(CN), 1700 (C=O), 1600, 1500, (aromatic C—C), 1010, and 1030 (-C(=O)O-) cm^{-1}; nmr 1.22 (t, 3, J = 7 Hz, CH_3CH_2), 4.22 (q, 2, J = 7 Hz, CH_3CH_2), 4.95 (s, 2, CH_2NPh), and 7.0–7.7 (m, 9, aromatic H).

Anal. Calcd for $C_{17}H_{16}N_2O_2$: C, 72.83; H, 5.75; N, 10.00. Found: C, 72.96; H, 5.85; N, 9.81.

General Procedure for the Reaction of *N*-(*p*-Cyanobenzyl)aniline Derivatives with the Disodium-Stilbene Complex and Ethyl Chloroformate. A THF solution of the disodium-stilbene complex was treated with a solution of an equivalent amount of the selected ester in THF (*ca.* 10 ml) at room temperature. The color changed from deep red of the stilbene complex to pale yellow or colorless immediately. The reaction was stirred and quenched with ethyl chloroformate. After 24 hr of additional stirring, this reaction mixture was diluted with water; the reaction product was isolated and analyzed by vpc using the same conditions as described earlier. The results are summarized in Table II.

Preparation of Ethyl α-(*N*-Carbethoxyanilino)-*p*-(*N*-carbethoxyaminomethyl)phenylacetate, 32. Ethyl α-(*N*-carbethoxyanilino)-*p*-cyanophenylacetate, **23** (0.704 g, 0.002 mol), was hydrogenated in ethanol (65 ml) with 5% rhodium on carbon (0.2 g) as a catalyst at atmospheric pressure of hydrogen for 24 hr, during which time 96 cm^3 of hydrogen was consumed. The crude hydrogenated product was then dissolved in anhydrous ether (20 ml) and ethyl chloroformate (0.216 g, 0.002 mol) was added. After being stirred for 24 hr, the mixture was treated with 3*N* sodium hydroxide (1.0 ml), and the organic product was isolated (0.69 g) and chromatographed with chloroform as eluent. Of the two fractions obtained, the first (0.21 g) contained incompletely hydrogenated material. The second fraction (0.26 g, 30% yield) was a pale yellow oil whose ir and nmr spectra were identical with those of **32** prepared by hydrogenation of the tricarbethoxy compound **25**.

Thermal Decomposition of 25. A small amount of **25** placed in a test tube under nitrogen was heated in a metal block at 260° for 6 hr. The product was analyzed by vpc and found to contain 90% of **23** and 10% of ethyl *N*-(*p*-cyanobenzyl)-*N*-phenylcarbamate, **22**. The latter compound was present in the initial **25** as an impurity.

Acknowledgment. This research was financially supported by the National Research Council of Canada.

Registry No.—**1** (M = Na), 53418-39-6; **1** (M = Li), 53418-40-9; **2**, 33672-87-6; **3**, 7714-87-6; **6** (R = Me), 33672-88-7; **7** (R = CH_3, Y = OEt), 53418-41-0; **7** (R = $PhCH_2$, Y = OEt), 53418-42-1; **7** (R = Me, Y = NMe_2), 53418-43-2; **8**, 53418-44-3; **9**, 53418-45-4; **10**, 42391-89-9; **11**, 42391-85-5; **12**, 53418-46-5; **13**, 42391-88-8; **14**, 42391-86-6; **15**, 42391-87-7; **17**, 53418-47-6; **18**, 53418-48-7; **19**, 42391-91-3; **20** (M = Na), 53418-49-8; **21**, 40577-15-9; **22**, 53418-50-1; **23**, 40577-09-1; **24**, 53418-51-2; **25**, 53418-52-3; **32**, 53418-53-4; ethyl chloroformate, 541-41-3; dimethylcarbamoyl chloride, 79-44-7; *N*-(*p*-cyanobenzyl)aniline, 37812-49-0.

References and Notes

(1) Preliminary reports on some aspects of this study have appeared: (a) J. G. Smith and G. E. F. Simpson, *Tetrahedron Lett.*, 3295 (1971); (b) *ibid.*, 1947 (1973).
(2) J. G. Smith and I. Ho, *J. Org. Chem.*, **38**, 2776 (1973).
(3) It was hoped to obtain evidence of an intramolecular nature for this rearrangement: T. A. Antkowiak, D. C. Sanders, G. B. Trimitsis, J. B. Press, and H. Shechter, *J. Amer. Chem. Soc.*, **94**, 5366 (1972).
(4) R. Heck, P. S. Magee, and S. Winstein, *Tetrahedron Lett.*, 2033 (1964).
(5) This synthesis is considerably more satisfactory than that reported in our preliminary communication.[1b]
(6) This interesting reaction is presently being investigated.
(7) In vpc analyses, the injection and detector temperatures were 210°; at 260°, **25** was not detected.
(8) See for example (a) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N.Y., 1965, pp 54–55; (b) V. R. Sandel and H. H. Freedman, *J. Amer. Chem. Soc.*, **85**, 2328 (1963); (c) R. Waack, L. D. McKeever, and M. A. Doran, *Chem. Commun.*, 117 (1969).
(9) R. M. Acheson, *Accounts Chem. Res.*, **4**, 177 (1971).
(10) J. Smid, "Ions and Ion Pairs in Organic Reactions," Vol. 1, M. Szwarc, Ed., Wiley-Interscience, New York, N.Y., 1972, pp 85–151.
(11) J. J. Eisch, "The Chemistry of Organometallic Compounds," Macmillan, New York, N.Y., 1962, pp 13–33.
(12) J. G. Smith and R. A. Turle, *J. Org. Chem.*, **37**, 126 (1972).
(13) E. Wertheim, *J. Amer. Chem. Soc.*, **55**, 2540 (1933).
(14) Spectral properties have been reported.[2]

Vinylogous Systems. III. Mass Spectra of Vinylogous Imides[1]

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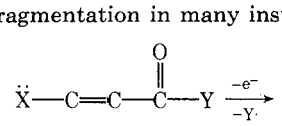
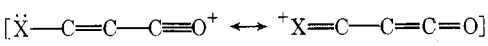
The mass spectra of sixteen acyclic, isocyclic, and heterocyclic vinylogous imides, -(O)CNC=CC(O)-, have been examined. Stereochemical and structural factors strongly influence the preferred fragmentation pathways, with oxazolium and/or isoxazolium fragment ions playing prominent roles in the decomposition of acyclic and isocyclic compounds.

Several reports have appeared concerning the mass spectral fragmentations of vinylogous amides (**1a**),[2-4] esters (**1b**),[3] urethanes (**1c**),[2] and *N*-acylurethanes (**1d**).[5] Loss of Y from the molecular ion of **1** to form the resonance stabilized α,β-unsaturated acylium ion **2** is the major initial fragmentation in many instances, and then **2** usually constitutes the base peak. Radical ions analogous to **2a** are also important intermediates in the fragmentation patterns of uracils.[6,7]



1a, X = R_2N; Y = R
b, X = RO; Y = R
c, X = R_2N; Y = OR
d, X = RC(O)NH; Y = OR



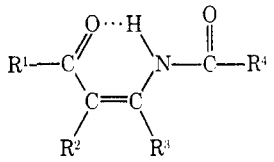
2a, X = R_2N
b, X = RO
c, X = RC(O)NH

The present study of vinylogous imides, β-amido α,β-unsaturated ketones, -(O)CNC=CC(O)-, had two main thrusts. First, we wanted to extend previous results by including compounds of greater stereochemical variety in our work.[8] Second, it seemed likely that the initial fragmentation of the imides would be unique, leading not to ion **2c**,[9] but, if stereochemically permissable, to highly stable oxazolium and/or isoxazolium daughter ions.[10] Earlier work in this laboratory[1,11] made available a number of acyclic, isocyclic, and heterocyclic vinylogous imides. We herewith report the mass spectral results for these compounds.

Experimental Section

Melting points are uncorrected. Mass spectra were obtained on an A.E.I. MS-9 mass spectrometer operating at 70 eV. Samples were introduced *via* a direct insertion probe. The inlet system tem-

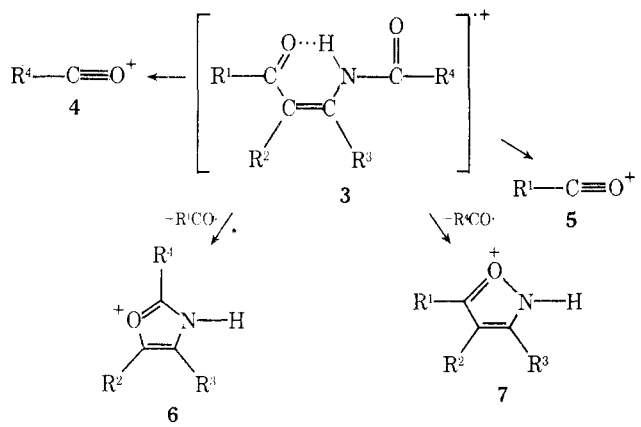
Table I
Relative Intensities of Principal Peaks in the Mass Spectra of Acyclic Cis-s-Cis Compounds



Compd	$[M]^{+\cdot}$ [a]	4	5	6	7	8	9	10	11
3a	15.2	55.4[a]	5.5[a]	59.0	2.1[b]	5.3[c]	100.0	13.7	11.6
3b	21.4	20.4	2.1[d]	100.0	3.6	10.5	96.2	12.4[d]	10.5
3c	12.8	9.8	45.8	100.0	7.1	3.8	90.0	24.8	3.3
3d	17.1	39.9	13.2[e]	84.1	100.0	2.6[c]	55.9	9.9[f]	0.9
3e	14.9	100.0[e]	4.7	28.5	0.8				
3f	8.7	100.0[e]	10.9	45.3	2.2				
3g[g]	17.8	100.0[e]	12.0	30.0	7.7				

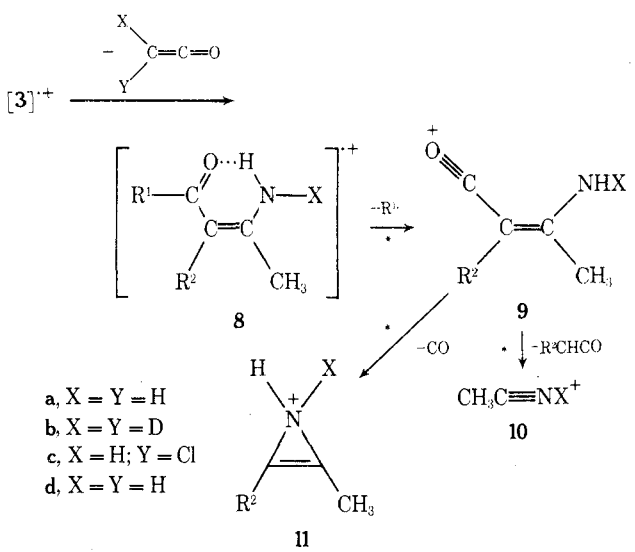
[a] Ions 4a and 5a are identical; relative importance of cleavage site is based upon results for compound 3b. [b] A single peak, m/e 112 (61.1%), is observed for ions 6a and 7a; values shown are based upon results for 3b. [c] Corrected for isotopic contribution from ion 6. [d] Ion 5b is CH_3CO^+ (m/e 43) and ion 10b is $CH_3C{\equiv}NH^+$ (m/e 42) plus $CH_3C{\equiv}ND^+$ (m/e 43). Experimental relative abundances of m/e 42 and 43 peaks are 4.3% and 10.2%, respectively. Assuming the fragmentation modes of ion 9 are of equal importance for compounds 3a and 3b, one can then assign the tabulated values of 12.4% for ion 10b and, indirectly, a value of 2.1% for ion 5b. [e] The characteristic stepwise fragmentation of $C_6H_5CO^+$ to $C_6H_5^+$ and $C_4H_3^+$ is observed along with the expected metastable transitions in every instance. [f] Based upon high-resolution results for 3c. [g] Although 3g does contain a cyclohexene ring, the compound is structurally very similar to 3f.

Scheme I



a, $R^1 = R^2 = R^3 = R^4 = CH_3$
b, $R^1 = R^2 = R^3 = CH_3$; $R^4 = CD_3$
c, $R^1 = R^3 = CH_3$; $R^2 = H$; $R^4 = ClCH_2$
d, $R^1 = C_6H_5$; $R^2 = H$; $R^3 = R^4 = CH_3$
e, $R^1 = R^3 = CH_3$; $R^2 = H$; $R^4 = C_6H_5$
f, $R^1 = R^2 = R^3 = CH_3$; $R^4 = C_6H_5$
g, $R^1 = CH_3$; $R^2 + R^3 = (CH_2)_4$; $R^4 = C_6H_5$

Scheme II



perature was maintained at 180–200°, except for deuterated compounds where it was 130–150°.[12] High-resolution mass spectra for 4-chloroacetylamino-3-penten-2-one (3c) and 3-acetylamino-5,5-dimethyl-2-cyclohexen-1-one (24b) were obtained on an A.E.I. MS-902 mass spectrometer. All values from exact mass measurement were accurate to within 15 ppm.

The preparation or source of each unlabeled compound utilized in the present work has been described earlier in this series.[1,11] Deuterated samples were prepared from acetic anhydride-d_6 and the appropriate vinylogous amide. Isotopically labeled compounds included 4-acetyl-d_3-amino-3-methyl-3-penten-2-one (3b), mp 47–48°, 2-(1-acetyl-d_3-aminoethylidene)cyclohexanone (12b), mp 33–35°, and 3-acetyl-d_3-amino-5,5-dimethyl-2-cyclohexen-1-one (24c), mp 157.5–158.5°.

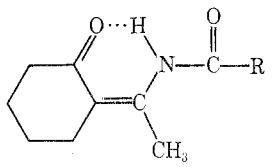
Results and Discussion

Spectral data are included in Tables I–V. The fragmentation pathways proposed below (Schemes I–VIII) are substantiated by (1) appropriate shifts in the spectra of labeled deuterium compounds 3b, 12b, and 24c; (2) appropriate metastable peaks (when present in all or most of the spectra this is indicated by an asterisk); and (3) selective high-resolution mass measurements.

Acyclic Compounds. Intensities of the major ions in the spectra of cis-s-cis[8] vinylogous imides 3a–g are collected in Table I. Inspection of this information supports the conclusion that the fragmentation pattern of the initially formed radical cation 3 (Schemes I and II) is directed by the location and nature of the particular acyl group involved.

Within Scheme I, a strong preference is noted for the formation of those ions, 4 and 6, which retain the *N*-acyl group. Assuming both acylium ions are formed directly from the molecular ion 3, it is not unreasonable that cation 4, a product of allylic cleavage, should be favored over 5, where the neutral fragment is a vinyl radical. High-resolution mass measurement (m/e 43 is greater than 99% C_2H_3O) plus the characteristic chlorine isotope pattern in the spectrum of 3c clearly indicate that acetyl cation 5c ($R^1 = CH_3$) prevails over ion 4c, $ClCH_2CO^+$. Although the latter ion's low abundance is presumably due to the inductive effect of the chlorine atom, a satisfactory rationalization of

Table II
Relative Intensities of Principal Peaks in the Mass Spectra of Isocyclic Cis-s-Cis Compounds



Peak	R: CH_3 (12a)	CD_3 (12b)	C_6H_5 (12c)
$[M]^{\cdot+}$	41.3	51.2	8.9
13	62.7	65.1	100.0[a]
14	61.9	56.3	20.0
15	64.7	40.5	16.5
16	31.8	26.0	20.0
17	15.8[b]	12.8	6.4
18	17.9[c]	20.9	
19	34.7[c]	36.7	
20	100.0	100.0	
21	19.7[b]	16.0	
22	17.1	14.9	
23	24.7	22.1	

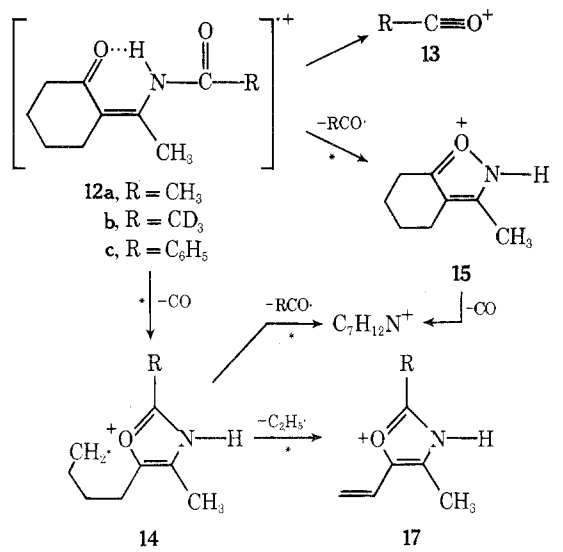
[a] See Table I, footnote *e*. [b] A single peak, *m/e* 124 (35.5%), is observed for ions **17a** and **21a**. Values shown are based upon results for **12b**. [c] Corrected for isotopic contribution from ion of next lower integral mass number.

the high intensity of ion **5c** is not apparent. The importance of the oxazolium[13] ion **6** compared to isoxazolium[13] ion **7** is consistent with the lower acidity of the former cation in aqueous solution.[14] Ring substituent effects are comparable or also favor **6** in all instances save that of **3d** (the only *C*-benzoyl compound), where the base peak is isoxazolium ion **7d** (*m/e* 160). Based upon high-resolution studies exact compositions were assigned to most of the important ions generated from compound **3g**: $[M]^{\cdot+}$, *m/e* 243, $C_{15}H_{17}NO_2$; **6g**, *m/e* 200, $C_{13}H_{14}NO$; **7g**, *m/e* 138, $C_8H_{12}NO$; **4g**, *m/e* 105, C_7H_5O; and *m/e* 77, C_6H_5.[15]

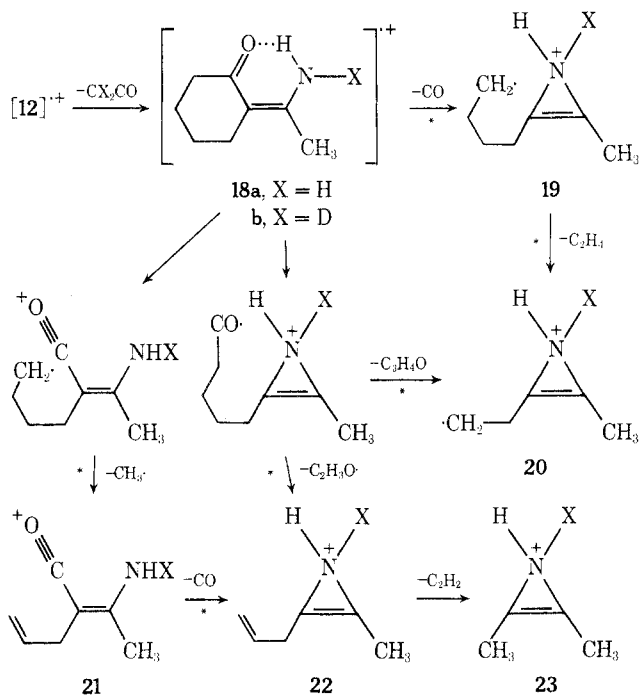
A very significant fragmentation pathway for acyclic *N*-alkanoyl imides **3a–d** is shown in Scheme II. Loss of the appropriate ketene with transfer of a hydrogen (or deuterium) atom to nitrogen (**3** → **8**) is followed by expulsion of methyl or phenyl radical (**8** → **9**), thereby affording resonance stabilized cation **9**.[16] Subsequent decomposition of even-electron ion **9** is unexceptional. The greater relative importance of azirinium cations **11a** and **11b** ($R^2 = CH_3$), compared to **11c** and **11d** ($R^2 = H$), is probably due to the electron-donating power of the additional methyl substituent. Exact mass measurement of all ions higher than *m/e* 39 in the spectrum of compound **3c** confirms the processes outlined in Scheme II, and in Scheme I as well. In particular the moderately intense peak (29.6%) at *m/e* 42 is primarily (84% C_2H_4N, 16% C_2H_2O) the even-electron nitrilium ion **10c** (X = H).

Isocyclic Compounds. Having established the basic behavior of representative acyclic compounds upon electron impact, it was of evident interest to determine what effect increasing stereochemical and/or structural restraint would have on the fragmentation pattern. We turn first to an examination of the principal ions in the mass spectra of 2-(1-acylaminoethylidene)cyclohexanones **12a–c** collected in Table II. Elemental compositions of all ions derived from **12a** and **12c** (see Schemes III and IV) are compatible with high-resolution data[15] and for **12a**, with the spectrum of labeled compound **12b** as well. Initial fragmentation of the

Scheme III

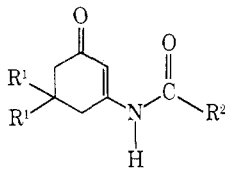


Scheme IV



molecular ion **12** is dominated by bond cleavage at carbonyl carbon, as was the case with acyclic compounds **3a–g**. Direct comparison of the relative intensities of related ions in Schemes I and III, *i.e.*, those from **3a** and **12a** and from **3f** and **12c**, reveals: (1) no dramatic difference between acylium ions **4** and **13**, (2) decreased abundance of oxazolium ion **14**, and (3) a large increase in importance of isoxazolium ion **15**. These results are reasonable, since incorporation of the *C*-acyl group into the six-membered ring of **12** not only means that formation of radical ion **14** requires an additional bond cleavage (compared to ion **6**), but also guarantees a more favorable entropy of activation for appearance of the isoxazolium ion **15** (compared to **7**). Ejection of the remaining carbonyl from **14** or **15** gives rise to a common product, even-electron ion **16**, as shown in Scheme III. Although high-resolution measurements confirm $C_7H_{12}N^+$ and compound **12a** exhibits a metastable peak at *m/e* 87.7 (**15** → **16**), what relatively stable structure corresponds to **16** is an open question for us.

Table III
Relative Intensities of Principal Peaks in the Mass Spectra of Isocyclic Trans-s-Trans Compounds



Peak	R^1, R^2 H, CH_3 (24a)	CH_3, CH_3 (24b)	CH_3, CD_3 (24c)	CH_3, C_6H_5 (24d)
$[M]^{\cdot+}$	34.9	27.0	28.2	7.8
25	25.5	13.8	13.5	4.8
26	0.3	14.1	15.2	2.2
27	46.8	100.0	100.0	10.6
28	79.7	66.9	70.9	100.0[a]
29	25.5	4.8	2.8	
30	100.0	89.9	77.8	
31	17.0	15.2	15.2	
32	1.8	37.2	34.3	8.2
33	4.1	37.2	36.0	

[a] See Table I, footnote *e*.

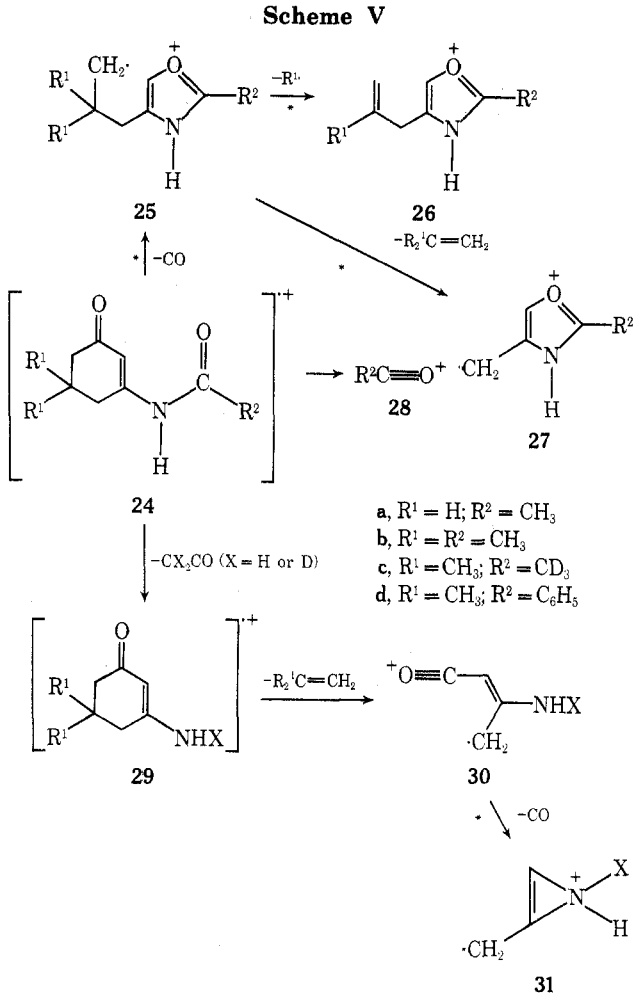
Scheme IV presents a competing fragmentation pattern open to molecular ions **12a** and **12b,** ordinary or labeled (X = D) ketene being eliminated in the first step to generate radical cation **18.** Further decomposition of **18** ultimately leads to azirinium radical ion **20** as the base peak, or to the less important even-electron azirinium ion **23.**

The mass spectra of trans-s-trans vinylogous imides **24a–d** were examined next (Table III), and the basic fragmentation pattern (see Scheme V) is clearly related to those of Schemes I–IV. Loss of an *N*-acyl radical ($R^2CO\cdot$) from molecular ion **24** is negligible,[17] for the resulting cation cannot attain the relatively stable isoxazolium structure (*cf.* ions **7** and **15**) unless ring cleavage[18] and subsequent trans → cis isomerization also occurs. On the other hand, no significant barrier to oxazolium ion formation (**24** → **25**) exists,[19] and indeed radical cation **27** constitutes the base peak in the mass spectra of compounds **24b** and **24c.**

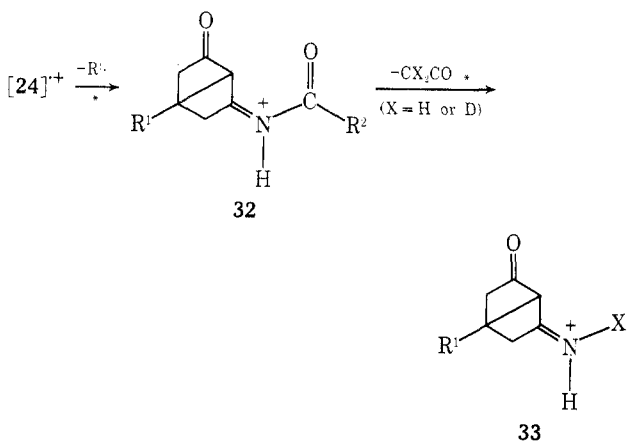
The most abundant ion produced upon electron impact of *N*-acetyl compound **24a** involves successive losses of ketene and ethylene, with appropriate metastable peaks being observed at *m/e* 80.6 (**24a** → **29a**) and *m/e* 62.1 (**29a** → **30a**). Highly conjugated radical cation **30** is also very important in the fragmentation of the two other *N*-acetyl compounds, **24b** and **24c.** Subsequent expulsion of carbon monoxide from **30** should give rise to azirinium[20] ion **31** as shown in Scheme V. In the case of compound **24a** exact mass measurements fully support the structures assigned to fragment ions **25, 27, 29,** and **30.**[15] Further substantiation of the pathways indicated in Schemes V and VI is provided by high-resolution data (ions of *m/e* greater than 39) for *gem*-dimethyl compound **24b** plus peak shifts in the spectrum of labeled compound **24c.** Examination of the *m/e* 55 peak (22.3%) in the high-resolution spectrum of **24b** showed it to be mainly (68% C_3H_5N, 32% C_4H_7) the azirinium radical cation **31b.**

Primary fission of a ring methyl group is significant in the mass spectra of compounds **24b–d,** the resulting tertiary carbocations **32b–d** possibly being stabilized *via* resonance involvement of the enamino system as envisioned in the bridged structures of Scheme VI. As expected, ejection of a hydrogen atom from molecular ion **24a** (R^1 = H) to form the secondary cation **32a** is not a favored process.

Scheme V



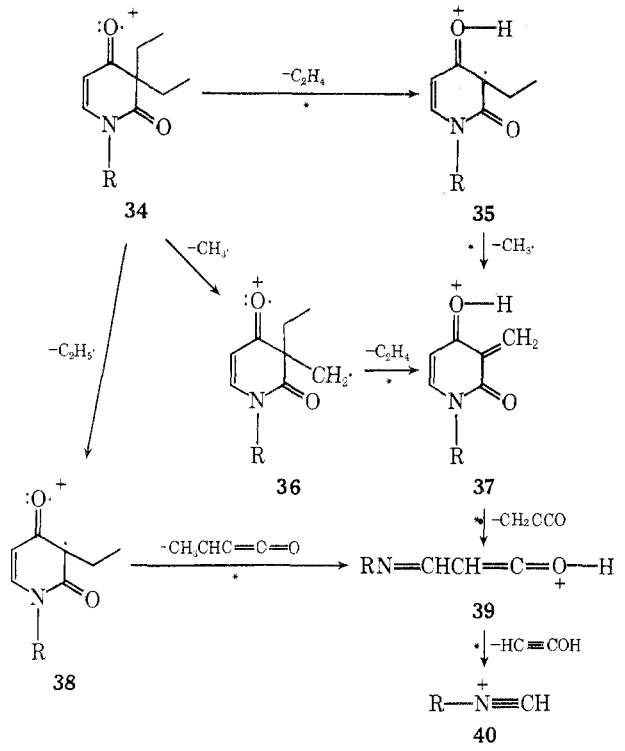
Scheme VI



Preferential loss of a methyl radical over a hydrogen radical is also evidenced in the low abundance of even-electron ion **26a.**

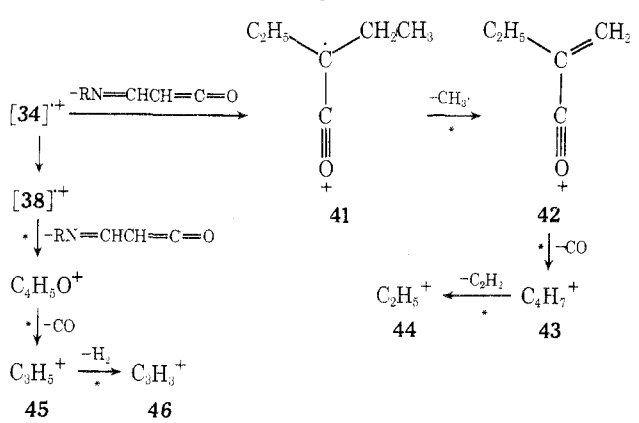
Heterocyclic Compounds. Finally, two groups of heterocyclic imides were studied, the stereochemistry of the conjugated system in each set being completely fixed. Schemes VII and VIII suggest decomposition mechanisms based upon mass spectral results for monocyclic cis-s-trans compounds **34a** and **34b** (Table IV). The abundance of metastable peaks plus elemental compositions for all charged species of *m/e* 69 or greater provide strong support for these fragmentation pathways. No oxazolium or isoxazolium fragment ions are observed, but rather the two most abundant high mass peaks in the spectra of **34** are due to

Scheme VII



a, R = H
b, R = CH_3

Scheme VIII



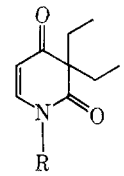
an initial McLafferty rearrangement (**34** → **35**, Scheme VII)[20] and an initial reverse Diels–Alder reaction (**34** → **41**, Scheme VIII), respectively.

Within Scheme VII all fragment ions retain the nitrogen atom, a relatively stable even-electron ion **39** being formed *via* ring cleavage (**37** → **39** or **38** → **39**). The structural relationship between cation **39** and cation **9** (Scheme II) is quite apparent.

Alternatively, the heterocyclic nitrogen atom can be ejected within a neutral vinylogous isocyanate molecule (RN=CHCH=C=O) in a first (**34** → **41**) or second (**38** → $C_4H_5O^+$) decomposition step (see Scheme VIII). Not suprisingly ion **42** dominates Scheme VIII, the ethacrylyl cation[22] being the base peak in the mass spectrum of compound **34a** and also very important in **34b**. Subsequent loss of carbon monoxide from **42** to yield a hydrocarbon fragment ion is as expected.[23]

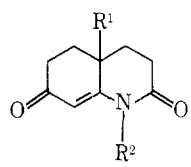
No consistent fragmentation pathway of high probability appears to exist for the three bicyclic compounds **47a–c**. Decomposition of the molecular ion to yield either an even-electron oxazolium or isoxazolium ion, or a highly resonance stabilized radical cation analogous to **35** (see Scheme VII), is incompatible with compound structure. Except for the high mass region of **47a**, the mass spectra of the three fixed trans-s-trans imides are characterized by ubiquitous ion clusters. In all cases the molecular ion peak is very abundant (see Table V) and either it or the [M − 28] radical ion constitutes the base peak. Ejection of an ethylene

Table IV
Relative Intensities of Principal Peaks in the Mass Spectra of Heterocyclic Cis-s-Trans Compounds



	R	
Peak	H (34a)	CH_3 (34b)
$[M]^{\cdot+}$	8.2	7.4
35	92.9	100.0
36	31.0	3.5
37	9.4	15.0
38	12.7	15.7
39	57.4	71.4
40	13.6	23.3
41	86.8	73.6
42	100.0	85.7
43	45.9	30.8
44	13.0	9.5
45	25.4	17.2
46	15.0	7.9

Table V
Relative Intensities of Principal Peaks in the Mass Spectra of Heterocyclic Trans-s-Trans Compounds



	R^1, R^2		
Peak	H, CH_3 (47a)		C_6H_5, H (47b) C_6H_5, CH_3 (47c)
$[M]^{\cdot+}$	54.4	$(C_{10}H_{13}NO_2)^a$	93.2 100.0
M − 28	100.0	$(C_8H_9NO_2)^a$	100.0 73.6
M − 29	12.6		31.2 17.4
M − 43	26.4	$(C_7H_6NO_2)^a$	2.8 5.9
M − 56	8.1	$(C_7H_9NO)^a$	21.8 15.6
M − 57	6.8	$(C_7H_8NO)^a$	25.4 8.9
M − 69	4.6	$(C_6H_8NO)^a$	6.1 3.2
M − 71	5.4	$(C_6H_6NO)^a$	7.6 17.3
M − 84	18.2	$(C_6H_9N)^a$	24.4 15.6
M − 85	7.6	$(C_6H_8N)^a$	13.0 7.4
M − 97	16.2	$(C_4H_4NO)^a$	7.0 2.8
M − 98	2.8	$(C_5H_7N)^a$	17.0 4.9

[a] Fragment ion compositions for compound **47a** were determined by high-resolution measurement. The nominal masses are comprised of greater than 90% of ion of the indicated elemental composition with the exception of [M − 71] (greater than 75%) and [M − 98] (greater than 60%).

molecule from $[M]^{\cdot+}$ is followed by stepwise loss of two carbon monoxide molecules,[24] the resulting [M − 28], [M − 56], and [M − 84] peaks all being relatively unstable odd-electron species. Confirming metastable transitions for the first two steps are found in the spectra of all three compounds. Additional experiments to further elucidate the results of Table V do not seem to be a compelling objective at the present time.

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Registry No.—**3a,** 23652-94-0; **3b,** 53432-94-3; **3c,** 23754-49-6; **3d,** 23652-96-2; **3e,** 23112-27-8; **3f,** 23652-95-1; **3g,** 23674-49-9; **12a,** 23652-79-1; **12b,** 53432-95-4; **12c,** 23652-80-4; **24a,** 23674-56-8; **24b,** 23645-83-2; **24c,** 53432-96-5; **24d,** 23674-57-9; **34a,** 77-04-3; **34b,** 1130-18-3; **47a,** 1130-77-4; **47b,** 1216-47-3; **47c,** 1149-82-2.

References and Notes

(1) Part II, D. L. Ostercamp, *J. Org. Chem.*, **35,** 1632 (1970).
(2) J. J. Jakobsen, S.-O. Lawesson, J. T. B. Marshall, G. Schroll, and D. H. Williams, *J. Chem. Soc. B,* 940 (1966).
(3) M. Vandewalle, N. Schamp, and M. Francque, *Org. Mass Spectrom.*, **2,** 877 (1969).
(4) R. T. Aplin and R. Mestres, *Org. Mass Spectrom.*, **3,** 1067 (1970).
(5) A. M. Duffield, C. Djerassi, G. Schroll, and S.-O. Lawesson, *Acta Chem. Scand.*, **20,** 361, (1966).
(6) J. M. Rice, G. O. DudeK, and M. Barber, *J. Amer. Chem. Soc.*, **87,** 4569 (1965).
(7) T. Nishiwaki, *Tetrahedron,* **22,** 3117 (1966).
(8) See ref 1 for details concerning stereochemical classification of compounds used in this project. Intramolecular hydrogen bonding (where possible) would be strongly favored within the mass spectrometer vacuum.
(9) Presence of an electron-withdrawing *N*-acyl substituent would destabilize this fragment ion (as compared to **2a**). Apparently contradictory results have been obtained for three *N*-acyl vinylogous urethanes and one vinylogous imide.[5] However, all four are heterocyclic compounds, and alternative fragmentation would disrupt the ring.
(10) Sucn ions would result from direct loss of an acyl group. Cyclic azirinium ions have been postulated as minor fragment ions in the mass spectra of vinylogous amides.[3,4] The present expectation regarding stability is based on the twin factors of favorable ring size and aromatic character.
(11) D. L. Ostercamp, *J. Org. Chem.*, **30,** 1169 (1965).
(12) Representative starting compounds were shown to be thermally stable at 200°, thus precluding any thermal reaction in the inlet system.
(13) Ions analogous to **6** and/or **7** are essentially absent whenever the appropriate carbonyl group is stereochemically barred from participation (see discussion of cyclic compounds). Alternative structures, *i.e.,* acyclic or azirinium cations, would not enjoy aromatic stability. Oxazolium ion structures have been assigned to base peaks in the mass spectra of 5-methyl- and 4,5-dimethyl-2-hexyloxazole and 2,5-dimethyl-4-hexyloxazole: J. H. Bowie, P. F. Donaghue, H. J. Rodda, R. G. Cooks, and D. H. Williams, *Org. Mass Spectrom.*, **1,** 13 (1968).
(14) D. J. Brown and P. B. Ghosh, *J. Chem. Soc. B,* 270 (1969). We refrain from commenting on the relative resonance stabilization of ions **6** and **7,** as we are unable to find a reference to heats of hydrogenation and/or combustion of oxazole and isoxazole.
(15) The results are limited here to ions whose *m/e* is equal to or greater than 69.
(16) The second step, **8** → **9,** is equivalent to a prominent first step, **1a** → **2a,** in the fragmentation of the molecular ion of a vinylogous amide. As **9a** is here, so is **2a** often the base peak.[2-4]
(17) Relative intensities of $[M - R^2CO]$ cations for the following compounds are, for **24c,** 0.4% and, for **24d,** 0.2%.
(18) This would produce a diradical, and so detract from product stability.
(19) Ring closure is accompanied by inversion of configuration at a vinyl carbon atom. The process may be viewed as an SNi reaction, carbon monoxide being the leaving group.
(20) Such fragmentation is also shown by analogous vinylogous esters and amides[3] and 5,5-dialkylbarbituric acids.[21]
(21) H.-F. Grutzmacher and W. Arnold, *Tetrahedron Lett.,* 1365 (1966).
(22) J. T. Watson and F. C. Falkner, *Org. Mass Spectrom.*, **7,** 1231 (1973).
(23) A. J. Bowles, E. F. H. Brittain, and W. O. George, *Org. Mass Spectrom.*, **2,** 809 (1969).
(24) See ion compositions for compound **47a** in Table V.

Site Selectivity on Hydrogenation of Bicyclo[4.2.1]nona-2,4,7-trien-9-one. A Possible Effect of Homoaromatic Delocalization

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The synthesis of bicyclo[4.2.1]nona-2,4-dien-9-one (**2**) by catalytic and diimide reduction of bicyclo[4.2.1]nona-2,4,7-trien-9-one (**1**) was investigated. It was found that direct reduction of **1** gave five reduced ketones, whose structures were determined spectroscopically, but none of **2.** An authentic sample of **2** was prepared in low yield by further reactions of two of the other reduced ketones. However, conversion of the ketone group of **1** to a dimethyl ketal, an ethylene ketal, or an alcohol prior to reduction, followed by treatment with diimide and then either hydrolysis or oxidation, respectively, gave high yields of **2.** The reduction *via* the dimethyl ketal has been developed into a useful preparative procedure for **2.** The reluctance of **1** to give **2** on direct reduction is attributed to homoaromatic interaction of the electrons on the isolated double bond at C_7–C_8 with the carbonyl at C_9 leading to sharply reduced electron density at C_7–C_8 compared to the diene moiety. The electron density in the diene may even be increased by bis(homocyclopentadienyl) interaction with the carbonyl. These effects are removed by conversion of C_9 to a tetrahedral configuration from the trigonal configuration in **1.** Steric effects in this system are analyzed and are concluded to be of less significance than the electronic effects.

We had need of bicyclo[4.2.1]nona-2,4-dien-9-one (**2**) for photochemical studies described elsewhere[2] and sought to prepare **2** by reduction of bicyclo[4.2.1]nona-2,4,7-trien-9-one (**1**). Compound **1** was recently synthesized through different routes by three groups.[3,4] We naively assumed that catalytic or diimide hydrogenation of **1** would preferentially reduce the isolated double bond (C_7–C_8) as opposed to the diene moiety.

Results

The synthesis of **1** utilized was essentially that of Antkowiak and Shechter.[3] The synthesis of **2** from **1** would seem to be simply accomplished by reduction of the C_7–C_8 double bond, since isolated double bonds are reduced preferentially to a conjugated diene grouping. However, **2** was not present in the complex product mixture derived from