tonated γ-valerolactone ($1H_O^+$) and, ultimately, O-protonated cyclopentenone ($10H_O^+$) as the most general result. This behavior could be correlated with the behavior of the same ions in the gas phase. Thus, it was possible to assign reasonable structures to the ions that resulted by the fragmentation of the ions initially formed from the parent compounds under the conditions of CIMS.

Experimental Section

^1H NMR spectra were recorded at 60 MHz with a Hitachi Perkin-Elmer Model R-24 NMR spectrometer. ^{13}C NMR spectra were recorded with a Bruker WP 80 SY NMR spectrometer or, when more resolution was necessary, with a Varian Gemini 200 NMR spectrometer. Dioxane or acetone (used for spectra recorded at low temperatures) served as the external standard (capillary tube). Chemical shifts (δ) are reported in ppm relative to TMS. CIMS spectra were recorded with a Hewlett-Packard 5988A spectrometer.

The $C_5H_8O_2$ acids and lactones were commercial materials. Ions were prepared by slowly adding, with efficient stirring, the cooled acid or lactone to a quantity of concentrated sulfuric acid (96%) or neat trifluoromethanesulfonic acid sufficient to give a ca. 1 M solution.

The cationic solutions were heated in tightly closed NMR tubes in a thermostated bath at the temperatures indicated in the text.

^1H NMR Data for the Isomeric $C_5H_9O_2^+$ Ions. $1H_O^+$: 1.6 (d, 3 H), 2.0–2.8 (m, 2 H), 3.3 (t, 2 H), 5.6 (q, 1 H). $2H_O^+$: 1.5 (d, 3 H), 2.6 (m, 2 H), 3.6 (m, 1 H), 5.1 (m, 2 H). $3H_O^+$: 2.0 (bs, 4 H), 3.0 (s, 2 H), 4.9 (s, 2 H). $5H_O^+$: 1.9 (m, 3 H), 2.3 (m, 2 H), 5.9 (d, 1 H), 7.8 (dt, 1 H). $6H_O^+$: 1.9 (s, 3 H), 2.1 (d, 3 H), 7.7 (q, 1 H). $7H_O^+$: 1.2 (s, 3 H), 1.4 (m, 1 H), 1.7 (m, 1 H). $8H_O^+$: 1.2 (d, 3 H), 1.7–1.9 (m, 2 H), 1.9–2.5 (m, 2 H). $9H_O^+$: 1.6–2.6 (m, 6 H), 3.2–3.6 (m, 1 H).

Acknowledgment. This research was supported in part by the Comision Interministerial de Ciencia y Tecnología (CICYT Project PB87-0989).

Registry No. 1, 108-29-2; $1H_O^+$, 140843-82-9; 2, 1679-47-6; $2Ho^+$, 140858-54-4; 3, 542-28-9; $3Ho^+$, 113020-82-9; 4, 591-80-0; 4^+, 94285-35-5; $4Ho^+$, 143430-81-3; 4_{sc}^+, 143430-83-5; 5, 13991-37-2; $5Ho^+$, 115120-39-3; 6, 80-59-1; $6Ho^+$, 143430-77-7; $6H_{ac}^+$, 87676-52-6; $6H_{sc}^+$, 143430-82-4; 7, 6914-76-7; $7Ho^+$, 143430-78-8; 8, 29555-02-0; $8Ho^+$, 143430-79-9; 9, 3721-95-7; $9Ho^+$, 143430-80-2; 9^+, 45377-78-4; $10H_{sc}$, 143446-05-3; $11Ho^+$, 18639-88-8; $12Ho^+$ (R = H), 143430-84-6; $12Ho^+$ (R = SO_3H), 143430-85-7; $13Ho^+$, 143430-86-8; $14Ho^+$, 104598-62-1; 15^+, 35335-83-2; butane ion, 96347-32-9.

Nucleophilic Substitution in 1-Substituted 3-Iodobicyclo[1.1.1]pentanes. A New Synthetic Route to Functionalized Bicyclo[1.1.1]pentane Derivatives

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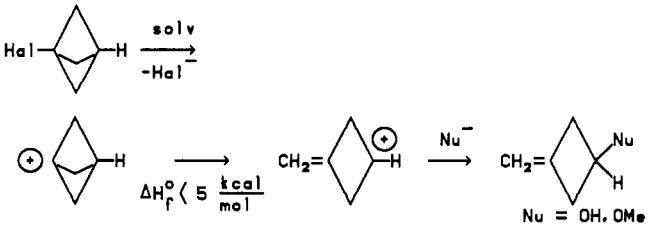
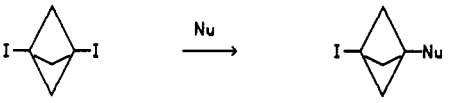
Nucleophilic substitution of the iodine in 1-substituted 3-iodobicyclo[1.1.1]pentanes [R = I (1), CF_3 (2)] was investigated. The results of the reaction are strongly dependent on the nature of the nucleophile and the substituent. Whereas the trifluoromethyl derivative 2 is found to be inert in the reactions and gave substitution products only with organolithium reagents, the 1,3-diiodide 1 is much more reactive and affords normal substitution products with nitrogen bases and MeONa but gives [1.1.1]propellane with Grignard and organolithium reagents and with triaryl(alkyl)phosphines. Other synthesized 3-iodobicyclo[1.1.1]pentanes did not give substitution products. A general scheme for the transformations of 1 is also proposed.

Nucleophilic substitution in cage systems is of great interest in both theoretical and synthetic organic chemistry.[1] However, for the simplest cage molecules such as 1-halobicyclo[1.1.1]pentanes, nucleophilic substitution was believed to be of no practical value,[2] since in 1967 it was discovered that 1-chlorobicyclo[1.1.1]pentane underwent abnormally fast solvolysis with 100% rearrangement.[2a] The same rearrangement was found for other 1-halobicyclo[1.1.1]pentanes.[2b]



It was not until late 1991 that the first successful results for fast unrearranged nucleophilic substitution in 1,3-diiodobicyclo[1.1.1]pentane were reported.[3]



If these reactions are of a general nature, a new effective method for synthesis of 1,3-substituted bicyclo[1.1.1]pentanes is available.

In this paper we present the results of our investigation of these reactions.

Results and Discussion

1,3-Diiodobicyclo[1.1.1]pentane (1) and 1-(trifluoromethyl)-3-iodobicyclo[1.1.1]pentane (2) were chosen as starting materials. Both compounds are very easily prepared in good yield from [1.1.1]propellane in a one-step process.

It was found that 2 has a very low reactivity. Common nucleophiles such as OH^-, MeO^-, RS^-, or R_3N and even

(1) For reviews, see: (a) Fort, R. C., Jr.; Schleyer, P. R. In *Advances in Alicyclic Chemistry*; Academic Press: New York, 1966; Vol. 1, pp 284–370. (b) Müller, P.; Mareda, J. In *Cage Hydrocarbons*; Wiley-Interscience: New York, 1990; pp 189–217.

(2) (a) Wiberg, K. B.; Williams, V. Z. *J. Am. Chem. Soc.* **1967**, *89*, 3373. (b) Della, E. W.; Taylor, D. K. *Aust. J. Chem.* **1990**, *43*, 945. (c) Kaszynski, P.; McMurdie, N. D.; Michl, J. *J. Org. Chem.* **1991**, *56*, 307. (d) Applequist, D. E.; Renken, T. L.; Wheeler, J. W. *J. Org. Chem.* **1982**, *47*, 4985.

(3) (a) Wiberg, K. B.; McMurdie, N. *J. Am. Chem. Soc.* **1991**, *113*, 8995. (b) Adcock, J. L.; Gakh, A. A. *Tetrahedron Lett.* **1992**, *33*, 4875–4878.

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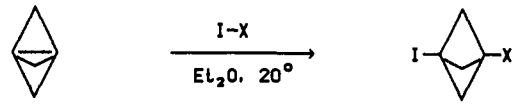
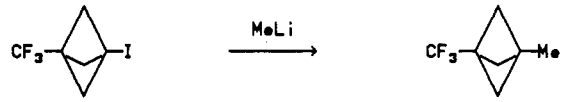


1, X = I, 92%
2, X = CF_3, 76%

Grignard reagents did not react with **2** either at ambient temperature or at 60 °C. As much as 60–85% of **2** was recovered unchanged from all reaction mixtures without the desired substitution products being detected.

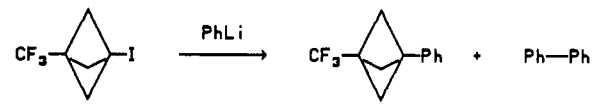
More reactive nucleophiles, such as alkyl- and aryllithium reagents, were found to react with **2**, but the results of the reactions depended strongly on the nature of R in RLi.

The clearest substitution reaction was found to proceed in the case of methyllithium, where only one volatile product remained in the reaction mixture after the reaction was completed.



2 3, 50%

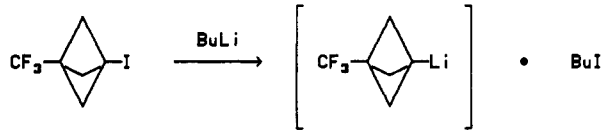
A similar reaction of **2** with phenyllithium gave the desired substitution product **4** together with biphenyl.



2 4, 40%

Intensive color changes during the reaction (from green to deep purple) as well as formation of biphenyl clearly indicate radical character in the reaction.

n-Butyl- and *tert*-butyllithium reagents reacted with **2** faster than methyl and phenyllithium but gave a mixture of volatile products, principally butyl iodides. This clearly indicates halolithium exchange in the reaction.[4] However, 1-lithio-3-(trifluoromethyl)bicyclo[1.1.1]pentane has not been isolated.



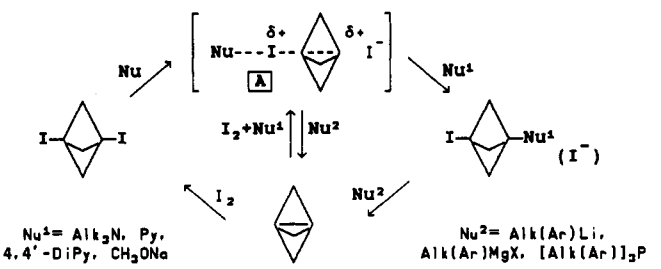
It is unlikely that nucleophilic substitution of iodine in **2** could go through a heterolytic S_N2 or S_N1 pathway. Radical substitution S_R of iodine in **2**, on the other hand, may present a useful pathway with some restrictions. Our attempts to substitute iodine in **2** with hydrogen were unsuccessful. Compound **2** does not react with neat tri(*n*-butyl)tin hydride even at 70 °C for 24 h. This behavior is strange taking into account the well-known good reactivity of iodobicyclo[1.1.1]pentanes toward the reagent.[2c]

In contrast to **2**, the diiodide **1** reacts smoothly with nucleophiles.

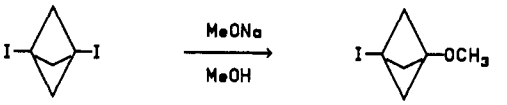
Thus **1** slowly reacts with methanolic NaOMe[3a] at room temperature and even with such a weak nucleophile as pyridine.[3b] Many other nitrogen bases react the same way.[3b] In each case only unrearranged substitution products could be detected.[3a,b]

(4) (a) Wiberg, K. B.; Waddell, S. T. *J. Am. Chem. Soc.* **1990**, *112*, 2194. (b) Eaton, P. E.; Tsanaktsidis, J. *J. Am. Chem. Soc.* **1990**, *112*, 876. (c) Kaszynski, P.; Friedli, A. C.; Michl, J. *J. Am. Chem. Soc.* **1992**, *114*, 601.

Scheme I

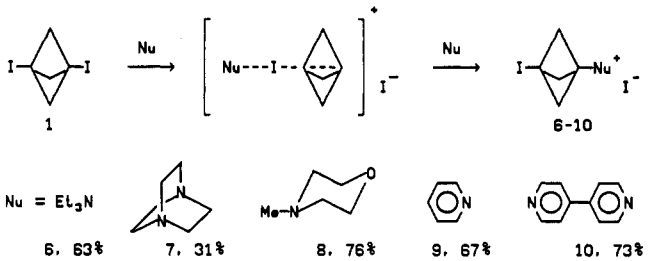


The best yield of the methoxy derivative **5** was obtained using a 5-fold excess of 5% MeONa in MeOH at room temperature for 48 h.



1 5, 68%

For the reactions of nitrogen bases with **1** acetone was found to be the best solvent.[3b] The desired substitution products usually precipitated during the reaction and were pure enough for NMR assay. Best yields were obtained using a 3–5-fold excess of nucleophile.[5]



1 6-10

6, 63% 7, 31% 8, 76% 9, 67% 10, 73%

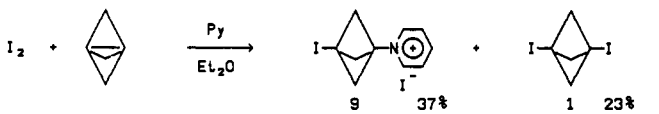
Triethylamine, *N*-methylmorpholine, and even cage amines, such as 1,4-diazabicyclo[2.2.2]octane (DABCO) may be easily quaternized in this manner. With hindered diisopropylamine, however, we isolated only diisopropylammonium iodide and some [1.1.1]propellane. This result indicates another pathway for the reaction of **1** with nucleophiles leading to [1.1.1]propellane.[3a]

The same picture was observed for the reaction of **1** with nitrogen heterocycles. Whereas pyridine and 4-substituted pyridines readily react with **1** to afford the desired substitution products with good yields and purity, α-substituted pyridines (e.g. *sym*-collidine, 2,4-lutidine) or quinoline cause only decomposition of **1**. Low-basicity (low-nucleophilicity) nitrogen heterocycles (pyrazine, thiazole) do not react with **1** properly either. Some [1.1.1]propellane was always detected in these unsuccessful reactions.

The formation of [1.1.1]propellane became a major process when nucleophiles such as trialkyl(aryl)phosphines or any carbon nucleophiles (phenylmagnesium bromide, methyllithium, phenyllithium) were used.

To generalize these results we propose Scheme I where a nucleophile-stabilized iodobicyclo[1.1.1]pentyl cation A is an intermediate.[3b]

(5) Another approach to these salts is the reaction of iodine with [1.1.1]propellane in the presence of nitrogen bases. The mixtures obtained severely limit the utility of this approach.



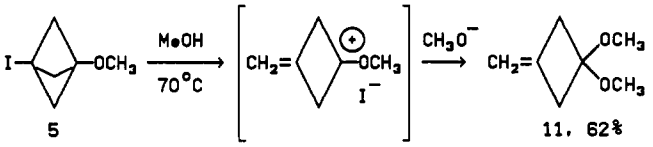
9 37% 1 23%

The choice between these two pathways (namely, to [1.1.1]propellane or to substitution products **5–10**) is determined by the strength of the Nu–I bond. The weaker the bond, the better is the chance to obtain the desired substitution product. However, the nucleophilicity of the reagent must be sufficient to drive the generation of cation A. Additionally, to obtain the substitution products the nucleophile must not be as sterically hindered as diisopropylamine or *sym*-collidine.

The proposed scheme postulates the involvement of a nucleophile capable of coordination with bound iodine so as to stabilize the cationic intermediate A which our results indicate is essential for obtaining unrearranged products. Offered in evidence is the reaction of **1** with silver fluoride in acetone which did not lead to detectable amounts of the desired iodo fluoride, but gave only rearranged product, tentatively identified as 3-methylenecyclobutanone. Also unsuccessful was an attempt at electrophilic replacement of iodine with fluorine in **1** using XeF_2. Only a complex mixture of products could be obtained.[6]

From all the 1-substituted 3-iodobicyclo[1.1.1]pentanes, **1, 5–10**, only diiodide **1** is capable of smooth, unrearranged nucleophilic substitution. Any attempts to continue substitution in **1** to replace both iodine atoms failed.

Thus, the 1-substituted 3-iodobicyclo[1.1.1]pentanes **5–10** would not react with nitrogen bases or MeONa under mild conditions. Stronger nucleophiles, such as organolithium or Grignard reagents, did react with these compounds with liberation of [1.1.1]propellane. Boiling in methanolic MeONa produced only the rearranged dimethyl ketal of 3-methylenecyclobutanone.



5 **11**, 62%

Conclusion

Several methods are known for the preparation of 1,3-disubstituted bicyclo[1.1.1]pentanes. The utilization of [1.1.1]propellane[4a,c] is the most convenient and general one.

This work has introduced another approach, namely through nucleophilic substitution of the iodine in some 1-substituted 3-iodobicyclo[1.1.1]pentanes. Although this method has limitations as to structure of the starting iodide and the nucleophile, it is a valuable procedure for synthesis of these cage compounds, which were difficult to prepare by previous methods. In addition, a new class of cage quaternary salts **6–10** has been obtained. This class of strained cage compounds has unusual structural and chemical characteristics and deserves further attention.[7]

Experimental Section

^1H NMR, ^{13}C NMR, and ^{19}F NMR were recorded at 89.6, 22.5, and 84.3 MHz, respectively. Chemical shifts (ppm) are relative to TMS (^1H, ^{13}C) or $CFCl_3$ (^{19}F) as internal standards. High-resolution mass spectra were obtained at 70 eV EI or 8 kV Xe atoms FAB in 3-nitrobenzyl alcohol. GLC was carried out on a preparative 20-ft × $^3/_8$-in. column with 10% SE-52 on 60–80-mesh Chromosorb P. Solvents and reagents were generally used as received from Baxter Scientific Products or Aldrich Chemical Co. [1.1.1]Propellane and 1,3-diiodobicyclo[1.1.1]pentane (**1**) were prepared as described elsewhere.[4c]

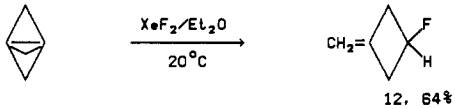
1-(Trifluoromethyl)-3-iodobicyclo[1.1.1]pentane (2). To a frozen Et_2O solution of [1.1.1]propellane (180 mL, 0.25 M; 3.0 g, 45 mmol) at −196 °C in a 1-L glass cylinder with pressure valve was condensed CF_3I (20.0 g, 100 mmol). After the addition (vacuum line) was complete, the valve was closed and the cylinder allowed to warm in a safety box. The reaction mixture was allowed to stand 3 days at room temperature. The solvent was then removed in vacuo at 0 °C (**2** is very volatile!) to afford 11.0 g of crude **2**. Low-temperature crystallization from pentane gave 8.5 g (75%) of **2** as colorless crystals: ^1H NMR (CCl_4) δ 2.39 (s, 6 H, CH_2); ^{19}F NMR (CCl_4) δ −72.6 (s, 3 F, CF_3); ^{13}C NMR ($CDCl_3$) δ 121.2 (q, $^1J_{CF}$ = 276.5 Hz, CF_3), 57.6 (q, $^3J_{CF}$ = 1.8 Hz, CH_2), 45.0 (q, $^2J_{CF}$ = 40.1 Hz, CCF_3), 2.7 (q, $^4J_{CF}$ = 2.0 Hz, CI); HRMS (EI) *m/e* calcd for $C_6H_6F_3$ (M − I) 135.0423, found 135.0429.

1-(Trifluoromethyl)-3-methylbicyclo[1.1.1]pentane (3). A solution of MeLi in Et_2O (70 mL of 1.4 M, low halide content, 98 mmol) was added dropwise to a solution of **2** (12 g, 48 mmol) in 60 mL of Et_2O at 0 °C under nitrogen with stirring. The addition was completed in 30 min, and the mixture was stirred at room temperature for an additional 2 h. The excess of MeLi was destroyed by adding dry ice (exothermic reaction!), and 100 mL of water was then added dropwise with intensive cooling and stirring to maintain a temperature below 10 °C. The organic phase was separated and washed with water (2 × 60 mL) at 0 °C to afford **9** as a 4.5% ethereal solution (110 mL, 3.6 g of pure **3**, yield 50%). The isolation of **3** was accomplished by GLC (160 °C) to give 0.3 g of the desired compound (from 11 mL of the Et_2O solution) as a colorless volatile liquid: ^1H NMR ($CDCl_3$) δ 1.83 (s, 6 H, CH_2), 1.19 (s, 3 H, CH_3); ^{19}F NMR ($CDCl_3$) δ −74.0 (s, 3 F, CF_3); ^{13}C NMR ($CDCl_3$) δ 122.8 (q, $^1J_{CF}$ = 275.3 Hz, CF_3), 50.2 (q, $^3J_{CF}$ = 1.8 Hz, CH_2), 37.4 (q, $^2J_{CF}$ = 37.6 Hz, CCF_3), 36.3 (q, $^4J_{CF}$ = 1.9 Hz, CCH_3), 17.6 (s, CH_3); HRMS (EI) *m/e* calcd for $C_7H_8F_3$ (M − H) 149.0578, found 149.0573.

1-Phenyl-3-(trifluoromethyl)bicyclo[1.1.1]pentane (4). A solution of **2** (1.3 g, 5.2 mmol) in 5 mL of dry THF was treated dropwise with PhLi (5.5 mL of a 1.8 M solution in cyclohexane–Et_2O, 9.9 mmol) under nitrogen with stirring at 0 °C. The reaction mixture immediately turned green in color and then deep purple. An additional quantity of PhLi (3.0 mL of a 1.8 M solution in cyclohexane–Et_2O, 5.4 mmol) was added after stirring for 4 h at room temperature. The reaction mixture was allowed to stand for 2 days at 20 °C until the reaction was complete (GLC assay, 175 → 210 °C, 10 min). The reaction mixture was then quenched with 50 g of ice; 20 mL of pentane was added, and the mixture was filtered to remove insoluble materials. The pentane solution was separated and the water layer was then extracted with 20 mL of pentane. The combined pentane extracts were washed with water (3 × 70 mL) and dried ($MgSO_4$). The organic solvents were evaporated in vacuo. The oily residue (1.3 g), which contain 34% w/w of **4** (yield 0.44 g, 2.1 mmol, 40%) and 15% w/w of biphenyl (0.2 g, 1.3 mmol), was separated by means of GLC (162 → 210 °C, 15 min) to afford 0.3 g of pure **4** as a colorless liquid, which slowly solidified upon cooling in a refrigerator overnight: ^1H NMR ($CDCl_3$) δ 7.37–7.15 (m, 5 H, Ph), 2.21 (s, 6 H, CH_2); ^{19}F NMR ($CDCl_3$) δ −73.7 (s, 3 F, CF_3); ^{13}C NMR ($CDCl_3$) δ 128.8, 128.4, 127.2, 126.0 (4 s, Ph), 123.1 (q, $^1J_{CF}$ = 275.3 Hz, CF_3), 50.4 (q, $^3J_{CF}$ = 2.1 Hz, CH_2), 41.4 (q, $^4J_{CF}$ = 1.8 Hz, *C*-Ph), 36.4 (q, $^2J_{CF}$ = 38.4 Hz, CCF_3); HRMS (EI) *m/e* calcd for $C_{12}H_{11}F_3$ (M) 212.0813, found 212.0810.

1-Methoxy-3-iodobicyclo[1.1.1]pentane (5). A suspension of **1** (3.2 g, 10 mmol) in 40 mL of methanolic MeONa (prepared from 40 mL MeOH and Na (0.5 g, 22 mmol)) was stirred at room temperature for 3 days. The reaction mixture was diluted with 100 mL of water and extracted with pentane (5 × 50 mL). The pentane solution was washed with water (4 × 100 mL) and dried ($MgSO_4$). The evaporation of solvent in vacuo gave crude (85% purity according to ^1H NMR) **5** (1.8 g, 68%). The analytical sample was obtained by sublimation in vacuo. **5** is a colorless liquid, unstable at room temperature: ^1H NMR ($CDCl_3$) δ 3.18 (c, 3 H, OCH_3), 2.26 (c, 6 H, CH_2); ^{13}C NMR ($CDCl_3$) δ 71.5 (CO),

(6) [1.1.1]Propellane in ether and XeF_2 gave only the rearranged product of electrophilic addition of HF (generated probably from the reaction of XeF_2 with the solvent). It seems that XeF_2 reacts faster with ether under these conditions than with [1.1.1]propellane.



12, 64%

(7) Adcock, J. L.; Gakh, A. A.; Pollitte, J. L.; Woods, C. *J. Am. Chem. Soc.* **1992**, *114*, 3980.

60.1 (CH_2), 54.4 (CH_3), -3.1 (CI); HRMS (EI) m/e calcd for C_6H_9O (M - I) 97.0653, found 97.0655.

1-(1-Pyridinio)-3-iodobicyclo[1.1.1]pentane Iodide (9). Diiodide 1 (3.2 g, 10 mmol) was dissolved in 70 mL of dry acetone, and pyridine (7.9 g, 100 mmol) was added. The resulting solution was allowed to stand for 3 days at room temperature with occasional shaking. The precipitate formed was filtered and recrystallized from the minimum volume of hot water to afford 9 (2.7 g, 67%) as cream-colored crystals: ^1H NMR (DMSO-d_6) δ 8.95 (d, 2 H, α-H), 8.54 (t, 1 H, γ-H), 8.07 (t, 2 H, β-H), 2.86 (s, 6 H, CH_2); ^{13}C NMR (DMSO-d_6) δ 146.6 (α-C), 142.4 (γ-C); 127.8 (β-C), 61.2 (CN^+), 60.7 (CH_2), -4.8 (CI); HRMS (FAB) m/e calcd for $C_{10}H_{11}NI$ (M - I) 271.9936, found 271.9929.

1-(4,4'-Bipyridinio)-3-iodobicyclo[1.1.1]pentane Iodide (10). The same procedure as for 9; 4,4'-bipyridyl (5.3 g, 34 mmol) was used instead of pyridine, and the reaction mixture was allowed to stand for 4 days at room temperature. Yield of 10, 73%: ^1H NMR (DMSO-d_6) δ 9.04 (d, J = 6.5 Hz, 2 H, α-H), 8.72 (d, J = 5.5 Hz, 2 H, α-H), 8.52 (d, J = 6.5 Hz, 2 H, β-H), 7.93 (d, J = 5.5 Hz, 2 H, β-H), 2.83 (c, 6 H, CH_2); ^{13}C NMR (DMSO-d_6) δ 153.3 (γ-C), 151.0 (α-C), 143.0 (α-C), 140.6 (γ-C), 125.1 (β-C), 122.1 (β-C), 61.0 (CN^+), 60.9 (CH_2), -4.8 (CI); HRMS (FAB m/e calcd for $C_{15}H_{14}N_2I$ (M - I) 349.0202, found 349.0237.

1-(Triethylammonio)-3-iodobicyclo[1.1.1]pentane Iodide (6). The same procedure as for 9; Et_3N (5.0 g, 50 mmol) was used instead of pyridine, and the reaction mixture was allowed to stand for 24 h at room temperature. Yield of 6, 63%: ^1H NMR (CD_3CN) δ 2.88 (q, 6 H, CH_2N^+), 2.34 (s, 6 H, CH_2), 0.86 (t, 9 H, CH_3); ^{13}C NMR (DMSO-d_6) δ 64.4 (CN^+), 59.5 (CH_2), 53.1 (CH_2), 8.6 (CH_3), -4.9 (CI); HRMS (FAB) m/e calcd for $C_{11}H_{21}NI$ (M - I) 294.0719, found 294.0719.

1-(1,4-Diazabicyclo[2.2.2]pent-1-yl)-3-iodobicyclo[1.1.1]-pentanylium Iodide (7). The same procedure as for 9; DABCO (3.0 g, 27 mmol) was used instead of pyridine, and the reaction mixture was allowed to stand for 20 h at room temperature. Yield of 7, 31% (after recrystallization from water): ^1H NMR (DMSO-d_6) δ 3.24-2.73 (m, 12 H, CH_2CH_2), 2.42 (c, 6 H, CH_2); ^{13}C NMR (DMSO-d_6) δ 62.4 (CN^+), 55.9 (CH_2), 49.1 (CH_2), 44.3 (CH_2), -4.6 (CI); HRMS (FAB) m/e calcd $C_{11}H_{18}N_2I$ (M - I) 305.0515, found 305.0532.

1-(*N*-Methylmorpholinio)-3-iodobicyclo[1.1.1]pentane Iodide (8). The same procedure as for 9; *N*-methylmorpholine was used instead of pyridine, and the reaction mixture was allowed to stand for 20 h at room temperature. Yield of 8, 76% (after recrystallization from water): ^1H NMR (DMSO-d_6) δ 3.91-3.62 (m, 4 H, CH_2), 3.34-3.12 (m, 4 H, CH_2), 3.03 (s, 3 H, CH_3), 2.51 (s, 6 H, CH_2); ^{13}C NMR (DMSO-d_6) δ 65.7 (CN^+), 59.6 (2 CH_2), 56.2 (5 CH_2), 42.9 (CH_3), -5.5 (CI); HRMS (FAB) m/e calcd for $C_{10}H_{17}ONI$ (M - I) 294.0355, found 294.0264.

Reaction of [1.1.1]Propellane with I_2 in the Presence of Pyridine. A solution of [1.1.1]propellane in Et_2O (10 mL of 0.25 M solution, 2.5 mmol) containing pyridine (0.6 g, 7.6 mmol) was treated dropwise with a solution of I_2 (13 mL of 0.2 M solution in Et_2O, 2.6 mmol) with stirring at -10 °C. The precipitate was collected and washed several times with Et_2O and acetone to afford 9 (370 mg, 37%). The filtrate was washed several times with 5% sodium thiosulfate, dried ($MgSO_4$), and evaporated in vacuo. The solid residue was then recrystallized from hexanes to give 1 (180 mg, 23%). All spectral characteristics of compounds prepared in this manner (1 and 9) were identical to samples prepared according to earlier procedures.

Reaction of Diiodobicyclo[1.1.1]pentane (1) with Diisopropylamine. The same procedure as for 9; diisopropylamine (3.0 g, 30 mmol) was used instead of pyridine, and the reaction mixture was allowed to stand for 20 h at room temperature. The precipitate (0.9 g) was filtered off and dried. ^1H NMR (CD_3CN) showed that it was pure diisopropylammonium iodide: δ 3.12 (m, J = 6.0 Hz, 2 H, CH), 0.94 (d, J = 6.0 Hz, 12 H, CH_3).

Reaction of 1,3-Diiodobicyclo[1.1.1]pentane (1) with AgF. A suspension of AgF (1.5 g, 12 mmol) and 1 (3.2 g, 10 mmol) in anhydrous acetone (60 mL) was stirred at room temperature for 2 days in darkness. The reaction mixture was filtered, the filtrate was poured onto 200 mL of ice and extracted with pentane (2 × 50 mL). The extract was washed with water (3 × 100 mL) and dried over $MgSO_4$. Evaporation of solvent in vacuo gave 0.6 g of a semisolid residue, which contained unreacted 1 and another compound tentatively identified as 3-methylenecyclobutanone according to ^1H NMR ($CDCl_3$) δ 5.04 (quintet, J = 2.1 Hz, 2 H, CH_2=), 4.23 (t, J = 2.1 Hz, 4 H, CH_2). No additional attempts to elucidate the structure of this compound have been made.

Reaction of 1,3-Diiodobicyclo[1.1.1]pentane (1) with Phenylmagnesium Bromide. The diiodide 1 (3.2 g, 10 mmol) was treated dropwise with a solution of PhMgBr (20 mL of a 1.4 M solution in THF, 28 mmol) with stirring in an ice bath. After the exothermic reaction was complete (20 min), 3.0 mL of reaction mixture was transferred in vacuo and treated with excess of 5% iodine in Et_2O. Evaporation of the resulting solution followed by crystallization in hexane gave 28 mg of pure diiodide 1; estimated yield of [1.1.1]propellane, 58%. The remaining reaction mixture was stirred for an additional 10 h at room temperature and then poured into 100 mL of 0.1 N HCl, filtered from insoluble materials, and extracted with pentane (3 × 30 mL). The pentane extract was washed twice with water (100 mL), dried ($MgSO_4$), and evaporated in vacuo. Chromatographic separation of the residue (190 °C) gave 1.3 g (32%) of a colorless liquid, which proved to be pure iodobenzene by comparison with an authentic sample [GLC, ^1H NMR ($CDCl_3$) δ 7.56 (d, 2 H, Ph), 7.28-6.81 (m, 3 H, Ph)].

The same results were obtained with phenyllithium and *n*-butyllithium, both of which gave [1.1.1]propellane and either iodobenzene or *n*-butyl iodide.

Reaction of 1,3-Diiodobicyclo[1.1.1]pentane (1) with Triphenylphosphine. Diiodide 1 (0.8 g, 2.5 mmol) was dissolved in dry acetone (20 mL). Triphenylphosphine (0.8 g, 3.1 mmol) and *sym*-collidine (to prevent acidification, 0.6 g, 5.0 mmol) were added to the solution. The reaction mixture was stirred for 2 days at room temperature. During the reaction a small part of the reaction mixture was transferred under vacuum and treated with 5% ethereal iodine. Some 1 was obtained indicating the presence of volatile [1.1.1]propellane in the reaction mixture. When the reaction was complete the dark brown reaction mixture was evaporated in vacuo to dryness, and the oily residue was treated with a small amount of Et_2O and chilled in a refrigerator. The semicrystalline product was dissolved in MeOH; water was added to cause precipitation. After 5 h at 0 °C the crystals were filtered off (0.25 g): mp 154-157 °C; ^1H NMR ($CDCl_3$) δ 7.83-7.22 (m, 3 Ph). The compound obtained was proved to be triphenylphosphine oxide by comparison with an authentic sample (^1H NMR, mp).

The same results were obtained with tributylphosphine, which gave some [1.1.1]propellane and tributylphosphine oxide.

Reaction of 1-(1-Pyridinio)-3-iodobicyclo[1.1.1]pentane Iodide (9) with Phenyllithium. By using the same procedure as was used for the reaction of diiodide 1 with phenylmagnesium bromide, the pyridinium salt 9 (2.0 g, 5 mmol) was reacted with a solution of phenyllithium (10 mL of a 1.8 M solution in cyclohexane-Et_2O, 18 mmol) to give mainly pyridine (26%, GLC and ^1H NMR), iodobenzene (32%, GLC and ^1H NMR), and small amounts of [1.1.1]propellane (converted to diiodide 1 with 5% ethereal I_2).

3-Methylenecyclobutanone Dimethyl Ketal (11). A solution of 5 (2.2 g, 10 mmol) in 30 mL of methanolic MeONa (prepared from 30 mL of MeOH and Na (0.5 g, 22 mmol)) was stirred and heated at reflux for 6 h under nitrogen. The mixture was then diluted with 50 mL of pentane, washed with water (100 mL), and dried ($MgSO_4$). Evaporation of the organic solvent in vacuo gave 1.0 g of a crude pale yellow liquid, which contained 79% (GLC) 11, yield 62%. The purification of the sample by GLC (145 °C) gave 0.4 g of pure 11 as a colorless liquid: ^1H NMR ($CDCl_3$) δ 4.95 (quintet, 2 H, J = 2.5 Hz, =CH_2), 3.19 (s, 6 H, OCH_3), 2.81 (t, 4 H, J = 2.5 Hz, CH_2); ^{13}C NMR ($CDCl_3$) δ 138.6 (=C), 108.6 (=CH_2), 100.3 (CO), 49.2, 41.6 (CH_2, CH_3); HRMS (EI) m/e calcd for $C_7H_{12}O_2$ (M) 128.0837, found 128.0831.

1-Methylene-3-fluorocyclobutane (12). To a stirred solution of [1.1.1]propellane in Et_2O (50 mL of a 0.3 M solution, 15 mmol, 1.0 g of pure [1.1.1]propellane) contained in a polyethylene flask connected to a U-tube containing H_2SO_4 was added XeF_2 (3.4 g, 20 mmol) in small portions over 15 min. The reaction mixture was allowed to stand for an additional 20 h at room temperature. The ethereal solution was washed twice with water (2 × 50 mL) and then three times with a 5% $NaHCO_3$/2% $Na_2S_2O_3$ solution (3 × 40 mL) and finally washed 5-7 times with 50-mL portions

of water until the volume of the organic layer was ca. 12 mL. The organic layer was dried overnight with $MgSO_4$. GLC separation (75 °C) of 2.0 mL of the ethereal solution (total volume after drying 11 mL) gave 0.15 g of **12** as a colorless volatile liquid (calculated total yield 0.83 g, 64%): ^1H NMR ($CDCl_3$) δ 5.13 (d quintet, J_{HF} = 56.5 Hz, J_{HH} = 6.2 Hz, 1 H, CHF); 4.95 (m, 2 H, CH_2=), 3.10–2.96 (m, 4 H, CH_2); ^{19}F NMR ($CDCl_3$) δ −170.6 (d m, J_{HF} = 56.9 Hz, CHF); HRMS (EI) *m/e* calcd for C_5H_7F 86.0532, found 86.0539.

Supplementary Material Available: ^1H NMR spectra of compounds **2–12** as well as an Ortep plot for compound **9** (13 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

The Photochemical Reaction between Aromatic Nitriles and Allylsilane

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The results obtained from the irradiation of aromatic nitriles and allyltrimethylsilane (ATMS) depend on the redox parameters of these molecules and their singlet energies. The reaction between 1-naphthalenecarbonitrile (NN) and ATMS in apolar solvents leads to [2 + 2] cycloaddition at positions 1 and 2 (via the exciplex); in polar solvents, electron transfer becomes a possibility, and loss of the trimethylsilyl cation followed by allylation of NN at positions 2 and 4 is also observed. When naphthalene-1,4-dicarbonitrile (NDN) is used, electron-transfer-initiated allylation (both addition and cyano group substitution) is the main pathway, but in apolar solvents cycloaddition at positions 4a and 5 occurs as a minor pathway. The reaction with benzene-1,2,4,5-tetracarbonitrile (BTN) gives substitution of an allyl for a cyano group as the only process. Finally, with both NDN and BTN and a high ATMS concentration in apolar solvents, the reaction pathway changes to photosensitized [2 + 2] dimerization of ATMS, proposed to occur via a terplex. Rationalizations for the observed reactions (including regiochemistry of addition and cycloaddition and nature of the intermediates) are offered.

In contrast to the variety of processes observed with benzene derivatives, the photoreactions between naphthalenes and alkenes are limited to [2 + 2] cycloadditions at positions 1 and 2;[2,3] with dienes, both [2 + 2] and [4 + 4] cycloadditions are observed.[4] Under conditions favoring electron transfer new paths become available. Thus, with naphthalenenitriles and arylalkenes the stabilized radical cations of the latter compounds are formed and undergo ionic addition and dimerization.[5] (However, we recently observed that cycloaddition takes place competitively in these systems as well).[3m] In other cases, the alkene radical cation is fragmented. Thus, with naphthalene-1,4-dicarbonitrile (NDN) and 2,3-dimethylbutene, the radical cation deprotonates and the alkenyl radical adds to NDN;[6] similarly, when allyltrimethylsilane (ATMS) is used as the donor, desilylation and addition of the allyl radical to NDN take place (Scheme I).[7]

Scheme I

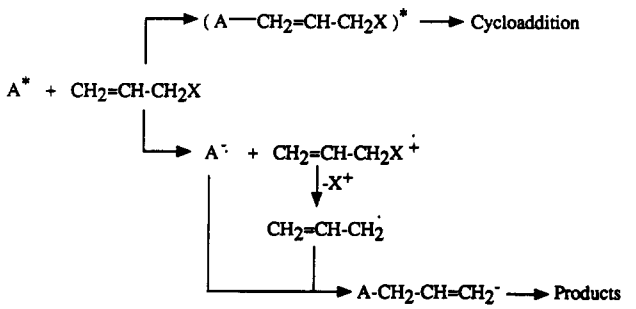

Table I. Products (Isolated Yield) from the Irradiation of Arenecarbonitriles in the Presence of 0.1 M Allyltrimethylsilane

arene	solvent	products (% yield)[a]
NN	MeCN	**1** (8), **2** (12), **3** (29), **4** (2), **5** (20)
NN	C_6H_6	**1** (23), **2** (35)
NDN	MeCN[b]	**6** (40), **7** (15), **8** (8), **9** (8)
NDN	C_6H_6	**6** (8), **7** (13), **8** (2), **9** (2), **10** (5), **12** (27),[c] **13** (23)[c]
BTN	MeCN	**11** (61)
BTN	CH_2Cl_2	**11** (85), **12** (79),[c] **13** (63)[c]

[a] Calculated on the converted nitriles. [b] In acetonitrile containing 0.1% D_2O the yields are unchanged, but compounds **7–9** are replaced by the deuterated analogues **7′–9′**. [c] Molar percentage of ATMS dimerized per mol of ATMS chemically reacting with the nitriles.

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