m, adamantyl), 2.78 (3 H, s, NCH_3), 5.51 (1 H, d, J_{ab} = 2.1 Hz, H_a or H_b), 6.11 (1 H, d, J_{ab} = 2.1 Hz, H_b or H_a), 6.20–6.98 (4 H, m, indolyl); IR (CCl_4) 1610 (C=C).

The 1,2-diox-4-ene **6b**, prepared in over 90% yield, was too unstable for combustion analysis: ^1H NMR (CCl_4, Me_4Si as external standard) δ 0.17 (6 H, s, $Si(CH_3)_2$), 0.88 (9 H, s, $SiC(CH_3)_3$), 2.80 (3 H, s, NCH_3), 3.20 (3 H, s, OCH_3), 5.27–5.48 (2 H, m, vinyl and CH), 6.16–7.00 (4 H, m, indolyl); IR (CCl_4) 1620 cm^{-1} (C=C).

The 1,2-diox-4-ene **6c** was prepared in 30% yield (based on NMR analysis): ^1H NMR (CCl_4, Me_4Si) 1.60 (3 H, s, CH_3), 2.68 (3 H, s, NCH_3), 5.32 (1 H, d, J_{ab} = 2.0 Hz, H_a or H_b), 5.68 (1 H, d, J_{ab} = 2.0 Hz, H_b or H_a), 6.20–7.45 (9 H, m, aromatic); IR (CCl_4) 1605 cm^{-1} (C=C).

Methanol Treatment of Dioxane 6a. A 50-mL, two-necked, round bottomed flask equipped with a spinbar and a rubber septum was charged with 171 mg (0.5 mmol) of dioxene **6a** and connected to a nitrogen manifold. The flask was evacuated, subsequently flushed with nitrogen, and cooled to −10 °C with a dry ice/methanol bath. Dry methanol (35 mL) which had been cooled to −20 °C was syringed in, and the mixture was stirred at −10 °C for 3.5 h. The solvent was rotoevaporated (5 °C, 1 mm), and NMR analysis of the crude product showed that the dioxene **6a** was converted to *N*-methylindole-3-carboxaldehyde (38%), 2-adamantanone (38%), and oxindole compound **7** (62% yield based on dioxene **6a** used). The latter was isolated by silica gel chromatography, eluting with CH_2Cl_2–EtOAc, 1:2: mp 222–225 °C ($CHCl_3$–hexane); ^1H NMR ($CDCl_3$, Me_4Si) δ 0.88–2.53 (14 H, m, adamantyl), 3.06 (3 H, s, NCH_3), 2.90 (1 H, d, J_{ab} = 8.4 Hz, H_a or H_b), 3.35 (1 H, d, J_{ab} = 8.4 Hz, H_b or H_a), 6.41–7.21 (4 H, m, indolyl); IR ($CHCl_3$) 1700 cm^{-1} (C=O); mass spectrum *m/e* (relative intensity) 309 (M, 43), 159 (100).

Silica Gel Treatment of Dioxene 6a. A 50-mL, two-necked, round-bottomed flask equipped with a magnetic spinbar and a rubber septum was charged with 200 mg of silica gel and connected to a nitrogen manifold. The flask was flame-dried under reduced pressure while being flushed with dry nitrogen and was cooled to −20 °C by means of a dry ice/methanol bath. The dioxene **6a** (25 mg) in 10 mL of dry CH_2Cl_2 (freshly distilled from P_2O_5) was syringed in, and the mixture was stirred at −20 °C for 2 h. The silica gel was filtered off under a nitrogen atmosphere, and the solvent was rotoevaporated (5 °C, 2 mm). NMR analysis of the crude product showed that the dioxene **6a** was converted to *N*-methylindole-3-carboxaldehyde and 2-adamantanone quantitatively.

Acknowledgment is made to the donors of the Petroleum Research Fund (Grant No. 11022-AC1), administered by the American Chemical Society, the National Science Foundation (Grant No. 78-12621), and the National Institutes of Health (Grant No. GM-00141-04 and RR-8102-07) for their financial support. We thank Hector Martinez and Veronica Cruz, both undergraduate research participants in the Support for University Biomedical Education (SUBE) program sponsored by NIH-MS, for technical assistance.

Registry No. A, 72228-34-3; **B**, 72228-35-4; **C**, 72228-36-5; **D**, 72228-37-6; **E**, 72228-38-7; **1a**, 72228-39-8; **1b**, 72228-40-1; **1c**, 72228-41-2; **1d**, 72228-42-3; **1e**, 72228-43-4; **2a**, 72228-44-5; **2b**, 72244-59-8; **3a**, 72244-60-1; **3b**, 72228-45-6; **3c**, 72228-46-7; **4a**, 72228-47-8; **4b**, 72228-48-9; **5a**, 72244-61-2; **5b**, 72244-62-3; **5c**, 72228-49-0; **6a**, 72228-50-3; **6b**, 72228-51-4; **6c**, 72228-52-5; **7**, 72228-53-6; indole-3-acetic acid, 87-51-4; 1-methylindole-3-acetic acid, 1912-48-7; 1,2-dimethylindole-3-acetic acid, 2597-28-6; methyl 1-methylindole-3-acetate, 58665-00-2; β-(*N*-methyl-3-indolyl)styrene, 72228-54-7; methyl iodide, 74-88-4; benzyl bromide, 100-39-0; trimethylchlorosilane, 75-77-4; dimethyl-*tert*-butylsilyl chloride, 18162-48-6; 2-adamantanone, 700-58-3; cyclopentanone, 120-92-3; methanol, 67-56-1; *N*-methylindole-3-carboxaldehyde, 19012-03-4.

The π–π Interaction between Nitrile and Ethylene Functionalities

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The axial/equatorial free-energy difference for 3-cyano-1-methylenecyclohexane-*2,2,4,4,6,6-d*$_6$ is 0.26 kcal/mol in CF_2Cl_2 and 0.07 kcal/mol in $CHFCl_2$ at −102 °C in favor of the equatorial conformer. The decreased equatorial preference in the polar, hydrogen-bonding solvent results from a less repulsive interaction between the 3-substituent and the 1-*exo*-methylene group. For the low-polarity solvent (CF_2Cl_2), the equatorial preference of cyano in the *exo*-methylene system is about the same as that in cyanocyclohexane (0.24 kcal/mol), which lacks the π–π interaction in the axial conformation. These results contrast with polar, lone-pair-containing substituents such as methoxyl, which have dramatically increased equatorial preferences in the *exo*-methylene systems compared to their cyclohexyl counterparts. The π–π interaction between the cyano group and the $C{=}CH_2$ group appears to offer very little repulsion in comparison with the strong electrostatic interactions between methoxyl, hydroxyl, or thiomethyl and the same $C{=}CH_2$ group.

Interactions between functional groups containing π electrons have traditionally been studied by their effects on electronic and photoelectronic spectra. In a phenomenological sense, these interactions may also be studied through their influence on conformational equilibria. It is necessary to construct a molecular system with two available conformations, one in which the π-containing functionalities are forced together and the other in which they are forced apart. The conformational equilibrium constant would be interpreted by reference to similar equilibria lacking the π electrons.

We have recently described a system designed for the study of the interaction between the carbon–carbon double bond and either groups that are fully saturated and bonding (e.g., CH_3) or groups that contain nonbonding electrons (e.g., CH_3O or CH_3S).[2] The π electrons are located in an *exo*-methylene group on a cyclohexane ring, and the interacting group is located at the 3-position. The

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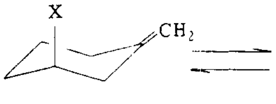
[1] (a) This work was supported by the National Science Foundation (Grant No. CHE77-08384 and CHE79-05542) and by the donors of the Petroleum Research Fund, administered by the American Chemical Society. (b) Fellow of the African-American Institute, 1975–1979.

[2] Lambert, J. B.; Clikeman, R. R. *J. Am. Chem. Soc.* **1976**, *98*, 4203. Lambert, J. B.; Clikeman, R. R.; Magyar, E. S. *Ibid.* **1974**, *96*, 2265.

axial/equatorial conformational equilibrium (eq 1) com-

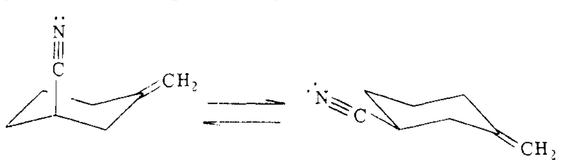


(1)

pares a strong interaction between the π electrons and the substituent X in the axial conformation with a negligible one in the equatorial conformation. This equilibrium constant may be compared to that in cyclohexyl itself in order to assess the difference between the interactions of a $C{=}CH_2$ group and those of a saturated CH_2 group.

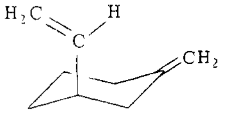
We found that a fully σ-bonded substituent (CH_3) has decreased interactions with the π-electron group, as compared to the saturated CH_2 group, since there is a larger proportion of axial conformer in the equilibrium of eq 1 than there is in cyclohexyl.[2] Furthermore, this observation is independent of solvent. On the other hand, substituents that are polar and contain nonbonding electrons (HO, CH_3O, CH_3S) were found to experience larger interactions with the π-electron group than with CH_2 in the nearly nonpolar solvent CF_2Cl_2, as indicated by increased proportions of the equatorial conformer in eq 1, compared to cyclohexyl.[2] We concluded that the repulsive interaction between the group X and the *exo*-methylene group is polar in nature and can result from either a dipole–dipole or a dipole–quadrupole interaction.[2] These conclusions were reinforced by examination of the equilibrium constants for the same equilibria in a polar, hydrogen-bonding solvent, $CHFCl_2$. The intramolecular polar interactions are partially neutralized by solvation, so that the interaction between the substituent and the π group is lower than that in cyclohexyl; i.e., the proportion of X axial in eq 1 is larger than that in cyclohexyl for polar solvents. It should be emphasized that solvent effects in cyclohexyl equilibria are in the opposite direction.[3]

In this fashion, we were able to probe the steric interactions between various groups and a π-electron functionality. None of these groups, however, possessed π electrons on the atom attached to the cyclohexane ring. We did study acetoxyl, but its π-electron system is directed away from the π electrons on the ring. In order to study π–π interactions within the context of eq 1, we selected cyano as the X group (eq 2). In cyano, not only are the



(2)

π electrons located on the atom attached to the cyclohexane ring but also their cylindrical distribution and the axial symmetry of the group assure that the cyano π electrons are directed toward the *exo*-methylene group in the axial conformer. The vinyl substituent, for example, would be an unacceptable subject, since any number of arrangements are possible, e.g., **1**, in which the π electrons



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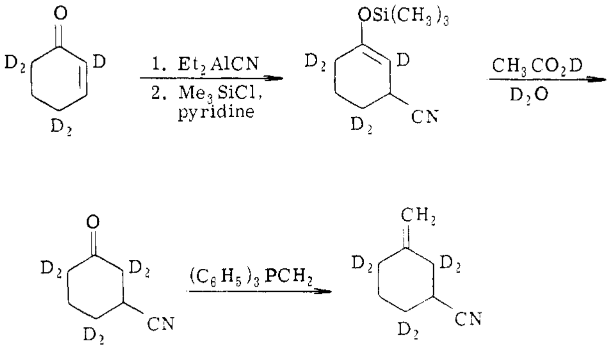
are directed away from the *exo*-methylene group. The lone pair on nitrogen in cyano is not directed toward the *exo*-methylene group, so it cannot give rise to any direct interaction. Nonetheless, the group is polar, so that dipolar interactions can be expected. We report in this paper the preparation and conformational study of 3-cyano-1-methylenecyclohexane in order to examine the π–π interaction between the nitrile and ethylene groups.

Scheme I



Results

Direct determination of the axial/equatorial equilibrium constant requires examination of the ^1H NMR spectrum at temperatures below the coalescence that arises from slowing of the ring reversal process. At these temperatures, separate resonances are observable for the axial and equatorial conformers, and direct integration gives the equilibrium constant. The 3-proton, which is geminal to the cyano group, should be most sensitive to the substituent location and hence give the largest and most reliable peak separation. The axial proton resonates at higher field, as determined in our earlier study.[2] In order to sharpen this pair of peaks through removal of vicinal coupling, we found it necessary to replace the 2- and 4-protons with deuterium. In addition, peak overlap dictated that the 6-protons also be replaced with deuterium. Consequently, the synthetic goal was 3-cyano-1-methylenecyclohexane-*2,2,4,4,6,6*-d_6.

The preparation of the desired material is outlined in Scheme I. Although we had previously prepared 2-cyclohexen-1-one-*2,4,4,6,6*-d_5,[2] we found that a superior procedure involved ethylation of the enol of 1,3-cyclohexadione, deuterium exchange and trans-etherification with sodium methoxide, and reduction by $LiAlH_4$.[4] Reaction of the deuterated enone with diethylaluminum cyanide followed by quenching with trimethylsilyl chloride gave the cyanated silyl ether.[5] Successful hydrolysis without deuterium exchange or ketal formation was effected with 2/1 CH_3CO_2D/D_2O. Conversion of the ketone to the *exo*-methylene compound was carried out with a normal Wittig procedure.

The ^1H spectra were taken at 270 MHz in order to obtain maximum peak separation, to have optimal sensitivity, and to raise the temperature of coalescence. Spectra were recorded as a function of temperature for two solvents, CF_2Cl_2 (Figure 1) and $CHFCl_2$ (Figure 2). The coalescence temperature was found to be about the same (−83 °C) for both solvents, so that the free energy of activation ($\Delta G^{\ddagger} = 8.7$ kcal/mol) was experimentally identical. Even the axial/equatorial chemical shift difference was the same (0.65 ppm) for the two solvents. It is clear from the low-temperature extreme, however, that the equatorial/axial equilibrium constants are different. These were measured

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(3) Eliel, E. L.; Gilbert, E. C. *J. Am. Chem. Soc.* **1969**, *91*, 5487.

(4) Taba, K. M. Ph.D. Dissertation, Northwestern University, Evanston, IL, 1979.

(5) Samson, M.; Vandewalle, M. *Synth. Commun.* **1978**, *8*, 231.

Table I. Equilibrium Data for 3-Substituents on 1-Methylenecyclohexane[a]

X	σ_I[b]	$-\Delta G°(CF_2Cl_2)$	$-\Delta G°(CHFCl_2)$	A	Δ[c]	Δ'[d]
CN	0.52	0.26	0.07	0.24	0.02	0.19
OH[e]	0.27	1.12	0.69	0.97	0.15	0.43
OCD_3[e]	0.26	0.80	0.11	0.55	0.25	0.69
SCH_3[e]	0.19	1.22	0.65	1.07	0.15	0.57

[a] Positive numbers indicate an equatorial preference. [b] Taft, R. W.; Deno, N. C.; Skell, P. S. *Annu. Rev. Phys. Chem.* **1958**, *9*, 287. [c] $-\Delta G°(CF_2Cl_2) - A$. [d] $-\Delta G°(CF_2Cl_2) - [-\Delta G°(CHFCl_2)]$. [e] Data from ref 2.

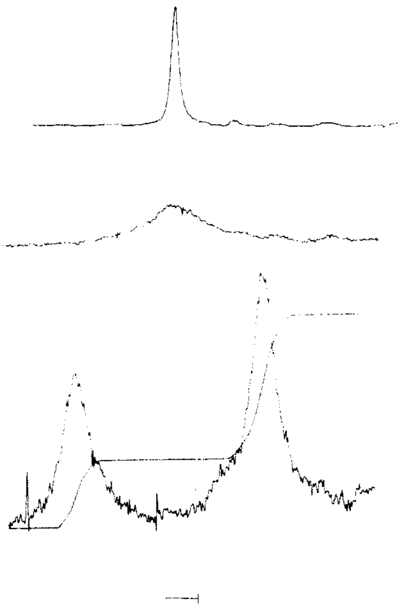


Figure 1. 270-MHz ^1H spectrum of 3-cyano-1-methylenecyclohexane-*2,2,4,4,6,6*-d_6 in CF_2Cl_2 as a function of temperature (top to bottom): −50, −82, and −102 °C. The calibration bar represents 30 Hz.

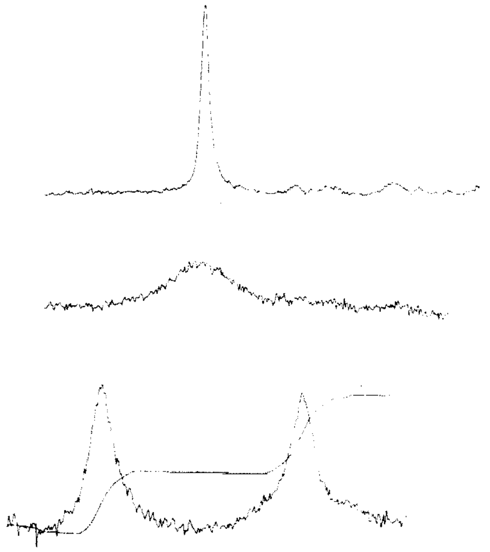


Figure 2. 270-MHz ^1H spectrum of 3-cyano-1-methylenecyclohexane-*2,2,4,4,6,6*-d_6 in $CHFCl_2$ as a function of temperature (top to bottom): −50, −82, and −102 °C. The calibration bar represents 30 Hz.

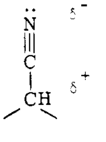
at −102 °C to be 2.14 (corresponding to a $-\Delta G°$ of 0.26 kcal/mol) for CF_2Cl_2 and 1.23 ($-\Delta G° = 0.07$ kcal/mol) for $CHFCl_2$. For comparison, the equatorial/axial equilibrium constant for cyanocyclohexane in CS_2 was measured at −79 °C to be 1.88 ($-\Delta G° = 0.24$).[6]

Discussion

Interpretation of the cyano data requires comparison with the results from polar substituents containing only σ bonds and lone pairs. The relevant information is given in Table I. The qualitative pattern is the same for hydroxyl, methoxyl, and thiomethyl. The equatorial preference in CF_2Cl_2 as solvent is higher for the *exo*-methylene system than for cyclohexyl; i.e., the negative free-energy difference is larger than the *A* value. The repulsive interaction of the substituent is larger with the $C{=}CH_2$ group than with the CH_2 group. The polar solvent $CHFCl_2$ considerably reduces the interaction in the *exo*-methylene system, so that the equatorial preference is lower than in cyclohexyl.

The most interesting aspect of the cyano equilibrium is that the increase in equatorial preference between cyclohexyl and *exo*-methylenecyclohexyl in CF_2Cl_2 is much smaller for cyano than for any other substituent (Δ in Table I), yet cyano is the most polar as measured by σ_I. This conclusion holds even after taking into consideration that cyano is the smallest substituent (smallest *A* value) in the series because the percent change ($100\Delta/A$) is half as large as any other. In a similar fashion, the change in equatorial preference between CF_2Cl_2 and $CHFCl_2$ (Δ′) is smallest for cyano. These results are unexpected, since the primary interaction between the substituent and the *exo*-methylene group almost certainly has to be electrostatic, either dipole–dipole or dipole–quadrupole.[2]

At least two reasons may be proffered for this behavior. First, there may be fundamental differences between π–π and π–n interactions. The π–π interactions may be inherently weaker, or a distance factor may be significant. Certainly the lone pair is directed from the substituent toward the *exo*-methylene double bond for OH, OCD_3, and SCH_3, whereas the cylindrical π cloud of the cyano group is distributed closely around the C–N bond axis. Second, the effective polarity of the cyano group may be reduced because the critical electronegative atom is further removed from the *exo*-methylene double bond; cp. **2** and **3**.



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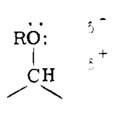

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The center of negative charge in the dipole is further away for CN, so that dipolar interactions might be expected to be reduced. The difference in conformational preference between CF_2Cl_2 and $CHFCl_2$ (Δ′) as solvent for these methylenecyclohexanes has been taken as a measure of the polar interaction between the 3-substituent and the 1-methylene double bond.[2] The small size of Δ′ for CN is consistent with a reduced electrostatic interaction with the double bond.

It is clear from these results that the π–π interactions per se have very little effect on the conformational equi-

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[6] Jensen, F. R.; Bushweller, C. H.; Beck, B. H. *J. Am. Chem. Soc.* **1969**, *91*, 344.

librium under study. The equilibrium constants are determined primarily by the magnitude and spatial arrangement of the component dipoles and quadrupoles. As a result, the π substituent cyano has a less repulsive interaction with the *exo*-methylene group than do the various n substituents.

Experimental Section

Infrared spectra were measured on Beckman IR-10 and Perkin-Elmer 283 spectrometers. Routine ^{1}H NMR spectra were recorded at 60 MHz on Varian Associates T60 and Perkin-Elmer R20B spectrometers. The low-temperature ^{1}H NMR spectra were taken at 270 MHz on a Bruker HX-270 spectrometer at the Southern New England High Field NMR Facility, New Haven, CT. Mass spectra were obtained on a Hewlett-Packard Model 5985A mass spectrometer.

3-Ethoxy-2-cyclohexen-1-one. In a 2-L flask fitted with a total-reflux variable-takeoff distillation head were placed 40 g (0.35 mmol, Aldrich) of dihydroresorcinol, 2.3 g of *p*-toluenesulfonic acid monohydrate, 250 mL of absolute ethanol, and 900 mL of benzene. The mixture was heated to boiling, and the azeotrope of benzene/alcohol/water was removed at the rate of 80 mL/h. The distillation was stopped when the temperature reached 78 °C. The cooled solution was washed with 10% aqueous NaOH saturated with NaCl (4 × 100 mL). The resulting organic layer was washed successively with 50 mL of H_2O until the aqueous washings became neutral. The organic layer was then dried ($MgSO_4$), filtered, and concentrated. Distillation of the residual liquid gave 38 g (86%) of colorless product: bp 192 °C (2 mm) [lit.[7] 66–68.5 °C (0.4 mm)]; NMR (CCl_4) δ 0.98 (t, 3, CH_3), 1.16–2.16 (m, 6, CH_2), 3.46 (q, 2, OCH_2), 5.0 (s, 1, alkene).

3-Methoxy-2-cyclohexen-1-one-*2,4,4,6,6-d*$_5$. In an adaptation of the procedure described by Clikeman,[8] 25 g (0.20 mmol) of 3-ethoxy-2-cyclohexen-1-one in 100 mL of 0.50 N sodium methoxide/methanol-*d* (from Na metal and methanol-*d*) was stirred for 1 day at room temperature under N_2. The solution was then neutralized with a solution of 15 N DCl/D_2O (from the addition of 13 mL of PCl_3 to 43 mL of D_2O). About two-thirds of the methanol-*d* was removed by rotary evaporation. The remaining mixture was brought to a total volume of 300 mL by addition of a 1/1 THF/ether solution. The mixture was filtered, and the filtrate was dried ($MgSO_4$), filtered, concentrated, and distilled. The main fraction was subjected to a second and a third cycle using the same quantities of reagents. Distillation gave for the first, second, and third cycles, respectively, 20, 16, and 13 g (50%) of product. The extent of deuterium incorporation was followed by NMR spectroscopy for each cycle and was, respectively, 77, 92, and at least 98%: NMR (CCl_4) δ 1.92 (br s, 2, CH_2), 3.8 (s, 3, OCH_3). The level of deuteration (98%) remained constant throughout the subsequent transformations.

2-Cyclohexen-1-one-*2,4,4,6,6-d*$_5$. A solution of 23 g (15 mmol) of 3-methoxy-2-cyclohexen-1-one-*2,4,4,6,6-d*$_5$ in 40 mL of dry ether was added dropwise to a stirred suspension of 3.5 g (46 mmol) of $LiAlH_4$ in 200 mL of dry ether. After the addition, the reaction mixture was refluxed for 1 h and then cooled in an ice bath. It was hydrolyzed by cautious addition of 20 mL of D_2O, followed by addition of 30 mL of a 15 N DCl/D_2O. The two layers were separated, and the aqueous layer was extracted with ethyl ether (3 × 100 mL). The combined ether layers were dried ($MgSO_4$), filtered, concentrated, and distilled to give 13.2 g (73%) of the desired product as a colorless liquid: bp 45 °C (1.5 mm); NMR ($CDCl_3$) δ 2.0 (s, 2, CH_2), 6.9 (s, 1, alkene).

3-Cyano-1-(trimethylsiloxy)cyclohex-1-ene-*2,4,4,6,6-d*$_5$. Diethylaluminum cyanide (22.17 mL, 37.5 mmol, 1.69 M solution in toluene, Alfa Ventron) was added to a solution of 3 g (29.7 mmol) of 2-cyclohexen-1-one-*2,4,4,6,6-d*$_5$ in 50 mL of pentane (distilled from Na metal) at 0 °C under N_2. After 1.5 h of continuous stirring, chlorotrimethylsilane (14.28 mL, 115 mmol, Aldrich) and dry pyridine (10 mL) were added at 0 °C. The mixture was brought slowly to room temperature and stirred for an additional hour. It was then diluted with pentane and carefully poured into cold, saturated, aqueous NH_4Cl solution. The aqueous layer was removed, and the organic layer was washed rapidly with 5% cold aqueous HCl (3 × 20 mL) and twice with 50 mL of cold aqueous $NaHCO_3$ solution. The organic layer was dried (Na_2SO_4), concentrated, and distilled to yield 2.8 g (47%) of the desired product: bp 68–70 °C (0.2 mm) [lit.[5] 112 °C (13 mm)]; NMR ($CDCl_3$) δ 0.10 (s, 9, CH_3), 1.65 (s, 2, CH_2), 3.2 (s, 1, CH).

3-Cyanocyclohexan-1-one-*2,2,4,4,6,6-d*$_6$. To 2.8 g (14 mmol) of 3-cyano-1-(trimethylsiloxy)cyclohex-1-ene-*2,4,4,6,6-d*$_5$ was added 8 mL of a 2/1 mixture of acetic acid-*d*/D_2O. The reaction mixture was stirred at room temperature for 1 h, and 50 mL of ethyl ether was added. It was neutralized by slow addition of solid K_2CO_3 solution. The ether was removed, and the aqueous layer was extracted with more ether. The combined ether layers were dried ($MgSO_4$), filtered, concentrated, and distilled to afford 1.5 g (83%) of the pure product: bp 80 °C (1.5 mm); NMR ($CDCl_3$) δ 1.9 (s, 2, CH_2), 3.2 (s, 1, CH); IR (film) 2240 ($C{\equiv}N$), 1710 ($C{=}O$) cm^{-1}.

3-Cyano-1-methylenecyclohexane-*2,2,4,4,6,6-d*$_6$. In a 200-mL, three-necked, round-bottomed flask was placed 5.8 g (16.24 mmol) of methyltriphenylphosphonium bromide and 50 mL of anhydrous ethyl ether. To this solution was added 7.7 mL (15.4 mmol, 2 M solution in hexane, Alfa Ventron) of phenyllithium. After the mixture was stirred 30 min at room temperature, 3-cyanocyclohexan-1-one-*2,2,4,4,6,6-d*$_6$ (1 g, 0.0077 mol) in 10 mL of ether was added dropwise. The reaction mixture was stirred for 15 h. The excess ylide was then quenched by addition of 5 mL of acetone. The reaction mixture was filtered and concentrated. To the remaining liquid was added 10 mL of pentane. The solution was stored at 0 °C for 2 h, filtered, and concentrated. The crude product was passed through an alumina column eluted with hexane/ether to afford 0.8 g (0.0063 mol, 80%) of the desired product: NMR ($CDCl_3$) δ 1.6 (q, 2, CH_2), 2.7 (s, 1, CH), 4.8 (s, 2, *exo*-CH_2); IR (film) 2940 (CH), 2240 ($C{\equiv}N$), 2210, 2100 (CD), 1640 ($C{=}C$) cm^{-1}; mass spectrum (70 eV) *m/e* 127 (M^+). Anal. Calcd for $C_8H_{11}N$: C, 79.29; H, 9.14; N, 11.55. Found: C, 78.93; H, 8.96; N, 10.27.

Registry No. 3-Ethoxy-2-cyclohexen-1-one, 5323-87-5; dihydroresorcinol, 504-02-9; 3-methoxy-2-cyclohexen-1-one-*2,4,4,6,6-d*$_5$, 60174-62-1; 2-cyclohexen-1-one-*2,4,4,6,6-d*$_5$, 60174-63-2; 3-cyano-1-(trimethylsiloxy)cyclohex-1-ene-*2,4,4,6,6-d*$_5$, 72360-53-3; 3-cyanocyclohexan-1-one-*2,2,4,4,6,6-d*$_6$, 72360-54-4; 3-cyano-1-methylenecyclohexane-*2,2,4,4,6,6-d*$_6$, 72360-55-5.

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