partitioned between Et_2O and H_2O. Combined Et_2O extracts were washed with 1 N $NaHCO_3$ (4 × 50 mL) and with H_2O and were dried ($MgSO_4$) and filtered. Evaporation of solvent followed by distillation of the oily residue (1.28 g) gave **2** (1.10 g, 52%), bp 135–145 °C at 0.4 mm. Chromatography over silica gel and elution with $CHCl_3$–hexanes (60:40) gave a purer sample: IR 2950 s, 1950 w (C≡C), 1730–1720 s (ester CO), 1220 br s (CO_2CH_3), 1180–1160 br s (CO_2CH_3); ^1H NMR 7.30 (br s, 5 H, Ar), 3.65 (s, 3 H, -OCH_3), 3.57 (m, 2 H, -C$H_2C_6H_5$), 2.47 (m, 2 H, -C$H_2CO_2CH_3$), 2.25 (m, 2 H, -CH_2C≡C-), 1.90 (m, 2 H, -CH_2-); MS, 216 (1, M^+), 105 (100).

Anal. Calcd for $C_{14}H_{16}O_2$ (M^+): 216.1150. Found: 216.1144.

IR, ^1H NMR, and mass spectra as well as side-by-side and co-spotted thin-layer chromatograms of **2** were compared with those of an authentic sample. Comparisons showed the samples to be identical.

B. From Benzylation and Hydrolysis of 6,6,6-Trimethoxy-1-hexyne. Benzylation of **5**[12] and hydrolysis of the product also gave **2** as follows.

A mixture of **5** (1.34 g, 7.80 mmol) and CuI (0.670 g, 3.50 mmol) in dry THF (8 mL) was cooled to −70 °C under dry N_2. *n*-Butyllithium (7.76 mmol from a 1.15 M solution in hexanes) was added slowly. After 30 min at −70 °C, benzyl chloride (0.854 g, 6.70 mmol) in THF (8 mL) was added. After refluxing 5 h, the cooled reaction mixture was poured into cold H_2O (200 mL). Et_2O (200 mL) was added, and the mixture was filtered. Layers of the filtrate were separated, and the aqueous layer was extracted with Et_2O. Combined Et_2O solutions were dried ($MgSO_4$) and evaporated to give crude 7-phenyl-1,1,1-trimethoxy-5-heptyne (1.94 g): IR 2940 s, 2825 s, 2190 w (C≡C), 1100 s (COC); ^1H NMR 7.25 (s, 5 H, Ar), 3.53 (m, 2 H, -C$H_2C_6H_5$), 3.21 (s, 9 H, -OCH_3), 2.25 (m, 2 H, -CH_2C(OMe)$_3$), 1.8 (m, 2 H, -CH_2C≡C-), 1.53 (m, 2 H, -CH_2-). The product was used directly in the next step.

A solution of 7-phenyl-1,1,1-trimethoxy-5-heptyne (1.70 g, 6.50 mmol), pyridinium *p*-toluenesulfonate (80.4 mg), and MeOH (25 mL) was heated 40 min at 40 °C, after which solvent was evaporated. Distillation of the residue (1.4 g) gave **2** (53%), bp 105 °C at 0.2 mm, pure according to TLC and to ^1H NMR spectroscopy.

7-Phenyl-5-heptynoic Acid. Saponifications (1 equiv of KOH, H_2O, MeOH, 3 h at 20 °C of **2** followed by standard workups gave the desired acid (79%) as a semisolid: IR 3470 and 2940–2900 (OH), 1945 (C≡C), 1700 br s (CO_2H); ^1H NMR 10.0 (br s, 1 H, ex, -CO_2H), 7.33 (br s, 5 H, Ar), 3.56 (br t, 2 H, -C$H_2C_6H_5$), 2.52 (t, J = 6, 2 H, -CH_2CO_2H), 2.32 (m, 2 H, -CH_2C≡C), 1.92 (m, 2 H, -CH_2-); MS, 202 (5, M^+), 91 (100, $C_7H_7^+$).

Anal. Calcd for $C_{13}H_{14}O_2$ (M^+): 202.0933. Found: 202.0981.

2-Benzyl-3-[[(4-methylphenyl)sulfonyl]hydrazino]cyclohex-2-en-1-one (3). A mixture of 2-benzyl-1,3-cyclohexanedione (17.25 g, 82.5 mmol),[1] (*p*-toluenesulfonyl)hydrazine (16.25 g, 0.880 mmol), concentrated HCl (1 mL), and MeOH (290 mL) was allowed to stand 60 h at 25 °C. The mixture was treated with charcoal, filtered, and concentrated. A solution of the residue in $CHCl_3$ was also filtered, and $CHCl_3$ was then evaporated. The oily residue crystallized on trituration with Et_2O, and the crystals were collected, washed with Et_2O, and dried to give impure **3** (26.1 g, mp 122–125 °C). Several crystallizations from MeOH gave pure **3** (15.8%), mp 172.5–173.5 °C; IR (mineral oil) 3350 (NH), 1568 (CO), 1330, 1300, 1160; ^1H NMR (Me_2SO-d_6): 9.73 and 8.14 (2 NH, ex), 7.43 (d, 2 H, J = 7.5, Ar), 7.30 (d, 2 H, J = 7.5, Ar), 7.17 (m, 5 H, Ar), 3.5 (s, 2 H, -C$H_2C_6H_5$), 2.38 (s, 3 H, -$C_6H_4CH_3$), 2.14 (m) and 1.67 (m) (total of 6 H); MS, 370 (10, M^+), 215 (100, M − $SO_2C_6H_4CH_3$), 185 (14, M − NHNHS$O_2C_6H_4CH_3$).

Anal. Calcd for $C_{20}H_{22}N_2O_3S$: C, 64.84; H, 5.99; N, 7.56; S, 8.65. Found: C, 64.71; H, 6.13; N, 7.69; S, 8.74.

2-Benzyl-3-[[(4-methylphenyl)sulfonyl]hydrazino]cyclohex-2-en-1-one [(4-Methylphenyl)sulfonyl]hydrazone. Initial filtration of the MeOH reaction mixture from which **3** was obtained (vide supra) gave a byproduct (1.33 g, 2.9%), mp 192–195 °C.

Anal. Calcd for $C_{27}H_{30}N_4S_2O_4$: C, 60.20; H, 5.61; N, 10.40; S, 11.90. Found: C, 60.18; H, 5.35; N, 10.23; S, 12.04.

3-[[(4-Methylphenyl)sulfonyl]azo]cyclohex-2-en-1-one (6). Prepared from **7** according to ref 4, compound **6** was obtained as a bright orange solid, mp 59–60 °C, in a yield of 89%. Rapid decomposition ensued when **6** was allowed to dry in air on a funnel: IR 1670 (CO), 1590, 1460, 1380, 1160; ^1H NMR 7.78 (d, J = 7.5, Ar), 7.37 (d, J = 7.5, 2 H, Ar), 6.66 (s, 1 H, vinyl H), 2.47 (br s, 7 H, overlapping resonances of 2 -CH_2- and -CH_3), 2.15 (m, -CH_2-); MS, 278 (11, M^+), 91 (100, $C_7H_7^+$). Instability of **6** precluded recrystallization, and acceptable microanalytical data for N were not obtained despite analyses of two different samples.

Anal. Calcd for $C_{13}H_{14}N_2O_3S$: C, 56.10; H, 5.07; N, 10.06; S, 11.52. Found: C, 56.46; H, 5.01; N, 9.39; S, 11.86.

3-[[(4-Methylphenyl)sulfonyl]hydrazino]cyclohex-2-en-1-one (7). Prepared from 1,3-cyclohexanedione according to ref 3, compound **7** was obtained in a yield of 88%, had mp 205–207 °C, and was pure (^1H NMR): IR (mineral oil) 3280 (NH), 1580–1520 br s (CO), 1350, 1320, 1180; ^1H NMR (Me_2SO-d_6) 9.72 (br s, NH), 8.50 (br s, NH), 7.81 (d, J = 7.8, 2 H, Ar), 7.40 (d, J = 7.8, 2 H, Ar), 5.12 (s, 1 H, vinyl H), 2.6–1.6 (overlapping resonances of CHD_2SOCD_3, -(CH_2)$_3$-, and CH_3 (s at 2.35)); MS, 280 (22, M^+), 125 (100), 91 (76, $C_7H_7^+$).

Anal. Calcd for $C_{13}H_{16}N_2O_3S$: C, 55.70; H, 5.75; N, 9.99; S, 11.44. Found: C, 56.26; H, 5.74; N, 9.83; S, 11.73.

3-Ethoxycyclohex-2-en-1-one. A solution of **6** (12 g, 43 mmol) and EtOH (50 mL) was stirred 5 h at 25 °C under N_2. The dark red solution became black, depositing a precipitate (3.2 g; uninvestigated). EtOH was evaporated from the filtered mixture, and a solution of the residue (6.2 g) in $CHCl_3$ was washed with 1 M aqueous Na_2CO_3 (2 × 200 mL) and with H_2O (200 mL). The dried ($MgSO_4$) solution was filtered through diatomaceous earth containing activated carbon and was concentrated to give an oily black residue (1.5 g) of several components (TLC). Flash chromatography over 150 g of Merck silica gel (230–400 mesh) and elution with $CHCl_3$ followed by distillation afforded 3-ethoxycyclohex-2-en-1-one (0.25 g, 4%) as a yellow liquid, bp 85 °C at 1 mm. Side-by-side and co-spotted thin-layer chromatograms of synthetic and commercial (Aldrich) samples were identical in two solvent systems. Indentity of the samples was confirmed by comparisons of ^1H NMR, IR, and mass spectra. Both samples contained a trace of the same, unidentified impurity (TLC, ^1H NMR).

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Registry No. **1**, 102921-09-5; **2**, 88255-19-0; **3**, 102940-19-2; **5**, 82709-37-3; **6**, 102940-20-5; **7**, 102921-12-0; $PhCH_2C$≡C-$(CH_2)_3C(OMe)_3$, 102921-10-8; $PhCH_2C$≡$C(CH_2)_3CO_2H$, 88255-07-6; 2-benzyl-1,3-cyclohexanedione, 22381-56-2; 2-benzyl-3-[2-[(4-methylphenyl)sulfonyl]hydrazino]cyclohex-2-en-1-one [(4-methylphenyl)sulfonyl]hydrazone, 102921-11-9; 3-ethoxycyclohex-2-en-1-one, 5323-87-5.

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Preparation of Secondary and Tertiary Cyclic and Polycyclic Hydrocarbon Azides[1]

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The azido functionality is one of the progenetorial groups for the synthesis of nitrogen-containing organic compounds.[2] In polycyclic bridgehead compounds such

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Table I. Preparation of Cyclic and Polycyclic Azides

substrate	substrate: azide ratio[a]	amount of $SnCl_4$ catalyst	reactn time and conditns	product	% yield[b]	mp, °C (bp/mm)	lit. mp, °C (bp/min)	50-MHz ^{13}C NMR data[f]
1-bromoadamantane	1:1.2	1 mL	12 h at rt, CH_2Cl_2	1	92	76–77	80–81[21]	C_1 = 58.5; C_2,C_8,C_9 = 41.2; C_3,C_5,C_7 = 29.6; C_4,C_6,C_{10} = 35.6
1-bromo-3-methyladamantane	1:1.2	1 mL	12 h at rt, CH_2Cl_2	2	72	13–14	$C_{11}H_{17}N_3$[d]	C_1 = 59.6; C_2 = 48.1; C_3 = 32.5; C_4,C_{10} = 40.7; C_5,C_7 = 30.2; C_6 = 35.1; C_8,C_9 = 42.9
1-bromo-3,5-dimethyladamantane	1:1.2	1 mL	12 h at rt, CH_2Cl_2	3	71	25–26	27[4]	C_1 = 60.1; C_2,C_9 = 47.4; C_3,C_9 = 32.9; C_4 = 40.0; C_6,C_{10} = 42.2; C_7 = 30.5; C_8 = 50.1
1-bromo-3,5,7-trimethyladamantane	1:1.2	1 mL	12 h at rt, CH_2Cl_2	4	65	16	15[4]	C_1 = 60.8; C_2,C_8,C_9 = 49.6; C_3,C_5,C_7 = 33.4; C_4,C_6,C_{10} = 46.8
2-bromoadamantane	1:2	1 mL	18 h reflux, CH_2Cl_2	5	92	40–41	30–35[3]	C_1,C_3 = 31.7; C_2 = 66.4; C_4,C_9[f] = 36.6; C_5[f] = 27.1; C_6 = 37.2; C_7[f] = 26.9; C_8,C_{10}[f] = 31.4
2-chloroadamantane	1:2	1 mL	18 h reflux, CH_2Cl_2	5	87	40–41	30–35[3]	
1-bromodiamantane	1:1.2	1 mL	15 h at rt, CH_2Cl_2	6	90	114	113–116[22]	C_1 = 63.7; C_2,C_{12} = 40.2; C_3,C_{14} = 33.0; C_4 = 24.9; C_5 = 37.0; C_6 = 36.5; C_7,C_{11} = 39.1; C_8,C_{10} = 37.8; C_9 = 29.0; C_{13} = 41.8
4-bromodiamantane	1:1.2	1 mL	12 h at rt, CH_2Cl_2	7	92	85	84–86[22]	C_1,C_7,C_{11} = 36.1; C_2,C_6,C_{12} = 38.8; C_3,C_5,C_{14} = 41.9; C_4 = 58.0; C_8,C_{10},C_{13} = 37.0; C_9 = 25.3
3-bromodiamantane	1:1.3	1 mL	8 h at 0 °C, CH_2Cl_2	8[g]	87	46–47	$C_{14}H_{19}N_3$[e]	C_1 = 37.2; C_2 = 40.7; C_3 = 67.1; C_4 = 31.7; C_5 = 37.7; C_6 = 36.2; C_7 = 36.9; C_8 = 37.2; C_9 = 26.0; C_{10} = 32.3; C_{11} = 29.5; C_{12} = 36.5; C_{13} = 36.8; C_{14} = 37.4
cyclohexyl bromide	1:1.2	1 equiv	48 h reflux, $CHCl_3$	9	48	(60/25)	(72/30)[6b]	C_1 = 59.6; C_2,C_6 = 36.4; C_3,C_5 = 24.9; C_4 = 24.6
cyclopentyl bromide	1:1.2	0.5 equiv	48 h reflux, $CHCl_3$	10	58	(65/70)	(72/77)[6b]	C_1 = 61.7; C_2,C_5 = 36.9; C_3,C_4 = 22.8

[a] Mole ratio: 10 mmol of the halide was used in each reaction. [b] Isolated yield, product purity confirmed by ^{13}C NMR, IR analyses. [c] Melting points are uncorrected. [d] Anal. Found: C, 68.98; H, 9.02; N, 21.79. Calcd: C, 69.07; H, 8.96; N, 21.97. [e] Anal. Found: C, 73.59; H, 8.33; N, 17.84. Calcd: C, 73.32; H, 8.35; N, 18.32. [f] In $CDCl_3$ at ambient temperature. Assignments are interchangeable. [g] All ^{13}C chemical shifts assignments are only tentative.

as adamantane and diamantane, the azido group has been successfully employed to prepare aza-bridged polycyclic systems.[3-6a] The general procedure for the preparation of polycyclic adamantyl and diamantyl azides involves reaction of the corresponding hydroxy compounds with sodium azide in sulfuric acid.[3-5] Although this procedure works well with tertiary alcohols, the reaction is sluggish with secondary systems and is often accompanied by rearranged products. Thus in the case of secondary alcohols such as 2-adamantanol only rearranged product 3-hydroxy-4-azahomoadamantane was obtained.[3] The cyclic azides have been prepared by treating the corresponding halides with sodium azide in carbitol solvents.[6b] In recent years trimethylsilyl azide has been developed into a convenient synthon to introduce the azide moiety into organic molecules.[7-9] It reacts with a variety of functional groups such as epoxides,[10] carbonyl compounds,[10,11] orthoesters,[12] acetals, ketals,[13] nitriles,[14] acid chlorides,[15,16] isocyanates,[17] phosphines,[18] etc. Nishiyama and Karigomi[19] have reported that trimethylsilyl azide reacts with activated organic halides such as allylic and benzylic halides in HMPT

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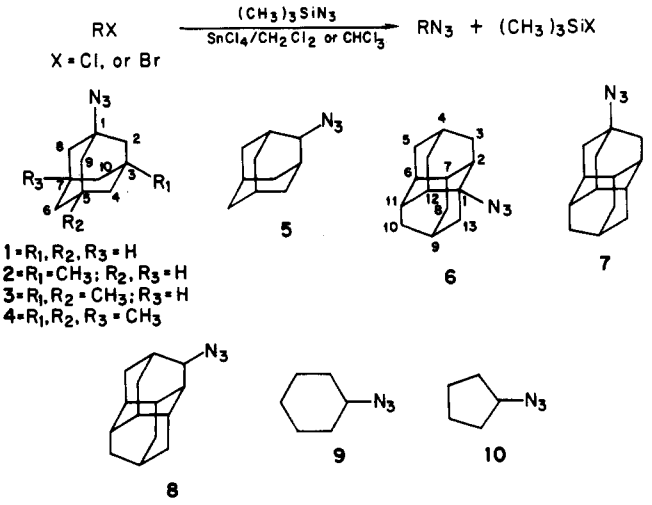

solvent to provide the corresponding azides. However, the reaction does not proceed with unactivated alkyl halides. We have found now in our studies that polycyclic adamantyl,[20] diamantyl related halides and cyclic cyclohexyl and cyclopentyl halides react with trimethylsilyl azides under stannic chloride 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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Nucleophilic S_N2 Displacements on (Pivaloyloxy)methyl 6α-[(Fluorosulfonyl)oxy]penicillanate

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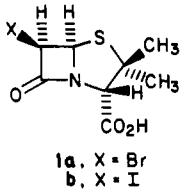
Since the discovery that 6β-bromo-[2,3] (**1a**) and 6β-iodopenicillanic acid[3,4] (**1b**) are inhibitors of β-lactamase enzymes, the synthesis of penicillanic acid derivatives with simple substituents in the 6β-orientation has become an area of considerable interest. Three principal routes for



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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