mL, 40.7 mmol) with cooling at −78 °C in a liquid N_2–EtOH bath. The mixture was stirred at −78 to −60 °C for 30 min, and to the resulting solution was added a solution of *N*-(1,1-dimethylpropargyl)acetamide (1.27 g, 10.1 mmol) in THF (10 mL) at −78 °C. Stirring was continued for 30 min at −78 to −60 °C, and to the mixture was added dropwise a solution of benzaldehyde (2.0 mL, 20 mmol) in THF (10 mL) at −78 °C. The mixture was stirred at −78 to −60 °C for 1 h and at −60 to −20 °C for 4 h. To the mixture was added dropwise acetic anhydride (3.8 mL, 40.3 mmol), and the resulting mixture was stirred at −20 °C for 5 h and then allowed to warm to room temperature. The mixture was poured into aqueous cold 10% tartaric acid (100 mL), the organic layer separated, and the aqueous layer extracted with ethyl acetate (100 mL). The combined organic layers were washed with brine (100 mL), aqueous $NaHCO_3$ (100 mL × 2), dried ($MgSO_4$), and concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2, hexane:AcOEt = 5:1) to give 1.50 g (55%) of **8a** as colorless crystals: mp 85–87 °C (from ether–CH_2Cl_2); IR (KBr) 1738, 1651 cm^{-1}; ^1H NMR (200 MHz) δ 1.67 (s, 6, CH_3), 1.94 (s, 3, CH_3CO), 2.09 (s, 3, CH_3CO), 5.70 (brs, 1, NH), 6.49 (s, 1, CH-O), 7.31–7.43 (m, 3, ArH), 7.48–7.57 (m, 2, ArH); ^{13}C NMR (50 MHz) δ 21.1, 24.1, 28.7 (2 C), 48.0, 65.5, 77.4, 90.6, 127.8 (2 C), 128.6 (2 C), 128.8, 137.0, 169.0, 169.8. Anal. Calcd for $C_{16}H_{19}NO_3$: C, 70.31; H, 7.01; N, 5.12. Found: C, 70.01; H, 7.35; N, 5.12.

4-Acetamido-1-acetoxy-2,2-dibromo-4-methyl-1-phenyl-3-pentanone (10a, X = Br) from 8a by Electrobromination. A side-armed cylindrical vessel (2.5-cm diameter and 10.0-cm height) equipped with a magnetic stirring bar was used for the electrolysis. Into this vessel was placed a solution of propargyl amide **8a** (R^1 = Me, R^2 = Ph, 82.2 mg, 0.30 mmol) in CH_2Cl_2 (5.0 mL), which was covered with aqueous 25% NaBr (10 mL, buffer solution at pH 7 with 3% Na_2HPO_4 and 3% KH_2PO_4). The mixture was electrolyzed with two platinum foil electrodes (3 cm^2) under a constant current density of 20 mA/cm^2 (applied voltage, 2.0 V), and 5 F/mol of electricity was charged. Two layers were separated, and the aqueous phase was extracted with ethyl acetate (20 mL). The combined organic layers were washed with brine, dried ($MgSO_4$), and concentrated under vacuum. The residue was purified by column chromatography (SiO_2, hexane–AcOEt (5:1)) to give 2.1 mg (2.2%) of **9a** (X = Br) and 122.0 mg (90%) of **10a** (R^1 = Me, R^2 = Ph, X = Br). **1-Acetyl-2,2-dimethyl-3-(2-acetoxy-1-bromo-2-phenethylidene)aziridine (9a, X = Br)**: mp 140–141 °C; IR (KBr) 2936, 1744 (CO), 1705 (CO), 1667, 1450, 1383, 1238, 1067, 1025, 969, 698 cm^{-1}; ^1H NMR (200 MHz) δ 1.52 (s, 3, CH_3), 1.58 (s, 3, CH_3), 2.13 (s, 3, CH_3CO), 2.21 (s, 3, CH_3CO), 6.92 (s, 1, CH), 7.36 (m, 5, ArH); ^{13}C (50 MHz) δ 13.9, 21.1, 25.0, 25.2, 71.4, 72.0, 99.6, 126.0 (2 C), 128.0, 128.4 (2 C), 137.7, 159.0, 159.2, 169.5. Anal. Calcd for $C_{16}H_{17}BrNO_3$: C, 54.72; H, 4.88; N, 3.99. Found: C, 54.45; H, 4.29; N, 4.30. **10a** (X = Br): mp 142–143 °C (ethyl acetate); IR (KBr) 3266, 3074, 1760 (CO), 1717 (CO), 1659, 1562, 1373, 1224, 1073, 1025, 787, 706 cm^{-1}; ^1H NMR (200 MHz) δ 1.74 (s, 3, CH_3), 1.78 (s, 3, CH_3), 1.99 (s, 3, CH_3CO), 2.12 (s, 3, CH_3CO), 6.06 (brs, 1, NH), 6.65 (s, 1, CH), 7.35–7.38 (m, 3, ArH), 7.56–7.59 (m, 2, ArH); ^{13}C (50 MHz) δ 20.9, 23.9, 25.8, 26.3, 62.9, 63.0, 78.2, 127.6 (2 C), 129.2, 130.1 (2 C), 134.2, 168.3, 169.1, 196.3. Anal. Calcd for $C_{16}H_{19}Br_2NO$: C, 42.79; H, 4.26; N, 3.12. Found: C, 42.99; H, 4.31; N, 3.05.

Spectral data of the compounds listed in Table II are as follows.

1-Acetyl-2,2-dimethyl-3-(2-acetoxy-1-iodo-2-phenylethylidene)aziridine (9a, X = I): IR (KBr) 3290, 1682, 1636, 1593, 1539, 1450, 1363, 1102, 690 cm^{-1}; ^1H NMR (200 MHz) δ 1.54 (s, 3, CH_3), 1.60 (s, 3, CH_3), 2.13 (s, 3, CH_3CO), 2.21 (s, 3, CH_3CO), 6.62 (s, 1, CH), 7.34 (s, 5, ArH); ^{13}C (50 MHz) δ 13.7, 21.3, 25.6, 27.1, 71.4, 72.6, 74.9, 125.8 (2 C), 127.9, 127.3 (2 C), 138.4, 159.0, 160.5, 169.4.

4-Acetamido-1-acetoxy-2,2-dichloro-4-methyl-1-phenyl-3-pentanone (10a, X = Cl): mp 47–48 °C (from ethyl acetate); IR (KBr) 3390, 1765 (CO), 1731 (CO), 1659, 1537, 1373, 1220 cm^{-1}; ^1H NMR (200 MHz) δ 1.64, 1.70 (s, 6, CH_3), 1.98 (s, 3, CH_3CO), 2.11 (s, 3, CH_3CO), 6.18 (brs, 1, NH), 6.62 (s, 1, CH), 7.34–7.39 (m, 3, ArH), 7.50–7.55 (m, 2, ArH); ^{13}C (50 MHz) δ 20.8, 23.5, 25.3, 25.6, 62.1, 78.0, 85.1, 127.7 (2 C), 129.2, 129.7 (2 C), 133.4, 168.4, 169.2, 197.0.

2-Acetamido-5-acetoxy-4,4-dibromo-2,6-dimethyl-3-heptanone (10b, X = Br): mp 138–140 °C (from hexane); IR (KBr) 3290, 1744 (CO), 1611, 1539, 1468, 1375, 1230, 1044 cm^{-1}; ^1H NMR (200 MHz) δ 0.96, 1.10 (d, J = 6.9 Hz, 6, CH_3), 1.84, 1.86 (s, 6, CH_3), 1.97 (s, 3, CH_3CO), 2.10 (s, 3, CH_3CO), 2.16–3.32 (m, 1, CH), 5.54 (d, J = 3.6 Hz, 3, CHOAc), 6.22 (brs, 1, NH); ^{13}C (50 MHz) δ 18.4, 20.6, 21.0, 22.9, 23.7, 26.6, 27.1, 31.5, 62.8, 64.6, 80.4, 169.2, 169.6, 196.2.

2,5-Dihydroxy-4,4-dibromo-3-hexanone (11). A solution of **2a** (3.74 g, 10 mmol) and concd sulfuric acid (five drops) in aqueous 50% ethanol (100 mL) was heated at reflux for 2 h under Ar. The mixture was concentrated under vacuum and taken up in ethyl acetate (100 mL). The organic layer was washed with 5% sodium hydrogen carbonate and brine, dried (Na_2SO_4), and concentrated under vacuum. The crude products were purified by column chromatography (SiO_2, hexane–AcOEt (1:1)) to give 2.61 g (90%) of **11** as an oil: (nonpolar component) IR (neat) 3322 (OH), 1729 (CO), 1456, 1429, 1373, 1321, 1116, 1077, 936, 870, 785 cm^{-1}; ^1H NMR (500 MHz) δ 1.52 (d, J = 6.2 Hz, 3, CH_3), 1.61 (d, J = 6.5 Hz, 3, CH_3), 2.65 (brs, 1, OH), 2.98 (brs, 1, OH), 4.38 (q, J = 6.2 Hz, 1, CH), 5.11 (q, J = 6.5 Hz, 1, CH); ^{13}C (126 MHz) δ 18.9, 22.6, 69.0, 72.4, 72.6, 201.8; (polar component) IR (neat) 3306 (OH), 1723 (CO), 1454, 1375, 1270, 1110, 1081, 1038, 934, 874, 822 cm^{-1}; ^1H NMR (500 MHz) δ 1.52 (d, J = 6.2 Hz, 3, CH_3), 1.64 (d, J = 6.8 Hz, 3, CH_3), 2.58 (br, 2, OH), 4.36 (q, J = 6.2 Hz, 1 CH), 5.12 (q, J = 6.8 Hz, 1, CH); ^{13}C (126 MHz) δ 18.9, 22.5, 69.6, 72.0, 72.6, 202.3.

4-Hydroxy-2,5-dimethyl-3(2*H*)-furanone (Furaneol, 12). A solution of diol (**11**, 1.02 g, 3.5 mmol) and triethylamine (1.06 g, 10.5 mmol) in ethanol (167 mL) was heated at reflux under Ar for 2 h. The mixture was concentrated under vacuum and dissolved in ethyl acetate (100 mL). The organic layer was washed with brine (10 mL × 2), dried (Na_2SO_4), and concentrated under vacuum. The crude products were purified by column chromatography (SiO_2, hexane–AcOEt (1:1)) to give the furaneol **12** as solid: mp 77–78 °C (lit.[16a] mp 77–79 °C).

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Supplementary Material Available: ^1H or ^{13}C NMR spectrum of **2c**, **2e**, **4f**, **9a** (X = I), **10a** (X = Cl), and **10b** (X = Br) (6 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.

2,2-Dichloro[1.1.1]propellane

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The synthesis and study of strained hydrocarbons has been an active area of organic chemistry for many years.[1] Recently, much attention has been devoted to small-ring propellanes, compounds in which the two bridgehead carbons of a bicyclo[*p.q.r*]alkane ring system are connected by a transanular bond. These compounds have attracted interest both for their unusual structural properties and for their synthetic utility in the generation of a number of novel compounds and materials.[2]

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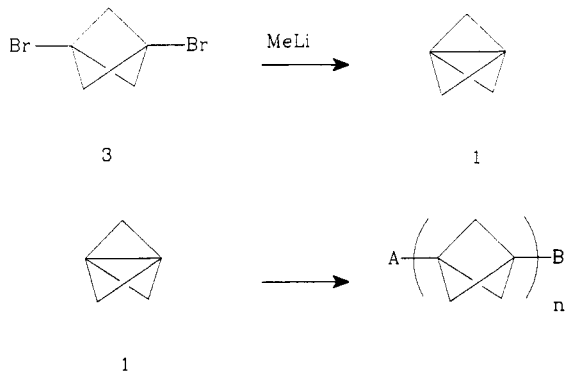
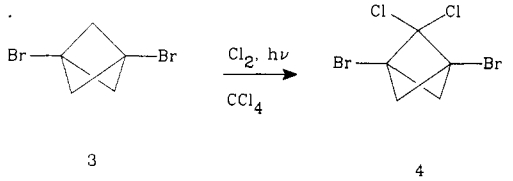
0022-3263/92/1957-5027$03.00/0

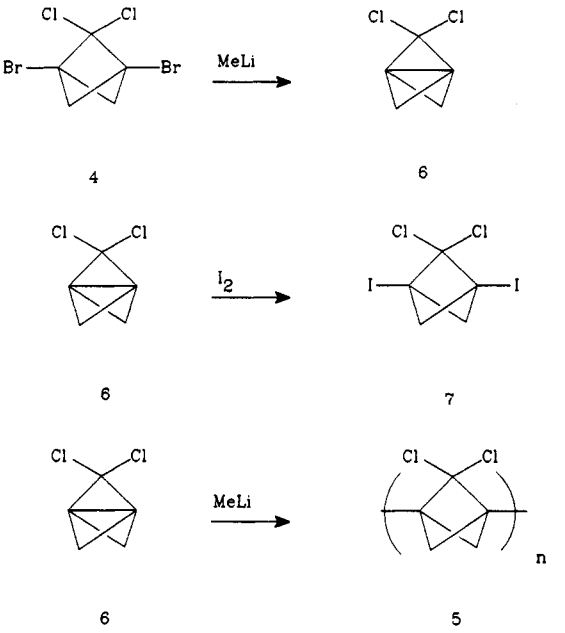
Scheme I



Scheme II



Scheme III



The smallest propellane, [1.1.1]propellane (1), was first prepared by Wiberg and Walker in 1982.[3] This surprisingly stable, highly strained compound has found application in this laboratory as a building block for rigid hydrocarbon rods, called staffanes, whose difunctional derivatives we have proposed for use in a molecular-size "Tinkertoy" construction set (Scheme I).[2c,d,f,4] The ability to substitute these hydrocarbon rods laterally, via functionalization of the bicyclopentane subunits, is essential for the general utility of such a Tinkertoy set. The most convenient precursor for these laterally derivatized staffanes would be substituted [1.1.1]propellanes. Only several alkyl-, vinyl-, and aryl-substituted [1.1.1]propellanes are known,[5,6] and no compounds with other types of substituents have been prepared. Such compounds would allow much greater flexibility in the functionalization of the staffane rods. Additionally, these compounds might have interesting properties in their own right. With this motivation, we attempted the syntheses of halogenated derivatives of [1.1.1]propellane, and here we report the observation of the first member of the series.

Results

Halogenated derivatives of bicyclo[1.1.1]pentane (2) were first prepared by Wiberg and Williams in 1969.[7] They found that incomplete chlorination of the parent 2 with molecular chlorine produced a complex mixture of mono and dichloro derivatives in low yield (11%). Use of larger amounts of chlorine produced polychloro compounds. Some years later it was found that chlorination of several 1,3-disubstituted bicyclo[1.1.1]pentanes could be achieved in high yields by irradiating these compounds and chlorine in either $CFCl_3$ or CCl_4 solutions.[8] In particular, 1,3-dibromobicyclo[1.1.1]pentane was chlorinated to give the dichloro derivative 4 in a yield of over 80% (Scheme II). It appeared likely that debromination of this tetrahalo compound with alkyllithium compounds could lead to 1,1-dichloro[1.1.1]propellane (6) in a reaction analogous to that of the parent 3, which yields 1.[3,9]

We find that the reaction of 4 with 1 equiv of methyllithium at −78 °C followed by room-temperature workup gives only an insoluble polymer. IR spectroscopy indicates its structure to be 5. In particular, an intense peak at 1203 cm^{-1} is assigned to the CH_2 wag, characteristic of bicyclo[1.1.1]pentane cages.[2f,10] Results of a more detailed examination of the polymer will be reported separately. This mode of polymerization would also be consistent with the alkyllithium-induced polymerization of the parent compound 1.[2c] The results indicate that the desired propellane 6 is being formed prior to polymerization.

It would thus appear that a direct observation of 5 might be possible under conditions that avoid excess methyllithium and keep the temperature low. Indeed, mixing a small amount of 4 and methyllithium (0.5 equiv) at −78 °C in THF-d_8 in an NMR tube, followed by immediate transfer to the probe of an NMR spectrometer, showed a spectrum with three absorptions in addition to those of the starting material. These were a sharp singlet at δ 2.64, assigned to MeBr by comparison with the literature value,[11] and two broad singlets of equal intensity at δ 3.06 and 2.26. If the solution was subsequently allowed to stand at room temperature for ca. 0.5 h, the two broad singlets gradually disappeared and numerous unidentified peaks between δ 2 and 5 appeared. However, if a small amount of I_2 was added to the solution prior to warming, the two broad peaks disappeared immediately and another pair of

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(11) Aldrich Catalogue of NMR Spectra, Aldrich Chemical Co. Milwaukee, WI, 1974.

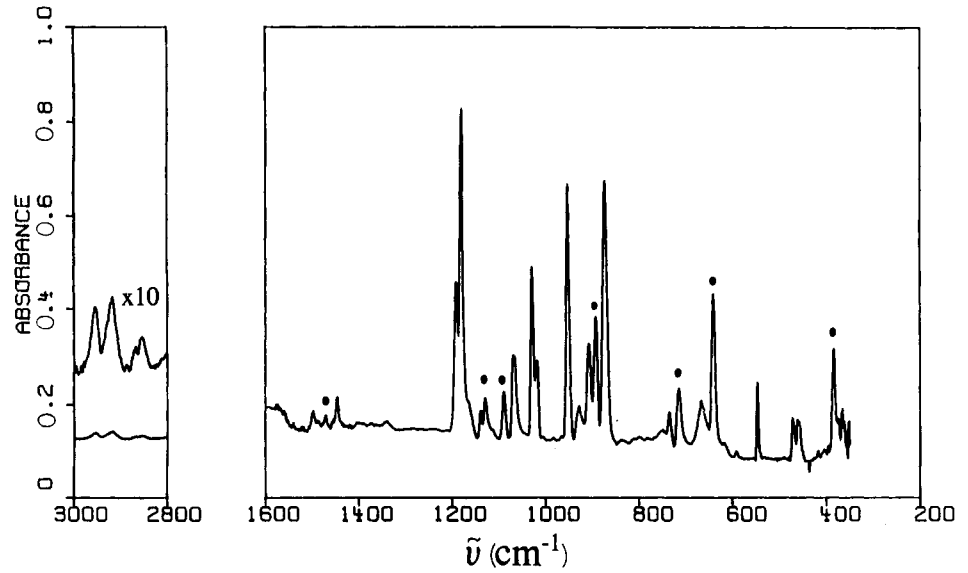

Figure 1. Infrared spectrum of the argon matrix obtained from the reaction of 4 with cesium followed by trapping in an argon matrix at 28 K (● indicates a new peak).

peaks appeared at δ 3.04 and 2.61. The latter belong to a stable product which was isolated and identified as 2,2-dichloro-1,3-diiodobicyclo[1.1.1]pentane (7) (Scheme III). These results are consistent with the assignment of the singlets at δ 3.06 and 2.26 to 6.

Several reactive organic molecules, including some small-ring propellanes, have been generated by the reaction of dihalides with sodium or potassium vapor in the gas phase, followed by trapping in a rare gas matrix.[12] In these experiments it was found that alkyl iodides mixed with potassium vapor gave the best results. It seemed to us that this procedure should convert 3 to 1 and 4 to 6. Since we required the elimination of bromine, we chose to use the more reactive alkali metal cesium in this study. We first attempted to form the parent [1.1.1]propellane (1) by the gas-phase dehalogenation of the dibromo compound 3. As expected, mixing 3 with cesium vapor in a stream of argon at ca. 130 °C, followed by trapping on a CsI window at 28 K, produced an argon matrix which was shown by IR spectroscopy to contain both the starting material and 1. Submitting the dibromo compound 4 to these reaction conditions gave rise to a matrix whose IR spectrum contained several new peaks in addition to starting material (Figure 1). The positions and intensities of these peaks correlated well with those predicted for 2,2-dichloro-[1.1.1]propellane (6) by ab initio calculations (Table I). In particular, the most intense stretch at 642 cm^{-1} seems to be characteristic of the strained propellane ring system; it occurs at 605 cm^{-1} in 1. In light of this agreement, and of the analogy to the behavior of the parent, there is every reason to believe that the new compound formed is 2,2-dichloro[1.1.1]propellane (6). Attempts to isolate it from the argon matrix were unsuccessful, probably due to the small amount and to the thermal instability of 6.

Discussion

The conversion of the dibromide 4 to the propellane 6 promises a wide range of new oligomeric structures, likely to be ultimately useful for our molecular Tinkertoys.

Table I. Calculated (6-31G*HF) and Experimental (Ar Matrix) Infrared Frequencies (Relative Intensities) for 6 (cm^{-1})

calcd	expl	calcd	expl
183 (0.00)	–	1092 (0.27)	1130 (0.44)
275 (0.00)	–	1102 (0.00)	–
291 (0.00)	–	1123 (0.11)	*a*
383 (0.17)	384 (0.67)	1141 (0.10)	*a*
450 (0.03)	–	1149 (0.00)	–
465 (0.01)	–	1188 (0.25)	*a*
576 (0.05)	–	1236 (0.32)	*a*
612 (1.00)	642 (1.00)	1480 (0.00)	–
721 (0.25)	715 (0.44)	1519 (0.03)	1470 (0.11)
761 (0.00)	–	3028 (0.07)	2852 (0.10)
906 (0.69)	893 (0.84)	3032 (0.08)	2917 (0.21)
920 (0.09)	–	3105 (0.00)	–
1007 (0.00)	–	3107 (0.02)	–
1028 (0.18)	1089 (0.40)		

[a] Obscured by the starting material.

The close agreement of the observed and calculated IR spectra is gratifying. The assignment of the vibrations involves no surprises, and the similarity to the parent 1 is obvious. The features of the proton NMR spectrum of 6 are also consistent with our expectations. The broad singlets due to unresolved couplings are similar to those observed for 2,2-dichlorobicyclo[1.1.1]pentanes, as are the chemical shifts.[8]

The calculated geometry of 6 also compares closely with that calculated for 1 at the same level of approximation.[13] The central bond in 1 has a calculated length of 1.544 Å, vs 1.559 Å in compound 6. The other calculated bond lengths in 6, 1.502 Å (C1–C2) and 1.506 Å (C1–C4), are also as expected, with C1–C3 being slightly shorter and C1–C4 being slightly longer than the corresponding bond in 1, 1.503 Å (C1–C2). The H–C–H bond angles are calculated to be somewhat smaller in 6 than in 1, 114.7° vs 118.7°, respectively. This reflects the close interaction between the chlorine and the hydrogen on the neighboring carbon atom (2.540 Å).

Our inability to convert 4 into 6 with methyllithium in greater than 50% yield is not surprising. One would expect 6 to be more reactive toward addition of alkyllithium

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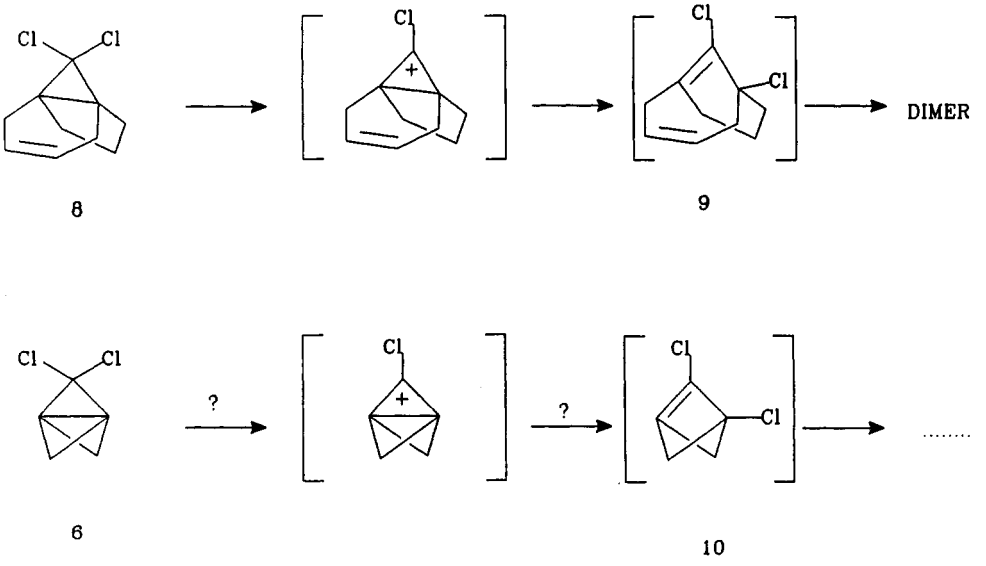
Scheme IV



compounds than the parent 1 due to the stabilizing effect of the chlorines on the intermediate bridgehead anion. More unexpected than the reactivity of **6** toward methyllithium is its thermal instability in THF solution in the absence of excess methyllithium. The radical intermediates usually associated with spontaneous polymerization of propellane should be destabilized by the substitution of chlorine on the bridges. Actually, the disappearance is clearly not due entirely to a clean polymerization to a bicyclo[1.1.1]pentane-based polymer and seems to yield a complex mixture. One possible explanation for these results is suggested in Scheme IV. It is based on analogy to the proposed mechanism of the spontaneous rearrangement of 9,9-dichloro[4,3,1]propell-3-ene **8** to the bridgehead olefin **9**,[14] which is complete within a few minutes in polar solvents. The rearrangement of **6** could yield **10**, but one might also envision other modes of decomposition of the intermediate cation. Force field calculations suggest similar strain in compounds **9** and **10** (OS = 21.6 and 21.0, respectively),[15] so that the formation of the remarkable structure **10** is not totally unrealistic. A halogenated [1.1.1]propellane has been proposed as a possible starting material for a bridgehead olefin such as **10**.[16]

Experimental Section

General. Compounds **3**[9] and **5**[8] were prepared by literature procedures. Matrix isolation was done with an Air Products CSA-202 Displex closed-cycle cryostat equipped with two CsI windows, one quartz window, and a gas inlet on the vacuum shroud. Argon was deposited onto a CsI window cooled to 28 K at a rate of ca. 0.2 mmol/min through a needle valve. Vacuum was maintained at 10^{-5}–10^{-6} Torr. After the matrices were cooled to 12 K, IR spectra were measured on a Nicolet 60-SX, 510, or 800 spectrophotometer. NMR spectra were taken on either a Bruker WP-250 or a Varian 300 spectrometer. Solvents were purified by standard procedures.[17]

Reaction of 4 with 1 equiv of Methyllithium (Room-Temperature Workup). Formation of Poly-2,2-dichloro[1.1.1]propellane (5). Compound **4** (0.041 g, 0.14 mmol) was dissolved in 1 mL of dry ether. The resulting solution was cooled to −78 °C, and 0.1 mL of 1.4 M MeLi in ether was added. The solution was stirred for 1.5 h and warmed to room temperature. This produced a white precipitate. No volatile material was detected by gas chromatographic analysis of the remaining solution. The precipitate was washed with ether and then water and then dried to give 0.016 g (85%) of a polymer: IR (KBr) 3020 (s), 2973 (s), 2924 (s), 2871 (m), 1203 (s), 1016 (s), 904 (s), 973 (m) 849 (vs) cm^{-1}.

Reaction of 4 with 0.5 equiv of Methyllithium at −78 °C and Trapping of 6 with I_2. 2,2-Dichloro-1,3-Diiodobicyclo-[1.1.1]pentane (7). Compound **4** (0.084 g, 0.28 mmol) was dissolved in 5 mL of dry ether. The solution was cooled to −78 °C, and 0.2 mL of 1.4 M MeLi in ether was added. The resulting solution was stirred an additional 30 min and then warmed to −30 °C for 5 min. The solution was again cooled to −78 °C, and I_2 (0.100 g, 0.39 mmol) in 1 mL of ether was added, followed by warming to room temperature. GC analysis of the resulting mixture showed equal amounts of two compounds, the starting material **4** and compound **7**. The latter was isolated as a colorless solid by preparative GC (1.5 ft 25% carbowax column, 80 °C to 175 °C) in 18% yield: IR (neat) 2971 (w), 2955 (w), 1182 (s), 1022 (m), 928 (s), 884 (s) cm^{-1}; ^1H NMR (250 MHz; $CDCl_3$) δ 3.04 (dd, J = 1.57, 0.72 Hz), 2.61 (dd, J = 1.57, 0.72 Hz) ppm; ^{13}C NMR (50 MHz, $CDCl_3$) δ 98.50, 60.38, 13.04 ppm; EIMS m/z 261 (M^+ − I), 225, 186, 165, 134 (M^+ − 2I), 127 (I^+), 99, 73. Anal. Calcd for $C_5H_4Cl_2I_2$: C, 15.45; H, 1.04; Cl, 18.28; I, 65.28. Found: C, 15.55; H, 1.05; Cl, 18.29; I, 65.03.

Reaction of 4 with Methyllithium at −78 °C. NMR Observation of 2,2-Dichloro[1.1.1]propellane (6). Methyllithium (0.1 mL, 1.4 M) was placed in a screw-cap NMR tube, and the ether was removed by first passing a stream of dry nitrogen over it followed by brief exposure to vacuum. THF-d_8 was added, giving a clear solution. The solution was then cooled to −78 °C, and a solution of compound **4** (0.025 g, 0.08 mmol) in 0.5 mL of THF-d_8 was added slowly. The sample was placed in the probe of an NMR spectrometer, and spectra were taken while it was allowed to warm to room temperature. The NMR spectrum showed three new absorbances, a sharp singlet at δ 2.64, assigned to MeBr, and two broad singlets of equal intensity at δ 3.06 and 2.26. Addition of a small crystal of I_2 caused the immediate disappearance of the two broad singlets and gave rise to the spectrum of compound **7**. If the I_2 was not added, the two broad peaks disappeared in ca. 0.5 h, giving rise to numerous very small peaks between δ 2 and 5.

Reaction of Compound 4 with Cs in the Gas Phase: Observation of 6 by FTIR in an Argon Matrix. The reaction vessel was similar to those previously described.[12] The reaction zone consisted of a 1-in.-diameter glass tube about 5 in. long which was wrapped in heating tape and heated to ca. 130 °C. The temperature was monitored with a thermocouple mounted under the heating tape in the middle of the tube. Compound **4** was

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sublimed at room temperature into the hot zone, concurrent with Cs, which was held at a temperature of ca. 100–110 °C. Argon flow was controlled by a needle valve (0.2 mmol/min). The mixture deposited onto a CsI window held at 28 K. The matrices were a transparent, deep-sea blue.

Reaction of Compound 3 with Cs in the Gas Phase: Observation of 1 by FTIR in an Argon Matrix. This reaction was carried out in essentially the same manner as with 4, the main difference being that the dibromo compound 3 was mixed with the argon in a 500:1 ratio prior to deposition.

Computations. Ab initio SCF calculations were carried out on IBM RS-6000/540 and 6000/550 computers using the GAUSSIAN 88 and GAUSSIAN 90 program.[5,18,19] Calculation of the IR frequencies were done at the restricted Hatree–Fock level on optimized geometries, using a 6-31G* basis set. The standard 0.9 multiplicative correction factor was used.

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Trimethylsilyl Trifluoromethanesulfonate Mediated Dialkylcuprate Addition to Epoxy Esters: An Unusual Intramolecular Transesterification Process

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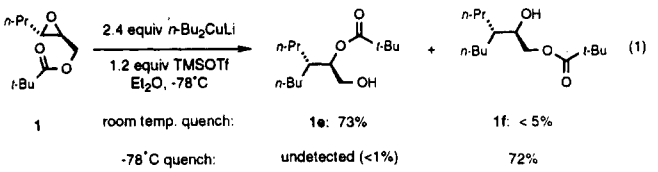
Epoxides are important starting materials and intermediates in organic synthesis because of their ready access and their high reactivity toward nucleophiles. The emergence of the Sharpless epoxidation procedure has increased the importance of these electrophiles by providing a route to 2,3-epoxy alcohols of high enantiomeric purity.[3] Development of synthetic methods allowing regioselective ring opening of 2,3-epoxy alcohols by a wide range of nucleophiles further enhances the utility of epoxides in organic synthesis.[4] While investigating the regiochemistry of Lewis acid promoted organocuprate addition to trimethylacetate-protected 2,3-epoxy alcohols,[5] we encountered an intriguing reaction providing products in which an unusual migration of the ester moiety[6] had occurred following the regiospecific addition of the cuprate to C-3 of 2,3-epoxy alcohol pivaloylates. Further investigation of this unexpected result has shown that this reaction is synthetically useful and provides a convenient protocol for the direct, regioselective preparation of an important class of monoprotected 1,2-diols that are only difficulty accessed by more traditional means.

At the outset of our investigations *trans*-3-propyloxiranemethanol trimethylacetate (1) was added to a solution of Bu_2CuLi/TMSOTf (2.4:1.2 equiv relative to 1) in Et_2O at −78 °C. After stirring for 30 min at −78 °C and then at room temperature for 30 min, the reaction was quenched with aqueous NH_4Cl/NH_4OH (10:1). Utilizing this protocol 1e was isolated as the major product, with the ester moiety residing on the secondary carbon. The transesterification was shown to be under thermodynamic control as the "unrearranged" addition product (1f) predominated when the reaction was quenched at −78 °C (eq 1).



(1)

The selectivity for acylation of the secondary alcohol in preference to the primary alcohol is reminiscent of the dibutyltin-promoted monoacylation of 1,2-diols reported previously by Roelens and co-workers.[7] However, given the uncertainty of the role that the trialkylsilyl triflates play in the present reaction,[8] a mechanistic rationale for the observations reported is difficult. It would seem reasonable that the usual intramolecular acyl migration through a dioxolanyl intermediate is operational in these transformations.[6,9] Thus, the primary alkoxide generated in this equilibrium process could be preferentially trapped by an electrophile (R_3SiOTf), shutting down the intramolecular acyl migration and leaving the carboxylate at the secondary alcohol center. However, all efforts to trap silyl ether products have failed, even in those instances where t-$BuMe_2SiOTf$ was utilized as the electrophile under conditions where these protected alcohols were stable.[10] Consequently, no evidence exists to document such a proposed mechanism.

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(10) For example, the reaction of 1 with Me_2CuLi/t-$BuMe_2SiOTf$ provides 57% of 1a and <5% of 1b. Furthermore, we have found that the *tert*-butyldimethylsilyl-protected alcohol of 1a is stable to the reaction and workup conditions for this reaction. Thus, a sample of this protected alcohol was recovered to the extent of 86% when it was present during the reaction between substrate 1 and Me_2CuLi/t-$BuMe_2SiOTf$. Products 1a and 1b were isolated in similar yields regardless of the presence (or absence) of the *tert*-butyldimethylsilyl-protected form of 1a.

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