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.

Acknowledgment. We are grateful to the Air Force Astronautics Laboratory, Edwards Air Force Base, for generous financial support.

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.

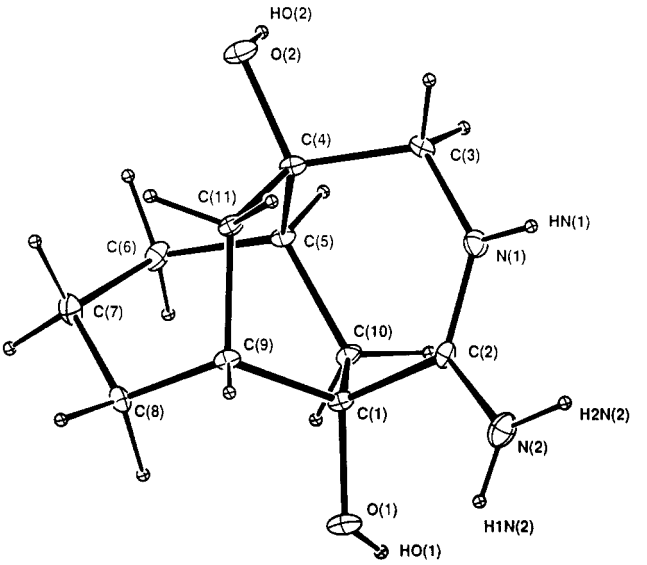

Figure 1. The crystallographic numbering system used for structure **6**.

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

(1) Wood, G.; Woo, E. P. *Can. J. Chem.* **1968**, *46*, 3713.
(2) Greenhouse, R.; Ravindranathan, T.; Borden, W. T. *J. Am. Chem. Soc.* **1976**, *98*, 6738.
(3) Greenhouse, R.; Borden, W. T.; Ravindranathan, T.; Hirotsu, K.; Clardy, J. *J. Am. Chem. Soc.* **1977**, *99*, 6955.
(4) For an outline of recent work in this area, see: Symposium on Pyramidalized Alkenes. ACS Division of Organic Chemistry. *Abstracts of Papers*, 196th National Meeting of the American Chemical Society, Los Angeles, CA; American Chemical Society: Washington, DC, 1988.
(5) Parham, W. E.; Roosevelt, C. S. *Tetrahedron Lett.* **1971**, 923.
(6) Evans, D. A.; Carroll, G. L.; Truesdale, L. K. *J. Org. Chem.* **1974**, *39*, 914.
(7) (a) Shriner, R. L.; Neumann, F. W. *Chem. Rev.* **1944**, *35*, 351. (b) Patai, S., Ed. *The Chemistry of Amidines and Imidates*; Interscience: New York, 1975. (c) Granik, V. G. *Russ. Chem. Rev.* (*Engl. Transl.*) **1983**, *52*, 377. (d) Oediger, H.; Möller, F.; Eiter, K. *Synthesis* **1972**, 591.

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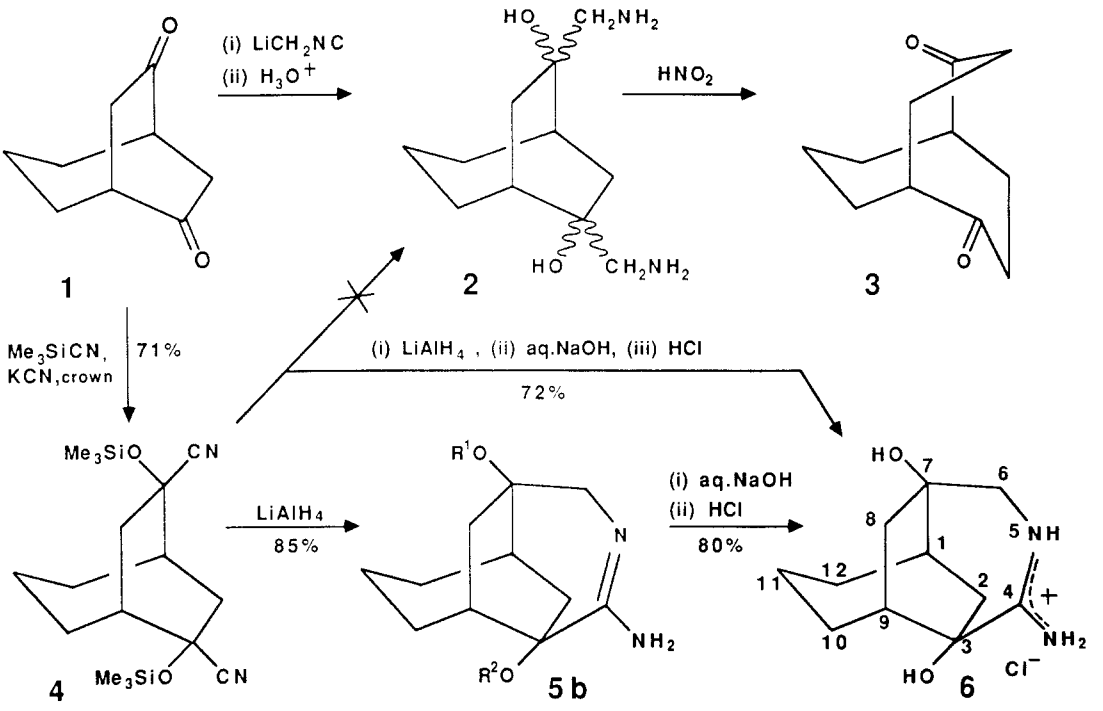
Scheme I



of which are arranged in doubly stranded chains (Figure II, supplementary material). Single chains are built up from molecules hydrogen bonded through the hydroxy groups by means of atoms HO(1) (acceptor) and O(2) (donor). Cross-linking between two adjacent single chains is effected by the chloride ions which hydrogen bond to HO(2) (acceptor) and only one of the amino hydrogens, H2N(2) (acceptor). Interactions between the resulting doubly stranded chains comprise only van der Waals forces. The crystal structure of **6** also reveals torsion angles of -179.7° for C(3)-N(1)-C(2)-N(2) and -0.7° for C(3)-N(1)-C(2)-C(1), with notable bond lengths of 1.311 Å for N(1)-C(2) and 1.307 Å for N(2)-C(2). These data are in full accord with the planar, delocalized configuration expected for amidine salts.[8]

Brief mention should also be made of the spectral data recorded for this compound. The amine salt proton chemical shifts mentioned earlier compare well with the values of δ 8.83 and 9.33 observed for acetamidinium chloride in dimethyl sulfoxide.[9] Although tertiary alcohol protons normally appear as sharp singlets in this solvent, those of **6** were recorded as very broad, ill-defined peaks. In marked contrast, the three nonequivalent amine salt protons all gave sharp signals with no discernible coupling, except for N5-H, which was coupled (J = 5.25 Hz) with one only of the C6 protons. [Atom numbers without parentheses are those for **6** in Scheme I.]

Although the C4 ^{13}C chemical shift value (δ 174.4) is high compared to the literature values of (δ (δ 148.9–160.5) reported for acyclic amidine derivatives,[10] Jackman and Jen[11] have observed greater values (δ 157.0–168.5) when the amidine comprises part of a ring, and values for the amidine salts are known to be higher than for the parent amidines.[12] All observed spectral data are therefore compatible with the structure **6**.

A well-established[13] synthetic route to amidines involves the addition of amines to nitriles. If the free amines are employed, then usually strong heating is required unless the nitrile group is activated by an electron-withdrawing group on the α-carbon atom.[14] A more effective procedure is to employ a metalated amine, usually the sodium salt or magnesium halide derivative.[13] Presumably in the present work reduction of one cyano group of **4** provides a lithium salt, allowing rapid intramolecular attack on the remaining cyano group.

In order to demonstrate that formation of the amidine group took place during the reduction step, the bis(cyanide) **4** was reacted with lithium aluminum hydride but the subsequent basic hydrolysis and hydrochloride salt formation steps were omitted. Further unexpected results were obtained. The single compound produced was clearly an amidine derivative because of the similarity of its spectral data with those of **6**, but it was not the anticipated product **5a**. The combustion analytical data are compatible with $(C_{14}H_{26}N_2O_2Si)_2 \cdot H_2O$, the hemihydrate of one of the two monodesilylated isomers **5b** and **5c**. This was confirmed by exact-mass measurement of the anhydrous fragment using chemical-ionization mass spectrometry. Trace amounts of **5a** could also be detected in the crude reaction product by using this technique.

(8) (a) Sax, M.; Pletcher, J.; Yoo, C. S.; Stewart, J. M. *Acta Crystallogr., Sect. B* **1971**, *27*, 1635. (b) Reck, G.; Hagen, V.; Wagner, G. *Cryst. Struct. Commun.* **1982**, *11*, 1099.

(9) Neuman, R. C.; Hammond, G. S.; Dougherty, T. J. *J. Am. Chem. Soc.* **1962**, *84*, 1506.

(10) (a) Naulet, N.; Filleux, M. L.; Martin, G. J.; Pornet, J. *Org. Magn. Reson.* **1975**, *7*, 326. (b) Oszczapowicz, J.; Raczynska, E.; Osek, J. *Magn. Reson. Chem.* **1986**, *24*, 9.

(11) Jackman, L. M.; Jen, T. *J. Am. Chem. Soc.* **1975**, *97*, 2811.

(12) Häfelinger, G. In *The Chemistry of Amidines and Imidates*; Patai, S., Ed.; Interscience: New York, 1975; Chapter 1, pp 69–74.

(13) (a) Gautier, J.-A.; Miocque, M.; Farnoux, C. C. In *The Chemistry of Amidines and Imidates*; Patai, S., Ed.; Interscience: New York, 1975; Chapter 7. (b) Söll, H. In Houben-Weyl, *Die Methoden der Organischen Chemie*, 4th ed.; Thieme, G.: Leipzig, 1958; Vol. XI(2), pp 38–69. (c) Tennant, G. In *Comprehensive Organic Chemistry*; Barton, D. H. R., Ollis, W. D., Eds.; Pergamon Press: Oxford, 1979; Vol. 2, Chapter 8.

(14) Curtiss, R. S.; Nickell, L. P. *J. Am. Chem. Soc.* **1913**, *35*, 885.

Although amidines can exist in two tautomeric forms, the ^{13}C NMR spectrum of this product clearly showed only one set of signals, and it is already known[15] that in alicyclic amidines the thermodynamically favored structure is that with the imine group endocyclic. Distinction between the possible structures **5b** and **5c** was less clear-cut, particularly since the ^{13}C NMR substituent parameters (α, β, and γ effects) for the (trimethylsilyl)oxy group[16] are almost identical with those for the hydroxy group.[17] However, the formation of an 85% yield of a single monosilylated isomer indicated a considerable difference in hydrolytic reactivity of the silyloxy groups of **5a**. We tentatively propose that this material has the structure **5b** since the spatial proximity of the C3 siloxy and C4 amino groups could lead to an intramolecular base-catalyzed hydrolysis. Unfortunately, definite proof of structure could not be obtained by X-ray crystallography because all crystals examined suffered from twinning disorder. On the other hand, this monosilylated derivative was readily converted (80% yield) into the amidinium chloride **6** by using the appropriate reaction conditions, thereby demonstrating its intermediacy in the original reaction.

Isolation of the products **5b** and **6** from a lithium aluminum hydride reduction reaction at first sight appears improbable, since amidines are known to react with reducing agents such as diisobutylaluminum hydride,[18] sodium borohydride,[19] and lithium aluminum hydride.[20] However, there are also literature reports where formamidines have been produced by reduction of carbodiimides using sodium borohydride,[21] and by reduction of 1,3-disubstituted ureas using either sodium borohydride[22] or lithium aluminum hydride.[23] The latter reaction gave excellent yields, provided excess reducing agent was avoided.

The ring system produced in these reactions, 5-azatricyclo[5.5.0.0^{3,9}]dodecane, is a novel example of an azabishomotwistane system and is previously unreported. Compared to tricyclo[4.4.0.0^{3,8}]decane (twistane), the central twist cyclohexane ring is retained but the two ethano bridges have each been expanded by one atom, nitrogen and carbon, repectively. This procedure may be applicable to the synthesis of other multicyclic amidine derivatives, and we identify several factors likely to be important in such attempts. Not only should potential precursors have two closely positioned nitrile groups but adjacent electron-withdrawing groups are also desirable. Excess reducing agent and reaction times should be avoided, and the concentration/solvent should be such that solubility of the lithium salts is limited. In support of the latter, we note that **6** was recovered unchanged when subjected to the reaction conditions used for its formation.

Experimental Section

Melting points were recorded on a Kofler instrument and are uncorrected. NMR spectra were recorded at 500 MHz for ^1H and 125.8 MHz for ^{13}C. Substitution of carbon atoms was determined by the DEPT procedure.

6,8-Bis[(trimethylsilyl)oxy]bicyclo[3.2.2]nonane-*endo*-6,*endo*-8-dicarbonitrile (4). Bicyclo[3.2.2]nonane-6,8-dione[1] (**1**) (3.80 g, 25.0 mmol), potassium cyanide (0.27 g), and dicyclohexyl-18-crown-6 (0.40 g) were added with stirring to dry 1,2-dimethoxyethane (30 mL; freshly distilled from $LiAlH_4$). Trimethylsilyl cyanide (5.00 g, 50.4 mmol) was then added, causing the solution to heat up and turn orange. After 10 min, the mixture had cooled to room temperature, but stirring was continued for a further 4.5 h. Evaporation of solvent under reduced pressure gave a yellow-brown solid, which was recrystallized from 60–80 °C petroleum to give the pure bis(cyanide) **4** (6.18 g, 71%): mp 83–85 °C; IR (paraffin mull) 2240 (w), 1260 (s), 1145 (m), 1105 (s), 1055 (m), 1035 (m), 1000 (m), 980 (w), 940 (s), 875 (s), 850 (s), 765 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.88–2.84 (m, 2 H), 2.36–2.33 (m, 2 H), 2.15–2.09 (m, 2 H), 2.06–2.02 (m, 2 H), 1.64–1.58 (m, 2 H), 1.52–1.46 (m, 2 H), 0.27 (s, 18 H); ^{13}C NMR ($CDCl_3$) δ 122.7 (C), 68.8 (C), 42.0 (CH), 40.9 (CH_2), 28.3 (CH_2), 20.3 (CH_2), 1.1 (CH_3). Anal. Calcd for $C_{17}H_{30}N_2O_2Si_2$: C, 58.24; H, 8.62; N, 7.99. Found: C, 58.43; H, 8.89; N, 8.43.

4-Amino-7-[(trimethylsilyl)oxy]-5-azatricyclo[5.5.0.0^{3,9}]-dodec-4-en-3-ol (5b). To a stirred solution of lithium aluminum hydride (0.30 g) in diethyl ether (30 mL) was added dropwise over several minutes a solution of the bis(cyanide) **4** (1.05 g, 3.0 mmol) in anhydrous ether (10 mL). After 4 h, the excess reagent was destroyed by cautious addition of wet ether and then water. The ether layer was decanted and the aqueous phase extracted several times with chloroform. The combined organic extracts were dried (Na_2SO_4) and filtered, and the solvent was evaporated to give a monosilylated amidine derivative tentatively identified as **5b** hemihydrate (0.74 g, 85%): mp 170–172 °C (from $CHCl_3$); IR (paraffin mull) 3520 (m), 3400 (m), 1640 (s), 1555 (w), 1250 (m), 1110 (s), 1085 (m), 940 (m), 900 (m), 870 (w), 840 (m), 755 (w) cm^{-1}; ^1H NMR [$(CD_3)_2SO$] δ 3.7 (v br s, exchanged with D_2O; NH_2, OH, and H_2O), 3.46 (d, 1 H, J = 14.0 Hz, C6-H_aH_b), 3.15 (d, 1 H, J = 14.0 Hz, C6-H_aH_b), 2.17–1.42 (m, 12 H), 0.09 (s, 9 H); ^{13}C NMR [$(CD_3)_2SO$] δ 168.8 (C), 76.9 (C), 72.5 (C), 59.7 (CH_2), 42.3 (CH), 40.4 (CH), 37.5 (CH_2), 35.3 (CH_2), 30.4 (CH_2), 26.7 (CH_2), 20.5 (CH_2), 2.9 (CH_3). Anal. Calcd for $(C_{14}H_{26}N_2O_2Si)_2 \cdot H_2O$: C, 57.69; H, 9.33; N, 9.61. Found: C, 57.48; H, 9.44; N, 9.68. Anal. Calcd for $[C_{14}H_{27}N_2O_2Si]^+$, self chemical ionization (self-CI) $[M + 1]^+$: m/z 283.1929. Found: m/z 283.1836.

Examination of the crude reaction product using MS revealed the presence of trace amounts of the bis(silyloxy) amidine **5a**. Anal. Calcd for $[C_{17}H_{35}N_2O_2Si_2]^+$, self-CI $[M + 1]^+$: m/z 355.2277. Found: m/z 355.2232. Anal. Calcd for $[C_{16}H_{31}N_2O_2Si_2]^+$, self-CI $[(M + 1) - CH_4]^+$: m/z 339.1932. Found: m/z 339.1919.

4-Amino-5-azatricyclo[5.5.0.0^{3,9}]dodec-4-ene-3,7-diol Hydrochloride (6). (A) The bis(cyanide) **4** (1.05 g, 3.0 mmol) dissolved in anhydrous ether (5 mL) was added dropwise over several minutes to a stirred solution of lithium aluminum hydride (0.30 g) in diethyl ether (15 mL) under dry nitrogen. After 2 h, the excess reductant was destroyed by cautious addition of wet ether and then water (5 mL). Dropwise addition of 15% aqueous sodium hydroxide (5 mL) caused dissolution of solid material and gave a clear solution, which was stirred at room temperature for 0.5 h. The ethereal solution was then decanted. Further organic material was extracted by using chloroform. The combined extracts were dried (Na_2SO_4), filtered, and evaporated to give the dihydroxy amidine **5d** as a viscous oil. This was dissolved in ether (20 mL), concentrated hydrochloric acid (2 mL) was added, and the mixture was shaken. After a few minutes, the precipitated amidinium chloride **6** was filtered off and dried (0.53 g, 72%): mp ca. 250 °C dec (from acetonitrile); IR (paraffin mull) 3400 (m), 3170 (s), 1660 (s), 1200 (w), 1150 (m), 1105 (m), 1075 (m), 1030 (w) cm^{-1}; MS, m/z (>20%) 211 (11), 210 (49, $C_{11}H_{18}N_2O_2^+$), 193 (24), 182 (32), 167 (21), 165 (27), 125 (23), 114 (53), 113 (21), 112 (27), 111 (56), 101 (98), 100 (47), 99 (100), 98 (34), 95 (29), 93 (21), 83 (27), 81 (21), 79 (28), 71 (27), 67 (27), 58 (70), 57 (41), 56 (27), 55 (53), 45 (36), 43 (60), 41 (53); ^1H NMR [$(CD_3)_2SO$] δ

(15) Sieveking, H. U.; Lüttke, W. *Justus Liebigs Ann. Chem.* **1977**, 189.

(16) (a) Beierbeck, H.; Saunders, J. K. *Can. J. Chem.* **1977**, *55*, 771. (b) Feshin, V. P.; Khamaganova, L. D.; Voronkov, M. G.; Dubinskaya, E. I.; Komarov, V. G.; Yasman, Ya. B.; Kuramshin, R. A. *J. Gen. Chem. USSR (Engl. Transl.)* **1982**, *52*, 1236. (c) Schraml, J.; Pola, J.; Jancke, H.; Engelhardt, G.; Cerny, M.; Chvalovsky, V. *Collect. Czech. Chem. Commun.* **1976**, *41*, 360.

(17) Wehrli, F. W.; Wirthlin, T. *Interpretation of Carbon-13 NMR Spectra*: Heyden and Son: London, 1976; p 37.

(18) Yamamoto, H.; Maruoka, K. *J. Am. Chem. Soc.* **1981**, *103*, 4186.

(19) (a) Moad, G.; Benkovic, S. J. *J. Am. Chem. Soc.* **1978**, *100*, 5495. (b) Okamoto, Y.; Kinoshita, T. *Chem. Pharm. Bull.* **1981**, *29*, 1165.

(20) Koikov, L. N.; Terent'ev, P. B.; Yufit, D. S.; Struchkov, Yu. T.; Zubarev, V. E. *J. Org. Chem. USSR (Engl. Transl.)* **1985**, *21*, 1664.

(21) Kaji, K.; Matsubara, H.; Nagashima, H.; Kikugawa, Y.; Yamada, S. *Chem. Pharm. Bull.* **1978**, *26*, 2246.

(22) Kikugawa, Y.; Yamada, S.; Nagashima, H.; Kaji, K. *Tetrahedron Lett.* **1969**, 699.

(23) Lettieri, G.; Larizza, A.; Brancaccio, G.; Monforte, P. *Atti Soc. Peloritana Sci. Fis., Mat. Nat.* **1978**, *24*, 77; *Chem. Abstr.* **1980**, *92*, 94028q.

9.51 (d, 1 H, J = 5.25 Hz, exchanged with D_2O, N5-H), 8.87 (s, 1 H, exchanged with D_2O, C4-NH_aH_b), 8.21 (s, 1 H, exchanged with D_2O, C4-NH_aH_b), 6.39 (br s, 1 H, exchanged with D_2O, OH), 5.17 (v br s, 1 H, exchanged with D_2O, OH), 3.43 (d, 1 H, J = 13.3 Hz, C6-H_aH_b), 3.15 (dd, 1 H, J = 13.3 Hz and 5.25 Hz, C6-H_aH_b, collapsed to d with J = 13.3 Hz on D_2O exchange of N5-H), 2.30, 2.28, 2.27 and 2.25 (dd, 1 H), 2.10-2.01 (m, 2 H), 1.98-1.87 (m, 4 H), 1.73-1.60 (m, 3 H), 1.52-1.45 (m, 2 H); ^{13}C NMR [$(CD_3)_2SO$] δ 174.4 (C), 72.4 (C), 70.8 (C), 56.5 (CH_2), 41.3 (CH), 40.0 (CH), 35.8 (CH_2), 34.8 (CH_2), 29.9 (CH_2), 26.6 (CH_2), 20.2 (CH_2). Anal. Calcd for $C_{11}H_{19}N_2O_2Cl$: C, 53.55; H, 7.76; N, 11.35. Found: C, 53.28; H, 7.97; N, 11.11.

(B) The amidine **5b** hemihydrate (0.40 g, 1.37 mmol) was dissolved in methanol (10 mL) and 15% aqueous sodium hydroxide (1.5 mL) added. After being stirred overnight at room temperature, the mixture was extracted several times with chloroform and the combined extracts were dried (Na_2SO_4). The material was then worked up as above to give the amidinium chloride **6** (0.27 g, 80%), which was identical with that obtained previously by procedure A.

Solution and Refinement of Structure 6. Numerical details pertaining to the collection and reduction of data are included in the supplementary material, and procedures have been described elsewhere.[24]

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Registry No. 1, 21173-67-1; 4, 123903-98-0; 5, 123904-01-8; 5b, 123903-99-1; 5d, 123904-02-9; 6, 123904-00-7.

Supplementary Material Available: Details of the solution and refinement of structure 6, crystal data, tables of atomic parameters and standard deviations, bond lengths and angles, hydrogen bonding parameters, and torsion angles with standard deviations, and Figure II showing the crystal packing arrangement of 6 (8 pages). Ordering information is given on any current masthead page.

(24) Dance, I. G.; Guerney, P. J.; Rae, A. D.; Scudder, M. L. *Inorg. Chem.* **1983**, *22*, 2883.

$VO(OR)Cl_2$-Induced Oxidative Aromatization of α,β-Unsaturated Cyclohexenones

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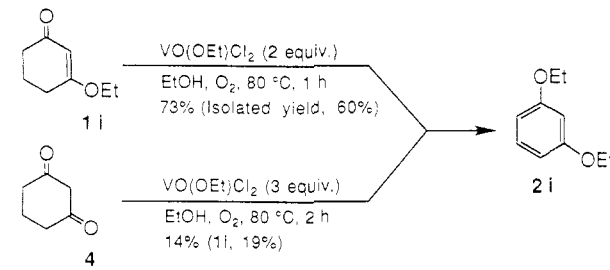
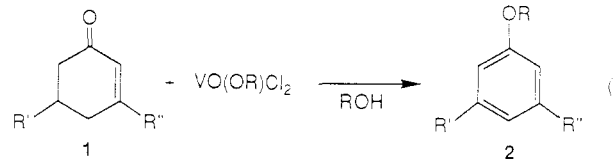
Vanadium compounds in a high oxidation state are considered to be versatile in oxidative transformations via one-electron transfer, but their synthetic utilization has been limited.[1] Our previous paper demonstrated that $VO(OEt)Cl_2$ catalyzes the ring-opening oxygenation of cyclic ketones in an alcohol under oxygen.[2] $VO(OR)Cl_2$ appears to be a Lewis acid with oxidation capability. We here report that oxidative aromatization[3] of α,β-unsaturated cyclohexenones to aryl ethers is achieved with $VO(OR)Cl_2$.

Scheme I



Treatment of 2-cyclohexen-1-ones (1) with $VO(OR)Cl_2$ in an alkanol led to the formation of the corresponding alkyl aryl ethers **2** in high yields (eq 1). The results are



(1)

listed in Table I. This oxidative transformation is characteristic of $VO(OR)Cl_2$; other oxovanadium compounds such as $VO(OEt)_3$, $VO(acac)_2$, and $VO(OSiPh_3)_3$ did not induce the aromatization of 2-cyclohexen-1-one (**1a**) in ethanol, giving only small amounts of the 1,4-addition product 3-ethoxycyclohexanone (**3a**).

It was found that 2 equiv of $VO(OEt)Cl_2$ was required to complete the dehydrogenative transformation. The reaction proceeded a little faster under oxygen than nitrogen. The conversion to ethyl phenyl ether (**2a**) with $VO(OEt)Cl_2$ was also observed in toluene although in low yield, suggesting that oxovanadium alkoxide plays an important role in the formation of the ether linkage. Use of 2-propanol as solvent gave predominantly the corresponding isopropyl ether **2c** even on treatment with $VO(OEt)Cl_2$. This may be due to a facile exchange within the oxovanadium alkoxide, which was independently confirmed by ^1H NMR. $VO(OEt)Cl_2$ in $CDCl_3$ was partially converted to $VO(OPr\text{-}i)Cl_2$ on addition of 2-propanol at room temperature. The ether **2c** was of course produced exclusively with $VO(OPr\text{-}i)Cl_2$ in 2-propanol. Methyl and cyclohexyl phenyl ethers (**2b** and **2d**) were similarly prepared. When allyl alcohol was employed, competitive oxidation to the acetal derivative 1,1,3-triallyloxypropane might account for the low yield of allyl ether **2e**. Running the reaction in 2-methyl-2-propanol did not give the *tert*-butyl ether.

Starting from the substituted 2-cyclohexen-1-ones **1f-g**, the expected ethers were obtained regioselectively, indicating that the alkoxyl group is introduced at the carbonyl carbon.

In the case of carvone (**1h**), the aromatization reaction was accompanied by oxidative bond cleavage between the carbon-carbon double bond of the 2-propenyl group, giving 4-acetyl-2-ethoxytoluene (**2h**) as the main product. This transformation probably is the result of oxidative cleavage after aromatization since it was also shown that α-methylstyrene was oxidized to acetophenone in 35% yield with $VO(OEt)Cl_2$ under oxygen at 80 °C for 5 h.

The present method was also applicable to oxidative aromatization of 3-ethoxy-2-cyclohexen-1-one (**1i**) into the resorcinol derivative **2i** (Scheme I). Treatment of 1,3-cyclohexanedione (**4**) with $VO(OEt)Cl_2$ in ethanol led to the same product **2i**, although in low yield. The latter transformation is assumed to proceed via **1i**, which was

(1) Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidations of Organic Compounds*; Academic Press: New York, 1981. Mijs, W. J.; de Jonge, C. R. H. I. *Organic Syntheses by Oxidation with Metal Compounds*; Plenum Press: New York, 1986.

(2) Hirao, T.; Mori, M.; Ohshiro, Y. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 2399.

(3) Copper-induced aromatization to phenols has been reported: Bondon, D.; Pietrasanta, Y.; Pucci, B. *Tetrahedron Lett.* **1977**, 821.

0022-3263/90/1955-0358$02.50/0