Synthesis of Doubly Bridgehead Substituted Bicyclo[1.1.1]pentanes. Radical Transformations of Bridgehead Halides and Carboxylic Acids

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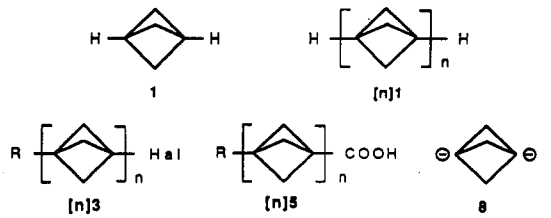
Synthetic transformations of the 1-bicyclo[1.1.1]pentyl bridgehead radicals **11** generated from the corresponding bridgehead iodides **3** and carboxylic acids **5** are described. The relatively high nucleophilicity of these radicals was utilized in reactions with carbonyl compounds. In the reaction sequence of preparation of the iodides **3** and their further transformations, [1.1.1]propellane (**2**) is a synthetic equivalent of the recently described bicyclo-[1.1.1]penta-1,3-dienyl dianion (**8**).

Introduction

We recently required synthetic transformation and replacement of functional groups at the bridgehead positions of bicyclo[1.1.1]pentane (**1**) and the higher [*n*]staffanes ([***n***]**1**).[1-4] Although quite a few bridgehead-substituted derivatives of **1** and [***n***]**1** have been synthesized over the years,[1-20] and although they are now readily accessible from [1.1.1]propellane (**2**),[1-15,20] relatively little is known about transformations in which a bond to the bridgehead carbon is broken, and this is the issue we address presently.

The starting materials for these transformations are of two types: (i) the members of the oligomeric series [***n***]**3** are generally accessible by photochemically induced oligomerizing addition of **2** across C–halogen bonds in organic halides **4**,[1-3,6-10,20] and (ii) the members of the series [***n***]**5** are accessible by oligomerization of **2** with methyl formate,[1-3] or by reaction of **2** with benzil[3] (in the case of [**1**]**5b**, also by reaction with biacetyl[11]), followed by oxidation. The overall synthetic sequence from starting



tetrahalide **6**, leading to the doubly bridgehead substituted bicyclo[1.1.1]pentanes **7**, is shown in Scheme I.

For the initial investigation,[21] we have selected bridgehead-substituted derivatives of **1**, the first member of the oligomeric series. The sequence **2** → **3** → **7** represents a fairly general way of inserting the bicyclo[1.1.1]pentane ring system between two moieties. In this sense, **2** acts as a synthetic equivalent of the recently described[12] dianion **8**.

Bicyclo[1.1.1]pentyl Halides 3. In principle, the carbon–halogen bond in **3** can be cleaved heterolytically, homolytically, or by electron transfer to give one of three potentially synthetically useful intermediates: (i) the carbocation **9**, (ii) the carbanion **10**, or (iii) the carbon radical **11**. Their further reactions then furnish the substitution products **7** (Scheme I). Direct metal insertion into the carbon–halogen bond represents another possibility.

(i) The solvolysis of the bridgehead halides **3** gives exclusively the ring-opened 3-methylenecyclobutyl cation **12**.[14,16]

(ii) The carbanion **10** can be generated from **3** by metal–halogen exchange,[2,3,10,17] by reduction of 1-(phenylthio)bicyclo[1.1.1]pentane with lithium 4,4′-di-*tert*-butylbiphenyl,[7,18] and by addition of organolithium compounds to **2**,[1,12,22,23] which however appears to suffer from serious limitations.[22]

(iii) The radical path[24] **3** → **11** → **7** is particularly mild.

Bicyclo[1.1.1]pentane-1-carboxylic Acids 5. Carboxylic acids can be converted to carbon radicals in several ways: decomposition of 2-mercaptopyridine *N*-oxide *O*-esters (Barton esters[25-28]), peroxy esters,[29,30] direct one-

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(21) Presented in part at 44th Southwestern Regional ACS Meeting, November 30–December 2, 1988; Corpus Christi, TX; Book of Abstracts, p 241.
(22) Morrison, R. W.; Michl, J., unpublished results.
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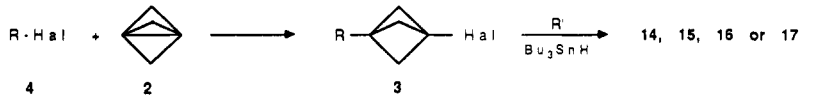
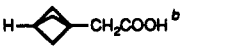
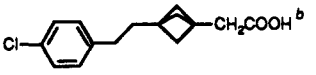
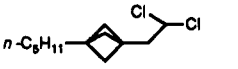
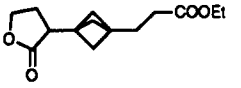
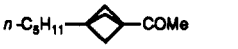
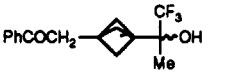
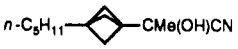
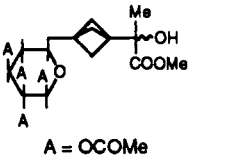
Table I. Formation of 1-Halobicyclo[1.1.1]pentanes and Their Reactions with Trapping Agents in the Presence of Tri-*n*-butyltin Hydride



entry	R-Hal (4)	R′		product	overall yield,[a] %
1	a: $BrCH_2COOMe$	-	14a		46
2	b: $BrCH(COOEt)_2$	-	14b		42
3	c: ICH_2COOEt	$4\text{-}ClC_6H_4CH{=}CH_2$	15a		24
			14a[b]		21
4	d: $n\text{-}C_5H_{11}I$	$CH_2{=}CCl_2$	15b		36
5	e: 	$CH_2{=}CHCOOMe$	15c		39
6	d: $n\text{-}C_5H_{11}I$	MeCOCOMe	16		43
7	f: $PhCOCH_2I$[c]	$MeCOCF_3$	17a		39
8	d: $n\text{-}C_5H_{11}I$	MeCOCN	17b		35[d]
9	g: 	MeCOCOOMe	17c		49[e]

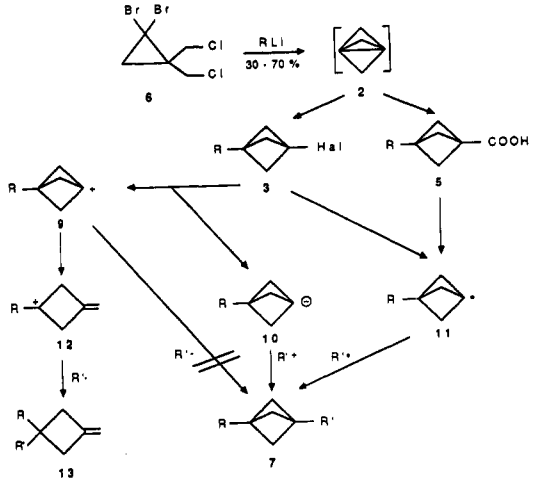
[a] Yields based on the [1.1.1]propellane precursor **6**. [b] After hydrolysis. [c] Iodides prepared from the corresponding bromides and used in situ: Perrier, M. *J. Am. Chem. Soc.* **1947**, *69*, 3148. [d] Yield of isolated **16** after hydrolysis of **17b**. [e] Yield based on **4g**.

electron oxidation of the carboxylate anion,[31-36] etc.[24]

Results and Discussion

Preparation of 3-Substituted 1-Halobicyclo[1.1.1]pentanes. The addition of **2** to alkyl iodides and bromides **4a–g** to produce the bridgehead halides **3a–g** (Table I) was induced photochemically. For the best overall yields, **2** is used as a 3% ethereal solution prepared from the 1,1-bis(chloromethyl)-2,2-dibromocyclopropane (**6**) and methyllithium[3,7,11,15] in about 70% yield. This solution also contains some methyl bromide, which does not interfere with the preparation of **3**. However, the methyl bromide is removed before the subsequent reaction of **3** with tri-*n*-butyltin hydride to yield **7**.

Scheme I



R:	a	b	c	d	e	f	g	h	i	j
3	CH_2COOMe	$CH(COOEt)_2$	CH_2COOEt	C_5H_{11}		$PhCOCH_2$		Br	I	$MeSO_2$
5	H	COOH	COOMe	BuS	MeCOO	2,5-$C_6H_3Cl_2$				

(26) Barton, D. H. R.; Garcia, B.; Togo, H.; Zard, S. Z. *Tetrahedron Lett.* **1986**, *27*, 1327.
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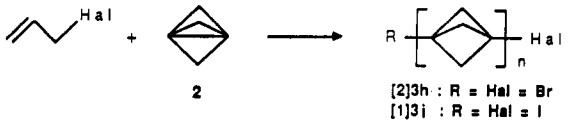
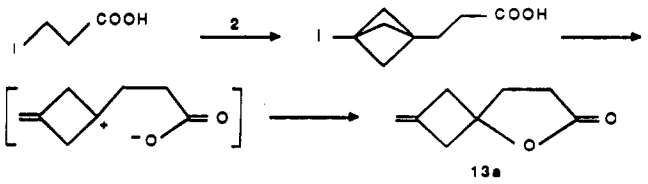
The radical addition of **2** to **4** usually proceeds cleanly, and the crude product can be used for the next step. This

is particularly important in the case of iodides, which are quite unstable.

Allyl bromide and iodide do not give the usual adducts **3**. Instead, halides [2]**3h** (R = Hal = Br) and **3i** (R = Hal = I) are produced in about 10% yield, probably by a mechanism responsible for the similar results obtained with benzyl bromide.[1,3]

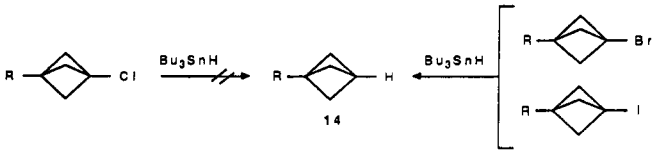


Replacement of Bridgehead Halogens as Anions. Solvolysis of bridgehead halides followed by reaction with a nucleophile lead to 3-substituted methylenecyclobutanes (**13**). We find that intramolecular carbocation trapping with a nucleophile works well. Thus, 3-iodopropionic acid is converted to 2-methylene-5-oxaspiro[4.3]octan-6-one (**13a**) in an overall yield of 31% based on the tetrahalo compound **6**. This process is likely to have general applicability, but we have not pursued it further at this time.



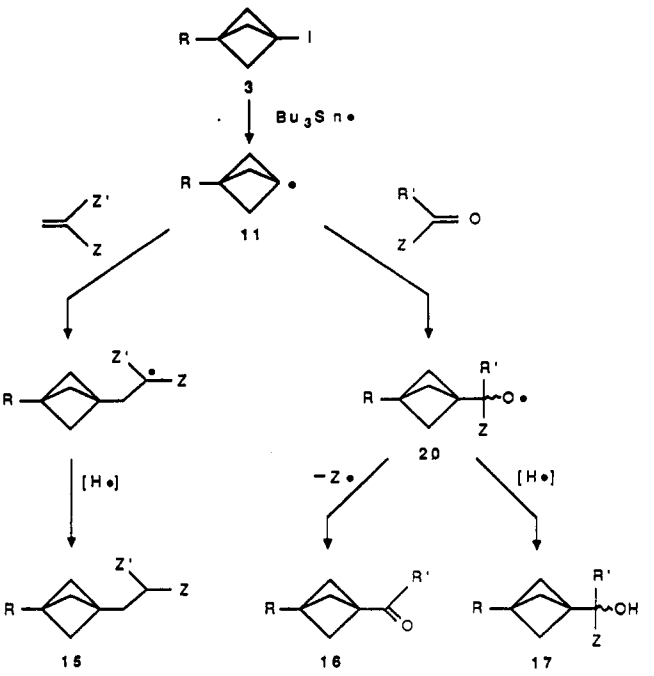
Replacement of Bridgehead Halogens as Atoms. Abstraction and Reaction with a Radical Trap (Table I). A. C–H Bond Formation. The simplest process of this kind is the replacement of the bridgehead halogen by hydrogen. The reactivity of **3** toward tri-*n*-butyltin hydride depends strongly on the choice of the halogen. The bridgehead chlorides do not undergo reduction to the parent **14**, and 3-chloro-3′-(methylsulfonyl)[2]staffane ([2]**3j**)[3] remains unchanged both photochemically and thermally even in boiling xylene. The difficulty of abstraction of chlorine in **3** by the stannyl radical can be expected from the extrapolation of existing experimental data for other bicyclic chlorides. In a series of tertiary chlorides, 1-methylcyclohexyl, adamantyl, bicyclo[2.2.2]-octyl, and bicyclo[2.2.1]heptyl, the relative rates of the chlorine abstraction are 1.0, 0.24, 0.12, and 0.010, respectively.[37] This clear trend of decreasing reactivity has been attributed to changes in the geometry at the radical center constrained by the polycyclic framework.

The bromides and the iodides are both reduced to **14** and serve as good intermediates for monosubstituted bicyclo[1.1.1]pentanes (Table I, entries 1–3). The bromides require longer reaction times and higher temperatures. This reaction sequence permits the substitution of an organic halide by the bicyclo[1.1.1]pent-1-yl group, with **2** acting as a synthetic equivalent of the bicyclo[1.1.1]-pent-1-yl anion. Examples are the acetic acid **14a**, R = CH_2COOH (obtained via the corresponding ester) and the malonate **14b**, R = $CH(COOEt)_2$, previously obtained by radical addition of **2** to diethyl malonate.[1]



(37) Fort, R. C., Jr.; Hiti, J. *J. Org. Chem.* **1977**, *42*, 3968.

Scheme II



Reduction of the dibromide [2]**3h** gives easy access to [2]staffane ([2]**1**), obtained earlier in moderate yields by the reduction of 3,3′-bis(methylthio)[2]staffane[15] and by hydrogen atom induced oligomerization of **2**.[38] In the synthesis of [2]staffane ([2]**1**) no solvent was used to avoid the formation of an azeotrope of the product with benzene and pentane. For instance, a mixture of [2]**1** and benzene (about 1:1 ratio) boils at 36–37 °C.

B. C–C Bond Formation. The ability of the bromides and iodides **3** to undergo reduction suggested that they may be useful for C–C bond formation reactions assisted by tri-*n*-butyltin hydride. However, we find that the bromides are not reactive enough and that the stannyl radicals react faster with the trapping agent, leaving behind unreacted **3**. Only the iodides **3** react under photochemical or thermal conditions to give new C–C bonds.

Scheme II shows reactions of the radical **11** with three distinct classes of multiple-bond radical traps, giving three types of products: **15**, **16**, and **17**. The reactants and products are summarized in Table I. In a typical experiment, a solution of crude **3** is concentrated to remove MeBr, mixed with Bu_3SnH and the trapping reagent in benzene, and either irradiated through Pyrex or refluxed for 1–2 h. The photochemical method generally is cleaner than the thermal one. Products are isolated by distillation or column chromatography, sometimes followed by hydrolysis (Table I, entries 1, 3, 8). The overall yields of the three-step synthesis based on **6** are about 40%.

Activated olefins, such as styrenes and unsaturated esters, are known to react easily with radicals to form new C–C bonds.[24] The radical **11** reacts with excess 4-chlorostyrene to give the acid **15a** (after hydrolysis), with 1,1-dichloroethylene to give **15b**, and with methyl acrylate to give **15c**. In the reaction of **3c** (R = CH_2COOEt) with the styrene, significant quantities of the reduced product **14a** were also isolated, even when an excess of the styrene was used. The reaction of **3d** (R = C_5H_{11}) with 1,1-dichloroethylene gives either some reduced product **14c**, when a small excess of the olefin is used or some oligomerization

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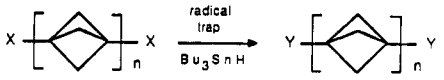
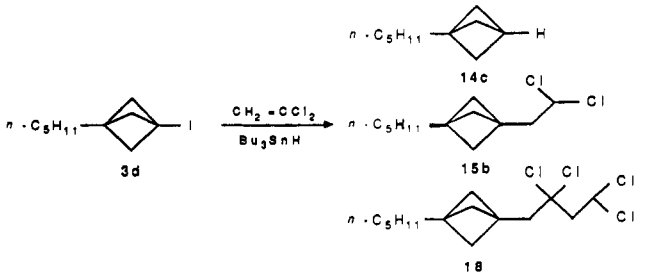
Table II. Radical Reactions of 3,3$^{(n-1)}$-Dihalo[n]staffanes ([n]3h,i) in the Presence of Tri-n-butyltin Hydride



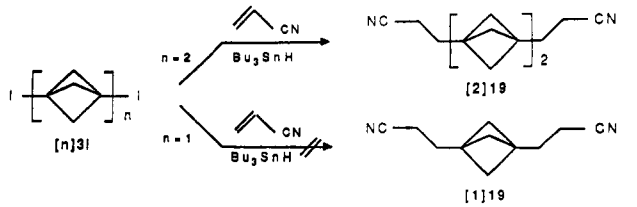
3	n	X	Y	product	yield, %
h	2	Br	H	[2]1	83
i	1	I	CH_2CH_2CN	[1]19	0[a]
i	2	I	CH_2CH_2CN	[2]19	73

[a] See text.

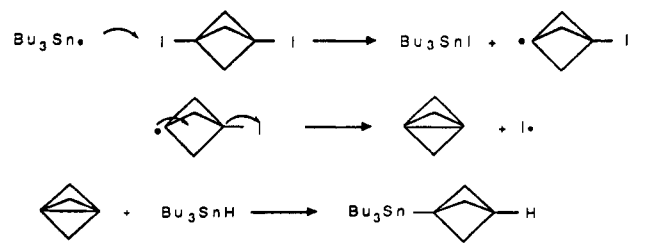
product **18**, when a large excess of the olefin is used. The side products **14c** and **18** were observed by GC-MS, but were not isolated.



The reaction of the diiodides [n]**3i** with acrylonitrile in the presence of tri-n-butyltin hydride gives the expected dinitrile [2]**19** only in the case of [2]**3i**. No dinitrile [1]**19**



was detected when [1]**3i** was used (Table II). This result can be explained by assuming a very fast sequential process of radical-induced elimination of two iodine atoms (in analogy to the anion-induced elimination of two bromine atoms;[14] note that the addition of the PhS$^{\bullet}$ radical to **2** is reversible[39]) and formation of the central bond of **2**. The resulting [1.1.1]propellane (**2**) can react further with tri-n-butyltin hydride.[40] In fact, GC–MS showed that one of the resulting organotin compounds[7] has a fragment m/z 67 (C_5H_7) beside the typical m/z 57 (C_4H_9).

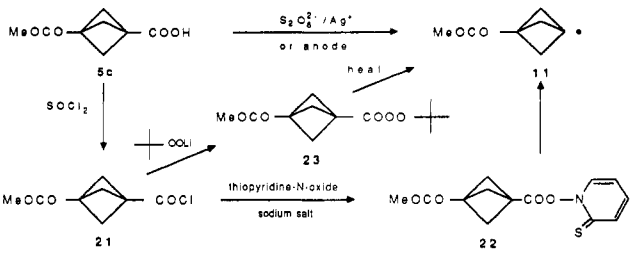


The most interesting products are formed in the addition of radicals **11** to a carbonyl group (Scheme II).[3,6,7,11] The bridgehead radical **11** reacts with activated carbonyl groups to give either the ketone **16** or the alcohol **17**, depending on the ability of the oxy radical **20** to fragment.[3]

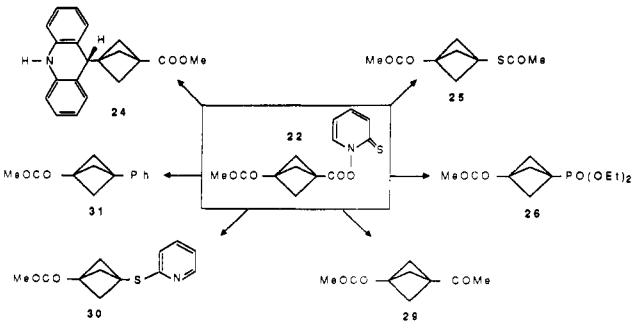
(39) McGarry, P. F.; Johnston, L. J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 3750.

(40) Radical addition of tri-n-butyltin hydride to a substituted [1.1.1]propellane was described by Belzner, J.; Szeimies, G. *Tetrahedron Lett.* **1987**, *28*, 3099.

Scheme III



Scheme IV



The radical **20a** (R′ = Me, Z = Ac) derived from the α-diketone, biacetyl, fragments easily to **16** (R′ = Me) and an acetyl radical, which abstracts hydrogen from tin hydride, propagating the radical chain. Radicals **20** derived from α-keto esters (Z = COOMe) or α-keto nitriles (Z = CN) do not fragment but instead abstract hydrogen from tin hydride and give the alcohols **17** (Table I, entries 7–9).

The generation of radical **11** from the iodide **3** and its subsequent reaction with a carbonyl group competes with both polar[41] and radical[42] addition of the tin hydride to the carbonyl group. The polar addition appears to be destructive, and this is particularly pronounced in the case of strongly electrophilic carbonyl compounds. In order to avoid the slower undesired polar pathway, the reaction sequence **3** → **11** → **20** → **16** or **17** (Scheme II) is best carried out photochemically as fast as possible. The reaction of **11** with a carbonyl compound serves as a unique and mild way of introducing a carbonyl group or its equivalent into the bridgehead position of bicyclo[1.1.1]-pentane.

Several examples of intramolecular addition of a carbon radical, generated from the corresponding halide, to the carbonyl group have been reported in the literature.[43] The reaction of alkyl halides with biacetyl in the presence of tin hydride was apparently first attempted by Bentrude.[44]

Replacement of a Bridgehead Carboxyl. Oxidation and Reaction with Radical Traps (Table III). We have explored some of the standard ways of generating the radical **11**, using the readily accessible[11] 3-(methoxycarbonyl)bicyclo[1.1.1]pentane-1-carboxylic acid (**5c**), which was converted, via the acyl chloride **21**, into the Barton ester **22** and the *tert*-butyl peroxy ester **23** (Scheme III). Quite a few of the reactions were successful but the yields were invariably low.

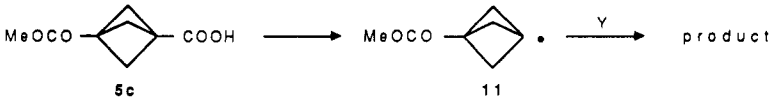
(41) Leusink, A. J.; Budding, H. A.; Marsman, J. W. *J. Organomet. Chem.* **1968**, *13*, 155. Leusink, A. J.; Budding, H. A.; Drenth, W. *J. Organomet. Chem.* **1968**, *13*, 163.

(42) Barker, P. J.; Davies, A. G.; Hawari, J. A.-A.; Tse, M.-W. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1488 and references cited therein.

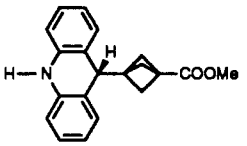
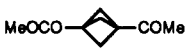
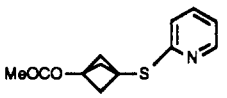
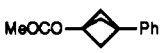
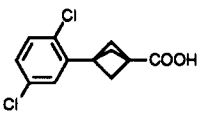
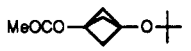
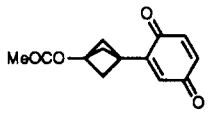
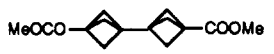
(43) For examples, see: Beckwith, A. L. J.; Kazlauskas, R.; Syner-Lyons, M. R. *J. Org. Chem.* **1983**, *48*, 4718. Flies, F.; Lalande, R.; Maillard, B. *Tetrahedron Lett.* **1976**, 439. Tsang, R.; Dickson, J. K., Jr.; Pak, H.; Walton, R.; Fraser-Reid, B. *J. Am. Chem. Soc.* **1987**, *109*, 3484.

(44) Bentrude, W. G.; Darnall, K. R. *J. Am. Chem. Soc.* **1968**, *90*, 3588.

Table III. Decarboxylative Alkylation with 3-(Methoxycarbonyl)bicyclo[1.1.1]pentane-1-carboxylic Acid (5c)



5c 11

Y		product	yield,[a] %	prod./30 ratio[b]
		Via Barton Ester 22		
Acridine	24		20	1
MeCOSSCOMe	25		15[c]	6
$P(OEt)_3$	26		28	3
MeCOCOMe	29		70	23
benzene	30		53,[d] 70[e]	0.03,[d] 0.14[e]
	31		2,[d] 10[e]	
		Via Decomposition of Peroxy Ester 23		
1,4-dichlorobenzene	5f		13[f]	
	33		7	
		Via Silver(I)/Ammonium Persulfate Oxidation		
1,4-benzoquinone	35		8	
		Anodic Oxidation		
–	36		4	

[a] Based on 3-(methoxycarbonyl)bicyclo[1.1.1]pentane-1-carboxylic acid (**5c**). [b] Ratio of the GC peaks areas of the intermolecular to the intramolecular trapping product. [c] Yield of isolated 3-(butylthio)bicyclo[1.1.1]pentane-1-carboxylic acid (**5d**). [d] 30 °C, *hν*. [e] 80 °C, *hν*. [f] After hydrolysis of the ester.

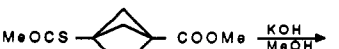
Table IV. Isomer Distribution of Alkylated Products 32 by ^1H NMR[a] Analysis

	X	ortho, % (δ)	other isomers,[b] % (δ)	
32a	Cl	60 (2.50)	25 (2.32)	15 (2.31)
32b	CN	54 (2.56)	33 (2.36)	13 (2.35)
32c	COOMe	43 (2.43)	57 (2.35)	

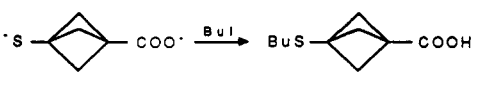
[a] See ref 47. [b] Meta and para assignment unclear.

A. Decomposition of the 2-Mercaptopyridine *N*-Oxide *O*-Ester 22. The Barton ester **22** was previously[45] used in situ, in the synthesis of bicyclo[1.1.1]pentane-1-carboxylic acid by reaction with *tert*-butylmercaptan. Without isolation, the radical precursor **22** was decomposed photochemically in the presence of a radical trap (Scheme IV). The reactions of the resulting radical **11** with acridine, diacetyl disulfide, or triethyl phosphite give access to the acridane derivative **24**, the thioacetate **25**, and the phosphonate ester **26**, respectively. The reductive alkylation of acridine with **22** resembles its alkylation with radicals generated from carboxylic acids.[46] In spite of the absence of the sulfur atom in the phosphite,[27] the ester **26** was obtained in 28% yield based on **5c**.

The thioacetate **25** was smoothly hydrolyzed and the resulting anion **27** was S-butylated to give 3-(butylthio)-bicyclo[1.1.1]pentane-1-carboxylic acid (**5d**). No ring fragmentation was observed in this process. In contrast,



25

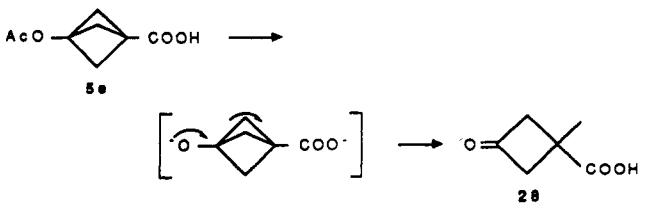


27 5d

the hydrolysis of 3-acetoxybicyclo[1.1.1]pentane-1-carboxylic acid (**5e**), a close oxygen analogue of **25**, is known to yield mostly the cyclobutanone product **28**.[16] The difference in the thermodynamic driving force is undoubtedly provided by the much lower C=S bond strength relative to C=O.

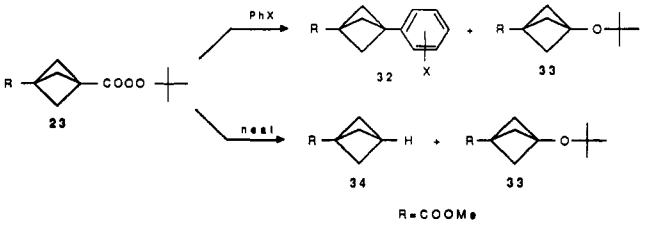
(45) Della, E. W.; Tsanaktsidis, J. *Aust. J. Chem.* **1986**, *39*, 2061.

(46) Noyori, R.; Kato, M.; Kawanisi, M.; Nozaki, H. *Tetrahedron* **1969**, *25*, 1125.



The tendency of **11** to react with the carbonyl group was demonstrated once again by the decomposition of **22** in the presence of biacetyl to form the keto ester **29** as the major product. Various amounts of the intramolecular trapping product **30** were detected in each of the reactions listed in Scheme IV. Irradiation of the ester **22** generated in situ in benzene either at ambient temperature or at reflux gives the intramolecular trapping product **30** in 53% and 70% yields, respectively. In addition to **30**, 3% (at room temperature) or 10% (at reflux) yield of the ester **31** was formed, apparently arising from the attack by the radical **11** on benzene.

B. Decomposition of the *tert*-Butyl Peroxy Ester 23. Unlike **22**, the crystalline peroxy ester radical precursor **23** (Scheme III) is relatively stable and insensitive to moisture and can be conveniently stored in the refrigerator. Thermal but not photochemical decomposition of **23** at 130 °C in the presence of *p*-dichlorobenzene gives, after hydrolysis, the dichloro acid **5f** in 13% yield (Table III). Other aromatic reagents give all possible isomers of the alkylated products **32**, although the ortho isomer is predominant in each case. Table IV contains results of the ^{1}H NMR analysis[47] of each of the isomeric fractions of **32**. GC–MS along with ^{1}H and ^{13}C NMR analysis of several reaction mixtures did not detect the starting acid **5c**, the ester **34**, or the ring-opened methylenecyclobutane products **13**. Thus it appears that the preferred pathway of decomposition of the peroxy ester **23** is a homolytic cleavage with the loss of a CO_2 molecule.

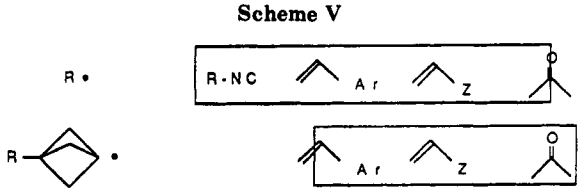


The apparent preference for the ortho substitution is presumably due to smaller spatial requirements of the bicyclo[1.1.1]pent-1-yl radical. This behavior resembles that of methyl[48] and phenyl radicals.[49] Larger bridgehead radicals like adamantyl,[29] norbornyl,[29] and even the closely related cubyl[31] give mostly the meta and para isomers.

A side product, the *tert*-butyl ether **33**, is formed in about 50% of the desired products in each of these reactions. No olefinic products are observed in any of these thermal reactions. Thermal decomposition of the neat peroxy ester **23** produces methyl bicyclo[1.1.1]pentane-1-carboxylate (**34**) and the *tert*-butyl ether **33** in an approximate 3:1 ratio, along with some intractable polymer.

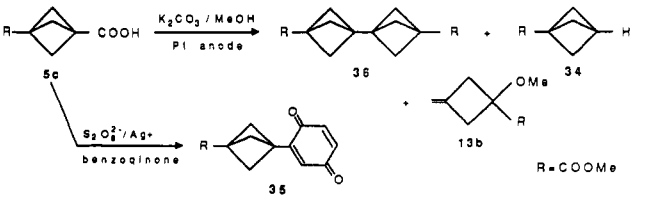
C. Direct Oxidation of the Acid 5c. Oxidation of the acid **5c** with persulfate in the presence of silver ions[34] also provides access to the radical **11** (R = COOMe), which

Scheme V

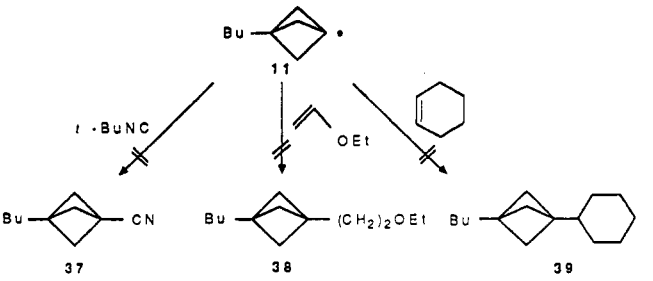


reacts under these conditions with 1,4-benzoquinone, giving a low yield of the quinone **35** as the only isolated product. This material slowly decomposes upon standing at room temperature in the dark.

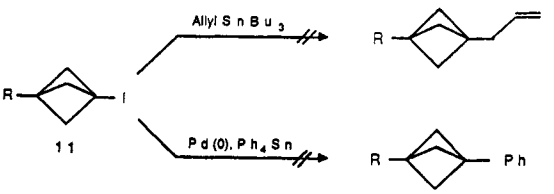
Anodic oxidation[50] of the acid **5c** in methanol gives only a small quantity of the expected diester **36** along with the reduced product **34** and other products, presumably rearranged, such as **13b**. No other solvent or solvent mixture was found to be superior or comparable to methanol in this reaction.



Unsuccessful Attempts To Form New C–C Bonds. Under conditions that were successful in the processes described so far, the attempted reaction of the bridgehead radical **11** (R = *n*-Bu) with *tert*-butyl isocyanide,[51] ethyl vinyl ether,[52] and cyclohexene failed to give the expected products **37**, **38**, and **39**. The iodides **3** were also found



to be unreactive with allyltri-*n*-butyltin under conditions reported in the literature.[53] Their coupling with tetraphenyltin catalyzed by tetrakis(triphenylphosphine)palladium(0)[54] failed as well, and the iodide was destroyed under the reaction conditions.



The carboxylic acid **5c** failed to displace the nitro group in *p*-dinitrobenzene and *p*-nitrobenzonitrile by an ipso substitution process.[32] It also failed in an attempted reaction with benzothiazole,[33] and no tractable product was obtained.

(47) The assignment is based on the assumption that the bridge methylene hydrogens in ortho-substituted products are shifted downfield relative to the meta and para isomers.
(48) Cowley, B. R.; Norman, R. O. C.; Waters, W. A. *J. Chem. Soc.* **1959**, 1799.
(49) Oldham, P. H.; Williams, G. H.; Wilson, B. A. *J. Chem. Soc. C* **1971**, 1094.
(50) Stork, G.; Meisels, A.; Davies, J. E. *J. Am. Chem. Soc.* **1963**, *85*, 3419.
(51) Stork, G.; Sher, P. M. *J. Am. Chem. Soc.* **1986**, *108*, 302.
(52) Giese, B.; Horler, H.; Leising, M. *Chem. Ber.* **1986**, *119*, 444.
(53) Keck, G. E.; Yates, J. B. *J. Am. Chem. Soc.* **1982**, *104*, 5829; *J. Organomet. Chem.* **1983**, *248*, C21.
(54) Stille, J. K. *Pure Appl. Chem.* **1985**, *57*, 1771 and references cited therein.

The experiments summarized in Schemes II and IV and in Tables I–IV, as well as those to be reported elsewhere,[3] suggest a pictorial representation of the synthetic utility of the bridgehead radicals **11** under conditions employed here, compared with typical aliphatic radicals (Scheme V). While most aliphatic radicals generated by a stannyl radical from the corresponding halides yield products with the electron-rich centers found in isocyanides, tri-*n*-butylallyltin, and the more electrophilic styrenes and Michael acceptors, the bicyclo[1.1.1]pent-1-yl radicals **11** yield products with electron-deficient centers such as Michael acceptors and carbonyl groups. Styrenes represent a borderline case. A quantitative study of the reaction rates is needed and would provide a better understanding of the reactivity of the bicyclo[1.1.1]pent-1-yl radical.

In summary, an initial survey of the generation and reactivity of the bridgehead radical **11** has been provided. It has been demonstrated that a large structural variety of 1,3-disubstituted bicyclo[1.1.1]pentanes is accessible via the bridgehead halides, which in turn are readily available from the addition of [1.1.1]propellane across carbon–halogen bonds. Also, it has been demonstrated that the bridgehead acids serve as precursors for the introduction of heteroatoms, and aromatic and heteroaromatic systems into the bridgehead position and thus are complementary to the bridgehead halides, but provide low yields. The methodology developed here for bicyclo[1.1.1]pentanes was successfully used in the synthesis of higher members of the $3^{(n-1)}$-butyl- and $3^{(n-1)}$-phenyl[*n*]staffane-3-carboxylic[55] acid series,[3] and it is expected that the reactions described herein will generally be useful also in other transformations of bridgehead functional groups in the higher [*n*]staffanes.

Experimental Section

Boiling points are uncorrected. Melting points were determined on a Boetius PHMK05 apparatus with microscope attachment (4 °C/min). ^{1}H and ^{13}C NMR spectra were run at 360 and 90 MHz, respectively, in $CDCl_3$ unless specified otherwise. Infrared spectra were recorded in $CHCl_3$ unless specified otherwise. Specific optical rotations were measured in $CHCl_3$. GC analysis and separations were done on SE-30 (20% on Chromosorb) 6-ft columns.

All operations and reactions involving [1.1.1]propellane were performed under an atmosphere of dry argon. Photochemical reactions were carried out in Pyrex vessels at ice-bath temperature, using a 450-W medium-pressure Hanovia mercury lamp.

[1.1.1]Propellane (2). Solutions of **2** in diethyl ether (3%) were prepared[3,11] from 1,1-bis(chloromethyl)-2,2-dibromocyclopropane[3,56] (**6**) and used without further purification or separation in subsequent transformations.

Alkyl Halides 4. Alkyl bromides were purchased and used without further purification. Alkyl iodides that were not available commercially (**4e** and **4f**) were prepared from the corresponding commercial bromides by halogen exchange[57] and used for subsequent transformations without isolation and characterization.

6-Deoxy-6-iodotetra-*O*-acetyl-β-D-glucopyranose (4g) was prepared according to literature:[58] mp 145 °C; $[\alpha]^{23}_D$ = +8.8° (*c* = 3.68) [lit.[58] mp 148 °C, $[\alpha]^{25}_D$ = +9.5° (*c* =1.15)]; ^{1}H NMR δ 2.00 (s, 3 H), 2.02 (s, 3 H), 2.05 (s, 3 H), 2.12 (s, 3 H), 3.13–3.18 (m, 1 H), 3.30–3.34 (m, 1 H), 3.53–3.59 (m, 1 H), 4.98 (t, *J* = 9.4 Hz, 1 H), 5.12 (t, *J* = 8.8 Hz, 1 H), 5.25 (t, *J* = 9.3 Hz, 1 H), 5.74 (d, *J* = 8.3 Hz, 1 H); ^{13}C NMR δ 2.21, 20.47, 20.60, 20.72, 70.45, 72.06, 72.52, 73.59, 91.51, 168.77, 169.07, 169.22, 169.96; EIMS *m/z* 399 (M – AcO, 4), 331 (M – I, 98), 169 (36), 157 (73), 115 (57), 43 (100).

Preparation of the Bridgehead Halides 3. The alkyl halide **4** was mixed with a [1.1.1]propellane solution (see above) under an argon atmosphere. The solution was kept in an ice bath and irradiated for 1 h (iodides) or 3 h (bromides). The solvents were evaporated, and the bridgehead halide product was used immediately for the next step.

Reaction of [1.1.1]Propellane with Allyl Bromide. The propellane derived from 0.10 mol of **6** (see above) was mixed with allyl bromide (18.2 g, 0.15 mol) under argon in a Pyrex vessel. The mixture was irradiated for 8 h. After evaporation of the solvents, the crystalline residue was crystallized from heptane to give 3,3′-dibromo[2]staffane[1,3] ([2]**3h**, 1.63 g, mp >175 dec, 11% yield based on **6**).

[2]Staffane ([2]1).[15,38] A mixture of 3,3′-dibromo[2]staffane ([2]**3h**, 1.61 g, 5.5 mmol), tri-*n*-butyltin hydride (4.5 mL, 15 mmol), and azobisisobutyronitrile (AIBN, 20 mg) was stirred without solvent under an atmosphere of argon at 80 °C overnight. The reaction mixture was distilled on Kugelrohr apparatus (95 °C (35 mmHg)), and the hydrocarbon (0.61 g, 83% yield) was collected in an ice-cooled bulb as a colorless semicrystalline liquid: ^{1}H NMR δ 1.61 (s, 12 H), 2.36 (s, 2 H) [lit.[38] δ 1.61 (s, 12 H), 2.36 (s, 2 H)]; EIMS *m/z* 133 (M – 1, 0.2), 131 (M – 2, 0.2), 105 (10), 91 (100), 79 (33), 77 (82), 65 (33), 51 (31).

Reaction of [1.1.1]Propellane with Allyl Iodide. The propellane derived from 10 mmol of **6** (see above) was mixed with allyl iodide (2.52 g, 15 mmol) under argon in a Pyrex vessel. The mixture was irradiated for 1 h. After evaporation of the solvents, the semicrystalline residue was crystallized from heptane, giving 1,3-diiodobicyclo[1.1.1]pentane[3,6–8] (**3i**, 0.32 g, 10% yield based on **6**).

2-Methylene-5-oxaspiro[4.3]octan-6-one (13a). 3-Iodopropionic acid (7.0 g, 35 mmol) and 3% ethereal propellane prepared from 35 mmol of **6** were irradiated for 1 h. The solvent was evaporated, and the resulting crystalline residue was refluxed overnight in triethylamine (30 mL) and chloroform (30 mL) with a catalytic amount of $ZnBr_2$. The reaction mixture was diluted with water, extracted with ether, and dried ($MgSO_4$), and the crude product (2.1 g) was distilled (53–54 °C (0.06 mm Hg)) to give 1.50 g (31% yield based on **6**) of a colorless oil: ^{1}H NMR δ 2.27 (t, *J* = 7.9 Hz, 2 H), 2.51 (t, *J* = 7.9 Hz, 2 H), 2.76 (d of quintets, J_1 = 14.26 Hz, J_2 = 2.1 Hz, 2 H), 3.15 (d of quintets, J_1 = 12.9 Hz, J_2 = 2.2 Hz, 2 H), 4.92 (quintet, *J* = 2.4 Hz, 2 H); ^{13}C NMR δ 28.73, 33.04, 44.51, 81.27, 108.66, 137.50, 176.05; IR (neat) 3078 (=CH_2), 1778 (C=O), 1685 (C=C), 1155 (C–O) cm^{-1}; EIMS *m/z* 138 (M, 0.7), 98 (7), 82 (22), 67 (13), 56 (31), 55 (100), 54 (60), 42 (54). Anal. Calcd for $C_8H_{10}O_2$: C, 69.54; H, 7.30. Found: C, 69.44; H, 7.27.

Bicyclo[1.1.1]pentane-1-acetic Acid (14a). Crude methyl 3-bromobicyclo[1.1.1]pentane-1-acetate, prepared from methyl bromoacetate (8.0 g, 52 mmol) and the propellane derived from 50 mmol of **6** as described above, was refluxed under argon with tri-*n*-butyltin hydride (15 mL) and AIBN (50 mg) in dry benzene (30 mL) for 2 h. Excess tin hydride was destroyed by addition of CCl_4 (5 mL) and 30-min reflux. The reaction mixture was hydrolyzed with 10% sodium hydroxide in methanol (50 mL). After the reaction mixture was refluxed for 30 min most of the methanol was evaporated, water (20 mL) was added, and the mixture was extracted with ether. The aqueous phase was acidified with hydrochloric acid and then extracted three times with ether. After drying (Na_2SO_4) and evaporation of the solvent, fractional distillation (54–55 °C (0.15 mmHg)) gave 2.90 g (46% yield based on **6**) of the acid: ^{1}H NMR δ 1.82 (s, 6 H), 2.49 (s, 1 H), 2.51 (s, 2 H); ^{13}C NMR δ 27.94, 38.16, 40.54, 51.20, 178.14; IR (neat) 1710 (C=O) cm^{-1}; EIMS *m/z* 125 (M – 1, 2), 111 (21), 84 (24), 81 (72), 80 (40), 79 (100), 69 (55), 67 (72), 65 (31), 55 (33), 53 (67), 45 (66), 43 (53); HRMS *m/z* (calcd for $C_7H_9O_2$ 125.0603) 125.0599. Anal. Calcd for $C_7H_{10}O_2$: C, 66.65; H, 7.99. Found: C, 66.63; H, 8.04.

Diethyl 2-(Bicyclo[1.1.1]pent-1-yl)propane-1,3-dioate (14b). The crude diethyl 3-bromobicyclo[1.1.1]pentane-1-malonate, prepared from diethyl bromomalonate (12.0 g, 50 mmol) and the propellane obtained from 50 mmol of **6** (see above), was reduced with Bu_3SnH as described above. Fractional distillation of the crude reaction mixture gave diethyl malonate (34–36 °C (0.2 mmHg); 2.87 g, 36 yield) and **14b** (60–70 °C (0.2 mmHg); 6.05 g) as a second fraction. The crude product was redistilled (58–59

(55) Position numbering in the individual bicyclo[1.1.1]pentane cages of an [*n*]staffane ([*n*]1) is distinguished by primes. A superscript in parentheses indicates the number of primes: $3'''' = 3^{(4)}$.

(56) Belzner, J.; Bunz, U.; Semmler, K.; Szeimies, G.; Opitz, K.; Schlüter, A.-D. *Chem. Ber.* **1989**, *122*, 397.

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°C (0.1 mmHg)) to give 4.75 g (42% yield based on **6**) of a colorless liquid: ^{1}H NMR δ 1.27 (t, J = 7.1 Hz, 6 H), 1.89 (s, 6 H), 2.51 (s, 1 H), 3.49 (s, 1 H), 4.19 (q, J = 7.1 Hz, 4 H); ^{13}C NMR δ 14.17, 28.07, 41.07, 41.66, 50.75, 54.25, 61.00, 167.57; IR (neat) 2981, 1740 (C=O) cm^{-1}; EIMS m/z 181 (M - OEt, 5), 153 (21), 125 (34), 107 (57), 81 (50), 79 (100), 77 (37), 67 (66); HRMS m/z (calcd for $C_{10}H_{13}O_3$ 181.0865) 181.0869. Anal. Calcd for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02. Found: C, 63.60; H, 8.03.

3-[2-(4-Chlorophenyl)ethyl]bicyclo[1.1.1]pentane-1-acetic Acid (15a). Crude ethyl 3-iodobicyclo[1.1.1]pentane-1-acetate, prepared from ethyl iodoacetate (2.14 g, 10 mmol) and the propellane derived from 10 mmol of **6** (see above), was refluxed under argon in dry benzene (4 mL) with 4-chlorostyrene (4.16 g, 30 mmol), Bu_3SnH (3.4 mL, 12 mmol), and AIBN (30 mg) for 1.5 h. After evaporation of the benzene, the mixture was passed through a silica gel column with hexanes as the eluent, followed by benzene. The crude product (2.3 g) was then hydrolyzed with 10% alcoholic KOH (10 mL), and the basic solution was extracted with ether. After acidification with HCl the acid was extracted with $CHCl_3$. The crude mixture of acids was then distilled on a Kugelrohr apparatus (60 °C (0.5 mmHg)) to give 0.27 g (21% yield based on **6**) of pure **14a**. The remaining solid product (1.15 g) was sublimed (130 °C (0.8 mmHg)) to give 0.81 g of material melting at 96–98 °C. This was then recrystallized from pentane at −78 °C to give 0.625 g (24% yield based on **6**) of the acid **15a**: mp 116–118 °C; ^{1}H NMR δ 1.65 (s, 6 H), 1.74–1.79 (m, 2 H), 2.41–2.54 (m with max 2.53, 4 H), 7.09 (d, J = 8.4 Hz, 2 H), 7.22 (d, J = 8.4 Hz, 2 H); ^{13}C NMR δ 32.32, 33.03, 35.32, 37.48, 40.09, 51.14, 128.32, 129.56, 131.35, 140.75, 177.96; IR 1714 (C=O) cm^{-1}; EIMS m/z 206 and 204 (M - MeCOOH, 1.5 and 5), 165 (8), 127 (33), 125 (100), 89 (21); HRMS m/z (calcd for $C_{15}H_{17}ClO_2$ 266.0888) 266.0907. Anal. Calcd for $C_{15}H_{17}ClO_2$: C, 68.05; H, 6.47; Cl, 13.39. Found: C, 67.96; H, 6.48; Cl, 13.33.

1-(2,2-Dichloroethyl)-3-pentylbicyclo[1.1.1]pentane (15b). The crude 1-iodo-3-pentylbicyclo[1.1.1]pentane, prepared from 1-iodopentane (20.0 g, 0.10 mol) and the propellane derived from 0.10 mol of **6** (see above), was refluxed under argon with vinylidene chloride (30 mL), Bu_3SnH (33 mL, 0.10 mol), dry benzene (4 mL), and AIBN (0.1 g) for 2 h. The reaction mixture was concentrated on a rotary evaporator, and the oily residue was distilled under vacuum to give 14.0 g of the major fraction (55–85 °C (0.2 mmHg)) of the crude product. Redistillation of the crude fraction (62–64 °C (0.1 mmHg)) gave 8.40 g (36% yield based on **6**) of colorless liquid: ^{1}H NMR δ 0.88 (t, J = 6.9 Hz, 3 H), 1.21–1.45 (m, 9 H), 1.61 (s, 6 H), 2.39 (d, J = 6.3 Hz, 2 H), 5.67 (t, J = 6.3 Hz, 1 H); ^{13}C NMR δ 14.03, 22.64, 26.25, 31.58, 32.00, 36.62, 41.06, 45.90, 51.25, 71.84; IR (neat) 2959 and 2924 (C-H stretch), 1260 cm^{-1}; EIMS m/z 167 (1), 165 (5), 163 (7), 127 (8), 95 (16), 91 (26), 81 (100), 79 (26), 67 (45), 55 (73). Anal. Calcd for $C_{12}H_{20}Cl_2$: C, 61.28; H, 8.57; Cl, 30.15. Found: C, 61.14; H, 8.50; Cl, 30.01.

2-[3-[2-(Methoxycarbonyl)ethyl]bicyclo[1.1.1]pent-1-yl]-butyrolactone (15c). The crude 2-(3-iodobicyclo[1.1.1]pent-1-yl)butyrolactone, prepared from 2-iodobutyrolactone[59] (obtained from 10 mmol of 2-bromobutyrolactone), and the propellane derived from 10 mmol of **6** (see above) were refluxed with methyl acrylate (3.0 mL, 33 mmol) and Bu_3SnH (3.0 mL, 11 mmol) in dry benzene (4 mL) under argon for 1 h. The reaction mixture was evaporated, and the oily residue was passed through a silica gel column. Hexanes followed by benzene were used to elute all tin compounds and side products. A mixture of ethyl acetate and hexanes (3:1) was then flashed through the column to give 1.3 g of crude product (75% pure by GC). The lactone was purified on a silica gel column (ethyl acetate and hexanes, 3:1) to give 0.93 g (39% yield based on **6**) of a colorless oil: ^{1}H NMR δ 1.61 and 1.67 (AB, dd, J_1 = 9.7 Hz, J_2 = 1.5 Hz, 6 H), 1.82 (t, J = 7.7 Hz, 2 H), 1.99–2.09 (m, 1 H), 2.27 (t, J = 7.7 Hz, 2 H), 2.26–2.35 (m, 1 H), 2.66 (dd, J_1 = 9.4 Hz, J_2 = 7.5 Hz, 1 H), 3.66 (s, 3 H), 4.17–4.29 (m, 2 H); ^{13}C NMR δ 25.89 (t), 26.61 (t), 31.02 (t), 37.67 (s), 39.34 (s), 40.36 (d), 48.95 (t), 51.33 (q), 66.33 (t), 173.61 (s), 176.87 (s); IR (neat) 2966, 1772 (C=O), 1738 (C=O), 1170 cm^{-1}; EIMS m/z 207 (M - MeO, 1), 160 (11), 119 (25), 105 (52), 93 (40), 91 (99), 86 (28), 79 (68), 77 (72), 67 (47), 65 (48), 59 (70), 55 (86), 53 (100), 51 (47); CIHRMS m/z (calcd for $C_{13}H_{19}O_4$ 239.1283) 239.1283. Anal. Calcd for $C_{13}H_{18}O_4$: C, 65.39; H, 7.60. Found: C, 65.54; H, 7.60.

1-Acetyl-3-pentylbicyclo[1.1.1]pentane (16). Method A. From Biacetyl. The crude 1-iodo-3-pentylbicyclo[1.1.1]pentane, prepared from 1-iodopentane (19.8 g, 0.10 mol) and the propellane derived from 0.10 mol of **6** (see above), was irradiated for 3 h in a Pyrex immersion photochemical apparatus under argon with biacetyl (15.0 mL), dry benzene (75 mL), and Bu_3SnH (35 mL). The mixture was fractionally distilled (58–63 °C (0.5 mmHg)) to give 8.0 g of 98% pure product. Redistillation (60–61 °C (0.5 mmHg)) gave 7.70 g (43% yield based on **6**) of pure ketone **16** as a colorless oil: ^{1}H NMR δ 0.85 (t, J = 6.8 Hz, 3 H), 1.21–1.27 (m, 6 H), 1.41 (t, J = 7.0 Hz, 2 H), 1.82 (s, 6 H), 2.07 (s, 3 H); ^{13}C NMR δ 13.91, 22.52, 25.90, 31.39, 31.88, 39.60, 44.41, 51.15, 206.66; IR (neat) 2965, 1925, 1706 (C=O), 1359 (COMe), 1171 (C—CO—C) cm^{-1}; EIMS m/z 137 (M - MeCO, 1), 123 (10), 81 (9), 55 (11), 43 (100); HRMS m/z (calcd for $C_{12}H_{20}O$ 180.1514) 180.1507. Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.77; H, 11.23.

Method B. From Pyruvonitrile. The crude 1-iodo-3-pentylbicyclo[1.1.1]pentane, prepared from 1-iodopentane (2.0 g, 10 mmol) and the propellane derived from 10 mmol of **6** (see above), was irradiated for 3 h in a Pyrex test tube under argon with pyruvonitrile (1.5 mL), dry benzene (5 mL), and Bu_3SnH (3.0 mL, 11 mmol). The reaction mixture was evaporated, and the oily residue was stirred with a mixture of 25% sodium fluoride (15 mL) and 3% methanolic NaOH (35 mL) for 1 h and poured into water. Organic products were extracted with hexanes, dried ($MgSO_4$), and concentrated. The oily residue was fractionally distilled (57–60 °C (0.5 mmHg)), giving 0.63 g (35% yield based on **6**) of the ketone.

2-(3-(Benzoylmethyl)bicyclo[1.1.1]pent-1-yl)-1,1,1-trifluoro-2-propanol (17a). The crude 2-(3-iodobicyclo[1.1.1]-pent-1-yl)acetophenone, prepared from phenacyl iodide[56] (obtained from 10 mmol of phenacyl bromide) and the propellane derived from 10 mmol of **6** (see above), was refluxed with 1,1,1-trifluoroacetone (2.24 g, 20 mmol) and Bu_3SnH (3.0 mL, 11 mmol) in dry benzene (5 mL) under argon for 1 h. The reaction mixture was evaporated, and the oily residue was passed through a silica gel column. Hexanes followed by benzene were used for elution of tin compounds and side products. A benzene–acetone (4:1) mixture was then used to elute 1.16 g (39% yield based on **6**) of yellowish oil: ^{1}H NMR δ 1.27 (s, 3 H), 1.81 and 1.84 (AB, J = 9.7 Hz, 6 H), 2.46 (s, 1 H), 3.17 (s, 2 H), 7.44–7.48 (m, 2 H), 7.54–7.56 (m, 1 H), 7.89–7.91 (m, 2 H); ^{13}C NMR δ 18.31, 34.79, 40.55, 42.26, 49.65, 71.57 (q, J_{CF} = 28.0 Hz), 126.05 (q, J_{CF} = 285.9 Hz), 128.27, 128.58, 133.19, 136.94, 198.51; ^{19}F NMR (CCl_3F) δ −80.0; IR (neat) 3456 (OH), 1673 (C=O), 1161 (CF_3) cm^{-1}; EIMS m/z 281 (0.1), 178 (1), 105 (100), 77 (55); CIMS m/z 300 (58), 299 (100), 281 (83), 279 (61), 179 (33), 106 (41), 105 (91); CIHRMS m/z (calcd for $C_{16}H_{18}F_3O_2$ 299.1259) 299.1261. (Dinitrophenyl)hydrazone: mp 175–6 °C; ^{1}H NMR δ 1.24 (s, 3 H), 1.83 and 1.84 (AB, d, J = 9.6 Hz, 6 H), 3.19 (s, 2 H), 7.45–7.51 (m, 3 H), 7.84–7.89 (m, 2 H), 8.15 (d, J = 9.5 Hz, 1 H), 8.37 (dd, J_1 = 9.5 Hz, J_2 = 2.3 Hz, 1 H), 9.17 (d, J = 2.4 Hz, 1 H), 11.53 (s, 1 H). Anal. Calcd for $C_{22}H_{21}F_3N_4O_5$: C, 55.23; H, 4.42; N, 11.71; F, 11.91. Found: C, 54.95; H, 4.41; N, 11.60; F, 11.81.

Methyl (2*SR*)-2-[3-(6-Deoxytetra-*O*-acetyl-β-D-glucopyranos-6-yl)bicyclo[1.1.1]pent-1-yl]-2-hydroxypropionate (17c). The crude 6-deoxy-6-(3-iodobicyclo[1.1.1]pent-1-yl)-tetra-*O*-acetyl-D-glucopyranose, prepared from iodo-D-glucopyranose[58] (1.38 g, 3 mmol) and the propellane derived from 6 mmol of **6** (see above), was mixed with methyl pyruvate (0.8 mL, 9 mmol), Bu_3SnH (0.9 mL, 3.3 mmol), dry benzene (5 mL), and irradiated for 3 h under an argon atmosphere. Then, pentane (25 mL) was added to the reaction vessel and the precipitated product was filtered off. The crude product was washed with 30% aqueous methanol (10 mL) and chromatographed on a silica gel column using benzene/acetone (4:1) as eluent to give 0.72 g (49% yield) of white powdery product: mp 171–2 °C; $[\alpha]^{25}_D$ = +6.3° (c = 1.95); ^{1}H NMR δ 1.283 and 1.285 (s, 3 H), 1.47–1.69 (m, 8 H), 1.95 (s, 3 H), 1.98 (s, 3 H), 1.99 (s, 3 H), 2.047 and 2.050 (s, 3 H), 2.918 and 2.922 (s, 1 H), 3.49–3.56 (m, 1 H), 3.74 (s, 3 H), 4.82 (t, J = 9.6 Hz, 1 H), 5.05 (t, J = 9.0 Hz, 1 H), 5.16 (t, J = 9.4 Hz, 1 H), 5.559 and 5.565 (d, J = 8.3 Hz, 1 H); ^{13}C NMR δ 20.45, 20.56, 20.63, 20.93, 32.55, 35.04, 44.09, 48.61, 52.24, 61.06, 70.49, 71.60, 73.04,

(59) Daremon, C.; Rambaud, R. *Bull. Soc. Chem. Fr.* **1971**, 294.

73.45, 91.74, 168.71, 169.13, 169.45, 169.99, 175.62; IR 1759 (C=O), 1254 cm^{-1}; CIMS m/z 483 (1), 442 (36), 441 (100); FABMS m/z 441 (100). Anal. Calcd for $C_{23}H_{32}O_{12}$: C, 55.19; H, 6.45. Found: C, 55.44; H, 6.49.

No attempt was made to separate the diastereoisomers.

[2]Staffane-3,3'-dipropionitrile ([2]19). A mixture of 3,3'-diiodo[2]staffane[5] ([2]**3i**, 0.39 g, 1 mmol), acrylonitrile (0.54 g, 10 mmol), dry benzene (8 mL), and Bu_3SnH (0.75 mL, 2.8 mmol) was irradiated through Pyrex with a medium-pressure mercury lamp for 8 h. The mixture was evaporated and passed through silica gel column using solvents in the following order: hexanes, benzene, benzene–ethyl acetate (3:1), and benzene–ethyl acetate (1:1). The crude product was recrystallized from heptane and sublimed (120 °C (0.6 mmHg)) to give 0.19 g of 96% pure product. One more recrystallization from heptane and sublimation gave 0.17 g (73% yield) of an analytical sample: mp 135–36 °C; ^{1}H NMR δ 1.53 (s, 12 H), 1.78 (t, J = 7.3 Hz, 4 H), 2.26 (t, J = 7.3 Hz, 4 H); ^{13}C NMR δ 14.38, 27.57, 37.40, 38.87, 48.83, 119.79; IR 2249 (CN) cm^{-1}; EIMS m/z 239 (M - 1, 1), 157 (10), 143 (29), 105 (100), 91 (79), 79 (52), 77 (46); HRMS m/e (calcd for $C_{16}H_{19}N_2$ 239. 1548) 239.1540. Anal. Calcd for $C_{16}H_{20}N_2$: C, 79.95; H, 8.39; N, 11.66. Found: C, 79.91; H, 8.42; N, 11.61.

Methyl 3-(Chlorocarbonyl)bicyclo[1.1.1]pentane-1-carboxylate (21). 3-(Methoxycarbonyl)bicyclo[1.1.1]pentane-1-carboxylic acid[11] (**5c**, 13.60 g, 80 mmol) and thionyl chloride (20 mL) were refluxed for 1.5 h. Excess thionyl chloride was evaporated, and the white crystalline residue was vacuum dried, giving 15.05 g (100% yield) of product with mp 90–91 °C. Vacuum sublimation (60 °C (0.1 mmHg)) gave an analytical sample: mp 90–91 °C; ^{1}H NMR (benzene-d_6) δ 1.97 (s, 6 H), 3.21 (s, 3 H); ^{13}C NMR (benzene-d_6) δ 37.07, 45.19, 51.32, 53.66, 168.04, 169.81; IR 1787 (C=O), 1730 (C=O) cm^{-1}; EIMS m/z 159 (M - MeO, 1.5), 157 (M - MeO, 4.5), 153 (M - Cl, 7), 125 (36), 66 (39), 65 (100), 59 (64); HRMS m/z (calcd for $C_7H_6ClO_2$ 157.0056) 157.0060. Anal. Calcd for $C_8H_9ClO_3$: C, 50.95; H, 4.81: Cl, 18.80. Found: C, 51.05; H, 4.84: Cl, 18.87.

***tert*-Butyl 3-(Methoxycarbonyl)bicyclo[1.1.1]pentane-1-peroxycarboxylate (23).** Crude vacuum dried chloride **21** (prepared from 510 mg, 3.0 mmol, of acid **5c**) was dissolved in dry THF (3 mL) and slowly added to a cold (0 °C) and stirred solution prepared from *tert*-butyl hydroperoxide (3.5 mmol, 1.15 mL of 3.0 M solution in 2,2,4-trimethylpentane), methyllithium (2.3 mL of 1.4 M solution in ether, 3.3 mmol), and dry THF (2 mL). The reaction mixture was stirred at room temperature for 1 h and filtered through silica gel, and the semicrystalline residue (0.68 g) was purified on silica gel column using pentane–methyl acetate mixture (3:1) as eluent. Crude product (0.60 g) was crystallized from pentane (-78 °C) to give 0.55 g (75% yield based on **5c**) of white cottonlike crystals: mp 41.5 °C; ^{1}H NMR δ 1.30 (s, 9 H), 2.36 (s, 6 H), 3.68 (s, 3 H); ^{13}C NMR δ 26.02, 35.65, 38.38, 51.85, 53.20, 83.84, 166.14, 169.08; IR 1765 (C=O), 1732 (C=O) cm^{-1}; EIMS m/z 153 (44), 125 (100), 97 (44), 93 (47), 79 (33), 73 (41), 65 (53), 59 (58), 57 (47), 43 (45). Anal. Calcd for $C_{12}H_{18}O_5$: C, 59.49; H, 7.49. Found: C, 59.50; H, 7.53.

General Procedure for Radical Decarboxylative Alkylation with 5c via the Barton Ester 22. The crude acid chloride **21** prepared as above from 5 mmol of the acid **5c** was dissolved in dry benzene (5 mL), and the dry sodium salt of 2-mercaptopyridine *N*-oxide (5.5 mmol, 0.82 g) was added. The reaction mixture was stirred in the dark for 2 h at 50 °C, and a dry trapping regent was added (25 mmol; acridine was added as a solution in 8 mL of dry benzene). The resulting mixture was stirred and irradiated for 1.5 h at 30 °C. The solvent was evaporated, and the residue was worked up as described for the individual products.

3-(Butylthio)bicyclo[1.1.1]pentane-1-carboxylic Acid (5d) via Methyl 3-(Acetylthio)bicyclo[1.1.1]pentane-1-carboxylate (25). The crude mixture obtained according to the general procedure was dissolved in glacial acetic acid (15 mL) and water (10 mL), and zinc dust (2.0 g) was added. The mixture was stirred at 30 °C for 3 h and washed with saturated sodium bicarbonate (200 mL), and the thioacetate **25** was extracted with hexanes. The extract was dried, the solvent was evaporated, and the residue was short path distilled (90 °C (0.5 mmHg)) to give 0.25 g (85% pure by GC) of ester **25** as a yellowish oil: ^{1}H NMR δ (major peaks) 2.22 (s, 3 H), 2.37 (s, 6 H), 3.62 (s, 3 H); ^{13}C NMR δ (major peaks) 31.05, 38.66, 41.22, 51.66, 55.27, 168.36, 195.49; EIMS m/z 169 (M - OMe, 1), 143 (3), 99 (7), 65 (4), 59 (8), 58 (8), 43 (100).

The crude thioester **25** (0.25 g) was stirred for 15 min with methanolic sodium hydroxide (0.2 g in 5 mL), and then butyl iodide (0.20 g) was added. The reaction mixture was stirred for 30 min at room temperature and then was refluxed for another 30 min. The solvent was evaporated, and the solution was extracted three times with methylene chloride. The aqueous phase was acidified with hydrochloric acid, chilled, and filtered to give 154 mg of crude carboxylic acid **5d**. The acid was distilled (90 °C (0.3 mmHg)) to give 145 mg (15% yield based on **5c**) of white waxy crystals of **5d**: mp 48–49 °C; ^{1}H NMR δ 0.90 (t, J = 7.3 Hz, 3 H), 1.33–1.43 (m, 2 H), 1.51–1.60 (m, 2 H), 2.21 (s, 6 H), 2.52 (t, J = 7.4 Hz, 2 H); ^{13}C NMR δ 13.59, 21.97, 30.68, 32.39, 38.75, 41.08, 54.76, 174.75; IR 1704 (C=O) cm^{-1}; EIMS m/z 155 (M - COOH, 5), 144 (16), 115 (17), 99 (100), 97 (20), 65 (27), 59 (43), 45 (46). Anal. Calcd for $C_{10}H_{16}O_2S$: C, 59.96; H, 8.05; S, 16.01. Found: C, 60.03; H, 8.16; S, 16.05.

Methyl 3-(Diethoxyphosphoryl)bicyclo[1.1.1]pentane-1-carboxylate (26). The crude product was purified on silica gel column using first ethyl acetate and then ethyl acetate–acetone mixture (2:1), and distilled on a Kugelrohr apparatus (110 °C (0.4 mmHg)) to give 367 mg (28% yield based on **5c**) of colorless oil: ^{1}H NMR δ 1.27 (t, J = 9.1 Hz, 6 H), 2.26 (s, 6 H), 3.63 (s, 3 H), 3.99–4.10 (m, 4 H); ^{13}C NMR δ 16.44 (d, J = 4.7 Hz), 32.44 (d, J = 165.1 Hz), 40.97 (d, J = 37.8 Hz), 51.62, 52.22, 61.85 (d, J = 5.7 Hz), 168.85 (d, J = 34.8 Hz); ^{31}P NMR (H_3PO_4) δ 18.1; IR (neat) 2983, 1727 (C=O), 1245, 1221, 1203, 1174, 1059, 1030, 966 cm^{-1}; EIMS m/z 263 (M + 1, 1), 261 (M - 1, 1), 234 (M - 28, 1.5), 203 (M - MeOCO, 18), 174 (47), 146 (58), 81 (45), 66 (35), 65 (100), 59 (30), 43 (33); HRMS m/z (calcd for $C_{11}H_{18}O_5P$ 261.0892) 261.0894. Anal. Calcd for $C_{11}H_{19}O_5P$: C, 50.08; H, 7.30; P, 11.81. Found: C, 50.08; H, 7.30; P, 11.64.

Methyl 3-(9-Acridanyl)bicyclo[1.1.1]pentane-1-carboxylate (24). The crude mixture was passed through an alumina column using a mixture of hexanes and ethyl acetate (5:1 ratio) as an eluent. The collected yellowish solid (0.40 g) was recrystallized from methanol and chloroform mixture to give 0.30 g (20% yield based on **5c**) of white crystals: mp 242–43 °C; ^{1}H NMR δ 1.69 (s, 6 H), 3.58 (s, 3 H), 3.97 (s, 1 H), 5.99 (s, 1 H), 6.70 (d, J = 7.9 Hz, 1 H), 6.88 (tm, J = 7.4 Hz, 1 H), 7.03 (d, J = 7.0 Hz, 1 H), 7.11 (tm, J = 7.7 Hz, 1 H); ^{13}C NMR δ 37.77, 43.92, 44.39, 49.63, 51.43, 113.36, 120.34, 120.41, 127.22, 129.05, 139.30, 170.75; IR 3431, 1722, 1609, 1584, 1482, 1336, 1303, 1204, 1176 cm^{-1}; EIMS m/z 305 (M, 3), 180 (100). Anal. Calcd for $C_{20}H_{19}NO_2$: C, 78.66; H, 6.27; N, 4.59. Found: C, 78.50; H, 6.30; N, 4.57.

Methyl 3-Acetylbicyclo[1.1.1]pentane-1-carboxylate (29). The crude reaction mixture was passed through silica gel column, initially using hexanes as an eluent. The product was eluted with hexanes/ethyl acetate (2:1) mixture, and sublimed (60 °C (25 mmHg)) to give 590 mg (70% yield based on **5c**) of white crystals: mp 57–58 °C; ^{1}H NMR δ 2.12 (s, 3 H), 2.27 (s, 6 H), 3.68 (s, 3 H); ^{13}C NMR δ 26.07, 37.01, 43.99, 51.71, 52.41, 169.79, 205.03; IR 1730 (C=O), 1703 (C=O), 1289 cm^{-1}; EIMS m/z 168 (M, 0.1), 136 (3), 108 (6), 65 (10), 59 (10), 43 (100); HRMS m/z (calcd for $C_9H_{12}O_3$ 168.0786) 168.0790. Anal. Calcd for $C_9H_{12}O_3$: C, 64.27; H, 7.19. Found: C, 64.09; H, 7.23.

Methyl 3-(2-Pyridylthio)bicyclo[1.1.1]pentane-1-carboxylate (30). A benzene solution of the crude acid chloride **21** prepared from 1.0 mmol of the acid **5c** was added at once to a stirred and refluxing suspension of dry sodium salt of 2-mercaptopyridine *N*-oxide (1.2 mmol, 180 mg) in benzene (1 mL). The mixture was stirred, heated, and irradiated for 1.5 h. Silica gel column separation of the reaction mixture using a benzene–ethyl acetate mixture (4:1) as an eluent gave methyl 3-phenylbicyclo[1.1.1]pentane-1-carboxylate (**31**, 20 mg, 10% yield based on **5c**) identified by comparison with the authentic sample.[3] Further elution gave the sulfide **30** (164 mg, 70% yield based on **5c**) as a colorless oily fraction: ^{1}H NMR δ 2.42 (s, 6 H), 3.65 (s, 3 H), 6.99–7.02 (m, 1 H), 7.19 (d, J = 8.0 Hz, 1 H), 7.47 (td, J_1 = 7.7 Hz, J_2 = 1.9 Hz, 1 H), 8.41–8.43 (m, 1 H); ^{13}C NMR δ 40.31, 40.59, 51.69, 55.56, 120.31, 124.10, 136.00, 149.60, 158.34, 168.86; IR (neat) 1733 (C=O), 1577, 1325, 1208 cm^{-1}; EIMS m/z 234 (M - 1, 33), 150 (51), 78 (50), 67 (68), 51 (46); HRMS m/z (calcd for $C_{12}H_{12}NO_2S$ 234.0589) 234.0586. Anal. Calcd for $C_{12}H_{13}NO_2S$: C, 61.25; H, 5.57; N, 5.95; S, 13.63. Found: C, 60.97; H, 5.60; N, 5.92; S, 13.48. The reaction performed at 30 °C under otherwise

the same conditions gave 53% yield of the sulfide **30** and 2% yield of the ester **31**.

Thermal Decomposition of Neat Peroxy Ester 23. The ester **23** (59 mg) was pyrolyzed at 130 °C for 3 h. The yellow viscous residue was washed with hot chloroform and analyzed by NMR and GCMS. The analysis showed, by comparison with an authentic sample,[3] that methyl bicyclo[1.1.1]pentane-1-carboxylate (**34**) was the major product. Methyl 3-*tert*-butoxybicyclo-[1.1.1]pentane-1-carboxylate (**33**, about 30% of the major product), acetone, and *tert*-butyl alcohol were also present in the mixture. Preparative GC allowed us to collect 8 mg (26% yield) of ester **34** and 4 mg (8% yield) of the *tert*-butyl ether **33**: ^{1}H NMR δ 1.26 (s, 9 H), 2.28 (s, 6 H), 3.67 (s, 3 H); ^{13}C NMR δ 29.16, 32.72, 51.74, 56.79, 63.67, 75.92, 170.51; IR (neat) 2982, 1735 (C=O), 1347, 1200, 1070 cm^{-1}; EIMS *m/z* 167 (M - OMe, 1), 110 (17), 82 (10), 68 (25), 57 (100), 41 (62). Anal. Calcd for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15. Found: C, 66.68; H, 9.12.

3-(2,5-Dichlorophenyl)bicyclo[1.1.1]pentane-1-carboxylic Acid (5f). The peroxy ester **23** (0.72 g, 3 mmol) and 1,4-dichlorobenzene (3.0 g, 20 mmol) were heated and stirred at 130 °C for 4 h. Excess dichlorobenzene was distilled off (65 °C (25 mmHg)), followed by *tert*-butyl ether **33** (50 mg, 7% yield, 75 °C (0.5 mmHg)). The residue (0.4 g) was boiled in 10% methanolic KOH (5 mL), evaporated to dryness, dissolved in water, washed with methylene chloride, and acidified with HCl. The product was extracted with methylene chloride, dried over sodium sulfate, and evaporated, and the residue was sublimed (115 °C (0.5 mmHg)) to give 120 mg of crude product. The acid was recrystallized from hexanes to give 100 mg (13% yield based on **23**) of white crystals: mp 135-36 °C; ^{1}H NMR 2.53 (s, 6 H), 7.12 (d, J = 2.3 Hz, 1 H), 7.18 (d, J = 2.3 Hz, 1 H), 7.22 (s, 1 H), 8.5 (br s, 1 H); ^{13}C NMR δ 38.14, 41.70, 53.30, 128.57, 129.12, 131.14, 132.21, 132.51, 137.80, 175.63; IR 2610, 1703 (C=O), 1463, 1096 cm^{-1}; EIMS *m/z* 223 and 221 (M - Cl, 0.9 and 2.3), 211 (M - COOH, 4.7), 177 (35), 175 (24), 142 (100), 141 (72), 136 (30), 99 (37), 75 (44), 74 (39), 63 (32), 51 (44), 45 (57). Anal. Calcd for $C_{12}H_{10}Cl_2O_2$: C, 56.05; H, 3.92; Cl, 27.58. Found: C, 56.01; H, 3.96; Cl, 27.52.

The peroxy ester **23** was also pyrolyzed in the presence of other derivatives of benzene. The mixtures of the regioisomers were collected by preparative GC and analyzed by GC-MS and ^{1}H NMR (Table IV).

Chlorobenzene adducts **32a**: GC EIMS *m/z* 221 (M - Me, 3), 201 (4), 179 (M - COOMe, 11), 177 (M - COOMe, 33), 142 (100), 141 (78), 115 (38), 101 (36), 75 (44), 63 (28), 59 (52), 51 (44).

Benzonitrile adducts **32b**: GC EIMS (t_R = 8.9 min, 53%) *m/z* 226 (M - 1, 1), 195 (31), 168 (54), 167 (100), 166 (92), 140 (32), 128 (25), 101 (30), 75 (42), 63 (38), 59 (37), 51 (72), 50 (43); (t_R = 9.1 min, 13%) *m/z* 226 (M - 1, 3), 168 (100), 167 (39), 166 (38), 153 (35), 141 (30), 140 (31), 128 (24), 101 (23), 77 (32), 75 (33), 63 (32), 59 (60), 51 (64), 50 (36); (t_R = 9.2 min, 34%) *m/z* 226 (M - 1, 1), 168 (100), 167 (36), 166 (32), 153 (35), 140 (25), 101 (24), 75 (28), 63 (29), 59 (59), 51 (45), 50 (31).

Methyl benzoate adducts **32c**: GC EIMS (t_R = 9.8 min, 44%) *m/z* 245 (M - Me, 1), 229 (M - OMe, 4), 201 (M - COOMe, 13), 169 (36), 168 (50), 142 (42), 141 (100), 129 (41), 115 (67), 77 (30), 76 (30), 63 (32), 59 (76), 51 (45); (t_R = 10.1 min, 15%) *m/z* 245 (M - Me, 1), 228 (4, M - OMe), 201 (M - COOMe, 17), 169 (25), 142 (47), 141 (60), 115 (40), 59 (100); (t_R = 10.3 min, 41%) *m/z* 245 (M - Me, 1), 229 (M - OMe, 4), 201 (M - COOMe, 18), 169 (21), 157 (17), 142 (54), 141, (42), 115 (33), 59 (100), 51 (22).

Methyl 3-(1,4-Benzoquinonyl)bicyclo[1.1.1]pentane-1-carboxylate (35). To a stirred and warm (70 °C) solution of acid **5c** (340 mg, 2 mmol), benzoquinone (230 mg, 2 mmol), and silver nitrate (10 mg) in water (4 mL) was added ammonium persulfate (500 mg) in water (1 mL) within 45 min. The mixture was stirred and heated for another 15 min and cooled down, and the organic products were extracted with methylene chloride. The extract was dried and evaporated, and the dark residue was passed through a silica gel column (benzene-ethyl acetate, 2:1 mixture). The yellow fraction containing the product and some benzoquinone was sublimed. After the removal of benzoquinone, 36 mg (8% yield based on **5c**) of the product was collected (95 °C (0.4 mmHg)): mp 141-42 °C; ^{1}H NMR δ 2.34 (s, 6 H), 3.67 (s, 3 H), 6.46 (d, J = 2.1 Hz, 1 H), 6.67-6.70 (m, 2 H); ^{13}C NMR δ 38.72, 38.77, 51.73, 53.52, 132.25, 136.34, 136.90, 145.20, 169.66, 187.05, 187.31; IR 1728 (C=O), 1661 (C=O) cm^{-1}; EIMS *m/z* 232 (M, 6), 217 (M - Me, 11), 201 (M - OMe, 22), 200 (22), 173 (43), 172 (100), 116 (37), 115 (73), 91 (31), 65 (30), 54 (58). Anal. Calcd for $C_{13}H_{12}O_4$: C, 67.23; H, 5.21. Found: C, 67.11; H, 5.24.

Electrolysis of the Acid 5c. A solution of acid **5c** (340 mg, 2 mmol) in a mixture of methanol (10 mL) containing sodium carbonate (15 mg) was electrolyzed using platinum electrodes (8 × 8 mm, 3 mm distance; 40 V, 60 mA) for 8 h at 55 °C. The solvent was evaporated, and the products were separated on preparative GC to yield 13 mg of methyl bicyclo[1.1.1]pentane-1-carboxylate (**34**) and 10 mg (4% yield) of the dimerization product, the diester **36**. These products were identified by comparison with the authentic samples.[3] There was also isolated an intermediate fraction (67 mg) containing three products. The ^{1}H NMR spectra of this mixture showed olefinic protons at 4.85-4.95 and 5.45-5.50 ppm.

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New Reagents for the Synthesis of *gem*-Halonitro Compounds from Oximes

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The utility of the *N*-haloheterocycles 1-sodio-3,5-dichloro-1,3,5-triazine-2,4,6(1*H*,3*H*,5*H*)-trione (**4**), 1,3,5-trichloro-1,3,5-triazine-2,4,6(1*H*,3*H*,5*H*)-trione (**5**), 1,3-dibromo-1,3,5-triazine-2,4,6(1*H*,3*H*,5*H*)-trione (**6**), and 1,3-dibromo-5,5-dimethylhydantoin (**7**) for the halogenation-oxidation of oximes to *gem*-halonitro compounds is reported. The triazine derivatives **4**, **5**, and **6** provided satisfactory yields when employed either alone or in combination with ozone as a supplemental oxidant. Hydantoin **7** required the use of a supplemental oxidant. The yields for the reactions were consistently 70% for simple oximes and 50% for molecules possessing two oxime functions. Occasional difficulties were encountered in reproducing the yields of the products from the bromination-oxidation sequence. The formation of modest amounts (20-30%) of 3,7-dinitronoradamantane via cyclization was observed in the reactions of bicyclo[3.3.1]nonane-3,7-dione dioxime.

gem-Halonitro compounds **1** and **2** have proven to be versatile intermediates in the synthesis of molecules possessing one or more nitro groups. They have been prepared traditionally by either the direct halogenation of nitronate

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