lations of this type were performed.[7] The former selected the 1 position and the latter the 3 position.

Attempts to show the position of protonation by observing the change in the $^1H$ NMR spectrum on formation of the conjugate acid were not successful. Concentrated (72%) perchloric acid effected reversible protonation but obscured the absorption of the conjugate acid.[8] Hexafluorophosphoric acid (65%) and tetrafluoroboric acid (48%) were not sufficiently strong.[8] Sulfuric acid (96%) led to rapid darkening and apparent decomposition,[8] and trifluoromethanesulfonic acid caused polymerization. The amount of 1 available did not permit the extension of these experiments.

Treatment of 1 with trifluoroacetic anhydride at room temperature afforded a 73% (ca. 100% net) yield of a crystalline monotrifluoroacetyl derivative with no indication of disubstitution products. The $^1H$ NMR spectrum of this compound was reasonably interpretable only with the structure 2 resulting from substitution in the 1 position. The assignments (with the corresponding chemical shift values for 1 given in parentheses) were $\delta$ 8.03 (s, 1, H-2) (8.4), 8.28 (d, 2, H-3 and H-5) (8.68), 6.975 (t, 1, H-4) (7.34), 8.64 (d, 2, H-6 and H-7) (8.4), 9.675 (d, 1, H-8) (8.68), 7.28 (t, 1, H-9) (7.34), and 8.36 (d, 1, H-10) (8.68). These assignments are consistent with shielding of H-2 by the adjacent trifluoroacetyl group, retention of the signals for H-3, H-5, H-8, and H-10 as doublets and, concomitantly, of the signals for H-4 and H-9 as triplets, absorption at lower field for H-9 than H-4 as the result of both inductive and resonance effects (the latter places a partial positive charge at C-9 but not at C-4), and H-10 shielded more than H-8.

Confirmation was provided by decoupling experiments. Irradiation at $\delta$ 7.28 (H-9) affected only the doublets at $\delta$ 9.675 (H-8) and 8.36 (H-10). Similarly, irradiation at $\delta$ 6.975 (H-4) affected only the doublet at $\delta$ 8.28 (H-3 and H-5). Thus the remaining doublet ($\delta$ 8.64) must be from H-6 and H-7, and the remaining singlet ($\delta$ 8.03) from H-2.

These results establish that 1 undergoes electrophilic aromatic substitution readily and in the 1 position.

## Experimental Section

Melting points were taken on a Fisher-Johns apparatus and are uncorrected. NMR spectra were recorded on a Varian HA-100 spectrometer in chloroform with tetramethylsilane as the internal reference. Ultraviolet and visible spectra were obtained with a Cary Model 14 spectrophotometer using 1-cm quartz cells. Trifluoroacetic anhydride was freshly distilled from $P_2O_5$. Triethylamine was distilled from KOH and stored over $Na_2SO_4$. Dichloromethane was distilled from $P_2O_5$ and stored over $Na_2SO_4$. *n*-Hexane was washed successively with sulfuric acid, water, aqueous $NaHCO_3$, and water and then dried ($Na_2SO_4$) and distilled tilled from Na. Chloroform was reagent grade. Analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

**1-Trifluoroacetyldicyclopenta[*ef*,*kl*]heptalene (2).** To a solution of 80.8 mg (0.4 mmol) of the hydrocarbon 1 in 7 mL of dichloromethane was added 0.28 mL (2 mmol) of triethylamine, and the whole was chilled (ice bath) while an atmosphere of $N_2$ was introduced through a condenser. Then 0.3 mL (2 mmol) of trifluoroacetic anhydride was added with stirring (magnetic bar). The bath was removed and the stirring continued at room temperature for 3-4 days.[9] The reaction mixture was then filtered through a short silica gel G column (chloroform eluant). The eluted material was concentrated and chromatographed over a silica gel CC-7 column. Elution with *n*-hexane removed unchanged 1 (20.31 mg, 25.1%) and a 1:1 chloroform-*n*-hexane mixture removed 2 (87.32 mg, 73.2%), mp 144-146 °C. Sublimation at 96 °C (0.5 torr) afforded fine, reddish brown needles: mp 144-145 °C; UV max (cyclohexane) 240 ($\epsilon$ 1.47 × $10^4$), 264 (2.1 × $10^4$), 300 (9.1 × $10^3$), 315 (7.35 × $10^3$), 334 (4.1 × $10^3$), 354 sh (8.65 × $10^2$), 384 (2.38 × $10^3$), 410 (1.21 × $10^3$), 438 (8.22 × $10^2$), 475 (9.5 × $10^2$), 499 sh (1.64 × $10^3$), 511 nm (5.1 × $10^3$); NMR ($HCCl_3$) $\delta$ 6.975 (t, 1), 7.28 (t, 1), 8.03 (s, 1), 8.28 (d, 2), 8.36 (d, 1), 8.64 (d, 2), and 9.675 (d, 1). Anal. Calcd for $C_{18}H_9OF_3$: C, 72.49; H, 3.04. Found: C, 72.56; H, 2.93.

**Registry No.** 1, 193-85-1; 2, 72541-89-0.

(7) We thank Professor Martin Gouterman for assistance with these.
(8) MacDonald, A. A., Ph.D. Thesis, University of Washington, 1968.
(9) The reaction progress could be monitored by TLC on silica gel G with *n*-hexane as the eluant.

# Electrophilic Addition of Benzeneselenenyl Chloride to Hydroxyalkynes[1]

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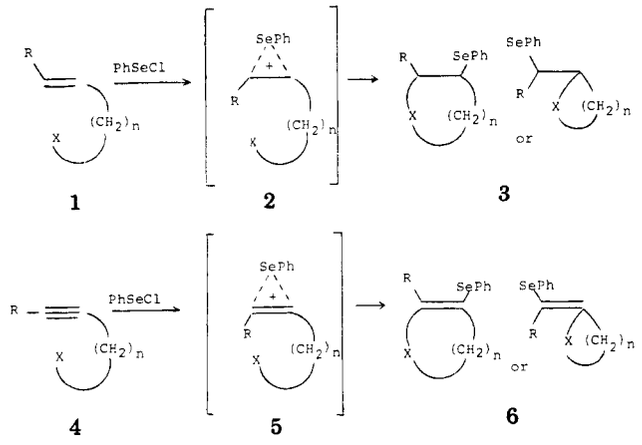
Cyclofunctionalization of compounds 1 (Scheme I) possessing proximate nucleophile X using benzeneselenenyl chloride (PhSeCl) is a powerful and elegant synthetic method leading to the formation of various heterocyclic compounds 3. Among the nucleophiles X successfully used in this synthon have been hydroxyl,[2] carboxyl,[3] urethane,[4] and carbon,[5,6] and the products derived from this cyclization have been those as predicted by Baldwin's rules for ring closure.[7] To date, however, only olefins have been reported as the unsaturated component in this cyclization scheme. We now report on the first attempt to utilize alkynes as the unsaturated moiety in a cyclofunctionalization reaction with PhSeCl.

Several lines of evidence suggested that alkynes might be substituted for olefins in a cyclofunctionalization reaction. It has been demonstrated that alkynes like olefins, in the absence of internal or external nucleophiles, electrophilically add PhSeCl in 1,2 fashion to yield well-characterized adducts.[8a] Since the cyclofunctionalization of olefins apparently proceeds through an intramolecular nucleophilic interception of a putative seleniranium cation 2,[2b] we reasoned that a similar utilization of alkynes 4 might allow for an intramolecular attack on an intermediate selenirenium cation 5,[8] yielding vinyl selenides 6 as shown in Scheme I. Also, Baldwin's rules for ring closure indicate that many favored modes of cyclization for alkynes exist.[7] It is not surprising then that there are numerous

(1) Presented in part at the 9th Northeast Regional Meeting of the American Chemical Society, Syracuse, NY, Oct 1979; see abstract No. ORGN-7.
(2) (a) D. L. J. Clive, G. Chittattu, N. J. Curtis, W. A. Kiel, and C. K. Wong, *J. Chem. Soc., Chem. Commun.*, 725 (1977); (b) D. L. J. Clive, G. Chittattu, and C. K. Wong, *Can. J. Chem.*, **55**, 3894 (1977); (c) K. C. Nicolaou and Z. Lysenko, *Tetrahedron Lett.*, 1257 (1977).
(3) K. C. Nicolaou and Z. Lysenko, *J. Am. Chem. Soc.*, **99**, 3185 (1977).
(4) D. L. J. Clive, C. K. Wong, W. A. Kiel, and S. M. Menchen, *J. Chem. Soc., Chem. Commun.*, 379 (1978).
(5) D. L. J. Clive, G. Chittattu, and C. K. Wong, *J. Chem. Soc., Chem. Commun.*, 441 (1978).
(6) Using PhSeBr, an amine [S. R. Wilson and R. A. Sawicki, *J. Org. Chem.*, **44**, (1979)] and a carbonyl oxygen [S. Current and K. B. Sharpless, *Tetrahedron Lett.*, 5075 (1978)] have also been used as nucleophiles (X) in a cyclofunctionalization reaction.
(7) J. E. Baldwin, *J. Chem. Soc., Chem. Commun.*, 734 (1976).
(8) (a) G. H. Schmid and D. G. Garratt, *Chem. Scr.*, **10**, 76 (1976); (b) G. H. Schmid and D. G. Garratt, *Tetrahedron Lett.*, 3991 (1975).

0022-3263/80/1945-1313$01.00/0 

Scheme I

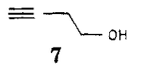
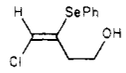
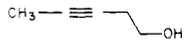
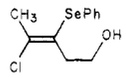
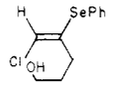
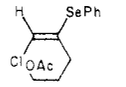
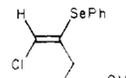
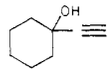
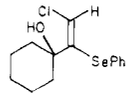


literature examples for such alkyne–proximate nucleophile cyclizations.[9] Such precedent encouraged us to try to effect the conversion of alkynes **4** to heterocyclic vinyl selenides **6** with PhSeCl as displayed in Scheme I.

Because various alkynyl alcohols were commercially available, they were the most attractive candidates for reaction with PhSeCl. For alkynes **7–12**, Table I presents yields of observed products **13–18** with PhSeCl in both $CH_2Cl_2$ at −78 °C and HOAc at ambient temperature. In all cases only 1,2 addition and *no* digonal cyclofunctionalization was observed. As can be seen, yields varied from poor to excellent. Reactions that produced only modest amounts of adduct also yielded significant amounts of diphenyl diselenide and as yet unidentified polar material. In the case of **9** especially, the hydroxyl group is implicated in these nonproductive side reactions by considering the contrasting high-yield conversion of alkynyl acetate **10** to vinyl selenide **16**.

The regiochemistry and stereochemistry of products **13–18** could in most cases be assigned by consideration of NMR spectra. In the $^{13}C$ spectra of **13** and **15–18**, the coupling of the chlorovinyl carbon ($C_1$) with the adjacent vinyl proton clearly established the regiochemistry of 1,2 addition as shown in Table I. The $^{13}C$ chemical shift and coupling of the chlorovinyl carbon ($C_2$) in product **14** was ambiguous, and we are only assuming that the regiochemistry of **14** is like that of the other products. The magnitude of the coupling between the $C_1$ vinyl proton and $C_3$ methylene protons ($J$ = 0.73 Hz) in the case of **13** and **15–17** and that between the $C_1$ methyl and $C_4$ methylene protons ($J$ = 0.98 Hz) in the case of **14** clearly indicated that the stereochemistry of these products was trans. Without the possibility of definitive proton coupling in **18**, we can only guess that its stereochemistry is also trans. Except in the case of **18**, whose proton NMR betrays a single vinyl proton, all other products **13–17** are contaminated by another chromatographically inseparable geometrical isomer. For **13** and **15–17**, the amount of side product is only a few percent by proton NMR integration of a downfield vinyl proton singlet, indicative of one of two possible cis isomers. In the case of **14**, the side product is 20% of the mixture as determined by the proton NMR integration of an upfield methyl triplet ($J$ = 0.85 Hz), most likely the only other possible trans isomer. In all cases the excellent correlation of calculated and found C, H, Cl, and Se elemental analyses for mixtures **13–17** confirmed that we were dealing with geometrical isomers.[10]

Table I. Addition Product Yield Data

| alkyne | major product | % yield[a] HOAc (24 °C) | % yield[a] $CH_2Cl_2$ (−78 °C) |
|---|---|---|---|
|  **7** |  **13** | 84 | 89 |
|  **8** |  **14** | 44 | 66 |
|  **9** |  **15** | 43 | 17 |
|  **10** |  **16** | | 90 |
|  **11** |  **17** | 55 | 60 |
|  **12** |  **18** | 80 | 90 |

[a] All yields are of analytically pure mixtures of chromatographically inseparable geometrical isomers.

Several factors may contribute to the lack of observed cyclofunctionalization and exclusive 1,2 addition of PhSeCl to hydroxyalkynes. In contrast to the case with olefins,[11] the addition of PhSeCl to alkynes is an irreversible process. We have found, for instance, that adducts **13–18** are perfectly stable in refluxing cyclohexene for 24 h without exchanging PhSeCl with the solvent and also in refluxing methanol for 24 h without solvent incorporation. It has been estimated[12] that carbonium ions like seleniranium ions **2** are more stable than vinyl cations like selenirenium ions **5** and thus are possibly easier to trap as cyclofunctionalized products by intramolecular nucleophilic attack. Also, the alignment of the necessary orbitals for cyclofunctionalization might not be as optimized in **5** as in **2**. We are currently examining ways to promote cyclofunctionalization of hydroxyalkynes and the possible conversion of products **13–15**, **17**, and **18** to the desired cyclized products.

## Experimental Section

**General Methods.** Alcohols **7–9**, **11**, and **12** were purchased from Chemsampco, Inc. (Farchan Division). Acetate **10** was prepared from **9**. Reactions were performed on a millimolar scale by the dropwise addition of 10% excess PhSeCl (Aldrich) in 5 mL of either HOAc or $CH_2Cl_2$ to a rapidly stirred solution of the alkynyl alcohol in 10 mL of the same solvent at the appropriate temperature. Workup simply entailed solvent evaporation and preparative TLC on 20 × 20 cm, 1000-μm Analtech silica gel GF plates eluted with EtOAc–hexane (1:4) and visualized by short-

(9) J. Bastide and O. Henri-Rousseau in "The Chemistry of the Carbon-Carbon Triple Bond", S. Patai, Ed., Wiley, New York, 1978, Part I, p 504, and references cited therein; (b) R. Fuks and H. G. Viehe in "The Chemistry of Acetylenes", H. G. Viehe, Ed., Marcel Dekker, New York, 1969, p 520, and references cited therein.

(10) Isomeric mixtures in the 1,2 addition of PhSeCl to triple bonds have been noted before; see ref 8a.

(11) K. B. Sharpless and R. F. Lauer, *J. Org. Chem.*, **39**, 429 (1974).

(12) K. Yates, G. H. Schmid, T. W. Regulski, D. G. Garratt, H. W. Leung, and R. McDonald, *J. Am. Chem. Soc.*, **95**, 160 (1973).

wave UV light. Analytical samples were dried at room temperature under high vacuum for 24 h. Analyses were performed by Galbraith Laboratories. Both proton and $^{13}C$ NMR spectra were obtained on a Bruker WP 200-MHz NMR. Chemical shift values are expressed in parts per million downfield from internal $(CH_3)_4Si$. The IR spectra were measured neat on salt plates with a Perkin-Elmer 283 spectrophotometer. Spectral and analytical data for each adduct now follow.

**Alcohol 13**: $^1H$ NMR ($CDCl_3$) $\delta$ 7.50–7.25 (m, 5, phenyl H), 6.50 (t, 1, $J$ = 0.73 Hz, $C_1H$), 3.80 (t, 2, $J$ = 6 Hz, $C_4H$), 2.70 (t, 2, $J$ = 6 Hz, $C_3H$), 1.70 (s, 1, OH); with the addition of trifluoroacetic anhydride (TFAA) the peak at $\delta$ 1.70 disappeared, and the peak at $\delta$ 3.80 shifted downfield to $\delta$ 4.50; $^{13}C$ NMR ($CDCl_3$) $\delta$ 133.18 (s, $C_2$), 121.13 (d, $C_1$), 60.67 (t, $C_4$), 35.98 (t, $C_3$); IR (film) 3400, 3080, 2960, 2900, 1600, 1580, 1480, 1440 $cm^{-1}$.

Anal. Calcd for $C_{10}H_{11}OClSe$: C, 45.91; H, 4.24; Cl, 13.55; Se, 30.18. Found: C, 45.92; H, 4.28; Cl, 13.80; Se, 29.95.

Alcohol 13 was contaminated by a minor isomer (2.5%) as determined by $^1H$ NMR integration at $\delta$ 6.70 (s, 1, $C_1H$).

**Alcohol 14**: $^1H$ NMR ($CDCl_3$) $\delta$ 7.50–7.25 (m, 5, phenyl H), 3.80 (t, 2, $J$ = 6 Hz, $C_5H$), 2.75 (t, 2, $J$ = 6 Hz, $C_4H$), 2.45 (t, 3, $J$ = 0.98 Hz, $C_1H$), 1.60 (s, 1, OH); with the addition of TFAA the peak at $\delta$ 1.60 disappeared, and the peak at $\delta$ 3.80 shifted downfield to $\delta$ 4.50; $^{13}C$ NMR ($CDCl_3$) $\delta$ 61.09 (t, $C_5$), 39.15 (t, $C_4$), 26.89 (q, $C_1$); $C_2$ and $C_3$ could not be assigned without ambiguity; IR (film) 3400, 3080, 2960, 2900, 1600, 1580, 1480, 1440 $cm^{-1}$.

Anal. Calcd for $C_{11}H_{13}OClSe$: C, 47.94; H, 4.75; Cl, 12.86; Se, 28.61. Found: C, 47.92; H, 4.75; Cl, 13.04; Se, 28.43.

Alcohol 14 was contaminated by a minor isomer (20%) as determined by $^1H$ NMR integration at $\delta$ 2.20 (t, 3, $J$ = 0.85 Hz, $C_1H$).

**Alcohol 15**: $^1H$ NMR ($CDCl_3$) $\delta$ 7.50–7.25 (m, 5, phenyl H), 6.40 (t, 1, $J$ = 0.73 Hz, $C_1H$), 3.65 (t, 2, $J$ = 6 Hz, $C_5H$), 2.50 (t, 2, $J$ = 6 Hz, $C_3H$), 1.80 (q, 2, $C_4H$), 1.50 (s, 1, OH); with the addition of TFAA the peak at $\delta$ 1.50 disappeared, and the peak at $\delta$ 3.65 shifted downfield to $\delta$ 4.30; $^{13}C$ NMR ($CDCl_3$) $\delta$ 133.47 (s, $C_2$), 119.45 (d, $C_1H$), 62.04 (t, $C_5$), 30.83 (t, $C_3$), 29.29 (t, $C_4$); IR (film) 3400, 2980, 2880, 1600, 1580, 1480, 1440 $cm^{-1}$.

Anal. Calcd for $C_{11}H_{13}OClSe$: C, 47.93; H, 4.75; Cl, 12.86; Se, 28.65. Found: C, 47.76; H, 4.89; Cl, 13.10; Se, 28.96.

Alcohol 15 was contaminated by a minor isomer (8%) as determined by $^1H$ NMR integration at $\delta$ 6.60 (s, 1, $C_1H$).

**Acetate 16**: $^1H$ NMR ($CDCl_3$) $\delta$ 7.60–7.20 (m, 5, phenyl H), 6.40 (t, 1, $J$ = 0.73 Hz, $C_1H$), 4.05 (t, 2, $J$ = 6 Hz, $C_5H$), 2.50 (t, 2, $J$ = 6 Hz, $C_3H$), 2.05 (s, 3, $COCH_3$), 1.90 (q, 2, $C_4H$); $^{13}C$ NMR ($CDCl_3$) $\delta$ 133.47 (s, $C_2$), 119.68 (d, $C_1$), 63.41 (t, $C_5$), 29.14 (t, $C_3$), 26.82 (t, $C_4$), 20.86 (q, $COCH_3$); IR (film) 3080, 2960, 1750, 1600, 1580, 1480, 1440 $cm^{-1}$.

Anal. Calcd for $C_{13}H_{15}O_2ClSe$: C, 49.15; H, 4.76; Cl, 11.16; Se, 24.85. Found: C, 49.35; H, 4.87; Cl, 11.40; Se, 25.17.

Acetate 16 was contaminated by a minor isomer (8%) as determined by $^1H$ NMR integration at $\delta$ 6.60 (s, 1, $C_1H$).

**Alcohol 17**: $^1H$ NMR ($CDCl_3$) $\delta$ 7.60–7.20 (m, 5, phenyl H), 6.40 (t, 1, $J$ = 0.73 Hz, $C_1H$), 3.65 (t, 2, $J$ = 6 Hz, $C_6H$), 2.45 (t, 2, $J$ = 6 Hz, $C_3H$), 1.60 (m, 4, $C_4$ and $C_5H$), 1.40 (s, 1, OH); with the addition of TFAA the peak at $\delta$ 1.40 disappeared, and the peak at $\delta$ 3.65 shifted downfield to $\delta$ 4.30; $^{13}C$ NMR ($CDCl_3$) $\delta$ 133.47 (s, $C_2$), 119.27 (d, $C_1$), 62.81 (t, $C_6$), 32.49 (t, $C_3$), 32.10 (t, $C_5$), 24.12 (t, $C_4$); IR (film) 3400, 3080, 2980, 2880, 1600, 1580, 1480, 1440 $cm^{-1}$.

Anal. Calcd for $C_{12}H_{15}OClSe$: C, 49.76; H, 5.23; Cl, 12.24; Se, 27.24. Found: C, 49.96; H, 5.44; Cl, 12.48; Se, 27.50.

Alcohol 17 was contaminated by a minor isomer (7%) as determined by $^1H$ NMR integration at $\delta$ 6.55 (s, 1, $C_1H$).

**Alcohol 18**: $^1H$ NMR ($CDCl_3$) $\delta$ 7.60–7.20 (m, 5, phenyl H), 5.90 (s, 1, $C_1H$), 2.30 (s, 1, OH), 2.30–2.10 (m, 2), 1.85–1.50 (m, 7), 1.40–1.10 (m, 1); $^{13}C$ NMR ($CDCl_3$) $\delta$ 134.34 (s, $C_2$), 113.44 (d, $C_1$), 34.79 (t), 25.12 (t), 21.66 (t); IR (film) 3600, 3030, 2960, 2870, 1580, 1480, 1450, 1440 $cm^{-1}$.

Anal. Calcd for $C_{14}H_{17}OClSe$: C, 53.26; H, 5.42; Cl, 11.23; Se, 25.01. Found: C, 53.39; H, 5.41; Cl, 11.44; Se, 24.90.

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**Registry No.** 7, 927-74-2; 8, 10229-10-4; 9, 5390-04-5; 10, 14604-46-7; 11, 928-90-5; 12, 78-27-3; (*E*)-13, 72726-34-2; (*Z*)-13, 72726-35-3; (*E*)-14, 72726-36-4; (*Z*)-14, 72726-37-5; (*E*)-15, 72726-38-6; (*Z*)-15, 72726-39-7; (*E*)-16, 72726-40-0; (*Z*)-16, 72726-41-1; (*E*)-17, 72726-42-2; (*Z*)-17, 72726-43-3; 18, 72726-44-4; PhSeCl, 5707-04-0.

## Synthesis and Nuclear Magnetic Resonance Study of 1,3-Diazacyclonona-1,2-diene: An Unusual Carbodiimide

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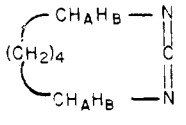
As early as 1932[1] Adams and co-workers recognized that carbodiimides might exist as chiral molecules because of their possible geometrical similarity to allenes. In addition, they recognized that "vibrations" of R groups through the NCN axis could lead to racemization. (In modern parlance, we discuss the configuration stability of the nitrogens in carbodiimides.) To date we are aware of only one report[2] of the preparation of an optically active carbodiimide whose optical activity arises solely from the molecular chirality of the NCN linkage. We[3] and others[4] have previously suggested that that report is in error.

Spectroscopic studies[5,6] carried out on various carbodiimides support structures with an NCN linkage analogous to that in allenes, although only limited work has been carried out[4] to examine the configurational stability of nitrogen in carbodiimides. Anet and co-workers[4] studied the low-temperature NMR spectrum of diisopropylcarbodiimide and found the free-energy barrier to interconversion of the diastereotopic methyl groups to be 6.6–6.7 kcal/mol. This barrier agrees with theoretical predictions.[7,8] Possible mechanisms leading to such barriers have been considered by using INDO calculations;[7] only nitrogen inversion and a rotation through a trans form (in which the angle between groups on nitrogen goes from 90 to 180°) were considered likely. Although the barrier measured for diisopropylcarbodiimide agreed with theoretical predictions, it gave no information about the mechanism for the interconversion process.

We synthesized 1,3-diazacyclonona-1,2-diene (I) in an




I

attempt to distinguish between these two possible mechanisms. We reasoned that although nitrogen inversion might be retarded by placing the linear NCN linkage in

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