1 H, CHO), 7.0–7.5 (m, 4 H, aromatic), 9.2 (s, 3 H, aromatic).

Anal. Calcd for $C_{18}H_{14}N_2O_6$: C, 61.02; H, 3.98. Found: C, 60.87; H, 4.06.

***endo*-1-Methylbicyclo[3.1.0]hexan-2-yl 3,5-Dinitrobenzoate.** The cyclopropanation of 8.6 g (88 mmol) of 2-methyl-2-cyclopenten-1-ol[8] with 17 g (260 mmol) of zinc dust, 2.6 g (26 mmol) of cuprous chloride, and 47 g (180 mmol) of methylene iodide in 30 mL of ether for 8 h in the usual manner[7] gave after workup and distillation 6.0 g (61% yield) of *endo*-1-methylbicyclo[3.1.0]hexan-2-ol: bp 50–52 °C (4.5 mm); n^{23}_D 1.4690°; NMR (CCl_4) δ 0.2 (m, 1 H, cyclopropyl), 0.7 (m, H, cyclopropyl), 1.0 (m, 1 H, cyclopropyl), 1.2 (s, 3 H, CH_3), 1.4–1.9 (m, 4 H), 3.2 (brs, 1 H, OH), 4.1 (m, 1 H, CHOH).

Following the usual procedure, 2.0 g (18 mmol) of *endo*-1-methylbicyclo[3.1.0]hexan-2-ol and 5.5 g (23 mmol) of 3,5-dinitrobenzoyl chloride in 50 mL of pyridine gave, after recrystallization from 100 mL of methylcyclohexane, 3.6 g (66% yield) of the ester as small needlelike, white crystals: mp 107–110 °C; NMR ($CDCl_3$) δ 0.5 (m, 1 H, cyclopropyl), 0.9 (m, 1 H, cyclopropyl), 1.2 (s, 3 H, CH_3), 1.0–2.3 (m, 5 H), 5.6 (t, 1 H, J = 7 Hz, CHO), 9.2 (s, 3 H, aromatic).

Anal. Calcd for $C_{14}H_{14}N_2O_6$: C, 55.03; H, 4.61. Found: C, 54.90; H, 4.63.

***exo*-1-Methylbicyclo[3.1.0]hexan-2-yl 3,5-Dinitrobenzoate.** Equilibration of 3.6 g (28 mmol) of *endo*-1-methylbicyclo[3.1.0]hexan-2-ol using 5.5 g (27 mmol) of aluminum isopropoxide, 65 mL of isopropyl alcohol, and 0.25 mL of acetone for 3 days at 100–105 °C in a Pyrex ampule gave after workup and distillation 2.9 g (81% yield) of a 70:30 mixture of *endo*- and *exo*-1-methylbicyclo[3.1.0]hexan-2-ols. The exo alcohol was isolated by preparative GLC: NMR (CCl_4) δ 0.2 (d, 2 H, J = 6 Hz, cyclopropyl), 1.2 (s, 3 H, CH_3), 0.9–2.2 (m, 6 H), 3.9 (m, 1 H, CHO).

Following the usual procedure, the reaction of 0.48 g (4.3 mmol) of *exo*-1-methylbicyclo[3.1.0]hexan-2-ol and 1.3 g (5.6 mmol) of 3,5-dinitrobenzoyl chloride in 30 mL of pyridine for 2 h at 0 °C gave, after recrystallization from 40 mL of methylcyclohexane, 0.90 g (69% yield) of the *exo*-3,5-dinitrobenzoate: mp 120–120.5 °C; NMR (CCl_4) δ 0.5 (d, 2 H, J = 5.5 Hz, cyclopropyl), 1.2 (s, 3 H, CH_3), 1.3–2.1 (m, 5 H), 5.4 (m, 1 H, CHO), 9.2 (s, 3 H, aromatic).

Anal. Calcd for $C_{14}H_{14}N_2O_6$: C, 55.03; H, 4.61. Found: C, 54.80; H, 4.64.

Kinetic Studies. The 80 vol % aqueous acetone solvent, sodium methoxide in methanol titrant, kinetic procedures, and controls were similar to those described previously.[2,3]

Hydrolysis Products. Hydrolysis product determinations and controls were similar to those described previously.[2,3] The *endo*- and *exo*-2-methylcycloprop[2,3]inden-1-yl 3,5-dinitrobenzoates gave only the corresponding endo and exo alcohols as products. These were readily determined by using ^{1}H NMR techniques as described earlier. The hydrolysis products of the *endo*- and *exo*-1-methyl-2-bicyclo[3.1.0]hexyl 3,5-dinitrobenzoates were determined by GLC on a 20% 3-nitro-3-methylpimelonitrile column to be a mixture of the *endo*- and *exo*-1-methyl-2-bicyclo[3.1.0]hexanols together with a major amount of 3-methyl-3-cyclohexen-1-ol. The structure of the latter material was demonstrated by comparing its GLC retention time and ^{1}H NMR spectrum with those of an authentic sample prepared according to literature procedures:[10] NMR (CCl_4) δ 1.3–2.4 (m, 6H), 1.6 (s, 3 H, CH_3), 3.4 (s, 1 H, OH), 3.7 (m, 1 H, CHOH), 5.3 (m, 1 H, CH=C).

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Synthesis of Cyclic Azomethine Imines from Aza β-Lactams. Conversion of 3-Oxo-1,2-diazetidinium Tosylates into 1-Substituted 3-Oxo-1,2-diazetidinium Inner Salts[1,2]

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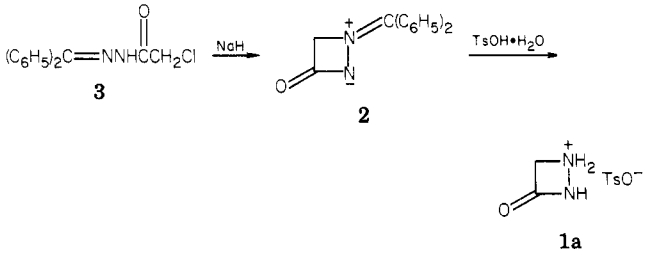
Dehydrohalogenation of (α-haloacyl)hydrazones of benzophenone gives 1-(diphenylmethylene)-3-oxo-1,2-diazetidinium inner salts (**2**, **5**, **6**), which are hydrolyzed with 1 molar equiv of *p*-toluenesulfonic acid monohydrate in CH_2Cl_2 to give 3-oxo-1,2-diazetidinium tosylates (**1**). Several procedures have been found for the transformation of these aza β-lactams to previously inaccessible 3-oxo-1,2-diazetidinium inner salts (**4**) by reaction with aromatic aldehydes, aralkyl ketones, and dialkyl ketones. 2,7-Disubstituted 1,3,6,8-tetraazatricyclo[6.2.0.0^{3,6}]decane-4,9-diones (**11**), which are dimers of ylides corresponding to **4**, are obtained by condensation of **1** with aliphatic aldehydes.

We have recently described a simple synthesis of the novel aza β-lactam 3-oxo-1,2-diazetidinium tosylate (**1a**) by stoichiometric acid-catalyzed hydrolysis of 1-(diphenylmethylene)-3-oxo-1,2-diazetidinium inner salt (**2**). This latter compound, as well as a number of related 1-(diarylmethylene) derivatives, resulted from an unexpectedly facile intramolecular dehydrohalogenation of (α-chloroacyl)hydrazones of the respective diaryl ketones (e.g., **3**).[3] Since preliminary experiments have shown that



3 2 1a

ylides such as **2**, as well as the parent 3-oxo-1,2-diazetidinium tosylate (**1a**), are versatile, reactive precursors of

(1) We are deeply indebted to Eli Lilly & Co. for their generous financial support of this work.

(2) Preliminary communication: Taylor, E. C.; Davies, H. M. L.; Clemens, R. J.; Yanagisawa, H.; Haley, N. F. *J. Am. Chem. Soc.* **1981**, *103*, 7660–7661.

(3) (a) Taylor, E. C.; Haley, N. F.; Clemens, R. J. *J. Am. Chem. Soc.* **1981**, *103*, 7743–7752. (b) Greenwald, R. B.; Taylor, E. C. *Ibid.* **1968**, *90*, 5272–5273.

0022-3263/83/1948-4567$01.50/0

aza analogues of the β-lactam antibiotics, we have investigated in some detail an alternate and considerably more flexible route to ylides related to **2**.

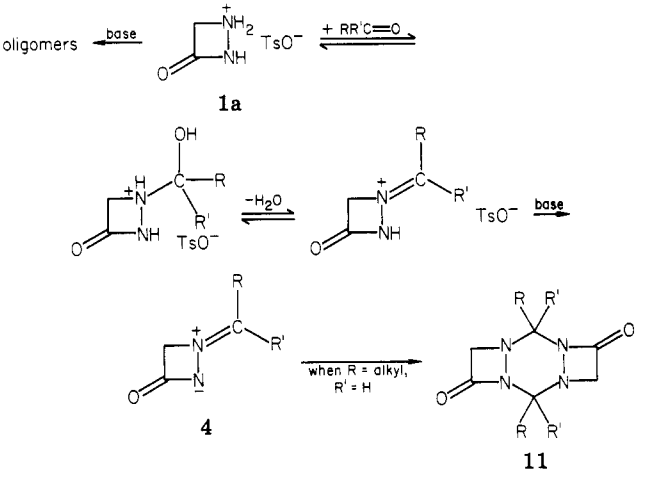
The condensation of 3-pyrazolidinones with carbonyl compounds to give pyrazolidinium ylides has been extensively studied.[4] Extension of this simple ylide synthesis to 1,2-diazetidinone, its lower homologue, would provide access to a large number of variously substituted ylides related to **2** but unavailable by the intramolecular dehydrohalogenation route. We describe below the scope and limitations of condensation reactions of 3-oxo-1,2-diazetidinium tosylates (**1**) with aromatic and aliphatic aldehydes and ketones to give new 3-oxo-1,2-diazetidinium ylides (**4**) related to **2**. Subsequent papers will describe the utilization of these highly reactive cyclic azomethine imines for the construction of both mono- and bicyclic bridgehead analogues of the β-lactam antibiotics.

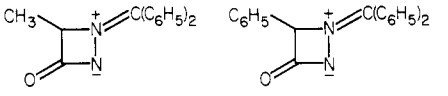
3-Oxo-1,2-diazetidinium tosylate (**1a**) is soluble only in polar solvents, and it decomposes rapidly upon treatment with base. Thus, the reaction conditions employed previously for the formation of 3-oxo-1,2-pyrazolidinium ylides from 3-pyrazolidinone (free base) were not applicable to the fragile diazetidinone system.[5] However, addition of benzaldehyde to a solution of **1a** in DMF at 0 °C, followed after 5 min by the addition of solid sodium bicarbonate and eventual aqueous workup (method A), led to the formation in excellent yield of a crystalline colorless solid whose IR spectrum (1760 cm^{-1}) showed that the four-membered aza β-lactam ring was still intact. The identity of this product as the desired ylide **4a** was confirmed by its ^1H NMR spectrum, which showed the characteristic downfield shift of the C-4 methylene protons, as well as a downfield shift of the two aromatic ortho protons, a consequence of the syn positioning of the aromatic ring with respect to the negatively charged nitrogen at position 2 (i.e., the product must be the *Z* isomer).[6]

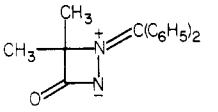
Other aromatic and heterocyclic aldehydes reacted similarly; yields varied with structure. For example, ortho-substituted benzaldeydes gave much lower yields of ylides than the corresponding para-substituted isomers (Table I). *p*-Nitrobenzaldehyde failed to give a stable, isolable ylide in contrast to its reaction with 3-pyrazolidinone.[4c] Both furfural and thiophene-2-carboxaldehyde gave the corresponding ylides **4j** and **4k** in 75% and 48% yields, respectively; once again only the *Z* isomers were isolated. Curiously enough, the *Z* ylide **4l** derived from condensation of **1a** with cinnamaldehyde rearranged in the presence of aluminum chloride to give predominantly the *E* isomer, a transformation that was clearly evident from the NMR spectrum of the rearranged product (see Experimental Section). An attempt to effect the same *Z* to *E* isomerization with the benzaldehyde ylide **4a** led only to ring opening to give the (α-chloroacetyl)hydrazone of benzaldehyde.

Several 4-substituted 3-oxo-1,2-diazetidinium tosylates were prepared by stoichiometric acid-catalyzed hydrolysis of the corresponding 4-substituted 1-(diphenylmethylene)-3-oxo-1,2-diazetidinium inner salts. The C-4 methyl (**5**) and C-4 phenyl (**6**) ylides were prepared as described previously[3] by intramolecular dehydrohalogenation of the corresponding benzophenone (α-haloacyl)hydrazones. 4,4-Dimethyl-3-oxo-1,2-diazetidinium tosylate (**1q**) was obtained by hydrolysis of the corresponding 4,4-dimethyl-3-oxo-1,2-diazetidinium inner salt (**7**), which

Scheme I







was prepared in turn by the method of Warkentin.[7] These 4-substituted derivatives of **1a** condensed satisfactorily with anisaldehyde and with cinnamaldehyde to afford the corresponding *Z* ylides (Table I), although yields decreased with increasing steric bulk at C-4.

We next examined the reaction of 3-oxo-1,2-diazetidinium tosylate (**1a**) with ketones. No ylide could be isolated with benzophenone, even when a large excess of benzophenone was employed, and reaction times were prolonged. A disappointingly low yield of ylide was obtained with 1,3-diphenylacetone under the reaction conditions established above (method A), and only a slight improvement in yield resulted from extended reaction times. These results can be rationalized as follows. Since 3-oxo-1,2-diazetidinium tosylate (**1a**) is unstable in base, we assume that initial condensation between N-1 of **1a** and the carbonyl component occurs before the addition of base (see Scheme I); i.e., it is acid catalyzed. In the case of aromatic aldehydes, the equilibrium between **1a** and the aldehyde apparently lies well to the right, but this is presumably not the case for the much less reactive ketones. Consistent with this interpretation is the observation that the use of activated molecular sieves in the reaction of 1,3-diphenylacetone with **1a** in DMF resulted in a dramatic improvement in the yield of the isolated ylide **4s**.

As can be seen from Table I, this DMF/molecular sieves/sodium bicarbonate procedure (method B) proved to be effective with a number of additional dialkyl and aralkyl ketones. Acetophenone gave a 70:30 mixture of *Z* and *E* ylide isomers, which was clearly revealed in the NMR spectrum of the product mixture. It should be noted that aliphatic as well as aromatic protons are deshielded

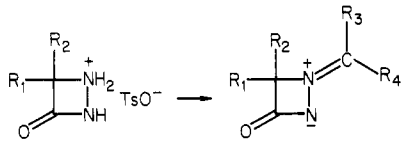
(4) (a) Gotfresden, W. O.; Vangedal, S. *Acta Chem. Scand.* **1955**, *9*, 1498–1509. (b) Howard, J. C.; Gever, G.; Wei, P. J. *J. Org. Chem.* **1963**, *28*, 868–870. (c) Dorn, H.; Otto, A. *Chem. Ber.* **1968**, *101*, 3287–3301. (d) Geissler, G.; Angermullen, K.; Behning, I.; Fürneisen, S.; Fust, W.; Hippius, M.; Müller, B.; Schauer, G.; Slezak, H.; Tomascheswki, G. *Z. Chem.* **1981**, *21*, 356–357.

(5) See ref 4c for experimental procedures.

(6) A more detailed explanation of this assignment, based on analogy with an ylide whose structure was confirmed by X-ray analysis, can be found in ref 3a.

(7) Ip, P. C.; Ramakrishnan, K.; Warkentin, J. *Can. J. Chem.* **1974**, *52*, 3671–3675.

Table I. 1-Substituted 3-Oxo-1,2-diazetidinium Inner Salts[a]



compd	R_1	R_2	R_3	R_4	method[a]	t_1,[b] min	t_2,[b] min	Z/E[c]	yield, %	mp, °C
a	H	H	H	C_6H_5	A	5	60	100/0	57	195-198 dec
b	H	H	H	4-$Me_2NC_6H_4$	A	5	60	100/0	74	210-212
c	H	H	H	4-$MeOC_6H_4$	A	5	60	100/0	71	190-191 dec
d	H	H	H	4-MeC_6H_4	A	5	60	100/0	58	196-197 dec
e	H	H	H	4-ClC_6H_4	A	5	60	100/0	70	220 dec
f	H	H	H	4-$MeO_2CC_6H_4$	A	5	60	100/0	80	220-221 dec
g	H	H	H	2-MeC_6H_4	A	5	60	100/0	38	139-140
h	H	H	H	2-ClC_6H_4	A	5	60	100/0	4	*d*
i	H	H	H	3,4-$(MeO)_2C_6H_3$	A	5	60	100/0	53	198-200 dec
j	H	H	H	2-furyl	A	5	60	100/0	75	198 dec
k	H	H	H	2-thienyl	A	5	60	100/0	48	199-200 dec
l	H	H	H	cinnamyl	A	5	60	100/0	92[e]	206 dec
m	CH_3	H	H	4-$MeOC_6H_4$	A	5	60	100/0	64	204-205 dec
n	CH_3	H	H	cinnamyl	A	5	60	100/0	85	212-213
o	C_6H_5	H	H	4-$MeOC_6H_4$	A	5	60	100/0	50	188 dec
p	C_6H_5	H	H	cinnamyl	A	5	60	100/0	64	201 dec
q	CH_3	CH_3	H	4-$MeOC_6H_4$	A	5	60	100/0	20	199 dec
r	CH_3	CH_3	H	cinnamyl	A	5	60	100/0	70	167-168
s	H	H	$C_6H_5CH_2$	$C_6H_5CH_2$	A	5	60		15[f]	187-189
					A	120	120		27[f]	
					B	120	120		52,[f] 42	
t	H	H	CH_3	$C_6H_5CH_2$	A	5	60		64	gum
					A	120	120		66	
					B	120	120	50/50	83	
u	H	H	CH_3	cinnamyl	A	5	60		64	
					A	120	120		63	
					B	120	120	30/70	75	195-197[g]
v	H	H	CH_3	C_6H_5	B	120	120	70/30	55	ref 3a
w	H	H	CH_3	4-$MeOC_6H_4$	B	120	120	85/15	50	*d*
x	H	H		α-tetralone	C	120	120	60/40	15	softens >135[h]
y	CH_3	CH_3	CH_3	$C_6H_5CH_2$	B	120	120	60/40	41	*d*
z	H	H	CH_3	$(MeO)_2CHCH_2$	B	120	120	50/50	68	gum
aa	H	H	CH_3	$(MeO)_2CH$	B	100	120	15/85	36	gum
ab	H	H		c-C_5H_{10}	B	120	120		71	157-159 dec
					C	120	120		90	
					D	1	60		71	
ac	CH_3	H		c-C_5H_{10}	C	120	120		99	150-151
ad	C_6H_5	H		c-C_5H_{10}	C	120	120		72	172-173
ae	CH_3	CH_3		c-C_5H_{10}	C	120	120		67	156-157
af	H	H		c-C_4H_8	B	120	120		33	109-112
ag	H	H	C_2H_5	C_2H_5	B	120	120		60	gum
ah	H	H	CH_3	CH_3	B	120	120		trace	
					D	1	60		90	>90 dec
ai	H	H	CH_3	CH_2=CH	D	1	60	25/75	27	149[g]
aj	H	H	CH_3	C_2H_5OCO	C	120	120	45/55	55	gum
ak	H	H	CH_3	CH_3COCH_2	C	120	120	70/30	37	oil

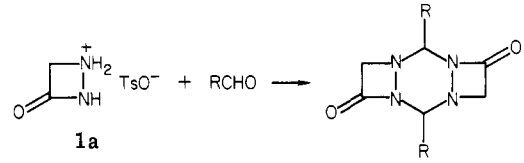
[a] See Experimental Section for methods A-D. [b] t_1 = time between addition of the carbonyl compound and sodium bicarbonate, t_2 = time between addition of sodium bicarbonate and water. [c] The *Z* isomer is the one with the larger (R_4) substituent cis to the anionic nitrogen. [d] Not determined. [e] The *E* isomer, mp 185 °C dec, was obtained in 25% yield by stirring the *Z* isomer with $AlCl_3/CH_2Cl_2$. [f] Yield determined by NMR. [g] *E* isomer. [h] *Z* isomer.

when adjacent to the anionic N-2; this phenomenon greatly facilitates isomer identification. Both the *Z* and *E* isomers of **4v** could be separated and obtained pure by HPLC, but each isomer slowly reverted upon standing in deuteriochloroform to approximately the same mixture of *Z* and *E* isomers obtained in the initial condensation reaction. Mixtures of *Z* and *E* isomers were also obtained with the other unsymmetrical ketones listed in Table I. Ylides derived from ketones proved to be much more soluble in organic solvents than ylides from aromatic aldehydes. In the case of ylides such as **4z**, **4aa**, **4ab**, **4af**, **4ag**, **4ah**, **4ai**, and **4aj** prepared from low molecular weight aliphatic ketones, reaction workup was complicated by water solubility; products could be isolated only after repeated or continuous extraction, and the ylide **4ak** derived from condensation of **1a** with 2,4-pentanedione required a nonaqueous workup (see Experimental Section for details).

Although a *Z*/*E* isomer ratio of 50:50 was obtained upon condensation of phenylacetone with **1a**, condensation with 4,4-dimethyl-3-oxo-1,2-diazetidinium tosylate (**1q**) shifted the *Z*/*E* isomer ratio to 60:40, consistent with the increase in steric bulk at C-4.

An alternative to the use of molecular sieves to shift the initial hemiaminal equilibrium (Scheme I) provide to be the use of excess ketone (method C). These conditions led to an excellent yield of ylides **4ab** and **4ac** from the condensation of **1a** and **1m** with cyclohexanone. Although only a trace of ylide **4ah** was obtained in an attempted condensation of **1a** with acetone in DMF in the presence of molecular sieves, the desired ylide could be obtained in

Table II. 2,7-Disubstituted 1,3,6,8-Tetraazatricyclo[6.2.0.0^{3,6}]decane-4,9-diones by Condensation of 3-Oxo-1,2-diazetidinium Tosylate with Aliphatic Aldehydes[a]



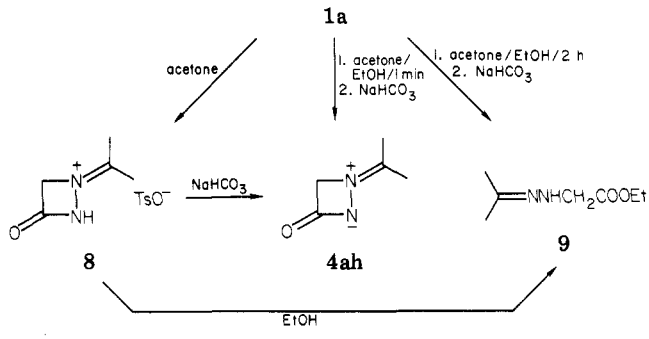
1a

11

compd	R	method[a]	t_1,[b] min	t_2,[b] min	yield, %	mp, °C
a	$(CH_3)_3C$	A	5	60	20	260-262
b	$(c\text{-}C_5H_{10})CH$	A	5	60	39	235 dec
c	$(CH_3)_2CH$	A	5	60	33	188-190
d	$C_6H_5CH_2$	A	5	60	7	222-223
e	CH_3	A	5	60	28	219
		D	1	60	38	

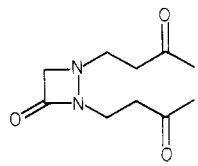
[a] See Experimental Section for Methods A and D. [b] t_1 = time between addition of carbonyl compound and sodium bicarbonate, t_2 = time between addition of sodium bicarbonate and water.

Scheme II



90% yield when the solvent was changed from DMF to ethanol to permit a nonaqueous workup. It is important to note, however, that the former procedure utilizing excess aldehyde or ketone was effective only with highly reactive carbonyl compounds, and that sodium bicarbonate must be added immediately after addition of **1a** to a solution of the aldehyde or ketone in ethanol. Delay in the addition of base led to the formation of hydrazones derived from ethyl hydrazinoacetate (i.e., **9**, Scheme II).

Condensation of 3-oxo-1,2-diazetidinium tosylate (**1a**) with methyl vinyl ketone followed two different reaction pathways, one leading to the expected mixture of *Z* and *E* ylides (**4ai**) and the other giving 1,2-bis(3-oxobutyl)-1,2-diazetidinone (**10**) by double Michael addition.



10

Condensation of pivaldehyde with **1a** under conditions employed successfully above for aromatic aldehydes (method A) resulted in the isolation of a colorless crystalline solid, which was purified by column chromatography. The IR spectrum of this product showed that the aza β-lactam ring had been retained (1762, 1728 cm^{-1}), but its mass spectrum (m^+, *m/e* 280) showed that the molecular weight of the product was twice that of the expected ylide. The simplicity of its ^{1}H and ^{13}C NMR spectra confirmed its identity as **11a**, a head-to-tail centrosymmetric dimer of the expected ylide (see Scheme I)[8]. This same reaction pathway was followed with other aliphatic aldehydes as well, except that mixtures of diastereomers and/or conformers were obtained that exhibited complex ^{1}H and ^{13}C NMR spectra. Dimeric products obtained by this procedure are listed in Table II. Although the reaction of 3-oxo-1,2-diazetidinium tosylate (**1a**) with formaldehyde appeared to follow a similar pathway leading to a head-to-tail dimer, the product was exceptionally unstable to hydrolysis and thus far has been obtained only in an impure form. Further experiments are in progress in an attempt to resolve this experimental difficulty.

Experimental Section

Yields are unoptimized and refer to isolated material (generally once recrystallized or distilled) free from visible impurities in the NMR spectrum, unless otherwise noted. Commercial reagents were utilized without further purification except where specifically mentioned. Molecular sieves were activated by drying in vacuo at 200 °C for 24 h.

Melting points were determined in open capillaries in a Thomas-Hoover apparatus, using analytically pure material, and are uncorrected. Infrared data were measured on a Perkin-Elmer 467 spectrophotometer.

^{1}H NMR data are reported in ppm downfield from Me_4Si as an internal standard, as determined on Perkin-Elmer R-32 or JEOL FX-90Q MHz instruments. ^{13}C NMR data were obtained on the JEOL FX-90Q instrument operating at 23 MHz. Heteronuclear decoupling was used, unless multiplicities, which were determined by off-resonance decoupling, are indicated. Mass spectral data were obtained on an AE-MS9 instrument operating at 70 eV. Peaks of greatest intensity and high mass peaks of importance are listed. HPLC refers to the use of a Perkin-Elmer Series 2 pump, LC-75 spectrophotometric detector and autocontrol, equipped for analytical (PE Silica A-10) and semipreparative operation (Knauer SI100, 16 × 250 mm). Ultraviolet scans were run from 200 to 400 nm in a stopped-flow mode.

Elemental analyses were determined by Eli Lilly and Co., Indianapolis, In, of Hoffmann-La Roche, Inc., Nutley, NJ.

1-(Diphenylmethylene)-3-oxo-1,2-diazetidinium inner salt[3] (**2**) was obtained by an improved procedure for large-scale preparation by adding sodium hydride (0.26 mol, 10.4 g, 60% dispersion in mineral oil) in small portions to a solution of benzophenone (chloroacetyl)hydrazone (**3**; 0.25 mol, 68.3 g) in 600 mL of toluene over 5 min. The yellow solution was then stirred for 18 h at 20 °C, during which time a white precipitate separated. The reaction mixture was filtered, and the isolated solids were stirred for 15 min in 500 mL of water to remove NaCl. Refiltration and air-drying afforded 56.1 g (95%) of crude **2**, mp 188 °C

(8) This dimerization has been observed in 3-oxo-1,2-pyrazolidinium ylides: Dorn, H.; Zubek, A. *Z. Chem.* **1968**, *8*, 270-271.

(9) Correct microanalytical and/or high-resolution MS data were obtained for all compounds reported and are tabluated in the Supplementary Material.

(~90% pure). Recrystallization from toluene then gave 33.2 g (56%) of fine, white needles, mp 194–195 °C dec, which were used in subsequent transformations. (An additional recrystallization from ethanol raised the melting point to 199–200 °C dec.) IR (KBr) 1780 (s), 1765 (s), 1755 (s), 1610, 1085, 1070 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.02 (m, 2 H), 7.55 (m, 8 H), 5.40 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 171.79, 142.30, 137.33, 131.49, 131.11, 131.0, 130.6, 130.4, 129.5, 128.8, 74.88.

3-Oxo-4-phenyl-1,2-diazetidinium tosylate (1o) was prepared on a 0.1-mol scale by hydrolysis of 1-(diphenylmethylene)-3-oxo-4-phenyl-1,2-diazetidinium inner salt[3a] (**6**), as previously described for the preparation of **1a**:[3a] yield 57%, mp 173–175 °C dec; IR (KBr) 3040, 1800 (s), 1125, 1035, 1010 cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 7.46 and 7.08 (d, J = 8 Hz, 2 H), 7.46 (s, 5 H), 6.32 (s, 1 H).

Anal. Calcd for $C_{15}H_{16}N_2O_4S$: C, 56.23; H, 5.03; N, 8.75; S, 10.01. Found: C, 55.94; H, 5.13; N, 8.40; S, 9.62.

4,4-Dimethyl-3-oxo-1,2-diazetidinium tosylate (1q) was prepared by the above procedure on a 0.01-mol scale by hydrolysis of 1-(diphenylmethylene)-4,4-dimethyl-3-oxo-1,2-diazetidinium inner salt[8] (**7**) except that the reaction solvent was 5 mL of CH_2Cl_2 and 5 mL of pentane. A second crop of excellent purity was obtained by the addition of more pentane to the filtrate: yield 55%, mp 159 °C dec; IR (KBr) 3000 (br), 1825 (s), 1210, 1150, 1010, 680, 570 cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 7.51 and 7.11 (d, J = 8 Hz, 2 H), 2.28 (s, 3 H), 1.62 (s, 6 H); ^{13}C NMR (Me_2SO-d_6) δ 168.0, 145.0, 137.8, 127.9, 125.4, 85.4, 20.6, 19.3.

Anal. Calcd for $C_{11}H_{16}N_2O_4S$: C, 48.51; H, 5.92; N, 10.29; S, 11.78. Found: C, 48.43; H, 5.74; N, 10.10; S, 11.47.

Preparation of 3-Oxo-1,2-diazetidinium Inner Salts (4). Four different experimental procedures were used for the synthesis of 3-oxo-1,2-diazetidinium inner salts from 3-oxo-1,2-diazetidinium tosylates (**1**). In method A, the carbonyl compound (5 mmol) in DMF (1–5 mL) was added to a stirred solution of **1** (5 mmol) in DMF (4 mL) at 0 °C. after t_1 (see Table I), sodium bicarbonate (1.0 g) was added and after a further t_2, water (80 mL) was added. In method B, the reaction was carried out as described above, but in the presence of activated 4-Å molecular sieves (5.0 g). After addition of sodium bicarbonate, followed by water (80 mL) and dichloromethane (80 mL), the molecular sieves were filtered and washed with dichloromethane. In method C, the reaction was carried out as described above, but excess carbonyl compound was added as indicated. In method D, the 3-oxo-1,2-diazetidinium tosylate (**1**; 5 mmol) was added to a stirred solution of 1 mL of the carbonyl compound in ethanol (10 mL) at 20 °C. After 1 min, sodium bicaronate (1.0 g) was added and the mixture was stirred for 1 h at 20 °C. Filtration, followed by evaporation of ethanol under reduced pressure, afforded the ylide **4**.

In many cases using methods A–C, the aqueous workup resulted in the formation of a precipitate, which was isolated and dried. If no precipitate formed, the aqueous phase was extracted with dichloromethane. For ylides **4a**, **4aa**, **4ab**, **4af**, and **4ag** it was necessary to saturate the aqueous phase with sodium chloride prior to continuous extraction with dichloromethane. The organic phase was dried ($MgSO_4$), and dichloromethane, DMF, and any excess carbonyl compound were evaporated under reduced pressure.

Ethyl *N*-isopropylidene hydrazinoacetate (8)[10] was prepared by stirring 3-oxo-1,2-diazetidinium tosylate (**1a**; 4 mmol, 1 g) in 0.5 mL of acetone and 10 mL of ethanol for 3 h at 20 °C. Sodium bicarbonate (1 g) was added and stirring was continued for 15 min, after which time the solvent was evaporated and the residue eluted through a short Florisil column with ether to give 0.22 g (35%) of an oil whose spectral properties were identical with those reported.

Registry No. **1a**, 79289-49-9; **1m**, 79289-51-3; **1o**, 87370-90-9; **1q**, 87370-92-1; **2**, 20958-76-3; **3**, 29043-58-1; (*Z*)-**4a**, 80350-92-1; (*Z*)-**4b**, 87393-18-8; (*Z*)-**4c**, 80350-93-2; (*Z*)-**4d**, 87370-93-2; (*Z*)-**4e**, 80350-94-3; (*Z*)-**4f**, 87370-94-3; (*Z*)-**4g**, 87370-95-4; (*Z*)-**4h**, 87370-96-5; (*Z*)-**4i**, 87370-97-6; (*Z*)-**4j**, 87370-98-7; (*Z*)-**4k**, 87370-99-8; (*Z*)-**4l**, 79559-05-0; (*E*)-**4l**, 79559-07-2; (*Z*)-**4m**, 87371-00-4; (*Z*)-**4n**, 87371-01-5; (*Z*)-**4o**, 87371-02-6; (*Z*)-**4p**, 87371-03-7; (*Z*)-**4q**, 87371-04-8; (*Z*)-**4r**, 87371-05-9; **4s**, 80350-96-5; (*Z*)-**4t**, 87371-28-6; (*E*)-**4t**, 87371-06-0; (*Z*)-**4u**, 87371-29-7; (*E*)-**4u**, 87393-19-9; (*Z*)-**4v**, 79289-31-9; (*E*)-**4v**, 80350-95-4; (*Z*)-**4w**, 87371-07-1; (*E*)-**4w**, 87371-08-2; (*Z*)-**4x**, 87371-09-3; (*E*)-**4x**, 87393-20-2; (*Z*)-**4y**, 87371-10-6; (*E*)-**4y**, 87393-21-3; (*Z*)-**4z**, 80351-00-4; (*E*)-**4z**, 80350-99-8; (*Z*)-**4aa**, 80350-98-7; (*E*)-**4aa**, 80350-97-6; **4ab**, 80351-01-5; **4ac**, 87371-11-7; **4ad**, 87371-12-8; **4ae**, 87371-13-9; **4af**, 87371-14-0; **4ag**, 87371-15-1; **4ah**, 87371-16-2; (*Z*)-**4ai**, 87371-18-4; (*E*)-**4ai**, 87371-17-3; (*Z*)-**4aj**, 87371-19-5; (*E*)-**4aj**, 87371-20-8; (*Z*)-**4ak**, 87371-21-9; (*E*)-**4ak**, 87371-22-0; **6**, 79289-83-1; **7**, 54848-25-8; **9**, 4666-64-2; **10**, 87393-22-4; **11a**, 80351-02-6; *cis*-**11b**, 87371-23-1; *trans*-**11b**, 87371-30-0; *cis*-**11c**, 87371-24-2; *trans*-**11c**, 87371-31-1; *cis*-**11d**, 87371-25-3; *trans*-**11d**, 87371-32-2; *cis*-**11e**, 87371-26-4; *trans*-**11e**, 87371-27-5; C_6H_5CHO, 100-52-7; 4-$Me_2NC_6H_4CHO$, 100-10-7; 4-$MeOC_6H_4CHO$, 123-11-5; 4-MeC_6H_4CHO, 104-87-0; 4-ClC_6H_4CHO, 104-88-1; 4-$MeO_2CC_6H_4CHO$, 1571-08-0; 2-MeC_6H_4CHO, 529-20-4; 2-ClC_6H_4CHO, 89-98-5; 3,4-$(MeO)_2C_6H_3CHO$, 120-14-9; C_6H_5CH=$CHCHO$, 104-55-2; $C_6H_5CH_2COCH_2C_6H_5$, 102-04-5; $C_6H_5CH_2COCH_3$, 103-79-7; C_6H_5CH=$CHCOCH_3$, 122-57-6; $C_6H_5COCH_3$, 98-86-2; 4-$MeOC_6H_4COCH_3$, 100-06-1; $(MeO)_2CHCH_2COCH_3$, 5436-21-5; $(MeO)_2CHCOCH_3$, 6342-56-9; $(C_2H_5)_2CO$, 96-22-0; $(CH_3)_2CO$, 67-64-1; CH_2=$CHCOCH_3$, 78-94-4; $C_2H_5OCOCOCH_3$, 617-35-6; $CH_3COCH_2COCH_3$, 123-54-6; $(CH_3)_3CCHO$, 630-19-3; $(CH_3)_2CHCHO$, 78-84-2; $C_6H_5CH_2CHO$, 122-78-1; CH_3CHO, 75-07-0; furfural, 98-01-1; 2-thiophenecarboxaldehyde, 98-03-3; α-tetralone, 529-34-0; cyclohexanone, 108-94-1; cyclopentanone, 120-92-3; cyclohexanecarboxaldehyde, 2043-61-0.

Supplementary Material Available: Microanalytical and or high-resolution MS data for all compounds reported (12 pages). Ordering information is given on any current masthead page.

(10) Dolgii, I. E.; Meshcheryakov, A. P.; Okonnishnikova, G. P.; Shvedova, I. B. *Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.)* **1969**, 2122–2126.