ternal standard. All IR spectra were recorded on a Perkin-Elmer 1420 spectrophotometer. The GLC analyses were carried out on a Carlo Erba HRGC 5300 chromatograph equipped with a Nordibond OV-1 column (25 m length, i.d. 0.32 mm) and a flame ionization detector. High-performance liquid chromatography (HPLC) was performed with a SHIMADZU LC-8 apparatus on a LiChrosorb RP-18 (7 μm) column using $CH_3CN/CH_3OH/H_2O$ (52/15/33 by volume) as eluent. Thin-layer chromatography (TLC) was performed on E. Merck precoated silica gel 60 F-254 plates (0.25 mm). Flash chromatography was carried out on Merck silica gel 60 (230-400 mesh), as described by Still.[15] Elemental analyses were performed by the microanalytical laboratory of the Instituto G. Donegani.

1,4-Dioxane and toluene were distilled from sodium and stored over activated 4A sieves. DMF was distilled from calcium hydride and stored over activated 4A sieves.

Aryl Triflates. Compounds **1a** and **4a** were prepared according to literature method.[11]

1-(((Trifluoromethyl)sulfonyl)oxy)naphthalene (1a) (84%): colorless oil; bp (bulb-to-bulb) 108-110 °C (0.4 mmHg); IR (neat) 1600, 1420, 1210 cm^{-1}; ^1H NMR δ 8.10 (br d, J = 8.3 Hz, 1 H), 7.94-7.8 (m, 2 H), 7.68-7.55 (m, 2 H). Anal. Calcd for $C_{11}H_7F_3O_3S$: C, 47.83; H, 2.55. Found: C, 48.07; H, 2.58.

1-(((Trifluoromethyl)sulfonyl)oxy)-9,10-anthraquinone (4a) (88%): yellow solid; mp 151-152 °C; IR (Nujol) 1670, 1580, 1420 cm^{-1}; ^1H NMR δ 8.45 (dd, J = 7.8, 1.2 Hz, 1 H), 8.39-8.20 (m, 2 H), 7.97-7.75 (m, 3 H), 7.63 (d, J = 8.2 Hz, 1 H). Anal. Calcd for $C_{15}H_7F_3O_5S$: C, 50.57; H, 1.98. Found: C, 50.45; H, 2.09.

Aryl Alkane- and Arenesulfonates. The following compounds were prepared in an analogous manner to aryl triflates, substituting trifluoromethanesulfonic anhydride with the corresponding sulfonyl chloride.

1-(((4-Fluorophenyl)sulfonyl)oxy)naphthalene (1b) (92%): white solid; mp 86-88 °C; IR (Nujol) 1450, 1370, 1180 cm^{-1}; ^1H NMR δ 8.10-7.65 (m, 5 H), 7.60-7.31 (m, 3 H), 7.24 (br d, J = 7.6 Hz, 1 H), 7.14 (br t, J = 7.9 Hz). Anal. Calcd for $C_{16}H_{11}FO_3S$: C, 63.57; H, 3.67. Found: C, 63.31; H, 3.64.

1-((Phenylsulfonyl)oxy)naphthalene (1c) (94%): white solid; mp 106-108 °C; IR (Nujol) 1440, 1365, 1180 cm^{-1}; ^1H NMR δ 8.1-7.1 (m, 11 H). Anal. Calcd for $C_{16}H_{12}O_3S$: C, 67.59; H, 4.25. Found: C, 67.50; H, 4.41.

1-(((4-Methylphenyl)sulfonyl)oxy)naphthalene (1d) (90%): white solid; mp 90-92 °C; IR (Nujol) 1450, 1360, 1175 cm^{-1}; ^1H NMR δ 8.35-8.06 (m, 3 H), 7.92-7.58 (m, 5 H), 7.50 (dd, J = 8.1, 1.3 Hz, 1 H), 7.31 (d, J = 8.5 Hz, 2 H), 2.38 (s, 3 H). Anal. Calcd for $C_{17}H_{14}O_3S$: C, 68.44; H, 4.73. Found: C, 68.12; H, 4.42.

1-(((4-Methoxyphenyl)sulfonyl)oxy)naphthalene (1e) (95%): white solid; mp 101-103 °C; IR (Nujol) 1450, 1370, 1180 cm^{-1}; ^1H NMR δ 8.02-7.60 (m, 5 H), 7.53-7.28 (m, 3 H), 7.21 (br d, J = 8.2 Hz, 1 H), 6.90 (br d, J = 9.0 Hz, 2 H), 3.82 (s, 3 H). Anal. Calcd for $C_{17}H_{14}O_4S$: C, 64.95; H, 4.49. Found: C, 64.79; H, 4.41.

1-((Methylsulfonyl)oxy)naphthalene (1f) (85%): colorless oil; bp (bulb-to-bulb) 183-185 °C (0.4 mmHg); IR (neat) 1590, 1370, 1180 cm^{-1}; ^1H NMR δ 8.16 (dd, J = 9.0, 1.0 Hz, 1 H), 7.92-7.69 (m, 2 H), 7.66-7.22 (m, 4 H), 3.16 (s, 3 H). Anal. Calcd for $C_{11}H_{10}O_3S$: C, 59.44; H, 4.53. Found: C, 59.61; H, 4.65.

4-(((4-Fluorophenyl)sulfonyl)oxy)benzonitrile (2b) (89%): white solid; mp 102-104 °C; IR (Nujol) 2230, 1580, 1485, 1370, 1160 cm^{-1}; ^1H NMR δ 7.96-7.75 (m, 2 H), 7.63 (td, J = 8.8, 2 Hz, 2 H), 7.23 (tt, J = 8.2, 1.9 Hz, 2 H), 7.13 (td, J = 8.7, 1.9 Hz, 2 H). Anal. Calcd for $C_{13}H_8FNO_3S$: C, 56.31; H, 2.91. Found: C, 56.46; H, 3.04.

4-(((4-Fluorophenyl)sulfonyl)oxy)-1-acetophenone (3b) (90%): white solid; mp 75-77 °C; IR (Nujol) 1670, 1370, 1150 cm^{-1}; ^1H NMR δ 8.05-7.70 (m, 4 H), 7.36-7.00 (m, 4 H), 2.59 (s, 3 H). Anal. Calcd for $C_{14}H_{11}FO_4S$: C, 57.14; H, 3.77. Found: C, 57.32, H, 3.70.

1-(((4-Fluorophenyl)sulfonyl)oxy)-9,10-anthraquinone (4b) (90%): yellow solid; mp 158-160 °C; IR (Nujol) 1665, 1580, 1370 cm^{-1}; ^1H NMR δ 8.34 (dd, J = 7.8, 1.3 Hz, 1 H), 8.30-8.00 (m, 4 H), 7.89-7.68 (m, 3 H), 7.6 (dd, J = 8.2, 1.3 Hz, 1 H), 7.35-7.15 (m, 2 H). Anal. Calcd for $C_{20}H_{11}FO_5S$: C, 62.82; H, 2.90. Found: C, 62.69; H, 2.78.

1-((Phenylsulfonyl)oxy)-9,10-anthraquinone (4c) (95%): yellow solid; mp 144-146 °C; IR (Nujol) 1665, 1570, 1350 cm^{-1}; ^1H NMR δ 8.32 (dd, J = 7.8, 1.2 Hz, 1 H), 8.27-8.13 (m, 2 H), 8.08-7.98 (m, 2 H), 7.86-7.45 (m, 7 H). Anal. Calcd for $C_{20}H_{12}O_5S$: C, 65.93; H, 3.32. Found: C, 65.99; H, 3.36.

1-(((4-Methylphenyl)sulfonyl)oxy)-9,10-anthraquinone (4d) (94%): yellow solid; mp 156-158 °C; IR (Nujol) 1670, 1580, 1370 cm^{-1}; ^1H NMR δ 8.31 (dd, J = 7.8, 1.2 Hz, 1 H), 8.28-8.10 (m, 2 H), 7.95-7.60 (m, 5 H), 7.53 (dd, J = 8.2, 1.2 Hz, 1 H), 7.40-7.24 (m, 2 H), 2.40 (s, 3 H). Anal. Calcd for $C_{21}H_{14}O_5S$: C, 66.66; H, 3.73. Found: C, 66.82; H, 3.81.

1-(((4-Methoxyphenyl)sulfonyl)oxy)-9,10-anthraquinone (4e) (91%): yellow solid; mp 154-156 °C; IR (Nujol) 1670, 1585, 1370 cm^{-1}; ^1H NMR δ 8.3 (dd, J = 7.8, 1.3 Hz, 1 H), 8.27-8.10 (m, 2 H), 8.00-7.85 (m, 2 H), 7.85-7.66 (m, 3 H), 7.55 (dd, J = 8.2, 1.3 Hz, 1 H), 7.02-6.85 (m, 2 H), 3.8 (s, 3 H). Anal. Calcd for $C_{21}H_{14}O_6S$: C, 63.95; H, 3.58. Found: C, 63.79; H, 3.45.

1-((Methylsulfonyl)oxy)-9,10-anthraquinone (4f) (95%): yellow solid; mp 186-188 °C; IR (Nujol) 1660, 1580, 1360 cm^{-1}; ^1H NMR δ 8.40-8.15 (m, 3 H), 7.90-7.65 (m, 4 H), 3.50 (s, 3 H). Anal. Calcd for $C_{15}H_{10}O_5S$: C, 59.90; H, 3.33. Found: C, 60.15; H, 3.44.

Palladium-Catalyzed Reduction of Aryl Sulfonates. General Procedure (Table I, Entry 1). To a stirred solution of **1a** (1 g, 3.62 mmol) in DMF (25 mL) under an argon atmosphere at room temperature were sequentially added Et_3N (1.46 g, 2.01 mL, 14.48 mmol), formic acid (0.67 g, 55 mL, 14.48 mmol), PPh_3 (0.19 g, 0.724 mmol), and $Pd(AcO)_2$ (0.041 g, 0.181 mol). The reaction temperature was raised to 40 °C. After 5 h the reaction mixture was diluted with methylene chloride (100 mL) and brought to pH 7.0 with sequential washes of 5% aqueous hydrochloric acid (2 × 30 mL) and water, dried (anhydrous Na_2SO_4), filtered, and concentrated in vacuo. The crude product was purified by flash chromatography (hexane/ethyl acetate, 95/5 by volume), affording naphthalene **5** (0.417 g, 90%). This procedure was used in all of the reactions described in Tables I-V. Anthraquinone **8** in Table V was purified by flash chromatography (hexane/ethyl acetate, 8/2 by volume).

Acknowledgment. We thank Professor Gian Paolo Chiusoli for helpful and stimulating discussions.

Registry No. **1a**, 99747-74-7; **1b**, 123412-32-8; **1c**, 15161-04-3; **1d**, 68211-49-4; **1e**, 123412-33-9; **1f**, 38262-42-9; **2b**, 123412-34-0; **3b**, 123412-35-1; **4a**, 123412-36-2; **4b**, 123412-37-3; **4c**, 123412-38-4; **4d**, 107035-89-2; **4e**, 123412-39-5; **4f**, 123412-40-8; **5**, 91-20-3; **6**, 100-47-0; **7**, 98-86-2; **8**, 84-65-1; **9**, 129-43-1; DPPP, 6737-42-4; DPPM, 2071-20-7; DPPE, 1663-45-2; DPPB, 7688-25-7; DPPF, 12150-46-8; DpTPE, 70320-30-8; $Pd(AcO)_2$, 3375-31-3; $P(p\text{-}ClPh)_3$, 1159-54-2; $P(p\text{-tolyl})_3$, 1038-95-5; PCH_3Ph_2, 1486-28-8; $P(CH_3)_2Ph$, 672-66-2.

(15) Still, W. C.; Kahn, M.; Mita, A. *J. Org. Chem.* **1978**, *43*, 2923.

Decarboxylation of Sodium 1-Nitrocyclopropanecarboxylates. A Facile Synthesis of Nitrocyclopropanes

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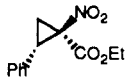
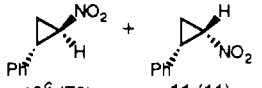
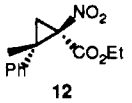
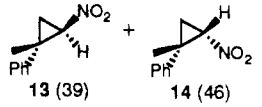
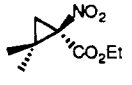
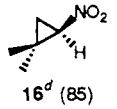
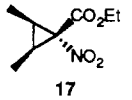
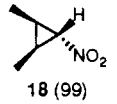
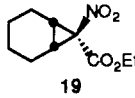
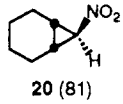
Nitroacetic acid is stable in acidic aqueous solution, and its dianion is stable in basic solution, yet in neutral aqueous solution the monoanion (**1**) decarboxylates within seconds to nitronate (**2**).[1] Other acyclic 1-nitrocarboxylic acids behave similarly.[2] However, 1-nitrocyclopropane-

(1) (a) Finkbeiner, H. L.; Stiles, M. *J. Am. Chem. Soc.* **1963**, *85*, 616. (b) Pedersen, K. S. *Acta Chem. Scand.* **1947**, *1*, 437.

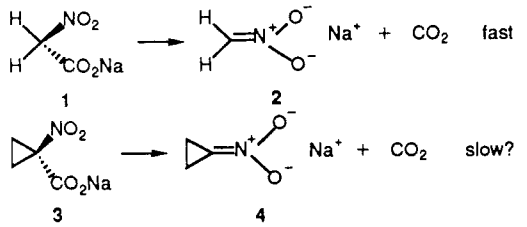
0022-3263/90/1955-0353$02.50/0

Table I. Preparation of Nitrocyclopropanes by Saponification and Decarboxylation of Ethyl 1-Nitrocyclopropanecarboxylates

entry	nitrocyclopropyl ester	nitrocyclopropane (yield, %)
1[a]	 **9**	 **10**[c] (79) + **11** (11)
2[b]	 **12**	 **13** (39) + **14** (46)
3[b]	 **15**	 **16**[d] (85)
4[a]	 **17**	 **18** (99)
5[b]	 **19**	 **20** (81)

[a] Yield based on sodium cyclopropanecarboxylate. [b] Yield based on cyclopropyl ester. [c] Reference 9a. [d] Schöllkopf, U.; Markusch, P. *Justus Liebigs Ann. Chem.* **1971**, *753*, 143.

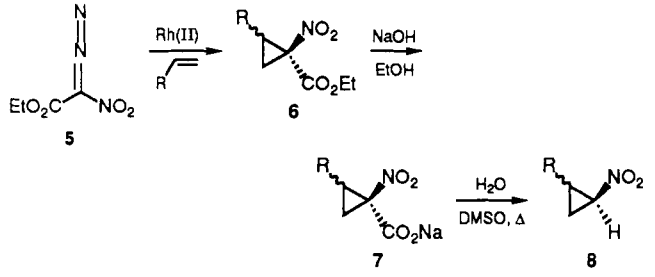
carboxylic acid and its sodium salt (**3**) should be much more resistant to decarboxylation because of the additional ring strain associated with the introduction of an sp^2 atom into a three-membered ring (**4**).[3]



1 **2** **3** **4**

While acyclic malonic acids and β-keto acids undergo thermal decarboxylation,[4] their cyclopropyl analogues require more forcing conditions[5] and generally give poorer results.[6] We have recently detailed the preparation of a series of ethyl 1-nitrocyclopropanecarboxylates[7] (**6**) and report here that these compounds may be easily converted to the corresponding nitrocyclopropanes (**8**) in high yields. We believe that this is now the method of choice for the preparation of many substituted nitrocyclopropanes.[8-10]

Ethyl 1-nitrocyclopropanecarboxylates (**6**) are conveniently available from the reaction of ethyl nitrodiazoacetate (**5**)[11] with alkenes in the presence of rhodium(II) acetate.[7] The esters can be converted to the sodium carboxylates (**7**) with ethanolic NaOH solution at room temperature. Decarboxylation of these salts in wet DMSO solution occurs at 80 °C to produce nitrocyclopropanes (**8**) in almost quantitative yield. This reaction presumably proceeds via the 1-nitrocyclopropyl anion (**4**),[12] which is quickly protonated under the reaction conditions. The separation of the diastereomeric nitrocyclopropyl esters (**6**) is not required since both isomers yield almost the same ratio of diastereomeric nitrocyclopropanes (**8**) after decarboxylation.



5 **6** **7** **8**

Several representative examples of this decarboxylation reaction are shown in Table I.

Further studies on the reaction and on the intermediate nitrocyclopropyl anion are in progress.[13]

Experimental Section

General Methods. ^1H NMR spectra were obtained in $CDCl_3$ at 250 or 500 MHz. Chemical shifts are reported in δ units with $CHCl_3$ as an internal standard at 7.20 ppm. ^{13}C NMR spectra were obtained at 125 MHz. Chemical shifts are reported in δ units with $CDCl_3$ as an internal standard at 77.0 ppm. High-resolution mass spectra were obtained on a VG-ZAB-E mass spectrometer under ammonia chemical ionization conditions. Infrared spectra were obtained as thin films. Ethyl 1-nitrocyclopropanecarboxylates were prepared by rhodium(II) acetate cyclopropanation of the appropriate alkene with ethyl nitrodiazoacetate as previously described.[7] All reagents were used as supplied.

Saponification of Ethyl 1-Nitrocyclopropanecarboxylates. To 5 mmol of ester in 5 mL of absolute ethanol are added 5 mL of 1 M NaOH/ethanol solution with stirring at room temperature. The solution turns yellow and solidifies after a few minutes. More ethanol is added to ensure efficient stirring. The reaction is usually complete within 30 min as indicated by thin-layer chromatography, although hindered esters **17** and **19** may require up to 12 h. Most of the ethanol is then removed under reduced pressure at 35 °C. If desired, dry purified salt may be obtained by removing the residual ethanol under high vacuum followed by washing of the solid with methylene chloride and continued drying under vacuum at 50 °C.

Decarboxylation of Sodium 1-Nitrocyclopropanecarboxylates. The sodium salts from 5 mmol of ester are dis-

(2) (a) O'Bannon, P. E.; Carroll, P. J.; Dailey, W. P. *Tetrahedron Lett.* **1988**, *29*, 6031. (b) Black, A. P.; Babers, F. H. *Organic Syntheses*; Wiley: New York, 1943; Collect. Vol. II, p 512.

(3) (a) The difference in strain energy between cyclopropane and methylenecyclopropane is 14 kcal/mol: Greenberg, A.; Liebman, J. *Strained Organic Molecules*; Academic Press: New York, 1978. (b) De Boer, T. J.; van Velzen, J. C. *Recl. Trav. Chim.* **1960**, *79*, 231.

(4) (a) March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley: New York, 1985. (b) Clark, L. W. In *The Chemistry of Carboxylic Acids and Esters*; Patai, S., Ed.; Wiley: New York, 1969.

(5) Musso, H. *Chem. Ber.* **1968**, *101*, 3710.

(6) (a) For instance, see: McCloskey, C. M.; Coleman, G. H. *Organic Syntheses*; Coll. Vol. 3, Wiley: New York, 1955; Collect. Vol. III, p 221. Reference 4b. (b) Vaidyanathan, G.; Wilson, J. W. *J. Org. Chem.* **1989**, *54*, 1810.

(7) (a) O'Bannon, P. E.; Dailey, W. P. *J. Org. Chem.* **1989**, *54*, 3096. (b) The spectral data for compound **12** have not been previously reported and are included in this paper.

(8) O'Bannon, P. E.; Dailey, W. P. *Tetrahedron Lett.* **1988**, *29*, 987.

(9) Other methods for the synthesis of nitrocyclopropanes: (a) Asunskis, J.; Shechter, H. *J. Org. Chem.* **1968**, *33*, 1164. (b) Parham, W. E.; Braxton, H. G.; Serres, C. *J. Org. Chem.* **1961**, *26*, 1831. (c) Kuwajima, I.; Ryochi, A.; Tomso, S. *Tetrahedron Lett.* **1983**, *24*, 4429. (d) Valades, L.; Siminez, M.; Rodreguez-Hahn, L. *Rev. Latinoam. Quim.* **1975**, *6*, 152. (e) Russell, G. A.; Makosza, M.; Hershberger, J. *J. Org. Chem.* **1979**, *44*, 1195. (f) Lampman, G. M.; Horne, D. A.; Hager, G. D. *J. Chem. Eng. Data* **1969**, *14*, 396.

(10) Wade, P. A.; Dailey, W. P.; Carroll, P. J. *J. Am. Chem. Soc.* **1987**, *109*, 5452.

(11) Schöllkopf, U.; Tonne, P. *Justus Liebigs Ann. Chem.* **1971**, *753*, 135.

(12) (a) Kai, Y.; Knochel, P.; Kwiatkowski, S.; Dunitz, J. D.; Oth, J. F. M.; Seebach, D.; Kalinowski, H.-O. *Helv. Chim. Acta* **1982**, *65*, 137. (b) Wagner, H.-U.; Boche, G. *Helv. Chim. Acta* **1983**, *66*, 842. (c) For a review, see: Boche, G.; Walborsky, H. M. In *The Chemistry of the Cyclopropyl Group*; Rappoport, Z., Ed.; Wiley: New York, 1987.

(13) O'Bannon, P. E.; Dailey, W. P. *J. Am. Chem. Soc.*, in press.

solved in 10 mL of a 10:1 DMSO/water solution in a 25-mL round-bottom flask equipped with a reflux condenser, and the solution is heated in an oil bath at 80 °C for 30 min. After cooling, the solution is diluted with water and extracted with diethyl ether. The organic layer is thoroughly washed with water to remove all traces of DMSO and dried. After careful concentration of a rotary evaporator, pure nitrocyclopropane is obtained.[14] Cyclopropanes **10**, **11**, **13**, and **14** are nonvolatile and are easily separated by flash column chromatography (ether/hexane, 0–5%).

***cis*-(2-Nitrocyclopropyl)benzene (11)**: ^{1}H NMR δ 1.58 (m, 1 H), 2.30 (m, 1 H), 2.80 (m, 1 H), 4.57 (m, 1 H), 7.16–7.23 (m, 5 H); ^{13}C NMR δ 13.5, 28.5, 61.6, 128.0, 128.4, 129.2, 132.4; IR 1540, 1360 cm^{-1}.

Ethyl *trans*-2-methyl-1-nitro-*cis*-2-phenylcyclopropanecarboxylate (12): ^{1}H NMR δ 0.81 (t, J = 7.2 Hz, 3 H), 1.45 (s, 3 H), 2.08 (d, J = 6.8 Hz, 1 H) 2.36 (d, J = 6.8 Hz, 1 H), 3.83 (q, J = 7.2 Hz, 2 H), 7.22–7.30 (m, 5 H); ^{13}C NMR δ 13.4, 24.9, 26.3, 39.1, 62.4, 76.1, 127.6, 127.7, 128.6, 139.1, 163.5; IR 1740, 1540 cm^{-1}; HRMS (M + NH$_4^+$) 267.131, calcd for $C_{13}H_{19}N_2O_4$ 267.133.

***trans*-(1-Methyl-2-nitrocyclopropyl)benzene (13)**: ^{1}H NMR δ 1.49 (s, 3 H), 1.62 (apparent t, J = 6.8 Hz, 1 H), 2.01 (dd, J = 6.6, 4.6 Hz, 1 H), 4.34 (dd, J = 7.1, 4.6 Hz, 1 H), 7.13–7.27 (m, 5 H); ^{13}C NMR δ 19.3, 21.8, 33.9, 66.3, 127.2, 127.4, 128.8, 142.5; IR 1540, 1360 cm^{-1}; HRMS (M + H$^+$) 178.086, calcd for $C_{10}H_{12}NO_2$ 178.087.

***cis*-(1-Methyl-2-nitrocyclopropyl)benzene (14)**: ^{1}H NMR δ 1.36 (apparent t, J = 6.5 Hz, 1 H), 1.38 (s, 3 H), 2.28 (dd, J = 5.9, 4.0 Hz), 4.32 (dd, J = 6.6, 4.0 Hz), 7.16–7.23 (m, 5 H); ^{13}C NMR δ 21.6, 26.7, 35.3, 65.8, 127.6, 128.0, 128.6, 138.3; IR 1540, 1360 cm^{-1}; mp (from CH_2Cl_2) 61–62 °C.

***trans,trans*-1,2-Dimethyl-3-nitrocyclopropane (18)**: ^{1}H NMR δ 1.08 (m, 6 H), 2.06 (m, 2 H), 3.63 (t, J = 3.2 Hz, 1 H); ^{13}C NMR δ 10.2, 24.7, 66.8; IR 1540, 1360 cm^{-1}. HRMS (M + NH$_4^+$) 133.096, calcd for $C_5H_{13}N_2O_2$ 133.097.

***anti*-7-Nitrobicyclo[4.1.0]heptane (20)**: ^{1}H NMR δ 1.11 (m, 2 H), 1.30 (m, 2 H), 1.74 (m, 2 H), 1.92 (m, 2 H), 2.20 (m, 2 H), 4.03 (t, J = 3.0 Hz, 1 H); ^{13}C NMR δ 18.7, 20.4, 21.5, 64.7; IR 1540, 1360 cm^{-1}; HRMS (M + H$^+$) 142.088, calcd for $C_7H_{12}NO_2$ 142.087.

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Supplementary Material Available: ^{1}H and ^{13}C NMR spectra for all new compounds (**11–14**, **18**, and **20**) (12 pages). Ordering information is given on any current masthead page.

(14) Product nitrocyclopropanes were judged to be >90% pure by ^{1}H and ^{13}C NMR and TLC.

Formation and Crystal Structure of a Novel Azabishomotwistane

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The reaction of bicyclo[3.2.2]nonane-6,8-dione[1] (**1**) with (isocyanomethyl)lithium, followed by hydrolysis, produces the bis(amino alcohol) **2**.[2,3] The latter underwent efficient Tiffeneau–Demjanov ring expansion to bicyclo[3.3.3]undecane-2,6-dione (**3**), which was used as the precursor for generation of, and studies on, the strained pyramidalized alkene[4] tricyclo[3.3.3.0^{2,6}]undec-2(6)-ene. Recently we have attempted to prepare the bis(amino alcohol) **2** by an alternative route and encountered unexpected results, which are presented here.

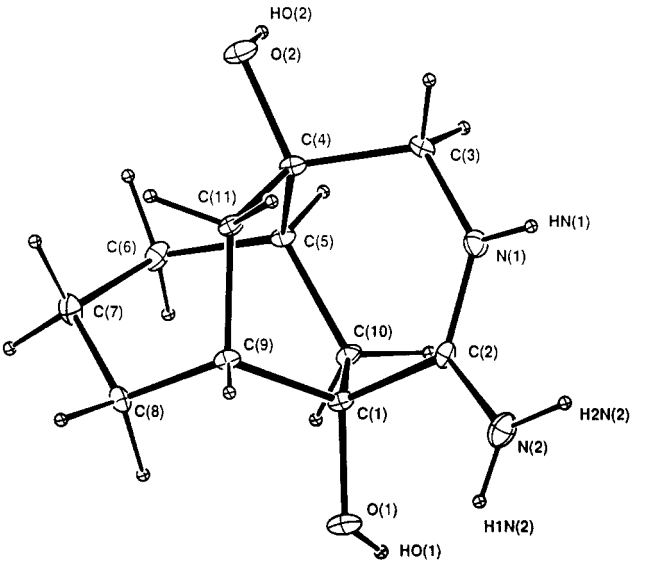

Figure 1. The crystallographic numbering system used for structure **6**.

β-Amino alcohols for use in the Tiffeneau–Demjanov procedure are commonly obtained by reduction of the corresponding trimethylsilyl cyanohydrin ethers,[5] which, in turn, are readily available from the reaction of ketones with trimethylsilyl cyanide.[6] Reaction of diketone **1** with trimethylsilyl cyanide and potassium cyanide in the presence of dicyclohexyl-18-crown-6 gave a single product (71% yield) with average C_2 symmetry (as revealed by its ^{13}C NMR spectrum). Subsequent events demonstrated that the two cyano groups were anti to the propano bridge and that this material therefore had the structure **4** (see Scheme I).

Reduction of **4** with lithium aluminum hydride in diethyl ether, followed by alkaline hydrolysis to remove the silyl groups, gave a high yield of a single product as an oil. Mass spectral and combustion analysis of its crystalline hydrochloride salt provided the formula $C_{11}H_{19}N_2O_2Cl$. The ^{13}C NMR spectrum comprised 11 signals (demonstrating lack of the anticipated C_2 symmetry), and the ^{1}H NMR data included three one-proton resonances due to amine salt hydrogens at δ 8.21, 8.87, and 9.51. It was therefore clear that this product did not have the anticipated structure **2**.

The structure of this highly crystalline product was determined by X-ray crystallography and found to be the amidinium derivative[7] 4-amino-5-azatricyclo[5.5.0.0^{3,9}]dodec-4-ene-3,7-diol hydrochloride (**6**). The crystallographic numbering system used is shown in Figure 1. Each crystal contains only one enantiomer of **6**, individual molecules

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