Mass Spectra of 2,4,5-Triphenyl-3*H*-pyrrol-3-one 1-Oxide and Derived Heterocycles Heavily Substituted with Phenyl Groups

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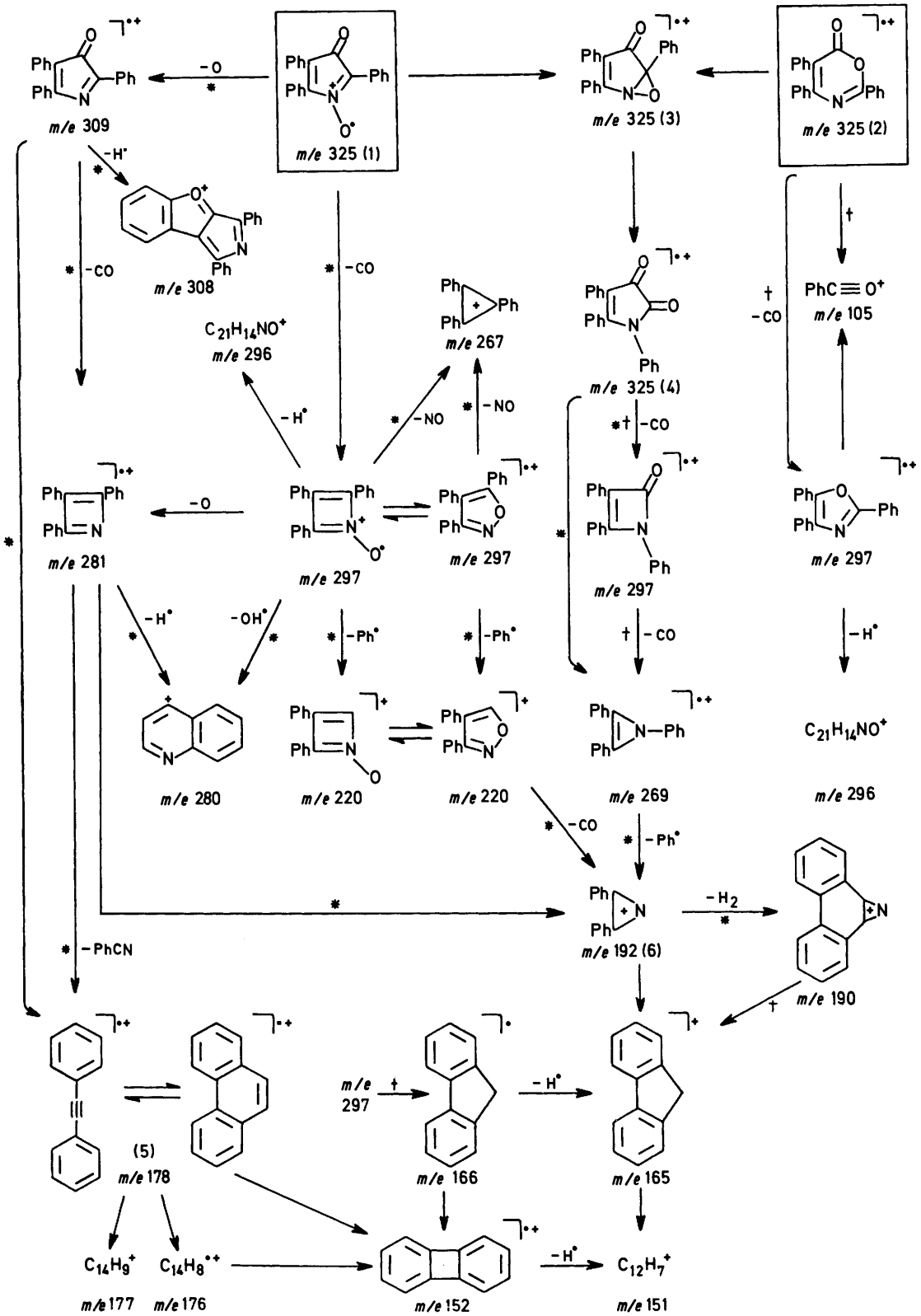
High resolution mass spectra are described for the title compound and the isomeric oxazinone, for 1- and 3-hydroxy-2,4,5-triphenylpyrrole, for the oxime, semicarbazone, and 2,4-dinitrophenylhydrazone of 5-benzoyl-3,4-diphenylisoxazole, for 2,5,6-triphenyl- and 2,3,5,6-tetraphenyl-pyrimidone, for 2-benzoyltriphenyl-4-pyridone, and for 3,4-bismethoxycarbonyl-2,5,6-triphenylpyridine. For most of these molecules detailed fragmentation paths are proposed.

WE have recently studied [1] some reactions of the title compound (1) a monocyclic analogue of the isatogens. The products of these reactions are in the main five- or six-membered heterocycles heavily substituted with phenyl groups. We here describe the high resolution mass spectra of some of these compounds.

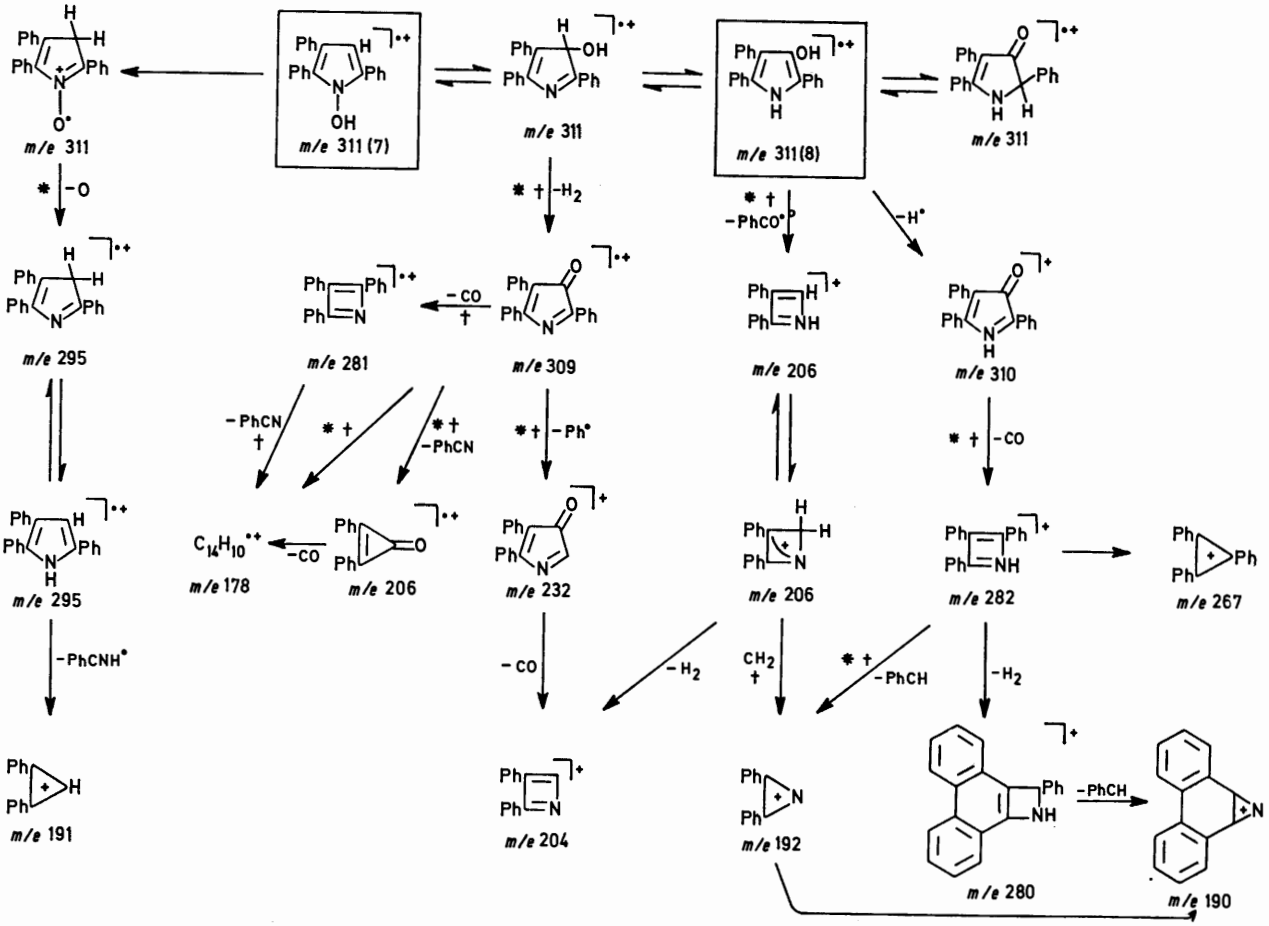
RESULTS AND DISCUSSION

2,4,5-Triphenyl-3H-pyrrol-3-one 1-Oxide (1) *and 2,4,5-Triphenyl-6H-1,3-oxazin-6-one* (2).—Scheme 1 illustrates the major fragmentation paths of these two isomers; fragmentations supported by metastable peaks are marked with an asterisk for the pyrrol-3-one oxide and with a dagger for the oxazinone. The consecutive loss of two molecules of carbon monoxide from the molecular ion is a feature of both spectra and suggests the intermediacy of the oxaziridine and pyrroledione isomers (3) and (4); the spectra of the analogous isatogen and benzoxazinone systems show similar behaviour.[2] On the other hand there are also marked differences between the spectra. The pyrrol-3-one oxide, as expected, readily loses an oxygen atom to give an ion with *m/e* 309; this is totally absent from the oxazinone spectrum. Further fragmentation leads to the base peak at *m/e* 178, deriving from the isomeric phenanthrene and diphenylacetylene radical cations (5) and characterised by abundant doubly charged fragment ions.[3] Indeed this peak occurs in all the spectra described in this paper, but in the oxazinone it is very weak with $<2\%$ abundance and no metastable indication of its precursor. For the oxazinone the base peak is the benzoyl cation at *m/e* 105. Other important fragment ions which occur not only in these spectra but in all or most of the others are at *m/e* 192 [diphenylazirinyl (6)], 166 and 165 (fluorene and fluorenyl), 151 and 152 (biphenylene and biphenylenyl), and 103 (benzonitrile).

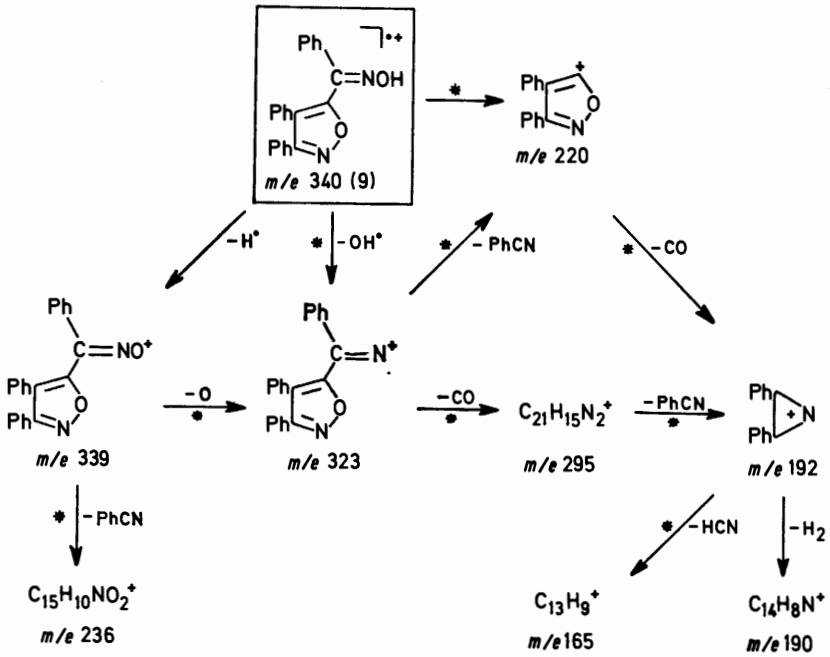
[1] R. A. Y. Jones and N. Sadighi, *J.C.S. Perkin I*, 1976, 2259.
[2] *Cf.* T. H. Kinstle and J. G. Stam, *Chem. Comm.*, 1968, 185; D. R. Eckroth, *Chem. Comm.*, 1970, 465.
[3] M. E. Wacks and V. H. Dibeler, *J. Chem. Phys.*, 1959, **31**, 1557; P. Natalis and J. L. Franklin, *J. Phys. Chem.*, 1965, **69**, 2935.


m/e 309
m/e 325 (1)
m/e 325 (3)
m/e 325 (2)
m/e 308
C21H14NO+
m/e 296
m/e 267
m/e 325 (4)
PhC≡O+
m/e 105
m/e 281
m/e 297
m/e 297
m/e 297
m/e 297
m/e 280
m/e 220
m/e 220
m/e 269
C21H14NO+
m/e 296
m/e 192 (6)
m/e 190
(5)
m/e 178
m/e 297
m/e 166
m/e 165
C14H9+
C14H8·+
m/e 177
m/e 176
m/e 152
C12H7+
m/e 151

SCHEME 1



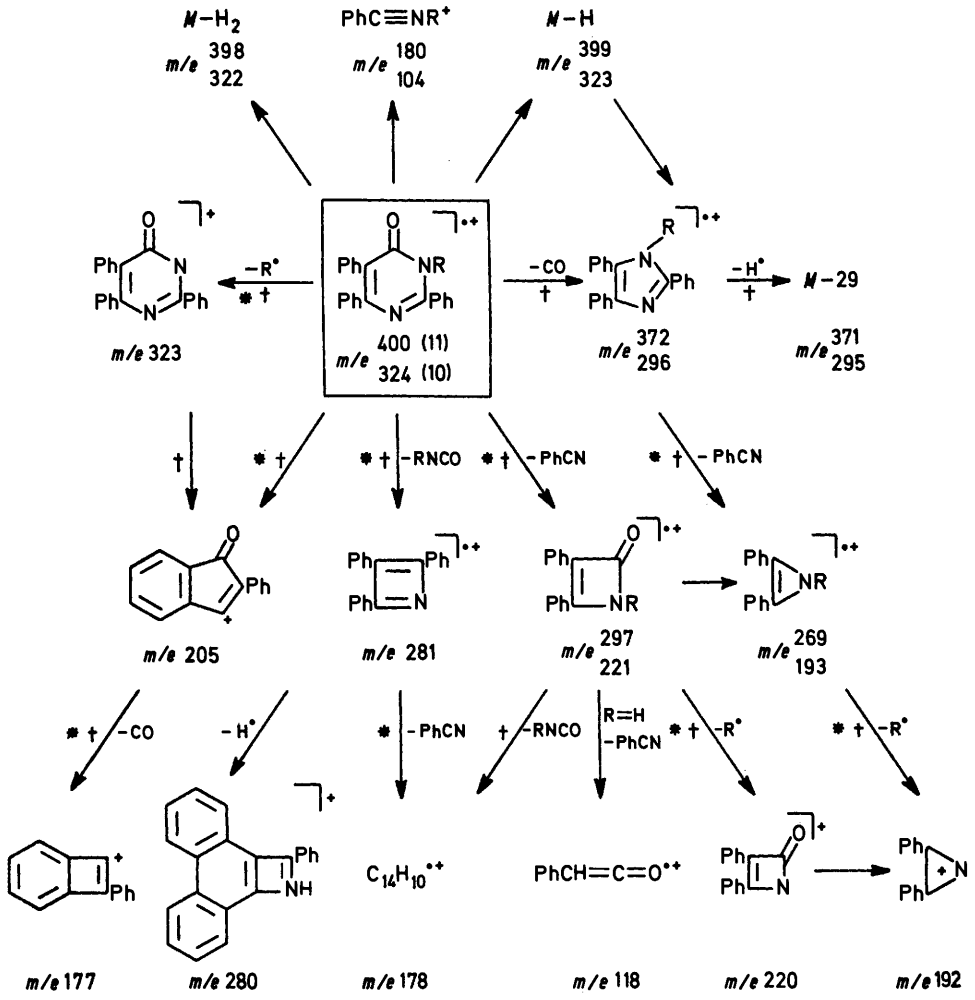
SCHEME 2



SCHEME 3

A brief report of the fragmentation of the oxazinone (2) has previously been published.[4] It gives little detail and only the most abundant ions are tabulated but the data are entirely compatible with our own.

1-Hydroxy-2,4,5-triphenylpyrrole (7) *and* *3-Hydroxy-2,4,5-triphenylpyrrole* (8).—The spectra from these two compounds are remarkably similar. The only major difference is the presence in the spectrum of the 1-hydroxy-isomer of an ion with *m/e* 295 (*M* − O; 17%). Moreover in this isomer the peak at *m/e* 191 [1.3% compared with 0.3% in isomer (8)] corresponds to $C_{15}H_{11}$ rather than $C_{14}H_9N$ as found in the breakdown of the diphenylazirinyl cation. This suggests the fragmentation of Scheme 2, involving tautomerism between the *N*-hydroxy and *N*-oxide isomers in the parent molecule or molecular ion. It is not immediately obvious why, this apart, the two isomers should follow apparently identical fragmentation pathways: the oxygen atom is retained in several of the fragment ions so it cannot arise simply from tautomerism among alternative deoxygenated fragments. We are forced to consider a direct isomerisation of the molecular ion of the parent *N*-hydroxy-isomer, perhaps *via* a 1,3-hydroxy-migration as shown. The fragmentation pattern of Scheme 2 implies that there are two isobaric ions of *m/e* 206; the high resolution spectra indicate that the predominant ion is $C_{15}H_{12}N$ formed by loss of the benzoyl radical from the molecular ion, but metastable peaks reveal that the alternative $C_{15}H_{10}O$ is also present. Metastables in the spectra of the 1- and 3-hydroxy-isomers are indicated in Scheme 2 by asterisks and daggers respectively.



SCHEME 4

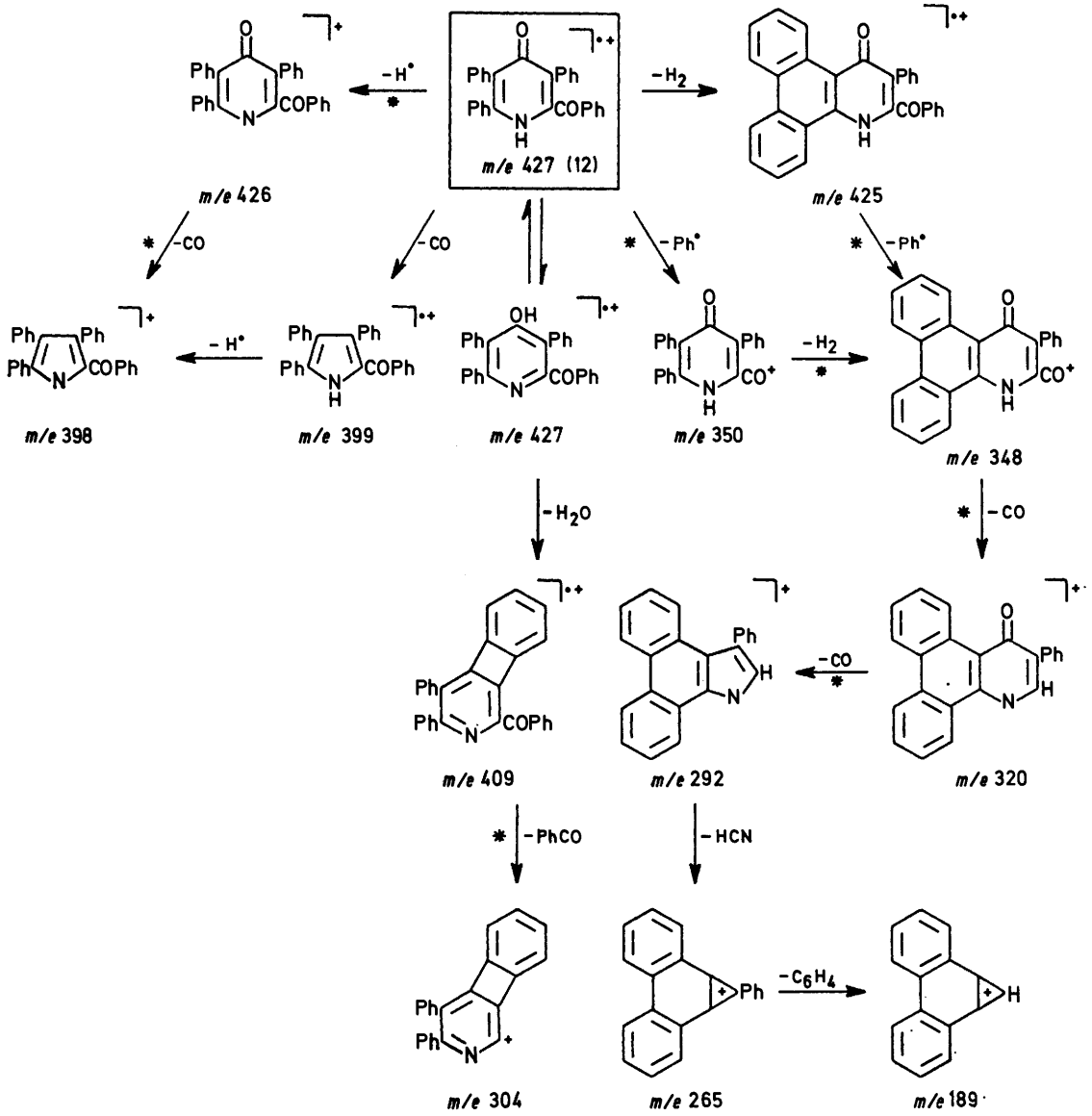
5-Benzoyl-3,4-diphenylisoxazole Oxime (9).—The proposed fragmentation pathway is shown in Scheme 3. Metastable peaks (marked with an asterisk) confirm the majority of these steps, and also the step *m/e* 340 ⟶ 207 which seems to entail the simultaneous loss of PhCN and NO from the molecular ion; neither of the possible intermediates for two consecutive steps are present. The structures of some of the fragment ions must be tentative. A peak at *m/e* 209 correspond-

[4] T. Sasaki, K. Kanematsu, and A. Kakehi, *J. Org. Chem.*, 1971 **36**, 2451.

ing to $C_{14}H_{11}NO$ has not been assigned; it could be rationalised as the radical ion from 1-hydroxydiphenylazirine or diphenyloxazete, but both should readily lose a hydrogen atom and there is no peak at *m/e* 208.

The corresponding 2,4-dinitrophenylhydrazone seems to follow a similar fragmentation path. The molecular ion is absent, but the major peaks at *m/e* 323, 295, 220, 192, 178, and 165 correspond to peaks in the oxime spectrum. The semicarbazone, on the other hand, fragments differently, though a detailed analysis is not possible without isotopic labelling studies. Again the molecular ion is absent; the highest peak corresponds to $M - H_2O$. The main sequence of fragmentation appears to proceed *via* successive losses of HNCO, PhCN, H, and CO giving ions at *m/e* 339, 236, 235, and 207 respectively. The 339 ion also loses a hydrogen atom to give a peak at 338. An abundant ion at *m/e* 322 corresponds to $C_{22}H_{16}N_3$ and is clearly different from the isobaric $C_{22}H_{14}N_2O$ which appears in the oxime and hydrazone spectra. An ion at *m/e* 220 corresponds to the complete loss of the isoxazole side chain, as in the other two systems.

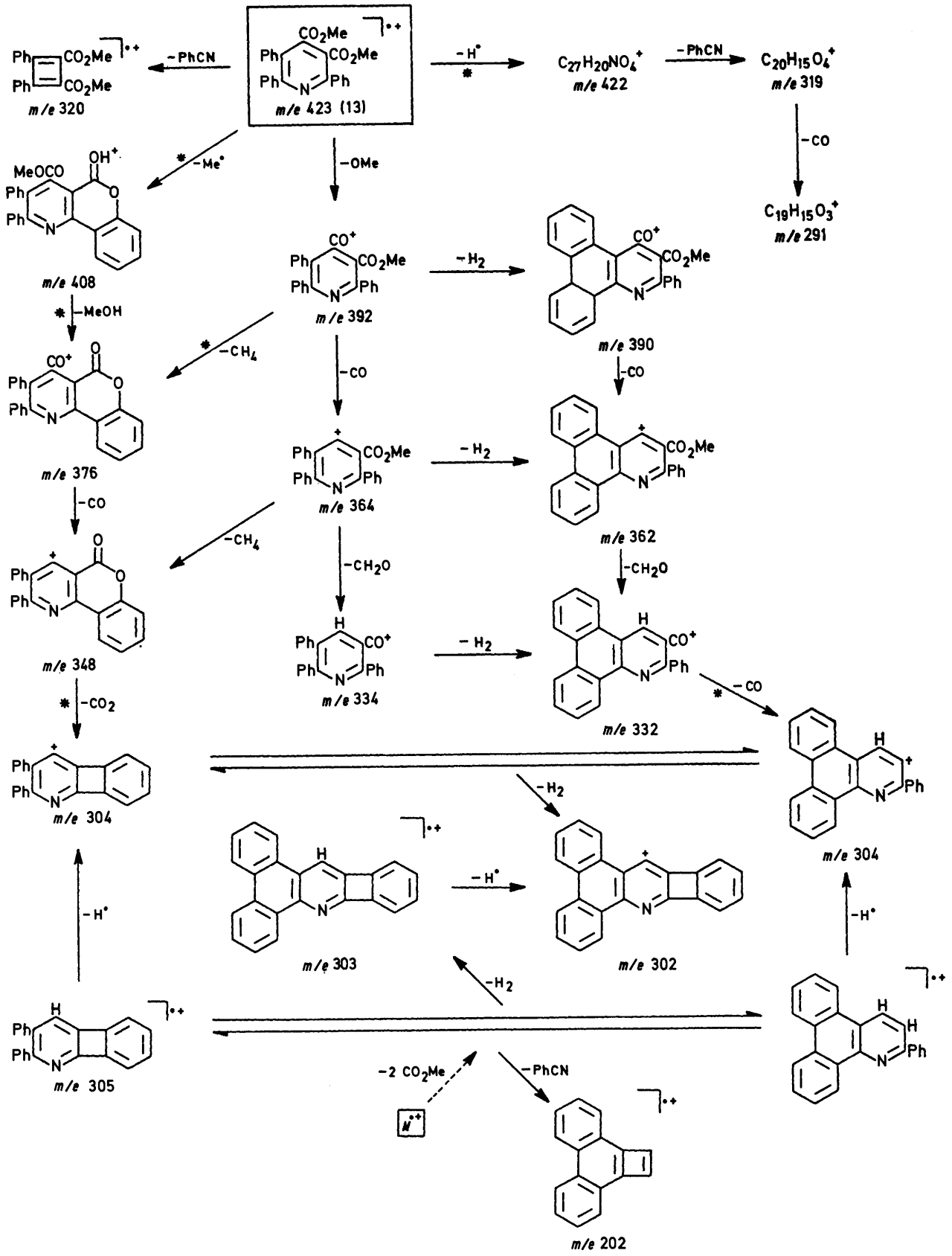
2,5,6-*Triphenyl*-4-*pyrimidone* (10) *and* 2,3,5,6-*Tetraphenyl*-4-*pyrimidone* (11).—The fragmentation patterns of these two compounds follow closely similar paths, shown in Scheme 4. Fragmentations confirmed by metastable peaks are marked with asterisks and daggers for the two compounds respectively.



SCHEME 5

2-*Benzoyl*-3,5,6-*triphenyl*-4-*pyridone* (12).—The main fragmentation paths are shown in Scheme 5.

3,4-*Bismethoxycarbonyl*-2,5,6-*triphenylpyridine* (13).—The proposed fragmentation pathway is shown in Scheme 6. Some of the suggested structures must be tentative.


m/e 423 (13)
m/e 320
m/e 422
m/e 319
m/e 291
m/e 408
m/e 392
m/e 390
m/e 376
m/e 364
m/e 362
m/e 348
m/e 334
m/e 332
m/e 304
m/e 303
m/e 302
m/e 305
m/e 202
-PhCN
-H•
-Me•
-OMe
-MeOH
-CH4
-CO
-H2
-CH2O
-CO2
-2 CO2Me
M•+

Scheme 6

EXPERIMENTAL

High resolution mass spectra were measured on the A.E.I. MS902 instrument of the Food Research Institute, Norwich. We are grateful to Dr. R. Fenwick of the F.R.I. for help and discussion. Metastable spectra were obtained on a Hitachi RMU-6E spectrometer.

Tabulated mass spectral data are included in Supplementary Publication No. SUP 21896 (7 pp.).*

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