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 ($CDCl_3$) δ 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 δ 1.70 disappeared, and the peak at δ 3.80 shifted downfield to δ 4.50; ^{13}C NMR ($CDCl_3$) δ 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 δ 6.70 (s, 1, C_1H).

Alcohol 14: ^1H NMR ($CDCl_3$) δ 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 δ 1.60 disappeared, and the peak at δ 3.80 shifted downfield to δ 4.50; ^{13}C NMR ($CDCl_3$) δ 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 δ 2.20 (t, 3, J = 0.85 Hz, C_1H).

Alcohol 15: ^1H NMR ($CDCl_3$) δ 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 δ 1.50 disappeared, and the peak at δ 3.65 shifted downfield to δ 4.30; ^{13}C NMR ($CDCl_3$) δ 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 δ 6.60 (s, 1, C_1H).

Acetate 16: ^1H NMR ($CDCl_3$) δ 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 ($CDCl_3$) δ 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 δ 6.60 (s, 1, C_1H).

Alcohol 17: ^1H NMR ($CDCl_3$) δ 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 δ 1.40 disappeared, and the peak at δ 3.65 shifted downfield to δ 4.30; ^{13}C NMR ($CDCl_3$) δ 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 δ 6.55 (s, 1, C_1H).

Alcohol 18: ^1H NMR ($CDCl_3$) δ 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 ($CDCl_3$) δ 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.

Acknowledgment. We gratefully acknowledge the technical assistance of Professor Lawrence Altman (Stony Brook) and Mr. Larry Thomas (NEN) in obtaining and interpreting the ^1H and ^{13}C NMR spectra. We also acknowledge communication with and encouragement from Professors Derrick L. J. Clive (University of Alberta), George H. Schmid (University of Toronto), Dennis Garratt (National Research Council of Canada), and K. N. Houk (Louisiana State University).

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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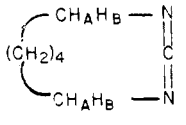
Received October 22, 1979

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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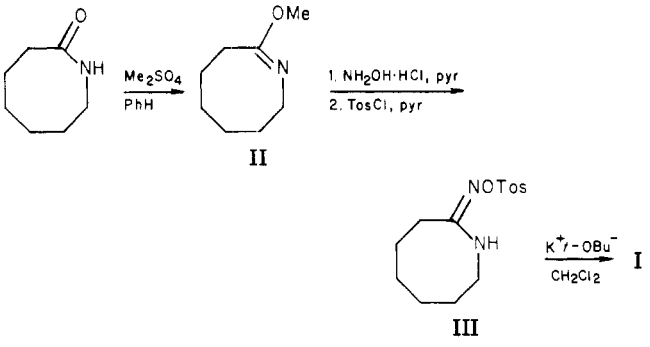
Scheme I



a small ring, rotation through the 180° trans form would appear to be impossible.

Results and Discussion

Although compound I had been reported in 1957,[9] it had not been prepared in a pure state. Furthermore, repeated attempts by us to prepare I by the reported method failed. We, therefore, designed the alternate synthesis shown in Scheme I. *O*-Methylation was carried out to prepare II in 60% yield. Reaction to prepare III in 47% yield was carried out without isolation of the intermediate oxime. Finally, I was prepared in 73% yield by reaction with potassium *tert*-butoxide. Compound I has been fully characterized spectroscopically and prepared in analytical purity.

Study of the low-temperature spectrum of I was carried out from ambient temperatures to −160 °C in CF_2Cl_2. At ambient temperatures, H_A and H_B appeared as a single sharp signal at 3.3 ppm (with decoupling of other methylene hydrogens). As the temperature decreases, H_A and H_B first split as two broad singlets (<−130 °C) and then at ∼−140 °C split further into an AB quartet. Under the conditions which we have examined, the AB quartet is not as sharply delineated as we would like; it is, however, clearly indicated by distinct separate shoulders developing on the outsides of the broad singlets. We have been able to closely simulate this behavior by using Binsch's dynamic NMR (DNMR) program.[10] Because of the difficulty of getting good slow-exchange spectra (see Experimental Section for further details), we have been unable to carry out a complete line-shape analysis. We have, however, calculated the free energy of activation for the interconversion of H_A and H_B at the coalescence temperature (−131 °C). As recognized by a number of workers,[11-13] excellent $\Delta G^{\ddagger}$ values may be obtained this way. We have calculated $\Delta G^{\ddagger}$ by using the approximate equation[10] $\Delta G^{\ddagger} = -RT_c \ln (k_c h/kT_c)$, where (1) k_c, the rate constant at the coalescence temperature, is taken from the best-fit DNMR simulations or (2) k_c is calculated[11] from $k_c = (\pi/2^{1/2})(\Delta\nu^2 + 6J^2)^{1/2}$. Furthermore, we have closely examined what effect various errors in the measurement of experimental parameters (temperature, $\Delta\nu$, and J) would have on $\Delta G^{\ddagger}$. Consistent with the findings of others,[11-13] we find that $\Delta G^{\ddagger}$ is not a very sensitive function of either the method of calculation or variations of the experimental parameters. A value of 6.7 ± 0.2 kcal/mol for $\Delta G^{\ddagger}$ takes these considerations into account. Additional details may be found in the Experimental Section.

The free-energy barrier measured for I is essentially identical with that in diisopropylcarbodiimide.[4] One might expect that the linear NCN linkage in a nine-membered ring would introduce considerable strain and that any process interconverting H_A and H_B would require difficult conformational reorganization. Such a view is somewhat simplistic, appearing at odds with the experimental results. The small free-energy barrier measured for interconversion of H_A and H_B suggests that other processes, in addition to those caused by the configurational instability of nitrogen, may affect the barrier. Recent work by Anet and Yavari[14] indicates that a nine-membered cyclic allene possesses considerable strain and undergoes a variety of conformational changes. These have been studied by using low-temperature ^{13}C NMR spectroscopy and analyzed with the aid of force-field calculations. Anet's work suggests to us that compound I may be undergoing a variety of measurable conformational changes at low temperatures. As a result, the interconversion barrier for H_A and H_B may be a composite of effects caused by the configurational instability of nitrogen and various conformational effects. We are at present unable to separate these, but we plan more detailed NMR studies in the future.

The recently reported[15] synthesis of V (see Scheme II) is an example of an unusually substituted nine-membered cyclic carbodiimide. Hydrogens H_A and H_B of V are nonequivalent by virtue of the nonplanarity of the biphenyl moiety. Indeed, the methylenes in both IV and V are nonequivalent, suggesting that there is no way of telling whether nitrogen inversion is occurring in V. That is, it is impossible to tell whether H_A and H_B are nonequivalent solely because of the biphenyl moiety or also because of nitrogen configurational stability.

Finally, we have recently prepared the eight-membered-ring analogue of I. So far it has eluded isolation, but we are hopeful that we will be able to study its DNMR properties.

Experimental Section[16]

Preparation of 1-Methoxy-2-azacyclooct-1-ene (II). The general procedure of "Organic Syntheses"[17] was followed. To a refluxing solution of 2-azacyclooctanone (Aldrich, 25.0 g, 0.197 mol) in benzene (50 mL) was added dimethyl sulfate (19 mL, 0.2 mol). After being refluxed for 24 h and cooled to room temperature, a K_2CO_3 solution (30 g in 30 mL of H_2O) was added. The resulting precipitate was separated, and the benzene layer was separated and dried over Na_2SO_4. Distillation (39 °C, 1.1 mm) gave II (16.8 g, 60.5%) [lit.[18] bp 44–48 °C (1.6 mm)].

Preparation[19] of 1-[[(*p*-Tolylsulfonyl)oxy]imino]-2-azacyclooctane (III). Compound II (16.8 g, 0.119 mol) was added to hydroxylamine hydrochloride (9.09 g, 0.131 mol) and pyridine (100 mL). The white suspension was stirred for 44 h and cooled to below 6 °C, and *p*-toluenesulfonyl chloride (22.7 g, 0.119 mol) in pyridine (50 mL) was slowly added. After 3.5 h, water (2000 mL) was added to the yellow suspension. The resulting white precipitate was filtered and recrystallized from a minimal amount of a 1:1 mixture of benzene–cyclohexane. White crystals (16.6 g, 47%, mp 104–106 °C) were obtained: IR (KBr) 3410, 3080, 2950, 1610 cm^{-1}; NMR ($CDCl_3$) δ 1.43 (s, 8 H), 2.20 (m, 2 H), 2.42

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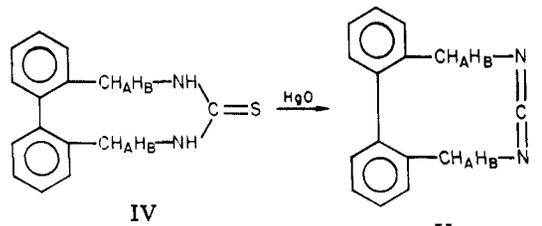
Scheme II



IV V

(s, 3 H), 3.20 (m, 2 H), 5.70 (m, 1 H), and 7.63 (m, 4 H).

Preparation of 1,3-Diazacyclonona-1,2-diene (I). In scrupulously dried equipment under nitrogen, III (5.00 g, 0.0169 mol), potassium *tert*-butoxide (MSA Research, 2.37 g, 0.0211 mol), and freshly distilled (from P_2O_5) methylene chloride (225 mL) were refluxed for 1 h. After the mixture was filtered, solvent was removed, and the resulting yellow liquid was distilled. I (1.54 g, 73.3%) was obtained [bp 48 °C (0.85 mm)]: IR (neat) 3000–2850, 2100 (s) cm^{-1}; NMR ($CDCl_3$) δ 3.30 (m, 4 H), 1.80 (s, 8 H). Anal. Calcd for $C_7H_{12}N_2$: C, 67.70; H, 9.74. Found: C, 67.55; H, 9.55.

Low-Temperature NMR Experiments and $\Delta G^{\ddagger}$ Calculations. The low-temperature NMR experiments were carried out on a JEOL PS-100 (most of the experiments) and a Varian FX-100 (a few experiments). The solvent used was CF_2Cl_2, and the temperature ranged between ambient temperature and −160 °C. The probe temperature was calibrated by placing a thermocouple in a tube of CF_2Cl_2 (without spinning). Frequent thermocouple measurements were made; we feel our temperatures are accurate to ±2 °C.

Free energy of activation ($\Delta G^{\ddagger}$) calculations were made by using $\Delta G^{\ddagger} = -RT_c \ln (k_c h/kT_c)$, where R, h, and k are the gas, Planck's, and Boltzmann's constants, respectively, and k_c is the rate constant at the coalescence temperature, T_c. Values for k_c were obtained either from (1) visual comparison of the simulated[10] and experimental spectra or (2) $k_c = (\pi/2^{1/2})(\Delta\nu^2 + 6J^2)^{1/2}$, where $\Delta\nu$ is the separation of H_A and H_B at the slow-exchange limit, and J is J_{AB}. Because the slow-exchange spectra are not as definitive as we would like, we can only estimate $\Delta\nu$ and J. This is a common problem,[4] and we have dealt with it by calculating $\Delta G^{\ddagger}$ for the ranges of $\Delta\nu$ and J which are possible. These are 55–60 Hz for $\Delta\nu$ and 12–15 Hz for J. All $\Delta G^{\ddagger}$ values calculated are between 6.6 and 6.8 kcal/mol. Uncertainties in our temperature measurements have also been considered; a ±2 °C range leads to only minor effects. We feel confident that a $\Delta G^{\ddagger}$ of 6.7 ± 2 kcal/mol is quite reasonable.

Acknowledgment. We thank Professor S. S. Eaton for simulating the spectra and for helpful discussions, M. Ashley for running most of the low-temperature spectra, the Regional NMR Center for running some low-temperature spectra, and the Research Corp. for partial support of this work.

Registry No. I, 6248-74-4; II, 1889-06-1; III, 72796-10-2; 2-azacyclooctanone, 673-66-5; hydroxylamine hydrochloride, 5470-11-1.

Novel Rearrangement of a Diaziridine

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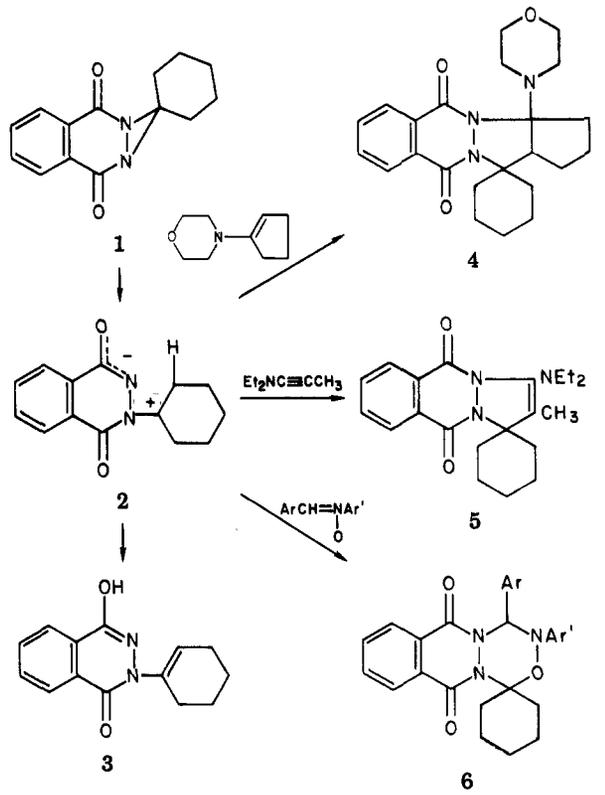
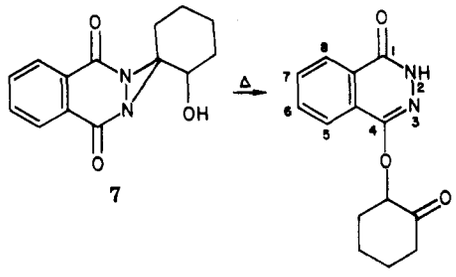
Recent work in these laboratories established that 1,1-dialkyl-1*H*-diazirino[1,2-*b*]phthalazine-3,8-diones isomerize in refluxing toluene into 2-(1-alken-1-yl)-4-hydroxy-1-

Scheme I



(2*H*)-phthalazinones. For example, **1** in refluxing toluene formed **3**. Presumably an azomethine imine, **2**, was initially formed which subsequently stabilized itself by loss of a proton (Scheme I). It was possible to intercept **2** by heating **1** with enamines,[1] ynamines,[1] and nitrones[2] to yield compounds **4**–**6**, respectively (Scheme I). We now report that a derivative of **1**, namely, **7**, in refluxing toluene or in Me_2SO containing potassium *tert*-butoxide undergoes an unusual isomerization.

Heating of **7** in anhydrous toluene for 2 h caused gradual precipitation of compound **8** (55%). The same product



was obtained in 85% yield when **7** was treated with potassium *tert*-butoxide in Me_2SO at ambient temperature. The constitution of **8** was established by ^{13}C NMR and ^1H NMR spectroscopy, chemical degradation, mass spectroscopy, and elemental analysis. That **8** was a 4-alkoxy-1(2*H*)-phthalazinone was indicated by its acid and alkaline hydrolysis. In hot hydrochloric acid **8** formed 4-hydroxy-1(2*H*)-phthalazinone (**9**) in 95% yield. Compound **8** in hot aqueous 10% sodium hydroxide followed by acidification of the reaction mixture gave **9** (95%) and 2-hydroxycyclohexanone (35%, isolated as the 2-4-dinitrophenylhydrazone). The alkaline hydrolysis probably occurred through the intermediacy of **10** (Scheme II). The

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