Addition of Trimethylsilyl Azide and of "Mixed Anhydrides" to the N-C(3) σ-Bond in 3-Substituted-1-azabicyclo[1.1.0]butanes†

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Received February 2, 1996

This paper is dedicated to the memory of Professor Nicholas Alexandrou

Trimethylsilyl azide adds smoothly to the highly strained N-C(3) σ-bond in 3-ethyl-1-azabicyclo[1.1.0]-butane (**1**) to afford an adduct, **2**, that reacts *in situ* with a variety of electrophilic reagents (*i.e.*, ethyl chloroformate, *p*-toluenesulfonyl chloride, benzoyl chloride, acetyl chloride, and oxalyl chloride) to afford the corresponding *N*-substituted-3-azido-3-ethylazetidines **3-7**, respectively in 62-72% yield. Similarly, **1** reacts regiospecifically with "mixed anhydrides" (*i.e.*, *p*-toluenesulfonyl acetate, methanesulfonyl acetate, and benzoyl trifluoromethanesulfonate) to afford the corresponding adducts, **8-10**, respectively) in 38-68% yield. Reaction of *p*-toluenesulfonyl azide with 1-aza-3-phenylbicyclo[1.1.0]butane (**12**) produces two products: *N*-(*p*-toluenesulfonyl-3-azido-3-phenylazetidine (**13**, 15%) and a dimeric product, *N*-(*N'*-*p*-toluenesulfonyl-3'-phenyl-3'-azetidinyl)-3-azido-3-phenylazetidine (**14**, 28%). Ethyl chloroformate adds to the *N*-C(3) σ-bond in 1-aza-3-(bromomethyl)bicyclo[1.1.0]butane (**15**) to afford *N*-carboethoxy-3-(bromomethyl)-3-chloroazetidine (**16**) in 73% yield.

J. Heterocyclic Chem., **33**, 837 (1996).

In 1969, syntheses of 1-azabicyclo[1.1.0]butane and of 3-substituted-1-azabicyclo[1.1.0]butanes were reported by Funke [1,2]. Since that time, relatively little interest has been shown in these unusual and highly strained nitrogen heterocycles. The past few years have witnessed a heightened awareness of the existence of 1-azabicyclo[1.1.0]-butanes, particularly with regard to their potential usefulness as intermediates for the synthesis of *N*,3-disubstituted azetidines [3-8]. We now report the results of studies of the addition of trimethylsilyl azide and of "mixed anhydrides" to some 3-substituted-1-azabicyclo[1.1.0]butanes.

Reaction of Trimethylsilyl Azide with 3-Ethyl-1-azabicyclo-[1.1.0]butane (**1**).

A two-step reaction sequence is reported herein that results in net electrophilic addition of reagents of the type $X^{\delta+}$-$Y^{\delta-}$ across the N-C(3) σ-bond in **1**. Initially, substrate **1** is treated with trimethylsilyl azide (*i.e.*, an electrophile for which X = $SiMe_3$ and Y = N_3), thereby affording an adduct, **2** (Scheme 1), which is not isolated. Subsequently, the reaction mixture is quenched *via* rapid addition of an electrophilic reagent, X-Y, with the result that the N-$SiMe_3$ bond in **2** is replaced *in situ* by N-X. In the present study, X-Y = Cl-CO_2Et, Ts-Cl, PhC(O)-Cl, Ac-Cl, and Cl-C(O)C(O)-Cl have been used for this purpose, thereby providing convenient routes for preparing compounds **3-7**, respectively (Scheme 1) in 68-72% yield. Thus, this two-step reaction sequence provides a useful method for synthesizing *N*-substituted-3-azido-3-ethylazetidines.

Reactions of **1** with "Mixed Anhydrides".

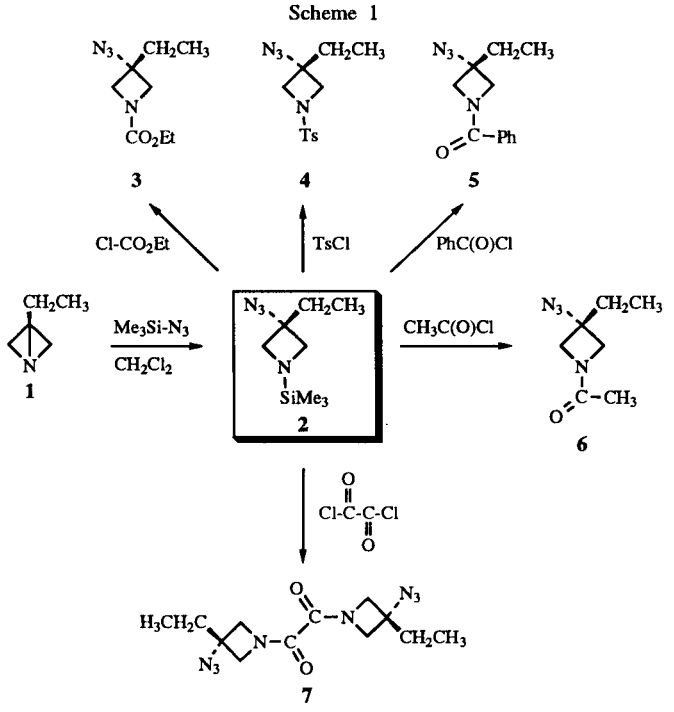
Here, the term "mixed anhydride" denotes mixed carboxylic acid-sulfonic acid anhydrides (e. g., *p*-toluenesulfonyl acetate [9], methanesulfonyl acetate [9], and benzoyl trifluoromethanesulfonate [10]. For the three examples studied herein, we find that these electrophilic reagents add regioselectively to the N-C(3) σ-bond in **1** to afford in each case only one of two possible adducts (Scheme 2).

Interestingly, spontaneous elimination of the elements of trifluoromethanesulfonic acid occurs under the conditions wherein benzoyl trifluoromethanesulfonate adds across the N-C(3) σ-bond in **1** [6]. Subsequent ozonolysis of the resulting product, **10**, affords *N*-benzoyl-3-azetidinone (**11**) [11]. This reaction sequence provides a general method for converting **1** into *N*-substituted 3-azetidinones, which constitute a useful class of organic synthetic intermediates.

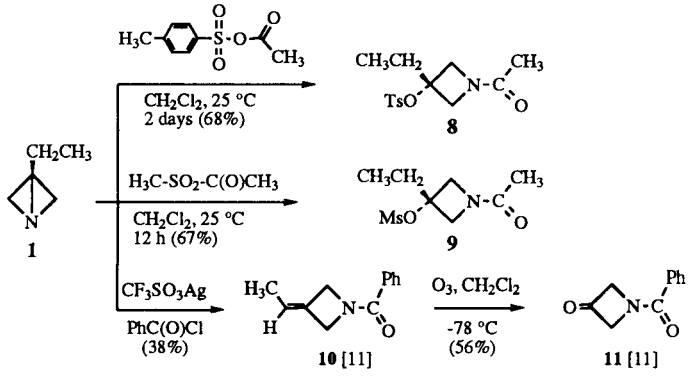
Reactions of other 3-Substituted-1-azabicyclo[1.1.0]-butanes with Electrophiles.

As part our study of electrophilic additions to the N-C(3) σ-bond in 1-azabicyclo[1.1.0]butanes, we have investigated the reaction of *p*-toluenesulfonyl azide [12] with 3-phenyl-1-azabicyclo[1.1.0]butane (**12**) [13]. The expected adduct, **13**, was formed in low yield; in addition, a dimeric product, **14**, was also obtained in this reaction (Scheme 3). Under the reaction conditions, partial polymerization of **12** occurs, concomitant with the formation of products **13** and **14**. Thus, after the reaction had proceeded for ten days, a broad resonance signal could be observed at δ 3.5-4.2 in the proton nmr spectrum of the reaction mixture (see the Experimental).

Scheme 1

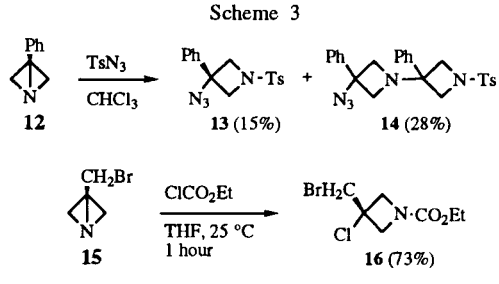


Scheme 2



Finally, we recently reported the synthesis of 1-aza-3-(bromomethyl)bicyclo[1.1.0]butane (**15**), which was used as an intermediate in a novel synthesis of 1,3,3-trinitroazetidine, an important energetic material [8]. In the present study, we have examined electrophilic addition of ethyl chloroformate across the highly strained N-C(3) σ-bond in **15**. In our hands, this reaction proceeded smoothly to afford the corresponding adduct, **16** (Scheme 3), in good yield.

Scheme 3



EXPERIMENTAL

Melting points are uncorrected. IR spectra were obtained by using a Midac high-resolution FTIR spectrometer. Proton and ^{13}C nmr spectra of **13** and **14** were obtained at 60 MHz and 20 MHz, respectively; the corresponding nmr spectra of the other compounds reported herein were obtained at 100 MHz and 25 MHz, respectively. Elemental microanalyses were performed by personnel at M-H-W Laboratories, Inc., Phoenix, AZ and by the Microanalytical Laboratory of the Polish Academy of Sciences (CBMiM Łódź, Poland). Low-resolution chemical ionization mass spectra were obtained at 70 eV with ammonia by using an MAT-112 mass spectrometer. High-resolution mass spectra (hrms) were obtained by personnel at the Midwest Center for Mass Spectrometry, University of Nebraska, Lincoln, NE.

Reaction of **1** with Trimethylsilyl Azide. General Procedure.

A solution of **1** (370 mg, 4.45 mmoles) in dichloromethane (10 ml) was cooled to 0°*via* application of an external ice-water bath. To this cooled solution was added with stirring trimethylsilyl azide (770 mg, 6.6 mmoles). After the addition of the azide had been completed, the external cold bath was removed, and the stirred reaction mixture was allowed to warm gradually to ambient temperature over 3 hours. Subsequently, the electrophile of interest (1.5 equivalents) was added with stirring to the resulting mixture. After all of the electrophilic reagent had been added, the reaction mixture was stirred at ambient temperature for 1 hour. The reaction mixture then was concentrated *in vacuo*, and the residue was purified *via* column chromatography on silica gel by eluting with 1:5 ethyl acetate-ligroin. The various reaction products, *N*-substituted-3-azido-3-ethylazetidines, were thereby obtained in 62-72% yield.

N-Carboethoxy-3-azido-3-ethylazetidine (**3**).

Sequential reaction of **1** with trimethylsilyl azide and then with ethyl chloroformate (716 mg, 6.6 mmoles) was performed by using the method described above. Workup of the reaction mixture afforded pure **3** (635 mg, 72%) as a colorless oil. The IR, ^1H nmr, and ^{13}C nmr spectra of this material were identical in all respects with the corresponding spectra for **2** that have been reported previously [7].

N-(*p*-Toluenesulfonyl)-3-azido-3-ethylazetidine (**4**).

Sequential reaction of **1** with trimethylsilyl azide and then with *p*-toluene-sulfonyl chloride (1.26 g, 6.6 mmoles) was performed by using the method described above. Workup of the reaction mixture afforded pure **4** (870 mg, 70%) as a colorless microcrystalline solid; mp 81-82°; ir (film): 2110 (m), 1477 (s), 1388 cm^{-1} (s); ^1H nmr (deuteriochloroform): δ 0.89 (t, J = 10.0 Hz, 3 H), 1.71 (q, J = 10.0 Hz, 2 H), 2.46 (s, 3 H), 3.70 (q, J = 7.5 Hz, 4 H), 7.40 (AB, J_{AB} = 10.0 Hz, 2 H), 7.75 (AB, J_{AB} = 10.0 Hz, 2 H); ^{13}C nmr (deuteriochloroform): δ 8.2 (q), 22.1 (q), 30.1 (t), 59.4 (s), 59.7 (t), 128.8 (d), 130.4 (d), 131.5 (s), 145.1 (s).

Anal. Calcd. for $C_{12}H_{16}N_4O_2S$: C, 51.41; H, 5.75. Found: C, 51.60; H, 5.87.

N-Benzoyl-3-azido-3-ethylazetidine (**5**).

Sequential reaction of **1** with trimethylsilyl azide and then with benzoyl chloride (920 mg, 6.6 mmoles) was performed by

using the method described above. Workup of the reaction mixture afforded pure **5** (730 mg, 72%) as a colorless viscous oil; ir (film): 2972 (s), 2114 (vs), 1645 (vs), 1414 cm^{-1} (s); ^1H nmr (deuteriochloroform): δ 0.98 (t, J = 10.0 Hz, 3 H), 1.85 (q, J = 10.0 Hz, 2 H), 4.12 (br s, 4 H), 7.38 (br s, 3 H), 7.48 (br s, 2 H); ^{13}C nmr (deuteriochloroform): δ 8.4 (q), 30.4 (t), 58.3 (s), 61.1 (t), 62.8 (t), 128.3 (d), 128.9 (d), 131.8 (d), 133.1 (s), 170.9 (s).

Anal. Calcd. for $C_{12}H_{14}N_4O$: C, 62.59; H, 6.10. Found: C, 62.38; H, 5.94.

N-Acetyl-3-azido-3-ethylazetidine (**6**). Method A.

Sequential reaction of **1** with trimethylsilyl azide and then with acetyl chloride (518 mg, 6.6 mmoles) was performed by using the method described above. Workup of the reaction mixture afforded pure **6** (508 mg, 68%) as a colorless oil; ir (film): 2984 (s), 2887 (m), 2114 (s), 1640 (s), 1458 (s), 1275 cm^{-1} (m); ^1H nmr (deuteriochloroform): δ 1.02 (t, J = 10.0 Hz, 3 H), 1.91 (q, J = 10.0 Hz, 2 H), 1.97 (s, 3 H), 3.98 (q, J = 5.0 Hz, 2 H), 4.02 (q, J = 15.0 Hz, 2 H); ^{13}C nmr (deuteriochloroform): δ 8.4 (q), 19.5 (q), 30.5 (t), 57.5 (t), 60.0 (t), 60.1 (s), 171.2 (s).

Anal. Calcd. for $C_7H_{12}N_4O$: C, 49.99; H, 7.19. Found: C, 50.05; H, 7.48.

N-Acetyl-3-azido-3-ethylazetidine (**6**). Method B.

Similarly, sequential reaction of **1** with trimethylsilyl azide and then with acetic anhydride (0.67 g, 6.6 mmoles) also afforded **6** (448 mg, 60%). The ir, ^1H nmr, and ^{13}C nmr spectra of the material thereby obtained were identical in all respects with the corresponding spectra obtained for **6** which had been prepared by using Method A (*vide supra*).

1,2-Di(3-azido-3-ethylazetidinyl)ethane-1,2-dione (**7**).

Sequential reaction of **1** (370 mg, 4.45 mmoles) with trimethylsilyl azide (770 mg, 6.6 mmoles) and then with oxalyl chloride (830 mg, 6.6 mmoles) was performed by using the method described above. Workup of the reaction mixture afforded pure **7** (570 mg, 62%) as a colorless microcrystalline solid; mp 44-45°; ir (nujol): 2980 (m), 2931 (m), 2121 (s), 1647 (s), 1467 (w), 1419 cm^{-1} (m); ^1H nmr (deuteriochloroform): δ 0.94 (t, J = 9.5 Hz, 3 H), 1.80 (q, J = 9.5 Hz, 2 H), 3.95 (br s, 2 H), 4.48 (br s, 2 H); ^{13}C nmr (deuteriochloroform): δ 8.3 (q), 30.3 (t), 58.1 (t), 61.3 (s), 63.3 (t), 159.1 (s).

Anal. Calcd. for $C_{12}H_{18}N_8O_2$: C, 47.05; H, 5.92. Found: C, 47.31; H, 6.04.

N-Acetyl-3-ethyl-3-(*p*-toluenesulfonyloxy)azetidine (**8**).

A solution of **1** (250 mg, 3.0 mmoles) in dichloromethane (10 ml) under argon was cooled externally to 0°*via* the application of an external ice-water bath. To this cold solution was added with stirring a solution of *p*-toluenesulfonyl acetate [9] (642 mg, 3.0 mmoles). The external ice-water bath was removed, and the reaction mixture was allowed to warm gradually to ambient temperature and then was stirred at this temperature for 48 hours. The resulting mixture was concentrated *in vacuo*. The residue thereby obtained, a viscous yellow oil, was purified *via* column chromatography on silica gel by eluting with 25% ethyl acetate-hexane. Pure **8** (604 mg, 68%) was thereby obtained as a viscous pale yellow oil; ir (neat) 2978 (w), 1655 (vs), 1457 (s), 1355 (s), 1176 cm^{-1} (s); ^1H nmr (deuteriochloroform): δ 0.83 (t, J = 7.3 Hz, 3 H), 1.79 (s, 3 H), 2.06 (m, 2 H), 2.36 (s, 3 H), 3.89 (AB, J_{AB} = 12.0 Hz, 1 H), 4.03 (AB, J_{AB} = 10.0 Hz, 1 H), 4.12 (AB, J_{AB} =12.0 Hz, 1 H), 4.41 (AB, J_{AB} = 10.0 Hz, 1 H), 7.26 (AB, J_{AB} = 8.0 Hz, 2 H), 7.68 (AB, J_{AB} = 8.0 Hz, 2 H); ^{13}C nmr (deuteriochloroform): δ 7.0 (q), 18.8 (q), 21.3 (q), 29.8 (t), 57.9 (t), 60.4 (t), 82.9 (s), 127.0 (d), 129.7 (d), 134.8 (s), 144.8 (s), 170.3 (s).

Anal. Calcd. for $C_{14}H_{19}NO_4S$: C, 56.55; H 6.44. Found: C, 56.35; H 6.33.

N-Acetyl-3-ethyl-3-(*p*-toluenesulfonyloxy)azetidine (**9**).

A solution of **1** (332 mg, 4.0 mmoles) in dichloromethane (10 ml) under argon was cooled externally to 0° *via* application of an external ice-water bath. To this cold solution was added with stirring methanesulfonyl acetate [9] (550 mg, 3.98 mmoles). The external ice-water bath was removed, and the reaction mixture was allowed to warm gradually to ambient temperature and then was stirred at this temperature for 12 hours. The resulting mixture was concentrated *in vacuo*. The residue thereby obtained, a viscous yellow oil, was purified *via* column chromatography on silica gel by eluting with 25% ethyl acetate-hexane. Pure **9** (590 mg, 67%) was thereby obtained as a colorless oil; ir (neat): 2971 (w), 2937 (w), 2878 (w), 1650 (vs), 1445 (w), 1337 (s), 1166 cm^{-1} (m); ^1H nmr (deuteriochloroform): δ 0.91 (t, J = 8.0 Hz, 3 H), 1.75 (s, 3 H), 1.91-2.13 (m, 2 H), 2.97 (s, 3 H), 3.86 (AB, J_{AB} = 10.0 Hz, 1 H), 3.99 (AB, J_{AB} = 10.0 Hz, 1 H), 4.02 (AB, J_{AB} =10.0 Hz, 1 H), 4.34 (AB, J_{AB} = 10.0 Hz, 1 H); ^{13}C nmr (deuteriochloroform): δ 7.1 (q), 18.7 (q), 29.7 (t), 40.2 (q), 57.7 (t), 60.2 (t), 82.6 (s), 170.4 (s);

Anal. Calcd. for $C_8H_{15}NO_4S$: C, 43.43; H, 6.83. Found: C, 43.29; H, 6.75.

N-Benzoyl-3-(ethylidene)azetidine (**10**) [11].

To a suspension of silver trifluoromethanesulfonate (1.2 g, 5.0 mmoles) in dichloromethane (10 ml) under argon was added dropwise with stirring benzoyl chloride (700 mg, 5.0 mmoles), and the resulting mixture was stirred at room temperature for 2 hours. The reaction mixture then was cooled to 0°*via* application of an external ice-water bath. To the resulting cooled suspension was added dropwise with stirring under argon a solution of **1** (415 mg, 5.0 mmoles). The external ice-water bath was removed, and the reaction mixture was allowed to warm gradually to ambient temperature and then was stirred at this temperature for 48 hours. The reaction mixture was filtered, and dichloromethane (50 ml) was added to the filtrate. The combined organic layers were washed sequentially with water (50 ml) and brine (50 ml), dried (sodium sulfate), and filtered, and the filtrate was concentrated *in vacuo*. The residue thereby obtained, a viscous yellow oil, was purified *via* column chromatography on silica gel by eluting with 25% ethyl acetate-hexane. Pure **10** (370 mg, 38%) was thereby obtained as a colorless viscous oil. The ir and ^1H nmr spectra of the material thereby obtained, agreed with the corresponding values for **10** that have been published previously [11].

N-Benzoylazetidin-3-one (**11**).

A solution of **11** (100 mg, 0.5 mmole) in dichloromethane (10 ml) was cooled to -78° *via* application of an external dry ice-acetone bath. Ozone gas was bubbled through this cold solution. Aliquots were withdrawn periodically and subjected to tlc analysis (silica gel stationary phase, 2:1 ethyl acetate-hexane used as eluent). The flow of ozone was stopped immediately after tlc analysis indicated the absence of starting material. Dimethyl sulfide (5 ml, excess) was added to quench the reaction. The external cold bath was removed, and the reaction mixture was allowed to

warm gradually to ambient temperature during 1 hour. The resulting mixture was concentrated *in vacuo*. The residue thereby obtained, a viscous yellow oil, was purified *via* column chromatography on silica gel by eluting with 25% ethyl acetate-hexane. Pure **11** (49 mg, 56%) was thereby obtained as a colorless microcrystalline solid; mp 85-86°. The ir and ^{1}H nmr spectra of the material thereby obtained, agreed with the corresponding values for **11** that have been published previously [11].

Preparation of *p*-Toluenesulfonyl Azide.

Crude *p*-toluenesulfonyl azide was prepared from *p*-toluenesulfonyl hydrazide (2.74 g, 15 mmoles) by using a previously published procedure [12]. Ether (50 ml) was added to the material thereby obtained, and the resulting mixture was washed sequentially with 1 *N* aqueous sodium hydroxide (30 ml, to remove acidic impurities) and with water (3 x 50 ml). The ether layer was dried (magnesium sulfate) and filtered, and the filtrate was concentrated *in vacuo*. This procedure afforded *p*-toluenesulfonyl azide (2.20 g, 74%) as a colorless oil, which was used as obtained without further purification.

Reaction of **12** with *p*-Toluenesulfonyl Azide.

To a solution of 3-phenyl-1-azabicyclo[1.1.0]butane [13] (**12**, 130 mg, 1.00 mmoles) in chloroform (0.5 ml) at ambient temperature was added freshly prepared *p*-toluenesulfonyl azide (236 mg, 1.20 mmoles). The reaction mixture was placed in an nmr sample tube and allowed to stand at ambient temperature for several days. The progress of the reaction was monitored periodically *via* analysis of its ^{1}H nmr spectrum. After ten days, **12** could no longer be detected in the reaction mixture; instead, a new set of signals could be seen in the region δ 3.5-4.2. The crude reaction mixture was concentrated *in vacuo*, and the residue was purified *via* preparative thick layer chromatography (silica gel stationary phase) by using 99:1 dichloromethane-methanol as eluent. Workup of the first chromatography fraction afforded unreacted *p*-toluenesulfonyl azide (120 mg, 0.61 mmoles). Workup of the second chromatography fraction gave *N*-*p*-toluenesulfonyl-3-azido-3-phenylazetidine (**13**, 50 mg, 15%) as a colorless, viscous oil that slowly solidified upon standing at ambient temperature. The resulting solid, mp 88-92°, was further purified by recrystallization from dichloromethane-hexane, thereby affording pure **13** as a colorless microcrystalline solid; mp 90-92°; ir (potassium bromide): 2050 (s), 1350 (vs), 1295 (m), 1270 (m), 1250 (w), 1170 (vs), 1100 (s), 770 (m) 730 (m), 685 cm^{-1} (s); ^{1}H nmr (deuteriochloroform): δ 2.50 (s, 3 H), 4.10 (AB, J_{AB} = 9.1 Hz, 2 H), 4.25 (AB, J_{AB} = 9.1 Hz, 2 H), 7.27-7.43 (m, 7 H), 7.80 (AB, J_{AB} = 8.2 Hz, 2 H); ^{13}C nmr (deuteriochloroform): δ 22.3 (q), 61.1 (s), 62.4 (t), 125.9 (d), 129.0 (d), 129.4 (d), 129.6 (d), 130.6 (d), 131.9 (s), 138.8 (s), 145.3 (s); ms: (CI, 70 eV), *m/z* (relative intensity) 346 [$(M + NH_3)^+$, 6], 329 [$(M + 1)^+$, 100], 286 [$(M - N_3)^+$, 5].

Anal. Calcd. for $C_{16}H_{16}N_4O_2S$: C, 58.52; H, 4.91; N, 17.06; S, 9.76. Found: C, 58.32; H, 4.87; N, 17.35; S, 10.03.

Continued elution of the chromatography plate gave *N*-(*N'*-*p*-toluenesulfonyl-3'-phenyl-3'-azetidinyl)-3-azido-3-phenylazetidine (**14**, 63 mg, 28%) as a viscous oil that slowly solidified upon standing at ambient temperature for several days. The resulting solid, mp 123-128°, was further purified by recrystallization from dichloromethane-hexane, thereby affording pure **14** as a colorless microcrystalline solid, mp 127-129°; ir (potassium bromide) 2050 (s), 1350 (s), 1250 (m), 1215 (m), 1175 (vs), 1100 (s), 770 (s), 720 (s), 690 cm^{-1} (vs); ^{1}H nmr (deuteriochloroform): δ 2.44 (s, 3 H), 3.45 (br s, 4 H), 3.95 (AB, J_{AB} = 8.7 Hz, 2 H), 4.07 (AB, J_{AB} = 8.7 Hz, 2 H), 7.23-7.42 (m, 12 H), 7.75 (AB, J_{AB} = 8.2 Hz, 2 H); ^{13}C nmr (deuteriochloroform): δ 21.6 (q), 56.9 (t), 58.7 (t), 59.9 (s), 61.2 (s), 125.5 (d), 126.1 (d), 127.9 (d), 128.4 (d), 128.6 (2 C, d), 128.9 (d), 130.0 (d), 131.3 (s), 139.4 (s), 139.9 (s), 144.4 (s); ms: (CI, 70 eV), *m/z* (relative intensity) 461 [$(M + 2)^+$, 16], 460 [$(M + 1)^+$, 100], 432 (32), 304 (13), 276 (12).

Anal. Calcd. for $C_{25}H_{25}N_5O_2S$: C, 65.34; H, 5.48; N, 15.24; S, 6.98. Found: C, 65.05; H, 5.51; N, 15.21; S, 7.01.

N-Carboethoxy-3-(bromomethyl)-3-chloroazetidine (**16**).

To a solution of **15** [5] (300 mg, 2.02 mmoles) in water (50 ml) was added a solution of ethyl chloroformate (10 ml, excess) in tetrahydrofuran (10 ml), and the resulting mixture was stirred at room temperature for 1 hour. The reaction mixture was diluted with water (100 ml), and the resulting aqueous suspension was extracted with ethyl acetate (3 x 25 ml). The combined organic extracts were washed sequentially with water (50 ml) and brine (50 ml), dried (sodium sulfate), and filtered, and the filtrate was concentrated *in vacuo*. The residue thereby obtained, a viscous, pale yellow oil, was purified *via* column chromatography on silica gel by eluting with 20% ethyl acetate-hexane. This procedure afforded pure **16** (380 mg, 73%) as a colorless oil, bp 150° (2 mm Hg); ir (film): 2973 (w), 1701 (vs), 1413 (s), 1376 (m), 1338 (sh, m), 1251 (m), 1213 cm^{-1} (m); ^{1}H nmr (deuteriochloroform): δ 1.20 (t, J = 8.0 Hz, 3 H), 3.73 (s, 2 H), 4.10 (q, J = 8.0 Hz, 2 H), 4.18 (AB, J_{AB} = 10.0 Hz, 2 H), 4.26 (AB, J_{AB} = 10.0 Hz, 2 H); ^{13}C nmr (deuteriochloroform): δ 14.5 (q), 38.6 (t), 60.1 (s), 61.2 (t), 62.3 (t), 156.2 (s).

Anal. Calcd. for $C_7H_{11}BrClNO_2$: C, 32.78; H, 4.32. Found: C, 33.00; H, 4.57.

Acknowledgment.

We thank the Office of Naval Research (Grant N00014-94-1-1039 to A. P. M.), the United States Air Force (Contract F29601-92-K-0018 to A. P. M.), and the Robert A. Welch Foundation (Grant B-963 to A. P. M.) for financial support of this study.

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