spectrum was determined on a CEC-110-21B spectrometer by Dr. Susan Rottschaefer.

4-Methyl-5,6,7,8-tetrahydrocarbostyril (4).—Sodium carbonate (100 mg, 0.94 mmol), adduct **3** (201 mg, 0.865 mmol), and 80% ethanol (5 ml) were heated at reflux for 1 hr. Chloroform (20 ml) was added, and the mixture was washed with water (2 × 20 ml) and brine (1 × 20 ml), dried ($MgSO_4$), filtered, and concentrated to yield 127 mg of solid residue (about 60% **4** by nmr). Recrystallization from acetone gave 30.8 mg (22%) of compound **4**. A portion after further purification by recrystallization from chloroform had mp 256°: nmr ($CDCl_3$) broad signal δ 12.76 (1 H), singlet 6.26 (1 H), broad signal 2.68 (2 H), broad signal 2.39 (2 H), singlet 2.11 (3 H), complex multiplet 1.77 (4 H); mass spectrum *m/e* (rel intensity) 163 (100), 148 (10), 135 (42), 107 (47). The compound was identical with an authentic sample of 4-methyl-5,6,7,8-tetrahydrocarbostyril as judged by nmr spectral, melting point, and mixture melting point criteria.

Registry No.—**3**, 36286-99-4; **4**, 36287-00-0; cyanoallene, 1001-56-5; 1-(*N*-morpholino)cyclohexene, 670-80-4.

Electron Impact Induced Fragmentations Mimicking Retro-1,3-dipolar Cycloadditions

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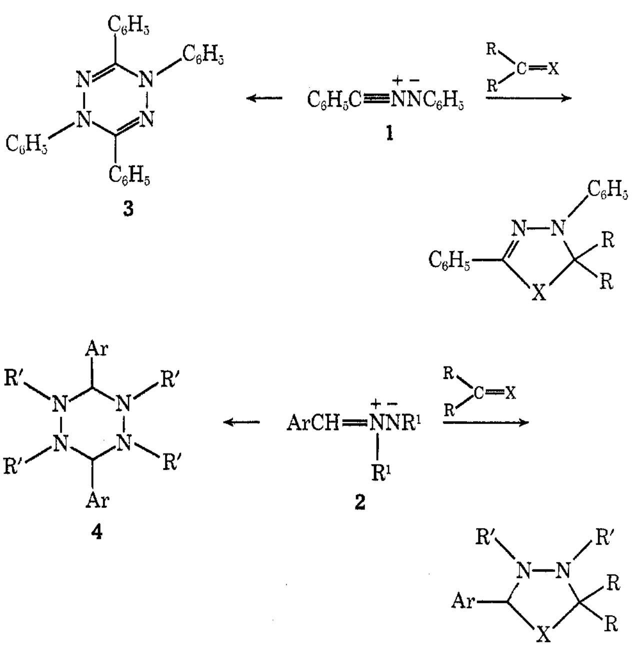
Correlation of thermal and photochemical processes with reactions that occur after electron impact has received considerable attention. The best known examples of successful analogies are the similarity of the mass spectrometric McLafferty rearrangement–decomposition process and the Norrish type 2 photofragmentation, and the occurrence of thermal, photochemical, and mass spectrometric retro-Diels–Alder reactions.[1] Recently, Nomura, Furusaki, and Takeushi[2] have proposed that retro-1,3-dipolar cycloadditions also have mass spectrometric counterparts, since 4- and 5-aminoisoxazolidines formed by 1,3-dipolar cycloaddition of enamines to nitrones yield ionized enamines upon electron impact. Earlier, at least one other well-established mass spectrometric retro-1,3-dipolar cycloaddition has been reported,[3] namely, the elimination of *tert*-butyl isocyanide from the molecular ion of the 3-(*N*-*tert*-butylimino)-1,2-diazetidine formed by addition of *N*-(*p*-nitrophenylimino)-1,2,3,4-tetrahydroisoquinoline to *tert*-butyl isocyanide.

We wish here to report the preliminary results of an investigation of the mass spectrometric behavior of heterocyclic compounds formed by 1,3-dipolar cycloaddition reactions of nitrile imines and azomethine imines, to show that such compounds upon electron impact may fragment by way of a cycloelimination reaction corresponding, formally, to the reverse process of their formation.

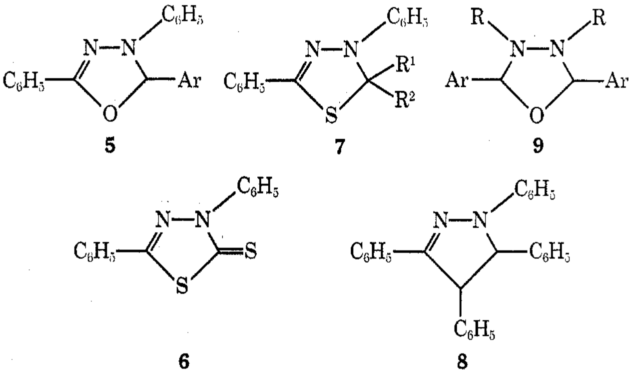
Addition of compounds incorporating C=C, C=O, or C=S double bonds to diphenylnitrileimine (1) or azomethine imines (2) usually yields five-membered ring compounds,[4] as illustrated in Scheme I.

SCHEME I



In the absence of dipolarophiles the 1,3-dipolar species dimerize to give dihydro-1,2,4,5-tetrazines (3) or hexahydro-1,2,3,4-tetrazines (4).[4] We have examined the mass spectra of several compounds formed in such reactions, **3**–**9**[5] (Scheme II).

SCHEME II



The mass spectrometric decomposition of the five-membered ring compounds **5**–**8** leads in all cases to ions corresponding in elemental composition to the parent 1,3 dipole (**1**, *m/e* 194), usually accompanied by minor peaks corresponding to the ionized dipolarophile. The most pronounced example of such retro-1,3-dipolar cycloaddition is found in the fragmentation of **5**, where more than 60% of Σ_{50} is carried by the three ions shown in Scheme III. Metastable ion peaks corresponding to both processes are observed in the spectra and have also been observed by metastable

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(1) T. W. Bentley and R. A. W. Johnstone, *Advan. Phys. Org. Chem.*, **8**, 151 (1970), and references cited therein.

(2) Y. Nomura, F. Furusaki, and Y. Takeushi, *J. Org. Chem.*, **37**, 502 (1972).

(3) J. A. Deyrup, *Tetrahedron Lett.*, 2191 (1971).

(4) R. Huisgen, *Angew. Chem., Int. Ed. Engl.*, **2**, 565 (1963).

(5) Formulas **4**, **5**, **7**, and **9** each represent several compounds of the class in question. A full discussion of the mass spectra of these compounds will appear elsewhere.

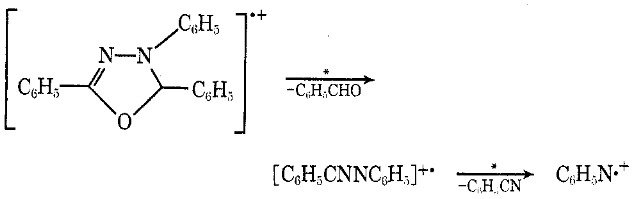
TABLE I

INTENSITIES OF PEAKS CORRESPONDING TO IONIZED DIPOLE AND DIPOLAROPHILE IN MASS SPECTRA OF REPRESENTATIVE 1,3-DIPOLAR CYCLOADDUCTS

Registry no.	Compd	Dipole[a]	Dipolarophile[a]	Base peak
36411-19-5	**4**, Ar = p-$CH_3OC_6H_4$; R′ = CH_2CH_3	206 (42)[b]	206 (42)[b]	C_8H_9O
36358-04-0	**4**, Ar = 3-pyridyl; R′ = CH_3	149 (25)[c]	149 (25)[c]	$C_7H_8N_2$
20561-17-5	**5**, Ar = C_6H_5	194 (48)	106 (2)	C_6H_5N
36358-06-2	**5**, Ar = p-$CH_3OC_6H_4$	194 (57)	136 (2)	C_6H_5N
36358-07-3	**7**, R^1 = H; R^2 = H	194 (5)	46 (2)	$M\cdot^+$
36358-08-4	**7**, R^1 = CH_2CH_3; R^2 = H	194 (10)	74 (3)	$[M^+ - H_2]$[d]
13187-62-7	**7**, R^1 = C_6H_5; R^2 = H	194 (26)	122 (2)	C_6H_5N
36358-10-8	**7**, R^1 = C_6H_5; R^2 = C_6H_5	194 (41)	198 (1)	$C_{13}H_{10}N$
36358-11-9	**7**, R^1 = C_6H_5; R^2 = $N(CH_2)_5$	194 (82)	205 (7)	C_6H_5N
36358-12-0	**7**, R^1 = p-$CH_3OC_6H_4$; R^2 = OCH_2CH_3	194 (98)	196 (3)	C_6H_5N
36358-13-1	**9**, Ar = m-$NO_2C_6H_4$; R = CH_2CH_3	221 (56)	151 (100)	$C_7H_5NO_3$

[a] m/e (rel intensity). [b] 205 (72). [c] 148 (94). [d] Possibly of thermal origin.

SCHEME III



defocusing, showing that the m/e 194 ion is not of thermal origin. Furthermore, the intensity ratio $M\cdot^+$ to m/e 194 does not change significantly when the temperature of the ion source is raised from 100 to 250°.

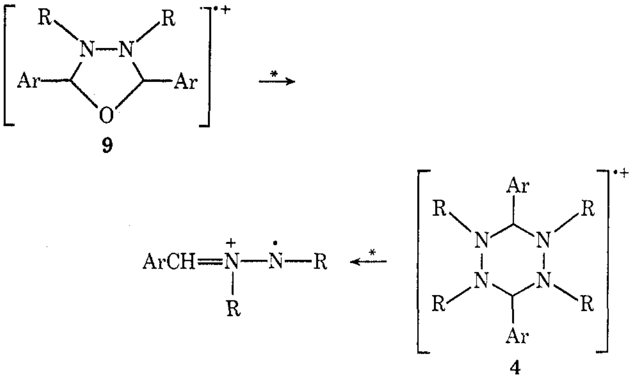
The mass spectrum of **6** likewise exhibits strong peaks corresponding to the fragment ions shown in Scheme III, whereas these are formed in lesser abundance in the decomposition of **7** and **8**. The intensity of the peaks corresponding to ionized **1** in the spectra of the various thiadiazolines **7** examined varies with R^1 and R^2, and is more intense when the eliminated fragment is aromatic (*cf.* Table I). This indicates that the retro-1,3-dipolar cycloaddition reaction within a class of compounds is dependent upon the stability of the eliminated neutral.

The retro-1,3-dipolar cycloaddition reaction occurs in compounds **5**–**7** principally with charge retention in the fragment corresponding to the dipolar species, while the ionized dipolarophiles only give rise to peaks of negligible intensity; only compound **8** produces ions of about equal abundance corresponding to **1** and to stilbene. These results contrast with the earlier suggestion of Nomura, Furusaki, and Takeushi[2] that this kind of cycloreversion reactions will proceed with charge retention mainly in the dipolarophile fragment.

The fragmentations of the cycloadducts of azomethine imines, **4** and **9** (Scheme IV), also give evidence of mass spectrometric retro-1,3-dipolar cycloadditions. The five-membered ring compounds **9** decompose to give abundant ions corresponding in elemental composition to azomethine imine as well as aldehyde, the latter producing the base peaks of the spectra.

Hexahydro-1,2,4,5-tetrazines **4** similarly produce ions corresponding in elemental composition to azomethine imines by bisection of the ring; this reaction is frequently accompanied by hydrogen transfer reactions leading to abundant ions 1 amu less (*cf.* Table I). The azomethine imine ions formed from **4** and **9** decompose further by nearly identical fragmentations, indicating these ions to be of similar structure. Hexahydro-1,2,4,5-tetrazines formed in reactions other than cyclodimerization of azomethine imines also undergo facile bisection of the ring to give abundant ions of half the mass of the molecular ion; these ions may likewise be regarded as ionized azomethine imines.[6]

SCHEME IV



Dihydro-1,2,4,5-tetrazines, however, fragment differently; the mass spectrum of **3** exhibits only a weak peak corresponding to ionized **1**. Instead [6 → 4 + 2][7] fragmentation reactions produce $PhCNPh^+$ and $PhCN\cdot^+$ ions. Similar [6 → 4 + 2] reactions are also of importance in the decomposition of **4**, leading to $ArCH{=}NR\cdot^+$ ions. This shows that mass spectrometric cycloreversion reactions formally resembling retro-1,3-dipolar cycloadditions are not always important in the decomposition of 1,3-dipolar cycloadducts. However, such reactions are expected to occur frequently among the mass spectrometric decomposition reactions of many compounds that may be formed through 1,3-dipolar cycloadditions.

(6) (a) S. Hammerum and J. Møller, *Org. Mass Spectrom.*, **5**, 1209 (1971). (b) W. Sucrow, H. Bethke, and G. Chondromatidis, *Tetrahedron Lett.*, 1481 (1971). (c) J. H. Cooley and J. W. Atchison, *ibid.*, 4449 (1969). (d) The M/2 ions formed in the fragmentation of 1,4-disubstituted hexahydro-1,2,4,5-tetrazines are probably an exception, since rearrangement by hydrogen migration to the isomeric hydrazone structure appears to be favored (ref 6a); the facile thermal dissociation of these compounds to give hydrazones (ref 6a,b,e) complicates an assignment of structure to the fragment ions of the same elemental composition. Evidence for similar rearrangements is not found in the mass spectra of other hexahydro-1,2,4,5-tetrazines. (e) S. R. Johns, J. A. Lamberton, and E. R. Nelson, *Aust. J. Chem.*, **24**, 1859 (1971).

(7) Simple cleavage of two ring bonds in a six-membered ring to give fragments containing, respectively, four and two ring atoms.