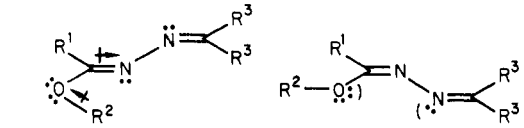
Equilibrium Configurations of Azines of Esters

Diane Keus and John Warkentin*

Department of Chemistry, McMaster University, Hamilton, Ontario L8S 4M1

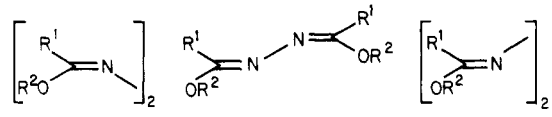
Received August 8, 1983

The equilibrium configuration of hydrazonates (ester azines) such as $R^2O(R^1)C{=}NN{=}C(R^3)_2$ (**2**) and $[R^2O(R^1)C{=}N]_2$ (**3**) is found to be that in which the alkoxy group is anti (*E* configuration) even if the alkyl group (R^1) is larger than the alkoxy group. This is the same as the configuration of imidates ($CH_3O(R)C{=}NCH_3$)



2

(*E*, dipole alignment) (*Z*, repulsion)



3

(*Z*,*Z*) (*E*,*Z*) (*E*,*E*)

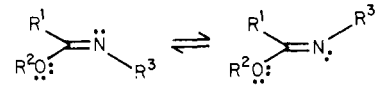
and opposite to the configuration observed for azines, hydrazones, and semicarbazones of aldehydes and ketones, where the more bulky group occupies the anti position. With $R^2 = CH_3$ or CH_2CH_3, R^1 groups smaller than *tert*-butyl do not force the hydrazonates into the *Z* configuration and even in the case R^1 = *tert*-butyl ($R^2 = CH_3$), the *E* isomer predominates in the two-component system (**2**) at equilibrium. Similarly, in the three component system (**3**) ($R^2 = CH_3$, $R^1 = C(CH_3)_3$) the order of predominance at equilibrium is *E*,*E*, > *E*,*Z*, > *Z*,*Z*. It is concluded that dipole alignment is an important factor stabilizing the *E* configuration and that there may also be some destabilization of the *Z* configuration resulting from repulsions between nonbonded electrons at nitrogen and at oxygen. Both factors are illustrated above with the isomers of **2**.

Introduction

Many studies of the configurations of imines, azines, hydrazones, semicarbazones, and oximes have been reported.[1] The results are consistent in implicating a dominant steric factor that determines which of the two configurations about the C=N functional group is thermodynamically the more stable. In simple systems having substituents such as H, alkyl, or aryl at sp^2 carbon, the most stable configuration is usually that in which the larger of two such substituents occupies the anti position.

Analogues of the above classes of compounds, but with a second heteroatom substituent (X) at sp^2 carbon (i.e., R(X)>C=N—Y, X = N, O, S, halogen) have also been studied extensively.[2] In those it is expected that the configuration of choice will be determined not only by substituent sizes but also by repulsions between unshared electron pairs at X, N, and Y and by interaction of the C=N dipole with dipolar bonds between X and its substituents (X = N, O, S).

The net effect of the various forces that determine the free energies of *E*, *Z* isomers of imino systems is clear in some cases and unknown or ambiguous in others. *O*-Methyl imidates were first reported to be most stable in the *Z* configuration[3] with a barrier greater than 23 kcal mol^{-1} for configurational isomerization, eq 1, where R^1 =

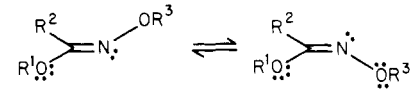


(1)

Z *E*

$R^2 = CH_3$, R^3 = *n*-alkyl or phenyl. Both the configurational preference and the high barrier to isomerization were explained in terms of 1,3-repulsions between unshared electrons at oxygen and nitrogen.[3] However, the opposite conclusion (*E* isomer more stable) was reached more recently by other groups,[4-7] and the importance of 1,3-interorbital repulsions was judged to be small relative to steric effects and dipolar interactions in imidates.[7]

If the group R^3 is bound to N through oxygen, there could be, in addition to the repulsions referred to above, a 1,4-repulsion between oxygens in the *Z* isomer, eq 2. In



(2)

E *Z*

R^1 = alkyl; R^2 = alkyl, aryl; R^3 = $COCH_3$, COAr, for example a series of ester oxime derivatives, eq 2, the *E* isomer is the one that predominates under conditions that cause equilibration,[8] although the *Z* isomer may be the exclusive kinetic product under nonequilibrating conditions. In the case of ester oximes rather than their *O*-alkyl derivatives,

(1) (a) For a review of the chemistry of such compounds see: "The Chemistry of the Carbon-Nitrogen Double Bond"; Patai, S., Ed.; Interscience: New York, 1970. Only a few references from that review are repeated here. For selected, more recent references, see ref 1b and 1c. (b) Hawkes, G. E.; Herwig, K.; Roberts, J. D. *J. Org. Chem.* **1974**, *39*, 1017. (c) Barber, G. A.; Olofson, R. A. *Ibid.* **1978**, *43*, 3015.

(2) For a review, see: "The Chemistry of Amidines and Imidates"; Patai, S., Ed.; Wiley: New York, 1975.

(3) Moriarty, R. M.; Yeh, C.; Ramey, K. C.; Whitehurst, P. W. *J. Am. Chem. Soc.* **1970**, *92*, 6360.

(4) Lumbroso, H.; Bertin, D. M.; Reynaud, P. *C. R. Acad. Sci. Paris, Ser. C* **1965**, *261*, 399.

(5) Lumbroso, H.; Bertin, D. M. *Bull. Soc. Chim. Fr.* **1970**, 1728.

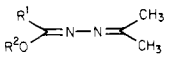
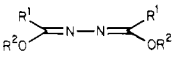
(6) Exner, O.; Schindler, O. *Helv. Chim. Acta* **1972**, *55*, 1921.

(7) Meese, C. O.; Walter, W.; Berger, M. *J. Am. Chem. Soc.* **1974**, *96*, 2259.

(8) Exner, O.; Jehlinčka, V.; Reiser, A. *Collect. Czech. Chem. Commun.* **1959**, *24*, 3207.

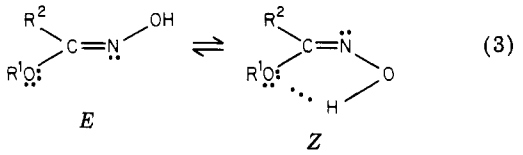
0022-3263/84/1949-3466$01.50/0

Table I. Spectra of Ester Azines 2 and 3

compd[a]	^{1}H NMR (δ, $CDCl_3$)[b]	MS, m/z (%)[c,d]
		
2a, $R^1 = CH_3$; $R^2 = C_2H_5$	1.31 (t, 3 H), 1.95 (s, 3 H), 2.01 (s, 3 H), 2.03 (s, 3 H, R^1), 4.18 (q, 2 H)	142 (35), 127 (14), 99 (69), 86 (100), 72 (51), 56 (85)
2b, $R^1 = C_2H_5$; $R^2 = C_2H_5$	1.08 (t, 3 H, R^1), 1.30 (t, 3 H, R^2), 1.94 (s, 3 H), 2.00 (s, 3 H), 2.48 (q, 2 H, R^1), 4.16 (q, 2 H, R^2)	156 (13), 141 (12), 128 (3), 113 (38), 99 (26), 86 (35), 72 (38), 56 (97), 42 (100)
2c, $R^1 = CH(CH_3)_2$; $R^2 = CH_3$	1.07 (d, 6 H), 1.92 (s, 3 H), 2.01 (s, 3 H), 3.50 (septet, 1 H), 3.73 (s, 3 H)	156 (16), 125 (14), 113 (20), 84 (10), 70 (14), 68 (100), 56 (30), 43 (45)
2d, $R^1 = CH(CH_3)_2$; $R^2 = C_2H_5$	1.07 (d, 6 H), 1.29 (t, 3 H), 1.94 (s, 3 H), 2.00 (s, 3 H), 3.39 (septet, 1 H), 4.14 (q, 2 H)	170 (25), 155 (15), 127 (19), 99 (20), 86 (39), 70 (24), 56 (93), 43 (100), 42 (90)
2e, $R^1 = C(CH_3)_3$; $R^2 = CH_3$ (*E*)	1.26 (s, 9 H), 1.90 (s),[e] 2.00 (s),[e] 3.68 (s, 3 H, R^2)	170 (14), 155 (19), 139 (16), 113 (44), 99 (25), 70 (85), 57 (100), 56 (90)[f]
2e, $R^1 = C(CH_3)_3$; $R^2 = CH_3$ (*Z*)	1.19 (s, 9 H), 1.90 (s),[e] 2.00 (s),[e] 3.91 (s, 3 H, R^2)	
		
3a, $R^1 = CH_3$; $R^2 = C_2H_5$	1.30 t, 6 H), 2.03 (s, 6 H), 4.16 (q, 4 H)	172 (100), 157 (11), 144 (16), 127 (40), 116 (54), 99 (14), 86 (12), 74 (72), 59 (98)
3b, $R^1 = C_2H_5$; $R^2 = C_2H_5$	1.20 (t, 6 H), 1.31 (t, 6 H), 2.46 (q, 4 H), 4.15 (q, 4 H)	200 (16), 88 (13), 72 (23), 57 (100), 56 (66)
3c, $R^1 = CH(CH_3)_2$; $R^2 = CH_3$	1.09 (d, 12 H), 3.51 (septet, 2 H), 3.72 (s, 6 H)	200 (6), 100 (13), 86 (13), 84 (10), 68 (91), 43 (100), 31 (40)
3d, $R^1 = CH(CH_3)_2$ $R^2 = C_2H_5$	1.11 (d, 12 H), 1.28 (t, 3 H), 3.48 (septet, 2 H), 4.12 (q, 4 H)	228 (83), 185 (21), 184 (12), 182 (29), 157 (25), 114 (10), 71 (92), 43 (100)
3e, $R^1 = C(CH_3)_3$; $R^2 = CH_3$ (*E,E*)	1.63 (s, 18 H), 3.77 (s, 6 H)	228 (10), 197 (23), 171 (73), 156 (19), 114 (63), 100 (100), 57 (42)[g]
3e, $R^1 = C(CH_3)_3$; $R^2 = CH_3$ (*E,Z*)	1.36 (s, 9 H), 1.64 (s, 9 H), 3.60 (s, 3 H), 4.07 (s, 3 H)	
3e, $R^1 = C(CH_3)_3$; $R^2 = CH_3$ (*Z,Z*)	1.30 (s, 18 H), 4.09 (s, 6 H)	

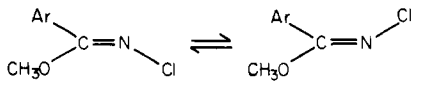
[a] Compounds **2** and **3** of unspecified configuration have the *E* and *E,E* configurations, respectively. See text. [b] The shifts are relative to δ ($CHCl_3$) 7.27. [c] Electron impact spectra obtained at 70 eV. [d] Peaks smaller than 10% of the parent peak were arbitrarily omitted from the list. This restriction was lifted in the case of molecular ion peaks. [e] Methyl signals from the ketone-derived portion of **2e** were not resolved for the two isomers. The total integral from those signals was twice that of the methoxy signals, as expected. [f] Mass spectrum of *E,Z* mixture. [g] Mass spectrum of *E,E*, *E,Z*, *Z,Z* mixture.

H bonding in the *Z* isomer is potentially an additional factor to be considered, eq 3. Synthesis of such com-



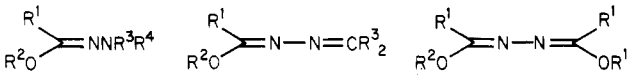
E *Z* (3)

pounds ($R^2 = C_6H_5$, $C_6H_4OCH_3$, $R^1 = C_2H_5$) gave both isomers in nearly equal yield[8] but it is not clear whether or not the reaction conditions equilibrated the isomers. Formamide oxime ($HC(NH_2)$=NOH) has the *Z* configuration.[9,10] Oximes of thio esters, $R^2C(SR^1)$=NOH, are reported to be more stable in the *Z* configuration at least for the cases R^1 and $R^2 = CH_3$, C_2H_5.[11] Some *N*-halo derivatives have also been found to prefer the *Z* configuration, eq 4. For the case where Ar = C_6H_5, the *Z* isomer predominated by a factor of 3 at 100 °C.[12]

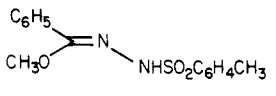


Z *E* (4)

Ester hydrazones (**1**)[13] and ester azines (**2, 3**)[13-15] have been reported without mention of their configurations. An



1 **2** **3**



4

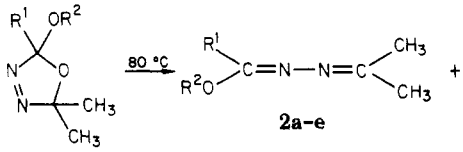
ester tosylhydrazone shows a small equilibrium preference for the *Z* configuration (**4**).[16] We now report the configurational preferences of a series of ester azines (hydrazonates) of types **2** and **3**.

Methods, Result, and Discussion

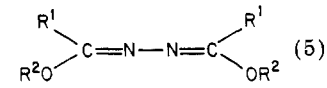
Compounds of type **2** and **3**, Table I, were obtained together from thermolysis of the appropriate oxadiazolines, either neat of as concentrated solutions in benzene, eq 5.[17]

(9) Hall, D.; Llewellyn, F. J. *Acta Crystallogr.* **1956**, *9*, 108.
(10) Hall, D. *Acta Crystallogr.* **1965**, *18*, 955.
(11) Davies, J. H.; Davis, R. H.; Kerby, P. *J. Chem. Soc. C* **1968**, 431.
(12) Papa, A. J. *J. Org. Chem.* **1970**, *35*, 2837.
(13) Chihaoui, M.; Baccar, B. *C. R. Acad. Sci. Paris C* **1978**, *287*, 69.
(14) Cohen, V. I. *J. Heterocycl. Chem.* **1979**, *16*, 365.
(15) Crawford, R. J.; Raap, R. *Can. J. Chem.* **1965**, *43*, 356.
(16) Crawford, R. J.; Raap, R. *Can. J. Chem.* **1965**, *43*, 126.
(17) Keus, D.; Kaminski, M.; Warkentin, J. *J. Org. Chem.* **1984**, *49*, 343.

Acetone azine was also formed in most cases and there were additional products, not shown in the equation, such as $R^1CO_2R^2$, $(CH_3)_2CO$, $R^1CH(OR^2)C(CH_3)=CH_2$, and propene. Evidence pointing to a carbene mechanism has been published.[17]



2a-e



3a-e (5)

a, $R^1 = CH_3$, $R^2 = C_2H_5$; b, $R^1 = C_2H_5$, $R^2 = CH_3$; c, $R^1 = CH(CH_3)_2$, $R^2 = CH_3$; d, $R^1 = CH(CH_3)_2$, $R^2 = C_2H_5$; e, $R^1 = C(CH_3)_3$, $R^2 = CH_3$

When all of the oxadiazoline had decomposed, aliquots of the reaction mixture were analyzed and separated by preparative gas chromatography. Acetone azine and the ester azines were separated from each other, but the configurational isomers (in the cases of **2e** and **3e**, Table I) were collected together. Gross structures of the azines (Table I) were assigned on the basis of their ^1H NMR spectra and their mass spectra. The ^1H NMR spectra showed that all the compounds were configurationally pure except for the two *tert*-butyl systems **2e** and **3e** (Table I).

Configurations were assigned on the basis of the well-known fact that the larger of two substituents (alkyl, aryl, or H) at sp^2 carbon of an azine is best accommodated at the anti site.[1b,18] On the basis of that precedent there is only one configuration for **2a–d** and for **3a–d** (Table I) which leads to a consistent picture. The alkyl groups must be in the syn position if a regular increase in their steric requirements ultimately leads (when R^1 = *tert*-butyl) to a change of configuration. If the uniconfigurational compounds (Table I) had the R^1 alkyl group in the less hindered anti position, then the compounds with R^1 = *tert*-butyl would surely have the same configuration (with an even greater perference) and there would be no configurational change in the series. We are therefore led to the conclusion that the preferred configuration of compounds like **2** and **3** is that with the alkoxy group(s) anti, the *E* configuration.

The configurations of the *tert*-butyl compounds (**2e** and **3e**, Table I) were assigned on the basis of their methoxy group chemical shifts in the ^1H NMR spectra by using **2c** and **3c**, the most hindered uniconfigurational analogues, as models. Thus, $\delta \sim 3.7$ (3.73 in **2c** and 3.72 in **3c**) was taken as the chemical shift characteristic of an *anti*-methoxy group. Chemical shifts near δ 4.0 (3.91 in **2e**, 4.07 and 4.09 in isomers of **3e**) were then assigned to *syn*-methoxy groups. The remaining signals in the ^1H NMR spectra of mixtures **2e** and **3e** were assigned on the basis of the integration. For example, the *tert*-butyl signal at δ 1.26 in the ^1H NMR spectrum of mixture **2e** was assigned to the *E* isomer of **2e** because that signal was thrice as intense as the methoxy signal at δ 3.68. Similarlty, the four *tert*-butyl signals in the ^1H NMR spectrum of the mixture **3e** were assigned on the basis of intensities relative to those of the four methoxy signals.

The assignments of configuration for isomers **3e** are consistent with the isomer populations at equilibrium. That is, if the relative isomer population (and the order of thermodynamic stability) for **2** is $E > Z$, as argued above, then one would expect the relative isomer populations for compounds **3e** to be $E,E > E,Z > Z,Z$, as observed.

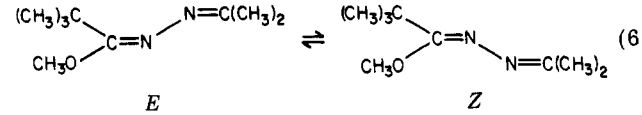
Table II. Equilibration of Configurational Isomers of 2 and 3[a]

compd[b]	T,[c] K	equilibrium composition,[d,e] % E	Z	E,Z	E,Z	Z,Z
2b–d	305	100	0			
	353	100	0			
	393	100	0			
2e	305	89	11			
	353	82	18			
	393	75	25			
3c–d	305	100	0			
	353	100	0			
	393	100	0			
3e	305			62	33	5
	353			53	40	7
	393			43	49	8

[a] In CD_3SOCD_3, which provided the lock signal for the Bruker WP80 spectrometer. For chemical shifts in Me_2SO see Experimental Section. [b] Structures are given in Table I. [c] Probe temperatures, ±1 K. [d] Compositions determined by repeated integration of ^1H NMR spectrum at equilibrium. In each case the low temperature composition was rechecked by cooling samples from the highest temperature. [e] In cases where only the one isomer was seen, the maximum amount of minor isomer that could have gone undetected was estimated to be 2%. In other cases the errors in the numbers are in the neighborhood of ±5% of the quoted values for the two component system **2e** and ±10% of the quoted values for the three component system **3e**.

Equilibration of the *E–Z* isomers at different temperatures was attempted for compounds **2b–e** and **3b–e**. The ones with smaller alkyl groups were unaffected by heating to 120 °C in Me_2SO but the compositions of the *tert*-butyl systems (**2e**, **3e**) changed with temperature. Results are gathered in Table II. Since the *tert*-butyl systems reached equilibrium quite rapidly, less than 0.5 h being required at 80 °C, it is clear that the barrier to isomerization is not very large. Although the barrier could be higher for the isopropyl systems and for those with even less bulky alkyl groups, it is very unlikely that they would not even begin to equilibrate in 2 h at 120 °C. We conclude that the isopropyl, ethyl, and methyl systems too were equilibrated and that the equilibrium concentrations of isomers other than *E* (for **2a–d**) and *E,E* (for **3a–d**) are below the detection limit of about 2% at 120 °C.

From the temperature dependence of K_{eq} for the isomerization of eq 6, the thermodynamic parameters $\Delta G° = 1.3$ kcal mol^{-1} (25 °C), $\Delta H° = 2.7$ kcal mol^{-1}, and $\Delta S° = 4.7$ cal deg^{-1} (all in the sense *Z* minus *E*) were calculated.

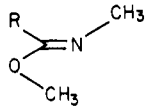


E ⇌ Z (6)

The higher entropy of the *Z* isomer can presumably be attributed, at least in part, to more freedom of motion of the *tert*-butyl group in that isomer. Although similar calculations could be carried out for the three-component system **3e**, the errors in the equilibrium constants are too large for the results to be meaningful.

Although the ester azines **2** and **3** are qualitatively the same as the imidates **5** investigated by Walter and coworkers[7], in that the *E* configuration is the more stable one thermodynamically, there is a quantitative difference. Whereas the imidates **5** (R = CH_3, CH_2CH_3) were uniconfigurational (*E*) in CCl_4 at 36 °C, both isomers were

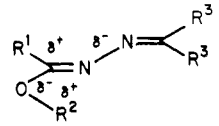
(18) Elguero, J.; Jacquier, R.; Marzin, C. *Bull. Soc. Chim. Fr.* **1968**, 713.



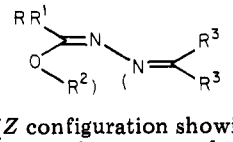
5

present in the more polar solvent methanol at 36 °C. Ester azines **2a–d** and **3a–d** do not contain a detectable percentage of *Z* isomer in either chloroform or Me_2SO at room temperature. Representative compounds from those groups also remained uniconfigurational, within experimental error, at 120 °C in Me_2SO (Table II). Moreover, the value of $\Delta G°$ for $E \rightleftharpoons Z$ isomerization of **5** (R = $C(CH_3)_3$), calculated from the data in the literature,[7] is 0.98 kcal mol^{-1} in CCl_4 and 0.46 kcal mol^{-1} in CD_3OD, both at −14 °C.[7] That for $E \rightleftharpoons Z$ isomerization of **2e** is substantially larger at 1.48 kcal mol (−14 °C) in Me_2SO. In view of the fact that the coalescence temperature for **5** (R = $C(CH_3)_3$) in CCl_4 is about 37.5 °C[7] whereas the spectra for **2e** were still sharp in Me_2SO at 120 °C, it is very likely that $\Delta G^{\ddagger}$ for isomerization of **2e** is also significantly higher than that (15.9 kcal mol^{-1}) of the imidate model **5** (R = $C(CH_3)_3$).

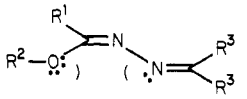
A plausible, but tentative, explanation for the more pronounced configurational preference of hydrazonates (**2**, **3**) as compared with imidates (**5**) is that the *Z* configuration of the former is destabilized by two factors, only one of which is present also in the *Z* configuration of the latter. These factors are illustrated below for the case of **2**, where



2 (*E* configuration showing favorable dipole alignment)



2 (*Z* configuration showing dipole alignment and steric hindrance)



2 (*Z* configuration showing interorbital repulsion)

Z configurations involve either a 1,4-steric repulsion between R^2 and N, if the favorable dipole alignment of the *E* configuration is maintained, or a 1,4-interorbital repulsion between nonbonding electrons if that dipole alignment is sacrificed. Although only two conformations of the OR^2 group are shown, it is clear that intermediate conformations will represent compromises containing part of the maximum steric interaction and part of the maximum repulsion between lone pair electrons. Imidates **5**, on the other hand, do not have the 1,4-interorbital repulsion feature and can therefore adopt the *Z* configuration at a lower cost.

Finally, it is unlikely that the crucial compounds for this study (**2e** and **3e**) could have been synthesized by the alternative routes that are known.[13,14] Those routes would require either an ortho ester[13] of pivalic acid or a selenone ester[14,19] of pivalic acid but no representatives of either class appear to be reported in the literature. The carbene route[17] which was used to prepare **2e** and **3e** may prove to be useful for the synthesis of other hindered systems.

(19) Cohen, V. I. *J. Org. Chem.* **1977**, *42*, 2645.

Experimental Section

Oxadiazoline precursors of all the azines except **2c**, **3c**, and **3e** have been reported earlier.[17] The new oxadiazolines prepared for this work were prepared by the same procedure.[17]

2-Methoxy-5,5-dimethyl-2-(1-methylethyl)-Δ^3-1,3,4-oxadiazoline, from oxidation of the acetone hydrazone of (2-methylpropanoyl)hydrazine with lead tetraacetate in methanol, was obtained as an oil: ^1H NMR ($CDCl_3$, Me_4Si) δ 1.09 (d, 3 H, J = 6.9 Hz), 1.13 (d, 3 H, J = 6.9 Hz), 1.50 (s, 3 H), 1.60 (s, 3 H), 2.03 (m, 1 H), 3.13 (s, 3 H).

2-Methoxy-5,5-dimethyl-2-(1,1-dimethylethyl)-Δ^3-1,3,4-oxadiazoline was obtained by oxidation of the hydrazone from acetone and (2,2-dimethylpropanoyl)hydrazine with lead tetraacetate in methanol. It was an oil: ^1H NMR ($CDCl_3$, Me_4Si) δ 1.02 (s, 9 H), 1.54 (s, 3 H), 1.60 (s, 3 H), 3.01 (s, 3 H).

Thermolysis of Oxadiazolines To Form Ester Azines. In a typical procedure a solution of the appropriate oxadiazoline (1–3 M) in benzene was degassed and sealed into a Pyrex tube. The tube was then heated at 80 °C (oil bath) for at least six half-lives. A half-life ranged from about 7×10^4 s for oxadiazolines with small alkyl groups at C-2 to 2×10^6 s for the 2-*tert*-butyloxadiazoline. At the end of the heating period the tube was opened and the contents were separated by preparative gas chromatography (OV-17, 10%, 6 ft × 0.25 in.) using a temperature program that increased the column temperature from 40 to 200 °C at a rate of 5 °C/min. The azines were eluted after propene, acetone, benzene, ester, and acetal[17] in the order acetone azine, **2**, **3**. Absolute yields (moles of product per mole of oxadiazoline) were, for R^1 = CH_3 and $C(CH_3)_3$, respectively, acetone azine (0.12), **2a** (0.26), **3a** (0.04), and acetone azine (trace), **2e** (0.08), **3e** (0.32); yields from the other oxadiazolines falling between those extremes.

Equilibration of Ester Azines. Samples of **2** and of **3**, collected from the gas chromatograph were dissolved in Me_2SO-d_6 and sealed into NMR tubes. The ^1H NMR spectrum and several integrals were recorded, first at the ambient probe temperature (305 K) of a Bruker WP-80 spectrometer and then at the two higher temperatures (Table II). Samples were left at a given temperature until after the composition had become constant and, for those samples whose composition did not change, for 2 h at the highest temperature. Chemical shifts in Me_2SO-d_6, relative to the solvent lock signal at δ 2.55, are listed for the two- and three-component systems. **2e** (*E*): 1.27 (s, 9 H), 1.91 (s, 3 H), 1.99 (s, 3 H), 3.67 (s, 3 H). **2e** (*Z*): 1.19 (s, 9 H), 1.86 (s, 3 H), 1.99 (s, 3 H), 3.90 (s, 3 H). **3e** (*E*,*E*): 1.35 (s, 18 H), 3.71 (s, 6 H). **3e** (*E*,*Z*): 1.21 (s, 9 H), 1.33 (s, 9 H), 3.71 (s, 3 H), 4.06 (s, 3 H). **3e** (*Z*,*Z*): 1.21 (s, 18 H), 4.04 (s, 6 H).

Isomer ratios for **3e** in Me_2SO-d_6 were determined from the methoxy signals for the mixture rather than from the *tert*-butyl signals. The peak at δ 4.04 indicated the relative amount of *Z*,*Z* isomer, that at δ 4.06 when multiplied by two gave the relative amount of *E*,*Z* isomer, and that at δ 3.71 gave (after substraction of an area equal to that of the δ 4.06 signal) the relative amount of *E*,*E* isomer. The relative intensities of the high field signals were matched to those of the methoxy signals to assign the former to particular isomers of **3e**.

Acknowledgment. This project was supported by the Natural Sciences and Engineering Research Council of Canada.

Registry No. (*E*)-**2a**, 87938-10-1; (*E*)-**2b**, 91190-16-8; (*E*)-**2c**, 91190-17-9; (*E*)-**2d**, 87938-14-5; (*E*)-**2e**, 91190-18-0; (*Z*)-**2e**, 91190-19-1; (*E*,*E*)-**3a**, 87938-04-3; (*E*,*E*)-**3b**, 91190-20-4; (*E*,*E*)-**3c**, 91190-21-5; (*E*,*E*)-**3d**, 87938-08-7; (*E*,*E*)-**3e**, 91190-22-6; (*E*,*Z*)-**3e**, 91190-23-7; (*Z*,*Z*)-**3e**, 91190-24-8; 2-methoxy-5,5-dimethyl-2-(1-methylethyl)-Δ^3-1,3,4-oxadiazoline, 91190-25-9; acetone hydrazone of (2-methylpropanoyl)hydrazine, 91190-26-0; 2-methoxy-5,5-dimethyl-2-(1,1-dimethylethyl)-Δ^3-1,3,4-oxadiazoline, 91190-27-1; acetone hydrazone of (2,2-dimethylpropanoyl)hydrazine, 90152-27-5.