 (s, 1 H), 2.10 (s, 6 H); GC–MS (70 eV) *m/e* 125 (M − 1), 111, 95, 83, 67*; HRMS (EI) calcd = 126.0681, obsd = 126.0671.

Reaction of [1.1.1]Propellane with Methyl Propionate. The reaction with methyl propionate was carried out as described above. The mass spectrum of the reaction mixture showed clean formation of 1:1, 2:1, 3:1 and 4:1 adducts (propellane to ester) in decreasing amounts. In the GC after solvent there were two peaks, with retention times of 1.5 min (methyl 2-(1-bicyclo[1.1.1]pentyl)propionate = 1:1 adduct) and 8 min (methyl 2-[3-(1,1′-bibicyclo[1.1.1]pentyl)]propionate = 2:1 adduct). The yield of the two products was 7.3 mg (45%) and 2.1 mg (18%), respectively.

Methyl 2-bicyclo[1.1.1]pentylpropionate: ^{1}H NMR δ 3.68 (s, 3 H), 2.55 (q, J = 6.95, 1 H), 2.49 (s, 1 H), 1.70 (s, 6 H), 1.08 (d, J = 6.95, 3 H); GC–MS (70 eV) *m/e* 153 (M − 1), 139, 123, 95*, 79, 67, 55.

Methyl 2-[3-(1,1′-bibicyclo[1.1.1]pentyl)]propionate: ^{1}H NMR δ 3.66 (s, 3 H), 2.56 (q, J = 6.95, 1 H), 2.39 (s, 1 H), 1.62 (s, 6 H), 1.48 (s, 6 H), 1.05 (d, J = 6.95, 3 H); GC–MS (70 eV) *m/e* 189 (M − OMe), 173, 159, 145, 131, 117, 105, 91*, 77, 65.

The 3:1 adduct was not isolated but was clearly seen in the GC–MS *m/e* 255 (M − OMe), 211, 197, 183, 169, 157, 143, 129, 117, 105, 91*, 77, 65, 59. In addition there were three peaks in the proton NMR which we believe may be tentatively assigned the three types of methylenes in this compound: δ 1.60, 1.46, 1.40.

The 4:1 adduct was not isolated but was clearly seen in the GC–MS: *m/e* 321 (M − OMe), 249, 235, 223, 209, 195, 181, 169, 157, 143, 129, 117, 105, 91*, 77, 65, 59.

Reaction of [1.1.1]Propellane with Methyl Acetoacetate: Methyl 2-(1-Bicyclo[1.1.1]pentyl)acetoacetate. The reaction with methyl acetoacetate was carried out as described above. In the GC (105 °C) after the solvent there was a single peak, with a retention time of 6 min. The yield was 7.5 mg of methyl 2-bicyclo[1.1.1]pentylacetoacetate (45%): ^{1}H NMR δ 3.73 (s, 3 H), 3.60 (s, 1 H), 2.55 (s, 1 H), 2.22 (s, 3 H), 1.90 (s, 6 H).

Reaction of [1.1.1]Propellane with Methyl Cyanoacetate: Methyl 2-(1-Bicyclo[1.1.1]pentyl)-2-cyanoacetate. The reaction with methyl cyanoacetate was carried out as described above. In the GC (130 °C) after the solvent, there was a single peak, with a retention time of 7 min. The yield was 7 mg of methyl 2-bicyclo[1.1.1]pentylcyanoacetate (45%): ^{1}H NMR δ 3.83 (s, 3 H), 3.65 (s, 1 H), 2.63 (s, 1 H), 1.93 (s, 6 H); GC–MS (70 eV) *m/e* 134 (M − OMe), 120, 106, 79, 67, 59*.

Reaction of [1.1.1]Propellane with Methyl Chloroacetate: Methyl 2-(1-Bicyclo[1.1.1]pentyl)-2-chloroacetate. The reaction with methyl chloroacetate was carried out as described above. In the GC (80 °C) after the solvent, there was a single peak, with a retention time of 6 min. The yield was 12 mg of methyl 2-bicyclo[1.1.1]pentyl-2-chloroacetate (75%): ^{1}H NMR δ 4.33 (s, 1 H), 3.79 (s, 3 H), 2.56 (s, 1 H), 1.84 (d of d, $J \approx 0.2$ Hz, 6 H); GC–MS (70 eV) *m/e* 139 (M − Cl), 107, 79*, 67, 59.

The 2:1 adduct was seen in the GC–MS spectrum but was not isolated: GC–MS *m/e* 205 (M − Cl), 173, 145, 131, 117, 105, 91*, 77, 67, 65, 59. No higher adducts were seen in the GC–MS.

Reaction of [1.1.1]Propellane with Methyl 2-Chloropropionate: Methyl 2-(1-Bicyclo[1.1.1]pentyl)-2-chloropropionate. The reaction with methyl 2-chloropropionate was carried out as described above. In the GC (110 °C) after the solvent, there was a single peak, with a retention time of 2.5 min. The yield was 13 mg of methyl 2-(1-bicyclo[1.1.1]pentyl)-2-chloropropionate (65%). ^{1}H NMR δ 3.79 (s, 3 H), 2.55 (s, 1 H), 1.83 (s, 6 H), 1.69 (s, 3 H); GC–MS (70 eV) *m/e* 153 (M − Cl), 121, 93*, 77, 65, 53.

Reaction of [1.1.1]Propellane with Tetrahydrofuran. The reaction with tetrahydrofuran was carried out as described above. The mass spectrum of the reaction product showed clean formation of 1:1, 2:1, 3:1, and 4:1 adducts (propellane to ester) in decreasing amounts. In the GC (60 °C) after solvent, there was a peak, with a retention time of 5.5 min (1-(1-bicyclo[1.1.1]pentyl)tetrahydrofuran = 1:1 adduct). The yield was 5.5 mg (44%). The 2:1 adduct was isolated from a separate, identically conducted experiment by preparative GC at 130 °C. There was a peak after solvent with a retention time of 7 min. The yield was 2.2 mg of 1-[3-(1,1′-bibicyclo[1.1.1]pentyl)]tetrahydrofuran (24%).

1-(1-Bicyclo[1.1.1]pentyl)tetrahydrofuran: ^{1}H NMR δ 3.9–3.7 (m, 3 H), 2.51 (s, 1 H), 1.9–1.6 (m, 4 H), 1.71 (d of d, $J \approx 8$ Hz, 6 H); GC–MS (70 eV) *m/e* 137 (M − 1), 123, 110, 97, 84, 71, 55*; HRMS (EI) calcd = 137.0967 (M − 1), obsd = 137.0980.

1-[3-(1,1′-Bibicyclo[1.1.1]pentyl)]tetrahydrofuran: ^{1}H NMR δ 3.9–3.7 (m, 3 H), 2.39 (s, 1 H), 1.9–1.8 (m, 4 H), 1.63 (s, 6 H), 1.49 (d of d, $J \approx 8$ Hz, 6 H); GC–MS (70 eV) *m/e* 189, 163, 145, 129, 117, 105, 91*, 79, 71, 67, 65, 55; HRMS (EI) calcd = 203.1437 (M − 1), obsd = 203.1452.

The 3:1 adduct was not isolated but was clearly seen in the GC–MS *m/e* 211, 195, 181, 169, 155, 143, 129, 117, 105, 91, 77, 71, 65, 55.

The 4:1 adduct was not isolated but was clearly seen in the GC–MS (70 eV): *m/e* 221, 207, 193, 181, 167, 155, 141, 129, 115, 105, 91*, 77, 71, 67, 65, 55.

Determination of Chain-Transfer Constant in Reaction of [1.1.1]Propellane with Tetrahydrofuran. In order to determine the chain-transfer constant, it was necessary to measure the ratio of the oligomeric products produced in the reaction for several concentrations of propellane in THF. The reactions were conducted as described in the previous experiment except that the propellane was first weighed in a gas storage bulb and the amount of THF was chosen to give the desired concentration. In addition, the tube was sealed as close to the meniscus as possible to minimize gas volume. Solutions of 0.06, 0.13, 0.19, and 0.57 M propellane in THF were prepared.

After photolysis the solutions were analyzed by capillary GC. With an initial temperature of 50 °C, raised at a rate of 10 °C/min to a final temperature of 290 °C, the oligomers had the following retention times: 1:1 eluted after 10 min, 2:1 after 23 min, 3:1 after 30 min, 4:1 after 35 min, and 5:1 after 42 min. Each peak was followed closely by a smaller peak (approximately one tenth the area of the major peak) which might be due to the isomeric product (attachment of bicyclopentyl at carbon 2 rather than carbon 1).

The results of the experiment and details of using the MSIM4 stochastic kinetics modeling program to fit the data are given in section 3.

Reaction of [1.1.1]Propellane with 1,3-Dioxolane: 2-(1-Bicyclo[1.1.1]pentyl)-1,3-dioxolane and 4-(1-Bicyclo[1.1.1]pentyl)-1,3-dioxolane. The reaction with 1,3-dioxolane was carried out as described above. The mass spectrum of the reaction mixture showed clean formation of 1:1, 2:1, and 3:1 adducts (propellane to ester) in decreasing amounts. In the GC (75 °C) after solvent, there was a peak, with a retention time of 3 min (a 3:1 mixture of the two 1:1 adducts 2-(1-bicyclo[1.1.1]pentyl)-1,3-dioxolane and 4-(1-bicyclo[1.1.1]pentyl)-1,3-dioxolane. The yield was 7.4 mg of the mixture of 1:1 adducts (50%).

2-(1-Bicyclo[1.1.1]pentyl)-1,3-dioxolane: ^{1}H NMR δ 4.79 (s, 1 H), 4.0–3.8 (m, 4 H), 2.52 (s, 1 H), 1.82 (s, 6 H); GC–MS (70 eV) *m/e* 139 (M − 1), 125, 112, 99, 79, 73*, 67, 55; HRMS (CI) of unseparated product mixture calcd = 141.0912 (M + 1), obsd 141.0909.

4-(1-Bicyclo[1.1.1]pentyl)-1,3-dioxolane: ^{1}H NMR δ 4.0–3.6 (m, 3 H), 2.56 (s, 1 H), 1.77 (d of d, $J \approx 8$ Hz, 6 H); GC–MS (70 eV) *m/e* 1139 (M − 1), 125, 112, 99, 79, 73*, 67, 55; HRMS (Cl) of unseparated product mixture calcd = 141.0912 (M + 1), obsd = 141.0909.

2:1 adduct(s): This compound was not isolated but is clearly seen in the GC–MS *m/e* 165, 149, 129, 117, 105, 91, 73*, 65, 55.

3:1 adduct(s): This compound was not isolated but is seen as a very small peak in the GC–MS, *m/e* 165, 149, 141, 129, 117, 105, 91, 73*, 65, 55.

Reaction of [1.1.1]Propellane with Triethylsilane: 1-Bicyclo[1.1.1]-pentyltriethylsilane and [1-(1-Bicyclo[1.1.1]pentyl)ethyl]diethylsilane. The reaction with triethylsilane was carried out as described above. The GC–MS showed formation of both 1:1 and 2:1 adducts. In the GC (105 °C) after solvent, there was a peak, with a retention time of 3 min (a 3:1 mixture of the two 1:1 adducts [1-(1-bicyclo[1.1.1]pentyl)ethyl]diethylsilane and bicyclo[1.1.1]pentyltriethylsilane). The yield was 7.7 mg of the mixture of 1:1 adducts (40%).

[1-(1-Bicyclo[1.1.1]pentyl)ethyl]diethylsilane: ^{1}H NMR δ 3.57 (q, $J \approx 3$ Hz, 1 H), 2.45 (s, 1 H), 1.69 (d of d, $J \approx 4$ Hz, 6 H), 1.1–0.9 (m, 5 H), 0.7–0.5 (m, 9 H); GC–MS *m/e* 153 (M – Et), 125, 115, 97*, 87, 69, 59.

1-Bicyclo[1.1.1]pentyltriethylsilane: ^{1}H NMR δ 2.70 (s, 1 H), 1.87 (s, 6 H), 0.99 (t, J = 8.3 Hz, 6 H), 0.50 (q, J = 8.3 Hz, 9 H); GC–MS (70 eV) *m/e* 153 (M – Et), 125, 115, 97*, 87, 69, 59.

Two to one adduct(s): This compound was not isolated but was clearly seen in the GC–MS, *m/e* 219 (M – Et), 205, 191, 177, 163, 149, 135, 115, 87*, 59.

Reaction of [1.1.1]Propellane with Triethylamine: *N,N*-Diethyl-1-(1-bicyclo[1.1.1]pentyl)ethylamine. The reaction with triethylamine was carried out as described above. In the GC (90 °C) after solvent, there was one peak, with a retention time of 3.5 min. The yield was 3.9 mg of *N,N*-diethyl-1-(1-bicyclo[1.1.1]pentyl)ethylamine (22%): ^{1}H NMR δ 2.76 (q, J = 6.93 Hz, 1 H), 2.6–2.4 (m, 4 H), 2.46 (s, 1 H), 1.74 (d of d, $J \approx 9$ Hz, 6 H), 1.01 (t, J = 7.5 Hz), 0.90 (d, J = 6.93 Hz, 3 H).

Reaction of [1.1.1]Propellane with Dimethyl Phosphite: Dimethyl 1-Bicyclo[1.1.1]pentylphosphonate. The reaction with dimethyl phosphite was carried out as described above. In the GC (180 °C) after the solvent, there was one peak, with a retention time of 3.5 min. The yield was 10.8 mg of dimethyl 1-bicyclo[1.1.1]pentylphosphonate (58%): ^{1}H NMR δ 3.74 (d, J = 10.6 Hz, 6 H), 2.70 and 2.48 (d, J = 55.92 Hz, 1 H), 2.46 (s, 1 H), 2.15 (d, J = 2.85 Hz, 6 H); HRMS (CI) calcd = 177.0681, obsd = 177.0718.

Reaction of [1.1.1]Propellane with Diphenylphosphine: 1-Bicyclo-[1.1.1]pentyldiphenylphosphine. The reaction with 50 mg of diphenylphosphine (3 equiv) in 0.5 mL of CH_2Cl_2 was carried out as described above. The solution was evaporated, and the residue was dissolved in $CDCl_3$. Proton NMR showed clean formation of 1-bicyclo[1.1.1]-pentyldiphenylphosphine along with excess diphenylphosphine. The product was not separated from excess starting material, and the yield was not determined. ^{1}H NMR δ 7.6–7.3 (m, 10 H), 2.83 and 2.71 (doublet with J = 29.61 Hz, 1 H), 2.46 (s, 1 H), 1.94 (s, 6 H).

After the tube was broken open and the solution sat exposed to air for several weeks, the proton NMR revealed that the bicyclo[1.1.1]pentyldiphenylphosphine was going away and a new product was growing in that had in addition to phenyl protons a doublet at 2.84 and 2.66 ($J \approx$ 45 Hz, 1 H) and a singlet at 2.17 (6 H) as well as phenyl protons. This new product proved to be 1-bicyclo[1.1.1]pentyldiphenylphosphine oxide: HRMS (CI) calcd = 269.1091 (M + 1), obsd = 261.1097.

1-Lithiobicyclo[1.1.1]pentane. At the start of the reaction a septum-capped Schlenck tube (hereafter referred to as the flask) was flame dried under vacuum and then filled with Ar, and then this was repeated. When the flask had cooled, 273 mg of 3,3′-di-*tert*-butylbiphenyl and a magnetic stirbar were introduced, and the flask was again evacuated and filled with Ar. Tetrahydrofuran (5 mL) freshly distilled from Na/K/benzophenone was added by syringe. Lithium wire was scraped with a spatula to remove the oxide coating, and 35 mg of it was freshly clipped in small pieces directly into the flask. The septum was replaced, and the solution became dark green within about 60 s. The solution was stirred at 0 °C under positive Ar pressure for 4 h. This gave 5 mL of ~0.17–0.20 M lithium dibutylbiphenyl radical anion solution (hereafter referred to as LiDBB solution).

A second Schlenck vessel was dried and filled with Ar as described above, and 70 μL (~77 mg = 0.44 mmol) of 1-bicyclo[1.1.1]pentyl phenyl sulfide and 2 mL of freshly distilled tetrahydrofuran were added along with a magnetic stir bar and cooled under Ar to −78 °C. The 5 mL of LiDBB solution prepared as described above was added dropwise. The acetone/dry ice bath was replaced with a chloroform/dry ice bath (−65 to −55 °C) and the reaction mixture was allowed to stir for 45 min. At the end of 45 min the reaction was recooled to −78 °C. It contained approximately two parts of 1-lithiobicyclo[1.1.1]pentane and lithium phenylthiolate to one part phenyllithium and lithium 1-bicyclo[1.1.1]-pentylthiolate. It was used in further reactions as described below.

1-Deuterobicyclo[1.1.1]pentane. 1-Bicyclo[1.1.1]pentyllithium solution was prepared as described from 2.5 mL of LiDBB solution and 35 mg of 1-bicyclo[1.1.1]pentyl phenyl sulfide. To the stirred solution at −78 °C was added 65 μL (~10 equiv) of 99% MeOD. The color of the solution changed to light purple. The solution was allowed to warm to room temperature and became clear. The reaction mixture was freeze–pump–thaw cycled three times to remove air, and the volatiles were vacuum transferred into a liquid N_2 cooled flask. The solution was separated by GC equipped with a $^1/_4$ in. × 15 ft 15% squalane on Chromosorb W HP column at 30 °C and collected in a liquid nitrogen cooled "U" tube. The yield was 3.5 mg (27%) of the known 1-deuterobicyclo[1.1.1]pentane. From the proton NMR deuteration appeared to be essentially complete, although the exact amount of deuteration was not precisely determined.

1-Deuterobicyclo[1.1.1]pentane: ^{1}H NMR δ 2.45 (center of three equally sized peaks, J = 2.45 Hz, 1 H), 1.85 (s, 6 H).

1-(Trimethylsilyl)bicyclo[1.1.1]pentane. 1-Bicyclo[1.1.1]pentyllithium solution was prepared as described above from 3 mL of LiDBB solution and 40 μL (44 mg = 0.25 mmol) of 1-bicyclo[1.1.1]pentyl phenyl sulfide. To the stirred solution at −78 °C was added quickly by syringe 40 μL of trimethylsilyl chloride (1.25 equiv). The solution color changed to reddish purple. The solution was allowed to warm to room temperature and stir overnight. After 12 h the solution was milky and colorless. Volatiles were separated from nonvolatiles by Kugelrohr distillation, and then separated via GC equipped with a 2.8 ft × $^1/_4$ in. 5% OV-101 50/60 V column at 30 °C. The desired product was the only peak besides solvent on the trace. The yield was 4.2 mg (12%): ^{1}H NMR δ 2.70 (s, 1 H), 1.78 (s, 6 H), −0.07 (s, 9 H).

1-Bicyclo[1.1.1]pentyltri-*n*-butyltin. 1-Bicyclo[1.1.1]pentyllithium solution was prepared as described above from 2.5 mL of LiDBB solution and 35 μL (39 mg = 0.22 mmol) of 1-bicyclo[1.1.1]pentyl phenyl sulfide. To the stirred solution at −78 °C was added 65 mL (1.1 equiv) of tri-*n*-butyltin chloride by syringe. The mixture was allowed to warm to room temperature and stir for 4 h at which time 15 mL of ether and 5 mL saturated NH_4Cl solution were added. This mixture was vigorously agitated, and then the organic layer was separated and dried over $MgSO_4$, and the ether was then removed. Silica gel chromatography with pentane allowed isolation of the rapidly eluting compound. The yield was 40 mg (50%) of the desired compound contaminated with a small amount of phenyltributyltin: ^{1}H NMR δ 2.89 (s, 1 H, methine for all nonmagnetic isotopes of Sn). In addition, three doublets centered at δ 2.89 were observed which arose from magnetic isotopes of Sn: J_{Sn119} = 179.5 Hz (8.58% isotopic abundance), J_{Sn117} = 171.0 Hz (7.61% isotopic abundance), J_{Sn115} = 156.1 Hz (0.35% isotopic abundance), 1.99 (s, 6 H), 1.5 (apparent sextet, 2 H), 1.3 (apparent sextet, 2 H), 0.9 (t, 9 H), 0.8 (m, 6 H); GC–MS (CI isobutane) *m/e* 357, 355, 353 (M's) 301, 299, 297, 291, 289, 287; HRMS (EI) calcd = 3557.1606 (M – 1), obsd = 357.1605.

1-Bicyclo[1.1.1]pentyl *tert*-Butyl Ether. 1-Bicyclo[1.1.1]pentyllithium solution was prepared as described above from 2 mL of LiDBB solution and 30 μL (33 mg = 0.19 mmol) of 1-bicyclo[1.1.1]pentyl phenyl sulfide. To the stirred solution at −78 °C was added 100 μL (~3.5 equiv) of *tert*-butyl peroxide. The solution turned red and was allowed to stir for 10 min at −78 °C. The mixture was allowed to warm to room temperature and turned from red to yellow slowly over the course of 40 min. The reaction solution was allowed to stir overnight and then 1 mL of saturated NH_4Cl was added. The solution was shaken and the organic layer was separated, dried over $MgSO_4$, and separated by GC equipped with a 2.8 ft × $^1/_4$ in. 5% OV-101 50/60 V column at 50 °C. The desired compound had a retention time of 4 min under these conditions, and no other peak besides solvent was observed. The yield was 2.5 mg (15%): ^{1}H NMR δ 2.29 (s, 1 H), 2.01 (s, 6 H), 1.28 (s, 9 H); GC–MS (79 eV) *m/e* 125 (M – Me), 83, 57*, 41.

1-Bicyclo[1.1.1]pentanecarboxylic Acid. 1-Bicyclo[1.1.1]pentyllithium solution was prepared as described above from 2 mL of LiDBB solution and 30 μL (33 mg = 0.19 mmol) of 1-bicyclo[1.1.1]pentyl phenyl sulfide. The solution was stirred at −78 °C, and a stream of CO_2 was bubbled into the solution by using a long needle. An exit needle vented the CO_2 stream. The solution instantly decolorized. The solution was allowed to warm to room temperature and turned first milky white then clear. Saturated $NaHCO_3$ (5 mL) and 5 mL of ether were added, and the mixture was shaken. The aqueous layer was separated, acidified with excess HCl, and then extracted four times with 25 mL of ether. This was dried over $MgSO_4$ and evaporated to give 10 mg (45%) of 1-bicyclo-[1.1.1]pentanecarboxylic acid which appeared to be pure by NMR except for some small absorbances in the aromatic region, presumably due to benzoic acid: ^{1}H NMR δ 2.45 (s, 1 H), 2.13 (s, 6 H), (lit.[25] δ 2.43, 2.10.)

1-Bicyclo[1.1.1]pentylphenylcarbinol. 1-Bicyclo[1.1.1]pentyllithium solution was prepared as described above from 2.5 mL of LiDBB solution and 40 μL (44 mg = 0.25 mmol) of bicyclo[1.1.1]pentyl phenyl sulfide. To the stirred solution at −78 °C was added 75 μL (3 equiv) of freshly distilled benzaldehyde. The color instantly faded to yellow. The solution was allowed to warm to room temperature. Ether (10 mL) and 1 mL of saturated NH_4Cl were added, and the mixture was vigorously agitated. The organic layer was separated, dried over $MgSO_4$, and then evaporated to remove solvent. The remaining oil was separated, dried over $MgSO_4$, and then evaporated to remove solvent. The remaining oil was dissolved

in a small amount of 1:4 ether/pentane and chromatographed with 1:10 ether/pentane on silica gel. TLC (20:1 pentane/ether) showed two blue spots with *p*-anisaldehyde development whose R_f values were approximately 0.6 and 0.1. The lower R_f spot proved to be the desired product, while the higher R_f spot was unreacted bicyclo[1.1.1]pentyl phenyl sulfide. There was isolated 10 mg of unreacted sulfide and 19 mg of 1-bicyclo[1.1.1]pentylphenylcarbinol (57% yield corrected for unreacted starting material): ^{1}H NMR δ 7.4–7.2 (m, 5 H), 4.65 (d, J = 2 Hz, 1 H), 2.52 (s, 1 H), 1.86 (d, J = 2 Hz), 1.66 (d of d, $J \approx$ 5 Hz); GC–MS (70 eV) m/e 173 (M − 1), 133, 107*, 79, 67; HRMS (EI) calcd = 173.0967 (M − 1), obsd = 173.0973.

Bicyclo[1.1.1]pentyl-*tert*-butylcarbinol. This reaction was performed precisely the same way as the preceding reaction to form 1-bicyclo-[1.1.1]pentylphenylcarbinol, except 35 μL (39 mg = 0.22 mmol) of sulfide with 2.5 mL of LiDBB solution was used, and the anion was quenched with 60 μL (3–4 equiv) of pivaldehyde. Chromatography with 15:1 pentane/ether on silica gel afforded 21 mg (60%) of the desired alcohol: ^{1}H NMR δ 3.21 (s, 1 H), 2.49 (s, 1 H), 1.86 (d of d, J = 1.65 Hz, 6 H), 1.56 (br s, 1 H), 0.98 (s, 9 H).

1-Bicyclo[1.1.1]pentanecarboxaldehyde. This reaction was performed in the same way as the preceding reaction to form bicyclo[1.1.1]-pentylphenylcarbinol, except 20 μL (22 mg = 0.13 mmol) of sulfide with 1.0 mL of LiDBB solution was used and the anion was quenched with 10 μL (2 equiv) of methyl formate. TLC showed two spots when developed with *p*-anisaldehyde: in 1:1 ether/pentane a blue spot of R_f = 0.9 and a brown spot of R_f = 0.8; in CH_2Cl_2 the R_f values were 0.8 and 0.5, respectively. Chromatography with CH_2Cl_2 on silica gel showed that the blue spot was unreacted sulfide and the brown spot was 1-bicyclo-[1.1.1]pentanecarboxaldehyde. There were isolated 3.5 mg of starting sulfide and 2.5 mg of a 3:1 mixture of 1-bicyclo[1.1.1]pentanecarboxaldehyde (21% corrected for recovered starting material) and benzaldehyde side product. It appeared that no bis(1-bicyclo[1.1.1]pentyl)-carbinol was formed (no low R_f spot was observed by TLC; NMR and GC–MS revealed no other product). ^{1}H NMR δ 9.50 (s, 1 H), 2.55 (s, 1 H), 2.09 (s, 1 H); GC–MS m/e 95 (M − 1), 67*, 53, 41.

Bis(1-bicyclo[1.1.1]pentyl)-*tert*-butylcarbinol. 1-Bicyclo[1.1.1]-pentyllithium solution was prepared as described above from 1.5 mL of LiDBB solution and 20 μL (22 mg = 0.13 mmol) of 1-bicyclo[1.1.1]-pentyl phenyl sulfide. To the stirred solution at −78 °C was added 50 μL (3 equiv) of methyl pivalate. The solution turned light yellow, was stirred for 10 min at −78 °C, and allowed to warm to room temperature. Ether (15 mL) and 5 mL of saturated NH_4Cl were added, and the solution was vigorously agitated. The organic layer was separated, dried over $MgSO_4$, and then evaporated. Chromatography in 20:1 pentane/ether on silica gel allowed for the isolation of 5 mg of pure bis(1-bicyclo[1.1.1]pentyl)*tert*-butylcarbinol (35% yield): ^{1}H NMR δ 2.41 (s, 2 H), 2.02 (s, 12 H), 1.56 (br s, 1 H), 1.03 (s, 9 H); GC–MS (CI isobutane) m/e 203 (M + H$^+$ − H_2O), 161, 147*, 133, 119, 109, 95, 81, 67.

Bis(1-bicyclo[1.1.1]pentyl)phenylcarbinol and 1-Bicyclo[1.1.1]pentyl Thiobenzoate. 1-Bicyclo[1.1.1]pentyllithium solution was prepared as described above from 1.5 mL of LiDBB solution and 24 μL (26 mg = 0.15 mmol) of 1-bicyclo[1.1.1]pentyl phenyl sulfide. To the stirred solution at −78 °C was added 35 μL (1 equiv) of benzoyl chloride in 1 mL of ether. The solution instantly decolorized and was allowed to warm to room temperature. Ether (15 mL) and 5 mL of saturated NH_4Cl were added, and the solution was vigorously agitated. The organic layer was separated, dried over $MgSO_4$, and then evaporated. Chromatography in 20:1 pentane/ether on silica gel allowed for the isolation of 9 mg of 1-bicyclo[1.1.1]pentyl thiobenzoate (30% yield) and 9.2 mg of bis(1-bicyclo[1.1.1]pentyl)phenylcarbinol (52% yield).

1-Bicyclo[1.1.1]pentyl thiobenzoate: ^{1}H NMR δ 8.1 (d, 2 H), 7.7–7.3 (m, 4 H), 2.90 (s, 1 H), 2.33 (s, 6 H); GC–MS (CI isobutane) m/e 205* (M + H$^+$), 105; FTIR ($CDCl_3$ solution) 1663 cm^{-1}.

Bis(1-bicyclo[1.1.1]pentyl)phenylcarbinol: ^{1}H NMR δ 7.5–7.2 (m, 6 H), 2.49 (s, 1 H), 1.80 (d of d, J = 10 Hz, 6 H); GC–MS (CI isobutane) m/e 223* (M + H$^+$ − H_2O); HRMS (EI) calcd = 240.1515, obsd = 240.1514.

1-Bicyclo[1.1.1]pentyl Benzoate. 1-Bicyclo[1.1.1]pentyllithium solution was prepared as described above from 1.5 mL of LiDBB solution and 20 μL (22 mg = 0.13 mmol) of 1-bicyclo[1.1.1]pentyl phenyl sulfide. The solution was stirred at −78 °C and a stream of O_2 was bubbled into the solution by using a long needle. An exit needle vented the O_2 stream. The solution turned red, and then light yellow in about 20 s. The solution was stirred under a gentle O_2 stream for 10 min at −78 °C, and then 46 μL (3 equiv) of benzoyl chloride was added. The solution was allowed to warm to room temperature. Saturated $NaHCO_3$ (1 mL) and 5 mL of ether were added, and the mixture was shaken. The organic layer was separated, dried over $MgSO_4$, and evaporated carefully. Chromatography in 20:1 pentane/ether on silica gel allowed the isolation of 17.3 mg of a mixture (~1:1 by proton NMR) of 1-bicyclo[1.1.1]pentyl thiobenzoate and 1-bicyclopentyl benzoate (34%).

1-Bicyclo[1.1.1]pentyl benzoate: ^{1}H NMR δ 8.0 (d, 2 H), 7.7–7.4 (m, 4 H), 2.63 (s, 1 H), 2.32 (s, 6 H); GC–MS (CI isobutane) m/e 189* (M + H$^+$), 123, 105, 67.

1-Bicyclo[1.1.1]pentyl Phenyl Ketone. 1-Bicyclo[1.1.1]pentyllithium solution was prepared as described above from 5.0 mL of LiDBB solution and 70 μL (77 mg = 0.44 mmol) of 1-bicyclo[1.1.1]pentyl phenyl sulfide. To the stirred solution at −78 °C was added 60 μL (1.25 equiv) of benzonitrile in 1 mL of ether. The solution was allowed to warm to room temperature and stir for 1 h. Ether (20 mL) and 5 mL of saturated NH_4Cl were added, and the solution was vigorously agitated. The organic layer was separated, dried over $MgSO_4$, and then evaporated. Chromatography in 20:1 pentane/ether on silica gel allowed the isolation of 69 mg of a 1.9:1.4:1 mixture (by proton NMR) of 1-bicyclopentyl phenyl ketone (50% yield), benzophenone, and benzonitrile.

1-Bicyclo[1.1.1]pentyl phenyl ketone: ^{1}H NMR δ 8.0 (d, 2 H), 7.6–7.4 (m, 3 H), 2.59 (s, 1 H), 2.35 (s, 6 H); GC–MS (CI isobutane) m/e 173* (M + H$^+$), 155, 105.

1-Bicyclo[1.1.1]pentyl *tert*-Butyl Ketone. 1-Bicyclo[1.1.1]pentyl-lithium solution was prepared as described from 2.5 mL of LiDBB solution and 35 μL (39 mg = 0.22 mmol) of 1-bicyclo[1.1.1]pentyl phenyl sulfide. To the stirred solution at −78 °C was added 90 μL (3 equiv) of pivalonitrile in 1 mL of ether. The solution turned red and was allowed to warm to room temperature, and stirred for 1 h. Ether (20 mL) and 5 mL of saturated NH_4Cl were added, and the solution was vigorously agitated. The organic layer was separated, dried over $MgSO_4$, and then evaporated. Chromatography in 20:1 pentane/ether on silica gel allowed the isolation of 32 mg of a 1:2 mixture (by proton NMR) of *tert*-butyl phenyl ketone and 1-bicyclo[1.1.1]pentyl *tert*-butyl ketone (60% yield): ^{1}H NMR δ 2.46 (s, 1 H), 2.17 (s, 6 H), 1.17 (s, 9 H); GC–MS (CI isobutane m/e 153* (M + H$^+$), 135.

1-Bicyclo[1.1.1]pentyl *tert*-butyl ketone: ^{1}H NMR δ 2.46 (s, 1 H), 2.17 (s, 6 H), 1.17 (s, 9 H); GC–MS (CI isobutane) m/e 153* (M + H$^+$), 135; HRMS (EI) calcd = 152.1202, obsd = 152.1210.

Conjugate Addition to Cyclohexenone Using CuI. 1-Bicyclo[1.1.1]-pentyllithium solution was prepared as described above from 1.5 mL of LiDBB solution and 24 μL (26 mg = 0.15 mmol) of 1-bicyclo[1.1.1]-pentyl phenyl sulfide. The stirred solution at −78 °C was quickly cannulated under Ar pressure into a second Schlenck tube containing 29 mg of CuI (15 mmol) in 0.5 mL of ether, also cooled to −78 °C. The solution was allowed to stir for 20 min, at which time it was dark olive/black. A solution of 9 mg of cyclohexenone in 1 mL of ether was added, and the solution was warmed to 0 °C and stirred for 2 h. The solution was then cannulated into 8 mL of rapidly stirred saturated NH_4Cl. Ether (10 mL) was added, the mixture was shaken, the organic layer was separated and dried over $MgSO_4$ and then evaporated. TLC in 1:1 pentane/ether and development with *p*-anisaldehyde stain showed a blue spot with $R_f \approx$ 0.85 (unreacted sulfide), a pink/brown spot at $R_f \approx$ 0.60 (conjugate addition product), and a blue spot at $R_f \approx$ 0.42 (1,2-addition product). The proton NMR of the reaction mixture showed that they were formed in ≈ 1:1 ratio. Chromatography in 5:1 pentane/ether on silica gel allowed the isolation of 3.2 mg of conjugate addition product (22% based on cyclohexenone) and 3.5 mg of the 1,2-addition product (25% based on cyclohexenone).

3-(1-Bicyclo[1.1.1]pentyl)cyclohexanone: ^{1}H NMR δ 2.51 (s, 1 H), 2.4–1.2 (series of small featureless multiplets, 9 H), 1.64 (s, 6 H); GC–MS m/e 163 (M − 1), 95, 79, 67, 55; FTIR (CCl_4 solvent) 1716 cm^{-1}.

3-(1-Bicyclo[1.1.1]pentyl)-3-hydroxycyclohexenone: ^{1}H NMR δ 5.87 (doublet of triplets, J = 10 Hz and 3 Hz, 1 H), 5.58 (broad doublet, J = 10 Hz, 1 H), 2.52 (s, 1 H), 2.1–1.4 (series of small featureless multiplets, 6 H), 1.73 (s, 6 H); FTIR (CCl_4 solvent) 3610 cm^{-1}.

Addition to Cyclohexenone without Using CuI. 1-Bicyclo[1.1.1]-pentyllithium solution was prepared as described from 1.5 mL of LiDBB solution and 24 μL (26 mg = 0.15 mmol) of bicyclo[1.1.1]pentyl phenyl sulfide. To the stirred solution at −78 °C was added 15 mg (1 equiv) of cyclohexenone in 0.5 mL of THF. The solution decolorized and was allowed to warm to room temperature. It was then cannulated into 10 mL of saturated NH_4Cl. Ether (10 mL) was added, and the organic layer was separated, dried over $MgSO_4$, and then evaporated. TLC in 1:1 pentane/ether and development with *p*-anisoaldehyde stain showed only a blue spot at $R_f \approx$ 0.42 (1,2-addition product). The proton NMR of the reaction mixture also showed that no conjugate addition product was formed. The 1,2-addition product was not isolated. This reaction was performed to verify that the CuI was responsible for conjugate addition.

Conjugate Addition to Alkyl Acrylates Using CuI. The reaction was performed with ethyl acrylate, *sec*-butyl acrylate, and *tert*-butyl acrylate. The same (1,2 and 1,4) addition product was formed in each case and the yields were similar.

1-Bicyclo[1.1.1]pentyllithium solution was prepared as described above from 3.0 mL of LiDBB solution and 55 μL (62 mg = 0.35 mmol) of 1-bicyclo[1.1.1]pentyl phenyl sulfide. The stirred solution at −78 °C was quickly cannulated under Ar pressure into a second Schlenk tube containing 60 mg of CuI (0.31 mmol) in 1.0 mL of ether, also cooled to −78 °C. The solution was allowed to stir for 20 min, at which time it was black. A solution of 1 equiv of ethyl, *sec*-butyl, or *tert*-butyl acrylate in 1 mL of ether was added, and the solution was warmed to 0 °C, stirred for 2 h, and then allowed to warm to room temperature and to stir overnight. The solution was then cannulated into 10 mL of rapidly stirred saturated NH_4Cl. Ether (10 mL) was added, and the mixture was shaken. The organic layer was separated, dried over $MgSO_4$, and then evaporated. Chromatography in 20:1 pentane/ether on silica gel allowed the isolation of the (1,2 and 1,4) addition product 1-bicyclo[1.1.1]pentyl 2-(1-bicyclo[1.1.1]pentyl)ethyl ketone. The yields ranged from 20% to 30%: ^1H NMR δ 2.48 (s, 1 H), 2.45 (s, 1 H), 2.36 (t, J = 7.68 Hz, 2 H), 2.06 (s, 6 H), 1.67 (t, J = 7.68 Hz, 2 H), 1.62 (s, 6 H); GC–MS (CI isobutane) m/e 191 ($M + H^+$), 95*.

Addition to *tert*-Butyl Acrylate without Using CuI. 1-Bicyclo-[1.1.1]pentyllithium solution was prepared as described above from 1.0 mL of LiDBB solution and 16 μL (18 mg = 0.10 mmol) of 1-bicyclo-[1.1.1]pentyl phenyl sulfide. To the stirred solution at −78 °C was added 19 mg (1 equiv) of *tert*-butyl acrylate in 0.5 mL of THF. The solution decolorized and was allowed to warm to room temperature. It was then cannulated into 10 mL of saturated NH_4Cl. Ether (10 mL) was added, and the organic layer was separated, dried over $MgSO_4$, and then evaporated. Chromatography on silica gel with 5:1 pentane/ether allowed isolation of the (1,2 and 1,4) adduct (spectral data as reported above) as well as two bis-1,2-addition products (~1:1 mixture by proton NMR) isolated as a mixture, bis(1-bicyclo[1.1.1]pentyl)vinylcarbinol [A] and 1-bicyclo[1.1.1]pentylphenylvinylcarbinol [**B**] (the latter from pentyllithium produced in the initial reduction).

Compounds [A] and [B]: No attempt to separate the compounds was made, so there is some ambiguity in the NMR assignment. One set of methylene protons appears as a singlet at δ 1.78 (presumably compound [**B**] because vinyl and phenyl might be fairly similar electronically); the other set appears as a doublet of doublets ($J \approx 5$ Hz) centered at δ 1.67 (presumable compound A). The two methine hydrogens appear as two singlets at δ 2.53 and 2.50. Four doublets overlap in the δ 5.4–5.1 region, presumably two from each molecule. Two addition set of doublets of doublets appear at δ 6.41 and 5.83 ($J \approx 10$ and 18 Hz in each). A multiplet from δ 7.3–7.6 represents the phenyl protons. The GC–MS (CI isobutane) (m/e) has two peaks in the chromatogram, one with a large peak at 173 (which is parent + H^+ − H_2O for compound [A]) and the other with a large peak at 183 (which is parent + H^+ − H_2O for compound [B]).

Addition to Benzoyl Chloride Using CuI. 1-Bicyclo[1.1.1]pentyllithium solution was prepared as described above from 5.0 mL of LiDBB solution and 85 μL (94 mg = 0.53 mmol) of bicyclo[1.1.1]pentyl phenyl sulfide. The stirred solution at −78 °C was quickly cannulated under Ar pressure into a second Schlenck tube containing 103 mg of CuI (15 mmol) in no solvent, also cooled to −78 °C. The solution was allowed to stir for 20 min, at which time it was dark olive/black. Benzoyl chloride (110 μL) was added, the solution was stirred for 20 min, and then 150 μL of MeOH was added. The solution was cannulated into 8 mL of rapidly stirred saturated NH_4Cl. Ether (10 mL) was added, the mixture was shaken, and the organic layer was separated, dried over $MgSO_4$, and then evaporated. The proton NMR of the reaction mixture showed 1-bicyclo[1.1.1]pentyl phenyl ketone, bis(1-bicyclo[1.1.1]pentyl)phenylcarbinol, 1-bicyclo[1.1.1]pentyl thiobenzoate, and unreacted sulfide in a 1.0:0.72:1.28:0.25 ratio. The compounds were not isolated, but all had been previously isolated and characterized.

With the CuI we found significant monoaddition to acid chlorides, but we also found some bis addition. In the absence of CuI exclusive bis addition was found. Probably not all of the alkyllithium was converted to the cuprate in this procedure. In any case, the method of choice for preparing 1-bicyclo[1.1.1]pentyl ketones is the addition of 1-bicyclo-[1.1.1]pentyllithium to nitriles.

1-Octylbicyclo[1.1.1]pentane. 1-Bicyclo[1.1.1]pentyllithium solution was prepared as described above from 1.5 mL of LiDBB solution and 24 μL (26 mg = 0.15 mmol) of 1-bicyclo[1.1.1]pentyl phenyl sulfide. The stirred solution at −78 °C was quickly cannulated under Ar pressure into a second Schlenck tube containing 31 mg of CuI (0.16 mmol) in 0.5 mL of THF, also cooled to −78 °C. The solution was allowed to stir for 20 min, at which time it was murky olive/black and appeared to be inhomogeneous. A solution of 13.5 μL (0.075 mmol = 0.5 equiv) of 1-iodooctane in 0.5 mL of THF was added, and the solution was stirred at −78 °C for 2 h, during which time the mixture turned to gray and then brown. The solution was then warmed to −20 °C and allowed to warm slowly to room temperature. The reaction was quenched with 75 μL of MeOH and turned translucent green. Saturated NH_4Cl (1 mL) was added, and the mixture was shaken. The aqueous layer turned blue, while the organic layer was yellow. The organic layer was separated, washed twice with 1 mL of 15% NaOH, dried over $MgSO_4$, and evaporated. The organic layer was separated by GC on a 2.8 ft × $^1/_4$ in. 5% OV-101 50/60 V column at 130 °C. There were three peaks: solvent came out from 0 to 2.5 min, 1-iodobicyclo[1.1.1]pentane and iodooctane came out from 3 to 5 min, and unreduced 1-bicyclo[1.1.1]pentyl phenyl sulfide came out from 5.5 to 8.5 min. The proton NMR revealed the central peak to contain 7 mg of a 1.8:1 mixture of octyl iodide and 1-octylbicyclo[1.1.1]pentane (21%): ^1H NMR δ 2.46 (s, 1 H), 1.65 (s, 6 H), 1.5–1.2 (br m, 14 H), 0.9 (br m, 3 H); GC–MS m/e 165 (M − Me), 151, 137, 123, 109, 95, 81, 67, 55, 41.

Reduction of 1,3-Bis(thiophenoxy)bicyclo[1.1.1]pentane Using Lithium Di-*tert*-butylbiphenyl Radical Anion and Attempted Trapping of Dianion with CO_2. To 2.1 mL of LiDBB solution cooled to −78 °C was added 30 mg (0.11 mmol) of 1,3-bis(thiophenoxy)bicyclo[1.1.1]pentane in 0.6 mL of THF. The mixture was stirred for 10 min, then warmed to −60 °C with a chloroform/dry ice bath, and stirred for 35 min. The solution remained dark green and was recooled to −78 °C. Carbon dioxide was bubbled into the reaction through a needle. An exit needle vented the CO_2. The solution decolorized instantly. The flow of CO_2 was maintained for 2 min, and the solution was allowed to warm to room temperature. Ether (5 mL) and 10 mL of saturated $NaHCO_3$ were added, the mixture was vigorously agitated, and the layers were separated. The aqueous layer was acidified with excess HCl, and the water and solvent were removed under high vacuum. The considerable amount of white precipitate was triturated with acetone-d_6 to separate any bicyclo-[1.1.1]pentane 1,3-diacid from the lithium salts. A proton NMR of this sample showed that no diacid (which has a sharp singlet at δ 2.29) was present.

A spatula tipful of I_2 was added to the organic layer (to trap any propellane), and the red solution was washed with saturated $NaHSO_3$ (to reduce excess iodine) and then dried over $MgSO_4$. A GC–MS showed a complicated mixture of products including 1,3-diiodobicyclo[1.1.1]-pentane and a product of the formula C_6H_7I of unknown structure.

Trifluoroperacetic Acid. Extreme caution must be exercised when transferring 70% H_2O_2: it should be transferred by glass pipet and not allowed to drip onto wood, paper, sugar, or any other easily oxidizable organic compound.[54] A spill should be diluted with a large quantity of water.

To 3.5 mL of CH_2Cl_2 in a 50-mL flask equipped with a magnetic stir bar and dropping funnel and cooled in an ice bath was added by pipet 0.72 mL of 70% H_2O_2 (~20 mmol of H_2O_2) without stirring.[55] When this addition was complete, stirring was begun. Through the dropping funnel was slowly added 5.1 mL of trifluoroperacetic anhydride. The resulting mixture was stirred 10 min at 0 °C, and then the ice bath was removed, and the solution was allowed to warm to room temperature and stirred 30 min more. This gave a 1.0 to 1.25 M solution of trifluoroperacetic acid contaminated with trifluoroacetic acid.

Baeyer–Villiger Reaction of 1-Bicyclopentyl *tert*-Butyl Ketone. In a 50-mL flask was combined 32 mg of a 2:1 mixture of 1-bicyclopentyl *tert*-butyl ketone and *tert*-butyl phenyl ketone (~0.2 mmol total), 600 mg of $NaHPO_3$ which had been ground very fine in a mortar and pestle, and 13 mL of CH_2Cl_2. To this solution was added by pipet 0.5 mL of the 1.0–1.25 M solution of trifluoroperacetic acid (~2.5 equiv), the preparation of which was described above. The solution was stirred at room temperature for 3 h, then filtered, washed once with 5 mL of saturated $NaHCO_3$, and gently evaporated. The NMR and GC–MS of the reaction mixture showed that it was very clean. The only products visible were *tert*-butyl benzoate, unreacted 1-bicyclopentyl *tert*-butyl ketone, unreacted *tert*-butyl phenyl ketone, *tert*-butyl 1-bicyclopentanecarboxylate, and 1-bicyclopentyl pivalate in a 2.23:2.35:1.00:4.31:1.88 ratio (as determined by integration of the proton NMR spectrum).

The products were not separated but the NMR assignments were easily made in the following manner. The NMR spectrum had three singlets in the δ 2.5–2.4 region (bicyclopentyl methine) at δ 2.52, 2.45, and 2.38, three singlets in the δ 2.2–2.0 region (bicyclopentyl methylene) at δ 2.17, 2.14, and 2.03, and six singlets in the δ 1.6–1.1 region (*tert*-butyl) at δ 1.60, 1.44, 1.35, 1.25, 1.18, and 1.16. The peaks at δ 2.46, 2.18, and 1.17 are known to correspond to bicyclopentyl *tert*-butyl ketone (starting material). The peaks at δ 2.52, 2.14, and 1.18 are known to correspond to *tert*-butyl bicyclopentanecarboxylate because it was inde-

(54) For a general discussion of the properties of and handling procedures for concentrated hydrogen peroxide, see: Shanley, E. S.; Greenspan, F. P. *Ind. Eng. Chem.* **1947**, 1536.

(55) Both this procedure and the procedure which follows for the Baeyer–Villiger oxidation are based on that of Emmons and Lucas: Emmons, W. D.; Lucas, G. B. *J. Am. Chem. Soc.* **1955**, *77*, 2287.

pendently synthesized (vide infra). Because two peaks are seen in the mass spectrum which correspond to $C_{10}H_{16}O_2$, we can assign the peaks at δ 2.38 and 2.03 to the isomeric ester bicyclopentyl pivalate. Only the peak at δ 1.44 integrates correctly to be the *tert*-butyl resonance for this compound. The peak at δ 1.36 is known to correspond to *tert*-butyl phenyl ketone (impurity in the starting material). A compound with a molecular weight corresponding to addition of one O atom to *tert*-butyl phenyl ketone is seen in the GC–MS; the peak at δ 1.60 is assigned to this compound and on the basis of chemical shift is reckoned to be *tert*-butyl benzoate. GC–MS (Cl isobutane) (*m/e*) for bicyclopentyl *tert*-butyl ketone is 153* (M + 1), 135, for *tert*-butyl bicyclopentanecarboxylate is 169* (M + 1), 103, 85, 67, for bicyclopentyl pivalate is 169* (M + 1), 113, for *tert*-butyl phenyl ketone is 163* (M + 1), and for *tert*-butyl benzoate is 179 (M + 1), 163, 123*; HRMS (CI) of mixture of isomers, calcd = 169.1229, obsd = 169.1236.

1-Bicyclopentyl Pivalate. 1-Bicyclopentyllithium solution was prepared as described above from 2.5 mL of LiDBB solution and 35 μL (39 mg = 0.22 mmol) of 1-bicyclopentyl phenyl sulfide. The solution was stirred at −78 °C, and a stream of O_2 was bubbled into the solution using a long needle. An exit needle vented the O_2 stream. The solution turned red and then light yellow in about 20 s. The solution was stirred under a gentle O_2 stream for 10 min at −78 °C, and then 80 μL (3 equiv) of pivaloyl chloride was added. The solution was allowed to warm to room temperature. Saturated NH_4Cl (1 mL) and 5 mL of ether were added, and the mixture was shaken. The organic layer was separated, dried over $MgSO_4$, and evaporated carefully. The NMR of the reaction mixture showed unreacted sulfide and a new product with resonances at δ 2.53, 2.16, and 1.19. GC–MS (Cl isobutane) *m/e* 169* (M + H^+), 103, 85, 67. The product was not isolated, and no yield was determined. This reaction was done after the Baeyer–Villiger oxidation to unambiguously identify the 1-bicyclopentyl pivalate. Its NMR and mass spectra matched one of the products formed in the Baeyer–Villiger reaction.

Tosylhydrazone of Bicyclopentyl Phenyl Ketone. To a 50-mL septum-capped flask was added 69 mg of a 1:1.4:2.9 mixture of benzonitrile/benzophenone/1-bicyclopentyl phenyl ketone along with 10 mL of EtOH and 100 mg of tosylhydrazine. The reaction was allowed to stir at room temperature and proceeded over the course of 12–15 h. When the reaction was complete, the EtOH was evaporated and the product was isolated by chromatography on silica gel, eluting with 4:1 pentane/ether. The yield was 97 mg (88%) of an approximately 2:1 mixture of the 1-bicyclopentyl phenyl ketone tosylhydrazone and benzophenone tosylhydrazone. The latter compound was not expected to interfere in further reactions (and in fact did not), and no further purification was attempted.

^{1}H NMR of the tosylhydrazone of bicyclopentyl phenyl ketone δ 7.82 (d, 2 H), 7.41 (m, 3 H), 7.33 (d, 2 H), 7.00 (m, 2 H), 2.46 (s, 3 H), 2.34, 2.32 (two singlets, 1 H), 1.90 (s, 6 H); DIP MS (70 eV) *m/e* 275, 260, 185 (parent − SO_2 − tosyl), 155, 141, 128, 115, 91, 77, 65, 51, 41.

Decomposition of the Tosylhydrazone of 1-Bicyclopentyl Phenyl Ketone with Ethoxide. A solution of 1 M NaOEt in EtOH was prepared by introducing 230 mg of freshly cut Na to 10 mL of absolute EtOH and allowing the solution to stir until all the Na had reacted.

To a 50-mL flask equipped with a reflux condenser and magnetic stir bar was introduced 20 mg of a 2:1 mixture of the bicyclopentyl phenyl ketone tosylhydrazone and benzophenone tosylhydrazone (0.06 mmol) and 8 mL of absolute EtOH. To this solution was added 100 μL of 1 M NaOEt in EtOH (1.6 equiv) and the solution was heated, refluxed, and followed by TLC. Eluting with 60:1 pentane/ether showed starting material as a baseline spot, and products grew in as a pair of overlapping blue spots at $R_f \approx 0.35$. As the reaction proceeded the solution turned pale rosy pink, presumably due to the presence of the diazo compound as first formed product. After 5 h of refluxing the solution turned from pink to orange. The base-line spot had not entirely disappeared, but the reaction was worked up at this point. The solution was diluted with 20 mL of ether, washed three times with 10 mL of water, and dried over $MgSO_4$. GC–MS of the reaction solution showed that it was clean. Four peaks were seen: the first three with MW 202 ($C_{14}H_{18}O$) and the last with MW 212 ($C_{15}H_{16}O$).

The ether solution was concentrated to 4 mL and then GC prepped on a 2.8 ft × $^1/_4$ in. 5% OV-101 50/60 V column at 150 °C. Four peaks were seen in the GC trace (retention times were 4, 6, 8, and 12 min) which corresponded to the four peaks in the GC–MS trace. Manual integration showed that the four products were present in a ratio of approximately 9:5:1:5. The products were collected from the GC and identified by their NMR spectra.

The first peak proved to be the ethyl ether of 1-bicyclopentylphenylcarbinol (**11**): ^{1}H NMR δ 7.4–7.2 (m, 5 H), 4.19 (s, 1 H), 3.40 (distorted quintet, $J \approx 8$ Hz, 2 H), 2.47 (s, 1 H), 1.62 (d of d, J = 6.95, 6 H), 1.18 (t, $J \approx 8$ Hz, 3 H); GC–MS (70 eV) *m/e* 202, 201, 161, 135*, 107, 79.

The second peak proved to be 2-ethoxy-2-phenylbicyclo[2.1.1]hexane (**12**) (the identity of this compound was confirmed by independent synthesis): ^{1}H NMR δ 7.4–7.2 (m, 5 H), 3.17 (apparent quintet, $J \approx 8$ Hz, 1 H), 3.02 (multiplet, 2 H), 2.52 (broad square peak, 1 H), 2.21 (doublet, $J \approx 10$ Hz, 1 H), 2.05 (d of d, $J \approx 10$ and 3 Hz, 1 H), 1.78 (m, 3 H), 1.13 (d of d, 1 H), 1.03 (t, 3 H); GC–MS (70 eV) *m/e* 202, 173, 161, 133, 105*, 91, 77, 55.

The third peak was isolated in too small a quantity to be identified, but by its MS is shown to be an isomer of the two previous compounds: GC–MS *m/e* 202, 156*, 141, 129, 115, 105, 91, 84, 72, 65, 41.

The last peak proved to be the ethyl ether of diphenylcarbinol (**14**): ^{1}H NMR δ 7.4–7.2 (m, 5 H), 5.36 (s, 1 H), 3.53 (q, 2 H), 1.28 (t, 3 H); GC–MS (70 eV) *m/e* 212, 167*, 135, 105, 77.

2-Hydroxy-2-phenylbicyclo[2.1.1]hexane. To a septum-capped 35-mL flask equipped with magnetic stirbar was introduced 1 mL of THF and 2 mL of 1.3 M phenyllithium in 3:1 benzene/ether. A nitrogen needle was inserted in the septum, and the mixture was cooled to −78 °C. It froze. The mixture was warmed until it just thawed, and 50 μL of 2-bicyclo[2.1.1]hexanone in 1 mL of THF was added by syringe. The reaction mixture was stirred and allowed to warm to room temperature. The solution was diluted with 15 mL of ether and quenched with 2 mL of saturated NH_4Cl. The organic layer was separated, washed with 10 mL of water, dried over $MgSO_4$, and then evaporated. The product was isolated by chromatography on silica gel with 4:1 pentane/ether and gave 30 mg of 2-hydroxy-2-phenylbicyclo[2.1.1]hexane (38%): ^{1}H NMR δ 7.6–7.2 (m, 5 H), 2.9 (d of t, $J \approx 7.5$ and 2.5 Hz, 1 H), 2.53 (broad square peak, 1 H), 2.38 (d, $J \approx 11$ Hz, 1 H), 2.02 (d of d, $J \approx 11$ and 2 Hz, 1 H), 1.9–1.7 (m, 3 H), 1.6 (br s, 1 H), 1.25 (d of d, $J \approx 8$ and 10 Hz, 1 H); GC–MS *m/e* 174 (M), 133*, 120, 105, 77, 55.

2-Ethoxy-2-phenylbicyclo[2.1.1]hexane (12). A 1 M solution of dimsyl anion in DMSO was prepared by adding 2 g of NaH (60% oil dispersion) to 20 mL of freshly distilled DMSO and heating for 1 h at 70 °C. The evolution of H_2 was vigorous at first and then ceased.

To a 25-mL septum-capped flask equipped with a magnetic stir bar were introduced 30 mg of 2-hydroxy-2-phenylbicyclo[2.1.1]hexane, a few grains of triphenylmethane, and 1 mL of DMSO. The solution was stirred, and the murky dimsyl anion solution was added by syringe until the red color (formed by deprotonating triphenylmethane) persisted. Two equivalents (54 mg) of ethyl iodide was then introduced by syringe and the reaction was allowed to stir 10 min. The mixture was diluted with 20 mL of ether and washed four times with 15 mL of water. The ether was carefully evaporated. The product was isolated by chromatography on silica gel.

2-Ethoxy-2-phenylbicyclo[2.1.1]hexane: ^{1}H NMR δ 7.4–7.2 (m, 5 H), 3.17 (apparent quintet, $J \sim 8$ Hz, 1 H), 3.02 (multiplet, 2 H), 2.52 (broad square peak, 1 H), 2.21 (doublet, $J \approx 10$ Hz, 1 H), 2.05 (d of d, $J \approx 10$ and 3 Hz, 1 H), 1.78 (m, 3 H), 1.13 (d of d, 1 H), 1.03 (t, 3 H); GC–MS *m/e* 202, 173, 161, 133, 105*, 91, 77, 55.

Reaction of Bicyclobutane with N_2O_4 in Ether: 3-Ethoxycyclobutanone (21). A solution of NO_2 (250 mL of gas at 1 atm, ~11 mmol of NO_2) was prepared in 20 mL of ether freshly distilled from Na/K/benzophenone. To this solution at −78 °C was added dropwise a solution of 30 mg of bicyclobutane in 5 mL of ether, and the resulting mixture was allowed to stir for 5 min at −78 °C (at which point the solution is a milky blue), then the cooling bath was removed, and the solution was allowed to warm to room temperature over 20 min. As the solution warmed it turned lime green and some white solid appeared on the sides of the flask above the level of the liquid. The ether and excess N_2O_4 were carefully removed under aspirator vacuum in a fume hood. The remaining greenish oil was taken up in a small amount of CH_2Cl_2. The proton NMR of the reaction product showed that it was almost pure 3-ethoxycyclobutanone. The product could be purified by flash chromatography on silica gel, eluting with CH_2Cl_2. The yield was 44.3 mg (68%) of 3-ethoxycyclobutanone: ^{1}H NMR δ 4.3 (quintet of doublets, J = 5 Hz, 1.5 Hz, 1 H), 3.52 (q, J = 8 Hz, 2 H), 3.15 (m, 4 H), 1.25 (t, J = 8 Hz, 3 H); FTIR ($CDCl_3$) 1793 cm^{-1}.

Reaction of the Oxime of 3-Ethoxycyclobutanone with N_2O_4 in Ether. A solution of NO_2 in ether was prepared as described above. To this solution at −78 °C was added dropwise a solution of 40 mg of 3-ethoxycyclobutanone in 5 mL of ether; the resulting mixture was allowed to stir for 5 min at −78 °C, then the cooling bath was removed, and the solution was allowed to warm to room temperature over 20 minutes. The ether and excess N_2O_4 were carefully removed under aspirator vacuum in a fume hood. The remaining greenish oil was taken up in a small amount of $CDCl_3$. TLC and proton NMR showed that the oxime of 3-ethoxycyclobutanone had been converted completely and rather cleanly back to 3-ethoxycyclobutanone.

Reaction of Bicyclobutane with N_2O_4 in Tetrahydrofuran: 3-(4-Nitrato-1-butoxy)cyclobutanone (22). A solution of NO_2 in tetrahydrofuran was prepared as described above. To this solution at −78 °C was added dropwise a solution of 12 mg of bicyclobutane in 4 mL of tetrahydrofuran and the resulting mixture was allowed to stir for 5 min at −78 °C; the cooling bath was then removed, and the solution was allowed to warm to room temperature over 20 min. As the solution warmed it turned lime green. The ether and excess N_2O_4 were carefully removed under aspirator vacuum in a fume hood. The remaining greenish oil was taken up in a small amount of CH_2Cl_2. The proton NMR showed that the product was almost pure 3-(4-nitratobutoxy)-cyclobutanone. It could be purified by flash chromatography on silica gel, eluting with 5:1 ether/pentane. The yield was 37 mg (82%) of 3-(4-nitrato-1-butoxy)cyclobutanone: ^{1}H NMR δ 4.40 (t, J = 7 Hz, 2 H), 4.28 (quintet of doublets, J = 4 Hz, 1.5 Hz, 1 H), 3.48 (t, J = 7 Hz, 2 H), 3.15 (m, 4 H), 1.83 (br quintet, J = 7 Hz, 2 H), 1.75 (br quintet, J = 7 Hz, 2 H); FTIR ($CDCl_3$) 1786, 1631, 1278 cm^{-1}. The IR bands at 1631 and 1278 cm^{-1} are characteristic of organic nitrates.

Reaction of Bicyclo[2.1.0]pentane with N_2O_4 in Ether: 3-Nitrocyclopentene, *cis*- and *trans*-1-Nitrato-3-nitrocyclopentane (23, 24), and Cyclopenten-3-one (25). A solution of NO_2 in ether was prepared as described above. To this solution at −78 °C was added dropwise a solution of 70 mg of bicyclo[2.1.0]pentane in 10 mL of ether, and the resulting mixture was allowed to stir for 5 min at −78 °C, the cooling bath was then removed, and the solution was allowed to warm to room temperature over 20 min. The ether and excess N_2O_4 were carefully removed under aspirator vacuum in a fume hood. The remaining greenish oil was taken up in a small amount of $CDCl_3$. The proton NMR of the reaction mixture revealed a complicated mixture of products, chief among them 3-nitrocyclopentene, *cis*- and *trans*-1-nitrato-3-nitrocyclopentane, and cyclopenten-3-one. The products were separated by flash chromatography on silica gel, eluting first with 5:1 pentane/ether and gradually increasing the proportion of ether. The cyclopenten-3-one coeluted with the *trans*-1-nitrato-3-nitrocyclopentane. Some of the early fractions were blue; this is believed to be due to trace amounts of nitroso compounds. The proton NMR showed that 3-nitrocyclopentene and *cis*-1-nitrato-3-nitrocyclopentane were the major products, formed in roughly a 1:1 ratio. There were a variety of minor products, among them *trans*-1-nitrato-3-nitrocyclopentane. The amount of cyclopenten-3-one varied from run to run and was perhaps a secondary product.

3-Nitrocyclopentene: ^{1}H NMR δ 6.30 (m, 1 H), 5.93 (m, 1 H), 5.48 (m, 1 H), 2.8–2.0 (m, 4 H); ^{13}C NMR δ 141.3, 126.4, 91.9, 31.8, 28.8; GC–MS (70 eV) m/e 67 (M − NO_2); FTIR ($CDCl_3$) 1549 cm^{-1}.

cis-1-Nitrato-3-nitrocyclopentane (**23**): ^{1}H NMR δ 5.6 (br m, 1 H), 5.1 (br m, 1 H), 2.9 (d of t, J = 16 Hz, 7 Hz, 1 H), 2.5–2.0 (br m, 5 H); ^{13}C NMR δ 84.9, 84.2, 37.0, 30.5, 29.8; GC–MS m/e 130 (M − NO_2), 112, 100, 84* (M − NO_2 − NO_2), 67, 55; FTIR ($CDCl_3$) 1635, 1552, 1276 cm^{-1}.

trans-1-Nitrato-3-nitrocyclopentane (**24**): ^{1}H NMR δ 5.4 (br m, 1 H), 4.9 (m, 1 H), 2.7–2.0 (m, 6 H); ^{13}C NMR δ 83.9, 83.1, 36.4, 29.8, 29.7; GC–MS m/e 130 (M − NO_2), 84* (M − NO_2 − NO_2), 67, 55; FTIR ($CDCl_3$) 1638, 1552, 1277 cm^{-1}.

Cyclopenten-3-one (**25**): ^{1}H NMR δ 7.78 (d of t, J = 6 Hz, 2 Hz, 1 H), 6.24 (d of t, J = 6 Hz, 2 Hz, 1 H), 2.65 (m, 2 H), 2.31 (m, 2 H); GC–MS (70 eV) m/e 82* (M), 54, 53; FTIR ($CDCl_3$) 1705 cm^{-1}.

3-Nitrocyclopentene, *cis*- and *trans*-1-nitrato-3-nitrocyclopentane, and cyclopenten-3-one have all been previously prepared, and their spectral data have been reported.[56] Our spectral data is in accord with that reported.

Reaction of [1.1.1]Propellane with NO in Carbon Disulfide: 1-Nitro-3-(thiocyano)bicyclo[1.1.1]pentane (16). A solution of NO (250 mL of gas at 1 atm, ~11 mmol) in 10 mL of carbon disulfide was prepared. To this solution at −78 °C was added dropwise a solution of 12 mg of [1.1.1]propellane in 5 mL of ether, and the resulting mixture was allowed to stir for 5 min at −78 °C (at which point the solution was pale blue), the cooling bath was then removed, and the solution was allowed to warm to room temperature over 20 min. The ether and excess NO were carefully removed under aspirator vacuum in a fume hood. The remaining wet solid was taken up in a small amount of $CDCl_3$. The proton NMR showed a large singlet at δ 2.77; the product was almost pure 1-nitro-3-(thiocyano)bicyclo[1.1.1]pentane. The product could be further purified by sublimation (70 °C bath, 0.1 Torr). The yield was 28 mg (90%) of 1-nitro-3-(thiocyano)bicyclo[1.1.1]pentane: ^{1}H NMR δ 2.77 (s, 6 H), ^{13}C NMR δ 108.5, 64.4, 57.6 (CH_2), 35.1; FTIR ($CDCl_3$) 2162, 1548 cm^{-1}; GC–MS m/e 124 (M − NO_2), 84, 80, 72, 65*, 58, 53; GC–MS (CI isobutane) m/e 171* (M + 1), 124; HRMS (CI) calcd = 171.0229, obsd = 171.0231.

(56) Borisenko, A. A.; Nikulin, A. V.; Wolfe, S.; Zefirov, N. S.; Zyk, N. K. *J. Am. Chem. Soc.* **1984**, *106*, 1074.

Reaction of [1.1.1]Propellane with NO in Methylene Chloride. A solution of NO (250 mL gas at 1 atm) in 10 mL of methylene chloride freshly distilled from CaH_2 was prepared. To this solution at −78 °C was added dropwise a solution of 16 mg of [1.1.1]propellane in 5 mL of methylene chloride, and the resulting mixture was allowed to stir for 5 min at −78 °C, the cooling bath was then removed, and the solution was allowed to warm to room temperature over 20 min, at which point the solution is emerald green. The ether and excess NO were carefully removed under aspirator vacuum in a fume hood (the solution turns from green to yellow). The remaining oil was taken up in a small amount of $CDCl_3$. The proton NMR showed that the reaction was not clean, but that the major product was product A. The yield was 13 mg: ^{1}H NMR δ 5.43 (approximately a septuplet, $J \approx$ 2.5 Hz, 1 H), 4.98 (s, 2 H), 3.01 (d of d, J = 15 Hz, 7 Hz, 2 H), 2.68 (d of d, J = 15 Hz, 4 Hz, 2 H); ^{13}C NMR δ 81.5, 71.9 (CH_2), 71.4 (CH), 36.7 (CH_2); FTIR ($CDCl_3$) 1652 (a sort of doublet), 1282 cm^{-1} (two large peaks bounded by two small peaks).

The spectral data clearly indicate that this compound has the carbon skeleton of methylcyclobutane, along with three substituents, one on the methyl group, one at the methine position, and one across the ring from the methine position. The substituents do not contain carbon or hydrogen and are most likely some combination of nitro, nitrite, and nitrate groups. The compound appears to be a single stereoisomer. No satisfactory mass spectrum could be obtained for this compound.

Reaction of [1.1.1]Propellane with N_2O_4 in Methylene Chloride or Carbon Disulfide. A solution of NO_2 in methylene chloride was prepared as described above. To this solution at room temperature was added dropwise a solution of 15 mg of propellane in 2 mL of methylene chloride, and the resulting mixture was allowed to stir for 15 min. The solvent and excess N_2O_4 were carefully removed under aspirator vacuum in a fume hood. The remaining greenish oil was taken up in a small amount of $CDCl_3$. The NMR showed two large peaks in a ratio of 1:2 at δ 5.04 and 3.52 (which we believe constitute the proton NMR spectrum of the major product, which we will call product **B**), as well as various smaller peaks. The mixture was flash chromatographed, eluting with 1:1 ether/pentane, but only unidentified rearrangement products with complicated proton spectra came off of the column. Product B could be sublimed (80 °C bath, 0.1 Torr), but unfortunately the impurities sublime as well, and no purification results. The yield was 36 mg of impure product **B**: ^{1}H NMR δ 5.04 (s, 1 H), 3.52 (s, 2 H); ^{13}C NMR major peaks δ 71.1 (CH_2), 56.0 (CH_2) minor peaks δ 70.0, 68.1, 57.0, 55.3, 41.4, 40.3, 39.8, 38.3, 37.7, 36.7, 25.6; GC–MS (70 eV) m/e 114, 97, 85, 67, 53; FTIR ($CDCl_3$) 1805, 1654, 1554, 1282 cm^{-1}.

The course of the reaction in carbon disulfide was essentially identical. As with methylene chloride, product B was the major product.

Reaction of [1.1.1]Propellane with N_2O_4 in the Absence of Solvent. First, 12 mg of purified [1.1.1]propellane was vacuum transferred into a 100-mL pear-shaped reaction flask, which was sealed and then attached via a stopcock to a flask containing NO_2. The first flask was warmed to room temperature, so that it was filled with propellane vapor. The stopcock at the second flask was opened, allowing the NO_2 gas to rush into the reaction flask. A cloud of vapor formed immediately inside of the flask. The flask was allowed to sit for 5 min, during which time the cloud settled. The excess N_2O_4 was removed by aspirator vacuum in a fume hood, and the oily residue was taken up in $CDCl_3$. The proton NMR of the reaction mixture showed predominantly product **B** described above.

Reaction of [1.1.1]Propellane with N_2O_4 in Ether: 1,3-Dinitrobicyclo[1.1.1]pentane. A solution of NO_2 in ether was prepared as described above. To this solution at room temperature was added dropwise a solution of 6 mg of propellane in 2 mL of ether, and the resulting mixture was allowed to stir for 15 min. The ether and excess N_2O_4 were carefully removed under aspirator vacuum in a fume hood. The remaining greenish oil was taken up in a small amount of CH_2Cl_2. The product can be purified by chromatography on silica gel, eluting with CH_2Cl_2. The yield was 3.5 mg (25%) of colorless, crystalline 1,3-dinitrobicyclopentane: mp 172–173 °C; ^{1}H NMR δ 3.04 (6 H); ^{13}C NMR δ 61.7 (C-NO_2), 57.1 (CH_2); GC–MS (CI isobutane) m/e 159 (M + 1), 157 (M − 1); FTIR 1549 cm^{-1}.

Reaction of Bicyclobutane with Tetracyanomethylene: 3-(1,1,2,2-Tetracyanoethyl)cyclobutene (46, 1:1 Adduct) and 2,2,3,3-Tetracyanotricyclo[8.1.1.0^{4,9}]dodeca-5,7-diene (1:1:1 Adduct). A solution of 18 mg of bicyclobutane (0.33 mmol) in 1.5 mL of benzene was added by syringe to a magnetically stirred solution of 40 mg (0.31 mmol) of tetracyanoethylene (hereafter TCNE) in 4 mL of benzene in a 25-mL septum-capped flask. The yellow color (which arises from a charge transfer complex between TCNE and benzene) disappeared in ~1 min, signaling the end of the reaction. For reactions in benzene-d_6, a proton NMR taken at this point revealed clean formation of 1:1 adduct (bicyclobutane to TCNE) and 1:1:1 adduct (bicyclobutane to TCNE to benzene) in

approximately a 4:1 ratio. Flash chromatography on silica gel eluting with methylene chloride allowed isolation of 15.5 mg (18%) of the 1:1:1 adduct. The 1:1 adduct decomposed somewhat on silica gel and appeared as a red band moving down the column. This band eluted to give orange fractions that evaporate to leave a reddish solid. NMR shows that this is principally the 1:1 adduct. No yield was determined.

3-(1,1,2,2-Tetracyanoethyl)cyclobutene (**46**, 1:1 adduct): ^{1}H NMR δ 6.52 (d, J = 2 Hz, 1 H), 6.16 (d, J = 2 Hz, 1 H), ~4.45 (variable s, 1 H), 3.68 (d, J = 3.5 Hz, 1 H), 3.10 (d of d, J = 3.5 Hz, 16 Hz, 1 H), 2.75 (d, J = 16 Hz, 1 H); ^{1}H NMR (benzene-d_6) δ 5.54 (d, J = 2 Hz, 1 H), 5.43 (d, J = 2 Hz, 1 H), 2.80 (t, J = 2 Hz, 1 H), 2.27 (s, 1 H), 2.09 (d, J = 2 Hz, 2 H); GC–MS m/e 182 (M), 154, 129, 117, 102, 90*, 77, 65, 53, 39.

2,2,3,3-Tetracyanotricyclo[8.1.1.0^{4,9}]dodeca-5,7-diene (1:1:1 adduct): ^{1}H NMR (the peaks marked with an asterisk are absent when benzene-d_6 is used in the reaction) δ 6.6* (br m, 1 H), 6.27* (br m, 1 H), 6.10* (d of d, J = 8 Hz, 11 Hz, 1 H), 5.64* (br d, J = 11 Hz, 1 H), 3.35 (br m, 2 H for benzene, 1 H for benzene-d_6), 3.25* (br dist t, 1 H), 3.0–2.8 (br m, 2 H), 2.71 (br dist t, 2 H), 2.11 (br d, J = 13 Hz, 1 H); ^{1}H NMR (spectrum of the d_0 compound at −25 °C) δ 6.6 (d of d, J = 7 Hz, 4 Hz, 1 H), 6.27 (5 peaks, apparent J = 4 Hz, 1 H), 6.10 (d of d, J = 8 Hz, 11 Hz, 1 H), 5.64 (d, J = 11 Hz, 1 H), 3.35 (br m, 2 H), 3.25 (d of d, J = 6 Hz, 7.5 Hz, 1 H), 3.0–2.8 (m, 2 H), 2.71 (m, 2 H), 2.11 (d of d, J = 13 Hz, 5 Hz, 1 H); ^{13}C NMR δ 131.52 (CH), 128.49 (CH), 127.05 (CH), 120.35 (CH), 111.71 (CN), 111.50 (CN), 111.38 (CN), 111.03 (CN), 45.88 (C), 45.35 (C), 44.64 (CH), 39.50 (CH), 37.47 (CH), 36.61 (CH), 28.56 (CH_2), 24.47 (CH_2); GC–MS m/e 234 (M − CN), 205, 177, 166, 153, 140, 129, 115, 104*, 91, 78, 63, 51; HRMS (EI) calcd = 260.1064, obsd = 260.1048.

The peaks in the room temperature proton NMR spectrum of the 1:1:1 adduct were almost all quite broad. We surmised that the compound was fluxional and recorded the spectrum at −25 °C. At this temperature all of the peaks sharpened dramatically, and additional splittings were revealed.

Reaction of Bicyclobutane with Fumaronitrile: 3-(1,2-Dicyanoethyl)-cyclobutene. An NMR tube containing 0.5 mL of benzene-d_6 and 17 mg of fumaronitrile was freeze–pump–thaw cycled twice, frozen in liquid nitrogen, and then 12 mg of bicyclobutane (1 equiv) was vacuum transferred into the tube. It was sealed by flame under vacuum and warmed carefully to room temperature. The reaction was monitored by NMR. After 24 h at room temperature there was not sign of reaction. After 24 h of heating the tube at 65 °C in an oil bath, all of the bicyclobutane had been cleanly converted to a 2:1 mixture of the two diastereomers of 3-(1,2-dicyanoethyl)cyclobutene. Flash chromatography on silica gel eluting with 3:1 pentane/ether allowed isolation of 25 mg (86%) of a 2:1 mixture of the two diastereomers of 3-(1,2-dicyanoethyl)cyclobutene.

3-(1,2-Dicyanoethyl)cyclobutene (diastereomer A): ^{1}H NMR (benzene-d_6) δ 5.71 (d, J = 2 Hz, 1 H), 5.63 (d, J = 2 Hz, 1 H), 2.37 (m, 1 H), 2.13 (d of d, J = 4 Hz, 13 Hz, 1 H), 1.75 (m, 1 H), 1.69 (d, J = 13 Hz), 1.38 (d of d, J = 2 Hz, 7.5 Hz, 2 H).

3-(1,2-Dicyanoethyl)cyclobutene (diastereomer B): ^{1}H NMR (benzene-d_6) δ 5.71 (d, J = 2 Hz, 1 H), 5.44 (d, J = 2 Hz, 1 H), 2.37 (m, 1 H), 2.22 (d of d, J = 4 Hz, 13 Hz, 1 H), 1.89 (d, J = 13 Hz), 1.75 (m, 1 H), 1.38 (d of d, J = 2 Hz, 7.5 Hz, 2 H).

3-(1,2-Dicyanoethyl)cyclobutene (mixture of diastereomers): ^{13}C NMR (benzene-d_6) δ 138.5, 135.9, 43.4 and 43.3, 34.7 and 34.3, 31.8 and 31.7, 18.6 and 18.5; GC–MS m/e 131 (M − 1), 104*, 92, 78, 65, 51; (Cl methane) 133* (M + 1), 106.

Reaction of Bicyclobutane with Methyl Propiolate: Methyl 2,4,6-Heptatrienoate and 3-(2-Carbomethoxyethenyl)cyclobutene. An NMR tube containing 0.5 mL of CD_3CN and 15 μL of methyl propiolate was freeze–pump–thaw cycled twice, frozen in liquid nitrogen, and then 6 mg of bicyclobutane (0.7 equiv) was vacuum transferred into the tube. It was sealed by flame under vacuum and warmed carefully to room temperature. The reaction was monitored by NMR. After 24 h at room temperature there was no sign of reaction. After heating the tube at 80 °C in an oil bath, product was formed. Early in the reaction (3–5 h at 80 °C) there was a mixture of methyl 2,4,6-heptatrienoate and 3-(2-carbomethoxyethenyl)cyclobutene; later in the reaction (24 h at 80 °C) only methyl 2,4,6-heptatrienoate was seen. After prolonged heating other unidentified products began to grow in (presumably arising from thermal reactions of methyl 2,4,6-heptatrienoate).

Methyl 2,4,6-heptatrienoate: ^{1}H NMR δ 7.32 (d of d, J = 11.34 Hz, 15.35 Hz, 1 H), 6.6–6.3 (m, 3 H), 5.91 (d, J = 15.34 Hz, 1 H), 5.42 (d, J = 15.72 Hz, 1 H), 5.32 (d, J = 9.14 Hz, 1 H), 3.76 (s, 3 H); GC–MS m/e 138 (M), 123, 107, 95, 79, 77*, 51.

trans-3-(2-Carbomethoxyethenyl)cyclobutene: ^{1}H NMR δ 6.99 (d of d, J = 11.7 Hz, 16.7 Hz, 1 H), 6.18 (d, J = 2 Hz, 1 H), 6.08 (d, J = 2 Hz, 1 H), 5.86 (d, J = 16.7 Hz, 1 H), 3.75 (s, 3 H), 3.80–3.60 (obscured, 1 H), 2.86 (d of d, J = 4 Hz, 16 Hz, 1 H), 2.32 (d, J = 16 Hz, 3 H); GC–MS (70 eV) m/e 138 (M), 123, 107, 95, 79*, 77, 51.

Reaction of Bicyclobutane with Dimethyl Acetylenedicarboxylate. An NMR tube containing 0.5 mL of $CDCl_3$, CD_3CN, CD_3OD, acetone-d_6, cyclohexane-d_{12}, benzene-d_6, or CD_2Cl_2 and 15 μL (17 mg) of dimethyl acetylenedicarboxylate was freeze–pump–thaw cycled twice, frozen in liquid nitrogen, and then 6 mg of bicyclobutane (1 equiv) was vacuum transferred into the tube. It was sealed by flame under vacuum and warmed carefully to room temperature. The reaction was monitored by NMR and took several days to consume all of the bicyclobutane at room temperature. In practical terms, the reaction is faster in more polar solvents, and acetone or acetonitrile are the solvents of choice.

The reaction could be monitored by NMR, which showed the clean formation of the 1:1 and 2:1 adducts. The ratio of these two adducts is sharply dependent on solvent polarity, with relatively more of the 2:1 adduct being formed in more polar solvents. No 2:1 adduct is formed in cyclohexane or benzene. The ratio of 1:1 to 2:1 adduct in chloroform is ~5. The same ratio in acetonitrile or methanol is ~1.5. The products were separated and purified by flash chromatography on silica gel eluting with 10:1 pentane/ether. When all of the bicyclobutane was consumed, the yield was essentially quantitative.

3-(1,2-Dicarbomethoxyethenyl)cyclobutene (**32**, 1:1 adduct): ^{1}H NMR δ 6.19 (d, $J \approx 2$ Hz, 1 H), 6.04 (d, $J \approx 2$ Hz, 1 H), 5.84 (s, 1 H), 3.82 (s, 3 H), 3.72 (d, 1 H), 3.71 (s, 3 H), 2.88 (d of d, $J \approx 14$ Hz, 4 Hz, 1 H), 2.56 (d, $J \approx 14$ Hz, 1 H); GC–MS 196 (M), 165, 149, 137, 105*, 91, 77, 59; HRMS (EI) calcd = 196.0736, obsd = 196.0736.

1,2-Dicarbomethoxy-1-(3-cyclobutenyl)-3-(3-propenyl)cyclopropane (**33**, 2:1 adduct): ^{1}H NMR δ 6.18 (d, $J \approx 2$ Hz, 1 H), 5.89 (m, 1 H), 5.83 (d, $J \approx 2$ Hz, 1 H), 5.09 (d, J = 16.5 Hz, 1 H), 5.02 (d, J = 10.5 Hz, 1 H), 3.70 (s, 3 H), 3.68 (s, 3 H), 3.34 (d, J = 4 Hz, 1 H), 2.68 (d of d, J = 4 Hz, 17.5 Hz, 1 H), 2.56 (dist t, $J \approx 4$ Hz, 2 H), 2.33 (d, J = 17.5 Hz, 1 H), 2.00 (d, J = 8.8 Hz, 1 H), 1.40 (q, J = 8.8 Hz, 1 H); ^{13}C NMR δ 139.5, 137.5, 134.9, 115.0, 51.9, 51.8, 45.5, 38.2, 35.6, 28.3, 24.9 (quaternary carbons were not seen); GC–MS m/e 250 (M), 219, 186, 156, 131*, 115, 105, 91, 77, 65, 59, 53, 39; HRMS (EI) calcd = 250.1205, obsd = 250.1209.

Reaction of Bicyclobutane with Dicyanoacetylene in Methylene Chloride. Into a reaction tube was introduced 1.5 mL of methylene chloride and a magnetic stir bar. The tube was frozen in liquid nitrogen and evacuated, and then ~10 mg of dicyanoacetylene was vacuum transferred into the reaction tube. The reaction tube was warmed to −78 °C, filled with N_2, and stirred to yield a gray solution. To this solution was added dropwise by syringe a solution of 12 mg of bicyclobutane in 1.5 mL of methylene chloride. After this addition the cooling bath was removed and the solution was allowed to stir and warm to room temperature, during which time it turned light orange. The solution was concentrated, the resulting material was dissolved in $CDCl_3$, and a proton NMR was taken which showed that the 1:1 adduct, the major 2:1 (bicyclobutane to dicyanoacetylene) adduct, and the minor 2:1 adduct were formed in a ratio of ~10:18:1. The GC–MS showed clean formation of the three adducts. Flash chromatography on silica gel eluting with 5:1 pentane/ether allowed isolation of 6.5 mg (22%) of the 1:1 adduct and 10.6 mg (52%) of the major 2:1 adduct. In addition a small amount of the minor 2:1 adduct was also isolated, but the yield was not determined.

3-(1,2-Dicyanoethenyl)cyclobutene (**39**, 1:1 adduct): ^{1}H NMR δ 6.36 (d, J = 2 Hz, 1 H), 6.08 (d, J = 2 Hz, 1 H), 5.95 (s, 1 H), 3.79 (d, J = 4 Hz, 1 H), 3.07 (d of d, J = 4 Hz, 12 Hz, 1 H), 2.57 (d, J = 12 Hz, 1 H); GC–MS (70 eV) m/e 130 (M), 129 (M − 1), 103*, 90, 76, 51; HRMS (EI) calcd = 130.532, obsd = 130.531.

1,2-Dicarbomethoxy-1-(3-cyclobutenyl)-3-(3-propenyl)cyclopropane (**40**, major 2:1 adduct): ^{1}H NMR δ 6.30 (d, J = 2 Hz, 1 H), 5.92 (m, 1 H), 5.84 (d, J = 1.5 Hz, 1 H), 5.29 (d of d, J = 17 Hz, 1.4 Hz, 1 H), 5.21 (d of d, J = 12 Hz, 1.4 Hz, 1 H), 3.15 (d, J = 4 Hz, 1 H), 2.89 (d of d, J = 4 Hz, 14 Hz, 1 H), 2.56 (t, J = 6 Hz, 2 H), 2.41 (d, J = 14 Hz, 1 H), 2.01 (d, J = 8 Hz, 1 H), 1.59 (q, J = 8 Hz, 1 H); GC–MS m/e 184 (M), 183 (M − 1), 169, 156, 143, 129, 116, 103, 91*, 77, 64, 54, 39; HRMS (EI) calcd = 184.1002, obsd = 184.0987.

5,6-Dicyanodeca-1,4,6,9-tetraene (**41**, minor 2:1 adduct): ^{1}H NMR δ 6.85 (t, J = 8 Hz, 1 H), 5.83 (m, 2 H), 5.22 (d of d, J = 3.5 Hz, 1 Hz, 1 H), 5.08 (s, 1 H), 3.25 (t, J = 8 Hz, 2 H); GC–MS (70 eV) m/e 184 (M), 183* (M − 1), 169, 155, 142, 129, 116, 103, 89, 77, 65, 51, 39; HRMS (EI) calcd = 184.1002, obsd = 184.1011.

Reaction of Bicyclobutane with Dicyanoacetylene in Benzene. This reaction was conducted in the same fashion as the previous reaction except that benzene (or benzene-d_6) was used in place of methylene chloride. A proton NMR was taken which showed that the 1:1 adduct, the major 2:1 (bicyclobutane to dicyanoacetylene) adduct, the minor 2:1 adduct, and the 1:1:1 adduct (bicyclobutane to dicyanoacetylene to benzene) were formed in a ratio of ~10:10:1:10. The GC–MS showed clean formation of the four adducts. Flash chromatography on silica gel

eluting with 5:1 pentane/ether allowed isolation of 8.0 mg (27%) of the 1:1 adduct, 5.1 mg (25%) of the major 2:1 adduct, and 14.3 mg (31%) of the 1:1:1 adduct. In addition a small amount of the minor 2:1 adduct was also isolated, but yield was not determined.

7-Cyano-7-(1-cyanopenta-1,4-dienyl)bicyclo[4.1.0]hepta-2,4-diene (**42**, 1:1:1 adduct): ^{1}H NMR δ 6.79 (t, J = 7 Hz, 1 H), 6.47 (d of d, J = 3 Hz, 7 Hz, 2 H), 6.27 (m, 2 H), 5.80 (m, 1 H), 5.20 (d, J = 4 Hz, 1 H), 5.15 (s, 1 H), 3.64 (d of d, J = 3 Hz, 2 Hz, 2 H), 3.22 (t of d, J = 7 Hz, 2 Hz, 2 H); GC-MS m/e 208 (M), 207 (M - 1), 192, 180, 167, 153, 140*, 127, 114, 89, 77, 63, 51, 39; HRMS (CI) calcd = 209.1080 (M + 1), obsd = 209.1085.

Reaction of [1.1.1]Propellane with Tetracyanoethylene: 1,1,2,2-Tetracyano-5-methylenespirohexane (44). Into a reaction tube was introduced 40 mg of TCNE, 3 mL of benzene, and a small magnetic stir bar. The solution was frozen and evacuated, and then 20 mg of [1.1.1]propellane was vacuum transferred into the tube. Finally, 1 mL more of benzene was vacuum transferred on top of the [1.1.1]propellane. The solution was stirred at room temperature for 36 h, during which time it turned from yellow to brown and a precipitate formed. The precipitate was collected by filtration and dried under vacuum to yield 32 mg (53%) of a tan solid that was shown by proton NMR to be essentially pure 1,1,2,2-tetracyano-5-methylenespirohexane. The remaining yellow solution was evaporated to a sticky solid that was shown by proton NMR to be a mixture of 1,1,2,2-tetracyano-5-methylenespirohexane and other unidentified compounds.

1,1,2,2-Tetracyano-5-methylenespirohexane: ^{1}H NMR δ 5.04 (q, J = 2.56 Hz, 4 H), 3.14 (t, J = 2.56 Hz, 2 H); ^{1}H NMR (acetone-d_6) δ 5.15 (q, J = 2.56 Hz, 4 H), 3.35 (t, J = 2.56 Hz, 2 H); ^{1}H NMR (CD_2Cl_2) δ 5.30 (q, J = 2.56 Hz, 4 H), 3.35 (t, J = 2.56 Hz, 2 H); ^{13}C NMR (acetone-d_6) δ 136.4 (CN), 111.4 (CH_2), 110.4, 44.8, 37.0 (CH_2), 27.3; GC-MS m/e 193 (M - 1), 181, 167, 154, 140, 129, 116, 103, 91, 77, 66*; HRMS (EI) calcd = 194.0594, obsd = 194.0594; mp 248-250 °C (decomposes).

Reaction of [1.1.1]Propellane with Dimethyl Acetylenedicarboxylate. An NMR tube containing 0.5 mL of $CDCl_3$, CD_3CN, acetone-d_6, cyclohexane-d_{12}, benzene-d_6, or CD_2Cl_2 and 16 mg of dimethyl acetylenedicarboxylate (dmadc) was freeze–pump–thaw cycled twice and frozen in liquid nitrogen, and then 15 mg of propellane (2 equiv) was vacuum transferred into the tube. It was sealed by flame under vacuum and warmed carefully to room temperature. The reaction was monitored by NMR and was mostly complete in 36 h at room temperature. In practical terms, the reaction is faster in more polar solvents, and acetone or acetonitrile are the solvents of choice.

Since the 2:1 adducts (propellane to dmadc) are formed via reaction of a second molecule of propellane with the 1:1 adduct, the amount of 1:1 adduct present at the end of the reaction depends on the starting ratio of propellane to dmadc. If only 2:1 adduct is desired then 0.5 equiv of dmacd should be used. Large excesses of dmadc are required to produce significant amounts of 1:1 adduct at the end of the reaction. A 3-fold excess of dmadc gives approximately a 1:1 mixture of 1:1 to 2:1 adduct. The major 2:1 and minor 2:1 adduct are formed in a ratio of ≈17-20:1. The products were separated by flash chromatography on silica gel eluting with 10:1 pentane/ether. Unfortunately, the 1:1 adduct (which is rather unstable) coeluted with excess dmadc, and no satisfactory means of separating the two was devised. When all of the propellane was converted to 2:1 adduct, the yield of the reaction was essentially quantitative.

1,2-Dicarbomethoxy-5-methylenespirohex-1-ene (**27**, 1:1 adduct): ^{1}H NMR δ 4.92 (quintet, $J \approx$ 2 Hz, 2 H), 3.86 (s, 3 H), 3.06 (t, $J \approx$ 2 Hz, 4 H); GC-MS m/e 208 (M), 193, 177, 149*, 134, 121, 11, 89, 77, 59.

Dimethyl 2,3-bis(3-methylenecyclobutylidene)succinate (**28**, major 2:1 adduct): ^{1}H NMR δ 5.00 (quintet, $J \approx$ 2 Hz, 2 H), 4.96 (quintet, $J \approx$ 2 Hz, 2 H), 3.80 (multiplet consisting of five closely spaced peaks, 4 H), 3.73 (s, 6 H), 3.31 (multiplet consisting of five closely spaced peaks, 4 H); ^{13}C NMR δ 106.7 (CH_2), 52.0 (CH_3), 40.5 (CH_2), 36.6 (CH_2) (quaternary carbons were not seen); GC-MS m/e 274* (M), 259, 242, 153, 128, 115; HRMS (EI) calcd = 274.1205, obsd = 274.1207.

Dimethyl 3,3″-bis(methylene)dispiro[cyclobutane-1,2′-bicyclo-[1.1.0]butane-4′,1″-cyclobutane]-1′,3′-dicarboxylate (**29**, minor 2:1 adduct): ^{1}H NMR δ 4.89 (quintet, J = 2 Hz, 2 H), 4.85 (quintet, J = 2 Hz, 2 H), 3.73 (s, 3 H), 3.58 (br s, 4 H), 2.84 (br s, 4 H); ^{13}C NMR δ 166.2, 157.5, 142.4, 120.6, 107.6 (CH_2), 51.6 (CH_3), 43.4 (CH_2), 41.2 (CH_2); GC-MS 274* (M), 259, 242, 153, 128, 115.

Reaction of [1.1.1]Propellane with Dicarbomethoxyacetylene in Methanol. This reaction was conducted in the same way as the above reaction except that MeOH or CD_3OD was used as a solvent. This lead to the formation of two additional products (both 1:1:1 adducts of propellane, dmadc, and methanol). Integration of the proton NMR shows that the 2:1 adduct, 1:1:1 adduct A, and 1:1:1 adduct B are formed in a ratio of ~4:1:1 under the given conditions. When allowed to proceed to completion, the reaction was essentially quantitative. The products were separated by flash chromatography on silica gel eluting with 10:1 pentane/ether. Separating the two 1:1:1 adducts was difficult and required very careful chromatography.

1,2-Dicarbomethoxy-1-methoxy-5-methylenespirohexane (**30**, 1:1:1 adduct A): ^{1}H NMR (peaks marked with an asterisk are absent when the solvent is CD_3OD) δ 4.95 (q, 2 H), 3.83 (s, 3 H), 3.76 (s, 3 H), 3.57* (s, 3 H), 3.36 (br d, $J \approx$ 17 Hz, 1 H), 3.10 (br d, $J \approx$ 17 Hz, 1 H), 2.83 (br d, $J \approx$ 17 Hz, 1 H), 2.78 (br d, $J \approx$ 17 Hz, 1 H), 2.08* (s, 1 H); GC-MS m/e 240 (M), 225, 208, 181, 149*, 121.

1-(1,2-Dicarbomethoxyethenyl)-1-methoxy-3-methylenecyclobutane (**31**, 1:1:1 adduct B): ^{1}H NMR (peaks marked with an asterisk are absent when the solvent is CD_3OD) δ 6.87* (s, 1 H), 4.89 (quintet, $J \approx$ 2 Hz, 2 H), 3.81 (s, 3 H), 3.80 (s, 3 H), 3.24* (s, 3 H), 2.99 (t, $J \approx$ 2 Hz, 4 H); ^{13}C NMR δ 129.6, 107.4, 52.5, 52.4, 52.2, 43.2 (quaternary carbons were not seen); GC-MS m/e 225 (M - Me), 208, 181, 149*, 121.

Isomerization of Dimethyl 3,3″-Bis(methylene)dispiro[cyclobutane-1,2′-bicyclo[1.1.0]butane-4′,1″-cyclobutane]-1′,3′-dicarboxylate to Dimethyl 2,3-Bis(3-methylenecyclobutylidene)succinate. A small amount (~2 mg) of dimethyl 3,3″-bis(methylene)dispiro[cyclobutane-1,2′-bicyclo[1.1.1]butane-4′,1″-cyclobutane]-1′,3′-dicarboxylate in 0.5 mL of $CDCl_3$ was freeze-degassed and sealed under vacuum in an NMR tube. An initial proton NMR was recorded, and then the sample was completely immersed in an oil bath at 190 °C for 2 h. A second proton NMR revealed that all starting material was gone and that dimethyl 2,3-bis-(3-methylenecyclobutylidene)succinate was the only visible product.

Reaction of [1.1.1]Propellane with Dicyanoacetylene in Methylene Chloride. Into a reaction tube was introduced 1.5 mL of methylene chloride and a magnetic stir bar. The tube was frozen in liquid nitrogen and evacuated, and then ~10 mg of dicyanoacetylene was vacuum transferred into the reaction tube. The reaction tube was warmed to -78 °C, filled with N_2, and stirred to yield a gray solution. To this solution was added dropwise by syringe a solution of 15 mg of [1.1.1]propellane in 1.5 mL of methylene chloride. After this addition the cooling bath was removed, and the solution was allowed to stir and warm to room temperature, at which time it appeared slightly cloudy. The solution was evaporated, the resulting solid was dissolved in $CDCl_3$, and a proton NMR was taken which showed 1:1 adduct and major 2:1 (propellane to dicyanoacetylene) adduct in a ratio of ~1:2.5. GC-MS showed 1:1 adduct and the major 2:1 adduct as well as small amounts of two other 2:1 adducts. Flash chromatography on silica gel eluting with 5:1 pentane/ether allowed 15 mg (63%) of the major 2:1 adduct to be isolated as a white solid. The extremely reactive 1:1 adduct was not isolated.

2,3-Bis(3-methylenecyclobutylidene)succinonitrile (**37**, major 2:1 adduct): ^{1}H NMR δ 5.09 (br s, 2 H), 3.84 (br s, 2 H), 3.69 (br s, 2 H); ^{1}H NMR (benzene-d_6) δ 4.68 (br s, 2 H), 3.45 (br s, 2 H), 3.08 (br s, 2 H); ^{13}C NMR δ 162.0, 138.4 (CN), 114.2, 109.4 (CH_2), 101.4, 42.3 (CH_2), 41.8 (CH_2); GC-MS m/e 208 (M), 207* (M - 1), 192, 180, 166, 153, 140, 128, 115, 104, 89, 77, 63, 51, 39; HRMS (EI) calcd = 208.1002, obsd = 208.0994.

1,2-Dicyano-5-methylenespirohex-1-ene (**36**, 1:1 adduct): ^{1}H NMR δ 5.04 (quintet, J = 2.56 Hz, 2 H), 3.14 (t, J = 2.56 Hz, 2 H); GC-MS m/e 142 (M), 141 (M - 1), 115, 102, 88, 75, 65, 51, 39.

Reaction of [1.1.1]Propellane with Dicyanoacetylene in Benzene. A reaction tube equipped with a small magnetic stir bar was frozen in liquid nitrogen and evacuated, and then ~24 mg of dicyanoacetylene was vacuum transferred into the reaction tube, followed by 5 mL of benzene (benzene-d_6 was also used), and finally 25 mg of [1.1.1]propellane. The reaction tube was warmed to room temperature and stirred for 1 h, during which time the solution changed from clear to gray to yellow. The solution was concentrated, the resulting solid was dissolved in $CDCl_3$, and a proton NMR was taken which showed 1:1:1 adduct (propellane to dicyanoacetylene to benzene) and major 2:1 adduct in a ratio of ~1:1. GC-MS showed 1:1:1 adduct and the major 2:1 adduct as well as small amounts of two other 2:1 adducts. No 1:1 adduct (propellane to dicyanoacetylene) was seen in this reaction (presumably it all reacted further to form 1:1:1 adduct). Flash chromatography on silica gel (sample was introduced to the column in 1 mL of benzene) eluting with 4:1 pentane/ether allowed isolation of 12 mg (30%) of the major 2:1 adduct and 30 mg (36%) of 7-cyano-7-[(3-methylenecyclobutenyl)-cyanomethyl]bicyclo[4.1.0]hepta-2,4-diene (1:1:1 adduct).

7-Cyano-7-[(3-methylenecyclobutenyl)cyanomethyl]bicyclo[4.1.0]-hepta-2,4-diene (**38**, 1:1:1 adduct): ^{1}H NMR (peaks marked with an asterisk were absent from the spectrum when the reaction is carried out in benzene-d_6) δ 6.40* (d of d, $J \approx$ 4 Hz, 7 Hz, 2 H), 6.21* (m, 2 H), 5.10 (br s, 2 H), 3.73 (d of d, $J \approx$ 3 Hz), 3.64 (d of d, $J \approx$ 3 Hz), 3.35* (d of d, $J \approx$ 4 Hz, 5 Hz); ^{13}C NMR δ 165.1, 138.1 (CN), 127.3 (CH), 122.3 (CH), 115.5, 109.5 (CH_2), 103.4, 49.6 (CH), 42.4 (CH_2), 41.2 (CH_2), 13.7; GC-MS m/e 220 (M), 219* (M - 1), 205, 192, 180, 165,

153, 140, 128, 116, 102, 89, 77, 63, 51, 39. GC–MS of the 1:1:1 adduct formed when the reaction is carried out in benzene-d_6 *m/e* 226* (M), 211, 197, 183, 170, 156, 144, 132, 122, 94, 66, 54, 39; HRMS (EI) calcd = 220.1002, obsd = 220.1002.

Reaction of [1.1.1]Propellane with 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone. An NMR tube containing 0.5 mL of CD_3CN and 32 mg of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (hereafter DDQ) was freeze–pump–thaw cycled twice, frozen in liquid nitrogen, and then 9 mg of propellane (1 equiv) was vacuum transferred into the tube. It was sealed by flame under vacuum and warmed carefully to −78 °C. No blue or green color was observed. The tube was warmed to room temperature, and NMR showed exclusive formation of 3,4-dichloro-1,5-dicyano-2,5-dioxo-3′-methylenespiro[bicyclo[4.1.0]heptane-7,1′-cyclobutane]. Flash chromatography on silica gel eluting with 5:1 pentane/ether allowed isolation of 27 mg (68%) of 3,4-dichloro-1,5-dicyano-2,5-dioxo-3′-methylenespiro[bicyclo[4.1.0]heptane-7,1′-cyclobutane] (**45**): ^{1}H NMR δ 5.22 (br s, 1 H), 5.16 (br s, 1 H), 3.47 (br s, 2 H), 3.05 (br s, 2 H); ^{1}H NMR (CD_3CN) δ 5.17 (quintet, J = 2.5 Hz, 1 H), 5.06 (quintet, J = 2.5 Hz, 1 H), 3.40 (br s, 2 H), 3.13 (br s, 2 H); GC–MS *m/e* 290 (M), 291 (M − 1), 257, 229*, 213, 201, 177, 165, 152, 139, 122, 104, 87, 66, 51, 39; HRMS (EI) calcd = 291.9806, obsd = 298.9812.

General Procedure for Measurement of Kinetics. The reaction rates were measured by sealing the carefully weighed reactants and an internal standard (along with a precisely measured volume of a suitable solvent) in an NMR tube. The reaction was followed by proton NMR over several days, and integration of the proton NMR was used to measure changing concentrations of reactants and products.

Because of the volatility of [1.1.1]propellane and bicyclobutane, their partition between gas phase and solution phase may complicate the measurement of rates of reaction. To eliminate this consideration we desired to eliminate the gas space above the solution in the NMR tube. This was accomplished by lowering a glass rod (with an outer diameter just less than the inner diameter of the NMR tube) into the NMR tube almost to the level of the frozen solution and then sealing the tube normally.

Naphthalene was chosen for an internal standard because it is available in very pure form (zone refined), it is inert, it is easy to weigh accurately, and it has a simple NMR spectrum confined to a region where no signal from either starting material or product appear.

In a typical kinetic experiment naphthalene was weighed and placed in the NMR tube. Next, the dimethyl acetylenedicarboxylate was transferred by syringe into the NMR tube, and, finally, about $^3/_4$ of the solvent to be used was syringed into the NMR tube. The naphthalene was allowed to dissolve. The NMR tube was then attached to the manifold, frozen in liquid nitrogen, and evacuated. Two freeze–pump–thaw cycles rid the solution of air. At this point a sample of purified [1.1.1]propellane or bicyclobutane (which had been carefully weighed in a gas storage bulb) was vacuum transferred into the NMR tube. Finally, the remaining $^1/_4$ of the solvent was freeze-degassed and transferred onto the top of the solution (this is to insure that the propellane or bicyclobutane does not all get sucked by capillary action into the small space between the rod and the tube). The top half of the solution was thawed so that it filled the tube and was not simply frozen onto the walls and then refrozen. The glass rod was lowered to just above the level of the frozen liquid, and the tube was sealed with an oxygen–methane flame. The tube was warmed carefully from the top down (failure to exercise sufficient care in warming the tube will cause it to break).

An initial NMR spectrum was recorded immediately after warming, and more spectra were recorded periodically until the reaction was near completion. The concentrations of reactants and products were measured by integration of the proton NMR spectrum using a 10-s relaxation delay between pulses. The methoxy proton signals were integrated to determine the concentration of dimethyl acetylenedicarboxylate and of all reaction products. The concentration of propellane was determined by integration of its singlet. The concentration of bicyclobutane was determined by integrating its farthest upfield or farthest downfield peak (which have almost identical integrations). The middle peak for bicyclobutane (corresponding to the bridgehead protons) integrates low for reasons that are unclear and was not used in the determination of concentration. Each integrand was normalized by dividing its value by the number of protons represented by the peak integrated and was then divided by the normalized integrand of the internal standard (naphthalene). Because the concentration of naphthalene is known and is unchanging, this allows calculation of absolute concentrations.

Measurement of the Kinetics of the Reaction of [1.1.1]Propellane and Bicyclobutane with Dicarbomethoxyacetylene in Acetone-d_6 (Competition Experiment): 1-(3-Cyclobutenyl)-1,2-dicarbomethoxy-5-methylenespirohexane (1:1:1 Adduct). The sample was prepared as described in the general procedure with use of 6.90 mg of bicyclobutane, 10.75 mg of [1.1.1]propellane, 6.5 μL (7.8 mg) of dimethyl acetylenedicarboxylate, 4.65 mg of naphthalene, and 620 μL of acetone-d_6. Proton NMR spectra were recorded at 0.2, 2, 12, 20, 26, 36.3, 47.8, and 60.3 h after thawing the tube. The data are given in the text.

This reaction gave an unexpected product mixture. While bicyclobutane/dicarbomethoxyacetylene 1:1 and 2:1 adducts were formed normally, essentially all of the propellane appeared in a 1:1:1 adduct of propellane/bicyclobutane/dicarbomethoxyacetylene (1-(3-cyclobutenyl)-1,2-dicarbomethoxy-5-methylenespirohexane). A trace of propellane/dicarbomethoxyacetylene 2:1 adduct was visible at the end of the reaction, but no propellane 1:1 adduct was ever observed (we presume that it is trapped by bicyclobutane as fast as it is formed to yield 1:1:1 adduct).

1-(3-Cyclobutenyl)-1,2-dicarbomethoxy-5-methylenespirohexane (1:1:1 adduct): ^{1}H NMR δ 6.13 (d, $J \approx 3.7$ Hz, 1 H), 5.76 (d, $J \approx 3.7$ Hz, 1 H), 4.88 (dist quintet, $J \approx 3$ Hz, 2 H), 3.68 (s, 3 H), 3.67 (s, 3 H), 3.18 (m, 3 Hz), 3.04 (d, J = 17 Hz, 1 H), 2.76 (apparent t of d, J = 15 Hz, 4.7 Hz, 2 H), 2.51 (d, J = 16 Hz, 1 H), 2.01 (s, 1 H); ^{13}C NMR δ 170.2, 169.7, 143.5, 138.6 (CH), 136.3 (CH), 115.5, 106.8 (CH_2), 51.7 (CH_3), 44.5 (CH), 40.9, 37.2 (CH_2), 36.4 (CH_2), 35.9 (CH_2), 33.1, 31.3 (CH); GC–MS *m/e* 262 (M), 231, 198, 169, 143, 128*; HRMS (EI) calcd = 262.1200, obsd = 262.1199.

Determination of the Initial Kinetic Profile of the Reaction of [1.1.1]Propellane with Dicarbomethoxyacetylene in Acetone-d_6. The sample was prepared using 8 mg of [1.1.1]propellane and 14 μL (~17 mg, 1 equiv) of dicarbomethoxyacetylene in 0.35 mL of acetone-d_6. The internal standard used was 40 μL of $CHCl_3$, and no glass rod was inserted in the tube before it was sealed. This reaction was carried out to verify the sigmoidal shape of the curve describing the appearance of the 2:1 adduct (because it is formed by reaction of the 1:1 adduct with an additional molecule of propellane). For this reason, the procedure used was different from that of all the other kinetics experiments. Because we wanted especially to examine the early stages of the reaction, the tube was left in the NMR, which was programmed to acquire a spectrum every 15 min for 8 h and to store the spectra on magnetic media. The spectra were integrated at the end of the experiment and the concentration data were obtained in the usual manner.

Reaction of [1.1.1]Propellane with Silver Tetrafluoroborate. Silver tetrafluoroborate is extremely moisture sensitive and should be handled in a glove bag. A solution of ~2 mg of $AgBF_4$ in 0.5 mL of benzene-d_6 was prepared in an NMR tube. The solution was freeze-degassed on a vacuum line, and then 25 mg of [1.1.1]propellane was vacuum transferred into the tube, which was then sealed by flame. The tube was carefully warmed to room temperature. As soon as the benzene thawed a large amount of brown flocculant precipitate formed in the tube. The reaction was monitored by NMR, and the reaction tube was protected from light. After three days the propellane was completely consumed; the brown precipitate was gone, and the NMR showed that the predominant products were bis(3-methylenecyclobutylidene) (**48**, propellane dimer) and propellane trimer (**49**, which we believe is 2,7-bis(methylene)-5-(3-methylenecyclobutylidene)spiro[3.4]octane] in a ratio of approximately 1.5:1. In addition a very small amount of methylenecyclobutene was seen in the NMR. The GC–MS of the reaction mixture showed the major dimer and the trimer as the principal products but also showed two other small peaks which appear to be dimers. In addition, a very small peak with MW = 150 (corresponding to two propellanes plus H_2O) was seen.

The reaction mixture was passed through florisil to remove the silver and was then separated by GC on a $2^3/_4$ ft × $^1/_4$ in. 1.5% OV-101 50/60 V column at 100 °C. Solvent eluted from 0 to 1 min, the two minor dimers eluted as a single small peak from 1.5 to 2.5 min, bis(3-methylenecyclobutylidene) eluted from 3 to 4.5 min, and two very small peaks eluted at 5 and 6 min (unidentified). At this point the column temperature was raised to 150 °C, and trimer came out with a retention time of 18 min.

Bis(3-methylenecyclobutylidene) (**48**, propellane dimer): ^{1}H NMR (benzene-d_6) δ 4.93 (br s, 4 H), 3.15 (br s, 8 H); ^{1}H NMR ($CDCl_3$) δ 4.90 (br s, 4 H), 3.23 (br s, 8 H); GC–MS (70 eV) *m/e* 132 (M − 1), 117, 91*, 77, 65, 51, 39; GC–MS (Cl isobutane) *m/e* 133 (M + 1).

2,7-Bis(methylene)-5-(3-methylenecyclobutylidene)spiro[3.4]octane (**49**, propellane trimer): ^{1}H NMR (benzene-d_6) δ 4.94 (imperfect quintet, $J \approx 2$ Hz, 3 H), 3.88 (imperfect quintet, $J \approx 2$ Hz, 3 H), 3.46 (br quintet, $J \approx 2$ Hz, 2 H), 3.13 (br quintet, $J \approx 2$ Hz, 2 H), 2.95 (d of m, $J \approx 18$ Hz, 2 H), 2.77 (br s, 2 H), 2.49 (d of m, $J \approx 18$ Hz, 2 H), 2.41 (br s, 2 H); ^{13}C NMR (CD_2Cl_2, ref = 53.8) δ 106.43, 106.37, 106.16, 49.68, 43.30, 40.98, 39.28, 37.42; GC–MS (70 eV) *m/e* 198 (M), 183, 168, 155, 143, 128*, 115, 103, 91, 77, 65, 51, 39; GC–MS (Cl isobutane) *m/e* 199 (M + 1), 143.

Mixture of the two minor dimers: The two dimers were separated by the mass spectrometer's gas chromatograph, and their mass spectra were essentially identical: GC–MS (70 eV) *m/e* 132 (M − 1), 117, 91*, 84,

65, 54, 39; GC-MS (CI isobutane) m/e 133 (M + 1), 11.

If the benzene was wet, large amounts of another product was formed: ^{1}H NMR (benzene-d_6) δ 4.84 (quintet, J = 2 Hz, 4 H), 3.88 (quintet, $J \approx 5.5$ Hz, 2 H), 2.90–2.40 (br m, 8 H); GC-MS (70 eV) m/e 149 (M - 1), 134, 109*, 82, 66, 54, 39; GC-MS (CI isobutane) m/e 151 (M + 1), 150, 149* (M - 1), 133, 110, 93, 83, 69. We believe that this product is bis(3-methylenecyclobutyl) ether (**50**). At least a small amount of this product was observed in the most carefully dry reaction, and it is usually the first product seen. It appears that the reaction dries itself initially by consuming all the water in making this ether.

Reaction of Bicyclobutane with Silver Tetrafluoroborate. A solution of ~2 mg of $AgBF_4$ in 0.5 mL of benzene-d_6 was prepared in an NMR tube. The solution was freeze-degassed on a vacuum line, and then 24 mg of bicyclobutane was vacuum transferred into the tube, which was then sealed by flame. The tube was carefully warmed to room temperature. As the benzene thawed the solution remained clear. Unlike the reaction with [1.1.1]propellane no brown precipitate was formed. The reaction was monitored by NMR, and the reaction tube was protected from light. The reaction proved to be extremely slow. After one week conversion was not complete. The predominant reaction product observed in the proton NMR was 1,4,7-octatriene. No butadiene was observed.

1,4,7-Octatriene: ^{1}H NMR (benzene-d_6) δ 5.72 (m, 2 H), 5.42 (m, 2 H), 4.95 (pair of overlapping doublets, $J \approx 16$ Hz, 4 H), 2.77 (br m, 4 H). The 1,4,7-octatriene seems to be a single stereoisomer, but whether it is cis or trans is uncertain.

Competition Experiment between Bicyclobutane and [1.1.1]Propellane with Silver Tetrafluoroborate. A solution of ~2 mg of $AgBF_4$ in 0.5 mL of benzene-d_6 was prepared in an NMR tube. The solution was freeze-degassed on a vacuum line, and then 18 mg (0.33 mmol) of bicyclobutane and 16 mg (0.24 mmol) of [1.1.1]propellane were vacuum transferred into the tube, which was then sealed by flame. The tube was carefully warmed to room temperature. As soon as the benzene thawed a brown flocculent precipitate formed, as in the reaction of [1.1.1]propellane alone. A proton NMR taken immediately after thawing the tube showed approximately 3 times as much bicyclobutane as propellane, although there was only 1.3 times as much bicyclobutane as propellane to start. This is consistent with instant formation of the brown insoluble propellane–silver complex. The reaction was monitored by NMR and the reaction tube was protected from light. After 16 h the propellane had been completely consumed, but about 80% of the bicyclobutane remained.

The proton NMR of the reaction mixture showed propellane dimer [bis(3-methylenecyclobutylidene)], a small amount of bicyclobutane dimer, and a great many other peaks belonging to heretofore unobserved compounds. No butadiene was observed. The GC-MS of the reaction mixture showed propellane dimer and trimer and small amounts of at least four different cross-dimers. In addition there were three new compounds with retention times between those of the dimers and that of propellane trimer. It is believed that these compounds are cross-trimers, but if so they do not show parents in the GC-MS. No attempt was made to separate or purify the cross-dimers or -trimers.

Cross-dimers: There were four peaks on the chromatogram with essentially identical mass spectra: GC-MS m/e 120 (M), 105, 91, 77*, 65, 51, 39.

Possible cross-trimers: Three peaks appeared, all with approximately identical mass spectra: GC-MS m/e 145, 129, 117, 115, 105, 91, 77, 65, 51, 39.

Reaction of [1.1.1]Propellane with Rhodium Dicarbonyl Chloride Dimer. A solution of ~2 mg of $[Rh(CO)_2Cl]_2$ in 0.5 mL of $CDCl_3$ was prepared in an NMR tube. The solution was freeze-degassed on a vacuum line, and then 10 mg of [1.1.1]propellane was vacuum transferred into the tube, which was then sealed by flame. The tube was carefully warmed to room temperature. An NMR spectrum taken immediately after the tube had warmed showed that no propellane remained. The reaction was clean, and bis(3-methylenecyclobutylidene) (**48**) was by far the major product. In addition, however, there was a small triplet at δ 3.66 and a small quintet at δ 5.28 (corresponding perhaps to trimer). The GC-MS of the reaction mixture showed bis(3-methylenecyclobutylidene) and also a small peak with mass 198 (trimer) as the only products. The reaction mixture was filtered through florisil and then evaporated to give 9.6 mg (96%) of almost completely pure propellane dimer.

Reaction of Bicyclobutane with Rhodium Dicarbonyl Chloride Dimer. A solution of ~2 mg of $[Rh(CO)_2Cl]_2$ in 0.5 mL of $CDCl_3$ was prepared in an NMR tube. The solution was freeze-degassed on a vacuum line, and then 11 mg of bicyclobutane was vacuum transferred into the tube, which was then sealed by flame. The tube was carefully warmed to room temperature. An NMR taken immediately after the tube had warmed showed that a small amount of bicyclobutane remained, but most of it had been converted to a 2:1 mixture of butadiene and 1,4,7-octatriene.

Competition Experiment between Bicyclobutane and [1.1.1]Propellane with Rhodium Dicarbonyl Chloride. A solution of ~2 mg of $[Rh(CO)_2Cl]_2$ in 0.5 mL of $CDCl_3$ was prepared in an NMR tube. The solution was freeze-degassed on a vacuum line, and then 11 mg (0.20 mmol) of bicyclobutane and 6 mg (0.09 mmol) of [1.1.1]propellane were vacuum transferred into the tube, which was then sealed by flame. The tube was carefully warmed to room temperature. A proton NMR taken immediately after thawing the tube showed that all of the propellane had been consumed, but only about two-thirds of the bicyclobutane had been consumed. The products were bis(3-methylenecyclobutylidene) (propellane dimer), a propellane derived compound with the small singlet at δ 3.66 (perhaps propellane dimer), butadiene, and 1,4,7-octatriene (bicyclobutane dimer). No cross-products of any sort were detected. Bicyclobutane and propellane seemed to react independently of each other.

Reaction of [1.1.1]Propellane with Rhodium Dicarbonyl Chloride in Methyl Acrylate. A solution of ~2 mg of $[Rh(CO)_2Cl]_2$ in 0.5 mL of methyl acrylate was prepared in an NMR tube. The solution was freeze-degassed on a vacuum line, and then 6 mg of [1.1.1]propellane was vacuum transferred into the tube, which was then sealed by flame. The tube was carefully warmed to room temperature. An NMR taken immediately after the tube had warmed showed that no propellane remained. The reaction was clean, and bis(3-methylenecyclobutylidene) (**48**) and 1-carbomethoxy-5-methylenespirohexane (**52**) in a ratio of approximately 1.5:1 were the only products seen. The GC-MS of the reaction mixture showed bis(3-methylenecyclobutylidene) and 1-carbomethoxy-5-methylenespirohexane as the only products.

1-Carbomethoxy-5-methylenespirohexane: ^{1}H NMR ($CDCl_3$) δ 4.89 (quintet, J = 2.5 Hz, 2 H), 3.0–2.8 (br m, 4 H), 1.72 (d of d, $J \approx 4$ Hz, 7 Hz, 1 H), 1.27 (t, $J \approx 4.5$ Hz, 1 H), 1.72 (d of d, $J \approx 4.5$ Hz, 7 Hz, 1 H); GC-MS 152 (M), 137, 121, 109, 91, 93*, 77, 66, 53.

Reaction of [1.1.1]Propellane with Various Complexes of Rhodium(I) and Palladium(II). The reaction of propellane with rhodium tris(triphenylphosphine) chloride, palladium cycloctadienyl dichloride, and palladium bis(benzonitrile) dichloride proceeded in much the same way (2 mg of complex, 0.5 mL of $CDCl_3$, 10 mg of [1.1.1]propellane). In each case the reaction was very fast (all of the propellane was consumed as soon as the tube was warmed to room temperature), and in each case bis(3-methylenecyclobutylidene) was essentially the only product formed.

Reaction of [1.1.1]Propellane with Various Complexes of Platinum(0), Platinum(II), and Iridium(I). The procedure for these reactions was identical to that given in the previous experiment. Approximately 4 mg of propellane, 1 mg of the transition-metal complex, and 0.4 mL of $CDCl_3$ were used in each case. The reaction of propellane with platinum bis(triphenylphosphine) dichloride, platinum tetrakis(triphenylphosphine), platinum bis(triphenylphosphine) ethylene complex, and iridium tris(triphenylphosphine) carbonyl chloride proceeded in much the same way. In each case the reaction was slow (propellane was consumed over the course of 1 or 2 days), and in each case both methylenecyclobutene and bis(3-methylenecyclobutylidene) were formed. The ratio of these two products seemed to be related to the oxidation state of the metal. The two platinum(0) complexes gave 8–10 times as much methylenecyclobutene as dimer, the iridium(I) complexes gave 3–4 times as much methylenecyclobutene as dimer, and the platinum(II) complex gave approximately equal amounts of methylenecyclobutene to dimer. In all cases ratios were determined by integration of proton NMR spectra.