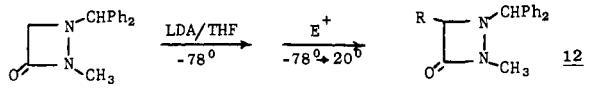
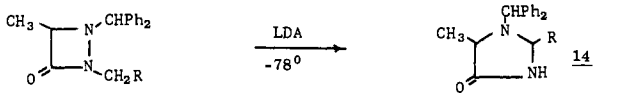
Scheme IV



	R	mp, °C	Yield, %
a,	CH_3	138-140	79
b,	$CHOHCH_3$	146-148	50
c,	CHOHPh	199-199.5	80
d,	$COOC_2H_5$	oil	70

Scheme V



	R	mp, °C	Yield, %
12a (R = H)	a, H	148-149	61
13a (R = CH_3)	b, CH_3	173.5-174	61
13b (R = Ph)	c, Ph	168-170	77

in-6-one (**11a**). Similarly, treatment of **9** with benzoyl chloride or benzyl chloroformate[6] in the presence of 2,6-lutidine gives **11b** and **11c**, respectively. Condensation of **9** with *p*-tolyl isocyanate leads directly to 4-benzhydryl-4,5-dihydro-2-(4-methylanilino)-1,3,4-oxadiazin-6-one (**11d**).

N-2 substituted derivatives (**10b–f**) of **9** are readily obtained either by reaction of the thallium(I) salt of **9** with an excess of the appropriate alkyl halide or preferably by reaction of the corresponding lithium salt of **9** (formed with *n*-butyllithium at −78 °C in anhydrous THF) with 1 equiv of the alkyl halide in the presence of 1 equiv of hexamethylphosphoric triamide. Treatment of the sodium salt of **9** (generated with NaH in DMF at 20 °C) with diphenyliodonium chloride provides the N-2 phenyl derivative **10g**. The Michael adduct **10h** is best prepared by addition of a catalytic amount of NaH to a solution of **9** and methyl acrylate in THF.

1-Benzhydryl-2-methyl-1,2-diazetidin-3-one (**10b**) can be readily substituted at C-4 by deprotonation with LDA in anhydrous THF at −78 °C, followed by addition of 1 equiv of methyl iodide (to give **12a**),[7] acetaldehyde or benzaldehyde (to give **12b** and **12c** respectively),[8] or ethyl chloroformate (to give **12d**). Remarkably, addition of 1 equiv of LDA to a solution of **12a** in anhydrous THF at −78 °C brings about *instantaneous ring expansion* to 1-benzhydryl-5-methylimidazolidin-4-one (**14a**); analogous ring expansions are observed with **13a** and **13b**, giving **14b** and **14c**, respectively. In each case the methylene group adjacent to N-2 is incorporated into the 2-position of the imidazolidinone ring. The extraordinary ease with which this reaction takes place is probably due to formation of a dipole-stabilized anion[10] derived from deprotonation of the methylene group attached to N-2; no deprotonation at C-4 or the benzhydryl methine position appears to take place, since no deuterium incorporation results from a D_2O quench of the reaction mixture. It is not known whether N–N bond cleavage is homolytic or heterolytic, but experiments are in progress to establish this point.

Since hydrolysis of these cyclic animals (e.g., **14**) gives aldehydes derived from the primary alkyl halides employed for N-2 alkylation of the precursor diazetidinone, this sequence of mild reactions holds promise as a general method for effecting the conversion of RCH_2X to RCHO.

(6) This ring expansion can also be carried out by treatment of the lithium salt of **9** with benzyl chloroformate at −78 °C for 2 min.

(7) This compound was prepared independently by sodium borohydride reduction of **1b**, followed by alkylation with methyl iodide.

(8) The aldehyde adducts **12b** and **12c** are formed as diastereomeric mixtures. A single recrystallization of **12b** (shrinks at 140 °C, mp 146–148 °C) failed to separate the diastereomers, while recrystallization of crude **12c** resulted in separation of the major diastereomer, mp 199–199.5 °C, in 80% yield.

(9) Yields of recrystallized analytically pure material. Crude yields appear (IR, TLC) to be quantitative.

(10) See: Beak, P.; Reitz, D. B. *Chem. Rev.* **1978**, *78*, 275–316.

3-Oxo-1,2-diazetidinium Tosylate[1]

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We describe in this communication the preparation of the novel small-ring heterocycle 3-oxo-1,2-diazetidinium tosylate (**2**) and our preliminary investigations of its utility for the preparation of several prototype fused aza-β-lactams, pyrazoles, and 4,5-dihydro-1,3,4-oxadiazin-6-ones.[2]

Stirring a solution of 1-(diphenylmethylene)-3-oxo-1,2-diazetidinium inner salt[3] (**1a**) with exactly 1 equiv of *p*-toluenesulfonic acid monohydrate in dry dichloromethane for 1 h at room temperature results in the separation of 3-oxo-1,2-diazetidinium tosylate (**2**), mp 147–149 °C dec (90%; IR 1820 cm^{-1}). Treatment of **2** with aromatic aldehydes in the presence of sodium bicarbonate in DMF or with ketones in the presence of sodium bicarbonate and activated 3-Å molecular sieves effects reconversion to azomethine ylides (**1b–j**). Aromatic aldehydes give only the *Z* isomers **1b–e**, while ketones invariably give mixtures of both possible stereoisomers. The isomers of ylide **1f** were separated by semi-preparative HPLC and found to isomerize very slowly upon standing in chloroform at room temperature.

No analogous azomethine ylide is isolated from the reaction of **2** with pivaldehyde; instead, the dimer **3**, mp 260–262 °C (20%), is formed.[4,5] Treatment of ylide **1b** with $BF_3{\cdot}Et_2O$ or *p*-toluenesulfonic acid monohydrate provides a different type of dimer **4**, mp 139–140 °C (19%), which we suggest may be formed as depicted below.

Addition of methylmagnesium bromide to the azomethine ylides **1i,j** gives, after purification by column chromatography, 1-substituted 1,2-diazetidinones (**5a,b**) as colorless gums. Although crystalline 1-substituted 1,2-diazetidinones appear to be indefinitely stable, these noncrystalline samples slowly undergo a virtually quantitative transformation to eight-membered-ring dimers (**6a,b**).

The azomethine ylides **1b–d** react smoothly at 20 °C with 1-pyrrolidinocyclopentene to afford excellent yields of adducts **7**. The potential of this remarkably simple ring annulation for the construction of highly strained aza analogues of the β-lactam antibiotics is under active investigation.

3-Oxo-1,2-diazetidinium tosylate (**2**) can also be employed for the synthesis of heterocycles no longer containing the aza-β-lactam ring. Thus, reaction of **2** with acetylacetone in methanol at room temperature gives the methyl ester of 3,5-dimethylpyrazole-1-acetic acid (**9**), mp 36–37 °C (41%).[6] Ylide **8**, prepared independently by condensation of **2** with acetylacetone in DMF in the presence of sodium bicarbonate, is also smoothly converted to **9** (70%) with

(1) This work was supported in part by grants to Princeton University from Eli Lilly & Company and the National Science Foundation (Grant CHE-7918676). Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

(2) Structural assignments for all new compounds reported are supported by microanalytical and/or mass spectral, IR, and NMR data. We are indebted to Mary Baum of this department for invaluable aid in the determination and interpretation of the ^1H and ^{13}C NMR spectra.

(3) (a) Greenwald, R. B.; Taylor, E. C. *J. Am. Chem. Soc.* **1968**, *90*, 5272–5273. (b) Taylor, E. C.; Haley, N. F.; Clemens, R. J. *J. Am. Chem. Soc.*, in press.

(4) Although dimer **3** has four chiral centers, the simple nature of its ^1H NMR spectrum [($CDCl_3$) δ 5.06 (2 H, d, *J* = 14Hz), 4.23 (2 H, d, *J* = 14Hz), 3.65 (2 H, s), 1.15 (18 H, s)] and ^{13}C NMR spectrum (δ 164.6, 79.0, 63.1, 37.5, 28.1) suggests that only one centrosymmetric diastereoisomer of **3** is formed.

(5) Azomethine imine ylides derived from aliphatic aldehydes are known to dimerize. See: Dorn, H.; Otto, A. *Chem. Ber.* **1968**, *101*, 3287–3301. Grashey, R.; Huisgen, R.; Sun, K. K.; Moriarty, R. M. *J. Org. Chem.* **1965**, *30*, 74–79.

(6) We are indebted to Professor Eldon H. Sund, on leave from Midwestern State University, Wichita Falls, TX, for carrying out this experiment.

(7) Only **10d** was formed under both sets of reaction conditions; no isomerization to **11** was observed.

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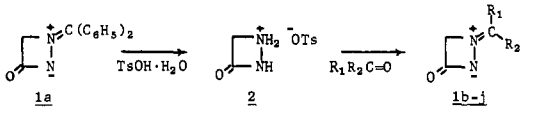
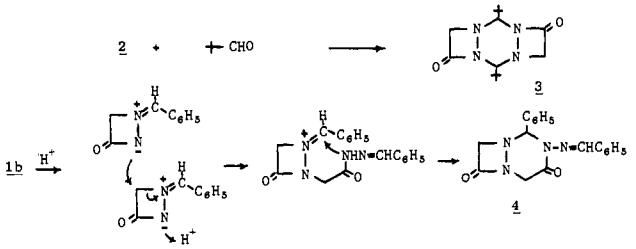
Scheme I



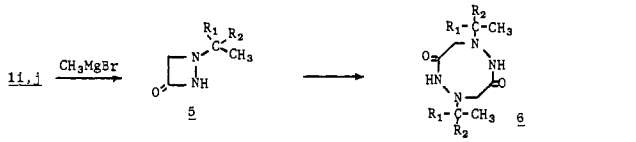
1	R_1	R_2	mp, °C	Yield, %	E/Z ratio[a]
a	C_6H_5	C_6H_5			
b	H	C_6H_5	196-198 d	57	
c	H	$C_6H_4OCH_3$-p	190-191 d	71	
d	H	C_6H_4Cl-p	220 d	77	
e	H	$C_6H_4CH{=}CH$	199-200 d	99	
f	~CH_3	~C_6H_5		55	30/70
g	$CH_2C_6H_5$	$CH_2C_6H_5$	87-89	42	
h	~CH_3	~$CH(OCH_3)_2$		36	85/15
i	~CH_3	~$CH_2CH(OCH_3)_2$		68	50/50
j		$-C_5H_{10}-$	157-159 d	90	

[a] As isolated from the reaction.

Scheme II

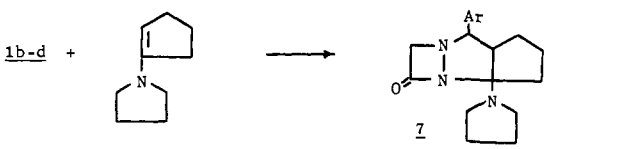


Scheme III



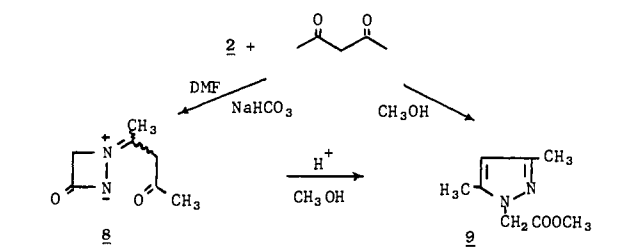
R_1	R_2	mp, °C	Yield, %
CH_3	$CH_2CH(OCH_3)_2$	149-151	53
	$-C_5H_{10}-$	310-315	36

Scheme IV



Ar	mp, °C	Yield, %
C_6H_5	138-140	97
$C_6H_4OCH_3$-p	117-119	90
C_6H_4Cl-p	136-137	91

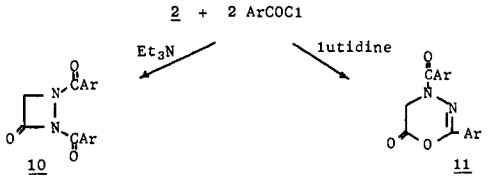
Scheme V



acidic methanol at room temperature (it is stable in neutral methanol).

It was not possible to monoacylate 3-oxo-1,2-diazetidinium tosylate (**2**) under a variety of reaction conditions. However, 1,2-diaroyl-1,2-diazetidinones (**10**) are formed on treatment of **2** with 2 equiv of an aroyl chloride in the presence of triethylamine in dichloromethane at −78 °C. When 2,6-lutidine is used as the base, ring expansion to 2-aryl-4-aroyl-4,5-dihydro-1,3,4-oxadiazin-6-ones (**11**) occurs. We are currently exploring the conversion of these now readily accessible heterocycles to 1,3,4-oxadiazin-6-ones, which should be of considerable interest as precursors to pyridazines, 2-pyrones, and unusually substituted acetylenes.

Scheme VI



	Ar	mp, °C	Yield, %	mp, °C	Yield, %
a	C_6H_5	111-113	42	91-93	35
b	$C_6H_4NO_2$-p	110 d	21	158 d	43
c	$C_6H_4OCH_3$-p	142 d	23	125-127	64
d	$C(CH_3)_3$	70-70.5	70	ref. 7	

Stereochemistry of an Alkoxide-Accelerated [1,3] Migration

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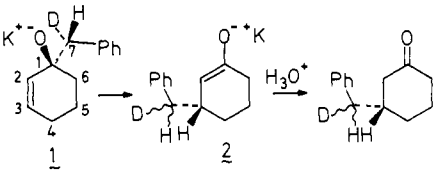
In 1975 Evans and Golob[1] reported the dramatic acceleration of a [3,3]-sigmatropic rearrangement caused by an alkoxide substituent. Subsequently it was found that similar rate enhancements occur for [1,3][2-6] and [1,5][7] migrations. In this communication we turn our attention to the stereochemistry of the alkoxide-accelerated [1,3] rearrangement **1** → **2**.



Recent work by Evans et al.[8] has shown that the potassium alkoxide substituent does not alter the stereochemistry of a [3,3]-sigmatropic migration. However, at the inception of the present study we had reason to believe that this constancy of mechanism upon substitution need not be universally true and that the [1,3]-sigmatropic shift might be a case where the rate acceleration would be accompanied by a change in stereochemistry.

The basis for this belief was a simple model for substituent effects on pericyclic reactions that we had found to be useful for interpreting a number of experimental observations[9,10] including

(1) Evans, D. A.; Golob, A. M. *J. Am. Chem. Soc.* **1975**, *97*, 4765–4766.
(2) Franzus, B.; Scheinbaum, M. L.; Waters, D. L.; Bowlin, H. B. *J. Am. Chem. Soc.* **1976**, *98*,, 1241–1247.
(3) Thies, R. W.; Seitz, E. P. *J. Chem. Soc., Chem. Commun.* **1976**, *846*–847.
(4) Wilson, S. R.; Mao, D. T. *J. Chem. Soc., Chem. Commun.* **1978**, 479–480.
(5) Laird, T.; Ollis, W. D.; Sutherland, I. O. *J. Chem. Soc., Perkin Trans. 1*, **1980**, 2033–2048.
(6) Danheiser, R. L.; Martinez-Davila, C.; Auchus, R. J.; Kadonaga, J. T. *J. Am. Chem. Soc.* **1981**, *103*, 2443–2446.
(7) Paquette, L. A.; Crouse, G. D.; Sharma, A. K. *J. Am. Chem. Soc.* **1980**, *102*, 3972–3974.
(8) Evans, D. A.; Nelson, J. V. *J. Am. Chem. Soc.* **1980**, *102*, 774–782.

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