sterically induced flattening in hydrocarbons.[21,22]

The data reported here indicated that hybridization at nitrogen is an important factor in determining δ_N, a hypothesis which ought to be tested on other amino compounds. Because the amount of pyrimidality at nitrogen is quite difficult to measure experimentally (a complete structure determination is now required), better understanding of the various factors influencing δ_N could ultimately promote a spectroscopic way of estimating the hybridization at nitrogen, which we expect to be important in determining the reactivity of amino compounds.

Experimental Section

Natural-abundance ^{15}N Fourier transform NMR spectra were obtained on a Varian XL-100-15 spectrometer equipped with a V4412 (12 mm) probe and a Varian FT data system using the GyroObserve option. Spectra were recorded at a spectral width of 5120 Hz, and 4096 data points (1.25 Hz/point) were obtained. A pulse width corresponding to a 30° flip angle was used at a 1.6–2.0-s repetition rate. Sample concentration was typically 1.5–3.0 M in 1/1 (v/v) acetone-d_6/nitromethane. This solvent mixture provided both the internal deuterium lock and nitromethane reference.[25] The solutions were approximately 0.085 M in $Cr(acac)_3$ to shorten relaxation times. Sample volumes of 2–3 mL were employed. Adequate signal-to-noise ratios were observed for 3 M hydrazine samples having two equivalent nitrogens in 4 h; more dilute samples required up to 16 h of data acquisition.

The observed ^{15}N chemical shifts are internally consistent to ±0.2 ppm relative to CH_3NO_2. While we recognize the deficiencies of internal standards for accurate and reproducible absolute chemical shift determination,[26] we feel that for compounds of similar structural type run under similar conditions these conditions provide the most consistent and convenient means of obtaining relative shifts. A study of chemical shift changes with substrate concentration was undertaken for 1,2-dimethyl-1,2-diethylhydrazine, in which a 0.2-ppm downfield shift was observed when the hydrazine concentration was increased from 1.3 to 2.7 M at a constant $Cr(acac)_3$ concentration of 0.087 M. Almost all of our hydrazine samples fall in this concentration range. The effect of paramagnetic relaxation reagents on ^{15}N shifts has been noted.[25] The circumvention of such effects by using internal referencing has been found to be quite adequate. Varying the concentration of $Cr(acac)_3$ from 0.05 to 0.10 M resulted in less than a 0.1-ppm change in the chemical shift for both nitrogens of isobutyltrimethylhydrazine relative to internal nitromethane, but a 0.6_6-ppm upfield shift relative to external $D^{15}NO_3$ [the hydrazine chemical shift was 294.1_8 ppm upfield from external $D^{15}NO_3$, 1.0 M in D_2O, which is 4.3_3 ppm upfield from neat external nitromethane, and the hydrazine shift was 295.7_0 ppm upfield from internal nitromethane, all experiments quoted being at 0.10 M $Cr(acac)_3$].

^{13}C NMR spectra were obtained at 15.9 MHz on a JEOL FX-60 spectrometer.

The tetraalkylhydrazines were prepared by previously reported methods.[3,5] Purification and drying was performed by distillation and/or allowing the sample to stand over NaOH pellets. Solids were crystallized or sublimed, as appropriate.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation for partial financial support of this work and Dr. D. F. Hillenbrand for valuable assistance in obtaining the ^{15}N spectra.

Registry No. 1, 6415-12-9; 2, 50599-41-2; 3, 23337-93-1; 4, 21849-74-1; 5, 60678-65-1; 6, 52598-10-4; 7, 68970-04-7; 8, 4267-00-9; 9, 60678-69-5; 10, 60678-71-9; 11, 6130-94-5; 12, 6523-29-1; 13, 26163-37-1; 14, 3661-15-2; 15, 5721-43-7; 16, 14287-92-4; 17, 14287-89-9; 18, 18389-95-2; 19, 38704-89-1; 20, 74096-71-2; 21, 5397-67-1; 22, 23211-28-1; 23, 60387-16-8; 24, 63892-83-1.

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Molecular Asymmetry in *trans*-Thiacycloalkenes. 2. Barriers to Interconversion of Diastereomeric Conformers of 2-Substituted Nine- to Eleven-Membered (*E*)-Thiacycloalk-4-enes[1]

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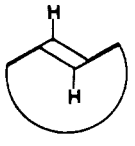
trans-Thiacycloalk-4-enes of ring size 9 to 11 carrying a substituent (CH_3 or $COOCH_3$) at C_2 were synthetized. These species have two elements of chirality (a plane and a center) and exist as diastereomeric pairs which may interconvert via a conformational process (180° revolution of the π plane inside out the ring). The energy barrier for this process has been measured by dynamic ^{13}C NMR and found to be 16.4, 10.7, and 8.3 (or 7.0) kcal/mol for the 9-, 10-, and 11-membered-ring compound, respectively, lower than those for their carbocyclic analogues. The lower barriers may arise from the heteroatom across the ring, which, unlike the corresponding carbon in the homocyclic counterpart, carries no ligand and allows for less steric compression in the transition state.

Eight-membered and larger rings may accommodate a double bond of *E* configuration. Rings having this feature are chiral enantiomeric pairs[2] whose interconversion occurs through configurational inversion of a chiral plane. This process requires a 180° rotation of the sp^2 plane around the σ bonds adjacent to the π bond and involves the passage of one of the olefinic hydrogens inside out the ring via a transition state in which the olefinic H was moved against the atoms across the ring and the ligands thereon.



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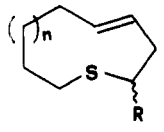
0022-3263/80/1945-3613$01.00/0

The height of the energy barrier for this process depends on ring size. Thus for carbocycles the barrier decreases from 35 kcal mol^{-1} for (*E*)-cyclooctene[3] to 19 and 11.7 kcal mol^{-1} for (*E*)-cyclononene[4] and (*E*)-cyclodecene.[5]

The nature of the atoms across the ring also affects the barrier. Thus in going from (*E*)-cyclooctene to (*E*)-thiacyclooct-4-ene, in which the methylene at position 5 has been replaced by an S atom, the barrier drops by 5 kcal mol^{-1}.[1] The lower barrier is likely to arise from the heteroatom across the ring, which, unlike the corresponding carbon in the homocyclic counterpart, carries no ligands, allowing for less steric crowding in the transition state. When ring size is increased, the differential barrier for chiral inversion, homocyclic vs. heterocyclic, is expected to gradually diminish.

As part of a broader study of the chemical and structural properties of medium-size heterocyclic olefins,[1,6,7c,8] we have synthesized (*E*)-thiacycloalk-4-enes of ring size 9–11, having a substituent (CH_3 or $COOCH_3$) at C_2 (1–3). Be-



1a, $n = 1$; R = CH_3
1b, $n = 1$; R = CO_2CH_3
2, $n = 2$; R = CH_3
3, $n = 3$; R = CO_2CH_3

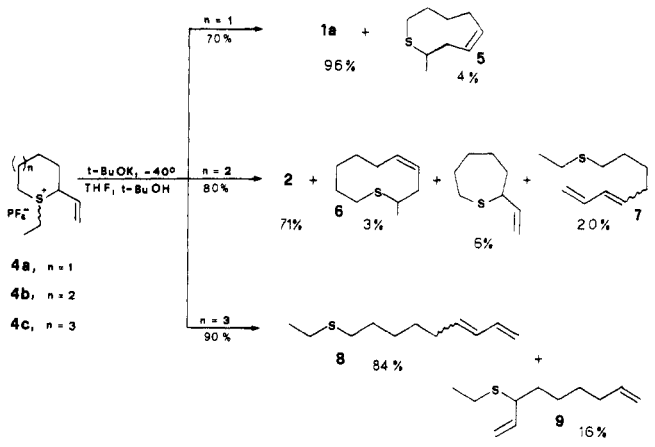
side the chiral plane, these species possess a second element of chirality, a chiral center at C_2, and therefore are diastereomerically rather than enantiomerically related. They give rise, at low temperature, to separate sets of resonances in the ^{13}C NMR spectrum, and their interconversion may be studied by dynamic ^{13}C NMR methods. The present paper reports this study.

Results and Discussion

Synthesis. The required 2-substituted (*E*)-thiacycloalk-4-enes were obtained via three-carbon ring expansion by [2,3] sigmatropic rearrangement of cyclic sulfonium ylides,[7] which for ring size six and larger produces cyclic homoallylic sulfides largely of *E* configuration ($E/Z \geq 20$).[7,8] Our initial plan was to synthetize 2-methyl substituted thiacycloalk-4-enes by rearrangement of 1-ethylides obtained by in situ deprotonation of 1-ethyl sulfonium salts. The method works well with the six-membered ($n = 1$) sulfonium salt, from which only products of ring expansion are obtained. It works less well with the seven-membered salt which, along with ring expansion, gives elimination products. It fails completely with the eight-membered salt (see Scheme I).

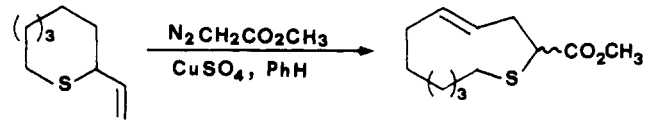
As the cyclic sulfonium salt grows in size and ring strain, β-elimination reactions that bring about ring opening be-

Scheme I



come more important and take over completely at ring size eight.

Since no opening had been previously observed in the ring expansion of 1-methyl-2-vinylthiepanium,[7c] the behavior of the 1-ethyl salt appears likely to be related to the lesser acidity of the exocyclic α protons. Their removal by base is not competitive with base catalyzed β-elimination in those ring systems where elimination results in the fission of a relatively strained ring. This observation and other ones,[7d,9] according to which ring expansion occurs without problems from eight- and nine-membered sulfonium salts carring an activated exocyclic C–H (e.g., *S*-allyl[9] and *S*-carbethoxy[7d] derivatives), indicate that the desired 2-substituted eleven-membered thiacycloalk-4-ene could be obtained from a stabilized ylide. A carbomethoxy stabilized ylide, prepared in situ by thermal Cu(II)-catalyzed decomposition of methyl diazoacetate[10] in the presence of 2-vinylthiocane, gives the expected eleven-membered 2-carbomethoxy derivative as the major product.



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Since the change from methyl to carbomethoxy may affect the energy barrier for chiral inversion, the carbomethoxy derivative **1b** of the nine-membered ring was also prepared. Its dynamic ^{13}C NMR behavior was observed along with that of **1a**.

Dynamic ^{13}C NMR. Table I lists the ^{13}C NMR shifts for the conformational isomers of compounds **1a**, **1b**, **2**, and (partially) **3**. The data for the corresponding eight-membered-ring compounds are also reported.[1,7c] For comparison, the shifts of the corresponding unsubstituted cyclic olefins are also included.

The room-temperature ^{13}C NMR spectrum of **1a** in $CDCl_3$ displays two sets of signals. The line width of the weaker signals appears to be larger than that of the more intense companions. This indicates a slow exchange between two unequally populated sites.[11] Indeed, on low-

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Table I. ^{13}C NMR Shifts (ppm from Me_4Si) of (E)-Thiacycloalk-4-enes and their Diastereomeric 2-Substituted Derivatives[a]

ring size	R	isomer	C_5	C_4	C_2	C_3	C_6	C_7	C_8	C_9	C_{10}	C_{11}	other
8	H[b,c]		137.5	130.4	43.5	37.8	(36.8)	(35.2)	(34.8)				
	CH_3[b,d]	*RR,SS*	136.6	131.7	54.3	44.9	(35.7)	(34.8)	(33.8)				21.2[m]
	CH_3[b,d]	*RS,SR*	139.6	127.5	49.9	41.8	(37.7)	(35.0)	25.9				21.4[m]
9	H[b,c]		134.6	126.6	(37.6)	(36.2)	(33.2)	(32.6)	(26.0)	(25.6)			
	CH_3[b,e]	major	134.8	127.4	46.5	42.5	(36.5)	(32.2)	(25.1)	(25.0)			23.3[m]
	CH_3[b,e]	minor	133.9	128.1	48.5	38.9	(36.2)	(33.8)	(30.0)	(29.0)			21.4
	$COOCH_3$[f]	major	136.3	124.7	51.6	37.8	(35.8)	(33.0)	(25.4)	(24.4)			172.0,[n] 51.7[o]
	$COOCH_3$[f]	minor	135.6	125.6	51.3	35.4	(34.6)	(33.0)	(28.1)	(27.5)			51.3[o]
10	H[b,c]		[131.6]	[130.3]	(34.2)	(34.2)	(33.5)	(31.3)	(27.2)	(25.4)	(23.6)		
	CH_3[g]	major	[131.4]	[130.5]	45.8	44.7	(32.8)	(30.0)	(27.7)	(25.6)	(23.9)		22.4[m]
	CH_3[g]	minor	[132.0]	[130.2]	42.8	37.7	(32.7)	(34.1)	(27.1)	(25.2)	(23.9)		23.9[m]
11	H[b,h]		[134.1]	[128.5]	(35.7)	(33.8)	(33.7)	(33.0)	(27.7)	(26.8)	(26.3)	(25.1)	
	$COOCH_3$[i]		[137.7][k]	[127.1]	50.4[l]	36.6	(34.7)	(30.4)	(28.9)	(27.2)	(26.8)	(25.1)	176.6,[n] 52.9[o]

[a] Shifts in parentheses or in brackets are interchangeable; for diastereomeric pairs, however, shifts in the same column are for the same carbon atom. [b] $CDCl_3$ solvent. [c] Reference 7c. [d] Reference 1. [e] At 0 °C. [f] C_2Cl_4 solvent, at 0 °C. [g] CD_2Cl_2, -90 °C. [h] Reference 20. [i] CHF_2Cl solvent, -20 °C; averaged shifts of two about equally populated conformers. See text and footnotes *k* and *l*. [k] At -120 °C, 138.2 and 137.3. [l] At -120 °C, 49.6 and 49.1. [m] CH_3. [n] CO. [o] OCH_3.

Table II. Activation Parameters for Interconversion of Diastereomeric Conformers of 2-Substituted (E)-Thiacycloalk-4-enes

compd	solvent	temperature range, K	$\Delta G^{\neq}$, kcal/mol	$\Delta H^{\neq}$, kcal/mol	$\Delta S^{\neq}$, kcal/mol
1a	$CDCl_3$	312-333	$16.3_8 \pm 0.4$[a]	15.9 ± 0.6	-1.5 ± 2
1b	C_2Cl_4	326-332	$17.1_5 \pm 0.15$[a]		
2	CD_2Cl_2	212-243	$10.7_2 \pm 0.09$[b]	10.1 ± 0.6	-3 ± 3
3	CHF_2Cl	161-168	8.3 ± 0.2		
		148-153	7.0 ± 0.3		

[a] For racemization of optically active (E)-cyclononene, $\Delta G^{\neq} = 19.1 \pm 0.2$ kcal/mol.[4] [b] For (E)-cyclodecene-1,2,4,4,9,9-d_6 and 3,3-difluoro-*trans*-cyclodecene, $\Delta G^{\neq} = 11.8$[5a] and 12.2 kcal/mol.[5b]

ering the temperature to 0 °C, the two sets of lines sharpen to the same line width (intensity 70:30; see Table I for shifts). The ^{13}C signals of **1a** broaden and coalesce to yield a sharp nine-line spectrum on warming above room temperature (about 75 °C, see Experimental Section). The kinetic parameters of the exchange process were evaluated by computer simulation of the line shapes.[12] Although any pair of corresponding signals may be used, the purpose is better served by pairs of lines having the largest chemical-shift difference (unencumbered by overlapping signals). The two pairs of low-field saturated-carbon lines C_2 (48.5 and 46.5 ppm) and C_3 (42.5 and 38.9 ppm), respectively, were suitable. The second pair, with a greater shift difference, allowed the line shape to be followed in a wider temperature range (312 to 335 K against 312 to 321 K). The values of the rate constants obtained at each temperature from either pair of lines were averaged and least-squares fitted to the Eyring equation to give the kinetic parameters reported in Table II. Table II also lists the corresponding parameters for the other ring systems. Since, for both **1a** and **2**, $\Delta S^{\neq}$ was found to be zero within experimental errors (Table II), $\Delta G^{\neq}$ is considered to be essentially temperature independent and will be used as the measure of the interconversion barrier.

The room-temperature spectrum (CD_2Cl_2 solvent) of the ten-membered-ring compound **2** shows ten signals (see Experimental Section) which on cooling at -90 °C separate into two sets (intensity 70:30; Table I). The two pairs of low-field saturated-carbon signals were used to analyze line shape. In this case the two pairs could not be analyzed independently of each other, because one pair crosses over

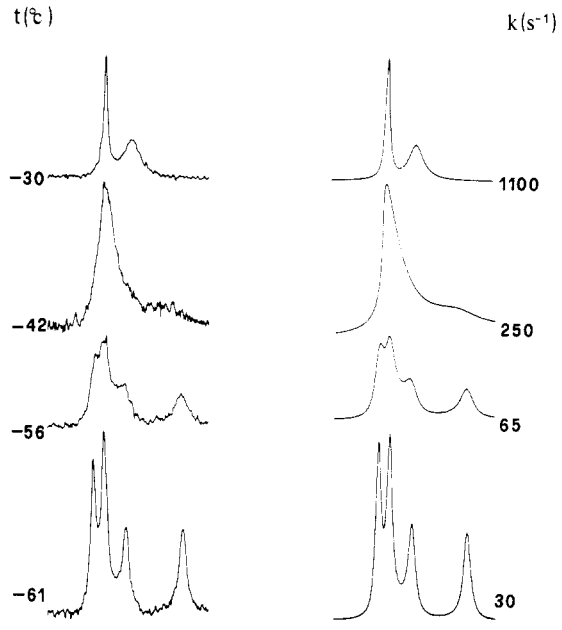

Figure 1. Experimental (left) and computer-simulated (right) line shapes of C_2 and C_3 of compound **2** as a function of temperature (°C).

the other: the 45.8-ppm line was found to exchange with the line at 42.8 ppm, and the 44.7-ppm line with the line at 37.7 ppm (see Figure 1). When the temperature was lowered further (below -110 °C, CHF_2Cl solvent), a second dynamic process became evident; however, no region of the ^{13}C spectrum was amenable to accurate line-shape analysis. Nonetheless, since the chemical-shift differences of the lines generated by the second process are in the range 10–50 Hz and broadening occurs between -110 and -125 °C, the barrier for this second process can be estimated to be in the 7–8 kcal/mol range. The higher of the two

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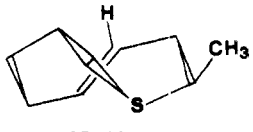
(13) Dale, J. *Top. Stereochem.* **1976**, *9*, 199. See, in particular, the discussion on pp 253–255.

barriers would be unreasonably elevated for a simple conformational change in a ten-membered ring and, in analogy with (*E*)-cyclodecene,[5,13] can be assigned to the process of rotation of the trans double bond through the ring.

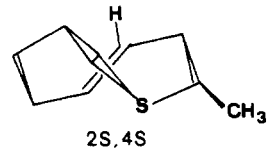
In CHF_2Cl at −20 °C, the eleven-membered compound **3** displays a sharp 12-signal spectrum (Table I). Stepwise lowering of the temperature down to −140 °C disclosed two dynamic processes. The more highly activated process was followed in the range −105 to −112 °C by monitoring the low-field aliphatic resonance at 50.4 ppm and the high-field olefinic resonance at 127.1 ppm. Both split into two equally intense signals at low temperature. The second process was evinced by a further splitting of the signals at lower temperature. The ^{13}C spectrum is extremely complex and only one carbon resonance (the olefinic carbon at 137.7 ppm) was found to be adequate for line-shape analysis. The two barriers are too close to one another to decide which of the two corresponds to the inversion of the chiral plane. However, their very closeness makes the assignment of little importance.

The conformational barriers reported in Table II confirm the expectations that for these heterocyclic *E* olefins the inversion of the chiral plane (involving a 180° rotation of the double bond through the ring) is less activated than for the carbocyclic homologues. The differential barriers, carbocyclic vs. heterocyclic, diminish with increasing ring size (Table II).

Unlike the eight-membered-olefin case,[1] where it was possible to attempt a rationalization (later confirmed to be correct)[6b] of the ^{13}C NMR shifts in terms of conformation and configuration of the diastereomers, in the present cases the ^{13}C shifts offer no clue to the prevailing conformation(s). Under these circumstances no analysis can be attempted for the interconversion processes. Consider the nine-membered olefin and its 2-methyl derivative **1a**. If the hypothesis is given that the ring conformation is similar to the C_2 conformation of (*E*)-cyclononene,[14] then the two diastereoisomers of **1a** would differ for the orientation of the Me group, as depicted. According to the argument developed for assigning the configuration of the eight-membered-ring homologues,[1] the *RS,SR* isomer is expected to have both C_4 and C_9 upfield (γ-effect) with respect to the *SS,RR* isomer, whose C_4 and C_9 shifts would in turn be about the same as those in the unsubstituted ring compound. The data in Table I do not bring forth this prediction: for both diastereomers of **1a** the shifts of C_4 are very close to each other, very close in turn to that of the unsubstituted oelfin. Neither diastereomer displays the γ-effect on C_4 that would be expected if both isomers adopt the twist conformation assumed. An explanation is that the *RS,SR* isomer adopts a different ring conformation, which allows a more effective relief of the strain that would arise from the Me group in a gauche arrangement to both C_4 and C_9. Such a requirement might be satisfied by a crown conformation, below, in which the dihedral angles $C_4C_3C_2CH_3$ and $C_9SC_2CH_3$ would be about 150°, and for which no appreciable γ-effect would arise.

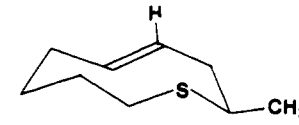


2R,4S



2S,4S

The idea that the two diastereomers adopt different ring conformations is supported by other shift considerations.



Although a precise assignment of C_9 could not be made, Table I shows a close correspondence between the shifts of the unsubstituted ring compound and those of the minor conformer of **1a** (except C_2 and C_3, of course). On the other hand, the major conformer has the two uppermost carbon shifts at very low field (30.0 and 29.0 ppm), indicating downfield shifts of at least 4.9 and 4.0 ppm. A deshielding of this magnitude, while unprecedented for carbons three or more bonds away from the CH_3 substituent, could be justified by a different ring shape. We suggest that the major conformer of **1a** adopts a ring conformation different from that of either the minor conformer or the unsubstituted ring.

A similar analysis of the ten-membered homologues leads to conclusions analogous to those for the nine-membered olefins. It is evident that more detailed work is necessary (high-field ^1H, ^2H, and ^{13}C NMR, molecular-mechanics calculations) to gain a satisfactory understanding of the static and dynamic properties of these molecules. Work in this direction has begun.

Experimental Section

General. Proton NMR spectra were recorded at 60 MHz on a JEOL C-60 HL instrument and at 100 MHz on a Varian XL-100 operating in the CW mode. Proton noise-decoupled ^{13}C NMR spectra were recorded at 25.16 MHz with a Varian XL-100 by Fourier transform. Unless otherwise stated, ^1H and ^{13}C shifts are given in parts per million from Me_4Si in $CDCl_3$ solvent. For low-temperature experiments in CHF_2Cl solvent, the samples were prepared by connecting the 10-mm NMR tube, containing the compound and some acetone-d_6 for deuterium locking, to a vacuum line. Gaseous CHF_2Cl was then admitted and condensed with liquid N_2, the tube being sealed in vacuo. The sample was allowed to warm to just below room temperature before insertion into the precooled spectrometer. The temperature was measured with a thermocouple inserted in a dummy tube before or after each spectral determination. Spectral simulations were run, using the DNMR program developed by Binsch,[12] on the computer facility of the University of Bologna.

GLC analysis was carried out with a Hewlett-Packard 5700 instrument equipped with a flame-ionization detector; preparative GLC separations were performed with a Varian-Aerograph 712 instrument. Two types of stationary phases were used, (A) 10% XE 60 and (B) 7% C 20M, both on Chromosorb W, 60–80 mesh.

Solvents and reagents were obtained dry as follows: methylene chloride, *tert*-butyl alcohol, benzene, and diisopropylamine were distilled from calcium hydride. Tetrahydrofuran, dried over sodium and distilled, was redistilled immediately before use.

2-Vinylthiane and 2-vinylthiepane were prepared by base-catalyzed dehydrobromination of 2-(2-bromoethyl)thiane and -thiepane, respectively, as described previously.[7c]

2-Vinylthiocane. Attempts to prepare the title compound from 2-(2-bromoethyl)thiocane by the dehydrobromination method[7c] failed, owing to extensive isomerization of the initially formed terminal olefin to internal olefins under the conditions required for dehydrobromination. The synthesis was eventually achieved by coupling 2-chlorothiocane with vinylmagnesium bromide by the procedure previously described for 2-vinylthiane.[7d] A benzene solution of 2-chlorothiocane, freshly prepared by the procedure of Tuleen and Bennett[15] from thiocane (5.6 g, 43 mmol, in 95 mL) and *N*-chlorosuccinimide (5.78 g, 43 mmol), was added dropwise over 45 min to an ice-cooled solution of the Grignard reagent [prepared from 9 mL (128 mmol) of vinyl bromide and 3 g (123 mmol) of magnesium in 160 mL of THF]. After warming to room temperature, the reaction mixture was decomposed with

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ice/20% sulfuric acid and extracted with pentane. The residue after solvent evaporation was fractionally distilled to give 3 g (45%) of 2-vinylthiocane: bp 113 °C (16 mm); ^{1}H NMR (60 MHz) δ 6.0–4.6 (m, 3 H, terminal vinyl group), 3.24 (m, 1 H, α-CH), 2.58 (unresolved m, 2 H, α-CH_2), 1.66 (wide, unresolved m, 10 H, β-, γ-, and δ-CH_2's). Anal. Calcd for $C_9H_{16}S$: C, 69.16; H, 10.32. Found: C, 68.7; H, 10.45.

Thiocane was prepared by diimide reduction of thiacyclooct-4-ene (85:15 mixture of *Z*/*E* isomers).[7c] Oxygen gas was bubbled (0.2 L/min) through a solution of the olefin (3.84 g, 30 mmol), hydrazine hydrate (75 g, 1.5 mol), and 3 mL of 0.2 M aqueous $CuSO_4$ in 215 mL of ethanol maintained at 20 °C by external cooling. After 5 h no unreacted starting material remained (GLC, column A). Water (50 mL) was added and the mixture, made acidic with 15% HCl, was extracted with pentane. The extracts, washed with H_2O and dried with $CaSO_4$, gave, after solvent removal and distillation under reduced pressure, 3 g (80%) of the title compound: bp 81–82 °C (14 mm) (lit.[16] bp 70.5 °C (10 mm); ^{1}H NMR δ 2.68 (m, 4 H, α-CH_2), 1.65 (m, 10 H, β-, γ-, and δ-CH_2). [Though comprising several steps, this synthesis of thiocane, which starts from thietane and allyl bromide,[17,7b] is superior to the direct cyclization method (overall 58%, against 34% in the final high-dilution cyclization of 1,7-dibromoheptane)].[16]

1-Ethyl-2-vinylthianium hexafluorophosphate (4a) was prepared by alkylation ($Et_3O^+BF_4^-$) of 2-vinylthiane (1.28 g, 10 mmol) followed by metathesis with aqueous NH_4PF_6. Extraction with CH_2Cl_2 gave, after evaporation of the solvent, 2.7 g (90%) of a viscous uncrystallizable material. The ^{1}H NMR spectrum (D_2O) indicates one isomer (probably the trans)[18] predominates (~10:1): δ 5.75 (m, 3 H, olefinic protons), 4.05 (m, 1 H, α-CH), 3.5 (m, 4 H, α-CH_2's), 2.1 (large m, 6 H, β- and γ-CH_2's), 1.56 (t, 3 H, CH_3). The presence of the minor isomer is indicated by a low-intensity triplet at δ 1.32. Anal. Calcd for $C_9H_{17}SPF_6$: C, 35.76; H, 5.67. Found: C, 35.63; H, 5.72.

1-Ethyl-2-vinylthiepanium hexafluorophosphate (4b) was obtained (83%) as a viscous material from 2-vinylthiepane as described for the corresponding thiane derivative. The ^{1}H NMR spectrum (60 MHz, D_2O) shows a large predominance of one isomer (probably the trans): δ 5.6 (m, 3 H, olefinic protons), 4.1 (m, 1 H, α-CH), 3.3 (large m, 4 H, α-CH_2's), 2.0 (large m, 8 H, β- and γ-CH_2's), 1.44 (t, 3 H, CH_3). The presence of a minor isomer (5–10%) is revealed by a low-intensity triplet at δ 1.38. Anal. Calcd for $C_{10}H_{19}SPF_6$: C, 37.97; H, 6.05. Found: C, 38.11; H, 6.10.

1-Ethyl-2-vinylthiocanium hexafluorophosphate (4c) was obtained (85%) as a viscous material from 2-vinylthiocane as described for the lower homologues. The presence of two geometrical isomers in ~6:1 ratio is apparent from both the ^{1}H and ^{13}C NMR spectra: ^{1}H NMR (100 MHz, D_2O) δ 5.72 (m, 3 H, olefinic protons), 4.24 (m, 1 H, α-CH), 3.4 (unresolved m, 4 H, α-CH_2), 2.0 (large unresolved m, 10 H, β-, γ-, and δ-CH_2), 1.48 (t, 3 H, CH_3). The minor isomer's CH_3 triplet shows up at δ 1.48. The ^{13}C NMR (CD_2Cl_2) is characterized by two low-field resonances of the major isomer at δ 130.8 (d, CH=) and 124.6 (t, =CH_2) while the corresponding resonances of the minor isomer occur at δ 127.5 and 125.9. This pattern confirms the major isomer is of the trans configuration.[8] The other resonances are (in parentheses the minor isomer) as follows: C_2, 59.8 (55.3); C_8, 39.4 (35.7); CH_2CH_3, 36.8 (35.6); C_3, 29.7 (28.9); C_5 and C_6, 25.6 and 25.1, interchangeable (25.7 and 24.6 interchangeable); C_3 and C_7, 23.8 and 22.8, interchangeable (23.7 and 23.8, interchangeable); CH_3, 8.9 (9.1). Anal. Calcd for $C_{11}H_{21}SPF_6$: C, 40.00; H, 6.41. Found: C, 39.92; H, 6.50.

(*E*)-2-Methylthiacyclonon-4-ene (1a) was obtained by ring expansion of **4a** under the conditions described for the synthesis of thiacyclonon-4-ene (*t*-BuOK in THF/*t*-BuOH, 10:1, at −40 °C).[7c] **4a** (10 mmol, 3.0 g) gave 1.1 g (70.5%) of crude sulfide containing (GLC) two products in a 25:1 ratio, unchanged after distillation, bp 95 °C (7 mm). The ^{13}C NMR spectrum at 0 °C displays three sets of signals (ratio 17.5:7.5:1). The two major sets (see Table I for shifts) coalesce on warming, indicating that they correspond to the conformational isomers of the trans olefin, while the minor set, of which only seven lines are visible, remains unaffected [δ 132.3 (C_5), 127.1 (C_4), 39.8 (C_2), 35.1 (C_3), 32.9, 27.6, and 26.4]. This minor product is probably the *Z* olefin **5**. The room-temperature ^{1}H NMR spectrum (100 MHz) has δ 6.0–5.1 (m, 2 H, olefinic H's), 3.03 (m, 1 H, α-CH), 1.5 and 2.7 (overlapping large and ill-resolved multiplets, indicating slow exchange between unequivalent sites, 10 H overall, α-, β-, γ-, and δ-CH_2's), 1.32 (d, 3 H, CH_3). Anal. Calcd for $C_9H_{16}S$: C, 69.16; H, 10.32. Found: C, 69.32; H, 10.35.

(*E*)-2-Methylthiacyclodec-4-ene (2). Ring expansion of **4b** (1.17 g) under the conditions[7c] gave 0.45 g (80%) of a sulfide fraction containing (GLC and ^{13}C NMR) four products, 1.7:6.1:22:1 (order of increasing retention time), which were separated by preparative GLC (column A, 130 °C).

The material with the shortest retention time is 2-vinylthiepane, arising from a β-elimination of ethylene. The material eluted second, *m*/*e* 170, was identified from its ^{1}H and ^{13}C NMR spectra as a ring-opened sulfide, **ethyl octa-5,7-dien-1-yl sulfide (7)**, arising from a β-elimination involving one of the protons at C_3: ^{1}H NMR δ 6.5–5.5 (m, 3 H, CH=CHCH=), 5.0 (m, 2 H, =CH_2), 2.54 (q, 7.5 Hz, superimposed to a m, 4 H overall, CH_2SCH_2), 2.11 (m, 2 H, CH_2CH=), 1.55 (m, 4 H, $SCH_2CH_2CH_2$), 1.24 (t, 3 H, CH_3); ^{13}C NMR δ 137.3 (C_7), 134.8 (C_6), 131.4 (C_5), 114.9 (C_8), 32.1 (C_1), 31.5 (C_2), 29.1 and 28.9 (C_3 and C_4 interchangeable), 26.0 ($C_{2'}$), 14.8 (CH_3).

Consistent with previous evidence,[7c] the minor and major products, both *m*/*e* 170, were assigned the **(*Z*)-(6)** and **(*E*)-2-methylthiacyclodec-4-ene (2)** structure. The assignment is in accord with the ^{13}C spectra, showing the resonances of the major isomer to be at low field relative to those of the minor isomer, as expected for a trans–cis pair: ^{13}C NMR (CD_2Cl_2; minor isomer in parentheses) δ 130.4 and 128.4 (130.4 and 128.4), C_5 and C_4, interchangeable; 44.2 (40.3), C_2; 42.4 (35.0), C_3; 31.9, 31.6, 28.3, 26.1, 24.0, and 23.6 (28.9, 26.5, 26.0, 24.4, 22.0, and 20.8), unassigned. (For the low-temperature spectrum of **2**, see Table I.) For either isomer the olefinic proton NMR absorption (100 MHz) is narrow and is unresolved by decoupling experiments.

***E* isomers**: NMR δ 5.56 (m, 2 H, olefinic H), 2.74 (m, 1 H), 2.54 (m, 2 H, α-CH_2), 2.4 (m, 1 H), 2.1 (large m, 3 H), 1.6 (m, 6 H), 1.21 (d, 3 H, CH_3). Anal. Calcd for $C_{10}H_{18}S$: C, 70.52; H, 10.65. Found: C, 70.24; H, 10.75.

***Z* isomer**: NMR δ 5.54 (m, 2 H, olefinic H), 2.91 (m, 2 H), 2.4 (m, 2 H), 2.1 (m, 1 H), 1.6 (m, 6 H), 1.42 (d, 3 H, CH_3). Anal. Calcd for $C_{10}H_{18}S$: C, 70.52; H, 10.65. Found: C, 70.77; H, 10.61.

Attempted Ring Expansion of 1-Ethyl-2-vinylthiocanium Hexafluorophosphate (4c). The title salt (0.74 g, 2.24 mmol), subjected to the usual ring-expansion conditions, gives 0.34 g of a sulfide fraction whose GLC (column A, 150 °C) shows two major peaks, 80% and 9%, respectively, besides five additional minor peaks. The materials giving the two more intense peaks were separated by preparative GLC (column A, 160 °C) and the major one was a ~1:1 mixture of **6-(*E*)-** and **6-(*Z*)-nona-6,8-dien-1-yl ethyl sulfide (8)**: ^{1}H NMR δ 6.8–4.9 (m, 5 H, olefinic H's), 2.52 (q superimposed to a m, 4 H overall, CH_2SCH_2), 2.13 (m, 2 H, C_5H_2), 1.44 (m, 6 H, β-, γ-, and δ-CH_2), 1.23 (t, 3 H, CH_3). That the material was a mixture of isomers is evident from the ^{13}C NMR showing eight olefinic carbon resonances (six doublets at δ 137.3, 135.0, 132.5, 132.3, 131.2, and 129.5 and two triplets at 116.8 and 114.7), whose intensities are too close to permit assignment to one or the other isomer. The aliphatic region has five double-intensity resonances at δ 31.6, 29.6, 28.5, 26.0 (SCH_2), and 14.8 (CH_3), in addition to four resonances at δ 32.5, 29.3, 28.9, and 27.6.

The second more abundant product is **ethyl 1-vinylhept-6-en-1-yl sulfide (9)** from its ^{1}H and ^{13}C NMR: ^{1}H NMR δ 6.03–5.43 (m, 2 H overall, 2 CH=), 5.12–4.85 (m, 4 H, 2 =CH_2), 3.17 (m, 1 H, SCH), 2.45 (q, 2 H, SCH_2), 2.05 (m, 2 H, C_6H_2), 1.46 (m, 6 H, β-, γ-, and δ-CH_2), 1.21 (t, 3 H, CH_3). The ^{13}C NMR spectrum has four olefinic [δ 139.6 and 138.8 (2 =CH), 114.7 and 114.4 (2 =CH_2)] and seven saturated carbon resonances δ 48.2 (CHS), 34.1, 33.6, 28.7, 26.8, 24.3 (S-CH_2), and 14.6 (CH_3).

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(*E*)-2-(Carbomethoxy)thiacycloundec-4-ene (3). A mixture of 2-vinylthiocane (0.78 g, 5 mmol), methyl diazoacetate (1.0 g, 10 mmol), and dry $CuSO_4$ (0.1 g) in 3 mL of benzene was heated at 40–45 °C under nitrogen. Gas evolution started immediately and continued without further external warming for about 5 min. The mixture was refluxed for 5 min, cooled, and filtered. Solvent evaporation left a residue (1.42 g) whose GLC (column B, 150 °C) showed one major peak (~65%) along with eight additional peaks of shorter retention time. The major product was separated by preparative GLC (150 °C): ^{1}H NMR δ 5.9–5.4 (m, 2 H, olefinic H's), 3.76 (s, 3 H, CH_3), 3.08 (q, J = 11.0 and 3.5 Hz, 1 H, SCH), 2.9–2.2 (m, 4 H), 2.1 (m, 2 H), 1.5 (m, 8 H). By irradiation at δ 2.6, the high-field part of an olefinic AB quartet can be decoupled, J = 15.0 Hz, confirming the E double bond configuration. (For the ^{13}C NMR spectrum, see Table I.) Anal. Calcd for $C_{12}H_{20}SO_2$: C, 63.11; H, 8.82. Found: C, 62.92; H, 9.01.

(*E*)-2-(Carbomethoxy)thiacyclonon-4-ene (1b) was prepared (50%) as described for the eleven-membered analogue, except that separation from the side products was performed via the $HgCl_2$ adduct. The sulfide was regenerated by aqueous KI treatment.[7c] The ^{13}C spectrum at room temperature shows slow exchange between two conformers (Tables I and II). Coalescence is observed on warming, and at 80 °C a sharp ten-signal spectrum is obtained (C_2Cl_4): δ 172.6 (CO), 136.5 (C_5), 125.0 (C_4), 51.9 and 51.6 (C_2 and OCH_3, interchangeable), 37.3 (C_3), 35.9, 25.8, 25.0 (unassigned). The room temperature ^{1}H NMR spectrum is also indicative of two diastereoisomers: the olefinic H absorption occurs as 2 multiplets at δ 6.1–5.5 and 5.4–5.0, 1.25 and 0.75 H, respectively. The latter is a neat ddd pattern (J = 15.0, 10.0, and 4.0 Hz), while the former is a ddd pattern (J = 15.0, 9.5, and 4.0 Hz) centered at δ 5.87 superimposed to an unresolved multiplet at δ 5.7. The behavior is consistent with the major isomer (~75%) giving raise to a two ddd pattern, with the minor isomer absorption occurring at δ 5.7 for both olefinic protons. This behavior is consistent with previous observations of the corresponding 2-carbethoxy derivative.[7d] Anal. Calcd for $C_{10}H_{16}O_2S$: C, 60.00; H, 8.06. Found: C, 59.63; H, 8.12.

Registry No. 1a, 74263-06-2; **1b** (isomer 1), 74263-07-3; **1b** (isomer 2), 74310-57-9; **2**, 74263-08-4; **3**, 74263-09-5; *cis*-**4a**, 74263-11-9; *trans*-**4a**, 74263-13-1; *cis*-**4b**, 74263-15-3; *trans*-**4b**, 74263-17-5; *cis*-**4c**, 74263-19-7; *trans*-**4c**, 74263-21-1; **5**, 74263-22-2; (*Z*)-**6**, 74263-23-3; **7**, 74263-24-4; (*E*)-**8**, 74263-25-5; (*Z*)-**8**, 74263-29-9; **9**, 74263-26-6; 2-chlorothiocane, 74263-27-7; vinyl bromide, 593-60-2; 2-vinylthiocane, 74263-28-8; (*E*)-thiacyclooct-4-ene, 64945-41-1; (*Z*)-thiacyclooct-4-ene, 64945-38-6; thiocane, 6572-99-2; 2-vinylthiepane, 66120-30-7.

Atropisomerism in *o*-Arylacetyl-*N*,*N*-dimethylbenzamides[1]

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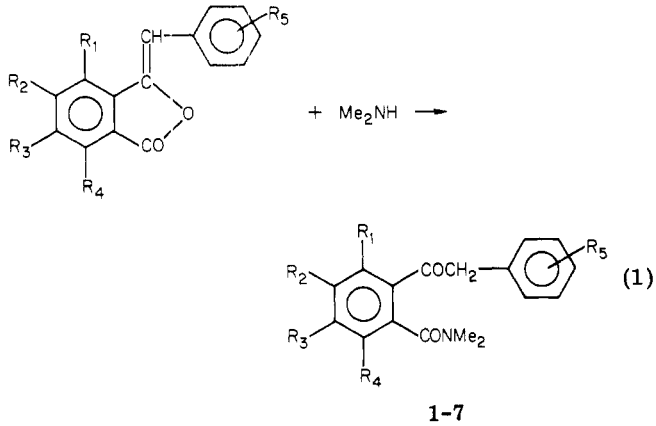
A series of *o*-arylacetyl-*N*,*N*-dimethylbenzamides, **1–7**, being studied as models for chain tautomers, differed markedly in their ^{1}H NMR spectral properties, as a function of the substituents R_1–R_4. In the two cases where substituents were placed ortho to the amide group, the benzylic protons were anisochronous at ambient temperatures. Reported dynamic ^{1}H NMR results are consistent with concomitant C–N and aryl–CO torsional processes. The ^{13}C carbonyl shifts are compared with those of model compounds.

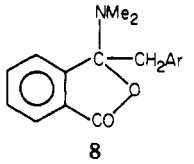
In connection with a dynamic NMR study of ring–chain tautomerism, we have prepared a series of *N*,*N*-dimethylamides, **1–7**, of *o*-arylacetylbenzoic acids from the corresponding enol lactones (eq 1). These, in turn, had each been prepared by condensation of an arylacetic acid under aldol conditions[3] with a phthalic anhydride; the exception was the enol lactone precursor of **3**,[4] which was obtained by aldol condensation of benzaldehyde with 6-nitrophthalide.[5] To our surprise, the benzylic protons in amides **2** and **4** were anisochronous, appearing as well-resolved AB quartets at ambient temperature. All the other amides exhibited the expected singlet for the COCH_2Ar group. Inasmuch as infrared spectra ruled out the nucleophilic[6] ring tautomeric structure **8**, we attribute the nonequivalence of the benzylic protons in **2** and **4** to atropisomerism,[7] the result of restricted rotation about the aryl–carbonyl bond of the amide functional group (vide infra).



(1)

1-7

compd	R_1	R_2	R_3	R_4	R_5
1	H	H	H	H	H
2	H	H	H	Me	H
3	H	H	NO_2	H	H
4	Cl	Cl	Cl	Cl	H
5	H	H	H	H	*o*-Me
6	H	H	H	H	*p*-Cl
7	H	H	H	H	*p*-NO_2



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Results of dynamic ^{1}H NMR studies of **2**, **4**, and **5** are given in Table I. Data for high-temperature coalescence of both the benzylic and *N*-methyl resonances are shown for **2** and **4**. Low-temperature dynamic behavior of the benzylic resonance of **5** is also reported. Calculation of

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