Robert L. Zey

Department of Chemistry, Central Missouri State University, Warrensburg, Missouri 64093

Michael L. Gross and Gary S. Groenewold

Department of Chemistry, University of Nebraska, Lincoln, Nebraska 68588

Received March 13, 1989

The mass spectrum of 3(2*H*)-cinnolinone indicates that it undergoes fragmentation in a fashion similar to other heterocyclic systems containing two vicinal nitrogens. The initial fragmentation, loss of CO, gives a 1*H*-indazole radical cation, as was shown by deuterium labelling and metastable ion spectra. Four 2-substituted-3(2*H*)-cinnolinones were also studied and it was found that their fragmentation patterns are highly influenced by the substituent groups.

J. Heterocyclic Chem., **27**, 209 (1990).

The mass spectra of various heterocyclic systems containing two vicinal nitrogen atoms, such as 3(2*H*)-pyridazinone (**I**) [1,2], 1(2*H*)-phthalazinone (**II**) [1] and 1*H*-indazol-3-ol (**III**) [3] were reported. This paper will discuss the mass spectra of 3(2*H*)-cinnolinone (**IV**) and various of its 2-substituted derivatives and compare their fragmentation patterns with those of other systems containing two vicinal nitrogen atoms.

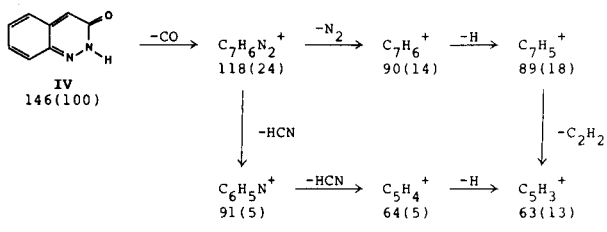
Results and Discussion.

3(2*H*)-Cinnolinone (**IV**) (see Table 1) undergoes fragmentation (Scheme 1) in a manner analogous to that of 3(2*H*)-pyridazinone (**I**) (Scheme 2); that is, it undergoes losses of CO, N_2, and then H. There is a subsequent loss of C_2H_2 from the $C_7H_5^+$ ion. This is also observed for 1(2*H*)-phthalazinone (Scheme 3). Interestingly, the initial fragmentation of 1(2*H*)-phthalazinone to give the $C_7H_6^+$ ion is reversed (*i.e.*, loss of N_2 and then loss of CO). There is no significant loss of CHO from 3(2*H*)-cinnolinone as is the case for 3(2*H*)-pyridazinone and 1(2*H*)-phthalazinone; however, one pathway for fragmentation of 1*H*-indazol-3-ol (**III**) (shown to exist primarily as the enol tautomer) involves loss of CHO (Scheme 4). The major fragmentation of 1*H*-indazol-3-ol involves the loss of N_2H. This occurs to a lesser extent for 1(2*H*)-phthalazinone and is not detected for 3(2*H*)-cinnolinone or 3(2*H*)-pyridazinone. Another fragmentation of 3(2*H*)-cinnolinone involves the loss of CO and two losses of HCN. This is also observed for 1*H*-indazol-3-ol and apparently for 1(2*H*)-phthalazinone. 3(2*H*)-Pyridazinone loses CO and at least one molecule of HCN.

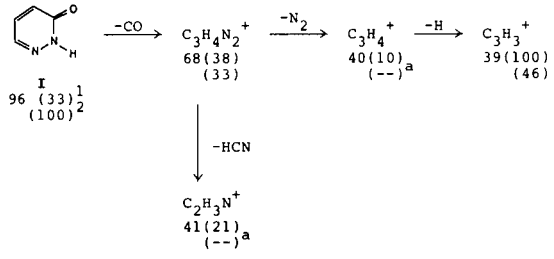
TABLE 1
Partial Mass Spectrum of 3(2H)-Cinnolinone (IV)

m/z	Composition	*m/z*	Composition
147	$^{13}CC_7H_6N_2O$ (11.4%)	89	C_7H_5 (18.3%)
146	$C_8H_6N_2O$ (100%)	86	C_7H_2 (6.2%)
118	$C_7H_6N_2$ (24.4%)	64	C_5H_4 (5.0%)
91	C_6H_5N (5.2%)	63	C_5H_3 (13.5%)
90	C_7H_6 (14.4%)	62	C_5H_2 (5.2%)

Scheme 1

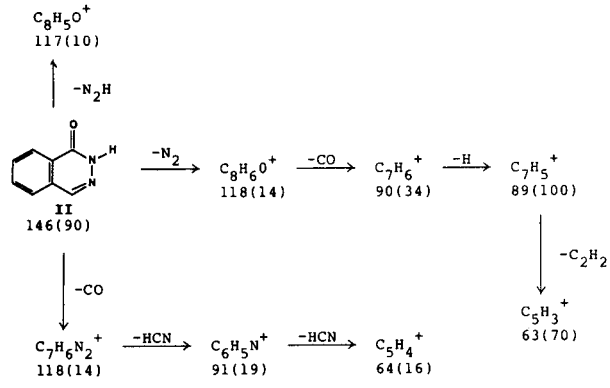


Scheme 2

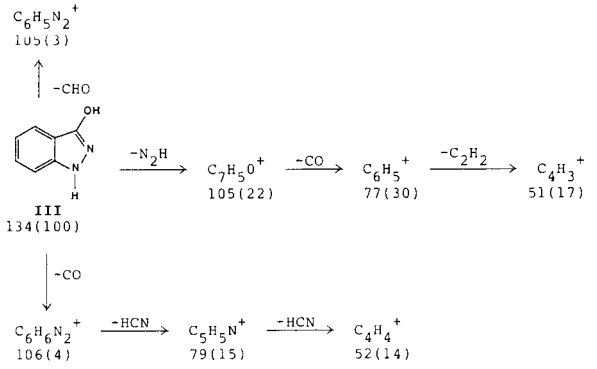


[a]This ion not reported in article.

Scheme 3

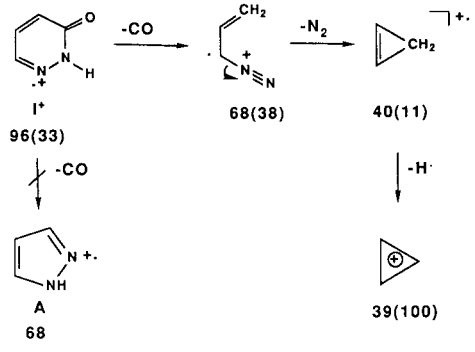


Scheme 4

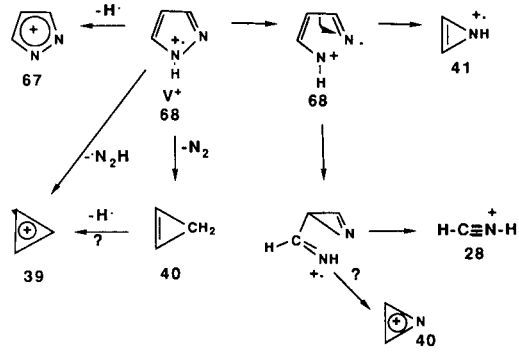


Porter and Baldas [4] gave a rational for the fragmentation of 3(2*H*)-pyridazinone (Scheme 5). They say that it is clear that ion A is not formed because it does not break down like pyrazole (**V**) [5] (Scheme 6). They based their rational on the work of Bowie, *et al.* [1]. Bowie, *et al.* do not mention the loss of HCN from the *m/z* 68 ion, but the mass spectrum published in the article shows a peak at *m/z* 41, which is 21% relative to the base peak.

Scheme 5

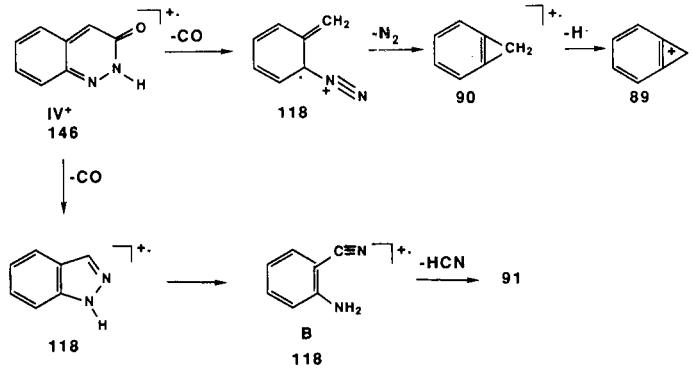


Scheme 6



It appears that the molecular ion of 3(2*H*)-cinnolinone loses CO to give two isomeric ions (Scheme 7) of *m/z* 118. A metastable ion kinetic energy spectrum (MIKES) of the *m/z* 118 species (Figure 1, A) shows an abundant ion at *m/z* 91 (loss of HCN) and a lower abundance one at *m/z* 90 (loss of N_2). A MIKES spectrum of the *m/z* 119 species of 2-d_1-3(2*H*)-cinnolinone (Figure 1, B) shows almost equal losses of DCN (to give the *m/z* 91 ion) and HCN (to give the *m/z* 92 ion). The species resulting from the loss of N_2 would have an *m/z* of 91 also, but the ion should be of low

Scheme 7



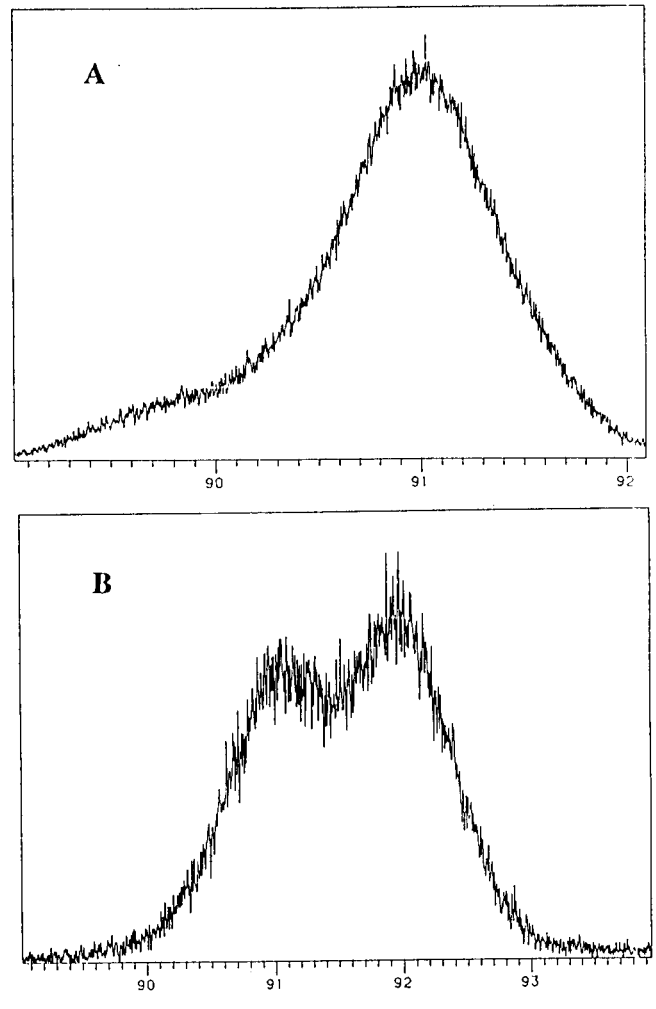
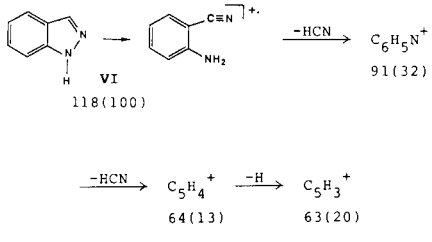


Figure 1. Decompositions of metastable ions.
A. Partial MIKES spectrum spectrum of the $[M - CO]^{+\cdot}$ ion from 3(2H)-cinnolinone ionized at 70 eV. Thirty 20-sec scans were signal averaged. B. Partial MIKES spectrum of the $[M - CO]^{+\cdot}$ ion from 2-d_1-3(2H)-cinnolinone ionized at 70 eV. Thirty 20-sec scans were signal averaged.

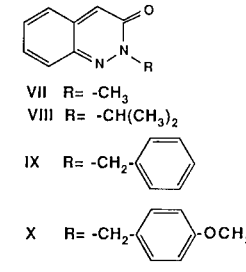
abundance compared to that formed by loss of DCN (note Figure 1, A). This gives some validity to species B (Scheme 7) in which both the H and D are attached to the nitrogen and thus would have equal opportunity to be lost as HCN and DCN, ignoring any kinetic isotope effects.

Further evidence for the fragmentation proposed for 3(2*H*)-cinnolinone (Schemes 1 and 7) is given in the study of 1*H*-indazole (Scheme 8) by Maquestiau, *et al.* [6]. They showed that the molecular ion of 1*H*-indazole (**VI**) isomerizes to that of *o*-aminobenzonitrile before fragmentation. They likewise observed virtually equal losses of HCN and DCN from the *m/z* 118 ion. Thus, one of the isomeric *m/z* 118 species formed by loss of CO from 3(2*H*)-cinnolinone is the 1*H*-indazole radical cation. A similar conclusion was reached for the structure of the ions arising by losses of CO from 2-pyrone and 4-pyrone, a classic question in mass spectrometry mechanisms. The structure of the principal fragment ion in those cases is that of the furan radical cation [7].

Scheme 8



Four 2-substituted-3(2*H*)-cinnolinones were also studied. They are 2-methyl-3(2*H*)cinnolinone (**VII**) (see Table 2), 2-isopropyl-3(2*H*)-cinnolinone (**VIII**) (see Table 3), 2-benzyl-3(2*H*)-cinnolinone (**IX**) (see Table 4) and 2-*p*-methoxybenzyl-3(2*H*)-cinnolinone (**X**) (see Table 5). The fragmentation patterns are highly influenced by the substituent groups.



The primary sequence of fragmentation of 2-methyl-3(2*H*)-cinnolinone (**VII**) is somewhat analogous to that of 3(2*H*)-cinnolinone. There is also a significant loss of CHO, which is not observed for 3(2*H*)-cinnolinone. 4-Methyl and 6-methyl-3(2*H*)-pyridazinone also show substantial abundances of the $[M - CHO]^+$ ion, but this loss does not occur for 3(2H)-pyridazinone. This result was explained by the influence of the *ortho*-effect of the methyl group [2]. The loss of CHO is much less important for the other three 2-substituted-3(2*H*)-cinnolinones (Scheme 9).

TABLE 2
Partial Mass Spectrum of
2-Methyl-3(2H)-cinnolinone (VII)

m/z	Composition	*m/z*	Composition
161	$^{13}CC_8H_8N_2O$ (9.4%)	90	$^{13}CC_6H_5$ (9.1%)
160	$C_9H_8N_2O$ (95.3%)	89	C_7H_5 (100%)
145	$C_8H_5N_2O$ (0.1%)	66	C_4H_4N (6.8%)
133	$^{13}CC_7H_8N_2$ (7.6%)	63	C_5H_3 (24.6%)
132	$C_8H_8N_2$ (84.6%)		C_4HN (0.2%)
131	$C_8H_7N_2$ (10.4%)	62	C_5H_2 (8.5%)
104	C_7H_6N (4.8%)	51	C_4H_3 (5.7%)
103	C_8H_7 (1.6%)	50	C_4H_2 (8.3%)
	C_7H_5N (1.4%)		

TABLE 3
Partial Mass Spectrum of
2-Isopropyl-3(2H)-cinnolinone (VIII)

m/z	Composition	*m/z*	Composition
189	$^{13}CC_{10}H_{12}N_2O$ (5.9%)	132	C_8H_6NO (13.8%)
188	$C_{11}H_{12}N_2O$ (48.7%)	118	$C_7H_6N_2$ (27.3%)
160	$C_{10}H_{12}N_2$ (2.1%)		C_8H_8N (0.6%)
159	$C_{10}H_{11}N_2$ (0.8%)	117	C_8H_5O (3.4%)
147	$C_8H_7N_2O$ (10.3%)	90	C_7H_6 (16.0%)
	$^{13}CC_7H_6N_2O$		$^{13}CC_6H_5$
146	$C_8H_6N_2O$ (48.9%)	89	C_7H_5 (100.0%)
145	$C_9H_9N_2$ (4.5%)	63	C_5H_3 (10.6%)
	$C_8H_5N_2O$ (4.0%)		

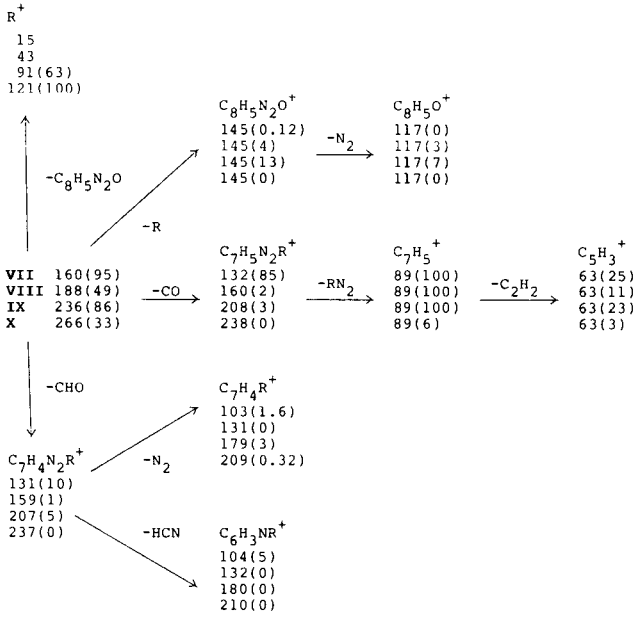
TABLE 4
Partial Mass Spectrum of
2-Benzyl-3(2H)-cinnolinone (IX)

m/z	Composition	*m/z*	Composition
237	$^{13}CC_{14}H_{12}N_2O$ (14.5%)	92	$^{13}CC_6H_7$ (5.4%)
236	$C_{15}H_{12}N_2O$ (85.9%)	91	C_7H_7 (62.7%)
235	$C_{15}H_{11}N_2O$ (7.1%)	90	$^{13}CC_6H_5$ (8.9%)
208	$^{13}CC_{13}H_{11}N_2$ (2.5%)	89	C_7H_5 (100.0%)
	$C_{14}H_{12}N_2$	83	C_6H_{11} (6.7%)
207	$C_{14}H_{11}N_2$ (4.9%)	81	C_6H_9 (6.7%)
179	$C_{14}H_{11}$ (3.3%)	71	C_5H_{11} (7.4%)
145	$C_8H_5N_2O$ (13.3%)	69	C_5H_9 (16.8%)
132	C_8H_6NO (5.7%)	65	C_5H_5 (30.5%)
117	C_8H_5O (7.3%)	63	C_5H_3 (23.4%)

TABLE 5
Partial Mass Spectrum of
2-*p*-Methoxybenzyl-3(2H)-cinnolinone (X)

m/z	Composition	*m/z*	Composition
267	$^{13}CC_{15}H_{14}N_2O_2$ (5.3%)	121	C_8H_9O (100.0%)
266	$C_{16}H_{14}N_2O_2$ (33.1%)	89	C_7H_5 (5.6%)
209	$C_{15}H_{13}O$ (0.3%)	77	C_6H_5 (5.2%)
122	$^{13}CC_7H_9O$ (7.9%)	63	C_5H_3 (2.5%)

Scheme 9

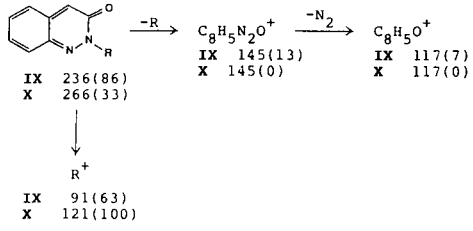


2-Isopropyl-3(2*H*)-cinnolinone (**VIII**) undergoes a number of other fragmentations that are dominated by the isopropyl group, particularly the loss of propene presumably by the McLafferty rearrangement to give an ion tautomeric with the $[M]^+$ of 3(2*H*)-cinnolinone (Scheme 10).

The $C_7H_5^+$ and $C_5H_3^+$ ions produced by fragmentation of the molecular ion of 3(2*H*)-cinnolinone are also produced in the decomposition of the various substituted compounds (see Scheme 9).

The benzyl derivatives fragment in the same manner as 3(2*H*)-cinnolinone (Scheme 1) and also show fragmentation between the 2-N of the cinnolinone and the R group as did 2-isopropyl-3(2*H*)-cinnolinone (Pathway A, Scheme 10). A considerable amount of the charge is carried by the R group. As might be expected because of the stablizing effect of the *p*-methoxy group, the $CH_3OC_6H_4CH_2^+$ ion is most abundant in the fragmentation of 2-*p*-methoxybenzyl-3(2*H*)-cinnolinone, and no detectable ion current is carried by the other fragment $[C_8H_5N_2O]^+$ (Scheme 11).

Scheme 11



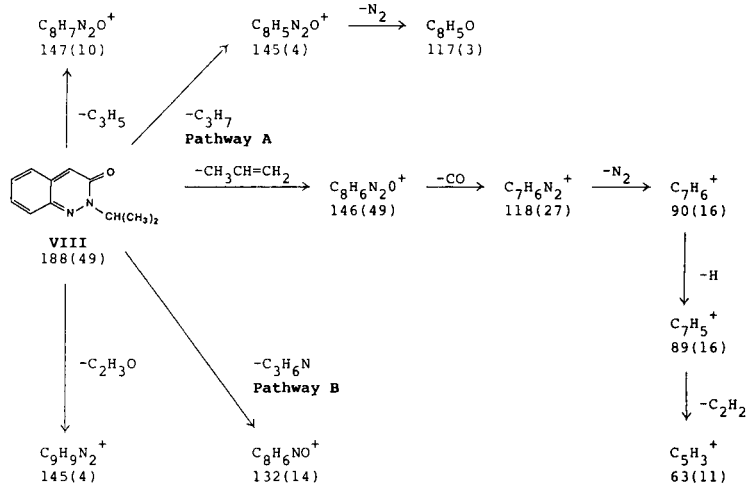
There is also some fragmentation involving the 2-N within the cinnolinone ring system as shown by 2-isopropyl-3(2*H*)-cinnolinone (Pathway B, Scheme 10). The relative abundance of the $[C_8H_6NO]^+$ ion from **IX** is 6%, but for *X*, only 0.42% $[C_8H_6NO]^+$ is formed.

EXPERIMENTAL

All full EI mass spectra were obtained on a Kratos MS-50 high resolution mass spectrometer operated at a mass resolving power of 10,000, an accelerating voltage of 8000 V, and an ionizing energy of 70 eV. The mass spectra reported were taken after 4-5 scans to insure that the spectra are reproducible from scan-to-scan. The reported elemental compositions have masses that are within at least 2.7 parts-per-million of the theoretical values.

The MIKES spectra were obtained by using a three sector Kratos MS-50 tandem mass spectrometer consisting of an EB

Scheme 10



mass spectrometer followed by an electrostatic analyzer (E) as the second mass spectrometer of the tandem [8]. The ions under study were separated at sufficient mass resolution to remove isobaric interferences by using the EB part of the spectrometer and obtaining the fragment ion spectrum by scanning the second E.

3(2*H*)-Cinnolinone (**IV**).

This material was prepared from isatin by the procedure previously reported by this author [9].

2-Methyl-3(2*H*)-cinnolinone (**VII**).

This material was prepared from 3(2*H*)-cinnolinone by the procedure previously reported by this author [10].

2-Isopropyl-3(2*H*)-cinnolinone (**VIII**).

The preparation of this material is discussed in an earlier article [11].

2-Benzyl-3(2*H*)-cinnolinone (**IX**).

The preparation of this material is discussed in an earlier article [11].

2-*p*-Methoxybenzyl-3(2*H*)-cinnolinone (**X**).

The preparation of this material is discussed in a earlier article [11].

REFERENCES AND NOTES

[1] J. H. Bowie, R. G. Cooks, P. F. Donaghue, J. A. Halleday and H. J. Rodda, *Aust. J. Chem.*, **20**, 2677 (1967).

[2] H. Ogura, S. Sugimoto, H. Igeta and T. Tsuchiya, *J. Heterocyclic Chem.*, **8**, 391 (1971).

[3] J. M. Desmarchelier and R. B. Johns, *Org. Mass Spectrom.*, **2**, 37 (1969).

[4] Q. N. Porter and J. Baldas, "Mass Spectrometery of Heterocyclic Compounds", Wiley-Interscience, New York, 1971, p 463.

[5] Q. N. Porter and J. Baldas, *ibid.*, p 443.

[6] A. Maquestiau, Y. Van Haverbeke and R. Flammang, *Org. Mass Spectrom.*, **10**, 558 (1975).

[7] H. F. Grutzmacher and R. Spilker, *Org. Mass Spectrom.*, **20**, 258 (1985) and references cited therein.

[8] M. L. Gross, E. K. Chess, P. A. Lyon, F. W. Crow, S. Evans and H. Tudge, *Int. J. Mass Spectrum. Ion Phys.*, **42**, 243 (1982).

[9] R. L. Zey, *J. Heterocyclic Chem.*, **9**, 1177 (1972).

[10] R. L. Zey, *J. Heterocyclic Chem.*, **24**, 1261 (1987).

[11] R. L. Zey, G. Richter, and H. Randa, *J. Heterocyclic Chem.*, **26**, 1437 (1989).