Synthesis of Some Bridgehead-Bridgehead-Disubstituted Bicyclo[1.1.1]pentanes

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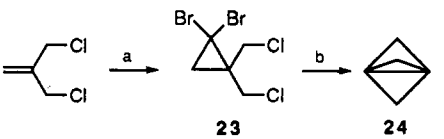
The synthesis of a wide variety of 1,3-disubstituted bicyclo[1.1.1]pentanes is described, with particular emphasis on the generation of a series of 3-X-substituted bicyclo[1.1.1]pentyl bromides required for solvolytic studies. Functional group manipulation at the bridgehead was readily accomplished in the majority of cases by radical processes; in some instances, transformations were effected via carbanionic-type intermediates.

We recently embarked on an investigation of the solvolytic behavior of the range of 3-X-substituted bicyclo-[1.1.1]pentyl bromides **1–22** as part of an experimental probe into the existence of the 1-bicyclo[1.1.1]pentyl cation as the primary intermediate in the ionization of these systems. The results of the solvolytic study were disclosed in a recent paper.[1] This contribution describes the synthesis of the bromides **1–17** as well as some rather novel transformations which occurred during attempted synthesis of the remaining substrates **18–22**.

1: X = H
2: X = $COOCH_3$
3: X = CH_2OH
4: X = CH_2OTs
5: X = CH_2Cl
6: X = CH_2OAc
7: X = CO_2^-
8: X = $COCH_3$
9: X = $OCOCH_3$
10: X = Cl
11: X = CH_3
12: X = CN
13: X = Ph
14: X = p-$O_2NC_6H_4$
15: X = Bu^t
16: X = p-$MeOC_6H_4$
17: X = Br
18: X = F
19: X = OMe
20: X = Me_3Si
21: X = Me_3Sn
22: X = PhSe

Until recently, the only viable synthetic entry into bridgehead-disubstituted bicyclo[1.1.1]pentanes in reasonable quantity was that reported 12 years ago by Applequist and co-workers.[2] While it fulfilled an important need, this route suffered from the combined disadvantage of being low-yielding and labor-intensive, and it has now been replaced by a procedure developed principally by Michl and his colleagues[3] and also by Wiberg and co-workers.[4] The more recent method, which is both efficient and rapid, is based on the discovery[3,4] that under photochemical irradiation, a variety of reagents can be induced to add to [1.1.1]propellane (**24**). Thus the considerable number of bridgehead derivatives that have been produced by the Michl and Wiberg groups are derived entirely through radical-mediated processes. The incorporation of such processes in the projected synthesis of the bromides **1–22** was thought to be highly attractive because we have demonstrated previously[5] that 1-bicyclo-[1.1.1]pentyl radicals are kinetically very stable intermediates, whereas the corresponding cations rearrange essentially without activation.[6] In order to simplify the syntheses and to minimize the intervention of undesirable side reactions, insertion of bromine at the bridgehead was delayed as late as possible in the sequence and was to be accomplished by bromodecarboxylation of the Barton ester.[7]

Scheme 1[a]



23 **24**

[a] (a) $CHBr_3$/NaOH; (b) MeLi.

1,3-Dicarbomethoxybicyclo[1.1.1]pentane (**26**) was regarded as the key precursor to the target bromides. Michl[3a] has reported that **26** is readily accessible in three steps by radical addition of biacetyl to [1.1.1]propellane to give the diketone **25**, followed by oxidation of the latter with sodium hypobromite to the corresponding 1,3-diacid. [1.1.1]Propellane (**24**) has been shown by Szeimies[8a,b] to be conveniently prepared via a two-step procedure from commercially available 2-(chloromethyl)allyl chloride (Scheme 1). A disadvantage of this route, however, is the low yield of **23** produced in the dibromocarbene addition reaction, and in view of the quantities of material required one of the objectives we set ourselves was to improve the yield of the tetrahalide **23**. In practice, this was achieved by controlling the rate of the carbene addition to ensure that it occurred over a shorter period and by using excess bromoform in the absence of solvent. These modifications also facilitated the workup procedure, making it very much simpler. Subsequent conversion of the propellane into the diester **26** essentially followed the directions reported.[3a] In order to manipulate one of the ester functions independently of the other, **28** was converted into the half-ester **27** as described previously[9] or, better, by employing

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(1) Della, E. W.; Taylor, D. K. *J. Am. Chem. Soc.* Submitted.
(2) Applequist, D. E.; Renkin, T. L.; Wheeler, J. W. *J. Org. Chem.* **1982**, *47*, 4985.
(3) (a) Kaszynski, P.; Michl, J. *J. Org. Chem.* **1988**, *53*, 4593. (b) Kaszynski, P.; McMurdie, N. D.; Michl, J. *J. Org. Chem.* **1991**, *56*, 307. (c) Kaszynski, P.; Friedli, A. C.; Michl, J. *J. Am. Chem. Soc.* **1992**, *114*, 601.
(4) (a) Wiberg, K. B.; Waddell, S. T.; Laidig, K. E. *Tetrahedron Lett.* **1986**, *27*, 1553. (b) Wiberg, K. B.; Waddell, S. T. *J. Am. Chem. Soc.* **1990**, *112*, 2194.
(5) Della, E. W.; Schiesser, C. H.; Taylor, D. K.; Walton, J. C. *J. Chem. Soc., Perkin Trans. 2* **1991**, 1329.
(6) Della, E. W.; Schiesser, C. H. *J. Chem. Res., Suppl.* **1989**, 172. Wiberg, K. B.; Hadad, C. M.; Sieber, S.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1992**, *114*, 5820.
(7) Della, E. W.; Tsanaktsidis, J. *Aust. J. Chem.* **1989**, *42*, 61.
(8) (a) Semmler, K.; Szeimies, G.; Belzner, J. *J. Am. Chem. Soc.* **1985**, *101*, 6410. (b) Alber, F.; Szeimies, G. *Chem. Ber.* **1992**, *125*, 757. (c) Belzner, J.; Szeimies, G. *Tetrahedron Lett.* **1987**, *28*, 3099.
(9) Della, E. W.; Tsanaktsidis, J. *Aust. J. Chem.* **1986**, *39*, 2061.

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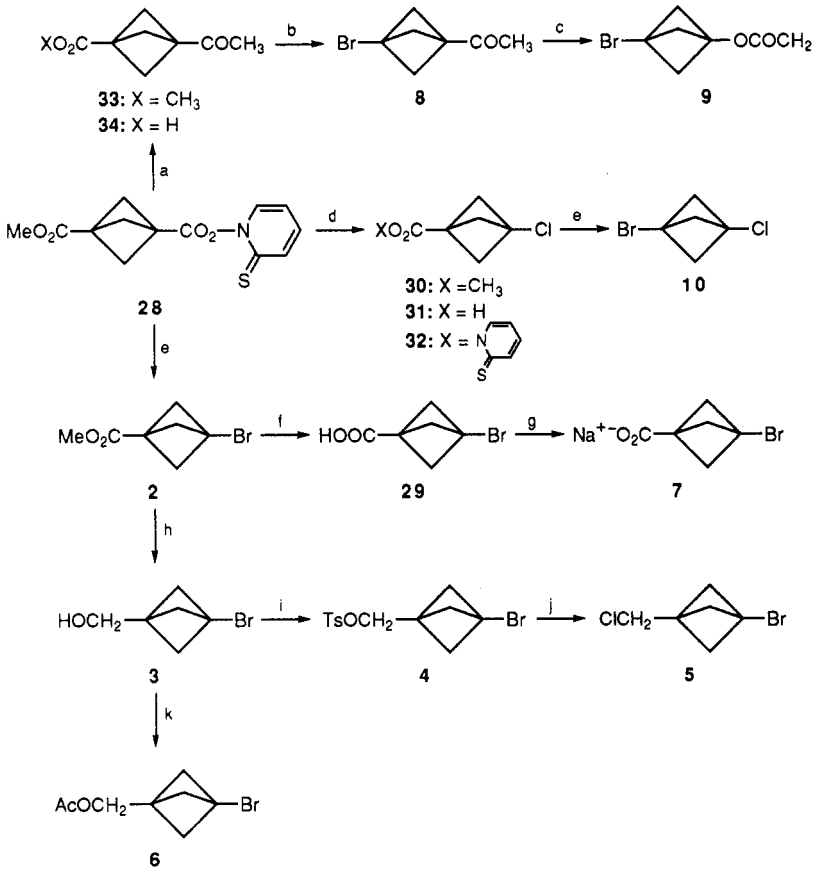
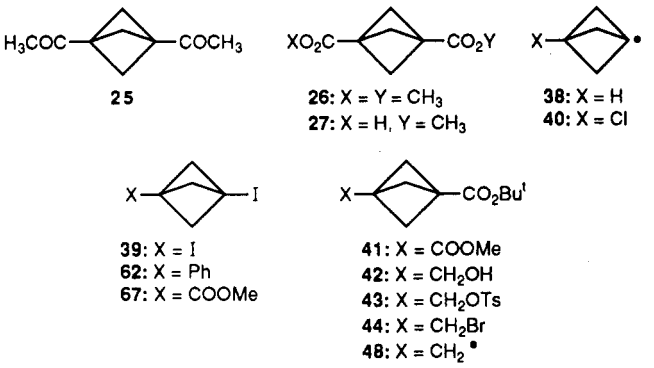
Scheme 2[a]



[a] (a) biacetyl, *hν*; (b) (i) *N*-hydroxypyridine-2-thione, DCC, (ii) $CF_3CHClBr$, *hν*; (c) *m*-CPBA; (d) (i) $CFCl_3$, *hν*; (ii) aqueous NaOH, (iii) *N*-hydroxypyridine-2-thione, DCC (e) $CF_3CHClBr$, *hν*; (f) H^+/THF; (g) NaH; (h) $LiAlH_4$; (i) TsCl, pyr.; (j) LiCl/THF; (k) AcCl, pyr.

the conditions for selective hydrolysis of cubane 1,4-diester devised by Eaton.[10]



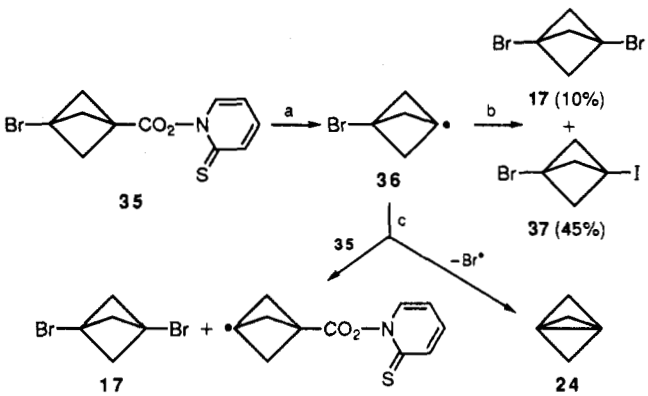
With reasonable quantities of the half-ester **27** now readily available, we turned our attention to the preparation of the first group of required substrates, **1–10**. These syntheses were achieved via the derived Barton ester **28**, which was obtained in near quantitative yield from reaction of half-ester **27** with *N*-hydroxypyridine-2-thione and dicyclohexylcarbodiimide in dichloromethane.[11] The thiohydroxamic ester **28** was found to be a stable yellow solid which could be stored in a refrigerator for several months if shielded from light. This versatile intermediate allowed easy access to 1-bromobicyclo[1.1.1]pentane (**1**),[12] and, as illustrated in Scheme 2, the bromo ester **2** as well as the chloro ester **30** by exposure to the appropriate reagent/solvent under photochemical irradiation. Synthesis of the keto ester **33** from **28** was achieved by using biacetyl as the source of the acetyl radical as described by Michl.[3b] After hydrolysis, the derived acid **34** was converted via its Barton ester into the bromo ketone **8**, Baeyer–Villiger oxidation of which gave the bromoacetate **9**.

Elaboration of the remaining compounds into the required bromides in Scheme 2 was performed by applying standard procedures and needs little comment apart from a precautionary note on the hydrolysis of the bromo ester **2** to the acid **29**. Acid-catalyzed hydrolysis is essential in this case because alkaline conditions lead predominantly to ring-opened material; as discussed in the solvolysis study,[1] the intermediate salt **7** generated in the alkaline medium solvolyzes with great rapidity, whereas its conjugate acid **29** ionizes several orders of magnitude slower. The salt **7** itself was obtained by vigorous stirring of an ethereal solution of **29** with NaH (0.9 equiv), and the precipitate was washed thoroughly with ether.

An interesting aspect of these transformations is that whereas the Barton chloro ester **32** is found to undergo bromodecarboxylation in $CF_3CHBrCl$ smoothly to afford the dihalide **10** in excellent yield, an attempt to insert the halogens in the reverse sense was unsuccessful. Conversion of the bromo acid **29** into the corresponding bromo ester **35** and irradiation of the latter in the chlorine atom donor/solvent CF_3CCl_3 gave 1,3-dibromobicyclo[1.1.1]pentane (**17**) only, and in lower yield (45%) (Scheme 3). The expected dihalide **10** was not detected, even in trace

(10) Eaton, P. E.; Xiong, Y.; Zhou, J. *J. Org. Chem.* **1992**, *57*, 4277.
(11) Barton, D. H. R.; Crich, D.; Motherwell, W. B. *Tetrahedron Lett.* **1983**, *24*, 4979. Barton, D. H. R.; Crich, D.; Motherwell, W. B. *Tetrahedron*, **1988**, *41*, 3901.
(12) Della, E. W.; Taylor, D. K. *Aust. J. Chem.* **1990**, *43*, 945.

Scheme 3[a]



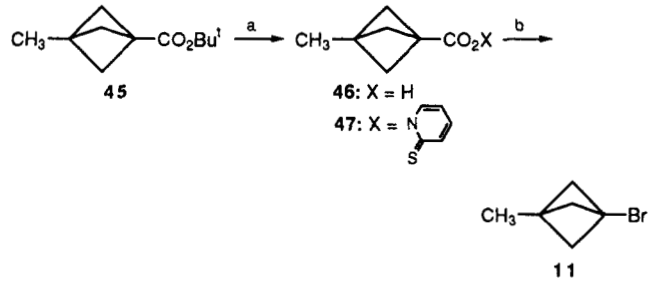
[a] (a) $h\nu$; (b) CF_3CH_2I, $h\nu$; (c) CF_3CCl_3, $h\nu$.

amounts; in fact, no other organic products were isolated. We suspect that the overall poor material balance is the result of a 1,3-elimination of bromine from the intermediate radical **36** to give [1.1.1]propellane, which exists as a gas under these conditions and escaped undetected from the warm reaction mixture. The dibromide presumably arises by extraction of a bromide atom from the ester **35** by the bicyclo[1.1.1]pentyl radical (**36**) as depicted in Scheme 3.

When the reaction was performed using CF_3CH_2I as solvent, the product consisted of a mixture of dibromide **17** (10% yield) and 3-iodobicyclo[1.1.1]pentyl bromide (**37**) (45% yield). Again, the remainder of the product was assumed to be [1.1.1]propellane. The formation of **37** reflects the more efficient halogen atom donor properties of trifluoroethyl iodide, which is capable of trapping some of the radical **36** before it decomposes. Production of propellane is a strong driving force for loss of a bromine atom from **36**, a process that is favored by the close proximity of the bridgehead carbons and the collinear disposition of the SOMO and the C–Br orbital. Strong through-space interactions of this kind were shown to occur by Walton[13] in an EPR study of the 1-bicyclo[1.1.1]pentyl radical (**38**), in which the H_γ hyperfine splitting was found to be 6.96 mT, one of the largest recorded. Michl[3b] has reported, and we ourselves have observed, that reduction of 1,3-diiodobicyclo[1.1.1]pentane (**39**) with Bu_3SnH occurs with explosive formation of [1.1.1]propellane, indicative of the leaving group ability of the iodine atom. As noted above, 1,3-elimination is not observed in the case of the chloro radical **40** and is presumably inhibited by the much higher bond strength of the C–Cl bond.

3-Methylbicyclo[1.1.1]pentyl bromide (**11**) was accessed from the half-ester **27** through the mixed diester **41** → alcohol **42** → tosylate **43** → bromide **44**, reduction of which gives the ester **45** presumably via the radical **48**. Conversion of *tert*-butyl 3-methylbicyclo[1.1.1]pentane-1-carboxylate (**45**) into the bromide **11** is outlined in Scheme 4. The half-ester **27** also provided ready access to the bicyclo[1.1.1]pentyl bromides **12**–**14** as illustrated in Scheme 5. Although dehydration of bicyclo[1.1.1]pentyl amides has been achieved quite successfully[14] using triflic anhydride,[15] it was found that in the route to the cyano bromide **12**, conversion of the amide **50** into the nitrile **51** could be effected in excellent yield (95%) by the use of the

Scheme 4[a]



[a] (a) (i) H^+, (ii) *N*-hydroxypyridine-2-thione, DCC; (b) $CF_3CHClBr$, $h\nu$.

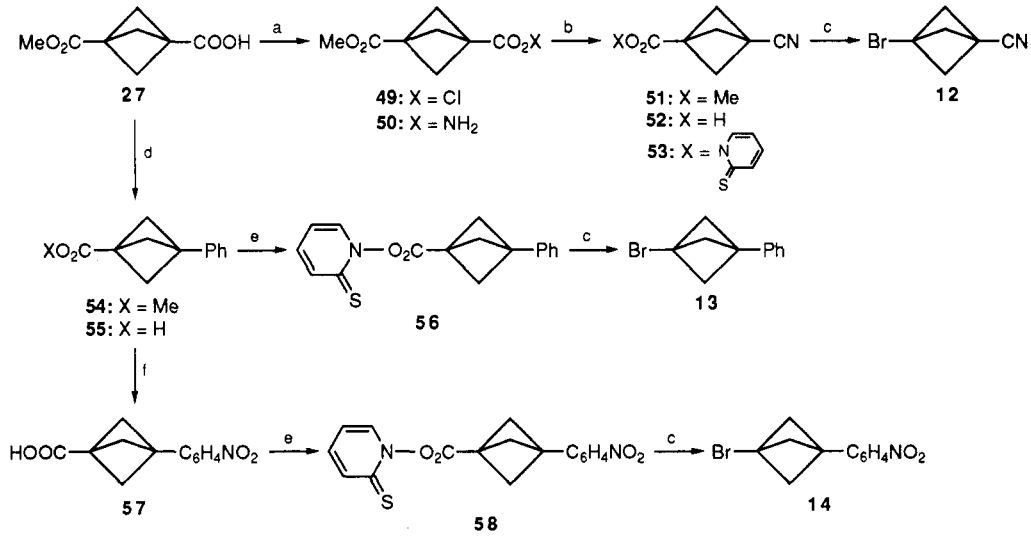
more economical reagent thionyl chloride.[16] Attention is drawn to the preparation of the ester **54** in which a phenyl group has replaced COOH at the bridgehead. This transformation was based on the method described recently by Moriarty[17] for the synthesis of 4-phenylcubyl esters, and is initiated by reaction of the half-ester **27** with lead tetraacetate to give the 3-carbomethoxybicyclo[1.1.1]-pentyl radical which reacts with benzene in an aromatic homolytic substitution process. It was found essential that thorough deoxygenation of the apparatus be performed prior to undertaking the reaction. If this precautionary measure is adopted, the yield of phenyl ester **54** is high, and the procedure represents a vastly improved one over that described[2] for the synthesis of **54**. Nitration of the derived acid **55** under standard conditions gave a 1:2 mixture if the *o*- and *p*-nitrophenyl derivatives which were separated by taking advantage of the much greater insolubility of the *para* isomer. Conversion of the aryl acids **55** and **57** into the corresponding bromides was accomplished successfully via their Barton esters.

[1.1.1]Propellane (**24**) was the precursor selected for the synthesis of the three bromides **15**–**17** as shown in Scheme 6. The route to the *tert*-butylated derivative **15** exploits the earlier observation[18] that *tert*-butyllithium adds to **24** to give (3-*tert*-butylbicyclo[1.1.1]pentyl)lithium (**59**), carbonation of which afforded the acid **60**. Conversion of the acid to the bromide was undertaken by Barton methodology. Production of **16** was based on the demonstration[3b,c,8c] that under photochemical irradiation, alkyl and aryl iodides can be induced to add across the 1,3-bond of **24**. During the course of this work, for example, Michl and his colleagues[3c] reported the preparation of the bromide **15** described above by this procedure. They also discovered that addition of iodobenzene gives 3-phenylbicyclo[1.1.1]pentyl iodide (**62**) in 40% yield. We find that use of *p*-iodoanisole affords a comparable yield of the adduct **63**, accompanied by what appeared to be oligomeric staffanes. The bulk of unreacted *p*-iodoanisole crystallized out when the product was triturated with cold ether, and the remainder of the product was treated with *tert*-butyllithium. Carbonation of the mixture and sublimation of the product yielded the target carboxylic acid **64**, which was converted into the bromide **16** under the standard Barton bromodecarboxylation procedure.

In view of the problems experienced above in preparing the symmetrical dibromide **17** from the ester **35** under

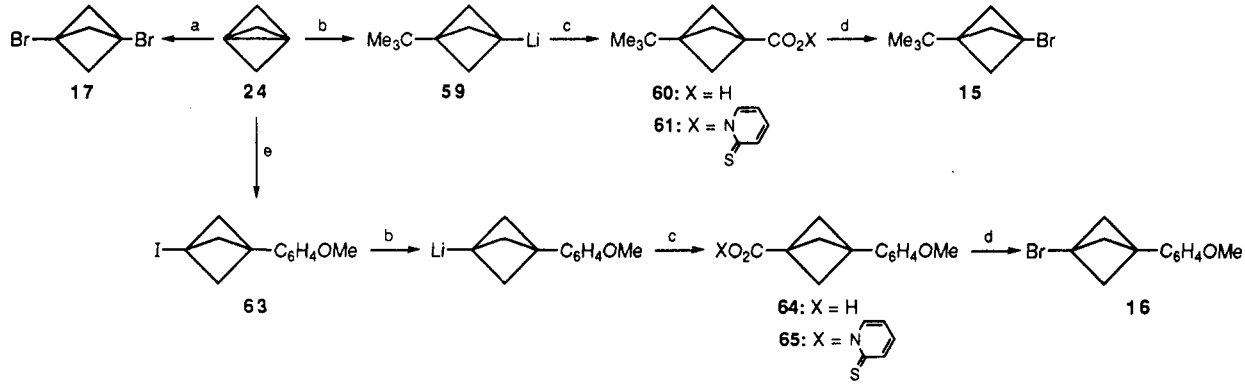
(13) Walton, J. C.; Maillard, B. *J. Chem. Soc., Chem. Commun.* **1983**, 901.
(14) Della, E. W.; Gangodawila, H. *Aust. J. Chem.* **1989**, *42*, 1485.
(15) Campagna, F.; Carotti, A.; Casini, G. *Tetrahedron Lett.* **1977**, 1813.
(16) March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley-Interscience: New York, 1985; p 933.
(17) Moriarty, R. M.; Khosrowshahi, J. S.; Miller, R. S.; Flippin-Andersen, J.; Gilardi, R. *J. Am. Chem. Soc.* **1989**, *111*, 8943.
(18) Della, E. W.; Taylor, D. K.; Tsanaktsidis, J. *Tetrahedron Lett.* **1990**, *36*, 5219.

Scheme 5[a]



[a] (a) (i) $SOCl_2$, (ii) NH_3; (b) (i) $SOCl_2$, (ii) aqueous NaOH, (iii) *N*-hydroxypyridine-2-thione, DCC; (c) $CF_3CHClBr$, *hν*; (d) (i) $Pb(OAc)_4$/benzene, *hν*, 80 °C, (ii) aqueous NaOH; (e) *N*-hydroxypyridine-2-thione, DCC; (f) HNO_3/H_2SO_4.

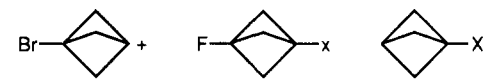
Scheme 6[a]



[a] (a) Br_2; (b) ^tBuLi; (c) (i) CO_2, (ii) H^+, (iii) *N*-hydroxypyridine-2-thione, DCC; (d) $CF_3CHClBr$, *hν*; (e) *p*-MeO-C_6H_4I.

Barton conditions (Scheme 3), we turned our attention to the possibility that **17** may be accessible by radical addition of bromide to [1.1.1]propellane (**24**) in the same way that good yields (65%) of 1,3-diiodobicyclo[1.1.1]pentane (**39**) are obtained from the analogous reaction of iodine.[3b,4b,8b] In agreement with the recent observation by Michl and his associates,[3c] however, the bromine/propellane reaction (Scheme 6) was found to be rather low-yielding. Although the proportion of dibromide could be increased by irradiating the reaction mixture during addition of bromide, the optimum yield of **17** obtained was 36%. These observations are a demonstration of the facility with which bromine and iodine participate in radical and ionic reactions. The poorer yield in the case of the bromination reaction is ascribed to the occurrence of an accompanying ionic process which competes effectively with radical bromination and gives the cation **66**. 1-Bicyclo[1.1.1]-pentyl cations are predicted by *ab initio* calculations to have an exceedingly short half-life[6] and the species **66** would be expected to ring-open before it had the opportunity to be trapped by bromide ion.

In summary, synthesis of the 3-X-substituted bicyclo-[1.1.1]pentyl bromides **1-17** can be accomplished by employing procedures which are seen to be readily performed and which generally afforded good yields. As illustrated in the various schemes, the making and breaking of bonds to the bridgehead position proceed quite successfully via homolytic reactions or by pathways mediated by bridgehead anions.

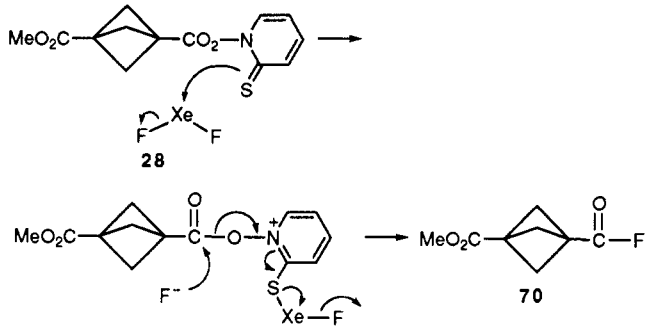


66 **68**: X = Ph, **69**: X = COOH **75**: X = Li, **76**: X = Me_3Si

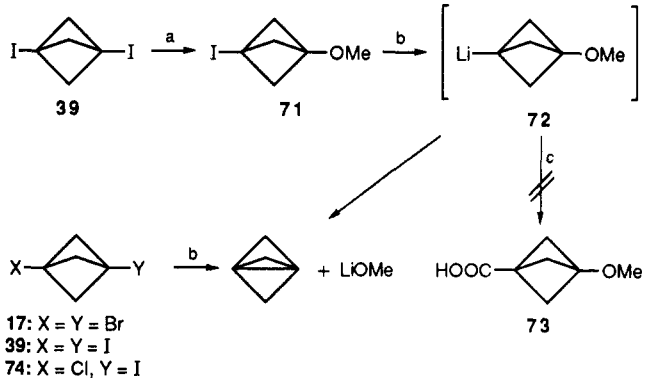
Our attempts to synthesize the bromides **18-22** met with failure and had to be abandoned. Several rather interesting observations were made during the course of the investigation, however. For example, where fluorodeiodination of bridgehead iodides with XeF_2 has been shown to be a general procedure for the introduction of fluorine at the bridgehead, it failed in the case of the iodoester **67**.[19] This was attributed to the intermediacy of a 1-bicyclo[1.1.1]pentyl cation which as mentioned above rearranges with little activation. So it was predictable that the reaction of xenon difluoride with 3-phenylbicyclo-[1.1.1]pentyl iodide (**62**) as attempted in this study would also lead to polymeric products; none of the fluoride **68** was isolated. It had been intended to oxidize the phenyl

(19) Della, E. W.; Head, N. J. *J. Org. Chem.* **1992**, *57*, 2850.

Scheme 7



Scheme 8[a]



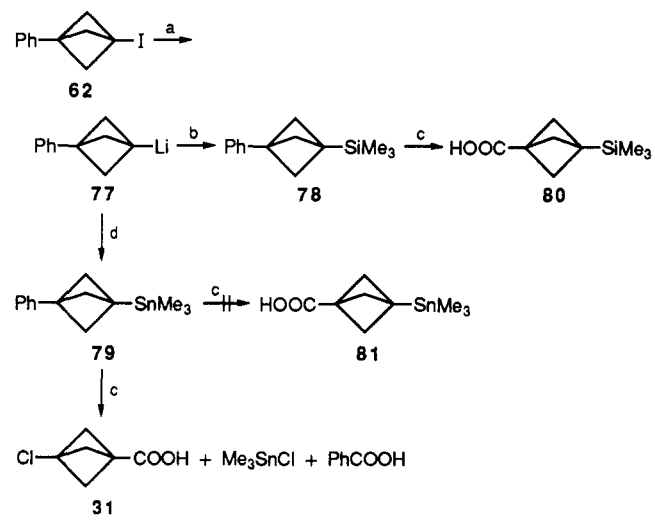
17: X = Y = Br
39: X = Y = I
74: X = Cl, Y = I

[a] (a) NaOH/MeOH; (b) ^{t}BuLi/ether, pentane; (c) (i) CO_2, (ii) H^+.

group in **68** with Ru(IV) to give the fluoro acid **69**, the precursor to the bromide **18**. Although this was a discouraging result, we felt that treatment of the Barton ester with XeF_2 held some promise as an alternate route. An instantaneous reaction occurred (either in the presence or absence of light) in which a gas was evolved and the characteristic color of the thiohydroxamic ester was discharged. The product of the reaction, identified as the acid fluoride **70**, was obtained in near quantitative yield. We suggest (Scheme 7) that formation of **70** is initiated by nucleophilic attack at XeF_2 to give the intermediate xenon ester which collapses under the influence of F^- as depicted or, alternatively, via a concerted process involving a seven-membered cyclic transition state. An analogous rearrangement has been proposed by Barton and coworkers[20] to account for the reaction between thiohydroxamic esters and activated azo compounds.

Since 3-bromobicyclo[1.1.1]pentyl methyl ether (**19**) was considered to be one of the more important substrates in the solvolysis study,[1] its synthesis was clearly of particular significance. Considering the facility with which cyclobutyloxide anions ring-open so rapidly, we wished to avoid synthetic pathways to **19** which involved the bicyclo[1.1.1]pentyloxy anion and therefore chose instead to follow the route depicted in Scheme 8. The key intermediate, 3-iodobicyclo[1.1.1]pentyl methyl ether (**71**), was prepared by reaction of 1,3-diiodobicyclo[1.1.1]pentane (**39**) with methanolic sodium hydroxide according to the procedure described by Wiberg.[21] Metalation of **71** with *tert*-butyllithium followed by treatment with CO_2 was attempted in the expectation that this would lead to the acid **73** and thence **19**. However, 3-*tert*-butylbicyclo[1.1.1]-

Scheme 9[a]



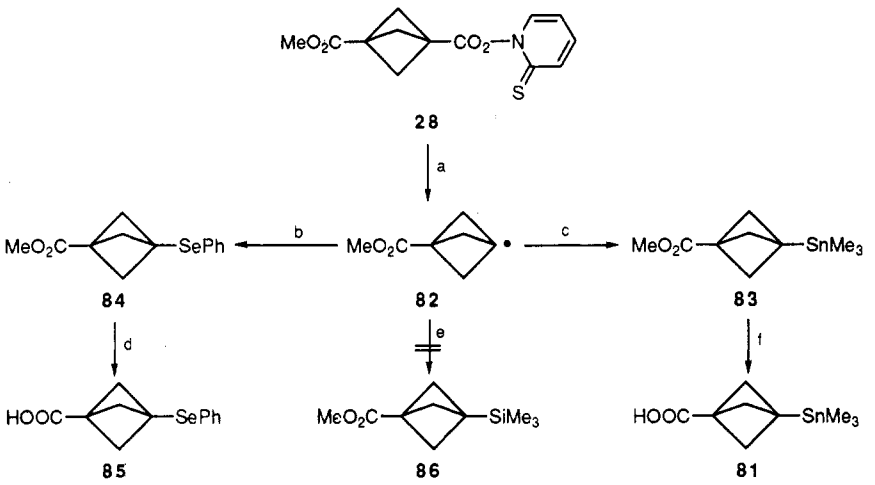
[a] (a) ^{t}BuLi; (b) Me_3SiCl; (c) RuO_4; (d) Me_3SnCl.

pentane-1-carboxylic acid (**60**) was produced instead. Evidently, the lithiated species **72** is more labile than we had anticipated and it collapses spontaneously[22] with extrusion of MeO^- to give [1.1.1]propellane which reacts with *tert*-butyllithium as noted previously.[18] Elimination of the elements of MeO and I in **71** is typical of a range of related elimination processes; for example, we find that treatment of 1,3-dibromo- and 1,3-diiodobicyclo[1.1.1]pentane (**17** and **39**) and 3-iodobicyclo[1.1.1]pentyl chloride (**74**) with *tert*-butyllithium leads essentially to complete conversion to [1.1.1]propellane (**24**) in all cases and is reminiscent of the production of **24** from dehydrobromination of 1-bromobicyclo[1.1.1]pentane (**1**) with *t*-BuLi.[18]

The synthetic strategy adopted for the metalloidal-substituted bromides **20** and **21** was based on a previous observation[18] that 1-(trimethylsilyl)bicyclo[1.1.1]pentane (**76**) can be prepared by nucleophilic displacement of chloride in chlorotrimethylsilane by 1-bicyclo[1.1.1]pentyllithium (**75**). The projected route is displayed in Scheme 9, in which it can be seen that the carboxylic acids **80** and **81** are the essential intermediates to the required bromides. (3-Phenylbicyclo[1.1.1]pentyl)lithium (**77**), generated by metalation of the corresponding iodide **62**, was quenched with Me_3SiCl (Me_3SnCl) and afforded the silane **78** (stannane **79**) as illustrated. Ru(IV) oxidation of the phenyl group in the silane was accomplished smoothly, giving the acid **80**. Interestingly, however, the stannane **79** did not survive these oxidative conditions; an array of products consisting of 3-chlorobicyclo[1.1.1]pentane-1-carboxylic acid (**31**), chlorotrimethylstannane, and benzoic acid in a ratio of 1:1:0.8 was obtained. The probable reaction channel accounting for the loss of the Me_3Sn group from the bicyclic moiety involves homolytic fission of the bridgehead carbon–tin bond and this is followed by abstraction of a chlorine atom from the solvent by the $Me_3Sn^\bullet$ and 1-bicyclo[1.1.1]pentyl radicals thus produced. Oxidation of 3-phenylbicyclo[1.1.1]pentyl chloride then affords the acid **31**. Formation of benzoic acid is a surprising result because oxidation of the alkyl side chain and retention of the aryl ring is uncharacteristic of the reactions of alkyl-substituted benzenes with Ru(IV).

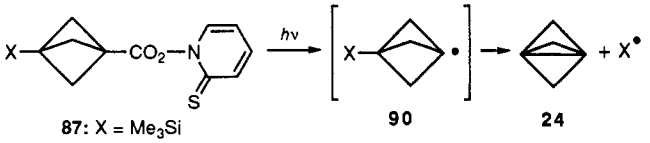
(20) Barton, D. H. R.; Ozbalik, N.; Vacher, B. *Tetrahedron*, 1988, *44*, 7385.
(21) Wiberg, K. B.; McMurdie, N.; *J. Am. Chem. Soc.* 1991, *113*, 8995.
(22) It may be, of course, that the reaction proceeds in a concerted fashion and that **72** has no finite existence at all.

Scheme 10 [a]



[a] (a) *hν*; (b) PhSeSePh; (c) $Me_3SnSnMe_3$; (d) aqueous NaOH; (e) $Me_3SiSiMe_3$; (f) H^+/THF.

Scheme 11



87: X = Me_3Si
88: X = Me_3Sn
89: X = PhSe

In an alternative route to the stannyl acid **81**, we decided to exploit the ease with which the Barton ester **28** can be induced to undergo photochemical decomposition to the 1-bicyclo[1.1.1]pentyl radical which, as depicted in Scheme 2, can be trapped by a variety of reagents such as biacetyl and the halogen atom donors. Potentially, generation of the radical **82** in the presence of $Me_3SnSnMe_3$ would lead via radical substitution to the ester **83** and ultimately the acid **81** (Scheme 10). In accordance with these expectations, the stannyl ester **83** was obtained in good yield. It is noteworthy that subsequent hydrolysis of the ester must be conducted under acidic conditions; treatment with alkali leads to decomposition of the stannane, giving unwanted unidentified products. Incidentally, this pathway also provided ready access to the selenyl ester **84** if diphenyl diselenide is used as the trapping agent in place of hexamethylditin. However attempts to insert the trimethylsilyl group by use of $Me_3SiSiMe_3$ in a similar fashion to give **86** were unsuccessful, and this is presumably a reflection of the relatively high Si–Si bond strength (81 kcal mol^{-1}) compared to the strengths of the Sn–Sn and Se–Se bonds.

With the three carboxylic acids **80**, **81**, and **85** now available, attention was directed to their conversion into the corresponding bromides **20**, **21**, and **22** under the typical Barton bromodecarboxylation conditions which had been employed so successfully above in the synthesis of the related bromides. However, irradiation of the derived thiohydroxamic esters **87**–**89** in 1-bromo-1-chloro-2,2,2-trifluoroethane did not yield even a trace of the respective bromide (Scheme 11). In the case of the selenyl ester **89**, for example, complete loss of the hydrocarbon moiety occurred, presumably as [1.1.1]propellane, and a quantitative recovery of diphenyl diselenide was isolated. Irradiation of the silyl and stannyl esters **87** and **88** also led to significant loss of the material; in these cases only a very small amount of an unidentified intractable product was obtained. Presumably here, too, the material imbalance was caused by loss of the bicyclic system as [1.1.1]-propellane. Thus, the intermediate radicals **90** produced in these reactions behave very much like their 3-halo-substituted analogs described above and collapse to give [1.1.1]propellane by elimination of PhSe• (completely) and Me_3Sn• and Me_3Si• radicals (substantially).

Experimental Section

General experimental procedures were as described previously.[19] 1-Bromobicyclo[1.1.1]pentane (**1**),[12] 1,3-diacetylbicyclo-[1.1.1]pentane (**25**),[3a] bicyclo[1.1.1]pentane-1,3-dicarboxylic acid,[3a] diethyl bicyclo[1.1.1]pentane-1,3-dicarboxylate (**26**),[3a] 3-carbomethoxybicyclo[1.1.1]pentane-1-carboxylic acid (**27**),[9] *tert*-butyl 3-bromomethylbicyclo[1.1.1]pentane-1-carboxylate (**44**),[23] and 1,3-diiodobicyclo[1.1.1]pentane (**39**)[6b] were prepared as reported in the literature.

1,1-Dibromo-2,2-bis(chloromethyl)cyclopropane (23). A modified procedure of that developed by Sziemies and co-workers[8] was used. A 16 M aqueous sodium hydroxide solution (500 mL), cooled to 15 °C, was added in one portion at room temperature to a vigorously stirred solution of 2-(chloromethyl)allyl chloride (100 g, 0.8 mol) dissolved in bromoform (500 g, 172 mL) containing aliquot 336 (2–3 g). The solution was then warmed to 40 °C for 5–6 h after which time the reaction was shown (^1H NMR) to be approximately 70% complete. After being left under these conditions for 2 days, the mixture was then poured into a separating funnel and diluted with water (2.5 L) before being allowed to phase. The organic layer was removed and the aqueous layer extracted with hexane (2 × 500 mL). The combined organic layers were dried ($MgSO_4$) and the solvent was removed in vacuo to afford the crude tetrahalide (**23**). Distillation (40 °C/1.5 mm) gave a forerun consisting of a mixture of starting alkene and bromoform, followed by the tetrahalide **23** (170 g) (60–70 °C/0.01 mm). Recrystallization from pentane (−20 °C) afforded pure **23** (165 g, 70%) as a white solid: mp 45.5–46 °C (lit.[8] mp 45–46 °C), which had physical properties identical with those reported.[8]

2-Thioxo-1,2-dihydropyridin-1-yl 3-(Methoxycarbonyl)-bicyclo[1.1.1]pentane-1-carboxylate (28). This ester was prepared following the general method (b) of Barton and colleagues[11] and had properties in agreement with those reported.[1]

Methyl 3-Bromobicyclo[1.1.1]pentane-1-carboxylate (2). Bromodecarboxylation was effected using the method described[7] by dissolving the thiohydroxamic ester (**28**) in 1-bromo-1-chloro-2,2,2-trifluoroethane (20 mL) and irradiating the solution with a tungsten lamp (300 W) for 1 h under a nitrogen atmosphere. The solution was then cooled and washed successively with cold concentrated HCl (10 mL) and saturated sodium bicarbonate solution (10 mL) before being dried ($MgSO_4$). The solvent was

(23) Pigou, P. E.; Taylor, D. K. *Aust. J. Chem.* **1991**, *44*, 1417.

removed and the residue distilled (Kugelrohr, 70 °C/0.05 mm) to give the bromide **2** (2.1 g, 95%), whose spectral properties were identical with those reported:[2] mp 49–50 °C (lit.[2] mp 49–49.5 °C).

3-Bromobicyclo[1.1.1]pentane-1-carboxylic Acid (29). Concentrated sulfuric acid (3 mL) was added to a vigorously stirred solution of the ester **2** (1.25 g, 6.1 mmol) in 50% aqueous tetrahydrofuran (40 mL) at 50 °C. After 8 h the tetrahydrofuran was removed under reduced pressure and the residue added to water (10 mL). Extraction with dichloromethane (3 × 20 mL) followed by desiccation ($MgSO_4$) of the organic extracts and concentration of the solution yielded the bromo acid **29** (1.0 g, 86%). An analytical sample was obtained by recrystallization from ether/pentane (1:1): mp 176–178 °C (sealed tube); IR (Nujol) 3300–2700 (OH), 1685 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.0 (bs, 1 H (exchangeable with D_2O)), 2.52 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 173.15, 59.11, 39.39, 36.03; mass spectrum *m/z* (relative intensity) 111 (M^+ – Br, 54), 110 (18), 93 (16), 82 (33), 66 (62), 65 (100), 54 (48); HRMS calcd for $C_6H_7O_2Br$ (M^+ – Br) 111.0483, found 111.0446. Anal. Calcd for $C_6H_7O_2Br$: C, 37.7; H, 3.7. Found: C, 37.9; H, 3.7.

Sodium 3-Bromobicyclo[1.1.1]pentane-1-carboxylate (7). Sodium hydride (80 mg, 50 wt % in mineral oil) was washed with hexane (3 × 10 mL) under nitrogen. Dry ether (50 mL) was added followed by the acid **29** (0.31 g, 1.63 mmol) in ether (10 mL). The mixture was stirred at room temperature for 12 h after which time the sodium salt **7** (322 mg, 93%) was filtered off and washed with pentane (2 × 10 mL) and ether (3 × 10 mL) before being dried under vacuum: mass spectrum *m/z* (relative intensity) 133 (M^+ – Br, 15), 111 (40), 97 (37), 82 (43), 71 (45), 57 (100); HRMS calcd for $C_6H_6O_2BrNa$ (M^+ – Br) 133.0266, found 133.0272.

3-Bromo-1-(hydroxymethyl)bicyclo[1.1.1]pentane (3). To a solution of lithium aluminum hydride (0.82 g, 2.2 equiv) in dry ether (25 mL) under nitrogen was added a solution of the bromo ester **2** (2.0 g, 9.76 mmol) in dry ether (10 mL) at 0 °C. The mixture was then heated to reflux for 1 h and then cooled and treated with saturated sodium sulfate solution (2 mL). After 10 min the solution was filtered, the salts were washed with fresh ether (2 × 15 mL), and the solvent was removed in vacuo to yield the desired alcohol **3** (1.59 g, 92%). An analytical sample was obtained by recrystallization from pentane: mp 64.5–65 °C; IR (Nujol) 3400–3000 (OH), 1512, 1146, 981 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.67 (s, 2H), 2.19 (s, 6H), 1.90 (bs, 1H (exchangeable with D_2O)); ^{13}C NMR ($CDCl_3$) δ 61.92, 57.05, 41.55, 37.43; mass spectrum *m/z* (relative intensity) 147 and 145 (M^+ – CH_2OH, 8), 97 (26), 79 (72), 77 (62), 69 (52), 57 (100), 53 (47); HRMS calcd for C_6H_9OBr $(M\text{-}CH_2OH)^+$ 146.9676 and 144.9677, found 146.9634 and 144.9653. Anal. Calcd for C_6H_9OBr: C, 40.7; H, 5.1. Found: C, 40.4; H, 5.4.

3-Bromo-1-((tosyloxy)methyl)bicyclo[1.1.1]pentane (4). *p*-Toluenesulfonyl chloride (1.27 g, 6.7 mmol) and pyridine (0.90 g, 11.3 mmol) were added to a solution of the alcohol **3** (1.0 g, 5.65 mmol) in dichloromethane (30 mL) under nitrogen. The mixture was allowed to stir for 3 days at room temperature after which time the solution was washed with water (3 × 20 mL) and then dried ($MgSO_4$) and concentrated to yield the tosylate **4** (1.60 g, 86%). An analytical sample was obtained by recrystallization from ether/pentane (3:1): mp 113–114 °C; IR (Nujol) 1598 (C=C), 1175, 997 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.84–7.27 (dd, J = 9.2 Hz, 4H), 4.07 (s, 2H), 2.45 (s, 3H), 2.16 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 145.03, 132.89, 129.91, 127.80, 68.26, 57.37, 38.52, 36.35, 21.64; mass spectrum *m/z* (relative intensity) 251 (M^+ – Br, 3.0), 160 (47), 158 (50), 155 (48), 95 (51), 91 (96), 79 (100), 65 (69); HRMS calcd for $C_{13}H_{15}O_3SBr$ $(M-Br)^+$ 251.0742, found 251.0719. Anal. Calcd for $C_{13}H_{15}O_3BrS$: C, 47.1; H, 4.6. Found: C, 47.1; H, 4.5.

3-Bromo-1-(chloromethyl)bicyclo[1.1.1]pentane (5). The tosylate **4** (1.0 g, 3.02 mmol) was dissolved in dry tetrahydrofuran (20 mL) containing anhydrous lithium chloride (4 equiv). The mixture was stirred at 60 °C for 12 h, after which the tetrahydrofuran was removed (0 °C/50 mm), ether was added (20 mL), and the solution was washed with water (3 × 20 mL). Desiccation ($MgSO_4$), concentration of the solution (0 °C/50 mm), and distillation of the residue (Kugelrohr, 100 °C/20 mm) afforded the bromide **5** (0.54 g, 92%) as a colorless liquid: ^1H NMR ($CDCl_3$) δ 3.58 (s, 2H), 2.22 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 57.53, 43.56, 40.85, 36.46; mass spectrum *m/z* (relative intensity) 147 and 145 (M^+ – CH_2Cl, (18), 79 (100), 77 (65), 65 (23), 53 (30); HRMS calcd for C_6H_8BrCl (M^+ – CH_2Cl) 146.9634 and 144.9653, found 146.9631 and 144.9658. Anal. Calcd for C_6H_8BrCl: C, 36.9; H, 4.1. Found: C, 37.0; H, 4.1.

3-Bromo-1-(acetoxymethyl)bicyclo[1.1.1]pentane (6). The alcohol **3** (0.75 g, 4.24 mmol) was dissolved in dry dichloromethane (20 mL) containing pyridine (0.67 g, 2.0 equiv) and treated at ambient temperature with a solution of acetyl chloride (0.40 g, 5.09 mmol) in CH_2Cl_2 over 15 h. The mixture was concentrated and then diluted with dichloromethane (30 mL) and washed with water (2 × 25 mL). Desiccation ($MgSO_4$) of the organic layer and removal of the solvent in vacuo followed by flash chromatography (ether/pentane, 1:9) of the residue afforded the acetate **6** (0.82 g, 88%): bp (Kugelrohr, 75 °C/2mm); IR (Nujol) 1747, 1365, 1038 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.11 (s, 2H), 2.19 (s, 6H), 2.05 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 170.54, 62.73, 57.70, 39.11, 36.57, 20.69; mass spectrum *m/z* (relative intensity) 160 (10), 139 (10), 138 (26), 97 (45), 79 (100), 67 (37); HRMS calcd for $C_8H_{11}O_2Br$ (M^+ – Br) 139.0759, found 139.0764. Anal. Calcd for $C_8H_{11}O_3Br$: C, 43.9; H, 5.1. Found: C, 44.0; H, 5.4.

Methyl 3-Chlorobicyclo[1.1.1]pentane-1-carboxylate (30). Exposure of the thiohydroxamic ester **28** (1.5 g, 5.38 mmol) to the conditions used above for the synthesis of **2** but employing trichlorofluoromethane as the solvent and distillation (Kugelrohr, 80 °C/6.0mm) of the product gave the chloride **30** (0.71 g, 82%): mp 63–64 °C; IR (Nujol) 1742 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.70 (s, 3H), 2.42 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 168.06, 58.15, 52.09, 48.32, 35.98; mass spectrum *m/z* (relative intensity) 120 (20), 125 (90), 101 (14), 93 (18), 65 (100), 59 (33); HRMS calcd for $C_7H_9O_2Cl$ (M^+ – Cl), 125.0603, found 125.0611. Anal. Calcd for $C_7H_9O_2Cl$: C, 52.4; H, 5.7. Found: C, 52.4; H, 6.0.

3-Chlorobicyclo[1.1.1]pentane-1-carboxylic Acid (31). The ester **30** (1.0 g, 6.25 mmol) was exposed to the same conditions used for the preparation of the bromo acid **29**. Workup followed by sublimation (Kugelrohr, 120 °C/3mm) yielded the acid **31** (0.88 g, 96%): mp 165–165.5 °C (sealed tube); IR (Nujol) 3300–2500 (OH), 1682 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 10.5 (bs, 1H (exchangeable with D_2O)), 2.43 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 173.81, 58.15, 48.22, 35.95; mass spectrum *m/z* (relative intensity) 111 (M^+ – Cl, (66), 101 (12), 93 (14), 83 (30), 65 (100); HRMS calcd for $C_6H_7O_2Cl$ (M^+ – Cl) 111.0446, found 111.0445. Anal. Calcd for $C_6H_7O_2Cl$: C, 49.2; H, 4.8. Found: C, 49.6; H, 5.0.

1-Bromo-3-chlorobicyclo[1.1.1]pentane (10). Application of the same method used above for the synthesis of the thiohydroxamic ester **28** to the acid **31** (0.38 g, 2.63 mmol) gave the thiohydroxamic ester **32** (0.65 g, 97%): mp 138–140 °C dec; IR (Nujol) 1800 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.79–6.50 (m, 4H), 2.66 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 174.50, 163.51, 137.43, 137.19, 133.36, 113.07, 58.93, 48.55, 34.56. Exposure of **32** (0.30 g, 1.18 mmol) to the conditions used for the synthesis of **2** and sublimation (Kugelrohr, 85 °C) of the product gave the desired bromide **10** (0.17 g, 80%): mp 84 °C (sealed tube); ^1H NMR ($CDCl_3$) δ 2.51 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 63.54, 45.71, 30.02; mass spectrum *m/z* (relative intensity) 145 and 147 (M^+ – Cl, 15), 101 (20), 65 (100); HRMS calcd for C_5H_6BrCl (M^+ – Cl) 144.9653 and 146.9634, found 144.9660 and 146.9633. Anal. Calcd for C_5H_6BrCl: C, 33.1; H, 3.3. Found: C, 32.8; H, 3.3.

Methyl 3-Acetylbicyclo[1.1.1]pentane-1-carboxylate (33). A solution of the thiohydroxamic ester **28** (3.0 g, 10.75 mmol) in dry deoxygenated dichloromethane (30 mL) (benzene could also be used) under nitrogen was treated with biacetyl (4.6 g, 5equiv). The mixture was subjected to irradiation from a tungsten lamp (300 W) for 30 min and then cooled and washed with cold concentrated HCl (2 × 20 mL) and saturated sodium bicarbonate solution (20 mL). Desiccation ($MgSO_4$) and removal of the solvent in vacuo yielded crude **33** (1.52 g, 84%), which was purified by flash chromatography (ether): mp 59–59.5 °C (lit.[3b] mp 57–58 °C); IR (Nujol) 1742 (C=O), 1713 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.70 (s, 3H), 2.29 (s, 6H), 2.14 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 205.03, 169.79, 52.41, 51.71, 43.99, 37.01, 26.07; mass spectrum *m/z* (relative intenstiy) 168 (M^+, 3.0), 153 (12), 136 (45), 125 (42), 121 (52), 108 (65), 97 (45), 93 (77), 66 (72), 59 (100); HRMS calcd for $C_9H_{12}O_3$ 168.0786, found 168.0798.

3-Acetylbicyclo[1.1.1]pentane-1-carboxylic Acid (34). Standard alkaline hydrolysis of **33** (1.0 g, 5.95 mmol) for 30 min

provided, after sublimation (80 °C/0.1 mm), a near quantitative yield of **34** (0.87 g, 95%): mp 95–96 °C; IR (Nujol) 3400–2500 (OH), 1700 and 1680 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.0 (bs, 1H (exchangeable with D_2O), 2.33 (s, 6H), 2.16 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 205.48, 175.04, 52.39, 43.94, 36.95, 26.22; mass spectrum *m/z* (relative intensity) 154 (M^+, 4.0), 136 (42), 121 (40), 108 (82), 93 (49), 83 (45), 66 (73), 65 (100); HRMS calcd for $C_8H_{10}O_3$ 154.0630, found 154.0631. Anal. Calcd for $C_8H_{10}O_3$: C, 62.3; H, 6.6. Found: C, 62.0; H, 6.8.

3-Bromo-1-acetylbicyclo[1.1.1]pentane (8). Using the method described above, the acid **34** (0.5 g, 3.25 mmol) was converted into the corresponding thiohydroxamic ester (0.81 g, 95%): mp 148–150 °C dec; IR (Nujol) 1785 (CO_2N), 1694 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.78–6.55 (m, 4H), 2.52 (s, 6H), 2.17 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 204.29, 174.6, 164.80, 137.66, 136.95, 133.59, 133.06, 53.20, 44.86, 35.70, 26.27; mass spectrum *m/z* (relative intensity) 220 ($M^+ - COCH_3$, 3), 187 (40), 127 (55), 111 (100), 95 (16), 78 (83), 67 (90); HRMS calcd for $C_{13}H_{13}O_3NS$ ($M - COCH_3$)$^+$ 220.0432, found 220.0466. Exposure of the hydroxamic ester (0.70 g, 2.66 mmol) to the bromodecarboxylation conditions used above and distillation (Kugelrohr, 90 °C/2.5 mm) of the product gave the bromide **8** (0.47 g, 94%): mp 43.5–44 °C; IR (Nujol) 1714 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.48 (s, 6H), 2.13 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 201.53, 58.83, 45.99, 37.11, 26.76; mass spectrum *m/z* (relative intensity) 131 (32), 119 (38), 107 (100), 108 (42), 93 (15), 79 (18), 65 (52); HRMS calcd for C_7H_9OBr ($M^+ - Br$) 109.0653, found 109.0647. Anal. Calcd for C_7H_9OBr: C, 44.5; H, 4.8. Found: C, 44.2; H, 4.8.

3-Bromo-1-acetoxybicyclo[1.1.1]pentane (9). A solution of the bromide **8** (0.62 g, 3.28 mmol) in dichloromethane (100 mL) was treated with *m*-chloroperbenzoic acid (2.3 equiv). The mixture was stirred at room temperature for 4 days, after which the solution was filtered and the salts were washed with fresh dichloromethane. The combined organic layers were evaporated in vacuo to furnish the crude acetate **9** (0.52 g, 77%). Flash chromatography (ether/pentane, 1:4) provided an analytical sample of **9**: mp 31–32 °C; IR (Nujol) 1756 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.53 (s, 6H), 2.01 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 69.57, 63.33, 60.19, 31.15, 21.02; mass spectrum *m/z* (relative intensity) 158 (55), 156 (97), 139 (100), 121 (90), 75 (70). Anal. Calcd for $C_7H_9O_2Br$: C, 41.0; H, 4.4. Found: C, 41.1; H, 4.4.

1,3-Dibromobicyclo[1.1.1]pentane (17). [1.1.1]Propellane (**24**) in ether/pentane (200 mL, 1:1) was prepared as described[8b] from the tetrahalide **23** (12.0 g, 40.5 mmol). A solution of bromine dissolved in ether was then added as the mixture was irradiated with light from a tungsten lamp (300 W) at −25 °C until the bromine color just persisted. The solution was washed with a saturated sodium metabisulfite solution (2 × 100 mL) and then dried ($MgSO_4$) and concentrated to yield the dibromide **17** (3.3 g, 36%), which crystallized from methanol as needles: mp 122–123 °C (lit.[24] mp 119.5-120.5 °C); IR (Nujol) 1152, 722 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.57 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 64.63, 30.50; mass spectrum *m/z* (relative intensity) 147 and 145 ($M^+ - Br$ 28), 66 (90), 65 (100); HRMS calcd for $C_5H_6Br_2$ ($M^+ - Br$) 144.9653 and 146.9633, found 144.9647 and 146.9615.

1-Bromo-3-iodobicyclo[1.1.1]pentane (37). The acid **29** (0.38 g, 1.99 mmol) was converted into the thiohydroxamic ester **35** (0.59 g, 1.98 mmol): mp 110–112 °C dec; IR (Nujol) 1795 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.80–6.49 (m, 4H), 2.74 (s, 6H). Exposure of **35** (0.59 g, 1.98 mmol) to the usual iododecarboxylation conditions and sublimation (Kugelrohr, 100 °C/80 mm) of the product gave, besides a small amount (10%) of 1,3-dibromobicyclo[1.1.1]pentane (**17**), the bromo iodide **37** (0.24 g, 45%): mp 125–127 °C (sealed tube); ^1H NMR ($CDCl_3$) δ 2.61 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 66.47, 32.49, −5.05; mass spectrum *m/z* (relative intensity) 274 and 272 (M^+, 22), 192 (10), 147 (48), 145 (48), 66 (100); HRMS calcd for C_5H_6BrI 273.8680 and 271.8700, found 273.8694 and 271.8721.

Decomposition of the Thiohydroxamic Ester 35 in 1,1,1-Trichloro-2,2,2-trifluoroethane. Treatment of the Barton ester **35** (0.2 g, 1.38 mmol) under the conditions used for the synthesis of the bromo ester **2** but substituting fluorotrichloromethane with 1,1,1-trichloro-2,2,2-trifluoroethane as solvent gave 1,3-dibromobicyclo[1.1.1]pentane (**17**) (0.14 g, 45%) which was identified by comparison with the sample obtained above.

1-Bromo-3-methylbicyclo[1.1.1]pentane (11). The *tert*-butyl ester **45** (0.5 g, 2.75 mmol) was stirred with concentrated sulfuric acid (20 mL) for 15 h at room temperature. Extraction with ether (3 × 30 mL) and sublimation (Kugelrohr, 90 °C/20 mm) of the extract gave the acid **46** (0.34 g, 98%): mp 121–122 °C (lit.[2] mp 122–122.5 °C); IR (Nujol) 3300–2600 (OH), 1693 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.70 (bs, 1H (exchangeable with D_2O), 1.95 (s, 6H), 1.19 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 176.34, 53.25, 37.54, 36.68, 17.82. Conversion of the acid **46** (0.25 g, 1.98 mmol) into the thiohydroxamic ester was effected in the usual way. The product **47** (0.43 g, 93%) had mp 113–115 °C: IR (Nujol) 1786 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.75–6.50 (m, 4H), 2.17 (s, 6H), 1.24 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 174.88, 165.23, 137.66, 137.17, 133.11, 112.74, 54.12, 38.03, 34.89, 17.72; mass spectrum *m/z* (relative intensity) 235 (M^+, 8), 187 (26), 157 (17), 127 (100), 111 (99), 81 (68), 67 (84), 51 (94); HRMS calcd for $C_{12}H_{13}O_2NS$ 235.0667, found 235.0678. Exposure of **47** (0.41 g, 1.74 mmol) to standard bromodecarboxylation conditions and distillation (Kugelrohr, 80 °C/50 mm) of the product gave the pure bromide **11** (0.23 g, 81%): ^1H NMR ($CDCl_3$) δ 2.12 (s, 6H), 1.25 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 60.24, 36.24, 35.05, 17.17; mass spectrum *m/z* (relative intensity) 143 (12), 126 (23), 110 (20), 98 (30), 81 (55), 67 (40), 56 (100); HRMS calcd for C_6H_9Br ($M^+ - Br$) 81.0704, found 81.0695. Anal. Calcd for C_6H_9Br: C, 44.7; H, 5.6. Found: C, 44.4; H, 5.9.

3-Phenylbicyclo[1.1.1]pentane-1-carboxylic Acid (55). Method A. 3-(Methoxycarbonyl)bicyclo[1.1.1]pentane-1-carboxylic acid (**27**) (7.0 g, 41.2 mmol) and lead tetraacetate (22 g, 1.2 equiv) were placed in dry deoxygenated benzene (500 mL) and heated to reflux under nitrogen while being irradiated by a tungsten lamp (300 W). After 6 h, the solution was cooled and filtered and the solids were washed with fresh benzene (50 mL). The combined organic solutions were washed with a solution of sodium metabisulfite (2 × 200 mL) and then saturated sodium bicarbonate (100 mL) before being dried ($MgSO_4$). Removal of the solvent evaporated in vacuo and flash chromatography (hexane/ether, 4:1) of the residue afforded methyl 3-phenylbicyclo-[1.1.1]pentane-1-carboxylate (**54**) (5.74 g, 69%), whose spectral properties were identical with those reported.[2,25] Standard hydrolysis with alkali and workup afforded the acid **55** (5.2 g) which after sublimation (100 °C/0.01 mm) had spectral properties consistent with those reported:[2,25] mp 177–177.5 °C (lit.[2] mp 176–176.5 °C).

Method B.[3b] [1.1.1]Propellane (**24**) in ether/pentane (1:4, 350 mL) was prepared as described from the tetrahalide **23** (12.0 g, 40.5 mmol). Iodobenzene (20 g, 98 mmol) was then introduced and the solution placed in a quartz vessel and irradiated (254 nm) for 5 h after which the solution was concentrated in vacuo. The residue was added to anhydrous ether/pentane (3:1, 50 mL) and treated with *tert*-butyllithium (2.5 equiv, 1.7 M in pentane) at −78 °C. After 10 min, carbon dioxide was bubbled through the mixture and the solution allowed to attain room temperature. The mixture was washed with water (3 × 15 mL) and the combined aqueous washings were acidified with concentrated HCl and saturated with sodium chloride before being extracted with ether (4 × 30 mL). Ether was removed and the residue sublimed (Kugelrohr, 100 °C/20 mm) to give a small amount of pivalic acid followed by (Kugelrohr, 100 °C/0.1 mm) benzoic acid and finally the acid **55** (1.5 g, 20%). No attempt was made to isolate the higher staffanes.

Methyl 3-Carbamoylbicyclo[1.1.1]pentane-1-carboxylate (50). Oxalyl chloride (2 equiv) was added at room temperature to a solution of the half ester **27** (2.0 g, 11.8 mmol) in dry ether (30 mL) under nitrogen. Two drops of dimethylformamide were then introduced and the mixture was stirred for 30 min. Removal of the solvent and excess oxalyl chloride under reduced pressure followed by distillation (Kugelrohr, 75 °C/0.05 mm) of the residue afforded the acid chloride **49** (2.15 g, 97%): IR (Nujol) 1792 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.72 (s, 3H), 2.45 (s, 6H). The acid chloride (2.15 g, 11.44 mmol) was taken up in dry dichloromethane (150 mL) and treated with gaseous ammonia for 45

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min at room temperature. Ammonium chloride was filtered off and washed with acetone (3 × 30 mL). The combined organic solutions were then concentrated in vacuo, yielding the amide **50** (1.79 g, 90%). An analytical sample was obtained by sublimation (Kugelrohr, 130 °C/0.01 mm): mp 235–236 °C; IR (Nujol) 3350–3100 (NH_2), 1737 (C=O), 1650 ($CONH_2$) cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.80–5.50 (bs, 2H), 3.68 (s, 3H), 2.29 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 171.47, 169.68, 52.46, 51.92, 38.88, 36.84; mass spectrum *m/z* (relative intensity) 168 ($M^+ - 1$, 2), 152 (39), 137 (26), 124 (33), 110 (100), 96 (35), 81 (64), 65 (88), 59 (43); HRMS calcd for $C_8H_{11}O_3N$ 168.0661, found 168.0653. Anal. Calcd for $C_8H_{11}O_2N$: C, 56.8; H, 6.6. Found: C, 56.7; H, 6.9.

3-Cyanobicyclo[1.1.1]pentane-1-carboxylic Acid (52). The amide **50** (1.5 g, 8.88 mmol) was dissolved in thionyl chloride (30 mL) and heated under reflux for 2 h. The mixture was then cooled and the excess thionyl chloride removed in vacuo at room temperature. Sublimation (Kugelrohr, 90 °C/0.8 mm) of the residue gave the pure ester **51** (1.27 g, 95%): mp 103–104 °C; IR (Nujol) 2230 (CN), 1735 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.69 (s, 3H), 2.50 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 167.97, 116.99, 55.18, 52.07, 41.02, 23.84); mass spectrum *m/z* (relative intensity) 150 ($M^+ - 1$, 3), 136 (9), 120 (53), 92 (93), 65 (100), 59 (43); HRMS calcd for $C_8H_9O_2N$ 150.0555, found 150.0559. The ester **51** (1.0 g, 6.62 mmol) was dissolved in 50% aqueous methanol (30 mL), sodium hydroxide (2 equiv) was added, and the mixture was stirred at room temperature for 1.5 h. Methanol was removed in vacuo and the mixture acidified (concentrated HCl) before being extracted with dichloromethane (3 × 30 mL). Desiccation ($MgSO_4$) of the organic layer and sublimation (Kugelrohr, 80 °C/0.05 mm) of the residue afforded the cyanide **52** (0.88 g, 97%): mp 191–192 °C (lit.[2] mp 189–189.5 °C).

3-Bromobicyclo[1.1.1]pentane-1-carbonitrile (12). Treatment of the acid **52** (0.38 g, 2.76 mmol) as described above gave the thiohydroxamic ester **53** (0.64 g, 95%): mp 167–168 °C dec; IR (Nujol) 2232 (CN), 1799 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.75–6.50 (m, 4H), 2.76 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 174.50, 163.23, 137.32, 137.20, 133.54, 116.46, 113.13, 56.03, 39.61, 24.73; mass spectrum *m/z* (relative intensity) 210 (22), 205 (10), 176 (40), 150 (18), 111 (100), 65 (70). Exposure of **53** (0.5 g, 2.03 mmol) to Barton decarboxylation conditions followed by sublimation (Kugelrohr, 110 °C) of the product gave the desired bromide **12** (0.29 g, 83%): mp 119–120 °C; IR (Nujol) 2238 (CN) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.65 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 115.38, 60.88, 35.85, 25.47; mass spectrum *m/z* (relative intensity ($M^+ - Br$, 63), 80 (78), 65 (100); HRMS calcd for C_6H_6NBr ($M^+ - Br$) 92.0500, found 92.0502. Anal. Calcd for C_6H_6NBr: C, 41.9; H, 3.5. Found: C, 41.6; H, 3.6.

1-Bromo-3-phenylbicyclo[1.1.1]pentane (13). Following the procedure described above, the acid **55** (1.5 g, 7.98 mmol) was converted into the thiohydroxamic ester **56** (2.23 g, 94%): mp 163–165 °C dec; IR (Nujol) 1800 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.78–6.52 (m, 9H), 2.55 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 174.92, 165.64, 138.87, 137.67, 137.30, 133.29, 128.42, 127.28, 126.09, 112.92, 54.28, 43.08, 35.69; mass spectrum *m/z* (relative intensity) 206 (22), 177 (21), 163 (58), 124 (58), 83 (88), 81 (92), 67 (57), 55 (100). Exposure of **56** (2.20 g, 7.41 mmol) to bromodecarboxylation conditions and distillation (Kugelrohr, 80 °C/0.1 mm) of the product gave the bromide **13** (1.47 g, 89%), whose spectral properties were identical with those reported:[25] mp 31–31.5 °C (lit.[25] mp 32 °C).

3-(*p*-Nitrophenyl)bicyclo[1.1.1]pentane-1-carboxylic Acid (57). A nitrating mixture (8 mL), prepared from nitric acid (4.2 g), water (6.4 g), and sulfuric acid 72 g), was added dropwise at 10 °C to a vigorously stirred solution of the acid **55** (2.0 g, 10.6 mmol) in nitromethane (100 mL). After 6 h, when the reaction was shown (^1H NMR) to be complete, the solution was poured onto ice water (100 mL) and extracted with dichloromethane (4 × 100 mL). The organic extracts were then dried ($MgSO_4$), and the solvent was removed in vacuo. The residue (2.40 g, 97%) was shown by ^1H NMR analysis to consist of a 2:1 mixture of the *ortho* and *para* isomers. Addition of ether (50 mL) caused a solid to separate, which was identified by spectral analysis as the *para* isomer **57** (1.6 g, 65%): mp 245–246 °C after sublimation (125 °C/0.05 mm); IR (Nujol) 3300–2500 (OH), 1692 (C=O), 1600 (C=C); ^1H NMR ($CDCl_3$/DMSO-d_6) δ 10.0 (bs, 1H (exchangeable with D_2O)), 8.28–7.31 (dd, J = 9.0 Hz, 4H), 2.39 (s, 6H); ^{13}C NMR ($CDCl_3$/DMSO-d_6) δ 172.11, 147.25, 146.87, 127.15, 123.57, 53.36, 41.23, 37.33; mass spectrum *m/z* (relative intensity) 233 (M^+, 2.0), 216 (15), 188 (32), 142 (100), 141 (77), 128 (45), 115 (59), 102 (35), 90 (24), 76 (22), 63 (30); HRMS calcd for $C_{12}H_{11}O_4N$ 233.0688, found 233.0680. Anal. Calcd for $C_{12}H_{11}O_4N$: C, 61.8; H, 4.8. Found: C, 62.0; H, 4.8.

1-Bromo-3-(*p*-nitrophenyl)bicyclo[1.1.1]pentane (14). Using the procedure above but with added DMSO to promote solubility, the acid **57** (1.0 g, 4.27 mmol) was converted into the thiohydroxamic ester **58** (1.31 g, 90%): mp 158–160 °C dec; IR (Nujol) 1791 (C=O); ^1H NMR ($CDCl_3$) δ 8.25–6.55 (m 4H), 2.64 (s, 6H); mass spectrum *m/z* (relative intensity) 315 (10), 224 (20), 187 (9), 143 (23), 127 (12), 99 (33), 67 (32), 56 (100). Exposure of **58** (0.93 g, 2.71 mmol) to the conditions used for the synthesis of **2** and sublimation (Kugelrohr, 110 °C/0.01 mm) of the product gave the bromide **14** (0.62 g, 85%): mp 131–132 °C; IR (Nujol) 1600 (C=C), 1526 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.25–7.23 (dd, J = 9.0 Hz, 4H), 2.57 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 147.03, 144.86, 127.15, 123.68, 60.09, 43.23, 35.97; mass spectrum *m/z* (relative intensity) 188 ($M^+ - Br$, 35), 142 (100), 141 (97), 128 (63), 115 (82), 102 (40), 86 (44), 77 (51), 63 (38); HRMS calcd for $C_{11}H_{10}O_2NBr$ ($M^+ - Br$) 188.0712, found 188.0730. Anal. Calcd for $C_{11}H_{10}O_2NBr$: C, 49.3; H, 3.8. Found: C, 49.2; H, 3.8.

3-*tert*-Butylbicyclo[1.1.1]pentane-1-carboxylic Acid (60). The diiodide **39** (6 g, 18.8 mmol) (dibromide **17** could also be used) in anhydrous ether/pentane (50 mL, 3:1) was treated with *tert*-butyllithium (3.2 equiv, 1.7 M in pentane) at −78 °C. After 10 min, carbon dioxide was bubbled through the solution which was then allowed to attain room temperature. The mixture was washed with water (3 × 25 mL), and the combined aqueous washings were acidified with concentrated HCl and then saturated with sodium chloride before being extracted with ether (4 × 30 mL). Desiccation ($MgSO_4$) of the ether extracts and removal of the solvent in vacuo afforded a residue, which was sublimed (Kugelrohr, 100 °C/20 mm) to give a small amounts of pivalic acid. Continued sublimation (Kugelrohr, 65 °C/0.1 mm) gave the acid **60** (2.72 g, 85%): mp 155–157 °C; IR (Nujol) 3300–2750 (OH), 1690 (C=O), 1215 cm^{-1}; ^1H NMR ($CDCl_3$) 11.10 (bs, 1H (exchangeable with D_2O), (1.86, s, 6H), 0.86 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 177.31, 48.05, 48.05, 35.38, 29.36, 25.73; mass spectrum *m/z* (relative intensity) 169 ($M^+ + 1$, 5), 153 (18), 107 (33), 83 (100), 67 (28); HRMS calcd for $C_{10}H_{16}O_2$ ($M^+ + 1$) 169.1229, found 169.1224. Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.4; H, 9.6. Found: C, 71.2; H, 9.3.

1-Bromo-3-*tert*-butylbicyclo[1.1.1]pentane (15). Using the conditions employed for the synthesis of the thiohydroxamic ester **28**, the acid **60** (0.93 g, 5.47 mmol) was transformed into the thiohydroxamic ester **61** (1.4 g, 91%): mp 149–150 °C dec IR (Nujol) 1790 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) 7.75–6.54 (m, 4H), 2.10 (s, 6H), 0.86 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 174.93, 165.99, 137.77, 137.17, 133.27, 112.85, 49.57, 49.08, 34.18, 29.53, 25.73; mass spectrum *m/z* (relative intensity) 277 (M^+, 12), 136 (23), 127 (34), 111 (72), 107 (88), 83 (81), 67 (90), 55 (100); HRMS calcd for $C_{15}H_{19}O_2NS$ 277.1136, found 277.1153. Exposure of **61** (1.4 g, 5.02 mmol) to the conditions used for the synthesis of **2** and sublimation (Kugelrohr, 80 °C/20 mm) of the product gave the bromide **15** (0.91 g, 89%): mp 83–84 °C (lit.[3c] mp 80.5–81 °C); ^1H NMR ($CDCl_3$) δ 2.06 (s, 6H), 0.87 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 55.42, 49.62, 37.76, 31.04, 26.44; mass spectrum *m/z* (relative intensity) 123 ($M^+ - Br$, 42), 107 (70), 91 (36), 83 (100), 81 (75), 67 (54), 55 (81); HRMS calcd for $C_9H_{15}Br$ ($M^+ - Br$) 123.1174, found 123.1170. Anal. Calcd for $C_9H_{15}Br$: C, 53.7; H, 7.5. Found: C, 53.2; H, 7.7.

3-(*p*-Methoxyphenyl)bicyclo[1.1.1]pentane-1-carboxylic Acid (64). *p*-Iodoanisole (15 g) and [1.1.1]propellane generated from the tetrahalide **23** (12.0 g, 40.5 mmol) were irradiated for 5 h as described above for the synthesis of the iodide **62**. The volatile constituents were then removed in vacuo. The residue consisted of a mixture of 1-iodo-3-(*p*-methoxyphenyl)bicyclo-[1.1.1]pentane (**63**), ^1H NMR ($CDCl_3$) δ 7.22–6.75 (m, 4H), 3.80 (s, 3H), 2.56 (s, 6H), and what appeared to be other staffanes as well as excess *p*-iodoanisole and some rearranged material. Trituration with cold ether led to precipitation of the majority of the *p*-iodoanisole. The ether layer was treated with *tert*-butyllithium and CO_2 in the usual fashion to convert iodides to the corresponding acids. Distillation (Kugelrohr, 150 °C/0.02

mm) removed volatile materials and the last traces of *p*-methoxybenzoic acid. The remaining solid now consisted of the desired acid **64** and other higher staffane acids. Sublimation (Kugelrohr, 175 °C/0.01 mm) afforded the acid **64**: mp 209–210 °C; IR (Nujol) 1689 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 10.0 (bs, 1H (exchangeable with D_2O)), 7.25–6.75 (m, 4H), 3.80 (s, 3H), 2.33 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 176.44, 158.75, 131.80, 127.23, 113.77, 55.38, 53.44, 41.45, 36.83; mass spectrum *m/z* (relative intensity) 218 (M^+, 34), 203 (23), 173 (100), 158 (27), 152 (14), 133 (91), 115 (19), 89 (17), 77 (32), 68 (33); HRMS calcd for $C_{13}H_{14}O_3$ 218.0943, found 218.0908. Anal. Calcd for $C_{13}H_{14}O_3$: C, 71.5; H, 6.4. Found: C, 71.7; H, 6.2.

1-Bromo-3-(*p*-methoxyphenyl)bicyclo[1.1.1]pentane (16). Treatment of the acid **64** (77 mg, 0.35 mmol) as described above gave the thiohydroxamic ester **65** (0.107 g, 93%): mp 164–165 °C dec; IR (Nujol) 1779 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.76–6.43 (m, 8H), 3.82 (s, 3H), 2.55 (s, 6H); mass spectrum *m/z* (relative intensity) 224 (54), 201 (5), 172 (12), 143 (60), 99 (83), 67 (47), 61 (76), 56 (100). Exposure of the thiohydroxamic ester **65** (0.10 g, 0.31 mmol) to the conditions used for the synthesis of **2** and sublimation (Kugelrohr, 120 °C/0.2 mm) of the product gave the desired bromide **16** (63 mg, 81%): mp 64–66 °C; ^1H NMR ($CDCl_3$) δ 7.20–6.75 (m, 4H), 3.77 (s, 3H), 2.46 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 158.77, 130.04, 127.36, 113.77, 60.29, 55.36, 43.51, 36.84; mass spectrum *m/z* (relative intensity) 173 (M^+ – Br, 80), 172 (100), 157 (51), 141 (30), 133 (43), 115 (16), 102 (10), 89 (17), 69 (53); HRMS calcd for $C_{12}H_{13}OBr$ (M^+ – Br) 173.0966, found 173.0942. Anal. Calcd for $C_{12}H_{13}OBr$: C, 56.9; H, 5.2. Found: C, 56.9; H, 5.5.

Treatment of the Thiohydroxamic Ester 28 with XeF_2. Xenon difluoride (1.5 equiv) was added at room temperature under a nitrogen atmosphere to a solution of the thiohydroxamic ester **28** (0.50 g, 1.79 mmol) in dry dichloromethane (35 mL). After 1 min, the solution was washed with hydrochloric acid (2 × 15 mL) and then dried ($MgSO_4$) and any volatile components were removed in vacuo. Spectral analysis of the residue revealed one component only which was identified as 3-carbomethoxybicyclo[1.1.1]pentane-1-carbonyl fluoride (**70**) (0.30 g, 95%) by spectral analysis [IR (Nujol) 1831 (C=O), 1735(C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.72 (s, 3H), 2.45 (s, 6H); mass spectrum *m/z* (relative intensity) 141 (M^+ – OCH_3 36), 124 (19), 113 (15), 96 (60), 85 (100), 65 (80), 59 (87)] and also by hydrolysis in ether/H_2O for 24 h to the half-ester **27**.

1-Iodo-3-methoxybicyclo[1.1.1]pentane (71). Following the method outlined by Wiberg and McMurdie,[21] the diiodide **39** (1.0 g, 3.13 mmol) was dissolved in methanol (20 mL) at room temperature, after which sodium hydroxide (0.5 g, 4 equiv) was added. The vessel was sealed and stirring was continued for 20 h, when the mixture was diluted with water (30 mL) and extracted with pentane (4 × 30 mL). Desiccation ($MgSO_4$) of the combined pentane extracts and removal of the solvent in vacuo at 0 °C afforded the iodide **71**:[21] ^1H NMR ($CDCl_3$) δ 3.30 (s, 3H), 2.32, (s, 6H).

Attempted Synthesis of 3-Methoxybicyclo[1.1.1]pentane-1-Carboxylic Acid (73). Treatment of the iodide **71** (0.5 g, 2.23 mmol) with *tert*-butyllithium and carbonation of the product in the usual fashion gave a white solid (0.42 g). The material was found to consist of a 1:3 mixture of pivalic acid and 3-*tert*-butylbicyclo[1.1.1]pentane-1-carboxylic acid (**60**). None of the acid **73** was isolated.

1-Iodo-3-phenylbicyclo[1.1.1]pentane (62). Exposure of the thiohydroxamic ester **56** (2.20 g, 7.41 mmol) to the conditions used for the synthesis of the bromo iodide **37** and sublimation (Kugelrohr, 110 °C/2 mm) of the product afforded the iodide **62** (1.86 g, 93%), mp 64.5–65.0 °C (lit.[3b] mp 64–65 °C), whose spectral properties were identical with those reported.[3b]

1-Phenyl-3-(trimethylsilyl)bicyclo[1.1]pentane (78). The iodide **62** (2.0 g, 7.41 mmol) was dissolved in anhydrous ether/pentane (50 mL, 3:1) and treated with *tert*-butyllithium (2.0 equiv, 1.7 M in pentane) at –78 °C. After 10 min, trimethylsilyl chloride (1.5 equiv) was added and the solution allowed to attain room temperature. The mixture was washed with water (2 × 10 mL) and then dried ($MgSO_4$) and the volatile components were removed in vacuo. Sublimation (Kugelrohr, 85 °C/0.1 mm) of the residue yielded the silane **78** (1.47 g, 92%). An analytical sample was obtained by recrystallization from methanol: mp 203–204 °C: IR (Nujol) 1599 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.22 (bs, 5H), 1.97 (s, 6H), –0.07 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 142.53, 128.07, 126.20, 125.55, 51.81, 47.46, 28.49, –3.36; mass spectrum *m/z* (relative intensity) 216 (2.0), 173 (20), 142 (6)0, 97 (38), 73 (100), 59 (40); HRMS calcd for $C_{14}H_{20}Si$ 216.1334, found 216.1338. Anal. Calcd for $C_{14}H_{20}Si$: C, 77.7; H, 9.3. Found: C, 77.9; H, 9.4.

3-(Trimethylsilyl)bicyclo[1.1.1]pentane-1-carboxylic Acid (80). A mixture of silane **78** (1.41 g, 6.54 mmol), acetonitrile (15 mL), carbon tetrachloride (15 ml), water (25 mL), sodium metaperiodate (12 g, 14 equiv), and ruthenium(III) chloride (30 mg) was stirred vigorously for 35 h at ambient temperature as prescribed by Ashby and Goel.[26] Water (20 mL) was then added and the mixture thoroughly extracted with dichloromethane (5 × 25 mL) before being dried ($MgSO_4$). Removal of the solvent in vacuo, addition of ether (45 mL) to the residue, filtration and evaporation of the solvent, and sublimation (Kugelrohr, 85 °C/0.01 mm) of the product yielded the silyl acid **80** (0.89 g, 74%): mp 165–166 °C; IR (Nujol) 3300–2500 (OH), 1699 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 10.0 (bs, 1H (exchangeable with D_2O)), 1.96 (s, 6H), –0.03 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 174.79, 51.07, 42.84, 30.67, –0.58; mass spectrum *m/z* (relative intensity) 184 (5), 169 (22), 147 (5), 94 (16, 75 (100), 74 (93), 69 (49); HRMS calcd for $C_9H_{10}O_2Si$ 184.0920, found 184.0924. Anal. Calcd for $C_9H_{10}O_2Si$: C, 58.7; H, 8.8. Found: C, 58.8; H, 9.1.

1-Phenyl-3-(trimethylstannyl)bicyclo[1.1.1]pentane (79). The iodide **62** (0.61 g, 2.27 mmol) was exposed to the conditions employed above for the synthesis of **78** except that chlorotrimethylstannane (1.5 equiv) was employed as the quenching agent. Workup followed by sublimation (Kugelrohr, 100 °C/0.1 mm) afforded the stannane **79** (0.62 g, 89%): mp 45–46 °C; IR (Nujol) 1605 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.33–7.14 (m, 5H), 2.12 (s, 6H), 0.06 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 141.92, 128.17, 126.62, 125.59, 55.65, 51.19, 26.90, –11.10; mass spectrum *m/z* (relative intensity) 293 (M^+ – CH_3, 10), 229 (15), 165, (100), 143 (55), 128 (45), 115 (31), 91 (12), 77 (20); HRMS calcd for $C_{14}H_{20}Sn$ (M^+ – CH_3) 293.0352, found 293.0361. Anal. Calcd for $C_{14}H_{20}Sn$: C, 54.8; H, 6.6. Found: C, 54.8; H, 6.5.

3-(Trimethylstannyl)bicyclo[1.1.1]pentane-1-carboxylic Acid (81). Method A. The thiohydroxamic ester **28** (0.67 g, 2.40 mmol) was treated with hexamethylditin (3.15 g, 4.0 equiv) in dry benzene (30 mL) and exposed to irradiation from a tungsten lamp for 30 min. The mixture was washed with concentrated hydrochloric acid (2 × 15 mL) and then dried ($MgSO_4$), and all volatile products were removed. ^1H NMR analysis revealed the presence of two components, the stannane **83** and hexamethylditin. Acid-catalyzed hydrolysis of the mixture was effected as described above for the preparation of the bromo acid **29**. Distillation (Kugelrohr, 130 °C/0.1 mm) of the product gave the acid **81** (0.27 g, 40%), which was identified by comparison with an authentic specimen:[27] ^1H NMR ($CDCl_3$) δ 10.5 (bs, 1H (exchangeable with D_2O)), 2.14 (s, 6H), 0.05 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 173.54, 54.61, 46.10, 28.87, –11.21.

Method B. 1-Phenyl-3-(trimethylstannyl)bicyclo[1.1.1]-pentane (**79**) (0.5 g, 1.63 mmol) was subjected to ruthenium tetraoxide oxidation in an identical manner to that used in the preparation of **80**. However workup gave none of the expected acid **81**. The material isolated was found to consist of a mixture of benzoic acid, 3-chlorobicyclo[1.1.1]pentane-1-carboxylic acid (**31**), and chlorotrimethyltin in a ratio of 0.8:1:1.

3-(Phenylseleno)bicyclo[1.1.1]pentane-1-carboxylic Acid (85). The thiohydrxamic ester **28** (1.1 g, 3.94 mmol) and diphenyl diselenide (1.69 g, 1.37 equiv) were dissolved in dry dichloromethane (30 mL) under nitrogen at room temperature. The solution was irradiated with light from a tungsten lamp (300 W) for 20 min before being washed with 4 M HCl (2 × 10 mL) and then dried ($MgSO_4$). The voltaile components were removed in vacuo and the residue was subjected to flash chromatography hexane then dichloromethane) to afford pure **84** (0.85 g, 77%): IR (Nujol) 1736 (C=O), 1578 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.72–7.21 (m, 5H), 3.64 (s, 3H), 2.21 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 168.65, 135.54, 128.99, 127.96, 127.96, 55.96, 40.85, 35.00; mass

(26) Ashby, E. C.; Geol, A. B. *J. Org. Chem.* **1981**, *46*, 3936.

(27) Adcock, W.; Krstic, A. Unpublished data. We thank Dr. Adcock and Mr. Krstic for these data on the authentic material prior to their publication.

spectrum m/z (relative intensity) 282 (M^+, 10), 183 (10), 158 (44), 125 (100), 112 (30), 93 (20), 77 (77), 65 (50), 59 (41); HRMS calcd for $C_{13}H_{14}O_2Se$ 282.0158, found 282.0147. Standard alkaline hydrolysis of **84** (0.80 g, 2.28 mmol) for 1 h provided, after sublimation (110 °C/0.02 mm), a near quantitative yield of 3-(phenylseleno)bicyclo[1.1.1]pentane-1-carboxylic acid (**85**) (0.73 g, 96%): mp 119–120 °C; IR (Nujol) 1682 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 10.10 (bs, 1H (exchangeable with D_2O)), 7.70–7.21 (m, 5H), 2.21 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 173.63, 135.60, 128.99, 128.07, 127.74, 55.82, 40.74, 34.89; mass spectrum m/z (relative intensity) 268 (M^+, 2.0), 234 (22), 232 (12), 158 (38), 156 (34), 154 (54), 114 (15), 77 (100), 69 (60), 51 (74); HRMS calcd for $C_{12}H_{12}O_2Se$ 268.0002, found 267.9997. Anal. Calcd for $C_{12}H_{13}O_2Se$: C, 53.9; H, 4.5. Found: C, 53.8; H, 4.6.

Attempted Synthesis of (1) 1-Bromo-3-(phenylseleno)bicyclo[1.1.1]pentane (22). The acid **85** (0.50 g, 1.87 mmol) was converted into the thiohydroxamic ester **89** (0.70 g, 99%): mp 140–142 °C dec; IR (Nujol) 1784 (C=O), 1609 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.80–6.40 (m, 9H), 2.42 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 174.39, 163.44, 137.49, 136.90, 135.65, 133.22, 129.04, 128.23, 127.31, 112.90, 56.50, 39.38, 33.86; mass spectrum m/z (relative intensity) 315 (26), 189 (17), 127 (100), 111 (88), 78 (98), 67 (80), 51 (67). Exposure of **89** (0.70 g, 1.86 mmol) to the conditions used for the synthesis of **2** afforded a pale yellow solid (0.28 g, 97%), which was shown to be diphenyl diselenide by comparison with authentic material.

(2) 1-Bromo-3-(trimethylstannyl)bicyclo[1.1.1]pentane (21). The acid **81** (0.06 g, 0.22 mmol) was converted into the thiohydroxamic ester **88** (0.084 g, 95%): mp 141–143 °C dec; IR (Nujol) 1787 (C=O), 1610 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.80–6.40 (m, 9H), 2.20 (s, 6H). Exposure of **88** (0.084 g, 0.22 mmol) to the conditions used for the synthesis of **2** gave a small amount of an intractable, unidentified material. None of the bromide **21** was isolated.

(3) 1-Bromo-3-(trimethylsilyl)bicyclo[1.1.1]pentane (20). The acid **86** (0.50 g, 2.72 mmol) was converted into the thiohydroxamic ester **87** (0.79 g, 98%): mp 146–147 °C dec; IR (Nujol) 1792 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.76–6.48 (m, 9H), 2.22 (s, 6H). Exposure of **87** (0.79 g, 2.70 mmol) to the conditions used for the synthesis of **2** did not afford the desired bromide **20** but gave a very small quantity of an intractable product the identity of which was not established.

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