mg, 20%) was identified as 17-methoxy-16-17-dihydrosecodine: NMR δ 8.8 (NH), 5.6 (=CH—), 3.9 (CO_2CH_3), 3.5 (CH_2OCH_3), 4.3 ($—CH_2OCH_3$, m), 1.15 (OCH_2CH_3, t). The more polar product (16 mg, 33%) was 16-methoxy-16,17-dihydrosecodine: NMR δ 8.9 (NH), 5.65 (=CH—), 3.9 (CO_2CH_3), 3.45 ($COCH_3$), 2.1 (>CCH_3), 1.1 (CH_2CH_3).

B. With Lithium Thiophenoxide. A solution of lithium thiophenoxide–thiophenol was prepared by addition of 2 N *tert*-butyllithium (1 mmol) to thiophenol (300 mg, 2.75 mmol) in anhydrous THF (25 mL). To this solution there was added 75 mg of compound **5** and the solution was refluxed for 5 h. The reaction mixture was then treated with a little methanol, diluted with methylene chloride, and washed throughly with sodium carbonate solution. TLC identified a single major product which was purified by preparative TLC to give 16,17-dihydrosecodine (30 mg, 60%): NMR δ 8.5 (NH), 5.6 (=CH—), 3.8 (OCH_3), 1.6 ($HCCH_3$), 1.15 (CH_2CH_3); MS, *m/z* 340, 309, 281, 230, 229, 216, 184, 170, 156, 125, 124.

C. With Sodium Amalgam in Methanol. A solution of **5** (~25 mg) was dissolved in 30 mL of anhydrous methanol. At three 1.5-h intervals there was added dry Na_2HPO_4 (250 mg each addition) and 5% sodium amalgam (150 mg each addition). The reaction mixture was then poured into 1% NaOH solution and extracted with methylene chloride. The solution was dried and evaporated to give the isosecodinol (**19**): NMR δ 8.50 (NH), 5.5 (=CH—), 3.81 (OCH_3), 1.90 (CCH_3), 1.03 (CH_2CH_3).

Thermal Decomposition of 12. A solution of **12** (10 mg) in distilled anisole (2 mL) was sealed in a small ampule and heated to 140 ± 5 °C for 3 h. The solution was cooled and the anisole was removed in a kugelrohr apparatus. The residue was purified on silica using ethyl acetate:hexane for elution to give **13**: NMR δ (recorded at 360 MHz) 8.11 (d), 7.45 (d), 7.38 (d), 7.2–7.35 (m), 7.0–7.10 (m), 6.90 (d), 2.70 (s).

Reduction of 6 with Sodium Amalgam. Reduction of **6** under the conditions described for **5** gave **18**. A reduction run at 0 °C using 10 mg of **6** and a single addition of Na_2HPO_4 and Na–Hg was terminated after 1 h. TLC indicated unreacted **6** and **18** as the principal components. This mixture was kept in a dilute methanol solution for 48 h at 0 °C. The mass spectrum of this material showed neither a methanol adduct nor a dimer derived from secodine.

Registry No. **3**, 82980-06-1; **4**, 82980-08-3; **5**, 89850-26-0; **6**, 89850-28-2; **7**, 89850-27-1; **9**, 89873-84-7; **10**, 89850-29-3; **12**, 89850-30-6; **13**, 89850-33-9; **17**, 89850-31-7; **18**, 27825-43-0; **19**, 89850-32-8; methyl pyruvate, 600-22-6.

Synthesis and Characterization of Anhydro-1,1-dialkyl-5-hydroxy-3-phenoxy-1,2,4-triazolium Hydroxides

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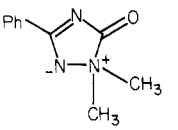
1,1-Dialkylhydrazines and phenyl *N*-(chlorocarbonyl)-1-chlorocarbonimidate react to give excellent yields of anhydro-1,1-dialkyl-5-hydroxy-3-phenoxy-1,2,4-triazolium hydroxides. The reaction is regiospecific, and the same products are obtained from phenyl N^3,N^3-dialkylcarbazimidate and phosgene. Thiophosgene and isocyanide dichlorides give exocyclic sulfur and nitrogen containing zwitterions, respectively. Alkylation of the triazolium hydroxides occurs exclusively on N2, and an *O*-Ph to *N*-Ph migration was observed at ca. 205 °C. Via dynamic NMR experiments, the diasteriotopic methylene hydrogens of the benzyl groups attached to the quaternary nitrogen atom gave thermodynamic exchange data of E_a = 21.7 ± 0.7 kcal mol^{-1}, $\Delta H^{\ddagger}$ = 21.0 ± 0.4 kcal mol^{-1}, $\Delta S^{\ddagger}$ = 6 ± 1 eu, and $\Delta G^{\ddagger}$ = 19.3 ± 0.5 kcal mol^{-1}.

As part of a conceptual approach to heterocyclic synthesis,[2] we have been investigating the reactions of appropriately substituted bielectrophiles with binucleophiles leading to heterocyclic zwitterions.[3-5] In this publication we describe our results utilizing 1,1-dialkylhydrazines as the 1,2-binucleophilic component.

Cyclic aminimides containing a pyrazole nucleus have been prepared[6] by the reaction of α,β-unsaturated esters, acid chlorides, or acid anhydrides with 1,1-dialkylhydrazines, by alkylation of the parent pyrazolinone, or by condensation of the pyrazolinone with an aldehyde or ketone. In contrast, relatively few ylides have been incorporated into the 1,2,4-triazole system, but successful syntheses have resulted from the reaction of 1,1-dimethylhydrazine with *N*-(α-chlorobenzylidene)carbamoyl chloride[7] giving **1**, from the dimerization of dialkylamino



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isocyanates,[8] and from the cycloaddition of amino isocyanates with heterocumulenes.[9] The above 1,1-dimethylhydrazine cyclocondensation could give isomeric products, and the structure **1** was assigned[7] solely on the basis of ν_{CO} 1765 cm^{-1}.

Phenyl cyanate readily adds phosgene in the cold to give phenyl *N*-(chlorocarbonyl)-1-chlorocarbonimidate (**2**) containing two highly electron deficient carbon atoms. The chlorine of the formyl group is more reactive, and both chlorines may be replaced[10] successively with appropriate

(1) (a) Acknowledgement is made to the donors of The Petroleum Research Fund, administered by the ACS, for support of this research. (b) Undergraduate Research Participant, B.S. Thesis, RPI, 1983.
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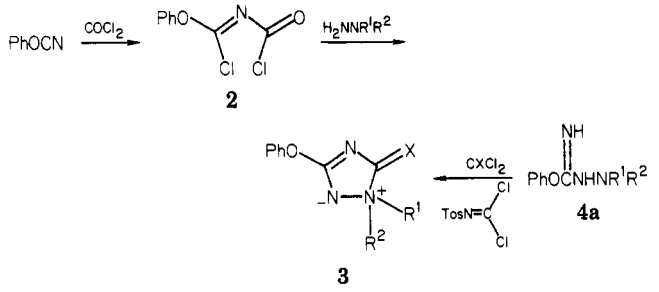


2

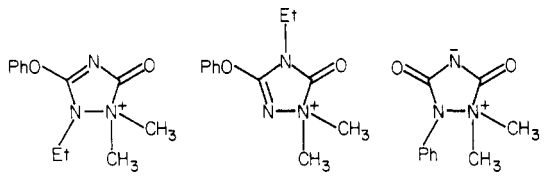
3

nucleophiles. Thus, in the reaction of **2** with 1,1-dialkylhydrazines, the disubstituted nitrogen should react at the formyl group and with 1,1-dimethylhydrazine in benzene, anhydro-1,1-dimethyl-5-hydroxy-3-phenoxy-1,2,4-triazolium hydroxide (**3a**) was obtained. Confirmation of the regiochemistry shown in this cyclocondensation was obtained by an independent synthesis of **3a** from phenyl N^3,N^3-dimethylcarbazimidate[11] (**4**) and phosgene/benzene/triethylamine.

These two routes to the triazolium ylides complement each other very effectively. Table I lists representatives prepared from **2** and 1-ethyl-1-methylhydrazine, 1,1-diethylhydrazine, and 1,1-dibenzylhydrazine. In all cases only one regioisomer was isolated. All products showed characteristic molecular ions in their mass spectra, these ions fragmenting to Ph^+, PhO^+, and NR^1R^{2+} ions, and a ν_{CO} in the range 1780–1790 cm^{-1}. Ring closure of **4** with thiophosgene and *p*-toluenesulfonyl isocyanide dichloride (**4a**) resulted in the introduction of an exocyclic sulfur and an *N*-tosylimino substituent into **3**, respectively (Table I).

The ylidic system **3** is soluble in most organic solvents but is insoluble in water and alcohols. It decomposes rapidly in the presence of mineral acid or alkali to phenol and e.g., dimethylhydrazine. Alkylation with ethyl iodide was unsuccessful for both exocyclic oxygen and sulfur systems. Reduction with sodium borohydride was also unsuccessful even though N–N bond cleavage has been observed in other cyclic aminimides under these conditions.[12]

Alkylation of **3a** with triethyloxonium hexafluorophosphate, however, was successful. O-alkylation was eliminated on the basis of ν_{CO} 1845 cm^{-1} and $\nu_{C=N}$ 1635 cm^{-1}. The observed NOE of the product showed that alkylation occurred at N2 as in **5** and not at N4 as in **6**.



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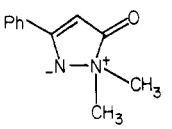

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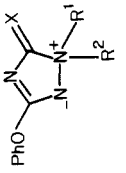
Irradiation of the methyl protons of the ethyl group resulted in a 12% ± 2% increase in intensity of the methylene signals and a 22% ± 2% increase in the intensity of the *N*-methyl hydrogens. Irradiation of the *N*-methyl or *N*-methylene groups produced no significant change in

Table I. Some Anhydro-1,1,3,5-tetrasubstituted 1,2,4-Triazolium Hydroxides (3)



no.	substituents R^1	substituents R^2	substituents X	yield, %	mp, °C	method	molecular formula	analytical data: calcd C	calcd H	calcd N	found C	found H	found N	M^+ (% rel intensity)	ν_{CO}, cm^{-1} (KBr)	NMR,[b,c] ppm: ^1H NCH_3	^{13}C NCH_3	^{13}C C3	^{13}C C5	R^1/R^2
a	Me	Me	O	75	195	A	$C_{10}H_{11}N_3O_2$	58.53	5.40	20.48	58.48	5.43	20.42	205 (100)	1790	3.09	49.4	179.3	167.4	49.4
				30		B														
b	Me	Et	O	37	134	A	$C_{11}H_{13}N_3O_2$	60.27	5.98	19.16	60.16	6.01	19.16	219 (100)	1790	3.07	48.7	179.6	166.7	56.1
																				48.7
																				8.4
c	Et	Et	O	72	124	A	$C_{12}H_{15}N_3O_2$	61.79	6.48	18.01	61.84	6.51	17.99	233 (62)	1790			179.9	165.8	57.7
																				8.1
d	CH_2Ph	CH_2Ph	O	51	178	A	$C_{22}H_{19}N_3O_2$	73.93	5.36	11.76	74.01	5.40	11.74	357 (42)	1780			178.7	165.9	63.8
																				132.4
																				127.7
e	Me	Me	*N*-Tos	60	195	B	$C_{17}H_{18}N_2O_3S$	56.97	5.06	15.63	56.82	5.07	15.61	358 (59)		3.19	52.5	177.0	170.8	52.5
f	Me	Me	S	24	160	B	$C_{10}H_{11}N_3OS$	54.23	5.01	18.99	54.02	5.05	18.94	221 (100)		3.20	53.0	178.5	199.1	53.0

[a] Other data all compounds: δ 7.5–7.1 (m, 5, aromatic). **3d**: δ 7.41 (s, 10, aromatic). **3e**: δ 8.1–7.9 (m, 4, aromatic), 2.42 (s, 3, CCH_3). [b] PhO chemical shifts: C_1, 152.0–152.3, C_2, 120.7–121.0, C_3, 129.5–129.7, C_4, 126.2–126.6 ppm. [c] Solvent $CDCl_3$.

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the intensities of the other absorptions.

Thermolysis of **3a** at ca. 200–205 °C, i.e., about 10 °C above its melting point, resulted in a crystalline product of the same molecular weight but with ν_{CO} 1760, 1725 cm^{-1} and with ^1H NMR data of δ 7.33 (s, 5) and 3.66 (s, 6). These data are accommodated by structure **7** whose formation most likely involved a phenyl migration. Fragment ions in the mass spectrum of **7** corresponded to PhN^+ and $PhNN^+$, consistent with this structure which is itself a new zwitterionic system.

The NMR data for these products offer additional insight into their structure. The ^{13}C chemical shifts (Table I) are consistent with carbon atoms in this environment. The downfield chemical shift of C3 (179.3 ppm) from that of C5 (167.4 ppm) in **3a** is attributable to the proximity of the phenoxy substituent as MINDO calculations (Table II) show C3 and C5 to carry nearly equal charge densities.

The ^1H NMR data of the N1 substituents are of interest as they provide a means of probing further the physical characteristics of these zwitterionic systems. The enantiotopic methyl substituents[13] give rise to a single signal at δ 3.09–3.20. The methylene hydrogens of the *N*-ethyl and *N*-benzyl groups are, however, diastereotopic. In $CDCl_3$, the *N,N*-diethyl groups of **3c** appear as overlapping ABX_3 systems (ddq, $J_{a,b}$ = 12.09 Hz, $J_{a,x}$ = 7.06 Hz, $J_{b,x}$ = 7.12 Hz) and with methyl, ethyl substituents (**3b**) a similar pattern was observed (ddq, $J_{a,b}$ = 12.26 Hz, $J_{a,x}$ = 7.06, $J_{b,x}$ = 7.11 Hz). With two benzyl substituents (**3d**) the above complex pattern was simplified to an AB spin system (dd, $J_{a,b}$ = 12.01 Hz). The 1,1-dibenzyl derivative **3d** with N1 being prochiral has diasteriotopic benzylic hydrogens. When **3d** was heated in $C_2D_2Cl_4$, the AB quartet broadened significantly by 70 °C and, with increase in temperature, the two outer peaks moved toward the inner two until, at 90 °C, the signal was that of a doublet. On further heating the signal coalesced to a broad singlet. At 125 °C (the coalescence temperature) a sharp singlet was observed. A similar phenomenon was observed in the coalescence of the ABX_3 pattern of **3c** to an A_2X_3 pattern over the same temperature range. The reversibility of the process was demonstrated by reproducibility of the observed spectra upon repeated heating to 135 °C and cooling of the same sample. In each case, the coalescence at 125 °C is due to interchange of the diasteriotopic methylene hydrogens.

A dynamic NMR experiment incorporating a full line shape analysis was used to determine the barrier to the inversion of the benzylic hydrogens of **3d**. The ^1H NMR spectrum was measured at six temperatures between 25 and 135 °C, and the results obtained are shown in Table III. Thermodynamic data for the exchange of the benzylic hydrogens were determined to be

$$E_a = 21.7 \pm 0.7 \text{ kcal mol}^{-1}$$

$$\Delta H^{\ddagger} = 21.0 \pm 0.4 \text{ kcal mol}^{-1}$$

$$\Delta S^{\ddagger} = 6 \pm 1 \text{ eu}$$

$$\Delta G^{\ddagger} = 19.3 \pm 0.5 \text{ kcal mol}^{-1}$$

However, use of an approximation formula[13] at the coalescence temperature to determine the activation parameters gave E_a = 20.5 kcal mol^{-1}. The largest source of error was introduced in the matching of experimental and calculated spectra (based on Heidberg's[14] equations for an exchanging AB system) as the latter assumes no line broadening. This line broadening accounts for the uncertainty in the rate constant k.

Table II. MINDO 3 Calculations on Anhydro-1,1-dimethyl-5-oxo-3-phenoxy-1,2,4-triazolium Hydroxide (3a)

atom	net charge density	π charge density
N1	+0.1	
N2	−0.3	−0.6
C3	+0.6	+0.3
N4	−0.4	−0.6
C5	+0.6	−0.4
oxo	−0.6	−0.7

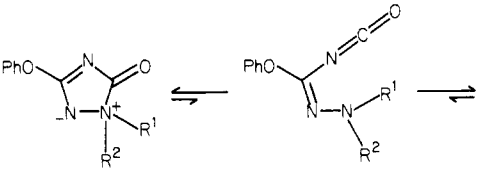
Table III. Chemical Shifts, Coupling Constants, T_2, and Rate of Exchange vs. Temperature for 3d

temp, K	ν_a	ν_b	$\nu_a - \nu_b$, Hz
295.7	912.82	873.18	39.64
324.5	906.74	867.97	38.77
353.1	900.70	862.79	37.91
372.3	(896.64)[a]	(859.32)[a]	(37.32)[a]
391.3	(892.61)[a]	(855.86)[a]	(36.75)[a]
401.0	(890.57)[a]	(854.12)[a]	(36.45)[a]

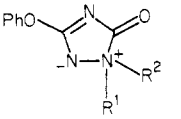
temp, K	$J_{a,b}$, Hz	T_2, s	k, s^{-1}
295.7	12.06	0.205	0.035 ± 0.005
324.5	12.06	0.300	0.86 ± 0.05
353.1	12.06	0.394	11 ● 1
372.3	(12.06)[a]	0.461	68 ± 2
391.3	(12.06)[a]	0.377	300 ± 2
401.0	(12.06)[a]	0.324	532 ± 3

[a] Parentheses denote extrapolated values.

In order for the diastereotopic hydrogens to interchange with each other, one of the bonds to the tetracovalent nitrogen atom must be cleaved to allow inversion at that center. In the X-ray structure of the similar compound **8**, the N1–C5 bond length was found[15a] to be 1.565 Å, appreciably longer than carbon–nitrogen bonds in amides (1.33 Å) and in amines (1.47 Å). This was attributed to an appreciable contribution to the structure of **8** of a canonical structure in which the N1–C5 bond does not exist. Similar acyclic resonance forms have been postulated to account for abnormal bond lengths of this nature in other zwitterionic systems.[15b] Due to the presumed abnormal bond length and consequent weakness of the N1–C5 bond in **3d**, it is believed that this bond is cleaved to form the valence tautomer **9**. This intermediate then



3 **9**



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can undergo N–N bond rotation with resultant exchange of the benzylic hydrogens on ring closure. In examining a space filling model of **3d**, it becomes clear that the benzyl groups are too close to the carbonyl group to allow rotation. Realignment of molecular geometry with small accompa-

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nying changes in bond angles and lengths in the transition state to allow the benzyl group exchange must therefore occur to some degree. The alternative pathways of N1–R and N1–N2 bond cleavage can both be ruled out; the former by the nearly identical behavior of **3d** and **3c** and the latter by the reversibility of the process with lack of nitrene insertion products.

No evidence for the heterocumulene **9** was observed in the infrared or NMR spectrum of the zwitterionic system at temperatures up to 135 °C. Attempts to trap the heterocumulene intermediate at these elevated temperatures via cycloaddition were also unsuccessful. These results demonstrate that the equilibrium strongly favors the cyclic zwitterion **3** over **9** and that no appreciable concentration of the open-chain tautomer is formed over the experimental temperature range. It should also be noted that in the alternative synthesis of **3** (X = O; R1 = R2 = CH_3), the isocyanate **9** (R1 = R2 = CH_3) is a possible intermediate and apparently undergoes a facile ring closure to **3**.

Experimental Section[16]

The following illustrate the two general routes to the zwitterionic systems. Established procedures were used for the synthesis of 1,1-diethylhydrazine,[17a] 1-ethyl-1-methylhydrazine,[17b] 1,1-dibenzylhydrazine,[18] phenyl N^3,N^3-dimethylcarbazimidate,[11] and *N*-*p*-toluenesulfonyl isocyanide dichloride.[19]

Method A. Anhydro-1,1-dimethyl-5-hydroxy-3-phenoxy-1,2,4-triazolium Hydroxide (3a). Phenyl *N*-(chlorocarbonyl)-1-chlorocarbonimidate[20] (**2**) (1.3 g, 6.0 mmol) was dissolved in CH_2Cl_2 (20 mL). A solution of dimethylhydrazine (1.3 g, 17.7 mmol) in CH_2Cl_2 (20 mL) was added dropwise over 20 min, and the mixture was stirred for 16 h. Separation on HPLC (silica, Prep 500) with $CHCl_3$:acetone (30:1) as eluent and recrystallization from CH_2Cl_2:hexane afforded colorless, irregular prisms: 0.92 g (75%); mp 194–195 °C (Table I).

Method B. Anhydro-1,1-dimethyl-5-mercapto-3-phenoxy-1,2,4-triazolium Hydroxide (3f). A solution of thiophosgene (0.70 g, 6.1 mmol) in dry benzene (50 mL) was treated with a solution of phenyl N^3,N^3-dimethylcarbazimidate[11] (1.01 g, 5.6 mmol), and triethylamine (1.40 g, 13.9 mmol) in benzene (25 mL) was added dropwise over 10 min. The mixture was stirred for 3 h as a white precipitate formed (triethylamine hydrobromide). The solid was filtered off, and the filtrate was passed through a small bed of silica. The solvent was evaporated, and recrystallization from CH_2Cl_2:CCl_4 afforded colorless needles: 0.32 g (24%), mp 159–162 °C (Table I).

1,1-Dimethyl-2-ethyl-5-oxo-3-phenoxy-1,2,4-triazolinium Hexafluorophosphate (5). Anhydro-1,1-dimethyl-5-hydroxy-3-phenoxy-1,2,4-triazolium hydroxide (0.50 g, 2.4 mmol) was dissolved in CH_2Cl_2 (10 mL), and a solution of triethyloxonium hexafluorophosphate (0.8 g, 3.2 mmol) in CH_2Cl_2 (25 mL) was added. After stirring for 18 h at room temperature, the colorless solid product was collected: 0.80 g (87%); mp 178–180 °C; IR (KBr) 3500, 2990 (CH), 1845 (C=O), 1635 (C=N) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.60–7.50 (m, 5, phenyl), 4.03 (q, 2, J = 7.33 Hz, CH_2CH_3), 3.71 (s, 6, CH_3), 1.50 (t, 3, J = 7.33 Hz, CH_2CH_3); ^{13}C NMR 165.4, 158.8, 151.7, 131.1, 128.8, 121.5, 52.7, 40.5, 12.6 ppm; mass spectrum, m/e (% relative intensity) [M^+ – ($MePF_6$)] 163 (35), $[PhO]^+$ 93 (17), $[EtNNMe_2]$ 87 (8), $[Ph]^+$ 77 (44).

Anal. Calcd for $C_{12}H_{16}N_3O_2PF_6$: C, 38.01; H, 4.25; N, 11.08. Found: C, 38.07; H, 4.29; N, 11.06.

Anhydro-1,1-dimethyl-3-hydroxy-5-oxo-2-phenyl-1,2,4-triazolinium Hydroxide (7). Anhydro-1,1-dimethyl-5-hydroxy-3-phenoxy-1,2,4-triazolium hydroxide (0.50 g, 2.4 mmol) was slowly heated to 215 °C for 30 min in a N_2 atmosphere. The residual red oil was filtered through a small bed of silica. Crystallization from CCl_4 afforded colorless plates: 0.36 g (72%); mp 172–174 °C; IR (KBr) 3100–2800 (CH), 2780, 2620, 1760 (C=O), 1725 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.33 (bs, 5, phenyl), 3.36 (s, 6, methyl); ^{13}C NMR 153.8, 152.5, 149.8, 129.8, 125.9, 119.7, 31.8 ppm; mass spectrum, m/e (% relative intensities) M^+ 205 (100), [M^+ – Ph] 148 (10), $[PhNN]^+$ 106 (35), $[PhN]^+$ 91 (29), $[Ph]^+$ 78 (80), $[NMe_2]^+$ 44 (21).

Anal. Calcd for $C_{10}H_{11}N_3O_2$: C, 58.53; H, 5.40; N, 20.48. Found: C, 58.63; H, 5.45; N, 20.48.

Dynamic NMR Experiments. All experiments were performed on a Varian XL-200 NMR spectrometer in an evacuated, sealed tube in sym-$C_2D_2Cl_4$ (bp 145 °C) using Me_4Si as standard. Degassing was carried out by using the freeze–thaw technique. Ethylene glycol was used to determine sample temperature,[21] and approximately 15 min was allowed for equilibration before temperature measurements were made. A Carr-Purcell-Merboom-Gil[22] pulsed NMR experiment was utilized to determine the value of $T2$, where $1/T2$ is the rate constant for relaxation in the transverse xy plane at each temperature.

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(16) Spectral characterizations were carried out on the following instrumentation: infrared spectra, Perkin-Elmer 337 spectrophotometer; ^1H NMR spectra, Varian XL-200 and Hitachi Perkin-Elmer R-600 spectrometers with Me_4Si as an internal standard; mass spectra, Hitachi-Perkin-Elmer RMU-6E mass spectrometer utilizing a direct insertion probe for solid samples with a source temperature of 175 °C; melting points were determined in capillaries, and all evaporations were carried out by using a rotary evaporator. Microanalyses were performed by Atlantic Microlab, Inc., Atlanta, GA. Coupling constants were determined by the use of a LAOCN3 program.

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