Additions of X–Y Across the C(3)–N σ-Bond in 1-Aza-3-ethylbicyclo[1.1.0]butane. Novel Routes to 3-Substituted Azetidines

Alan P. Marchand,* D. Rajagopal, and Simon G. Bott*

Department of Chemistry, University of North Texas, Denton, Texas 76203-0068

Thomas G. Archibald*

Aerojet, Propulsion Division, P. O. Box 13222, Sacramento, California 95813-6000

Received May 10, 1994

Introduction

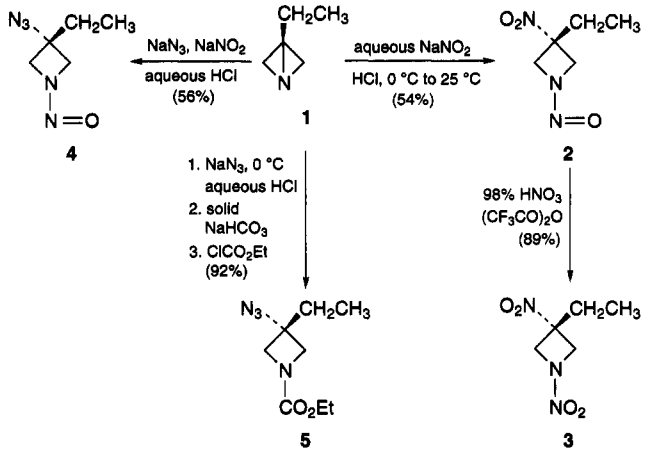
In 1969, Funke reported the synthesis of 3-ethyl-1-azabicyclo[1.1.0]butane (**1**) and some aspects of its chemistry.[1] Since that time, relatively little interest has been shown in this unusual ring system. Our own interest in **1** stems from its potential use as a key intermediate in the synthesis of *N*,3-disubstituted azetidines, which otherwise can be quite difficult to obtain [e.g., via S_N2 displacements on *N*-substituted-3-(tosyloxy)- (or mesyloxy-) azetidines].[2] Compounds of this type have attracted attention in recent years among members of the energetic materials community.[3] In addition, natural products chemists have been attracted to azetidine alkaloids, a class of strikingly bioactive compounds which have been isolated from marine organisms.[4] Finally, some unusual transformations of 3-functionalized azetidines which are of mechanistic interest have been reported recently.[5]

Previously,[6] we investigated reactions of **1** with a variety of electrophiles, e.g., N_2O_4, $ClCO_2Et$, Tf_2O, and Ms_2O. In each case, the observed reaction product(s) resulted via addition of the reagent, X–Y, across the highly strained C(3)–N σ-bond in the substrate, thereby affording new *N*,3-disubstituted azetidines. In the present study, we have extended the range of reagents studied in an effort to explore the scope and limitations of reactions of this type. In the course of this work, we performed several of the addition reactions in aqueous solution in an effort to design environmentally benign (i.e., "green") synthetic routes to novel 3-substituted azetidines.

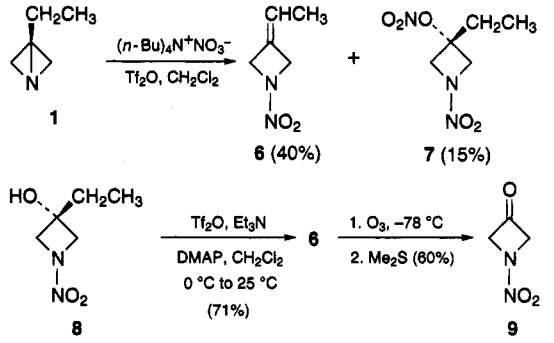
Results and Discussion

Compound **1** was synthesized by using a previously published modification[6] of a literature procedure.[1] Reaction of **1** with *in situ*-generated aqueous HNO_2 resulted in addition of the elements of HNO_2 across the C(3)–N σ-bond with concomitant *N*-nitrosation of the resulting intermediate azetidine, thereby affording **2** (54% yield, Scheme 1). Subsequent oxidation of the *N*-NO functionality by using 98% HNO_3–$(CF_3CO)_2O$ afforded the corresponding *N*-nitramine (**3**, 89% yield).

Scheme 1



Scheme 2



Addition of $X^+ N_3^-$ across the C(3)–N σ-bond in **1** was performed in aqueous medium in two separate experiments. Application of the first procedure, which employed aqueous NaN_3 and *in situ*-generated HNO_2, resulted in the formation of **4** (56% yield, Scheme 1). In the second procedure, **1** was reacted with an "azidoformate equivalent" which was generated by sequential reaction of **1** sith *in situ*-generated HN_3 followed by $ClCO_2Et$. Application of this procedure afforded **5** in excellent yield (Scheme 1).

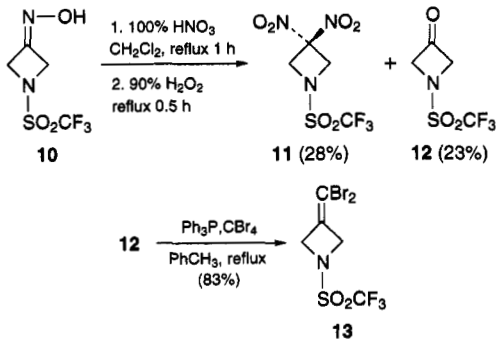
N-Nitro-3-ethylideneazetidine (**6**) was prepared in two ways. First, **6** was obtained in 40% yield via reaction of **1** with $(n\text{-}Bu)_4N^+ NO_3^-$ and Tf_2O.[7] Compound **7** (15%, Scheme 2) was also formed along with **6** as a product of this reaction. In addition, reaction of azetidinol **8**[6] with Tf_2O in the presence of tertiary amines afforded **6** in good yield. Subsequent low-temperature ozonolysis of **6** followed by reductive workup with Me_2S produced *N*-nitroazetidin-3-one (**9**), a potential precursor to 1,3,3-trinitroazetidine (TNAZ, an energetic material whose synthesis has attracted considerable attention in recent years[3]).

Compound **11**, another potential precursor to TNAZ, was synthesized from oxime **10** which was readily available to us from an earlier study.[6] Thus, sequential reaction of **10** with 100% HNO_3[8] and 90% H_2O_2 produced **11** and **12** (28 and 23% yield, respectively, Scheme 3), which could be separated conveniently by column chro-

(1) Funke, W. *Chem. Ber.* **1969**, *102*, 3148. (b) Funke, W. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 70.
(2) Archibald, T. G.; Gilardi, R.; Baum, K.; George, C. *J. Org. Chem.* **1990**, *55*, 2920.
(3) (a) Archibald, T. G.; Garver, L. C.; Baum, K.; Cohen, M. C. *J. Org. Chem.* **1989**, *54*, 2869. (b) Axenrod, T.; Watnick, C.; Yazdehkasti, H.; Dave, P. R. *Tetrahedron Lett.* **1993**, *34*, 6677.
(4) Kobayashi, J.; Cheng, J.-F.; Ishibashi, M.; Wälchli, M. R.; Yamamura, S.; Ohijumi, Y. *J. Chem. Soc., Perkin Trans 1* **1991**, 1135.
(5) (a) Bartholomew, D.; Stocks, M. J. *Tetrahedron Lett.* **1991**, *32*, 4795. (b) Bartholomew, D.; Stocks, M. J. *Ibid.* **1991**, *32*, 4799.
(6) Marchand, A. P.; Rajagopal, D.; Bott, S. G.; Archibald, T. G. *J. Org. Chem.* **1994**, *59*, 1608.
(7) Adams, C. M.; Sharts, C. M.; Shackelford, S. E. *Tetrahedron Lett.* **1993**, *34*, 6669.
(8) Bull, J. R.; Jones, E. R. H. *J. Chem. Soc.* **1965**, 2601.

0022-3263/94/1959-5499$04.50/0

Scheme 3



matography on silica gel (see the Experimental Section). Subsequently, ketone **12** was converted into the corresponding 3-(dibromomethylidene) derivative (**13**) in 83% yield via its reaction with Ph_3P-CBr_4.[9]

Experimental Section

Melting points are uncorrected. Elemental microanalyses were performed by M-H-W Laboratories, Phoenix, AZ. High-resolution mass spectra were obtained by personnel at the Midwest Center for Mass Spectrometry, University of Nebraska— Lincoln.

***N*-Nitroso 3-ethyl 3-nitroazacyclobutane (2).** To a solution of $NaNO_2$ (1.0 g, excess) in water (2 mL) was added **1**[1,6] (160 mg, 2.0 mmol), and the resulting mixture was cooled to 0 °C via application of an external ice–water bath. To this cooled mixture was added with stirring a solution of concd HCl (80 mg) in water (1 mL). The cold bath was removed, and the stirred reaction mixture was allowed to warm gradually to rt during 30 min. The reaction mixture then was again cooled to 0 °C, and 50% aqueous HCl (3 mL) was added dropwise with stirring. The cold bath was removed, and the reaction mixture was stirred for 3 h at rt and then was poured over crushed ice (100 g). The resulting suspension was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were washed sequentially with 10% aqueous $NaHCO_3$ (25 mL), water (25 mL), and brine (25 mL), dried (Na_2SO_4), and filtered. The filtrate was concd *in vacuo* to afford crude **2** as a pale yellow oil. This material was further purified via column chromatography on silica gel by eluting with 20% EtOAc–hexane. Pure **2** (180 mg, 54%) was thereby obtained as a pale yellow oil; IR (neat) 2973 (m, CH), 2935 (m, CH), 2885 (w), 1539 (s, NO_2), 1420 (s), 1326 (s), 1276 (s), 1188 cm^{-1} (m); ^1H NMR ($CDCl_3$) δ 0.96 (t, J = 7.3 Hz, 3 H), 2.26 (q, J = 7.3 Hz, 2 H), 4.25 (dd, J = 13.8, 2.4 Hz, 1 H), 4.58 (dd, J = 13.8, 2.4 Hz, 1 H), 4.96 (dd, J = 11.6, 2.2 Hz, 1 H), 5.35 (dd, J = 11.8, 2.4 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 7.7 (q), 29.8 (t), 60.6 (t), 62.6 (t), 83.6 (s); HRMS *m/z* 159.06439 (M^+), calcd for $C_5H_9N_3O_3$ 159.06442.

***N*-Nitro-3-ethyl-3-nitroazacyclobutane (3).** A mixture of trifluoroacetic anhydride (1.0 g) and 98% HNO_3 (1.0 g) was cooled externally to 0 °C via the application of an external ice bath. To this cooled solution was added dropwise with stirring a solution of **2** (50 mg, 0.31 mmol) in CH_2Cl_2 (2 mL). The cold bath was removed, and the stirred reaction mixture was allowed to warm gradually to rt during 1 h. The reaction mixture was then poured over crushed ice (25 g), and the resulting suspension was extracted with CH_2Cl_2 (2 × 10 mL). The combined organic layers were washed sequentially with 10% aqueous $NaHCO_3$ (10 mL), water (10 mL), and brine (10 mL), dried (Na_2SO_4), and filtered. The filtrate was concd *in vacuo*, thereby affording **3** (50 mg, 89%) as a colorless oil: IR (neat) 2971 (w, CH), 1534 (s, NO_2), 1507 (s, NO_2), 1449 (m), 1339 (m), 1264 cm^{-1} (m); ^1H NMR ($CDCl_3$) δ 0.97 (t, J = 8.0 Hz, 3 H), 2.24 (q, J = 8.0 Hz, 2 H), 4.46 (dd, J = 11.0, 1.1 Hz, 2 H), 4.87 (d, J = 11.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 7.7 (q), 29.9 (t), 64.1 (t), 80.5 (s); HRMS *m/z* 176.0674. [$(M + H)^+$], calcd for $C_5H_9N_3O_4$ 176.0671.

***N*-Nitroso-3-azido-3-ethylazetidine (4).** A mixture of **1**[1,6] (200 mg, 2.4 mmol) and NaN_3 (2.0 g, 30 mmol) in water (5 mL) was cooled to 0 °C via the application of an external ice–water bath. To this cooled solution was added dropwise with stirring concd HCl (2 mL, excess), and the resulting mixture was stirred at 0 °C for 30 min. Then, $NaNO_2$ (2.07 g, 30 mmol) was added, and concd aqueous HCl (5 mL, excess) was added dropwise to the resulting mixture. The cold bath was removed, and the stirred reaction mixture was allowed to warm gradually to rt during 30 min. Water (25 mL) was added, and the resulting suspension was extracted with EtOAc (3 × 25 mL). The combined organic extracts were washed sequentially with water (2 × 25 mL) and brine (25 mL). The organic layer was dried (Na_2SO_4) and filtered, and the filtrate was concd *in vacuo*. The residue, a pale yellow oil, was purified by column chromatography on silica gel by eluting with 15% EtOAc–hexane. Pure **4** (208 mg, 56%) was thereby obtained as a pale yellow oil: IR (neat) 2944 (m, CH), 2099 (vs, N_3), 1412 (s), 1317 (s), 1259 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.02 (t, J = 6.0 Hz, 3 H), 1.91 (q, J = 6.0 Hz, 2 H), 4.07 (d, J = 1.2 Hz, 2 H), 4.77 (t, J = 1.2 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 8.1 (q), 29.8 (t), 60.6 (s), 61.2 (t), 63.7 (t); HRMS *m/z* 155.0804. (M^+), calcd for $C_5H_9N_5O$ 155.0807.

***N*-Carbethoxy-3-azido-3-ethylazetidine (5).** A mixture of **1**[1,6] (200 mg, 2.4 mmol) and NaN_3 (2.0 g, 30 mmol) in water (5 mL) was cooled to 0 °C via application of an external ice–water bath. To this cooled solution was added dropwise with stirring concd aqueous HCl (2 mL, excess) and the resulting mixture was stirred at 0 °C for 30 min. Solid Na_2CO_3 (3.18 g, 30.0 mmol) then was added carefully, and the resulting mixture was stirred for 10 min. A solution of ethyl chloroformate (1 mL, excess) in THF (4 mL) was added dropwise with stirring. The cold bath was removed, and the reaction mixture was allowed to warm gradually to rt during 30 min. Water (25 mL) was added to the reaction mixture, and the resulting suspension was extracted with EtOAc (3 × 25 mL). The combined organic extracts were washed sequentially with water (2 × 25 mL) and brine (25 mL). The organic layer was dried (Na_2SO_4) and filtered, and the filtrate was concd *in vacuo*. The residue, a pale yellow oil, was purified by column chromatography on silica gel by eluting with 10% EtOAc–hexane. Pure **5** (437 mg, 92%) was thereby obtained as a colorless oil: IR (neat) 2965 (m, CH), 2923 (m, CH), 2881 (m), 2094 (vs, N_3), 1708 (vs, C=O), 1412 (s), 1375 (m), 1343 (m), 1254 (m), 1180 (m), 1095 cm^{-1} (m); ^1H NMR ($CDCl_3$) δ 0.89 (t, J = 7.2 Hz, 3 H), 1.16 (t, J = 7.2 Hz, 3 H), 1.75 (q, J = 7.2 Hz, 2 H), 3.80 (d *AB*, J_{AB} = 9.5 Hz, 2 H), 3.90 (d *AB*, J_{AB} = 9.5 Hz, 2 H), 4.03 (q, J = 7.2 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 7.7 (q), 14.4 (q), 29.8 (t), 58.2 (t), 60.2 (s), 61.1 (t), 156.4 (s); HRMS *m/z* 199.1193 [$(M + H)^+$], calcd for $C_8H_{14}N_4O_2$ 199.1195.

Reaction of 1 with Tetra-*n*-butylammonium Nitrate–Trifluoromethanesulfonic Anhydride.[7] A solution of $(n\text{-}Bu)_4N^+ NO_3^-$ (1.52 g, 5.0 mmol) in dry CH_2Cl_2 (25 mL) under argon was cooled to 0 °C via application of an external ice–water bath. To this cooled solution was added dropwise with stirring Tf_2O (1.41 g, 5.0 mmol). The resulting yellow reaction mixture was stirred at 0 °C for 1 h. A solution of **1** (415 mg, 5.0 mmol) in CH_2Cl_2 (5 mL) was added, and the cold bath was removed. The reaction mixture was allowed to warm gradually to rt during 2 h. Water (50 mL) was added, and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (2 × 25 mL). The combined organic layers were washed sequentially with 10% aqueous $NaHCO_3$ (50 mL), water (25 mL), and brine (25 mL). The organic layer was dried (Na_2SO_4) and filtered, and the filtrate was concd *in vacuo*. The yellow oily residue thereby obtained was purified by column chromatography on silica gel by eluting with 2% EtOAc–hexane. The first chromatography fractions afforded pure **6** (260 mg, 40%) as a colorless oil: IR (neat) 2971 (w, CH), 1639 (vs, C=C), 1534 (vs, NO_2), 1454 (w), 1338 (s), 1306 (s), 1259 (s), 1169 (m), 1137 (m), 842 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 1.55 (dt, J = 4.0, 2.0 Hz, 3 H), 4.83 (br s, 4 H), 5.46 (centrosymmetric multiplet, 1 H); ^{13}C NMR ($CDCl_3$) δ 13.9 (q), 64.5 (t), 65.3 (t), 119.8 (d), 121.7 (s). This compound was further characterized by conversion to the corresponding 3-azetidinone (**8**, *vide infra*).

Further elution of the chromatography column with 5% EtOAc–hexane afforded **7** (150 mg, 15%) as a pale yellow oil. The IR, ^1H NMR, and ^{13}C NMR spectra of the material thereby obtained were identical in all respects with the corresponding spectra of authentic **7**, which has been prepared previously in our laboratory.[6]

***N*-Nitro-3-ethylideneazetidine (6).** A mixture of **8**[6] (25 mg, 0.17 mmol), Et_3N (60 mg, 0.6 mmol), and (dimethylamino)pyridine (DMAP, 5 mg, catalytic amount) in CH_2Cl_2 (5 mL) under argon was cooled externally to 0 °C via application of an external

ice–water bath. To this cold mixture was added dropwise with stirring Tf_2O (58 mg, 0.20 mmol). The cold bath was removed, and the resulting mixture was allowed to warm gradually with stirring to rt during 2 h. The resulting mixture was concd *in vacuo*, and the resulting dark red residue was triturated with hexane. The combined hexane layers were decanted and then concd *in vacuo*. The residue, a pale yellow oil, was purified by column chromatography on silica gel by eluting with 10% EtOAc–hexane. Pure **6** (15 mg, 71%) was thereby obtained as a pale yellow oil. The IR, ^1H NMR, and ^{13}C NMR spectra of the material thereby obtained were identical in all respects with the corresponding spectra of **6** that had been prepared earlier via the reaction of **1** with $(n\text{-}Bu)_4N^+ NO_3^-$ and Tf_2O (*vide supra*).[7]

***N*-Nitroazetidin-3-one (9).** A solution of **6** (128 mg, 1.0 mmol) in CH_2Cl_2 (5 mL) was cooled externally to −78 °C via application of dry ice–acetone bath. Ozone was bubbled through this cold solution, and the reaction progress was monitored by thin layer chromatographic (TLC) analysis. The flow of ozone was stopped after all of the starting material had been reacted (as determined by TLC analysis). Argon was bubbled through the reaction mixture to purge it of excess ozone, and the resulting mixture was quenched by addition of Me_2S (3 mL, excess). The external cold bath was removed, and the reaction mixture was allowed to warm gradually to rt and then was stirred at rt for 12 h. The reaction mixture was concd *in vacuo*, and the pale yellow oily residue was purified via column chromatography on silica gel by eluting with 20% EtOAc–hexane. Pure **9** (70 mg, 60%) was thereby obtained as a colorless microcrystalline solid: mp 61–62 °C; IR (KBr) 3008 (w, CH), 2939 (w, CH), 1830 (s, C=O), 1523 (s, NO_2), 1329 (s), 1322 (vs), 1238 (s), 1159 (m), 1032 cm^{-1} (m); ^1H NMR ($CDCl_3$) δ 5.18 (s, 4 H); ^{13}C NMR ($CDCl_3$) δ 77.2 (t), 190.3 (s); Anal. Calcd for $C_3H_4N_2O_3$: C, 31.04; H, 3.47. Found: C, 31.02; H, 3.29.

***N*-(Trifluoromethanesulfonyl)-3,3-dinitroazetidine (11).** To a refluxing solution of oxime **10**[6] (150 mg, 0.68 mmol) in dry CH_2Cl_2 (100 mL) under argon was added dropwise with stirring a solution of 100% HNO_3 [20 mL, freshly distilled from a 1:1 mixture of concd H_2SO_4 and fuming HNO_3 which contains urea (100 mg)][8] in CH_2Cl_2 (25 mL). The initial blue green color faded as the addition of HNO_3 progressed. After the reaction mixture had been refluxed for 1 h, 90% aqueous H_2O_2 was added very carefully dropwise by using an addition funnel (**CAUTION**: addition of H_2O_2 results in a strongly exothermic reaction). The resulting mixture was refluxed for 30 min after the addition of H_2O_2 had been completed. The reaction mixture was allowed to cool gradually to rt and then was poured over crushed ice (200 g). The organic layer was separated, and the aqueous layer was washed sequentially with water (5 × 100 mL) and brine (100 mL). The combined organic extracts were dried (Na_2SO_4) and filtered, and the filtrate was concd *in vacuo*. The green oily residue thereby obtained was purified by column chromatography on silica gel by eluting with 2% EtOAc–hexane. The first chromatography fractions afforded pure **11** (53 mg, 28%) as a colorless microcrystalline solid: mp 73–74 °C; IR (KBr) 3051 (w, CH), 2991 (w, CH), 1589 (s, NO_2), 1437 (m), 1386 (s), 1332 (m), 1276 (m), 1213 (s), 1126 (m), 1055 cm^{-1} (w); ^1H NMR ($CDCl_3$) δ 5.02 (s, 4 H); ^{13}C NMR ($CDCl_3$) δ 59.3 (t), 103.7 (s), 109.5 (s), 115.9 (s), 122.2 (s), 128.6 (s). Anal. Calcd for $C_4H_4N_3O_6F_3S$: C, 17.21; H, 1.44. Found: C, 17.35; H, 1.28. The structure of **11** was established unequivocally via application of X-ray crystallographic methods (*vide infra*).

Further elution of the column with 5% EtOAc–hexane afforded **12** (32 mg, 23%, formed via hydrolysis of **9**) as a colorless oil. The IR, ^1H NMR and ^{13}C NMR spectra of the material thereby obtained were identical in all respects with the corresponding spectra of authentic **12** which has been prepared previously in our laboratory.[6]

***N*-(Trifluoromethanesulfonyl)-3-(dibromomethylidene)-azetidine (13).**[9] To a mixture of Ph_3P (2.26 g, 8.6 mmol) and CBr_4 (1.42 g, 4.3 mmol) in toluene (100 mL) under argon at ambient temperature was added **12**[6] (350 mg, 1.72 mmol). The resulting mixture was refluxed for 12 h. The reaction mixture was allowed to cool gradually to rt and then filtered. The filtrate was concd *in vacuo*, thereby affording a viscous pale yellow oil. This oil was purified via column chromatography on neutral alumina by eluting with pentane. Pure **13** (520 mg, 83%) was thereby obtained as a colorless micrycrystalline solid: mp 105–106 °C; IR (KBr) 2939 (w, CH), 1711 (vw), 1440 (sh, w), 1383 (vs), 1205 cm^{-1} (vs); ^1H NMR ($CDCl_3$) δ 4.60 (s, 4 H); ^{13}C NMR ($CDCl_3$) δ 61.5 (t), 84.3 (s), 110.0 (s), 116.4 (s), 122.7 (s), 129.1 (s), 130.5 (s). Anal. Calcd for $C_5H_4F_3Br_2NO_2S$: C, 16.73; H, 1.12. Found: C, 16.93; H, 1.19.

Table 1. X-ray Structure Data for 11

compound	11
formula	$C_4H_4F_3N_3O_6S$
size (mm)	0.18 × 0.21 × 0.52
space group	*P*1-bar
a (Å)	6.8171(5)
b (Å)	8.3445(7)
c (Å)	10.0106(7)
α (deg)	66.951(6)
β (deg)	70.812(6)
γ (deg)	83.019(7)
V (Å^3)	494.87(7)
Z	2
D_c (g cm^{-3})	1.873
μ (cm^{-1})	3.82
ω–2θ ($2\theta_{max}$)	44
total refl	1212
unique refl	1212
$I \geq 3\sigma(I)$	1073
parameters	154
R, R_w	0.0488, 0.0562
$(\Delta/\sigma)_{max}$	<0.01
ϱ_{min}; ϱ_{max}	0.27; −0.28

X-ray Crystal Structure of 11. Data were collected on an Enraf-Nonius CAD-4 diffractometer by using the ω–2θ scan technique, Mo Kα radiation (λ = 0.71073 Å) and a graphite monochromator. Standard procedures used in our laboratory for this purpose have been described previously.[10] Pertinent X-ray data are given in Table 1.[11] Data were corrected for Lorentz and polarization effects but not for absorption. The structures were solved by direct methods (i.e., SHELX-86[12]), and the model was refined by using full-matrix least-squares techniques. All non-hydrogen atoms were treated with anisotropic thermal parameters. Hydrogen atoms were included in the model in idealized positions [U(H) = 1.3B_{eq}(C)]. All computations other than those specified were performed by using MolEN.[13] Scattering factors were taken from the usual sources.[14]

Acknowledgment. We thank the Robert A. Welch Foundation (Grant No. B-963 to A.P.M., B-1202 to S.G.B.), the United States Air Force (Contract F29601-92-K-0018), the Office of Naval Research (Grant No. N00017-92-J-1999), and the University of North Texas Faculty Research Committee for financial support of this study.

Supplementary Material Available: Copies of the ^1H and ^{13}C NMR spectra of **2**–**5** (8 pages). This material is contained in 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.

(9) Posner, G. H.; Loomis, G. L.; Sawaya, S. H. *Tetrahedron Lett.* **1975**, 1373.

(10) Mason, M. R.; Smith, J. M.; Bott, S. G.; Barron, A. R. *J. Am. Chem. Soc.* **1993**, *115*, 4971.

(11) The author has deposited atomic coordinates for **11** with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.

(12) Sheldrick, G. M. in *Crystallographic Computing*; Sheldrick, G. M., Krüger, C., Goddard, R., Eds. Oxford University Press: Oxford, England; pp 184–189.

(13) *MolEN, An Interactive Structure Solution Program*. Enraf-Nonius: Delft, The Netherlands, 1990.

(14) Cromer, D. T.; Waber, J. T. *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, 1974; Vol. IV, Table 2.