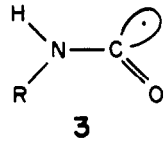
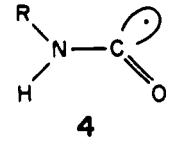
Table I. EPR Parameters for *trans*- (3) and *cis*-*N*-Alkylcarbamoyl (4) Radicals,[a] Their Percentage Yields,[a] and the Percentage of Trans (1) and Cis (2) Conformers of the Parent *N*-Alkylformamides

N-alkylcarbamoyl radicals								parent *N*-alkylformamide	
RNHĊO	conformer	*T*, K	*g*	a^N, G	a^H(NH), G	a^{other}, G	%	conformer	%[b]
CH_3NHĊO	3[c]	208	2.0015	24.0	0.9	0.9 (3 H)	93.6	1	92[4,15]
	4		2.0015	21.2	25.1	*d*	6.4	2	8[4,15]
CH_3CH_2NHĊO	3	219	2.0018	22.4	*e*	*e*	84	1	88[4,15]
	4		2.0017	20.2	25.3	0.7 (2 H)	16	2	12[4,15]
$CH_3(CH_2)_3$NHĊO	3	217	2.0018	22.6	*e*	*e*	89	1	86[15]
	4		2.0018	20.5	25.5	0.7 (2 H)	11	2	14[15]
$(CH_3)_3$CNHĊO	3	214	2.0017	20.6	0.9	0.9 (9 H) 151.9 (1 C)[f]	79	1	82,[4] 78[15,g]
	4		2.0017	18.5	25.7	0.3 (9 H) 150.5 (1 C)[f]	21	2	18,[4] 22[15,g]

[a] These data were obtained in toluene as solvent and were indistinguishable from the results obtained in cyclopropane as solvent. There was no significant change with temperature in the hfs or in the relative concentrations of 3 and 4 with temperature. [b] Note that the precision of these NMR derived population ratios is generally purported to be ca. ±1%. [c] The EPR parameters for this radical are in satisfactory agreement with those reported previously, viz., g = 2.00182, a^N = 22.2 G, a^H(NH) = 2.0 G, a^H(3 H) = 1.0 G;[9] g = 2.0017, a^N = 23.78 G, a^H(3 H) = 1.02 G.[10] [d] Not resolved. [e] An incompletely resolved complex multiplet was observed with hfs in the range 0.9–1.2 G. [f] Derived from measurements on $(CH_3)_3CNH^{13}CO$. [g] Reference 14 gives relative concentrations of 1 and 2 of 70 and 30, respectively, for this formamide. These values must be in error.



3



4

these isomeric radicals, which will have a σ electronic structure, should not interconvert (on the EPR time scale) since the electronic effects which produce high barriers in amides[3] will not be (appreciably) changed in these radicals. In addition, the relative yields of **3** and **4** should not differ significantly from the relative concentrations of **1** and **2** in the starting *N*-alkylformamide.

On searching the literature, we were surprised to find that the only *N*-alkylcarbamoyl radical for which an EPR spectrum has been reported is CH_3NHĊO and that although this radical has been observed by three separate groups of workers[8-10] only the trans isomer had been detected. We have therefore photolyzed solutions containing four different *N*-alkylformamides and di-*tert*-butyl peroxide in toluene and cyclopropane as solvents, directly in the cavity of a Varian E-104 EPR spectrometer. We were *not* surprised to see *two* *N*-alkylcarbamoyl radicals from each *N*-alkylformamide.[11] No other radicals were formed, i.e., there was no abstraction of the amide hydrogen[12] nor was there abstraction from the R group.

The EPR parameters for these carbamoyl radicals and their relative concentrations[13] in toluene are summarized in Table I. Within experimental error the hyperfine splittings (h.f.s.) for the individual radicals and the relative concentrations of each pair of carbamoyl radicals did not vary over the temperature range studied (ca. 210–300 K). The percentage yields of the trans and cis radical isomers are in excellent agreement with the NMR derived percentage concentrations of their individual parents as reported in the literature.[4,14,15] Since the trans and cis radicals are sterically nonhindered and are of identical molecular weight, they will decay (i.e., undergo their bimolecular self-reactions) at the same rates.[16] Their relative concentrations will therefore be determined only by their relative rates of formation. Since their relative concentration are equal to the relative concentrations of their individual parents, the rate constants for the reactions

$$(CH_3)_3C\dot{O} + \textit{trans}\text{-RNHCHO} \rightarrow (CH_3)_3COH + \mathbf{3}$$

$$(CH_3)_3C\dot{O} + \textit{cis}\text{-RNHCHO} \rightarrow (CH_3)_3COH + \mathbf{4}$$

must be equal.

Examination of the EPR data shows that within experimental error both radical conformers have the same g values. For the minor radical the value of a^H(NH) is always much larger than the value for the major radical. By analogy with other σ radicals (such as, for example, vinyl[17]) this serves to confirm that the minor radical has the cis structure, **4** with the NH hydrogen located trans to the orbital containing the unpaired electron. The value of a^N is about 10% smaller for **4** than for **3** which we considered might be due to differences in the hybridization or spin density[18] of the acyl carbons. With the hope of throwing some light on the origin of this difference in a^N values we therefore measured $a^{13C}\alpha$ for the two isomeric radicals derived from $(CH_3)_3CNH^{13}CHO$ (using 90% ^{13}C enriched material). However, the ^{13}C hfs obtained were within 1% of each other (see Table I) which implies that any changes in hybridization and spin density are either very small or mutually compensating with respect to a^{13C}.

(8) Bosco, S. R.; Cirillo, A.; Timmons, R. B. *J. Am. Chem. Soc.* **1969**, *91*, 3140–3143.
(9) Yonezawa, T.; Noda, I.; Kawamura, T. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 650–657.
(10) Hefter, H.; Fischer, H. *Chem. Ber.* **1970**, *74*, 493–500.
(11) Neither of these two radicals can be the corresponding formamidyl, RNĊHO, since we have found[12] that such radicals have g values in the range 2.0044–2.0056 and a^N values of 13–16 G.
(12) Sutcliffe, R.; Ingold, K. U. *J. Am. Chem. Soc.*, preceding paper in this issue.
(13) Obtained by double integration of appropriate lines in the spectra.
(14) Walter, W.; Maerton, G. *Liebigs Ann. Chem.* **1968**, *712*, 58–66.
(15) Nakanishi, H.; Roberts, J. D. *Org. Magn. Reson.* **1981**, *15*, 7–12.
(16) Griller, D.; Ingold, K. U. *Int. J. Chem. Kinet.* **1974**, *6*, 453–456. *Acc. Chem. Res.* **1980**, *13*, 193–200, 317–323.
(17) Cochran, E. L.; Adrian, F. J.; Bowers, V. A. *J. Chem. Phys.* **1964**, *40*, 213–220.
(18) Structure **4** might be expected to have a lower spin density on the acyl carbon because of the increased delocalization of the unpaired electron on to the NH hydrogen.

Stereospecific Reactions of Dichloroketene with Vinyl Sulfoxides: A New Type of Polar Cycloaddition

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The vinyl sulfide and sulfoxide functionalities have assumed an increasingly important role in synthetic chemistry.[1] During the course of our investigations on new methods for synthesizing α-methylene-γ-butyrolactone natural products, we sought a process

(1) For a general review, see: Block, E. "Reactions of Organosulfur Compounds"; Academic Press: New York, 1980. For a recent synthetic application, see: Danishefsky, S.; Harayama, T.; Singh, R. K. *J. Am. Chem. Soc.* **1979**, *101*, 7008.

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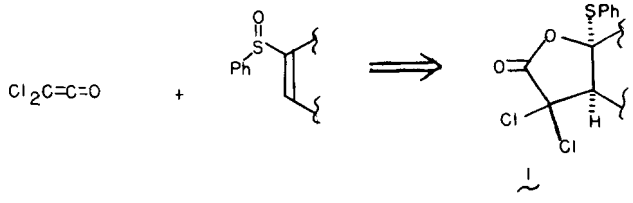
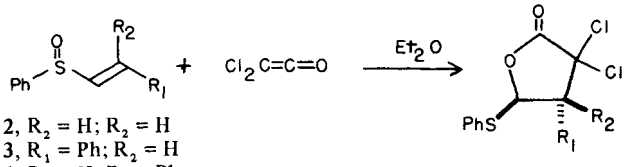
whereby a stereocontrolled addition of a functionalized acetic acid unit to a vinyl sulfoxide could be effected. While there are several literature examples of Michael-type additions of stabilized carbanions to simple phenyl vinyl sulfoxides,[2] there are no reports of an intramolecular process that involves the initial activation of the sulfoxide group. In this communication, we wish to report a new type of polar cyclization of dichloroketene and simple vinyl sulfoxides to stereospecifically yield functionalized *cis*-γ-butyrolactones of general structure **1**.



While the chemistry of ketenes and dichloroketene in particular has been investigated extensively,[3] no reports of their reactions with vinyl sulfoxides have come to our attention. This report focuses on the two most common methods for generating dichloroketene: (1) dehydrochlorination of dichloroacetyl chloride with triethylamine[4] and (2) reductive elimination of chlorine from trichloroacetyl chloride by activated zinc.[5] We have found that the generation of dichloroketene in the presence of a phenyl vinyl sulfoxide (**2**) results in the formation of α-dichloro-γ-(phenylthio)-γ-butyrolactone (**5**). The reactions of dichloroketene with *trans*-(**3**) and cis-phenyl styryl sulfoxide (**4**) yield different diastereomeric lactones **6** and **7**, respectively.[6,7]

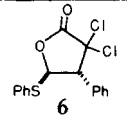
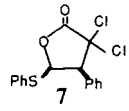
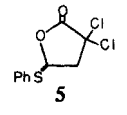
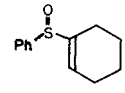
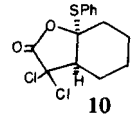
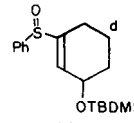
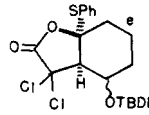


2, R_2 = H; R_2 = H
3, R_1 = Ph; R_2 = H
4, R_1 = H; R_2 = Ph

5, R_1 = H; R_2 = H
6, R_1 = Ph; R_2 = H
7, R_1 = H; R_2 = Ph

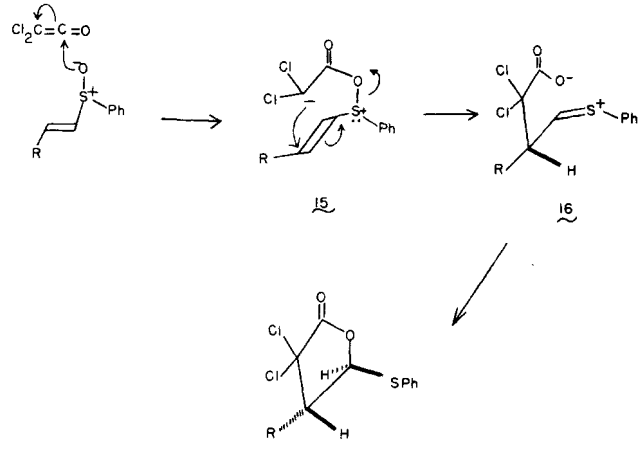
A variety of reaction conditions were examined in order to maximize the yields of the butyrolactones. We found that the highest yields (50–95%) of lactones were obtained when the zinc method of generating dichloroketene was used in refluxing ether.[8] In contrast to most [2 + 2] ketone cycloadditions,[4] the vinyl sulfoxide is not used in excess in these reactions. Generation of dichloroketene via triethylamine dehydrochlorinations routinely led to lower yields of lactones (10–30%) and resulted in the isolation of the deoxygenated vinyl sulfides. A summary of the vinyl sulfoxide reactions is given in Table I.

Table I

sulfoxide	ketene source[a]	solvent	product[b]	yield,[c] %
	A	Et_2O		65
PhCH=CHSOPh	B	Et_2O		54
(3), trans	B	CH_2Cl_2		30
			6	
PhCH=CHSOPh	A	Et_2O		25
(4), cis	B	Et_2O		20
			7	
CH_2=CHSOPh (**2**)	A	Et_2O		51
	B	Et_2O		40
	B	CH_2Cl_2		15
			5	
	A	Et_2O		72
	B	Et_2O		41
9			**10**	
	A	Et_2O		80
	B	Et_2O		20
11			**12**	
11a	A	Et_2O	**12a**	80[f]
11b	A	Et_2O	**12b**	95[b]

[a] Method A: 20 equiv of Zn to 5 equiv of Cl_3CCOCl. See ref 8 for details. Method B: 5–10 equiv of $Et_3N/Cl_2CHCOCl$. [b] Stereochemical assignments made on the basis of ^{13}C and 360-MHz ^1H NMR spectra. [c] Isolated yields from flash chromatography or direct crystallization. [d] A 1:1 mixture of diastereomers. [e] Product **12** is a 1:1 mixture of diastereomers. Product **12a** is the pure α isomer with regard to the OTBDMS group and the lactone ring, while **12b** is the pure β isomer. [f] HPLC analyses of reaction mixtures indicated that **11a** yielded a 90:10 ratio of **12a**/**12b**, while **11b** yielded a 95:5 ratio of **12b**/**12a**.

Scheme I



The results of the reactions of *cis*- and *trans*-styryl sulfoxides indicated that the cyclization process was probably intramolecular. Further evidence for a highly ordered transition state for the reaction can be obtained from the results of the reactions of the pure diastereomers **11a** and **11b**. These examples reveal a relationship between the sulfoxide group and the *tert*-butyldimethylsilyoxy (TBDMS) group. While it is not possible to rigorously assign the structures of **11a** and **11b** from spectral data, it is quite clear from the 360 ^1H NMR spectra of **12a** and **12b** that the TBDMS-oxy group is cis and trans to the lactone ring, respectively. Further confirmation of the *cis*-lactone stereo-

(2) (a) Tsuchihashi, G.; Mitamura, S.; Inoue, S.; Ogura, K. *Tetrahedron Lett.* **1973**, 323. (b) Tsuchihashi, G.; Mitamura, S.; Ogura, K. *Ibid.* **1976**, 855. (c) Koppel, G. A.; Kinnich, M. D. *J. Chem. Soc., Chem. Commun.* **1975**, 473.

(3) For some recent reviews, see: Patai, S. "The Chemistry of Allenes, Ketenes and Related Compounds"; Wiley: New York, 1980. Brady, W. T. *Synthesis*, **1971**, 415.

(4) Brady, W. T.; Waters, O. H. *J. Org. Chem.* **1967**, *32*, 3703.

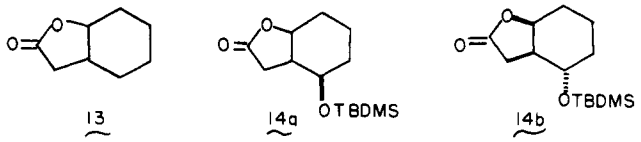
(5) Bak, D. A.; Brady, W. T. *J. Org. Chem.* **1979**, *44*, 107.

(6) All new compounds (**5**, **6**, **8**, **10–12**, **14**) gave satisfactory combustion analyses and had IR, ^1H, and ^{13}C NMR spectra consistent with the assigned structures.

(7) The J_{values} for the ring protons of **5** and **6** were 10 Hz and 4 Hz, respectively, making structure assignments possible. For analogous cases, see: Savostianoff, D.; Pfau, M. *Bull. Soc. Chim. Fr.* **1967**, 4162.

(8) Representative experimental procedure: (*E*)-β-styryl phenyl sulfoxide (134 mg, 0.6 mmol) was dissolved in 30 mL of ether and 0.8 g (12 mg-atom) of zinc[11] was added. The resulting suspension was heated to reflux under nitrogen. A solution of 0.35 mL (3 mmol) of freshly distilled trichloroacetyl chloride in 20 mL of ether was added dropwise to the refluxing zinc suspension over a period of 15 min. After the addition was complete, reflux was continued over 15 min. The reaction mixture was cooled to room temperature, filtered through Celite, and poured into 50 mL of cold $NaHCO_3$ (aqueous). The two-phase mixture that formed was stirred for 15 min at room temperature while a white precipitate formed. The aqueous layer was separated and extracted once with ether. The organic portions were combined, dried with $MgSO_4$, and evaporated. The solid residue was recrystallized from cyclohexane to give 108 mg of *trans*-2,2-dichloro-3-phenyl-4-(phenylthio)-γ-butyrolactone, mp 114–115 °C (55%). Another 10% yield of product was isolated from flash chromatography of the mother liquors with 9:1 petroleum ether/ether on silica.

chemistry was obtained from the complete reduction of products **10**, **12a**, and **12b** with Raney nickel. This transformation yielded the known *cis*-butyrolactone **13** and the isomeric lactones **14a** and **14b**.



13 14a 14b

On the basis of the stereoselectivity of this new cyclization process, we propose the following polar mechanism as shown in Scheme I. The highly electrophilic ketene molecule is sufficiently reactive to acylate the sulfoxide oxygen atom to generate the zwitterion **15**. Through a highly ordered transition state, we envisage a rearrangement initiated by the carbanion of **15** leading to a Pummerer-type[9] intermediate **16**. This latter species can be intramolecularly trapped by the carboxylate anion to produce the observed lactone products.[10] We believe that the rearrangement of zwitterion **15** to the lactones is the first example of an intramolecular and stereoselective addition of a carbanion to a vinyloxysulfonium cation. The lower yields of lactones using the triethylamine method B can be rationalized by the fact that the byproduct triethylammonium chloride protonates **15** and prevents the formation of **16**. The greater solubility of ammonium chlorides in methylene chloride also explains why ether is a better solvent for the reaction.

The utilization of vinylacyloxysulfonium intermediates in stereocontrolled formation of carbon–carbon bonds offers new strategies in the synthetic chemistry of vinyl sulfoxides and their precursors, vinyl sulfides. We are currently exploring the generality of this rearrangement/cycloaddition process and its applications to natural products synthesis.

(9) For an example of a vinylogous Pummerer rearrangement via an unsaturated (phenylthio)carbonium ion, see: Kosugi, H.; Uda, H.; Yamagawa, S. *J. Chem. Soc., Chem. Commun.* **1975**, 192.
(10) Scheme I only represents a simplified picture of the bond-forming process from **15** → **16** → lactone products. For Scheme I to apply, **16** must cyclize faster than it rotates about a carbon-carbon bond.
(11) Brady, W. T. *Synthesis* **1977**, 155.

Azocyclopropane

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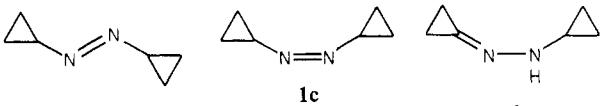
The stability of *trans*-azoalkanes toward loss of nitrogen depends primarily on the nature of the incipient alkyl radicals.[1] Although the same factor is prominent in *cis*-azoalkane chemistry, the cis–trans energy difference, which is a function of alkyl group size, is known to be equally important. When only poor alkyl radicals can be formed, *cis*-azoalkanes isomerize to trans at a rate determined by alkyl group size.[2]

The small size of cyclopropyl groups coupled with their high reactivity as free radicals[3,4] suggest that azocyclopropane (**1**) ought to be especially stable. We report here the first preparation of both the trans (**1t**) and the cis (**1c**) isomers of this simple but unusual azoalkane.[5] Tautomerism to the hydrazone (**2**), a troublesome side reaction in many azoalkanes, is not observed in **1** because of the high strain energy of methylenecyclopropanes[8] and presumably of iminocyclopropanes.

Table I. Properties of *trans*- and *cis*-Azocyclopropane

compd	bp (mp), °C	λ_{max}, nm	ϵ	$\Delta H^{\ddagger}$, kcal mol^{-1} [a]	$\Delta S^{\ddagger}$,[a] eu
1t	139	335	50	39.7 ± 0.7	−1.1 ± 1.4
1c	(38–39.5)	345	279	36.2 ± 0.5	−3.3 ± 1.1

[a] In hexadecane.



1t 1c 2

The synthesis of **1t**[9] was achieved by Si_2Cl_6 reduction[10] of the known azoxycyclopropane.[11] Irradiation of **1t** at 313 nm gave partial conversion to **1c**,[12] the mixtures being conveniently analyzed by HPLC on silica gel. After purification by chromatography on alumina (CH_2Cl_2/hexane), **1c** proved to be a solid (cf. Table I), not a very surprising result in view of the high dipole moment of *cis*-azoalkanes.[13] The UV spectrum of both isomers was unusual in that λ_{max} was lower than that of any previously reported azoalkanes; moreover, the difference between the isomers was only 10 nm, even smaller than the 16-nm separation between *cis*- and *trans*-azomethane. Since this UV band is normally attributed to an n,π^* transition, the cyclopropyl groups must stabilize the n orbital or raise the π^* energy. These possibilities are being evaluated by photoelectron spectroscopy.[14]

The most striking property of both isomers of **1** is their extraordinarily high thermal stability. The kinetics for disappearance of **1t** and **1c** were monitored by UV spectroscopy at five temperatures between 200 and 235 °C, giving the activation parameters shown in Table I.[15] While rearrangement of **1t** was a clean first-order process, disappearance of **1c** was treated as sequential first-order reactions with allowance for strongly overlapping UV absorption bands of the two isomers. A nonlinear least-squares computer program and the known rate constants for **1t** were used to extract rate constants for **1c**. Nitrogen evolution was not observed from **1c**, the exclusive reaction being isomerization to **1t**. The even more unreactive trans isomer underwent a vinylcyclopropane rearrangement to **4**[16] in strong preference to deazatization (<1%). 1,1′-Diphenylazocyclopropane exhibits the same behavior but at a lower temperature ($\Delta H^{\ddagger}$ = 31.6 kcal mol^{-1}, $\Delta S^{\ddagger}$ = −5.5 eu).[4] The observed 8.1 kcal mol^{-1} stabilization by phenyl is consistent with, but of course does not prove, a diradical mechanism for the rearrangement.[17] Because the observed $\Delta H^{\ddagger}$

(1) Engel, P. S. *Chem. Rev.* **1980**, *80*, 99.
(2) Chae, W. K.; Baughman, S. A.; Engel, P. S.; Bruch, M.; Özmeral, C.; Szilagyi, S.; Timberlake, J. W. *J. Am. Chem. Soc.* **1981**, *103*, 4824.
(3) For a recent review, see Walborsky, H. M. *Tetrahedron* **1981**, *37*, 1625.
(4) Bonnekessel, J.; Rüchardt, C. *Chem. Ber.* **1973**, *106*, 2890.
(5) Only three *trans*-azocyclopropyl compounds and no cis isomers have been reported previously.[4,6,7] As the parent compound of all azocycloalkanes, azocyclopropane is nearly as fundamental as azomethane.
(6) Chakravorty, K.; Pearson, J. M.; Szwarc, M. *J. Phys. Chem.* **1969**, *73*, 746.
(7) Rosenkranz, H. J.; Schmid, H. *Helv. Chem. Acta* **1968**, *51*, 1628.
(8) Greenberg, A.; Liebman, J. F. "Strained Organic Molecules"; Academic Press: New York, 1978; p 94.
(9) Properties of **1t**: NMR ($CDCl_3$) δ 1.08 (m, 2 H), 1.26 (m, 2 H) 3.38 (m, 1 H); MS, *m/e* (rel intensity) 110 (1), 109 (2), 68 (8), 54 (19), 41 (90), 40 (46), 39 (89), 38 (43), 28 (50), 27 (100), 26 (45). Anal. Calcd for $C_6H_{10}N_2$: 110.0844. Found: 110.0845.
(10) Greene, F. D.; Gilbert, K. E. *J. Org. Chem.* **1975**, *40*, 1409. Snyder, J. P.; Lee, L.; Bandurco, V. T.; Yu, C. Y.; Boyd, R. J. *J. Am. Chem. Soc.* **1972**, *94*, 3260.
(11) Iversen, P. E. *Chem. Ber.* **1971**, *104*, 2195.
(12) Properties of **1c**: NMR ($CDCl_3$) δ 1.08 (m, 2 H), 1.28 (m, 2 H), 3.60 (m, 1 H). MS, *m/e* (rel intensity) 110 (1), 109 (3), 68 (15), 54 (30), 41 (90), 40 (91), 39 (100), 38 (73), 27 (57), 26 (60).
(13) Stevens, J. F.; Curl, R. F.; Engel, P. S. *J. Phys. Chem.* **1979**, *83*, 1432.
(14) Houk, K. N.; Rozeboom, M. L.; Engel, P. S., work in progress.
(15) Rate data for azocyclopropane, temperature (°C), 10^5k (**1t** → **4**, s^{-1}), 10^5k (**1c** → **1t**, s^{-1}): 200.16, 0.264, 3.43; 209.95, 0.654, 7.97; 219.56, 1.51, 17.4; 230.04, 3.30, 36.3; 235.52, 5.55, 54.0.
(16) Properties of **4**: NMR ($CDCl_3$) δ 0.65 (m, 4 H), 2.1 (m, 1 H), 2.60 (distorted t, 2 H), 3.05 (distorted t, 2 H), 6.80 (m, 1 H); IR ($CDCl_3$) 3090, 3015, 2920, 2850, 1580 (C=N), 1020 cm^{-1}; MS, *m/e* (rel intensity) 110 (7), 109 (6), 83 (26), 68 (29), 55 (44), 54 (59), 41 (87), 40 (59), 39 (85), 28 (29), 27 (100), 26 (72). Anal. Calcd for $C_6H_{10}N_2$: 110.0844. Found: 110.0845.

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