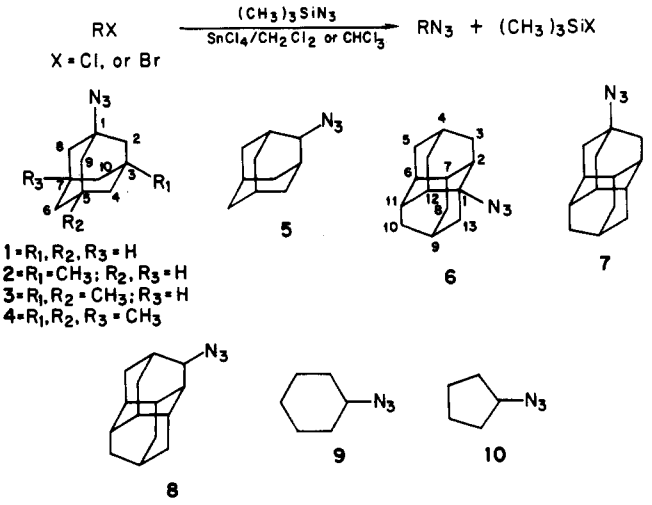

solvent to provide the corresponding azides. However, the reaction does not proceed with unactivated alkyl halides. We have found now in our studies that polycyclic adamantyl,[20] diamantyl related halides and cyclic cyclohexyl and cyclopentyl halides react with trimethylsilyl azides under stannic chloride catalysis to give the corresponding azides in moderate to excellent yields (Table I).

The reaction works well with both tertiary bridgehead as well as with secondary halides. This is significant, since secondary hydroxy compounds do not give the secondary azides directly using the NaN_3/H_2SO_4 method.[3] The presently developed procedure to prepare polycyclic and cyclic azides using readily available trimethylsilyl azide is superior to other existing methods for its convenience, good yields, and general applicability to both secondary and tertiary systems.

Experimental Section

To a stirred solution of the polycyclic or cyclic halide and trimethylsilyl azide[23a] (relative ratios in Table I) in 50 mL of dry dichloromethane or chloroform under nitrogen at 0 °C is added stannic chloride[23b] catalyst (see table for the exact amount). After the addition, the mixture was brought to room temperature followed by prolonged stirring or reflux for the stipulated period of time (Table I). After the reaction was complete the mixture was quenched with ice–water (100 mL) followed by methylene chloride or chloroform extraction (2 × 100 mL). The organic layer was dried over anhydrous $MgSO_4$ and evaporated to obtain the crude azide. The crude azide was further purified, when necessary, on a silica gel column using hexane–dichloromethane eluent (20:1) or fractional distillation. The purity of the product azide was confirmed by ^{13}C NMR (Table I), IR, and melting point measurement.

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Registry No. 1, 24886-73-5; 2, 102852-44-8; 3, 63534-29-2; 4, 63534-32-7; 5, 34197-88-1; 6, 87999-44-8; 7, 87999-45-9; 8, 102920-05-8; 9, 19573-22-9; 10, 33670-50-7; Me_3SiN_3, 4648-54-8; $SnCl_4$, 7646-78-8; 1-bromoadamantane, 768-90-1; 1-bromo-3-methyladamantane, 702-77-2; 1-bromo-3,5-dimethyladamantane, 941-37-7; 1-bromo-3,5,7-trimethyladamantane, 53398-55-3; 2-bromoadamantane, 7314-85-4; 2-chloroadamantane, 7346-41-0; 1-bromodiadamantane, 30545-17-6; 4-bromodiadamantane, 30545-30-3; 3-bromodiadamantane, 30545-30-3; bromocyclohexane, 108-85-0; bromocyclopentane, 137-43-9.

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(23) (a) Purchased from Petrarch Systems Inc., Bristol, PA 19007. (b) Purchased from Alfa Products, Danvers, MA 01923.

Nucleophilic S_N2 Displacements on (Pivaloyloxy)methyl 6α-[(Fluorosulfonyl)oxy]penicillanate

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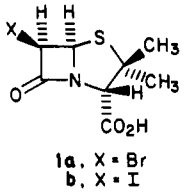
Since the discovery that 6β-bromo-[2,3] (**1a**) and 6β-iodopenicillanic acid[3,4] (**1b**) are inhibitors of β-lactamase enzymes, the synthesis of penicillanic acid derivatives with simple substituents in the 6β-orientation has become an area of considerable interest. Three principal routes for



1a, X = Br
b, X = I

preparing 6β-halopenicillanic acids have been explored: (i) epimerization by base of 6α-halopenicillanic acids (Br, Cl or I);[2,5,6] (ii) selective reduction by Bu_3SnH of 6,6-dibromopenicillanic acid[5] and its benzyl[7] and trimethylsilyl esters[8] and nucleophilic S_N2 displacement on penicillin 6-triflates or nonaflates with the soft nucleophiles iodide, bromide, and chloride, among others, leading to the 6β- or 6α-halopenicillanates.[4,9] However, in all the methods, the reported overall yields were poor.

We have recently begun to study the chemistry of the 6-position of penicillin,[10] and here we report a simple and efficient synthesis of three (pivaloyloxy)methyl (Pom) 6β-halopenicillanates **3a–c** by S_N2 nucleophilic displacement on Pom 6α-[(fluorosulfonyl)oxy]penicillanate (**2**).

It has been reported that fluorosulfonate is a very good leaving group,[11,12] and, moreover, we have found that this group can be conveniently and stereospecifically introduced at the 6α-position by a single step procedure in a reasonable yield (60%) by treatment of Pom 6β-aminopenicillanate with *tert*-butyl nitrite and fluorosulfonic acid in methylene dichloride. 6α-[(Fluorosulfonyl)oxy]-penicillanate (**2**) gave the 6β-halopenicillanates **3a–c** in high yields (better than 90%) upon treatment with 1.0 equiv of tetrabutylammonium halide (Cl^-, Br^-, and I^-) in THF (Scheme I). However, attempts to convert **2** into the corresponding 6β-fluoropenicillanate employing tetrabutylammonium fluoride (TBAF)[13,14] under the same

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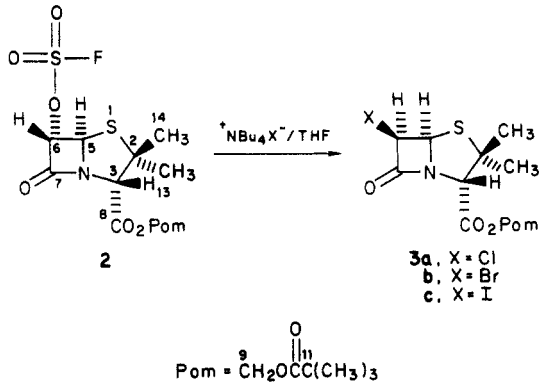
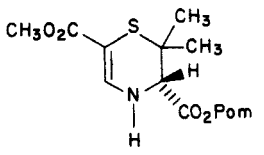
Scheme I



conditions led only to starting material. The same result was obtained when **2** was treated with TBAF/SiO_2[15] in THF or Amberlyst A-26 (F^-)[16] in refluxing benzene for 15 h. Longer periods of heating or higher temperatures resulted in an intractable mixtures of products. The use of KF–18-crown-6 complex,[17] dissolved in $CHCl_3$ with the aid of CH_3OH, led to the corresponding dihydrothiazine **4**



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through a well-established rearrangement process[4,18] initiated by attack of the hard methoxide or fluoride nucleophiles on the hard carbonyl group of the penam nucleus. The failure of these displacement reactions are presumably due to the fact that "naked" fluoride is harder[19] than other nucleophiles used successfully[4,9] and a rather strong base.

The Pom 6β-chloro- and 6β-iodopenicillanates (**3a** and **3c**) are quite stable and samples have been stored for one month at 0 °C without significant decomposition. In contrast, the Pom 6β-bromopenicillanate (**3b**) is less stable and decomposes in the atmosphere after 2 h at 20 °C or after 30 min in concentrated chloroform solution.[20]

The structures assigned to 6α-[(fluorosulfonyl)oxy]-penicillanate **2**, 6β-halopenicillanates **3a–c** and dihydrothiazine **4** are consistent with their spectroscopic data. The ^{1}NMR spectra of **2** and **3a–c** show H(5)–H(6) coupling constants of 1.6 and 4.0 Hz, respectively, consistent with the presence of a trans- or a cis-substituted β-lactam.[21] The assignment of the ^{13}C NMR signals was carried out by using the APT pulse sequence,[22] specific decoupling experiments, and correlation with related compounds. The low-resolution mass spectra of 6α-[(fluorosulfonyl)oxy]-penicillanate **2** shows, in addition to the ion arising from the known fragmentation pattern,[23] peaks at m/e 57 and 85 characteristic of the *tert*-butyl moiety and at m/e 330 (M-SO_2F) for a fragment that includes the β-lactam and thiazolidine rings.

Experimental Section

IR spectra were taken on a Beckman Acculab 8 Spectrometer. ^{1}H and ^{13}C NMR spectra were taken on a Bruker WP 80 SY at 80.13 and 20.15 MHz, respectively, and chemical shifts are expressed in parts per million downfield from internal tetramethylsilane. Low-resolution mass spectra (electron impact, 70 eV) were obtained with a Varian MAT 112 S. Silica gel 60 H (Merck) was utilized for column chromatography and silica gel GF_{254} (Type 60 Merck) for TLC. Spots were visualized by staining with anisaldehyde–sulfuric acid.[24]

(Pivaloyloxy)methyl 6β-Aminopenicillanate. A previously described procedure[25] was used to prepare this compound.

(Pivaloyloxy)methyl 6α-[(Fluorosulfonyl)oxy]-penicillanate (2). To a cooled solution (0 °C) of 0.485 g (1.5 mmol) of (pivaloyloxy)methyl 6β-aminopenicillanate in dry CH_2Cl_2 (50 mL) was added, dropwise, 0.36 mL (3.0 mmol) of freshly prepared *tert*-butyl nitrite. Then, a solution of fluorosulfonic acid (0.18 mL, 3.0 mmol) in 1.0 mL of dry CH_2Cl_2 was added at 0 °C. The reaction mixture was stirred at 0 °C for 30 min, neutralized with cold sodium bicarbonate solution, decanted, and washed with brine (20 mL). The organic layer was dried over sodium sulfate. The oil obtained upon removal of the solvent under reduced pressure was chromatographed on a short silica gel column, under a low pressure of nitrogen with $CHCl_3$, to afford 0.381 g (60%) of compound **2** as an oil. This material was one spot on TLC: R_f 0.5 ($CHCl_3$); IR (film) 1800 (β-lactam); 1760 and 1740 (ester) cm^{-1}; ^{1}H NMR ($CDCl_3$) 1.22 (s, 9 H), 1.51 (s, 3 H), 1.60 (s, 3 H), 4.59 (s, 1 H), 5.50 (asymmetrical d, 1 H, C-5 H, J = 1.6 Hz), 5.54 (tight m, 1 H), 5.78 (d, 1 H, C-9 H, AB system, J = 5.6 Hz), 5.88 (d, 1 H, C-9 H, AB system, J = 5.6 Hz); ^{13}C NMR ($CDCl_3$) 176.6 (C-10), 165.1 (C-8), 161.6 (C-7), 89.0 (C-5), 79.8 (C-9), 69.0 (C-3), 68.2 (C-6), 64.5 (C-2), 38.7 (C-11), 33.6 (C-14), 26.7 (C-12), 25.1 (C-13); mass spectrum, m/e (relative intensity) 330 (10.3), 254 (3.5), 199 (15), 114 (26.4), 85 (59.8), 57 (100).

6β-Halopenicillanate Preparation. General Procedure. A solution containing 0.2 mmol of compound **2** and 0.2 mmol of tetrabutylammonium halide in 3.0 mL of dry THF was stirred at 45 °C for 5 h. The solvent was removed under reduced pressure, and the crude residue was chromatographed on a short silica gel column with $CHCl_3$ as the eluant to give pure 6β-halopenicillanate.

3a: 94% yield, oil; R_f 0.27 ($CHCl_3$); IR (KBr) 1805 (β-lactam), 1780 and 1765 (ester) cm^{-1}; ^{1}H NMR ($CDCl_3$) 1.22 (s, 9 H), 1.50 (s, 3 H), 1.66 (s, 3 H), 4.52 (s, 1 H), 5.22 (d, 1 H, J = 4.0 Hz), 5.60 (d, 1 H, J = 4.0 Hz), 5.78 (d, 1 H, C-9H, AB system, J = 5.6 Hz), 5.86 (d, 1 H, C-9 H, AB system, J = 5.6 hz); ^{13}C NMR ($CDCl_3$) 176.6 (C-10), 168.8 (C-7), 166.0 (C-8), 79.7 (C-9), 70.3 (C-5), 68.5 (C-3), 64.1 (C-2), 60.3 (C-6), 38.7 (C-11), 31.8 (C-14), 26.8 (C-12), 26.2 (C-13).

3b: 95% yield, oil; R_f 0.20 ($CHCl_3$); ^{1}H NMR ($CDCl_3$) 1.22 (s, 9 H), 1.50 (s, 3 H), 1.67 (s, 3 H), 4.54 (s, 1 H), 5.33 (d, 1 H, J = 4.0 Hz), 5.56 (d, 1 H, J = 4.0 Hz), 5.78 (d, 1 H, C-9 H, AB system, J = 5.6 Hz), 5.85 (d, 1 H, C-9 H, AB system, J = 5.6 Hz).

3c: (prepared analogous to the general procedure except that the reaction mixture was stirred for 15 h) 90% yield, oil; R_f 0.35 ($CHCl_3$); IR (film) 1780 (br and 1760 cm^{-1}; ^{1}H NMR ($CDCl_3$) 1.21 (s, 9 H), 1.48 (s, 3 H), 1.70 (s, 3 H), 4.54 (s, 1 H), 5.37 (d, 1 H, J = 4.0 Hz), 5.62 (d, 1 H, J = 4.0 Hz), 5.78 (d, 1 H, C-9 H, AB system, J = 5.6 Hz), 5.85 (d, 1 H, C-9 H, AB system, J = 5.6 Hz); ^{13}C NMR ($CDCl_3$) 176.5 (C-10), 168.9 (C-7), 166.1 (C-8), 79.6 (C-9), 70.8 (C-5), 67.8 (C-3), 65.0 (C-2), 38.6 (C-11), 31.9 (C-14), 26.7 (overlapped C-6 and C-12), 25.9 (C-13).

(Pivaloyloxy)methyl 3,4-Dihydro-6-(methoxycarbonyl)-2,2-dimethyl-2*H*-1,4-thiazine-3-carboxylate (4). Powdered KF (0.010 g, 0.17 mmol) and 18-crown-6 (0.047 g, 0.17 mmol) were

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placed in a dry 10-mL flask equipped with a rubber stopper and magnetic stirrer. The flask was evacuated and flushed with dry N_2 several times, and $CHCl_3$ (3.0 mL) was introduced by means of a syringe. The suspension was stirred for 2 h and, after the addition of 2 drops of methanol, became a clear solution. The solvent was evaporated in vacuo, and the oily residue was dissolved in 2 mL of dry $CHCl_3$. This solution was added dropwise to a chloroform solution (5 mL) of 0.10 g (0.26 mmol) of compound 2 at room temperature and the mixture was stirred for 5 h. After the reaction was complete (TLC), the solvent was evaporated in vacuo, and the residue was purified by flash chromatography on a silica gel column using AcOEt–hexane (50:50) and affording a quantitative yield of 4 (0.083 g) as white crystals: mp 145–146 °C; R_f 0.19 ($CHCl_3$); IR (KBr) 3415, 2985, 1805, and 1760 cm^{-1}; ^1H NMR ($CDCl_3$), 1.22 (s, 12 H), 1.51 (s, 3 H), 3.73 (s, 3 H), 4.03 (d, 1 H, J = 1.6 Hz), 5.20 (br s, 1 H), 5.75 (d, 1 H, C-9 H, AB system, J = 5.6 Hz), 5.94 (d, 1 H, C-9 H, AB system, J = 5.6 Hz), 7.63 (d, 1 H, J = 6.4 Hz); mass spectrum, m/e (relative intensity) 345 (M^+, 2), 85 (25), 57 (100).

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Registry No. 2, 81658-78-8; 3a, 74772-34-2; 3b, 74772-33-1; 3c, 74772-35-3; 4, 102871-09-0; (pivaloyloxy)methyl 6β-aminopenicillanate, 25031-08-7.

A Silver Ion Catalyzed [3.1.1]Propellane Rearrangement. 2,4-Methano-2,4-didehydroadamantane Retro-Carbene Ring Opening

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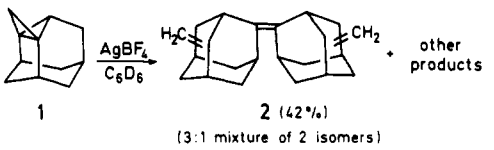
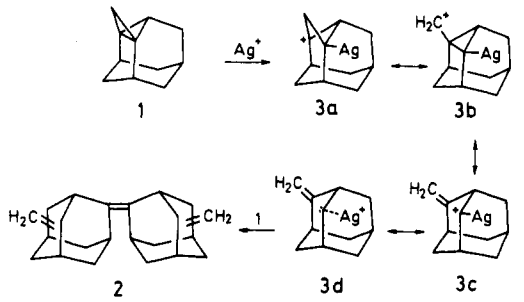
We report the first silver ion catalyzed retro-carbene rearrangement of a carbocyclic [3.1.1]propellane: 2,4-methano-2,4-didehydroadamantane (1).

Propellane 1 was readily prepared by an intramolecular cycloaddition of 4-methylene-2-adamantylidene to the olefinic bond.[1] It was thermally stable and completely inert toward nucleophiles but highly reactive toward electrophiles and free radicals.[1] This was explained by a high electron density at the reaction site, i.e., at the backside of the inverted carbon atoms, and a decrease in electron density between them. Such an electron density distribution in the central bond of 1 is in accord with theoretical considerations,[2] and X-ray,[3] vibrational,[4a] and electron-diffraction[4b] analyses, as well as with chemical

Scheme I



Scheme II



behavior of other small propellanes.[5-8] Hence, small propellanes should readily interact with transition metals having high electron affinities.

Transition metal catalyzed reactions of small propellanes have been only sparingly studied,[5,6,9] although such reactions of other small-ring organic molecules have been subjects of numerous investigations.[10] In the early 1970s, Gassman and Armour[9] reported a rearrangement of the parent [3.2.1]propellane to a mixture of diolefins, 4- and 5-methylenecycloheptenes, catalyzed by iridium, rhodium, or ruthenium chlorocarbonyl complexes. Recently, Szeimies and Szeimies-Seebach reported ring openings of a carbocyclic [4.1.1]propellane[5,6] and an oxa[3.1.1]propellane[6] to the structurally related conjugated diolefins catalyzed by silver ion or rhodium, palladium, or copper complexes. The same products were formed by the propellane thermolyses, presumably, via the respective carbene intermediates.

The main purpose of this investigation was to provide a further insight into the specific electron distribution in

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