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HERON Rearrangement of *N,N'*-Diacyl-*N,N'*-dialkoxyhydrazines — a Theoretical and Experimental Study

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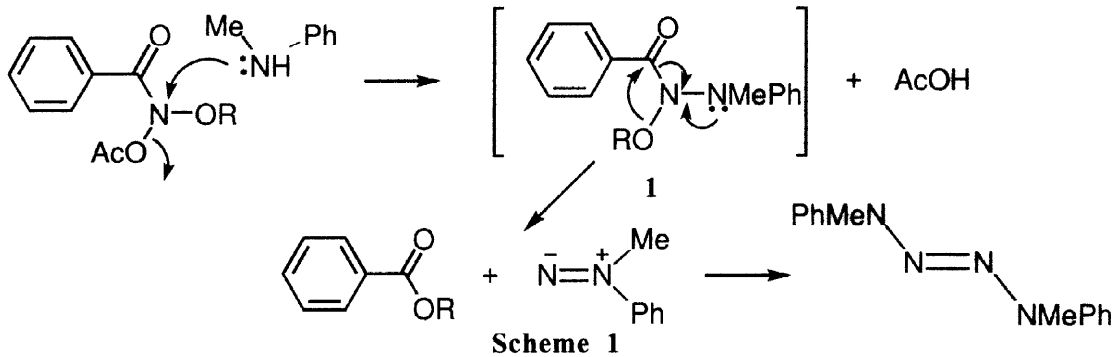
Abstract: *Ab initio* calculations at the B3LYP/6-31G* level on *N*-methoxy-*N*-dimethylaminoformamide and its rearrangement to methyl formate and 1,1-dimethyldiazene through the HERON reaction, have been carried out in conjunction with an experimental study of the HERON reactions of *N,N'*-diacyl-*N,N'*-dialkoxyhydrazines. Substituent effects are in accord with the theoretical properties of the transition state and point to an anomerically driven process in which donor groups on the anomeric nitrogen and withdrawing groups on the migrating alkoxy oxygen facilitate the rearrangement process. © 1999 Elsevier Science Ltd. All rights reserved.

INTRODUCTION

Amides which are geminally substituted with two electronegative heteroatoms at nitrogen have quite different physical and chemical properties when compared to normal amides or hydroxamic esters. In addition to the effects of the combined electronegativity of the substituents, the nonbonded electron pair(s) of one heteroatom may donate into the low-lying antibonding orbital of the other heteroatom's bond to the nitrogen and *vice versa*. The latter interactions, also called negative hyperconjugation, we refer to collectively as anomeric effects. We have explored, theoretically, the structural characteristics of this class of amides and confirmed the operation of anomeric effects.[1] In a comprehensive review, we recently focused on the relative anomeric effects, theoretical, spectroscopic and chemical properties of a number of different classes of bisheteroatom-substituted amides including *N,N*-dialkoxyamides (*ONO* systems), *N*-acyloxy-*N*-alkoxyamides (*AcONO* systems), *N*-alkoxy-*N*-haloamides (*ONX* systems) and *N*-alkoxy-*N*-aminoamides (*NNO* systems).[2] The *N*-alkoxy-*N*-methylanilinobenzamide **1**, an example of a *NNO* system, was first encountered in the reaction of mutagenic *N*-acetoxy-*N*-alkoxybenzamides and *N*-methylaniline (Scheme 1).[3] In methanol, S_N2 reaction at the amide nitrogen and displacement of acetate results in the formation of **1** which are unstable intermediates and which undergo a concerted migration of the alkoxy group to form benzoate esters and a 1,1-diazene. We have called these novel reactions, involving *HE*teroatom *R*earrangements *O*n *N*itrogen, HERON rearrangements.[4]



Scheme 1

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Extensive AM1 molecular orbital studies have been carried out which support the concerted nature of the process and point to the important structural elements that are necessary for it to occur.[4] The lowest activation energies were computed for amides bearing an *N*-amino group, and either an alkoxy or a chloro substituent. In such cases, the rearrangement is driven by the strength of the anomeric overlap of the high energy nitrogen lone pair, n_N, and the low energy *N—O* or *N—Cl* antibonding orbital, σ^*_{NO} or σ^*_{NCl} (Fig. 1).

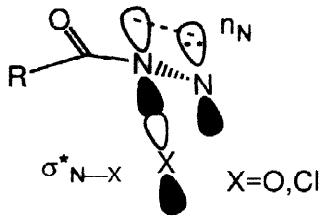
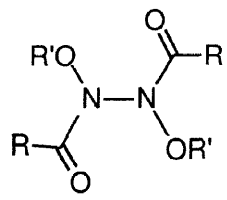


Fig. 1. Anomeric overlap in *NNX* systems.



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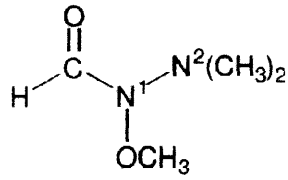
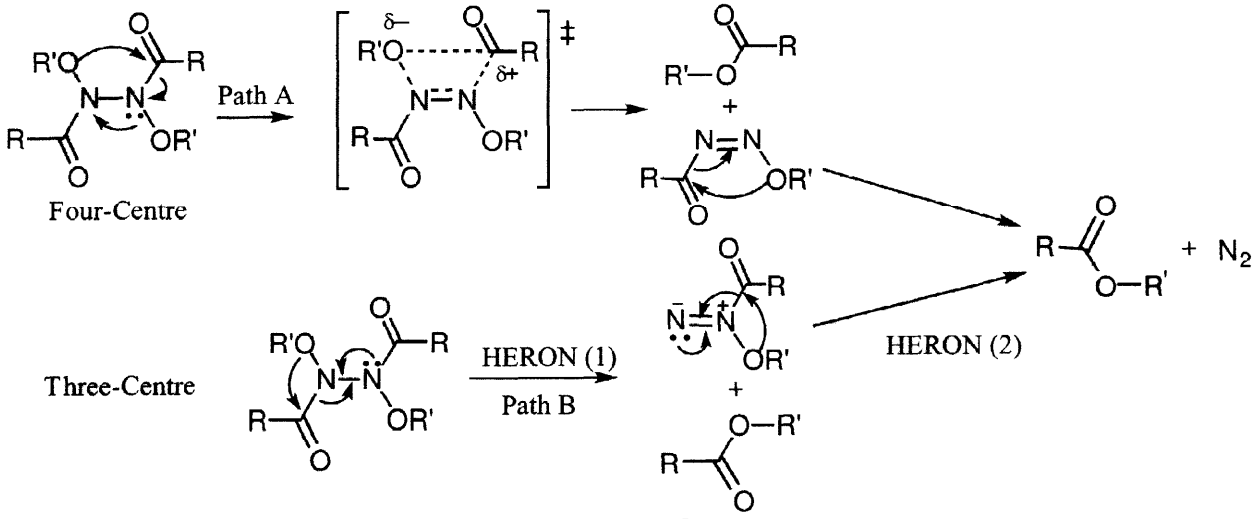


3

To date the only *N*-alkoxy-*N*-aminoamides that can be isolated are *N,N'*-diacyl-*N,N'*-dialkoxyhydrazine derivatives **2**, where the *N*-amino group bears both an acyl and an alkoxy group. They are however known to undergo a facile thermal decomposition giving two molecules of ester and a molecule of nitrogen.[5-8] Cooley and coworkers first explored the mechanism of this decomposition and proposed two consecutive four-centre transition states (Scheme 2, Path A). Rate-enhancing donor acyl substituents were believed to stabilise intrinsic acylium character in the first, rate-determining step.[7,8] Based on our results, however, we considered that **2** would be more likely to undergo two consecutive HERON reactions (Scheme 2, Path B). AM1 calculations supported this assertion and the preponderance of three-centre over four-centre rearrangements was confirmed by an internal crossover experiment.[4,9] About the same time, Barton and coworkers came to the same conclusions and, in addition, demonstrated that these reactions could be fashioned as an excellent synthesis of highly hindered esters.[10] Both our groups concluded from calculations that the second step, namely the HERON decomposition of 1-acyl-1-alkoxydiazene (Scheme 2, HERON (2)), would be extremely fast.



Scheme 2

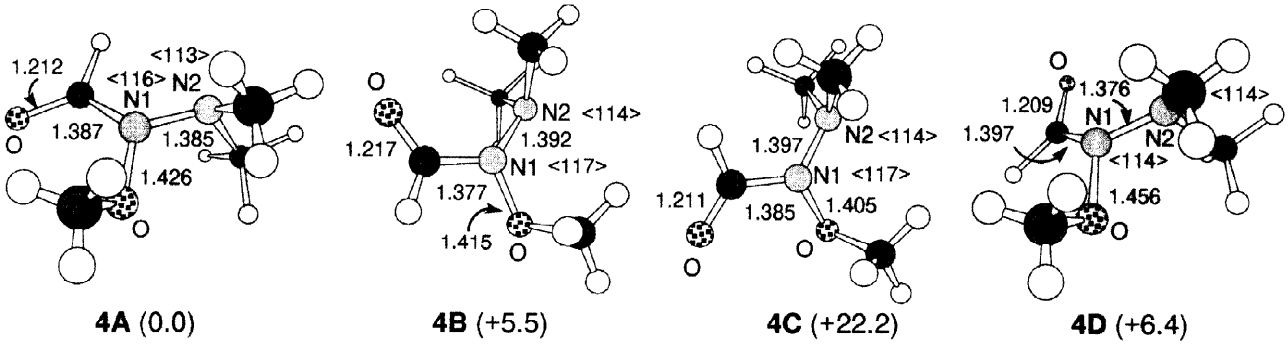
Ab initio calculations on the HERON rearrangement of *N*-methoxy-*N*-dimethylaminoformamide **3**, which is prototypical of this class of highly oxidized amides, have now been carried out which confirm the original calculations at the semiempirical level and the intimate details of the transition state point to a high degree of charge

separation in accordance with an anomerically driven process. Kinetic studies on the thermal decomposition of *N,N'*-diacyl-*N,N'*-dialkoxyhydrazines have been carried out which support these theoretical findings and shed a different light on Cooley's earlier interpretation of substituent effects.[8]

RESULTS AND DISCUSSION

N-*Methoxy*-N-*dimethylaminoformamide* — ab initio *results.*

Rigorous exploration of the ground-state structures for *N*-methoxy-*N*-dimethylaminoformamide has been carried out at the B3LYP/6-31G* level of theory and has identified four unique energy minima **4A-D** (Fig. 2) for which absolute and relative energies are presented in Table 1. **3** has four largely independent conformational degrees of freedom: rotation about the acyl *C—N* bond R(CN), rotation about the *N—N* bond, R(NN); rotation about the *N—O* bond, R(NO); and inversion at the nitrogen atom of the dimethylamino group, I(N2). There is a possible fifth degree of freedom, inversion at the acylated nitrogen atom, *N*1. This centre is a shallow pyramid and is formally the only stereogenic centre in **3**. However, I(N1) is coupled to R(NO) and does not give rise to additional conformations.



4A (0.0) **4B** (+5.5) **4C** (+22.2) **4D** (+6.4)

Fig. 2. Ground state conformations for *N*-methoxy-*N*-dimethylaminoformamide (bond lengths in Å, relative energies in kJmol^{-1} and average angles at *N*1 and *N*2 in degrees).

The most stable conformation **4A** has the oxygens *syn* . The formyl group in all geometries is turned into conjugation with the amide nitrogen atom, *N*1, which forms a shallow pyramid. In **4A** and **4D**, the more strongly pyramidal dimethylamino nitrogen, *N*2, is oriented such that its lone pair is *anti* to the vicinal *N—O* bond and the non-bonded electron pairs of the two nitrogen atoms are gauche to one another (Fig. 3a and 3d). This conformation facilitates an n_N—σ^*_{NO} anomeric interaction and the *N*1—*N*2 bond is extremely short when compared to hydrazines (*ca.* 1.45Å)[11] and hydrazides (1.40Å)[12,13] while the *N—O* bond is appreciably longer than that calculated for the hydroxamic ester (1.406Å)[1]. In **4B** and **4C** the inverted *N*2 places the *N*2 lone pair and the *N—O* bond in a *syn* orientation which is less favourable for anomeric overlap (Fig. 3b and 3c). This is clearly reflected in the longer *N*1—*N*2 and shorter *N—O* bonds in **4B** and **4C** relative to **4A** and **4D**. The methoxy group is, in all cases, oriented so that the *C—O* bond is quasi-perpendicular to the average plane at *N*1 with the methyl group turned *exo* to the pyramid rather than *endo* to it. The quasi-perpendicular geometry of the methoxy group also places the higher energy lone pair of the oxygen atom into the nodal plane of the lone pair at *N*1. Thus the equilibrium structures are determined by the requirement to maximize the stabilizing conjugation of the electron pair at *N*1 with the acyl group, to minimize the destabilizing lone pair—lone pair interactions between *N*1 and *N*2,

and between *N*1 and *O* (of methoxy) as well as to optimise the most favourable anomeric interaction (n_N—σ^*_{NO} rather than n_O—σ^*_{NN}). The average angles at *N*1 range between 114° and 117° and reflect pyramidality at that nitrogen as was the case for the *ONO* <115>, *ONCl*<113> and *NNCl* <112> systems studied previously[1] and this deviation from planarity is a response to the combined electronegativities of oxygen and nitrogen; electron demand by these atoms is best satisfied by sp^3 rather than sp^2 hybridisation at *N*1. As a consequence of reduced delocalisation, the *N*—*CO* bond is significantly longer and the *C*=*O* bond shorter than those found in formamide (1.362Å and 1.216Å, respectively). In summary, relative to amides and hydroxamic esters, *NNO* systems should exhibit higher carbonyl stretch frequencies in their infrared spectra, and lower barriers to *E*—*Z* isomerisation, both a consequence of sp^3 hybridisation at nitrogen which leads to reduced amide resonance. In addition, the strong anomeric effect should lead to high *N*—*N* rotation barriers as well as a weaker than normal *N*—*O* bond. A more detailed analysis of conformational isomerism in *N*-alkoxy-*N*-aminoamides together with spectroscopic evidence for these characteristics will be presented elsewhere.[14]

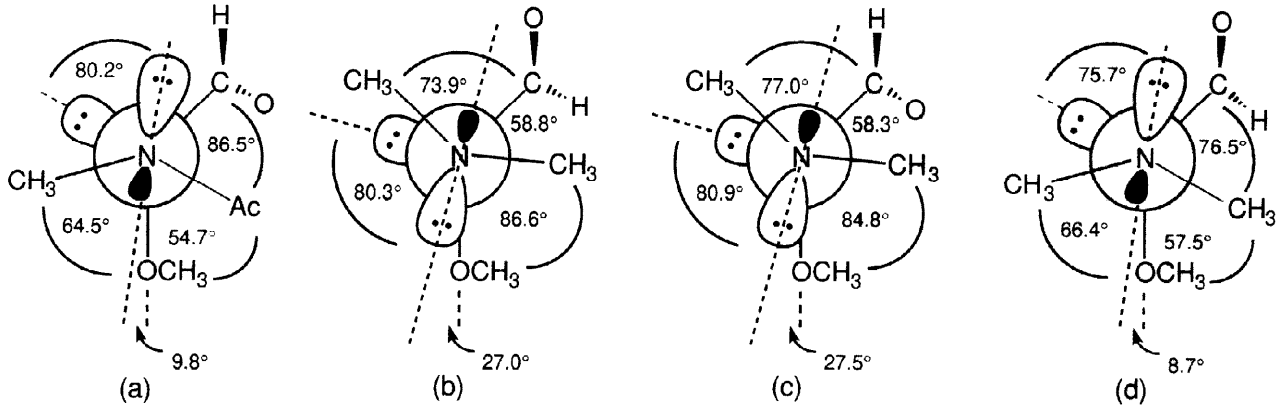


Fig. 3. Newman projections along the *N*2—*N*1 bonds in (a) **4A**, (b) **4B**, (c) **4C**, and (d) **4D**.

Table 1. B3LYP/6-31G* Energies, Zero Point Energies and Relative Energies of Ground State Conformations of *N*-Methoxy-*N*-dimethylaminoformamide and HERON Transition States.

Structure	Energy/hartrees	ZPE/kJmol^{-1}	ΔE/kJmol^{-1}
4A	-418.29799	397.2	0.0
4B	-418.28921	396.3	22.2
4C	-418.29589	397.3	5.5
4D	-418.29529	396.5	6.4
TS1	-418.26169	391.9	90.1
TS2	-418.26494	392.0	80.7
TS3	-418.25058	390.6	118.0
TS4	-418.26617	391.4	77.9

The HERON rearrangement.

The HERON rearrangement of the lowest energy conformation of *N*-methoxy-*N*-dimethylaminoformamide **4A** yields a complex between methyl formate and dimethylaminonitrene which is more stable than the individual products by 7 kJmol^{-1}. The overall reaction is exothermic by 23 kJmol^{-1} and the E_A is computed to be 90 kJmol^{-1}.

In the transition state (TS1, Fig. 4) the amino nitrogen, *N*2, is planar and the *N*—*N* bond (1.27Å) is shortened further relative the ground state (1.39Å). The migrating oxygen is 2.04 Å and 1.71 Å from the amide nitrogen and carbon, respectively. The *N*—*C(O)* bond (1.51Å) is virtually intact at the HERON transition state but breaks as the ester bond develops fully. The rearrangement is clearly driven by the n_N—σ^*_{NO} anomeric overlap which is strongly developed in the transition state complex.

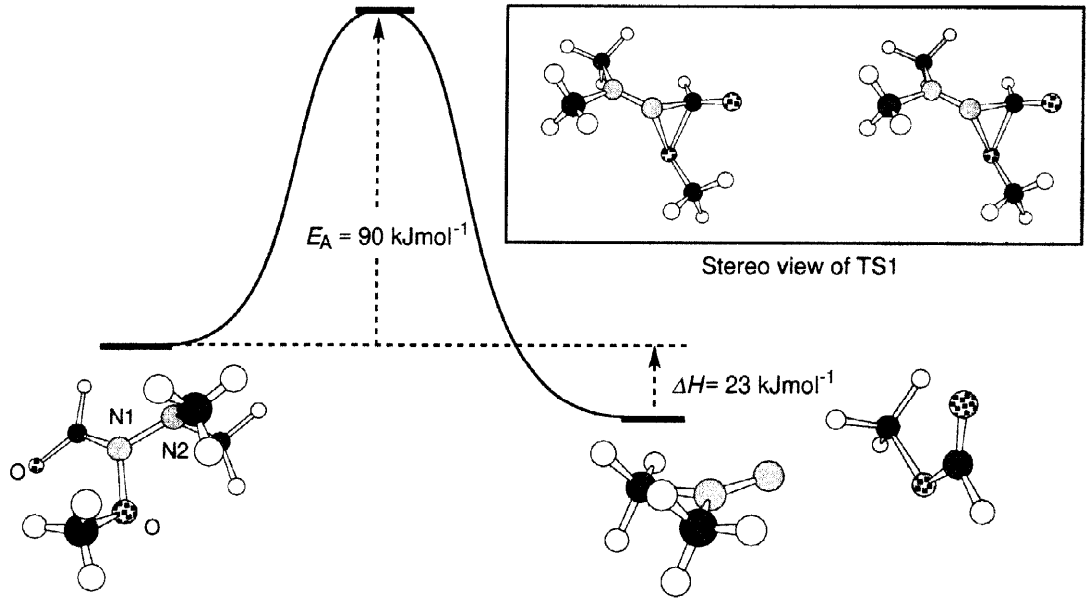


Fig. 4. B3LYP/6-31G* structures and energetics for the HERON rearrangement of **4A** to methyl formate and 1,1-dimethyldiazene.

In addition to this transition state, three other similar transition states, TS2-4 were located which are shown in Fig. 5; the transition state for the rearrangement may be characterised by the disposition of groups relative to the plane of the triangle formed by the formyl carbon, the amide nitrogen and the methoxy oxygen. At each site there is a group which projects out of the plane — the carbonyl oxygen, the dimethylamino group, and the methyl of methoxy, respectively. As there are four diastereomeric arrangements, all groups *cis*, or one group *trans* (in three different ways), one can expect eight transition states for the HERON rearrangement of **3** as four enantiomeric pairs of diastereomers. Absolute and relative energies are listed in Table 1.

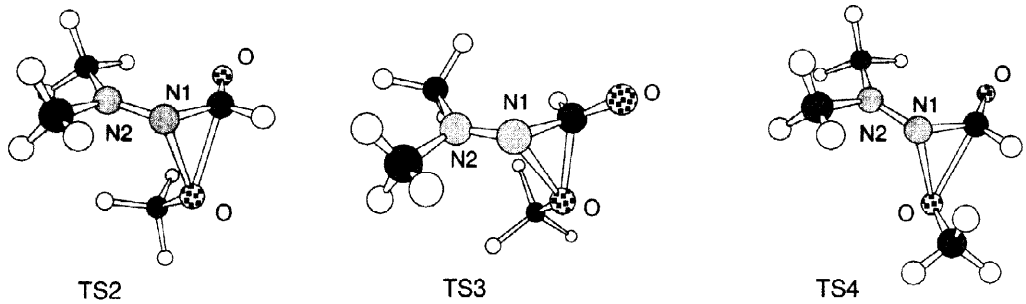


Fig. 5. Transition states for the HERON reaction of *N*-methoxy-*N*-dimethylaminoformamide **3**.

Group charges in the transition state for the rearrangement of **4A** are given in Table 2. They clearly indicate a high degree of charge separation in the transition state, *N*2 becoming positively charged while the bulk of the

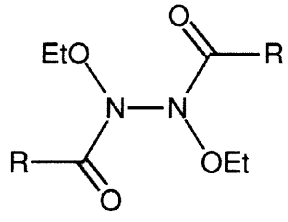
negative charge resides on the migrating oxygen. The formyl substituent is largely unaffected. The HERON reaction should thus be facilitated by both electron-donor substituents on the amino nitrogen, *N*2, and electron-withdrawing substituents on the migrating oxygen. Both substituents would enhance the anomeric interaction. Conversely, electronegative or electron-withdrawing substituents should slow the HERON reaction. In addition, polar solvents would be expected to lower the activation energy. Both conclusions accord with our earlier AM1 results.[4]

Table 2. 6-31G* Group Charges in the Transition State for the HERON Reaction of *N*-Methoxy-*N*-dimethylaminoformamide to 1,1-Dimethyldiazene and Methylformate.

Group	Ground State **4A**	Transition State from **4A**
—N2$(CH_3)_2$	0.00	+0.51
—N1—	0.00	-0.19
—OCH_3	-0.02	-0.34
—CHO	+0.02	-0.01

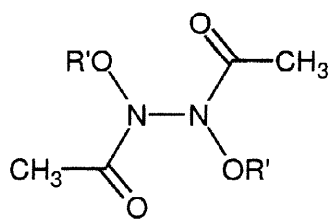
Decomposition of* N,N'-*diacyl*-N,N'-*dialkoxyhydrazines.

N-Alkoxy-*N*-methylanilinobenzamides **1** are only formed as reactive intermediates (Scheme 1). However, in light of the transition state properties described above, it is not surprising that *N*,*N*'-diacyl-*N*,*N*'-dialkoxyhydrazines **2** are relatively stable and can be isolated at room temperature since the positive polarity of the acyl carbon, as well as the electronegativity of the alkoxy oxygen, would reduce the anomeric driving force for the rearrangement. Since at higher temperatures they have been shown to undergo a concerted HERON decomposition rather than reaction through the four-membered transition state proposed by Cooley and coworkers,[8,15] we decided these would be ideal substrates to evaluate the influence of substituents on the HERON reaction process.



5

a: R=*p*-$CH_3OC_6H_4$
b: R=*p*-$CH_3C_6H_4$
c: R=C_6H_4
d: R=*p*-ClC_6H_4
e: R=*p*-$NO_2C_6H_4$



6

a: R'=*p*-$CH_3OC_6H_4CH_2$
b: R'=*p*-$CH_3C_6H_4CH_2$
c: R'=$C_6H_4CH_2$
d: R'=*p*-$ClC_6H_4CH_2$
e: R'=*p*-$NO_2C_6H_4CH_2$

Two hydrazine series, **5** and **6**, were synthesised by lead tetraacetate oxidation of the corresponding hydroxamic esters and were found to decompose unimolecularly in mesitylene giving esters and nitrogen. Arrhenius activation energies, entropies of activation and rate constants at 298K are given in Table 3.

Both series of data afforded excellent isokinetic relationships between E_A and $\Delta S^{\ddagger}$ indicating that, in each series, a uniform mechanism was operative. The rate determining step is characterised by small, mostly negative entropies of activation, in keeping with a highly ordered HERON transition state and are typical of an intramolecular process where bond cleavage—bond formation is appreciably in concert. Development of the transition state is also accompanied by a restriction in rotation about the *N*—*N* and *N*—*C(O)* bond, thus offsetting

any gain in entropy through stretching of the *N*—*O* bond. The activation barriers are in the region of those calculated for the HERON reaction of *N*-methoxy-*N*-dimethylaminoformamide (80-120 kJmol^{-1}).

Table 3. Arrhenius Activation Energies, Entropies of Activation[a] and Rate Constants at 298K for Decomposition of *N,N'*-Diacyl-*N,N'*-dialkoxyhydrazines, RCON(OR')N(OR')COR **2** in Mesitylene.

R	R'	E_A/kJmol^{-1}	$\Delta S^{\ddagger}$/JK^{-1}mol^{-1}	r^2	$10^6 \cdot k_{298}$/s^{-1}
p-$CH_3OC_6H_4$	Et	99.2 (4.3)	-21.2 (13)	0.996	5.564
p-$CH_3C_6H_4$	Et	100.7 (8.2)	-19.6 (25)	0.986	3.719
C_6H_5	Et	100.4 (5.1)	-23.8 (15)	0.994	2.521
b		86.4 (8.9)	-64.6 (26)	0.980	5.033
c		93.3 (6.4)	-44.4 (19)	0.990	3.528
p-ClC_6H_4	Et	107.7 (1.7)	0.9 (5)	1.000	2.502
p-$NO_2C_6H_4$	Et	104.0 (1.7)	-15.4 (5)	1.000	1.572
					$10^8 \cdot k_{298}$/s^{-1}
CH_3	*p*-$CH_3OC_6H_4CH_2$	111.4 (0.9)	-21.1 (2)	1.000	4.017
CH_3	*p*-$CH_3C_6H_4CH_2$	125.9 (1.0)	24.5 (3)	1.000	2.757
CH_3	$C_6H_5CH_2$	114.1 (3.9)	-8.7 (11)	0.998	6.206
CH_3	*p*-$ClC_6H_4CH_2$	125.1 (8.5)	27.4 (24)	0.990	5.436
CH_3	*p*-$NO_2C_6H_4CH_2$	98.8 (0.3)	-46.4 (1)	1.000	31.880

a $\Delta S^{\ddagger}=R(\ln A-\ln[kTe/h])=8.314(\ln A-30.457)$ at 298 *K*; *b* Tetralin; *c* Cyclohexanone

Table 2 indicates a significant increase in positive character at the anomeric nitrogen, *N*2, and virtually no change to the charge at the acyl carbon. Based on theoretical results, therefore, the migration occurs through a concerted transition state with increased positive charge on the amino nitrogen and increased negative charge on the migrating oxygen. Rate constants at 298K correlate with Hammett σ^+ with a low but negative sensitivity of ρ= –0.35 for the benzoyl series (Fig. 6) and with Hammett σ constants in the benzyloxy series (ρ=+1.02, Fig. 7). Thus, in accordance with the computed charge distribution in the model transition state for the HERON process, donor groups facilitate the rearrangement in the benzoyl series, as do withdrawing groups in the benzyloxy series. In the case of hydrazines, one nitrogen (the "anomeric" nitrogen) must function as an electron pair donor, while the other acyl carbon must behave as the alkoxy group recipient. At the anomeric nitrogen, the increased positive charge would be stabilised by *para* electron donor substituents on the adjacent benzoyl group as depicted in Fig. 8(a). These will reduce the polarity at the carbonyl carbon and raise the energy of the anomeric nitrogen lone pair thus promoting the electron donor interaction. The acceptor carbonyl moiety is computed to be nearly neutral in the transition state and thus relatively unaffected by donor or acceptor acyl groups. Thus Cooley's earlier assertion that the transition state has acylium character and is therefore stabilised by electron rich acyl groups is incorrect. Furthermore, the LFR reported by Cooley for decomposition of a series of *N,N'*-di-*p*-substitutedbenzoyl-*N,N'*-dibenzyloxyhydrazines in chloroform correlated with Hammett σ (ρ=–0.47) rather than σ^+.[8] We have observed σ^+ correlations in several other cases where a *para*-substituted aryl group exerts an electronic influence upon nitrogen through an acyl carbon.[16,17]

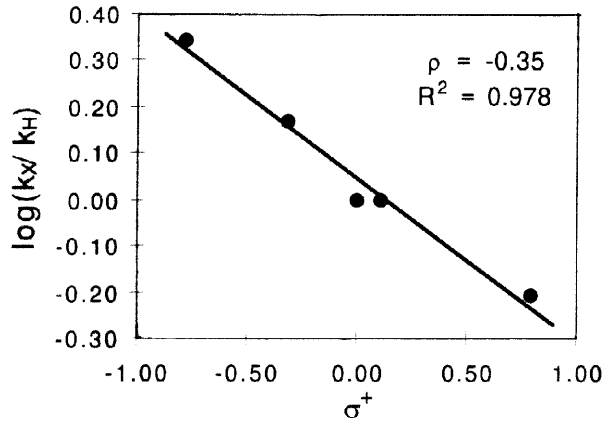


Fig. 6. Hammett correlation for the HERON reaction of *N,N'*-dibenzoyl-*N,N'*-diethoxyhydrazines **5**.

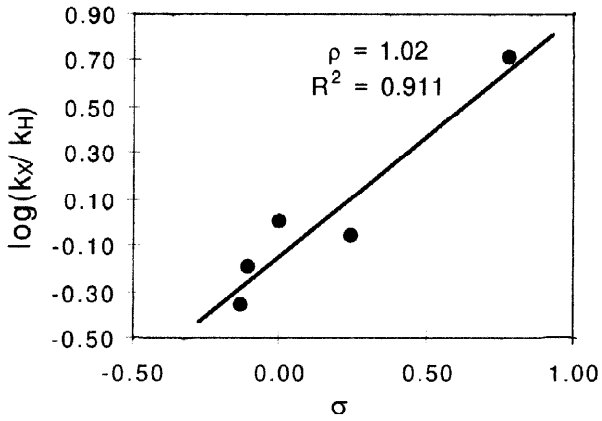


Fig. 7. Hammett correlation for the HERON reaction of *N,N'*-diacetyl-*N,N'*-dibenzyloxyhydrazines **6**.

The increased negative charge at the alkoxy group in the model transition state would also be stabilised by *para* electron-withdrawing substituents on the benzyloxy groups in accordance with the positive Hammett correlation for series **6** (Fig. 7). Furthermore, members of the benzoyl series react about two orders faster at 298K than the benzyloxy series. This can be understood in that, while an electron-withdrawing group on the alkoxy group will stabilise negative charge in the migrating group, it will destabilise a developing positive charge on the adjacent anomeric nitrogen (Fig. 8(b)). In the benzoyl series, a donor group facilitates positive charge at the anomeric nitrogen but has little effect upon the acyl carbon in the migration.

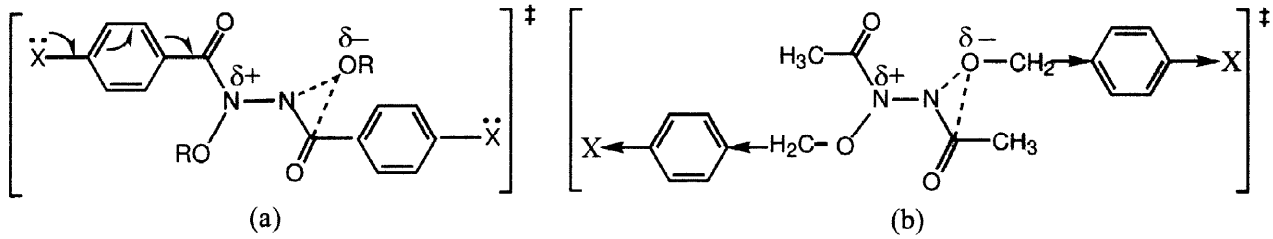


Fig. 8. Influence on the HERON transition states of (a) electron rich benzoyl groups in **5** and (b) electron deficient benzyloxy groups in **6**.

Arrhenius data for the decomposition of **5c** in both tetralin (ε=2.7) and cyclohexanone (ε=19) are listed together with the data for mesitylene (ε=2.4) in Table 3. Rates at 298K are similar although, in cyclohexanone, both E_A and $\Delta S^{\ddagger}$ are smaller than the corresponding values in mesitylene; increased charge separation in the transition state is stabilised by more polar solvents but leads to an ordering of polar solvent molecules resulting in a more negative entropy of activation. The error in the Arrhenius data for the tetralin reaction prevents a meaningful comparison from being made.

CONCLUSIONS

An *ab initio* study of the structural features and energetics of the anomeric amide, *N*-methoxy-*N*-dimethylaminoformamide, has been carried out at the B3LYP/6-31G* level together with an investigation of its HERON rearrangement to methylformate and 1,1-dimethyldiazene. The process is predicted to be concerted, exothermic by 23 kJmol^{-1} and to have a modest activation energy of *ca* 90 kJmol^{-1}. The HERON rearrangement of *N,N'*-diacyl-*N,N'*-dialkoxyhydrazines has been investigated by determining decomposition rates and Hammett correlations for reactions of two series, **5** and **6**. The results indicate that electron-donating groups on the acyl side chain in **5** accelerate the decomposition rates as do electron-withdrawing substituents on the benzyloxy groups in **6**. Stabilisation of a transition state, which is characterised by increased positive charge on the amino nitrogen and negative charge on the migrating oxygen, appears to be an important factor in facilitating the HERON rearrangement which is driven by an n_N—σ^*_{NO} anomeric interaction. Experimental results confirm the theoretically predicted properties of the HERON transition state in these *NNO* systems.

EXPERIMENTAL

Melting points were determined on a Reichert Microscopic Hot-Stage and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 1725X Fourier-transform instrument. 300MHz ^{1}H and 75MHz ^{13}C NMR spectra were recorded on a Bruker AC-300P FT spectrometer with variable-temperature probe. All routine samples were in $CDCl_3$, with tetramethylsilane (0.1%) as an internal standard. HPLC analyses were performed on a Waters 510 Analytical instrument using a model 481 UV absorbance detector linked to a Waters 740 data module. Microanalyses were obtained from the Research School of Chemistry at Australian National University.

Acetonitrile used was HiPerSolv, 'Far UV' grade (BDH). Ether refers to anhydrous diethyl ether stored over sodium wire. Dichloromethane (DCM), ethyl acetate, methanol (MeOH) and petroleum spirit were distilled before use. Hydrogen bromide solution was 48% w/w. Anhydrous sodium carbonate and sodium sulfate were used for drying all organic mixtures. Flash chromatography was executed on columns loaded with Kieselgel 60 (Merck). Thin layer chromatography (TLC) was performed on aluminium sheets pre-coated with 0.2mm of silica gel 60 F_{254} (Merck). Preparative plate chromatography was carried out centrifugally on a Harrison 7924T Research Chromatotron. Ethyl benzoate, *para*-substituted benzoic acid, ethyl bromide, *p*-nitrobenzyl bromide, *para*-substituted benzyl alcohols and acetohydroxamic acid were purchased from Aldrich.

General synthesis of alkyl benzohydroxamates (or benzyl acetohydroxamates).

Treatment of the appropriate ester with hydroxylamine hydrochloride under basic conditions afforded a precipitate of potassium hydroxamate salt from methanol after refrigeration.[18] The solution of the appropriate

potassium hydroxamate with the required alkyl bromide, and a 10% excess of sodium carbonate in 50% aqueous methanol was stirred for 24 hours then refluxed for 2 hours.[19] Removal of methanol *in vacuo*, acidification and extraction with dichloromethane (DCM) provided the appropriate alkyl arylhydroxamates or alkyl acetohydroxamates in high yield. (*para*-Substituted benzyl bromides (chlorides) were prepared from the appropriate alcohols by refluxing with HBr-H_2SO_4 (HCl-H_2SO_4) in ether, washing with conc. HCl, H_2O, 10% aq.Na_2CO_3, H_2O and extracting with DCM. Ethyl *para*-substitutedbenzoates were prepared by esterification of the appropriate *para*-substitutedbenzoic acid with an excess of ethanol under acidic conditions (HCl-H_2SO_4) and were identified by NMR. An alternative method was applied to make *p*-methoxybenzyl acetohydroxamate.

Ethyl benzohydroxamate. A solution of potassium benzohydroxamate (12.00 g, 0.07 mol), ethyl bromide (8.94 g, 0.08 mol), sodium carbonate (3 g) in methanol (50 mL) and water (50 mL) was stirred for 24 hours then refluxed for 2 hours. Methanol was removed *in vacuo*, and the remaining mixture was acidified with conc. HCl. Extraction with DCM afforded the ethyl benzohydroxamate (8.22 g, 73%) as pale pink crystals, m.p. 58-59°C (Lit.[16]m.p. 58-60°C); $\upsilon_{max}(CHCl_3)/cm^{-1}$ 3404 (NH) and 1685 (C=O); $\delta_H(CDCl_3)$ 1.30 (3H, t), 4.07 (2H, q), 7.40 (2H, d, *m*-ArH), 7.49 (1H, m, *p*-ArH), 7.75 (2H, d, *o*-ArH), 9.23 (1H, br); $\delta_C(CDCl_3)$ 13.51 (s), 72.32 (s), 127.07 (s), 128.62 (s), 131.94 (d).

Ethyl* p-*methylbenzohydroxamate. A solution of potassium *p*-methylbenzohydroxamate (37.50 g, 0.20 mol), ethyl bromide (28.07 g, 0.23 mol), sodium carbonate (10 g) in methanol (120 mL) and water (120 mL) was stirred for 24 hours then refluxed for 2 hours. Methanol was removed *in vacuo*, and the remaining mixture was acidified with conc. HCl. Extraction with DCM afforded the crude ethyl *p*-methylbenzohydroxamate (27.20 g, 77%). Recrystallisation from benzene provided pure ethyl *p*-methylbenzohydroxamate as colourless crystals, m.p. 100-101°C (Found: C, 66.96%; H, 6.98%; N, 7.53%. $C_{10}H_{13}O_2N$ requires C, 67.02%; H, 7.31%; N, 7.82%); $\upsilon_{max}(CHCl_3)/cm^{-1}$ 3406 (NH) and 1682 (C=O); $\delta_H(CDCl_3)$ 1.29 (3H, t), 2.38 (3H, s), 4.07 (2H, q), 7.21 (2H, d, *m*-ArH), 7.66 (2H, d, *o*-ArH); $\delta_C(CDCl_3)$ 13.46 (s), 21.44 (s), 72.22 (s), 127.09 (s), 129.21 (m), 142.41 (s).

Ethyl* p-*methoxybenzohydroxamate. A solution of potassium *p*-methoxybenzohydroxamate (24.00 g, 0.12 mol), ethyl bromide (16.56 g, 0.15 mol), sodium carbonate (6 g) in methanol (90 mL) and water (90 mL) was stirred for 24 hours then refluxed for 2 hours. Methanol was removed *in vacuo*, and the remaining mixture was acidified with conc. HCl. Extraction with DCM afforded the crude ethyl *p*-methoxybenzohydroxamate (18.02 g, 79%). Recrystallisation from benzene provided pure ethyl *p*-methoxybenzohydroxamate as colourless crystals, m.p. 81°C (Found: C, 61.26%; H, 6.46%; N, 7.04%. $C_{10}H_{13}O_3N$ requires C, 61.53%; H, 6.71%; N, 7.17%); $\upsilon_{max}(CHCl_3)/cm^{-1}$ 3402 (NH) and 1681 (C=O); $\delta_H(CDCl_3)$ 1.24 (3H, t), 3.79 (3H, s), 4.02 (2H, q), 6.84 (2H, d, *m*-ArH), 7.79 (2H, d, *o*-ArH), 10.10 (1H, br); $\delta_C(CDCl_3)$ 13.47 (s), 55.32 (s), 72.15 (s), 113.75 (m), 128.95 (m), 162.42 (s).

Ethyl* p-*chlorobenzohydroxamate. A solution of potassium *p*-chlorobenzohydroxamate (30.20 g, 0.14 mol), ethyl bromide (20.40 g, 0.18 mol), sodium carbonate (7 g) in methanol (100 mL) and water (100 mL) was stirred for 24 hours then refluxed for 2 hours. Methanol was removed *in vacuo*, and the remaining mixture was acidified with conc. HCl. Extraction with DCM afforded the crude ethyl *p*-chlorobenzohydroxamate (21.10 g, 73%). Recrystallisation from benzene provided pure ethyl *p*-chlorobenzohydroxamate as colourless crystals, m.p. 112-113°C (Found: C, 54.09%; H, 5.00%; N, 6.85%. $C_9H_{10}O_2NCl$ requires C, 54.15%; H, 5.05%; N, 7.02%); $\upsilon_{max}(CHCl_3)/cm^{-1}$ 1680 (C=O); $\delta_H(CDCl_3)$ 1.29 (3H, t), 4.06 (2H, q), 7.37 (2H, d, *m*-ArH), 7.72 (2H, d, *o*-ArH), 9.65 (1H, br); $\delta_C(CDCl_3)$ 13.49 (s), 58.16 (s), 72.22 (s), 128.25 (m), 129.79 (m), 137.62 (m), 165.12 (m).

Ethyl* p-*nitrobenzohydroxamate. A solution of potassium *p*-nitrobenzohydroxamate (54.18 g, 0.24 mol), ethyl bromide (29.43 g, 0.27 mol), sodium carbonate (12 g) in methanol (120 mL) and water (120 mL) was stirred for 24 hours then refluxed for 2 hours. Methanol was removed *in vacuo*, and the remaining mixture was acidified with conc. HCl. Extraction with DCM afforded the crude ethyl *p*-nitrobenzohydroxamate (22.58 g, 44%) as a yellow solid. Recrystallisation from benzene gave pure ethyl *p*-nitrobenzohydroxamate as pale yellow crystals, m.p. 132-142°C (Found: C, 51.10%; H, 4.65%; N, 12.96%. $C_9H_{10}O_4N_2$ requires C, 51.43%; H, 4.80%; N, 13.33%); $\upsilon_{max}(CHCl_3)/cm^{-1}$ 3407 (NH) and 1692 (C=O); $\delta_H(CDCl_3)$ 1.34 (3H, t), 4.15 (2H, q), 7.94 (2H, d, *o*-ArH), 8.28 (2H, d, *m*-ArH); $\delta_C(CDCl_3)$ 13.69 (s), 72.19 (s), 120.63 (s), 123.75 (s), 128.00 (s), 149.59 (s), 169.84 (s).

Benzyl acetohydroxamate. A solution of potassium acetohydroxamate (13.58 g, 0.12 mol), benzyl bromide (20.64 g, 0.12 mol), sodium carbonate (16 g) in methanol (160 mL) and water (160 mL) was stirred for 24 hours then refluxed for 2 hours. The solvents were removed *in vacuo*, and the remaining mixture was acidified with conc. HCl. Extraction with DCM afforded the crude benzyl acetohydroxamate (15.59 g, 79%). Purification by chromatotron (5% EtAc-95% Hexane) afforded pure benzyl acetohydroxamate as a yellow oil; n_D^{20} 1.5324 (Lit.[19] n_D^{28}1.5343); $\upsilon_{max}(CHCl_3)/cm^{-1}$ 3404 (NH) and 1682 (C=O); $\delta_H(CDCl_3)$ 1.78 (3H, br), 4.83 (2H, br), 7.31 (5H, m), 10.18 (1H, br); $\delta_C(CDCl_3)$ 19.33 (s), 77.67 (m), 128.25 (m), 135.12 (s), 148.81 (s), 168.13 (s), 174.49 (s).

p-*Methylbenzyl acetohydroxamate.* A solution of potassium acetohydroxamate (15.84 g, 0.14 mol), *p*-methylbenzyl bromide (25.91 g, 0.14 mol), sodium carbonate (18 g) in methanol (190 mL) and water (190 mL) was stirred for 24 hours then refluxed for 2 hours. The solvents were removed *in vacuo*, and the remaining mixture was acidified with conc. HCl. Extraction with DCM afforded the crude *p*-methylbenzyl acetohydroxamate (17.33 g, 69%). Recrystallisation from benzene gave pure *p*-methylbenzyl acetohydroxamate as colourless crystals, m.p. 56-57°C (Found: C, 66.93%; H, 7.27%; N, 7.74%. $C_{10}H_{13}O_2N$ requires C, 67.02%; H, 7.31%; N, 7.82%); $\upsilon_{max}(CHCl_3)/cm^{-1}$ 3403 (NH) and 1693 (C=O); $\delta_H(CDCl_3)$ 2.00 (3H, br), 2.36 (3H, s), 4.80 (2H, br), 7.18 (2H, d, *o*-ArH), 7.27 (2H, d, *m*-ArH), 8.32 (1H, br); $\delta_C(CDCl_3)$ 21.11 (s), 77.76 (s), 129.11 (m), 138.36 (s), 168.01 (s).

p-*Chlorobenzyl acetohydroxamate.* A solution of potassium acetohydroxamate (15.92 g, 0.14 mol), *p*-chlorobenzyl bromide (29.07 g, 0.14 mol), sodium carbonate (18 g) in methanol (190 mL) and water (190 mL) was stirred for 24 hours then refluxed for 2 hours. The solvents were removed *in vacuo*, and the remaining mixture was acidified with conc. HCl. Extraction with DCM afforded the crude *p*-chlorobenzyl acetohydroxamate (18.78 g, 67%). Recrystallisation from benzene gave pure *p*-chlorobenzyl acetohydroxamate as colourless crystals, m.p. 104-106°C (Found: C, 54.17%; H, 5.04%; N, 6.93%. $C_9H_{10}O_2NCl$ requires C, 54.15%; H, 5.05%; N, 7.02%); $\upsilon_{max}(CHCl_3)/cm^{-1}$ 3403 (NH) and 1693 (C=O); $\delta_H(CDCl_3)$ 1.86 (3H, br), 4.84 (2H, br), 7.32 (4H, m), 8.94 (1H, br); $\delta_C(CDCl_3)$ 19.64 (s), 96.50 (s), 128.82 (s), 130.48 (s), 134.71 (m).

p-*Nitrobenzyl acetohydroxamate.* A solution of potassium acetohydroxamate (15.84 g, 0.14 mol), *p*-nitrobenzyl bromide (30.24 g, 0.14 mol), sodium carbonate (18 g) in methanol (190 mL) and water (190 mL) was stirred for 24 hours then refluxed for 2 hours. The solvents were removed *in vacuo*, and the remaining mixture was acidified with conc. HCl. Extraction with DCM afforded the crude *p*-nitrobenzyl acetohydroxamate (18.50 g, 63%). Recrystallisation from benzene gave pure *p*-nitrobenzyl acetohydroxamate as colourless crystals, m.p. 131-132°C (Lit.[19]m.p.133.5-134.0) (Found: C, 51.36%; H, 4.71%; N, 13.28%. $C_9H_{10}O_4N_2$ requires C, 51.43%; H, 4.80%; N, 13.33%); $\upsilon_{max}(CHCl_3)/cm^{-1}$ 3403 (NH) and 1700 (C=O); $\delta_H(CDCl_3)$ 1.93 (3H, br),

5.01 (2H, br), 7.58 (2H, d, *o*-ArH), 8.23 (2H, d, *m*-ArH); $\delta_C(CDCl_3)$ 19.16 (s), 95.89 (s), 123.15 (s), 128.74 (s), 142.22 (m), 147.40 (s).

p-*Methoxybenzyl acetohydroxamate.* A solution of acetohydroxamic acid (5.26 g, 0.07 mol), *p*-methoxybenzyl chloride (10.97 g, 0.07 mol), and triethylamine (21.27 g, 0.21 mol) were refluxed in chloroform (210 mL) for 2 hours. The mixture was washed with 10% aq. sodium carbonate and dilute HCl after which the organic layer was dried and concentrated *in vacuo* to afford crude *p*-methoxybenzyl acetohydroxamate (1.20 g, 8.8%). Purification by chromatotron (5% EtOAc-95% Hexane) afforded pure *p*-methoxybenzyl acetohydroxamate as a colourless solid, m.p. 59-60°C (Found: C, 61.66%; H, 6.46%; N, 7.08%. $C_{10}H_{13}O_3N$ requires C, 61.53%; H, 6.71%; N, 7.17%); $\upsilon_{max}(CHCl_3)/cm^{-1}$ 3404 (NH) and 1693 (C=O); $\delta_H(CDCl_3)$ 1.88 (3H, br), 3.82 (3H, s), 4.85 (2H, br), 6.91 (2H, d, *o*-ArH), 7.31 (2H, d, *m*-ArH), 8.12 (1H, br); $\delta_C(CDCl_3)$ 55.28 (s), 113.99 (m), 128.61 (m).

***Synthesis of* N,N'-*diacyl*-N,N'-*dialkoxyhydrazines* 2.**

The title compounds were synthesised by oxidation of the appropriate hydroxamic esters using lead tetraacetate.

General synthetic procedure.[5] Freshly prepared lead tetraacetate[20] in DCM was added in portions to a stirred solution of the appropriate hydroxamate in DCM and the reaction mixture was stirred at room temperature for a further 1.5 hours. After filtration, the organic solution was washed with water and dried with sodium carbonate. Removal of solvent (DCM) *in vacuo* provided the title compound in good to high yield. Where solid samples could be recrystallised without decomposition, satisfactory microanalytical data was obtained. Oils and unstable solids could not be microanalysed but samples were characterised satisfactorily by spectroscopic means and were sufficiently pure by ^1H NMR for decomposition studies.

N,N'-*Diethoxy*-N,N'-*di*-(p-*methoxybenzoyl)hydrazine* 5a was prepared by the general method and recrystallised from MeOH as colourless crystals, m.p. 77-81°C (decomposition); $\upsilon_{max}(CHCl_3)/cm^{-1}$ 1700 (C=O); $\delta_H(CDCl_3)$ 1.18 (3H, t), 3.84 (3H, s), 4.12 (2H, br sextet [overlapping AB system]), 6.87 (2H, d, *m*-ArH), 7.73 (2H, d, *o*-ArH); $\delta_C(CDCl_3)$ 13.59 (s), 55.36 (s), 71.58 (s), 113.35 (s), 124.34 (s), 131.05 (s), 162.59 (s), 169.35 (s).

N,N'-*Diethoxy*-N,N'-*di*-(p-*methylbenzoyl)hydrazine* 5b was prepared by the general method and recrystallised from benzene as colourless crystals, m.p. 96-97°C (Found: C, 67.09%; H, 6.77%; N, 7.59%. $C_{20}H_{24}O_4N_2$ requires C, 67.40%; H, 6.79%; N, 7.86%); $\upsilon_{max}(CHCl_3)/cm^{-1}$ 1701 (C=O); $\delta_H(CDCl_3)$ 1.16 (3H, t), 2.37 (3H, s), 4.12(2H, br sextet [overlapping AB system]), 7.17 (2H, d, *m*-ArH), 7.59(2H, d, *o*-ArH); $\delta_C(CDCl_3)$ 13.49 (s), 21.51 (s), 71.58 (s), 128.68 (m), 129.46 (s), 142.48 (s), 169.92 (s).

N,N'-*Dibenzoyl*-N,N'-*diethoxyhydrazine* 5c was prepared by the general method and recrystallised from MeOH as colourless crystals, m.p. 85-87°C (Found: C, 65.59%; H, 6.07%; N, 8.30%. $C_{18}H_{20}O_4N_2$ requires C, 65.84%; H, 6.14%; N, 8.53%); $\upsilon_{max}(CHCl_3)/cm^{-1}$ 1708 (C=O); $\delta_H(CDCl_3)$ 1.16 (3H, t), 4.13 (2H, br sextet [overlapping AB system]), 7.39 (2H, d, *m*-ArH), 7.47 (1H, m, *p*-ArH), 7.65 (2H, d, *o*-ArH); $\delta_C(CDCl_3)$ 13.48 (s), 71.77 (s), 128.23 (d), 131.85 (s), 132.46 (s), 169.97 (s).

N,N'-*Di*-(p-*chlorobenzoyl)*-N,N'-*diethoxyhydrazine* 5d was prepared by the general method and recrystallised from MeOH as colourless crystals, m.p. 100-101°C (Found: C, 54.22%; H, 4.67%; N, 6.90%. $C_{18}H_{18}O_4N_2Cl_2$ requires C, 54.42%; H, 4.57%; N, 7.05%); $\upsilon_{max}(CHCl_3)/cm^{-1}$ 1711 (C=O); $\delta_H(CDCl_3)$ 1.18

(3H, t), 4.14 (2H, br sextet [overlapping AB system]), 7.37 (2H, d, *m*-ArH), 7.63 (2H, d, *o*-ArH); $\delta_C(CDCl_3)$ 13.49 (s), 72.00 (s), 128.46 (s), 130.03 (m), 138.36 (s), 168.73 (s).

N,N'-*Diethoxy*-N,N'-*di*-(p-*nitrobenzoyl*)*hydrazine* **5e** was prepared by the general method and recrystallised from MeOH as colourless crystals, m.p. 116-117°C (Found: C, 51.61%; H, 4.34%; N, 13.30%. $C_{18}H_{18}O_8N_4$ requires C, 51.68%; H, 4.34%; N, 13.39%); $\upsilon_{max}(CHCl_3)/cm^{-1}$ 1722 (C=O); $\delta_H(CDCl_3)$ 1.19 (3H, t), 4.17 (2H, br sextet [overlapping AB system]), 7.85 (2H, d, *o*-ArH), 8.28 (2H, d, *m*-ArH); $\delta_C(CDCl_3)$ 13.44 (s), 72.42 (s), 123.38 (m), 129.49 (m), 137.88 (s), 149.64 (s), 167.85 (s).

N,N'-*Diacetyl*-N,N'-*di*-(p-*methoxybenzyloxy*)*hydrazine* **6a.** Prepared by the general method as a yellow oil. $\upsilon_{max}(CHCl_3)/cm^{-1}$ 1733/1707 (C=O); $\delta_H(CDCl_3)$ 2.10 (3H, s), 3.81 (3H, s), 4.98 (2H, 2 x br d [AB system]), 6.89 (2H, d, *o*-ArH), 7.35 (2H, d, *m*-ArH); $\delta_C(CDCl_3)$ 21.06 (s), 55.19 (s), 77.30 (s), 113.86 (m), 131.12 (m), 160.02(s).

N,N'-*Diacetyl*-N,N'-*di*-(p-*methylbenzyloxy*)*hydrazine* **6b** was prepared by the general method as a yellow oil. $\upsilon_{max}(CHCl_3)/cm^{-1}$ 1734/1708 (C=O); $\delta_H(CDCl_3)$ 2.09 (3H, s), 2.33 (3H, s), 4.99 (2H, 2 x d[AB system]), 7.15(2H, d, *o*-ArH), 7.29 (2H, d, *m*-ArH); $\delta_C(CDCl_3)$ 20.97 (s), 53.28 (s), 77.26 (s), 128.97 (m), 138.45 (s), 171.28(s).

N,N'-*Diacetyl*-N,N'-*dibenzyloxyhydrazine* **6c** was prepared by the general method as a yellow oil. $\upsilon_{max}(CHCl_3)/cm^{-1}$ 1735/1711 (C=O); $\delta_H(CDCl_3)$ 2.10 (3H, s), 5.04 (2H, 2 x d[AB system]), 7.35(5H, m); $\delta_C(CDCl_3)$ 21.36 (s), 77.96 (m), 128.85 (m), 135.01 (s), 149.25(s).

N,N'-*Diacetyl*-N,N'-*di*-(p-*chlorobenzyloxy*)*hydrazine* **6d** was prepared by the general method as a yellow oil. $\upsilon_{max}(CHCl_3)/cm^{-1}$ 1738/1715 (C=O); $\delta_H(CDCl_3)$ 2.12 (3H, s), 4.98 (2H, 2 x d[AB system]), 7.32(4H, s); $\delta_C(CDCl_3)$ 20.91 (s), 53.35 (s), 76.58 (s), 128.55 (m), 130.50 (m), 133.02 (s), 134.56 (s), 171.35(s).

N,N'-*Diacetyl*-N,N'-*di*-(p-*nitrobenzyloxy*)*hydrazine* **6e** was prepared by the general method as pale yellow crystals, m.p. 127-128°C; $\upsilon_{max}(CHCl_3)/cm^{-1}$ 1744/1723 (C=O); $\delta_H(CDCl_3)$ 2.19 (3H, s), 5.14 (2H, 2 x d[AB system]), 7.57 (2H, d, *o*-ArH), 8.23 (2H, d, *m*-ArH); $\delta_C(CDCl_3)$ 21.11 (s), 33.13 (s), 76.17 (s), 123.75 (m), 129.46 (m), 148.06 (s).

Kinetic Studies.

The thermal decomposition of **2** was carried out at several temperatures in mesitylene. The rates were measured by analytical HPLC through integration of the hydrazine responses and employing diphenyl as an internal standard, or where appropriate, by ^1H NMR through integration of acetyl methyl singlet. In the HPLC method, 0.2-0.4 g of hydrazine and 0.02 g of diphenyl were dissolved in mesitylene (7 mL) in a flask, which was placed in a constant temperature bath. The disappearance of hydrazine was recorded on an analytical HPLC at various time intervals. In the ^1H NMR method, 0.04 g of hydrazine was dissolved in mesitylene (3 mL) in an NMR tube. ^1H NMR spectra were acquired automatically at pre-programmed intervals and the peak areas for the acetyl methyl singlet were recorded by integration. Four temperatures between 313 and 373K were used for each hydrazine. The rate constants at different temperatures are given in Table 4 and Table 5 while rate constants in tetralin and cyclohexanone are given in Table 6.

Table 4. Rate Constants (s^{-1}) for Decomposition of *N,N'*-Dibenzoyl-*N,N'*-diethoxyhydrazines **5** in Mesitylene.[a]

R	10^5k_{313}	10^5k_{325}	10^5k_{335}	10^5k_{345}	10^5k_{355}
p-$CH_3OC_6H_4$	—	16.38	41.10	137.50	344.00
p-$CH_3C_6H_4$	2.69	11.70	25.61	109.70	—
C_6H_5	—	7.54	22.49	54.71	184.00
p-ClC_6H_4	—	9.51	29.70	90.78	277.10
p-$NO_2C_6H_4$	—	5.29	15.46	48.43	134.40

[a] HPLC method

Table 5. Rate Constants (s^{-1}) for Decomposition of *N,N'*-Diacetyl-*N,N'*-dibenzyloxyhydrazines **6** in Mesitylene.

R'	10^5k_{333}	10^5k_{340}	10^5k_{343}	10^5k_{350}	10^5k_{353}	10^5k_{360}	10^5k_{363}	10^5k_{370}	10^5k_{373}
p-$CH_3OC_6H_4CH_2$[a]	—	1.06	—	3.16	—	9.20	—	25.75	—
p-$CH_3C_6H_4CH_2$[b]	—	—	2.20	—	7.46	—	24.34	—	76.74
$PhCH_2$[b]	—	—	2.64	—	8.33	—	21.43	—	68.80
p-$ClC_6H_4CH_2$[b]	1.24	—	3.68	—	12.14	—	53.13	—	—
p-$NO_2C_6H_4CH_2$[a]	—	4.37	—	11.86	—	30.74	—	73.99	—

[a] HPLC method; [b] ^1H NMR method

Table 6. Rate Constants (s^{-1}) for Decomposition of *N,N'*-Dibenzoyl-*N,N'*-diethoxyhydrazine.[a]

T/K	$10^5k_{mesitylene}$	$10^5k_{tetralin}$	$10^5k_{cyclohexanone}$
325	7.54	7.21	8.01
335	22.49	29.65	24.72
345	54.71	36.63	50.26
355	183.96	135.35	162.42

[a] HPLC method

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