

overnight the mixture was quenched with 0.55 ml each of water and 10% sodium hydroxide, followed by processing as in the natural series to give a colorless, sweet-smelling oil, which failed to crystallize upon trituration with pentane and cooling to -50° , or upon storage for several hours at -30° . The nmr spectrum of the synthetic specimen was virtually identical with that of authentic (–)-hinesol, and the spectra were virtually superimposable. Short-path distillation at $75-80^{\circ}$ (0.03 mm) afforded 34 mg (92% yield) of racemic hinesol (**38**).

Anal. Calcd for $C_{15}H_{26}O$: C, 81.02; H, 11.79. Found: C, 80.74; H, 11.66.

Registry No.—**2**, 13587-70-7; **3**, 26315-70-8; **5**, 26315-71-9; **9**, 26315-72-0; **10a**, 26310-73-6; **10a** dihydro thioketal, 26310-75-8; **10b**, 26310-74-7; **10b** dihydro thioketal, 26310-76-9; **10b** semicarbazone, 26310-77-0; **12b**, 26310-78-1; **13b**, 26310-79-2; **13b** thioketal, 26310-80-5; **15b**, 26310-81-6; **16b**, 26310-82-7; **17b**, 26310-83-8; **18a**, 26358-43-0; **18b**, 26310-

84-9; **18b** C-2 epimer, 26310-95-2; **19b**, 26310-85-0; **21b** semicarbazone, 26310-86-1; **22a** 2,4-DNP, 26310-94-1; **23b**, 26310-87-2; **25b**, 26310-88-3; **28**, 26310-89-4; **29**, 26310-90-7; **30**, 26310-91-8; **32**, 26310-92-9; **38**, 22196-40-3; **39**, 22196-41-4.

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Charge Migration in Odd- and Even-Electron Fragment Ions. The Mass Spectrum of a Bisaziridinone

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The synthesis and spectra of a bisaziridinone, *viz.*, 3,3'-(1,3-adamantylene)bis(1-*tert*-butyl-2-aziridinone) (**2**), are described. The 50- and 12-eV mass spectra exhibit an abundant ion at $M - 56$. The major component of this peak, identified by high resolution mass measurement, is due to the expulsion of two molecules of CO from the two α -lactam rings. Alternatively, part of the molecular ions undergoes two successive McLafferty rearrangements with elimination of two C_4H_8 fragments. Even-electron ions, m/e 287 ($M - 2CO - CH_3$)⁺ and m/e 273 ($M - CO - C_4H_8$)⁺, eject C_4H_8 to give m/e 231 and 217, respectively. These processes require migration of the positive charge through σ bonds as transfer through space is precluded by the rigidity of the adamantane nucleus. Some ions in the mass spectra originate from skeletal rearrangement.

One of the basic and widely accepted conventions¹ of mass spectrometry is that the unimolecular decomposition of ions occurs at the site of the positive charge. The charge is believed to be localized at the place of lowest ionization potential. Recent work from a number of laboratories²⁻⁵ yielded further experimental confirmation of the concept of charge localization.

However, Mandelbaum and Biemann presented evidence⁶ for charge migration within fragment ions. Their model compounds were para,para'-disubstituted 1,3-diphenylcyclopentanes of unknown stereochemistry. Subsequently, Kinstle and Oliver also found⁷ a similar example of charge migration: loss of two molecules of propylene in successive steps (McLafferty rearrangements) from *p,p'*-bis(valerylphenyl) ether. Both these reports describe cases in which the charge migrates within an odd-electron fragment ion.

If charge migration in ions can occur, the next as yet unanswered questions are *when* and *how* does it occur? Does the charge migrate through space or through

chemical bonds, and, if the latter, can it be transmitted by σ bonds alone?

The present report is an inquiry into these questions, *i.e.*, the "mechanism" of charge migration. It was felt that a suitable model compound would have to satisfy the following prerequisites. (1) It should contain two (or more) functional groups known to trigger facile eliminations to yield *major ions* in the mass spectrum. (2) The functionalities should be joined by σ bonds only, in order to exclude π systems as possible transmitters. (3) The *first* major loss should be that of a neutral fragment, as odd-electron fragment ions are more likely to undergo charge migration than even-electron ions.⁶ (4) Interaction of the (two) functionalities through space should be precluded on a stereochemical basis. (5) The difference in ionization potential between the two likely fragmentation sites should be small. (6) To avoid ambiguities, the thermal decomposition pathway of a good model compound should be different from the electron-impact induced decomposition path.

Results

Bisaziridinone **2**, a representative of a hitherto unreported class of compounds, appeared to be a promising model substrate, as it meets all the above conditions. The most favored primary fragmentation mode of monofunctional α lactams (aziridinones) upon electron impact is the loss of CO.^{8,9} This process appears to

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(1) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco, Calif., 1967, p 9-14, and references therein.

(2) H. Bruderer, W. Richter, and W. Vetter, *Helv. Chim. Acta*, **50**, 1917 (1967).

(3) T. Wachs and F. W. McLafferty, *J. Amer. Chem. Soc.*, **89**, 5044 (1967).

(4) P. Brown and C. Djerassi, *ibid.*, **89**, 2711 (1967).

(5) J. Cable, G. W. Adelstein, J. Gore, and C. Djerassi, *Org. Mass. Spectrom.*, **3**, 439 (1970).

(6) A. Mandelbaum and K. Biemann, *J. Amer. Chem. Soc.*, **90**, 2975 (1968).

(7) T. H. Kinstle and W. R. Oliver, *ibid.*, **91**, 1864 (1969).

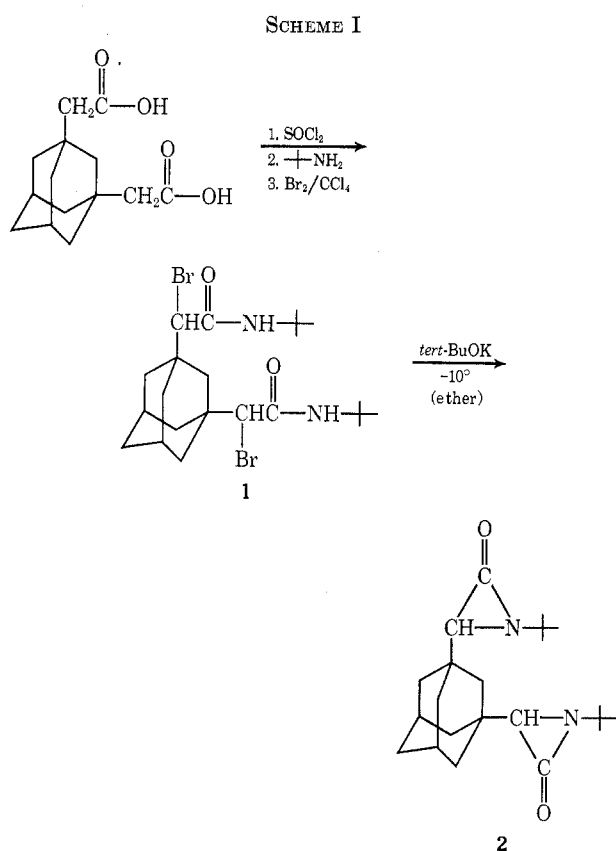
(8) I. Lengyel and D. B. Uliss, *Chem. Commun.*, 1621 (1968).

(9) I. Lengyel, D. B. Uliss, M. M. Nafissi-V., and J. C. Sheehan, *Org. Mass Spectrom.*, **2**, 1239 (1969).

have both a low activation energy and a high frequency factor due to the combined effect of (a) ring-strain release, (b) the large negative enthalpy¹⁰ associated with the formation of the neutral fragment (CO) eliminated, and (c) formation of an (ionized) C=N double bond. Thermolysis of 1,3-di-*tert*-alkyl or *tert*-cycloalkyl substituted α lactams, on the other hand, leads¹¹ to aldehydes or ketones and isocyanides as predominant products. To minimize competing thermal fragmentation, the *tert*-butyl group was chosen as the N substituent; it had been observed earlier¹¹ that tertiary substituents markedly increase the thermal stability of α lactams.

In bisaziridinone **2**, the two lactam rings are connected by the *rigid* 1,3-adamantylene moiety through C₃-C_{3'}, exclusively by σ bonds. The compound has a plane of symmetry and is inflexible, not permitting interaction of the functionalities in any conformation.

Our synthesis (Scheme I) followed the usual route,¹²



i.e., cyclization of the corresponding bis(bromoamide) with potassium *tert*-butoxide in dry ether at -10° . The structure was established by ir, pmr, uv, and mass spectral molecular weight determination. As expected, bisaziridinone (**2**) shows an $n \rightarrow \pi^*$ transition in the uv at the same wavelength (λ_{\max} 252 nm, *n*-hexane) as the corresponding monofunctional aziridinone, *viz.*, 1-*tert*-butyl-3-(1-adamantyl)aziridinone.¹³ Interestingly, the extinction coefficient more than doubles (from ϵ 144 to ϵ 346 for **2**). Moreover, a large hypsochromic shift is

(10) P. Brown and C. Djerassi, *Angew. Chem.*, **79**, 481 (1967); *cf. ibid.*, *Int. Ed. Engl.*, **6**, 477 (1967).

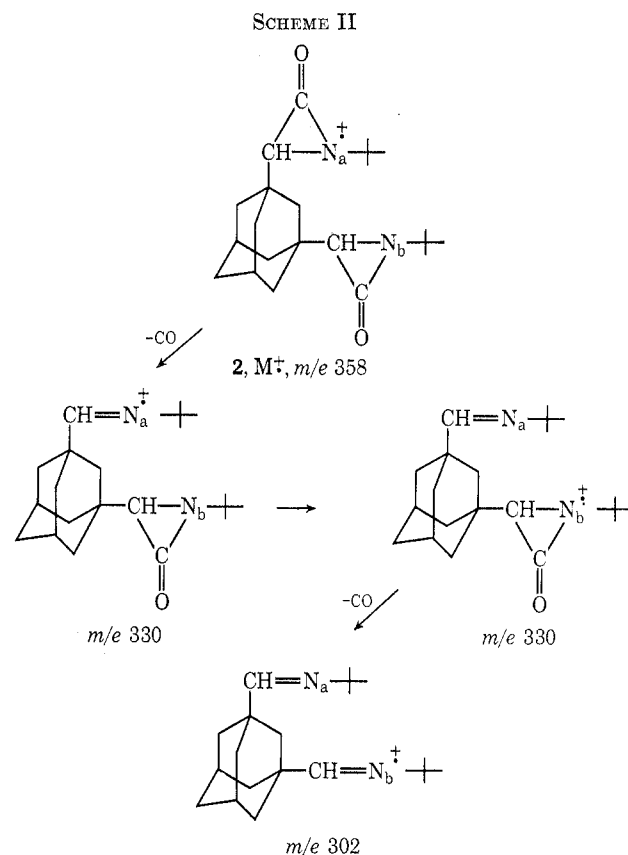
(11) I. Lengyel and J. C. Sheehan, *ibid.*, **80**, 27 (1968); *cf. ibid.*, *Int. Ed. Engl.*, **7**, 25 (1968).

(12) J. C. Sheehan and I. Lengyel, *J. Amer. Chem. Soc.*, **86**, 1356 (1964).

(13) E. R. Talaty, A. E. Dupuy, and T. H. Golson, *Chem. Commun.*, 49 (1969).

observed when the uv spectrum is recorded in ethyl alcohol ($\lambda_{\max}^{\text{EtOH}}$ 237 nm, ϵ 708).

The 50-eV conventional mass spectrum of bisaziridinone (**2**) (Figure 1) exhibits ions at both $M - 28$ (m/e 330) and $M - 56$ (m/e 302) (Scheme II). The $M - 56$



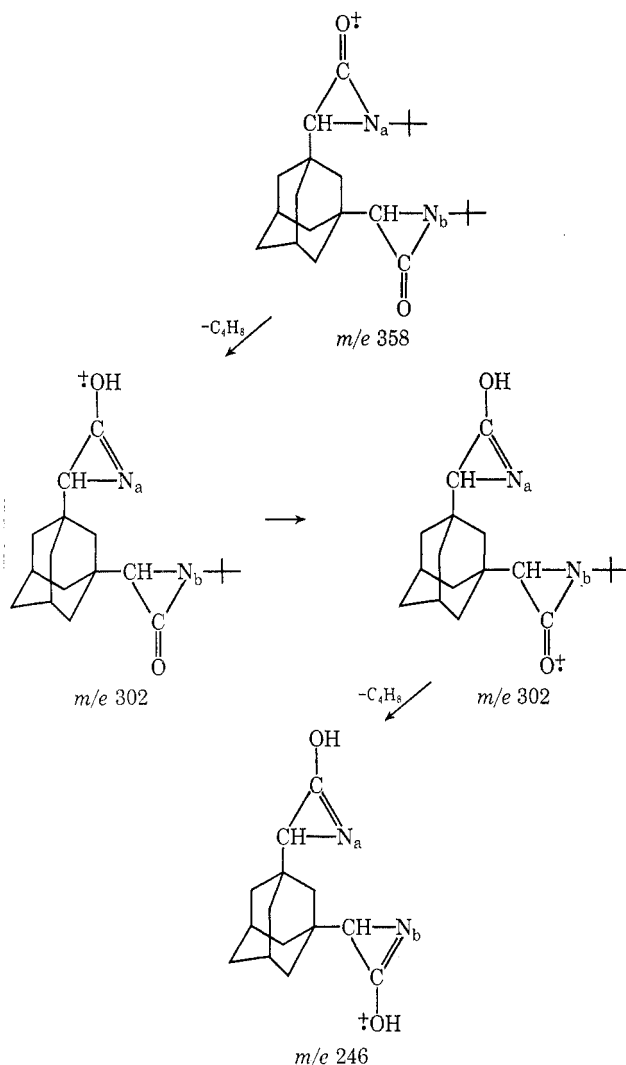
ion actually becomes the *base peak* at 12 eV (Figure 2), demonstrating that the elimination of 2CO molecules from the molecular ion is a very favored process. High resolution measurements, in the form of a complete "element map"¹⁴ confirmed ion $M - 28$ as a singlet due to the elimination of CO, while the $M - 56$ ion is a doublet, the major component (92%) being $M - 2CO$. A list of the accurate masses of selected ions in the high resolution mass spectrum of **2** is reproduced in Table I.

The second, minor component of the $M - 56$ ion (m/e 302) is $C_{18}H_{26}N_2O_2$, corresponding to elimination of C_4H_8 from the molecular ion (McLafferty rearrangement, involving one of the *N-tert*-butyl groups). Ion $C_{18}H_{26}N_2O_2$ eliminates a *second* C_4H_8 particle, accounting for one portion of the isobaric triplet at m/e 246, *viz.*, $C_{14}H_{18}N_2O_2$ (Scheme III). One path of further decomposition of ion m/e 302 ($M - 2CO$) is elimination of a methyl radical. The resulting even-electron ion, m/e 287, $C_{19}H_{31}N_2$, subsequently ejects C_4H_8 to give m/e 231, $C_{15}H_{28}N_2$ (Scheme IV). Metastable ions, calculated by computer, using a program similar to that of Rhodes, *et al.*,¹⁵ are present for both transitions (Table II). Applying the metastable defocusing technique (varying the accelerating voltage) provided positive proof that both processes, as depicted in Scheme IV are true one-step

(14) K. Biemann, P. Bommer, and D. M. Desiderio, *Tetrahedron Lett.*, 1725 (1964).

(15) R. E. Rhodes, M. Barber, and R. L. Anderson, *Anal. Chem.*, **38**, 48 (1966).

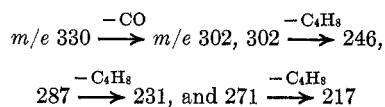
SCHEME III



electron-impact reactions. Part of ion $m/e\ 231$ arises from $m/e\ 246$ by expulsion of a methyl radical (m^* at $m/e\ 216.9$), a process not requiring charge migration.

Another even-electron ion of considerable interest is at $m/e\ 217$ (relative intensity 18%), predominantly $C_{13}H_{17}N_2O$. This ion originates from $m/e\ 273$ by loss of C_4H_8 (metastable supported, Scheme V).

A rationalization of transitions



requires charge migration. The first two are examples of charge migration in odd-electron fragments while the latter two in even-electron ions.¹⁶

Some of the ions present in the mass spectrum of 2 cannot be derived by simple bond cleavages. Thus, ion $m/e\ 83$ (C_5H_9N , *tert*-butylisocyanide) can arise only by skeletal rearrangement of one of the aziridinone rings to the isomeric imino- α -lactone (Scheme VI), a process analogous to the thermal decomposition.¹¹ Charge re-

(16) We did not foresee or anticipate the $287 \xrightarrow{-C_4H_8} 231$ and $273 \xrightarrow{-C_4H_8} 217$ transitions. Indeed, we are unaware of previous published reports on charge migration in even-electron ions substantiated by metastable evidence and high resolution data.

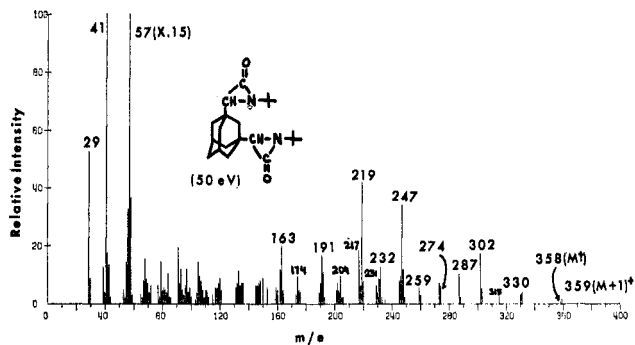


Figure 1.

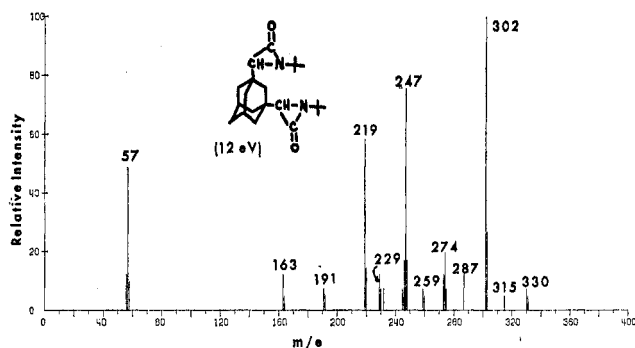
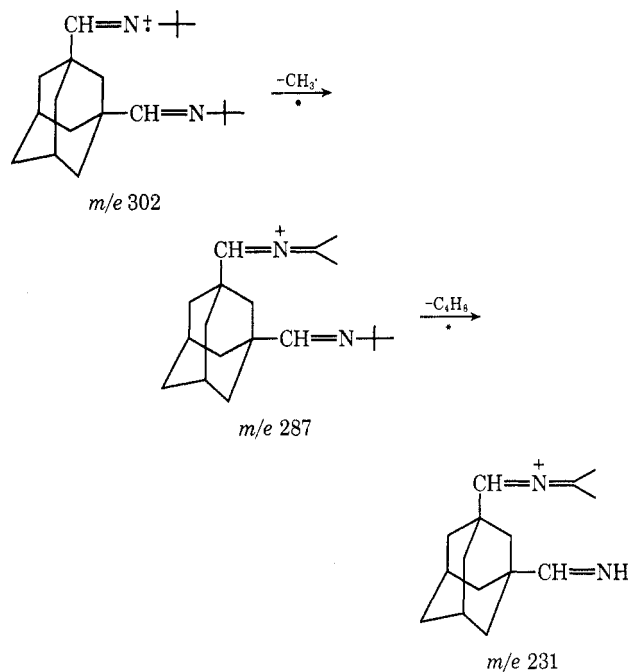


Figure 2.

SCHEME IV



tion by the oxygen-containing part leads to the abundant odd-electron ion $m/e\ 247$ ($C_{16}H_{25}NO$), which is the progenitor of ions $m/e\ 191$ (loss of C_4H_8) and 192 (elimination of C_4H_7 with double hydrogen rearrangement).

Other fragmentation reactions of bisaziridinone 2 are summarized briefly in the following. Alternative decomposition paths of the $M - CO$ ion ($m/e\ 330$) involve ejection of a methyl radical and C_4H_8 to give ions $m/e\ 315$ and 274 , respectively (Scheme VII). Either one of the latter (or both) may serve as precursor to ion

TABLE I
ELEMENTAL COMPOSITIONS OF SELECTED IONS IN THE HIGH RESOLUTION MASS SPECTRUM OF BISAZIRIDINONE 2

Nominal mass	Elemental composition	Difference between accurate mass found and calcd (\pm mmu)		Nominal mass	Elemental composition	Difference between accurate mass found and calcd (\pm mmu)		Nominal mass	Elemental composition	Difference between accurate mass found and calcd (\pm mm)		%
		found	calcd			found	calcd			found	calcd	
330	C ₂₁ H ₃₄ N ₂ O	0.0		145	C ₁₁ H ₁₃	-0.4		84	C ₇ H ₇	0.9		94
302	C ₂₀ H ₃₄ N ₂	-1.6		136	C ₈ H ₁₀ N ₂ O ₂	1.0		16	C ₆ H ₅ N	2.8		6
288	C ₁₉ H ₃₆ N ₂ O ₂	-0.1		135	C ₉ H ₁₄ N	3.4		62	C ₃ H ₁₂ N	1.9		50
287	C ₁₉ H ₃₂ N ₂	-1.2		134	C ₈ H ₁₀ NO	0.0		38	C ₅ H ₉ O	2.1		65
274	C ₁₉ H ₃₁ N ₂	0.1		133	C ₁₀ H ₁₅	-0.7		80	C ₄ H ₇ NO	-2.2		35
273	C ₁₇ H ₂₅ N ₂ O	1.7		132	C ₁₀ H ₁₄	-0.4		20	C ₄ H ₆ NO	0.9		92
259	C ₁₆ H ₂₅ N ₂ O	-0.2		131	C ₉ H ₁₂ N	0.2		64	C ₃ H ₉ N	-0.4		4
247	C ₁₆ H ₂₃ O ₂	-0.4		120	C ₈ H ₇ NO	1.1		18	C ₄ H ₇ N ₂	0.2		4
246	C ₁₆ H ₂₃ N ₂ O	1.3		120	C ₁₀ H ₁₃	-0.2		18	C ₃ H ₅ NO	0.0		89
245	C ₁₆ H ₂₁ N ₂	-0.8		120	C ₉ H ₁₁ N	0.1		66	C ₃ H ₈ N	0.9		11
232	C ₁₆ H ₂₁ N ₂ O	-1.4		119	C ₉ H ₁₀ N	0.4		34	C ₄ H ₄ NO	0.4		94
231	C ₁₄ H ₁₈ N ₂ O ₂	-1.2		118	C ₈ H ₆ NO	1.7		77	C ₆ H ₆	-1.2		6
229	C ₁₇ H ₂₆ O	-0.1		117	C ₁₀ H ₁₁	-0.4		88	C ₃ H ₇ N	0.7		97
219	C ₁₆ H ₂₅ N ₂ O	-0.4		115	C ₉ H ₉ N	0.5		7	C ₃ H ₅ N	-1.3		3
218	C ₁₅ H ₂₃ N ₂ O	-0.1		115	C ₇ H ₆ NO	-0.1		5	C ₆ H ₆	-1.0		96
217	C ₁₅ H ₂₃ N ₂ O	0.9		112	C ₉ H ₁₁	2.1		60	C ₃ H ₅ N	-1.6		4
203	C ₁₅ H ₂₁ N ₂	0.0		111	C ₈ H ₇ O	-1.3		25	C ₃ H ₄ N	-0.5		95
202	C ₁₄ H ₁₅ NO ₂	0.6		111	C ₈ H ₇ N	1.1		15	C ₆ H ₅	-0.1		5
201	C ₁₅ H ₂₁ N ₂ O	-0.4		110	C ₈ H ₆ N	-1.5		73	C ₃ H ₃ N	1.6		64
192	C ₁₅ H ₂₁ N ₂ O	0.2		110	C ₈ H ₉	0.6		27	C ₃ H ₁₀ NO	-2.8		36
191	C ₁₄ H ₂₀ N	-1.1		109	C ₈ H ₉	-0.4		75	C ₃ H ₉ N	-1.5		91
190	C ₁₄ H ₂₀ N ₂	0.3		108	C ₇ H ₆ NO	0.5		0	C ₃ H ₇ N	-3.2		6
189	C ₁₃ H ₁₇ N ₂ O	0.2		107	C ₇ H ₇ N	-0.1		19	C ₃ H ₁₁	1.0		3
176	C ₁₃ H ₁₇ N ₂ O	0.3		106	C ₄ H ₇ N ₂ O ₂	-2.1		6	C ₃ H ₁₁	-1.0		95
175	C ₁₃ H ₁₆ N ₂ O	-1.1		105	C ₆ H ₁₂ NO	0.0		50	C ₃ H ₈ N	-1.0		3
174	C ₁₃ H ₁₆ N ₂ O	-0.8		104	C ₆ H ₁₀ NO	-1.2		50	C ₃ H ₆ N ₂	-3.1		2
173	C ₁₃ H ₁₆ N ₂ O	2.3		104	C ₇ H ₉ N	-0.9		69	C ₃ H ₄ NO	0.0		93
163	C ₁₃ H ₁₆ N ₂ O	3.4		103	C ₇ H ₁₂ N	2.7		68	C ₃ H ₇ N	-0.9		7
162	C ₁₃ H ₁₆ N ₂ O	0.3		103	C ₆ H ₆ NO	0.8		66	C ₃ H ₆ N	-0.3		69
161	C ₁₃ H ₁₆ N ₂ O	2.9		103	C ₇ H ₁₂ N	0.3		34	C ₃ H ₇	-1.9		21
160	C ₁₃ H ₁₆ N ₂ O	0.3		103	C ₇ H ₁₁ N	0.3		60	C ₃ H ₇	-0.7		10
159	C ₁₃ H ₁₆ N ₂ O	2.9		103	C ₆ H ₇ NO	-0.5		40	C ₃ H ₈	-3.0		95
146	C ₁₃ H ₁₆ N ₂ O	-0.8		103	C ₇ H ₁₀ N	1.4		89	C ₃ H ₇ O	-1.6		5
145	C ₁₃ H ₁₆ N ₂ O	-1.9		103	C ₆ H ₆ NO	2.7		11	C ₃ H ₇ N	0.2		56
144	C ₁₃ H ₁₆ N ₂ O	-1.2		103	C ₇ H ₉ N	0.8		92	C ₄ H ₉	-3.3		21
143	C ₁₃ H ₁₆ N ₂ O	0.3		103	C ₇ H ₉ N	-0.3		8	C ₄ H ₆	-3.1		10
142	C ₁₃ H ₁₆ N ₂ O	-0.3		103	C ₇ H ₈ N	-1.4		21	C ₃ H ₂ NO	-2.0		95
141	C ₁₃ H ₁₆ N ₂ O	0.8		103	C ₇ H ₇ N	-0.9		79	C ₃ H ₆ N	-2.5		5
140	C ₁₃ H ₁₆ N ₂ O	-1.4		103	C ₈ H ₅	0.0		83	C ₃ H ₄ N	-2.3		56
139	C ₁₃ H ₁₆ N ₂ O	0.4		103	C ₈ H ₇	1.9		17	C ₃ H ₆	1.3		44
138	C ₁₃ H ₁₆ N ₂ O	-0.2		100	C ₃ H ₇ N ₂ O ₂	-3.1		83	C ₃ H ₆	-1.6		95
137	C ₁₃ H ₁₆ N ₂ O	-0.5		100	C ₃ H ₁₀ NO	0.8		17	C ₃ H ₅	-1.6		5
136	C ₁₃ H ₁₆ N ₂ O	-1.7		100	C ₃ H ₁₀ NO	0.8		17	C ₃ H ₃ N	-1.1		5

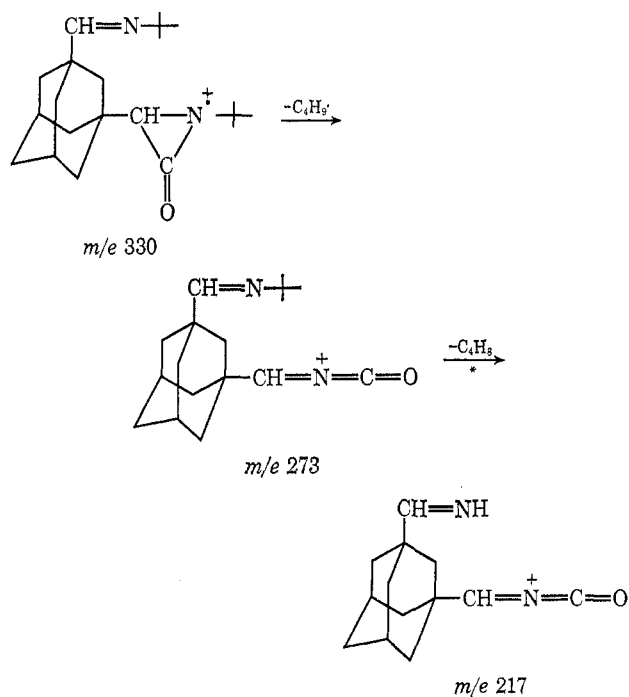
<i>m/e</i> (observed)	<i>M*</i> (calcd)	Transition	<i>M*</i> (observed)	<i>M*</i> (calcd)	Transition	<i>m/e</i> (observed)	<i>M*</i> (calcd)	Transition	<i>m/e</i> (observed)
159	14.7	57 → 29 -CH ₃	89.0	88.89	162 → 120 -C ₄ H ₉	44	190.03	219 → 204 -CH ₃	92
153	24.8	68 → 41 -HCN	139.9	139.84	190 → 163 -HCN	43	194.96	246 → 219 -HCN	8
150	29.5	57 → 41 -CH ₃	147.7	147.70	247 → 191 -C ₄ H ₉	60	198.76	302 → 245 -C ₄ H ₉	66
148	37.4	84 → 56 -CO	172.6	172.49	273 → 217 -C ₄ H ₉	38	216.91	246 → 231 -CH ₃	26
147	56.8	84 → 69 -CH ₃	186.0	185.93	287 → 231 -C ₄ H ₉	2	272.75	302 → 287 -CH ₃	6
						42			2
						92			64
146						8			36

TABLE II

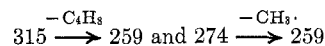
METASTABLE IONS AND TRANSITIONS IN THE 70-EV MASS SPECTRUM OF 2

<i>m/e</i> (observed)	<i>M*</i> (calcd)	Transition	<i>M*</i> (observed)	<i>M*</i> (calcd)	Transition	<i>m/e</i> (observed)
14.7	14.75	57 → 29 -CH ₃	89.0	88.89	162 → 120 -C ₄ H ₉	44
24.8	24.72	68 → 41 -HCN	139.9	139.84	190 → 163 -HCN	43
29.5	29.49	57 → 41 -CH ₃	147.7	147.70	247 → 191 -C ₄ H ₉	60
37.4	37.3	84 → 56 -CO	172.6	172.49	273 → 217 -C ₄ H ₉	38
56.8	56.68	84 → 69 -CH ₃	186.0	185.93	287 → 231 -C ₄ H ₉	2

SCHEME V



m/e 259 (80% C₁₆H₂₃N₂O). In the absence of the pertinent metastable peaks, routes



cannot be differentiated. Formation of *m/e* 259 may also involve charge migration.

Additional fragmentation modes of the *M* - 2CO ion (*m/e* 302) are depicted in Scheme VIII. The successive loss of two C₄H₉ fragments leads to C₁₆H₂₆N₂ (the major portion of ion *m/e* 246) and C₁₂H₁₈N₂ (*m/e* 190), respectively. Subsequent expulsion of HCN, supported by the appropriate metastable peaks, affords ions *m/e* 219 and 163, respectively. Finally, ejection of a C₄H₉ radical from *m/e* 302, supported by a metastable peak at *m/e* 198.8, leads to ion *m/e* 245.

The 70-eV mass spectrum of bisaziridinone 2 also exhibits an *M* + 1 ion, not uncommon for amides and amines. Expulsion of CO from the *M* + 1 species leads to ion *m/e* 331. It is noteworthy that the doubly charged analogs of (*M* - CO)⁺ (*m/e* 330/2 = 165) or (*M* - 2CO)⁺ (*m/e* 302/2 = 151) are absent both at 50 and 12 eV.

Discussion

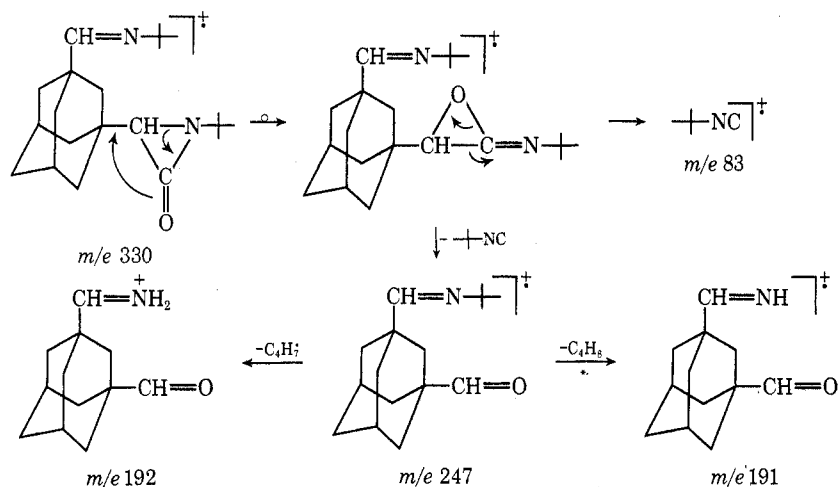
The electron-impact induced ejection of CO from non-terminal positions has been observed previously in numerous types of organic compounds.¹⁰ It was Beynon and coworkers^{17,18} who first called attention to the consecutive elimination of two molecules of carbon monoxide from *p*-benzoquinone¹⁷ 1,4-naphthoquinone and a wide variety of anthraquinones.^{17,18} Turro and coworkers reported¹⁹ the successive elimination of two molecules of carbon monoxide from tetramethylcyclobutane-1,3-

(17) J. H. Beynon, G. R. Lester, and A. E. Williams, *J. Phys. Chem.*, **63**, 1861 (1959).

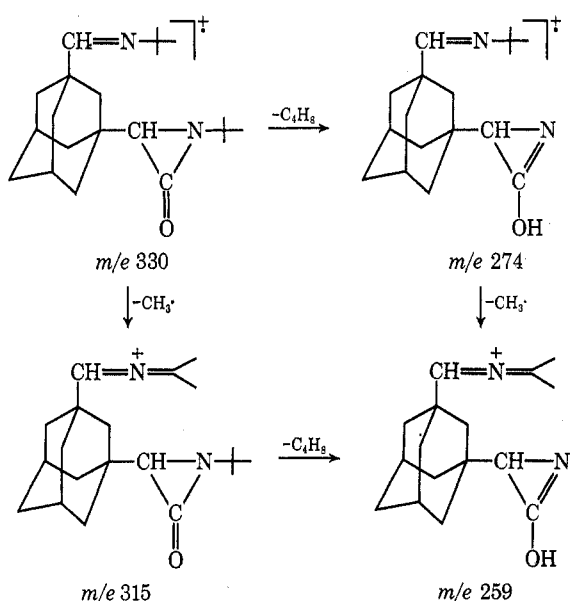
(18) J. H. Beynon and A. E. Williams, *Appl. Spectrosc.*, **14**, 156 (1960).

(19) N. J. Turro, D. C. Neekers, P. A. Leermakers, D. Seldner, and P. D'Angelo *J. Amer. Chem. Soc.*, **87**, 4097 (1965).

SCHEME VI



SCHEME VII

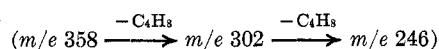


dione. Another derivative of cyclobutane-1,3-dione, *viz.*, the dimer of 2-carbonyladamantane is also reported²⁰ to expel two molecules of carbon monoxide upon electron impact.

In these examples, however, the eliminations occur from the *same* ring, the new site of the charge is in close proximity to the old one, and/or the two carbonyl groups are joined through a delocalized π -electron system, available for ready transmission. Also, in the above examples, the elimination of two molecules of CO results in the formation of at least one new carbon-carbon bond leading to a highly stable conjugated polyene^{17,18} or a tetrasubstituted olefin.^{19,20}

Unlike the literature examples dealing with multiple elimination of carbon monoxide from nonterminal positions,^{10,17-20} in the present example (i) elimination occurs from different rings; (ii) no delocalized π -electron system is part of the link, N_a is separated from N_b by *six* σ bonds, and no other type of bond is involved; (iii) a rigid skeleton makes steric interaction of the functionalities impossible. Similar considerations apply to a

comparison of the successive McLafferty rearrangements observed in bisaziridinone 2



with previous reports.⁶⁻⁷

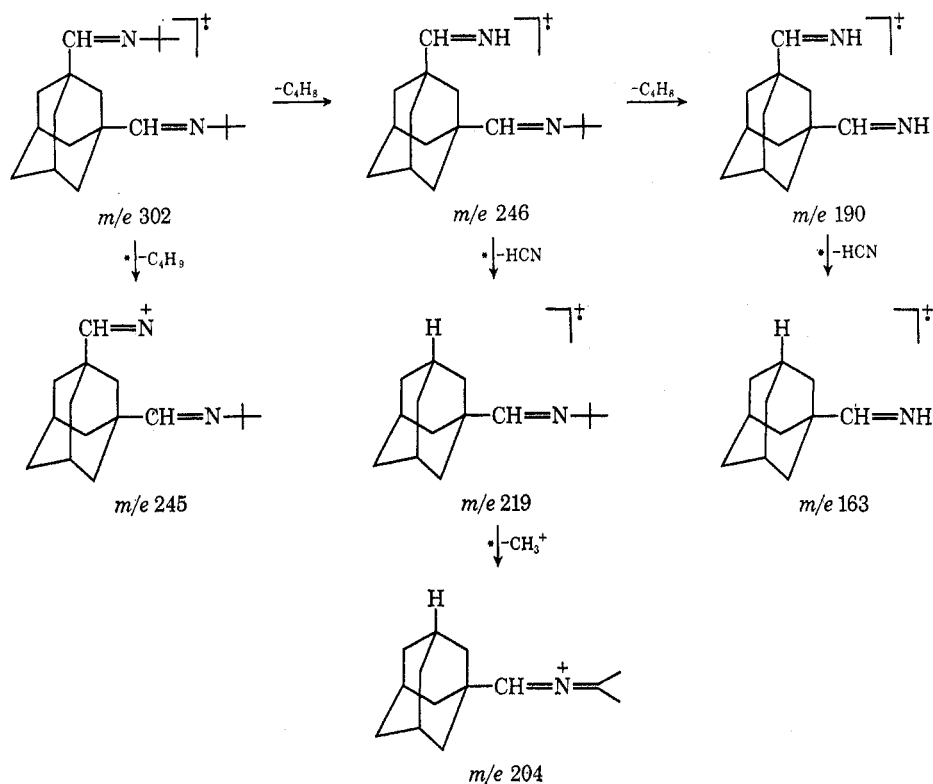
The presence and genesis of ions, *i.e.*, $m/e\ 302$ ($M - 2CO$)⁺, $m/e\ 246$ ($M - 2C_4H_5$)⁺, $m/e\ 231$ ($M - 2CO - CH_3 - C_4H_5$)⁺, $m/e\ 217$ ($M - CO - C_4H_5 - C_4H_5$)⁺, etc., in the mass spectrum of bisaziridinone 2 is clearly inconsistent with the concept¹ of charge localization at the site of initial fragmentation and cannot be rationalized by simple uncoupling of nearby π bonds or electron transfer effected by interaction of the functional groups (sites of lowest ionization potential) through space.²¹ It appears that the correlation between *secondary* fragmentation (competing reactions) and *initial* charge density distribution is not a simple one and that actual fragmentation is governed by a number of additional parameters such as product ion stability, activation energy, stability of the eliminated neutral particle, transition state geometry, etc.

The mechanism of charge migration, especially for even-electron ions such as $m/e\ 287$, 273, etc., may involve more than simple electron transfer, *viz.*, bond formation, H transfer, and skeletal rearrangements. For lack of compelling evidence, no such mechanisms are depicted in the schemes.

To explain the present findings one has to reckon with one of the following alternatives: (i) that charge migration in fragment ions is possible even if the two sites are separated *exclusively* by σ bonds and non-bonded interaction through space is precluded on stereochemical grounds;²¹ (ii) that fission of at least two carbon-carbon bonds in the adamantane moiety precedes or occurs concomitantly with elimination of the second molecule of CO, thus permitting steric interaction of the

(21) A further complication in the study of charge migrations originates from the following. Even though scale models, which represent ground state conditions, of bisaziridinone 2 indicate that the two functionalities cannot be brought into close proximity (to within reactive distance) without C-C bond fissions in the adamantane nucleus, interspatial electron transfer in the gas phase can still not be ruled out either experimentally or on theoretical grounds since intermolecular charge-transfer cross sections are often ten times greater than collision cross sections (*e.g.*, radii about 10 Å) and for ions living long enough to produce metastables, 10^{-6} sec or so, the Heisenberg uncertainty principle would make it difficult to assign definite charge locations, the more so, as the energy contents of the fragment ions in question can at present only be estimated. We thank one of the referees for calling attention to this point.

SCHEME VIII



functionalities, and/or elimination of C_4H_8 from the adamantane nucleus; (iii) that elimination reactions upon electron impact can occur without participation of the positive charge or a radical site, *i.e.*, that there are "quasithermal or quasiphotocemical reactions" in the mass spectrometer.

Conclusion

Since there is no precedent or evidence for alternatives ii and iii,²² we favor alternative i.²⁸ Indeed, our finding supports the conclusion⁶ that a fixation of the charge in fragment ions is "unwarranted." From the present examples in which electron transfer (*i.e.*, charge migration) by π bonds and/or through space is ex-

(22) In fact, for their compounds, Bruderer, *et al.* (ref 2), conclude that such reactions are "absent or insignificant."

(23) NOTE ADDED IN PROOF.—Alternative ii, even though presently without experimental proof, cannot be excluded. After the submission of this manuscript for publication, important papers dealing with charge redistribution in radical ions derived from structurally and conformationally rigid polyfunctional molecules appeared. From a study of a series of difunctional steroidal model compounds with isolated functional groups attached to rings A and D, Vetter, Meister, and Richter have concluded²⁴ that (1) charge localization at the potential site of reaction is a necessary prerequisite for mass spectral fragmentations to occur, (2) different fragmentation processes have varying minimum charge density requirements at the site of the event, (3) there is no simple relationship between IP differences of isolated sites and charge redistribution, and (4) charge redistribution to secondary sites in radical ions can involve migration of atoms or groups ("chemical charge transfer").

In a well-documented mass spectral study of steroidal alkaloids bearing nitrogen functions on rings A and D, Longevialle and Diatta report²⁵ a new type of fragmentation initiated by intramolecular interaction of the two amine functions involving hydrogen migration over four rings. The charge and the radical site, thus separated and localized at the two opposite peripheries of the ion, are shown to trigger separate sequences of competing fragmentation steps. Investigation of the possible operation of similar processes in our model requires specific labeling of the adamantylene connecting link.

(24) W. Vetter, W. Meister, and W. J. Richter, *Org. Mass Spectrom.*, **3**, 777 (1970).

(25) P. Longevialle and L. Diatta, *ibid.*, **3**, 803 (1970).

cluded, the feeling that the term "charge migration" might be inaccurate or inappropriate gathers strength. Rather, one tends to agree with Mandelbaum and Biemann⁶ who see a "dynamic distribution of charge... statistically maximized at the site of lowest ionization potential" within fragment ions.

It appears, however, that "charge migration" is not governed solely by the ionization potentials of the various sites but is influenced by other factors as well, *e.g.*, ion structure, stereochemistry, ring-strain release, etc.

Our present inability to predict for a polyfunctional molecule the *new* sites at which *secondary* fragmentation will occur in the gas phase, stems in part, we feel, from our poor understanding of these environmental factors. Additional work is necessary to gain further insight into the scope and mechanism of redistribution of the charge in ions.

Experimental Section

A. Synthesis of Model Compound.—All melting points are uncorrected and were measured on a Thomas-Hoover capillary melting point apparatus. The infrared spectra were measured on a Beckman IR-8, and the ultraviolet spectra were obtained on a Cary-14 spectrophotometer. The pmr spectrum was recorded on a Varian A-60 spectrometer using TMS as an internal standard. Microanalyses were performed by A. Bernhardt, West Germany.

2,2'-(1,3-Adamantylene)bis(2-bromo-*N*-*tert*-butylacetamide) (1).—Adamantane-1,3-diacetic acid (5.17 g, 20.5 mmol) was converted to the corresponding bis acid chloride by refluxing in excess thionyl chloride. The refluxing thionyl chloride solution was then treated with bromine (6.56 g, 41.0 mmol) and was allowed to reflux for 15 hr. The excess bromine and thionyl chloride were removed under vacuum. To the crude bromo acid chloride in 500 ml of dichloromethane and cooled in an ice bath, was added *tert*-butylamine (7.31 g, 100 mmol). After 2 hr at 0°, the mixture was extracted with water, 2 *N* hydrochloric acid, 2 *N* sodium hydroxide, and water. The dichloromethane solution was dried over magnesium sulfate, and the solvent was removed on a rotary evaporator. The crude amide was recrystallized from ethyl acetate to give 3.51 g (32.8% overall) of the product,

mp 258–259°. The ir spectrum (KBr) showed absorptions at 3360 (NH), 1650 (amide I), and 1530 cm^{-1} (amide II).

Anal. Calcd for $\text{C}_{22}\text{H}_{30}\text{Br}_2\text{N}_2\text{O}_2$: C, 50.78; H, 6.97; Br, 30.71. Found: C, 50.95; H, 6.86; Br, 30.49.

3,3'-(1,3-Adamantylene)bis(1-*tert*-butyl-2-aziridinone) (2).—Potassium *tert*-butoxide (0.740 g, 6.60 mmol) was added in one portion to a stirred slurry of 2,2'-(1,3-adamantylene)bis(2-bromo-*N*-*tert*-butylacetamide) (1.00 g, 1.92 mmol) in 50 ml of dry ether under nitrogen at 0 to -10° . The reaction was monitored by ir. When the reaction was complete (15 min), the mixture was extracted with 100 ml of cold water, and the organic phase was removed and dried over magnesium sulfate. Evaporation of the solvent gave 522 mg (75.8%) of a light yellow solid, mp 119–123°. An analytical sample was prepared by recrystallization from hexane, mp 121.5–123.5°. The ir (CCl_4) showed a strong carbonyl at 1835 cm^{-1} and no NH absorption. The pmr (CCl_4) showed 1.29 (singlet, 18 H, *tert*-butyl protons), 1.6–2.2 (hump, 14 H, adamantylene protons), and 2.52 ppm (singlet, 2 H, methine protons). The ultraviolet spectra showed (hexane) λ_{max} 252 nm ($\log \epsilon$ 2.54) and (EtOH) λ_{max} 237 nm ($\log \epsilon$ 2.85).

Anal. Calcd for $\text{C}_{22}\text{H}_{34}\text{N}_2\text{O}_2$: C, 73.70; H, 9.56; N, 7.82. Found: C, 73.55; H, 9.65; N, 7.74.

B. Mass Spectra.—The conventional (“low resolution”) mass spectra were recorded on a Hitachi RMU-6D instrument at

Morgan-Schaffer Corporation, Montreal, Canada, at 100° ion source temperature and 40–60° inlet temperature. Metastables were calculated by computer. Final selections were made manually, utilizing intensity data. The metastable-defocusing work was done on an AEI MS-902 instrument. The high resolution spectrum (“element map”) was recorded on a CEC 21-110B doubly focusing mass spectrometer in conjunction with an IBM 1801 computer.

Registry No.—1, 26431-15-2; 2, 26431-16-3.

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Aziridines. XVIII. The Pyrolytic and Iodide Ion Catalyzed Rearrangements of the *cis*- and *trans*-13-*p*-Nitrobenzoyl-13-azabicyclo[10.1.0]tridecanes¹

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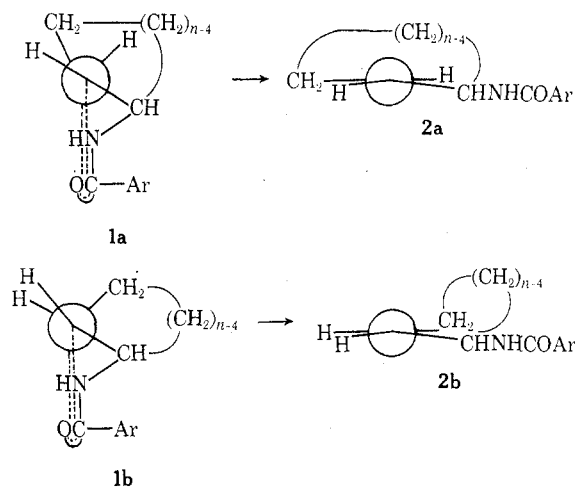
Received May 12, 1970

Pyrolysis of *trans*-13-*p*-nitrobenzoyl-13-azabicyclo[10.1.0]tridecane (3) in toluene at 110° gave a mixture of *trans-N*-(2-cyclododecenyl)-*p*-nitrobenzamide (6) and *cis-N*-(2-cyclododecenyl)-*p*-nitrobenzamide (5) in a ratio of 2:1. Pyrolysis of *cis*-13-*p*-nitrobenzoyl-13-azabicyclo[10.1.0]tridecane (4) in xylene at 140° gave a mixture of 6 and *trans*-2-*p*-nitrophenylcyclododecano[4,5-*d*]oxazoline (7) in a ratio of 7:1. Reaction of 4 with sodium iodide in acetone gave *cis*-2-*p*-nitrophenylcyclododecano[4,5-*d*]oxazoline (12). The formation of these products was rationalized in terms of the probable conformations of 3 and 4 and their respective transition states as deduced from the reported conformations of the corresponding aziridinium methiodides found by X-ray studies.

The thermal rearrangement of *N*-aroylaziridines to give unsaturated amides has been studied extensively and found to be in the category of pyrolytic *cis* eliminations such as the Chugaev reaction and the Cope elimination of tertiary amine oxides.^{2–5} In accord with this view, the isomerization of *N*-aroylaziridines fused to carbocyclic rings of 5, 6, 8, and 10 carbon atoms was found to yield only the unsaturated amide incorporating a *cis* double bond.^{6–9} This reaction must occur by way of the transition state **1b**. If a *trans* double bond were to be formed by a *cis* elimination in such compounds, it would have to occur by way of a transition state such as **1a** which obviously would impose a considerable strain on the smaller, less flexible rings, where $n \leq 10$. Furthermore, in such rings a *cis* double bond is thermodynamically more favorable than the *trans*. Only when a ring size of 11 carbon atoms is reached does

the *trans* isomer become the more favorable of the two isomers.¹⁰

In this connection, it seemed to us that an investigation of the pyrolytic rearrangement of the *cis*- and *trans*-13-*p*-nitrobenzoyl-13-azabicyclo[10.1.0]tridecanes would be of particular interest, since in this instance the carbocyclic ring system would be large enough to accommodate a conformation such as **1a** and the resulting *trans*-



(1) Preliminary work was initiated by B. S. Green and was reported in a Ph.D. Thesis submitted to Illinois Institute of Technology in 1967. The research was completed by I. J. Burnstein and reported in a Ph.D. thesis submitted to Illinois Institute of Technology in 1969. Inquiries should be addressed to P. E. Fanta.

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(3) P. B. Talukdar and P. E. Fanta, *ibid.*, **24**, 526 (1959).

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