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AS-TRIAZINE CHEMISTRY—VI

MASS SPECTRA OF AS-TRIAZINES AND THEIR N-OXIDES

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Abstract—The mass spectra of some substituted *as*-traizines and their N-oxides were measured, in order to investigate the intensity relationship between (M − 16) and (M − 17) ion peaks as functions of substituents and the positions of N-oxide groups in these compounds. These ion species proved useful for detecting an N-oxide group and predicting its orientation when the *as*-triazine ring is suitably substituted. The marked spectral correlation between these compounds permits certain crude generalizations of the cleavage processes. The observations implying electron impact induced 1,4-migrations of ether- and anilino-phenyl groups are also described.

THE mass spectral data on heteroaromatic N-oxides reported by Bryce *et al.*[1] are important in that they determined the mass spectra of a series of new quinoline N-oxides and concluded that (M − 16) and/or (M − 17) ions are of diagnostic value for aromatic N-oxides even if a nitro group is present in the molecule. In contrast, Grigg *et al.*[2] denied the diagnostic value of (M − 16) ions for Δ^1-pyrroline N-oxides. These reports prompted us to determine the mass spectra of *as*-triazine N-oxides[3–6] and for comparison, of substituted *as*-triazines as their chemical precursors. In this paper we discuss the merits of (M − 16) and (M − 17) ions of our N-oxides and compare their fragmentation mechanisms with those of the precursors.

Although very few metastable peaks are observed, several common patterns detected permit some generalization of the fragmentation mechanisms. Furthermore, the multiplicity of N and O atoms in these compounds makes prediction of the charged position in the molecule impossible and hence representation of the fragment ions may be incomplete. Nevertheless, these mechanisms provide possible explanations of our data.

I *Mass spectra of substituted* as-*triazines*

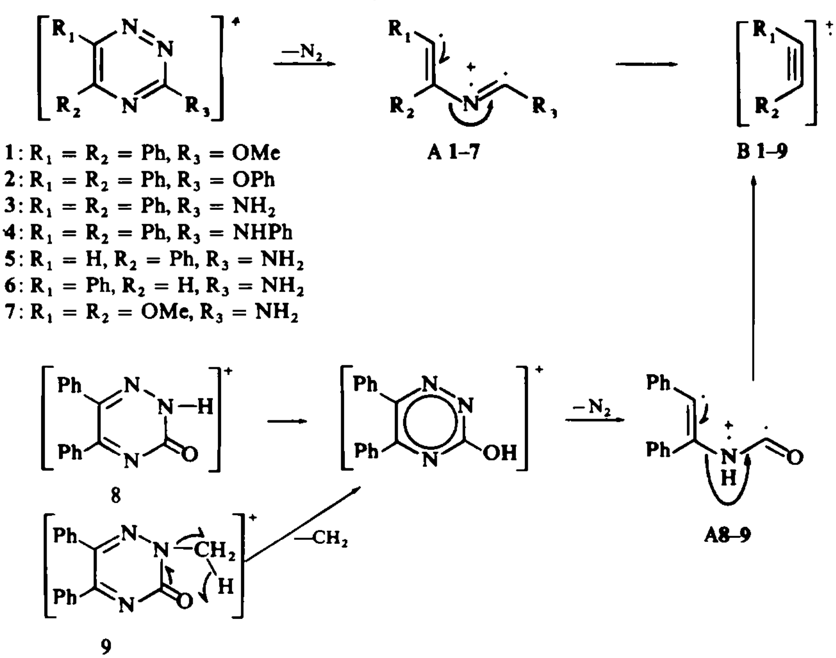
as-Triazines (**1–8**) release a nitrogen molecule to give A (**1–8**) which are then degradated to the fragments B (**1–8**) by loss of the nitrogen-containing parts in various forms as shown in Scheme I-1. This process of nitrogen-expulsion is unquestionable in view of the fragmentation of *as*-triazine itself.[7] The fragments B appear as base peaks in all cases with exception of 2-methyl-5,6-diphenyl-*as*-triazine-3(2*H*)-one (**9**). The abundance of molecular ions and fragment-A ions are summarized in (a) and (b) columns of Table 1. The actual spectra of some triazines (**1, 3** and **8**) are given in Figs. 1–3.

TABLE 1. PEAK INTENSITIES RELATIVE TO THE BASE PEAKS IN THE SPECTRA OF *as*-TRIAZINES

Compound	Fragments									
	(a)	M^+	(b)	A	(c)	C	(d)	D	(e)	F
	m/e	%	*m/e*	%	*m/e*	%	*m/e*	%	*m/e*	%
3-Methoxy-5,6-diphenyl-*as*-triazine (**1**)	263	20·3	235	0·9	192	1·7	190	2·8	165	4·8
3-Phenoxy-5,6-diphenyl-*as*-triazine (**2**)	325	18·0	297	0·6	192	3·8	190	3·2	165	6·7
3-Amino-5,6-diphenyl-*as*-triazine (**3**)	248	22·7	220	0·2	192	1·0	190	1·6	165	3·4
3-Anilino-5,6-diphenyl-*as*-triazine (**4**)	324	25·0	296	0·3	192	1·0	190	1·1	165	3·0
3-Amino-5-phenyl-*as*-triazine (**5**)	172	29·3	144	1·0	116	4·5	—	—	—	—
3-Amino-6-phenyl-*as*-triazine (**6**)	172	37·0	144	2·6	116	3·7	—	—	—	—
3-Amino-5,6-dimethyl-*as*-triazine (**7**)	124	28·0	96	18·7	68	8·6	—	—	—	—
5,6-Diphenyl-*as*-triazine-3(2H)-one (**8**)	249	35·0	221	5·3	192	19·6	190	20·3	165	57·5
2-Methyl-5,6-diphenyl-*as*-triazine-3(2*H*)-one (**9**)	263	100·0	221*	32·5	192	90·0	190	24·0	165	88·0

* $(M - 28)^+$ for compound 9: ca. 3·0%.

SCHEME I-1



1: $R_1 = R_2 = Ph, R_3 = OMe$
2: $R_1 = R_2 = Ph, R_3 = OPh$
3: $R_1 = R_2 = Ph, R_3 = NH_2$
4: $R_1 = R_2 = Ph, R_3 = NHPh$
5: $R_1 = H, R_2 = Ph, R_3 = NH_2$
6: $R_1 = Ph, R_2 = H, R_3 = NH_2$
7: $R_1 = R_2 = OMe, R_3 = NH_2$

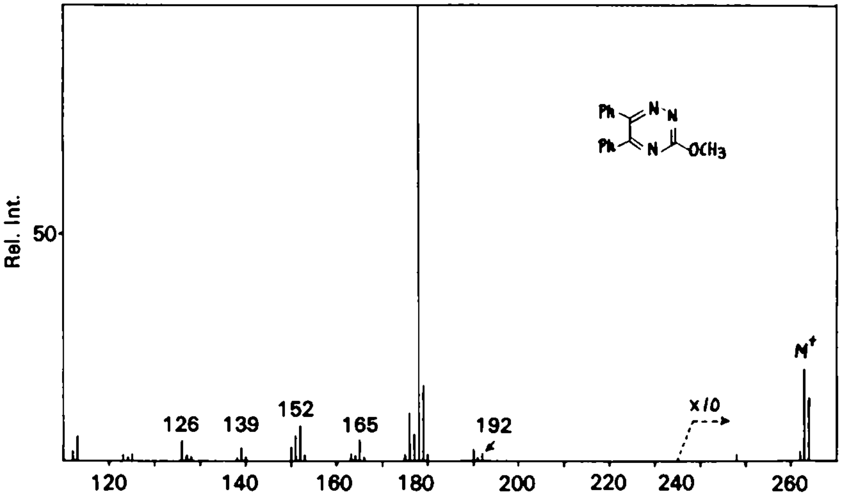


FIG. 1 Mass Spectrum of 3-Methoxy-5,6-diphenyl-*as*-triazine (1).

The *m/e* 221 ion in the spectrum of **8** may be due to both (M − N_2) and (M − CO) ions, but the major contribution is likely to be made by the former, since the 2-Me analogue **9** affords relatively smaller amounts of the *m/e* 235 ion (3·0%) presumed to be due to the (M—CO) ion. Recognition of an ion at mass 249 (M-14) (3·2%) and other ions common with **8** in the spectrum of compound **9** implies that **9** entered

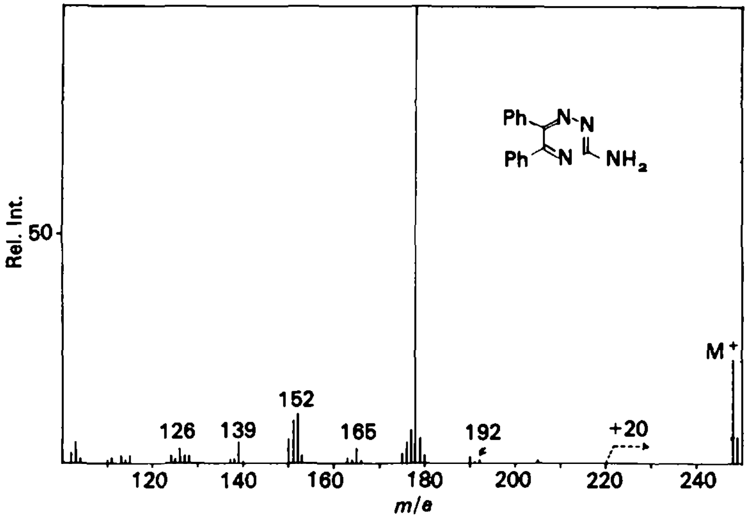


FIG. 2. Mass Spectrum of 3-Amino-5,6-diphenyl-*as*-triazine (3).

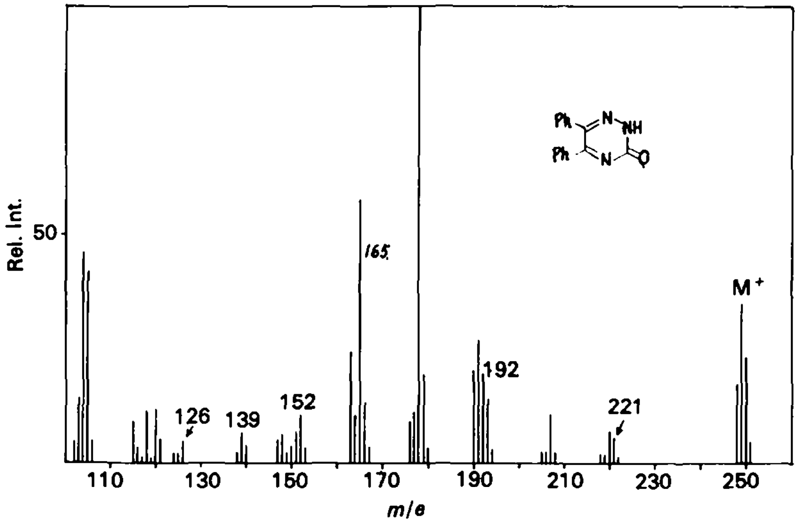
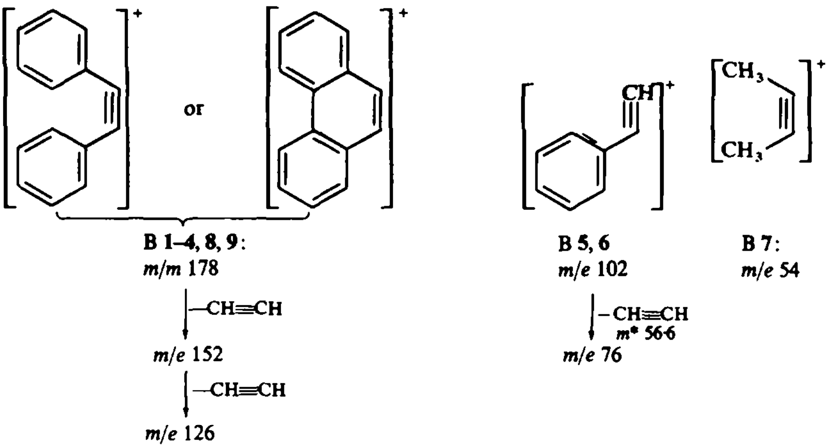


FIG. 3 Mass Spectrum of 5,6-Diphenyl-*as*-triazine-3 (2H)-one (8).

into the same fragmentation paths with those of **8** after expulsion of a methylene unit from the molecular ion as illustrated in Scheme 1-I. This *m/e* 249 ion cannot be due to contaminated **8**, because the purity of **9** was confirmed by TLC. Furthermore, if this ion (3·2%) was due to the contaimination, its contribution to fragment A, C, D and F would not be essential, as estimated from the intensity of the corresponding fragments in contrast with the molecular ion (35·0%) in the spectrum of **8** (Table 1). The reason why the *m/e* 221 ion in the spectrum of **9** is more intense than that of **8** is uncertain on the basis of our present data.

When $R_1 = R_2 = Ph$ (**1–4**, **8** and **9**), the fragment structure corresponding to B is diphenylacetylene or phenanthrene (B **1–4**, **8**, **9**), which expels an acetylene molecule to give ions of mass 152 and 126 as shown in Scheme I-2.

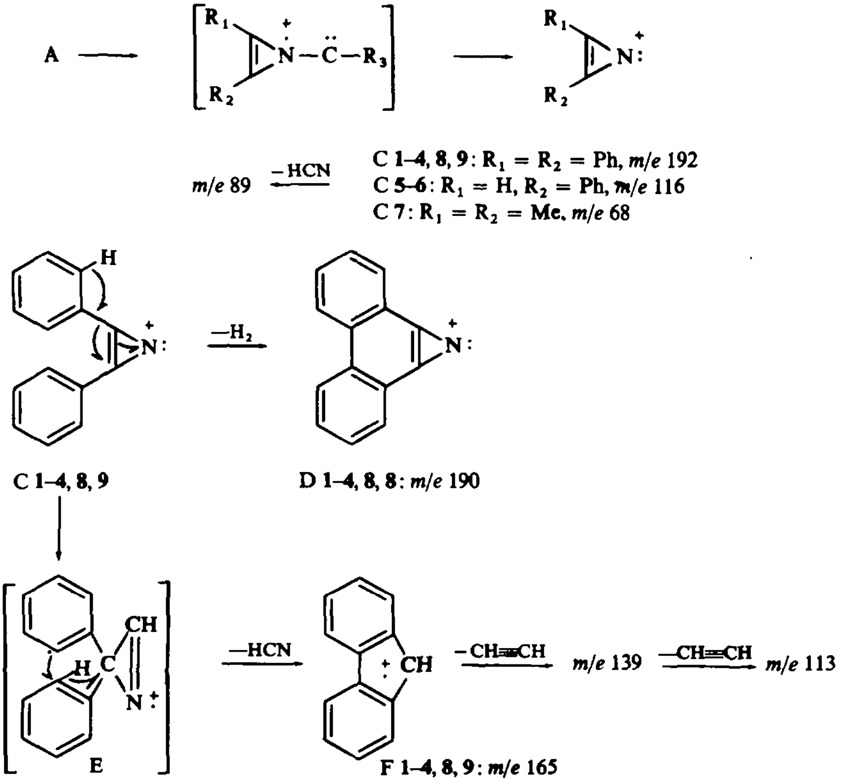
Scheme I-2



Similarly, a phenylacetylene ion (B 5, 6) generated from compound 5 or 6[8] gives rise to a peak at *m/e* 76, evidenced by the presence of a metastable ion at *m/e* 56·6 in the spectra of both compounds, 5 and 6.

The fragments A take another course of fission leading to azirine type fragments C (Scheme II and Table 1).

Scheme II



Fragment C **5** or C **6** loses hydrogen cyanide to yield a *m/e* 89 ion. These azirine type fragments have a precedence[9] and are justified by inspecting the mechanism of production of *m/e* 165 ion from C **1–4**, **8**, **9**. Namely, the spectra of **1–4**, **8** and **9** show the common peaks at mass 190 and 165 (Table 1, d and e columns, and Figs. 1–3), the former should denote the 9,10-azirinophenanthrene ion D **1–4**, **8**, **9** formed by loss of two phenyl hydrogen atoms from C **1–4**, **8**, **9**. On the other hand, the ion at mass 165, shown by high-resolution measurement to be $C_{13}H_9$, can be expressed by formula F **1–4**, **8**, **9**. This fragment seems most likely to be formed by removal of a hydrogen cyanide molecule from the intermediate E with hydrogen transfer and ring condensation. The formation of this intermediate can be interpreted by a 1,2-rearrangement of a Ph group accompanied by transfer of an *ortho*-H atom. The fragment F **1–4**, **8**, **9** seems to eject acetylene molecules to give ions at mass 139 and 113 whose structures are unknown at present.

It is to be noted that the spectrum of **8** as well as **9** exhibits a similar intensity of M − 29 peak (7–8%), which is not present or insignificant in the spectrum of any other compound. This fragment ion has not been characterized.

II *Mass spectra of substituted* as-*triazine* N-*oxides**

(1) (M − 16), (M − 17) *and* (M − 30) *ions*. The mass spectral behaviour of *as*-triazine N-oxides are generally more complicated and unsystematic when compared with those of *as*-triazines. The electron impact induced fragmentation starts with the formation of (M − 16), (M − 17) and/or (M − 30) ions. The intensity of these ions relative to the base peaks are summarized in Table 2 together with those of (M − 29) ions mentioned later. The important parts of the spectra of some N-oxides (**10**, **12**, **13** and **18**) are represented in Figs. 4–7.

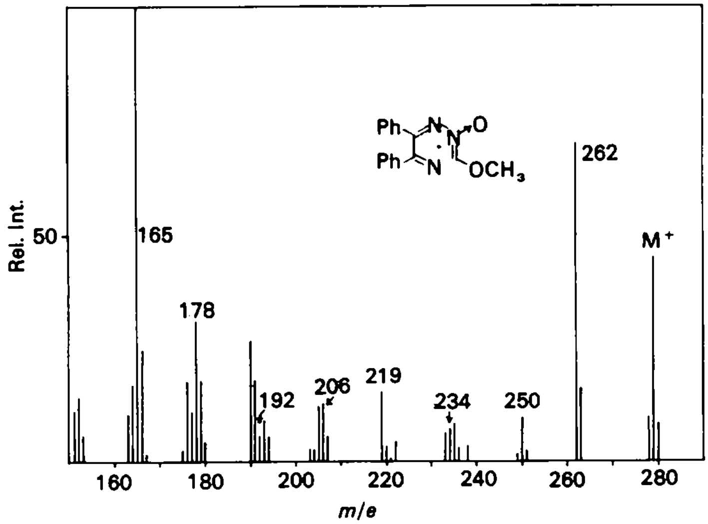


FIG. 4 Mass Spectrum of 3-Methoxy-5,6-diphenyl-*as*-triazine 2-oxide (**10**).

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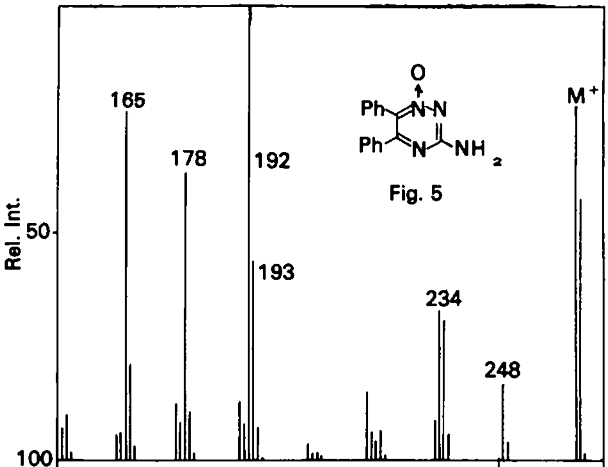
* The notation G and K denotes consistently the (M − 17) and (M − 30) ion, respectively. When a certain fragment is common between a N-oxide and its non-oxygenated precursor, the numbering of this fragment follows that of the precursor.

TABLE 2. PEAK INTENSITIES RELATIVE TO THE BASE PEAKS IN THE SPECTRA OF *as*-TRIAZINE N-OXIDES

Compound	% Abundance of					Base peak (m/e)
			G	K		
	M^+	$(M - 16)^+$	$(M - 17)^+$	$(M - 30)^+$	$(M - 29)^+$	
3-Methoxy-5,6-diphenyl-*as*-triazine 2-oxide (**10**)	45	16	70	1	9·6	165
3-Phenoxy-5,6-diphenyl-*as*-triazine 2-oxide (**11**)	18	11	23	2	2·7	77
3-Amino-5,6-diphenyl-*as*-triazine 1-oxide (**12**)	78	17	<1	33	31	192
3-Amino-5,6-diphenyl-*as*-triazine 2-oxide (**13**)	71	21	100	3	16·5	247
3-Anilino-5,6-diphenyl-*as*-triazine 1-oxide (**14**)	20·6	28	5·5	15·2	8·7	178
3-Anilino-5,6-diphenyl-*as*-triazine 2-oxide (**15**)	71	31·5	33·7	13·7	12	178
3-Amino-5-phenyl-*as*-triazine 2-oxide (**16**)*	69	20	7	15	7	102
3-Amino-5,6-dimethyl-*as*-triazine 2-oxide (**17**)	65	2·5	3	36	2·4	42
5,6-Diphenyl-*as*-triazine-3(2*H*)-one 2-oxide (**18**)	24	37	53	1	8·7	165
2-Aminopyridine oxide (**19**)	100	13	10	3	—	110

* $(M - 18)^+$: 2%. † $(M - 18)^+$: 21%.



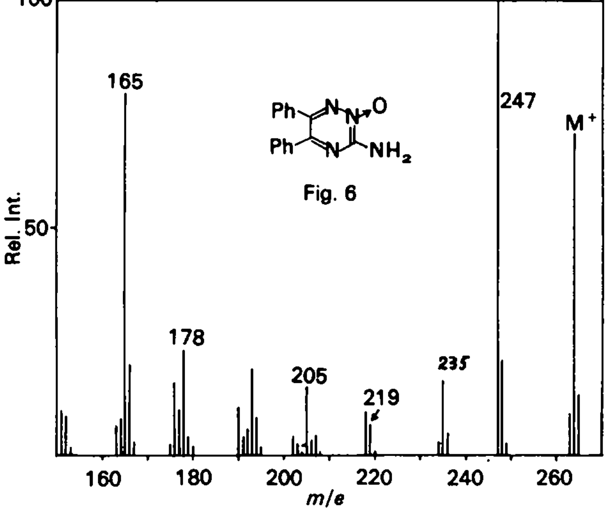


FIG. 5 Mass Spectrum of 3-Amino-5,6-diphenyl-*as*-triazine 1-oxide (12).
FIG. 6 Mass Spectrum of 3-Amino-5,6-diphenyl-*as*-triazine 2-oxide (13).

Table 3 shows the metastable peaks corresponding to (M − 17) ion peaks. It is seen from this Table and Table 2 that the compounds lacking the metastable peaks display (M − 16) ions in most cases more abundantly than (M − 17) ions. Under prevailing conditions, no metastable peaks were observed for the (M − 16) ions

TABLE 3. METASTABLE IONS FOR (M − 17) ION PEAKS

Comp. No.	Obs.	Calc.	Transition
10	246·04	246·04	279 262
11	307·8	307·85	341 324
12	—	231·09	264 247
13	231·1	231·09	264 247
14	—	306·85	340 323
15	306·6	306·85	340 323
16	—	155·54	188 171
17	—	108·06	140 123
18	232·09	232·09	265 248

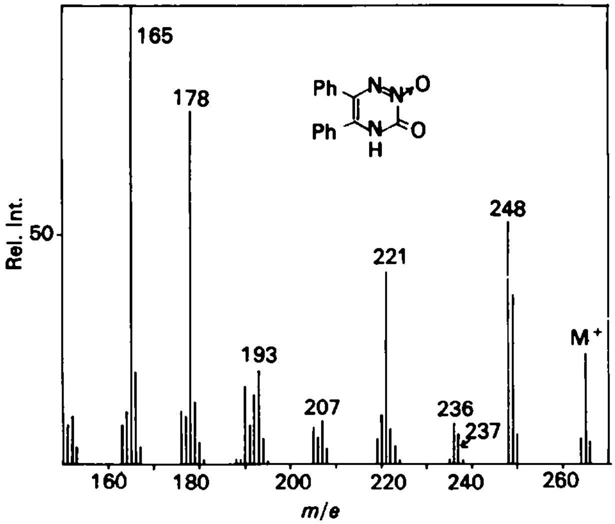


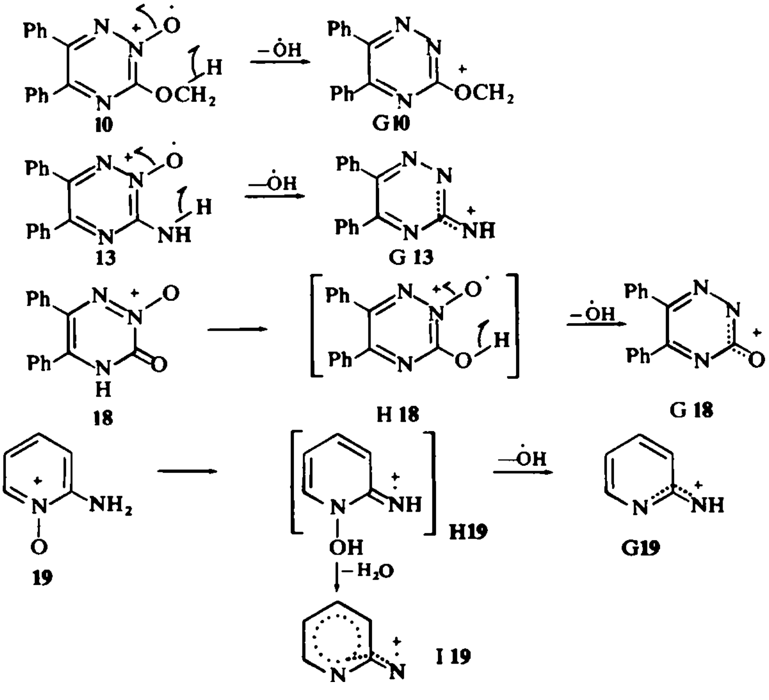
FIG. 7. Mass Spectrum of 5,6-Diphenyl-*as*-triazine-3(4H)-one 2-oxide (18).

while those for (M − 30) ions were found only in the spectrum of compound **12** (m: Obs., 207·40; Calc., 207·41). These three species of fragment ions were, however, not observed in the spectra of *as*-triazines (**1–9**).

The structures of these oxides (**10–18**) except compound **14** have been established by chemical methods and/or dipole moment measurements.[3–6]

It is noticeable that all the 2-N-oxides (except compound **16**) show more abundant (M − 17) ions than (M − 16) ions due to the operation of an *ortho*-effect as illustrated in Scheme III.

SCHEME III



Interestingly, 3-phenoxy compound **11** also displays a stronger (M − 17) peak, though in a moderate degree due to comparatively difficult requirements for taking a 7-membered cyclic transition state. The (M − 17) ions of compound **13** appear as a base peak possibly due to an amidine type of resonance stabilization (G **13**). Conversely, the corresponding peak intensity of the isomeric 1-N-oxide **12** is negligible, possibly due to an inhibited coplanarity of the 6-Ph group and the 1-oxide function by the presence of the bulky 5-Ph group. It is not clear, however, why the corresponding 3-anilino compound **14** shows a higher (M − 17) ion peak (5·5%) than that of **12**. It is noteworthy that the lactam oxide **18** presents the (M − 17) ion more abundantly than the (M − 16) ion. In this case, upon electron bombardment a prototropy seems to have occurred preferentially to give a hydroxyl type intermediate (H **18**). Whereas 3-anilino compound **15** may behave as compound **13**, the relatively lower (M − 17) ion peak (33·7%) is rather astonishing. This result may, however, be interpreted in terms of cation-destabilization by an inductive effect of a Ph group. Namely, the anilino Ph group in **15** may operate to destabilize the (M − 17) ion of the type G **13**.

The above compounds are all highly stabilized by the existence of two Ph groups in the 5- and 6-positions. In the case of the less stabilized N-oxide **17** the peak intensity of (M − 16) and (M − 17) ions are extremely low, the latter being slightly higher. This is due to predominance of ring degradation with loss of an N-oxide function. The irregularity of the spectrum of compound **16** may be explained in the similar terms.

It is to be noted that appearance of comparatively small amounts of (M − 16) and/or (M − 17) ions are generally accompanied by larger amounts of (M − 30) ions generated by loss of an N-oxide function in the *as*-triazine N-oxide series. For comparison, the spectrum of 2-aminopyridine N-oxide **19** was measured. Surprisingly, the (M − 16) ion peak is the stronger in spite of the fact that this substance exists mainly as the N-hydroxy tautomer (H **19**).[10] This irregular situation becomes consistent by appearance of more abundant (M − 18) ions, formed by dehydration, which causes remarkable lowering of the abundance of the expected (M − 17) ion. This (M − 18) ion peak is either absent or negligible (below 1%) in the other compounds.

In conclusion, the (M − 16) ion peak is of diagnostic value for N-oxide groups in suitably resonance-stabilized heteroaromatic systems and the abundance of (M − 16) and (M − 17) ions vary considerably according to the skeleton species, in which the inclination of emission of an N-oxide group is involved, and according to the nature of substitutuents, especially in *ortho*-position. However, the predominance of (M − 17) over (M − 16) ions often suggests an *ortho*-orientation of an N-oxide group to a substituent when this is hydrogen-donating through a 5- to 7-membered cyclic transition state and hence mass spectrometry will be useful for the structural elucidation of polyaza-heterocyclic N-oxides when these are suitably substituted.

(2) *Fragmentations.* As with the non-oxygenated precursors, all the N-oxides display molecular ions of appreciable intensity while the structures of base peak ions are very variable (Table 2). Although metastable ions could not be found in most cases, some main fragmentation paths could be pursued in the light of several common features.

Whereas electronic mechanisms of the electron impact induced emission of an

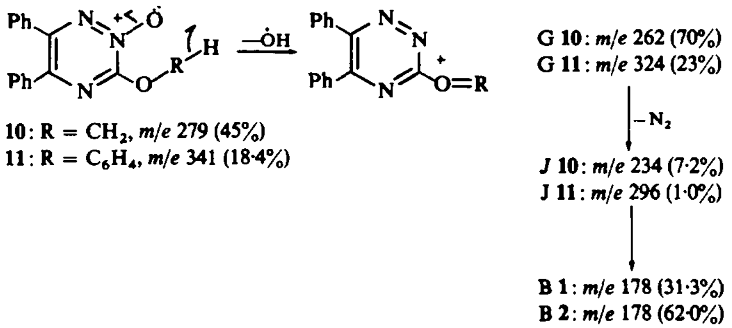
N-oxide function are unknown, we postulate a cleavage pattern involving ejection of a nitrogen oxide radical as this can explain subsequent fragmentations with the least inconsistency (see fragments K in Scheme IV-2, V-1 and V-2).

It must be added that some N-oxides present more abundant (M − 29) ions than (M − 30) ions as shown in Table 2. A high resolution experiment demonstrated that the (M − 29) ion (*m/e* 250) in the spectrum of compound **10** is due to a mixture of $C_{16}H_{14}N_2O$ (M − NO + H) and $C_{15}H_{12}N_3O$ (M − HCO). In this case, the latter fragment seems to be formed by ejection of an aldehyde group from the methoxyl with concomitant hydrogen transfers. This experiment suggests an over-all trend that (M − 30) ions are more or less stabilized by extracting hydrogen radicals from some parts of other molecules or fragments.

Here, fragmentations starting from (M − 16) ions are excluded since they can be regarded as analogous with *as*-triazines.

(a) 3-*Methoxy and* 3-*phenoxy compounds* (**10** *and* **11**). As shown in Scheme IV-1, the fragmentations through (M − 17) ions of both compounds (**10** and **11**) afforded the fragments B of appreciable intensity to which, of course, (M − 16) ions and other fragments make some contribution. The structural representations of ion J **10** and J **11** are difficult.

SCHEME IV-1



10: R = CH_2, *m/e* 279 (45%)
11: R = C_6H_4, *m/e* 341 (18·4%)

G **10**: *m/e* 262 (70%)
G **11**: *m/e* 324 (23%)

$-N_2$

J **10**: *m/e* 234 (7·2%)
J **11**: *m/e* 296 (1·0%)

B **1**: *m/e* 178 (31·3%)
B **2**: *m/e* 178 (62·0%)

Scheme IV-2 illustrates principal fragmentations subsequent to expulsion of an N-oxide group. The peak intensity of the *m/e* 190 and 165 ions displayed by compounds **10** and **11** is much stronger than in their precursors **1** and **2** (see Table 1, d and e columns). The peaks at *m/e* 219, 206 and 205 are of appreciable intensity for these N-oxides while the corresponding peak intensity displayed by compounds **1** and **2** is negligible (0–1%). The *m/e* 205 ion was demonstrated by high-resolution to consist of $C_{14}H_9N_2$. The structures of these new fragments can be illustrated by formula L, M and N derived from K **10** and K **11**. To add, the relatively lower abundance of all the fragments generated from K **11** seems to be in line with the higher stability of K **11** as compared with K **10**. This argument is also applicable in Scheme V-1, and seems to strengthen the validity of the proposed fragmentation processes.

(b) 3-*Amino and* 3-*anilino compounds* (**13, 15, 16** *and* **17**). The spectrum of compound **13** is represented in Fig. 6 in contrast with the isomeric 1-oxide **12** (Fig. 5). The main fragmentation routes of 3-amino- and 3-anilino-*as*-triazine 2-oxides are represented in Scheme V-1. The intensity of fragments J, B and O is summerized in Table 4 with those of G and K, which are again cited from Table 2 for the convenience of the readers.

SCHEME IV-2

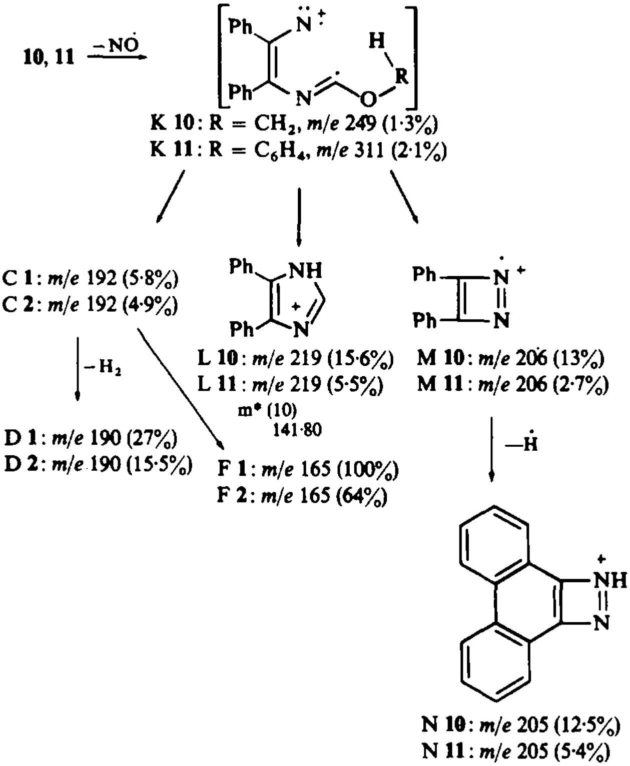


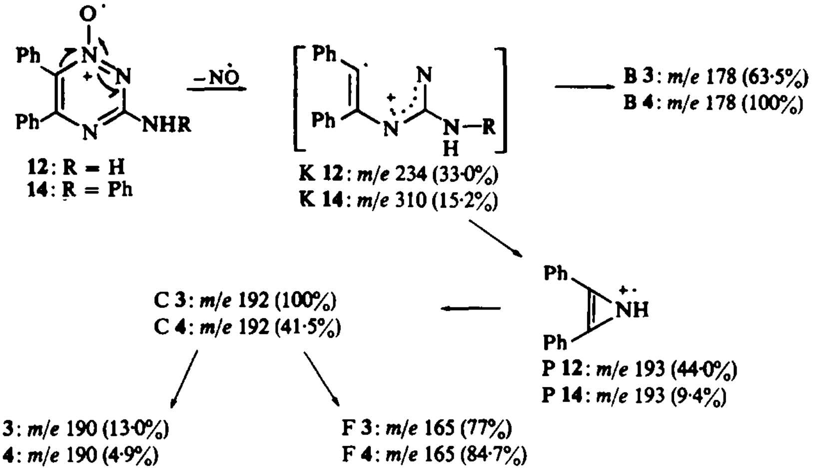
TABLE 4. PEAK INTENSITIES RELATIVE TO THE BASE PEAKS IN THE SPECTRA OF 3-AMINO- AND 3-ANILINO-*as*-TRIAZINE 2-OXIDES

Comp. No.	Fragments									
	(a) *m/e*	G %	(b) *m/e*	J %	(c) *m/e*	K %	(d) *m/e*	O %	(e) *m/e*	B %
13	247	100	219	6·7	234	3·0	207	4·2	178	23
15	323	33·7	295	2·6	310	13·7	207	1·2	178	100
16	171	7·0	143	1·8	158	15·0	131	11·8	102	100
17	123	3·0	95	30·4	110	36·0	83	6·7	54	19

The (M − OH) ions G lead to fragments B via fragments J. Here, ions B from compounds **15** and **16** appear as base peaks (Table 4). Compounds **13** and **15** ($R_1 = R_2 = Ph$) give the above mentioned fragments C, D, F, M and N. The appearances of fragments O with intensity over 1% are characteristic for this group of compounds. Fragment O **13** and **15** ($R_1 = R_2 = Ph$) could also be responsible for the formation of ions M and N.

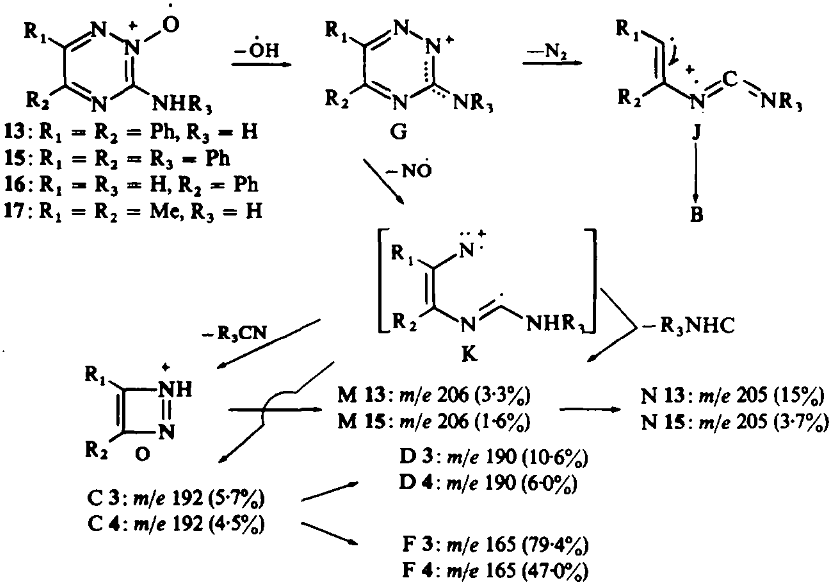
Regarding 1-oxides, **12** and **14**, disintegrations by expulsion of an N-oxide group are indicated in Scheme V-2. Characteristically, fragments P (*m/e* 193) appear with appreciable intensity.

SCHEME V-2



(c) 3-*Oxo compound* **18.*** This compound also exhibits a pattern similar to the above-mentioned compounds (Scheme VI and Fig. 7). A characteristic feature is the occurrence of ions at mass 236 (M – 29) and 237 (M – 28) with a similar intensity. The lost 29 as well as 28 mass unit can not be attributable to N_2H and N_2, respectively, except that an unreasonable rearrangement of the oxide O atom to some other part of the molecule is postulated. Thus, the former ion may be formed by loss of an aldehyde group, while the latter ion is formed by decarbonylation. Of course, an (M – NO + H) ion must also be taken into consideration for the *m/e* 236 fragment.

SCHEME V-1



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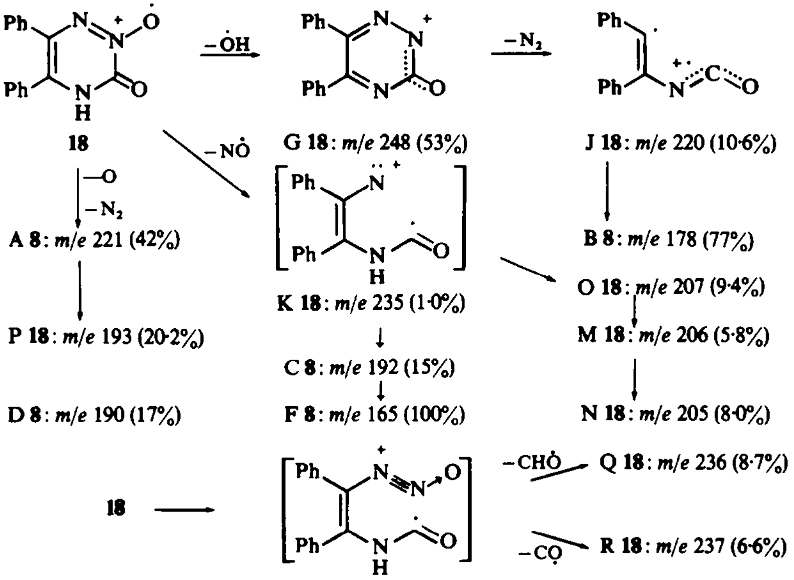
* This compound was obtained by hydrolysis of compounds **10** or **13** and chemically unrelated to compound **8**.[5]

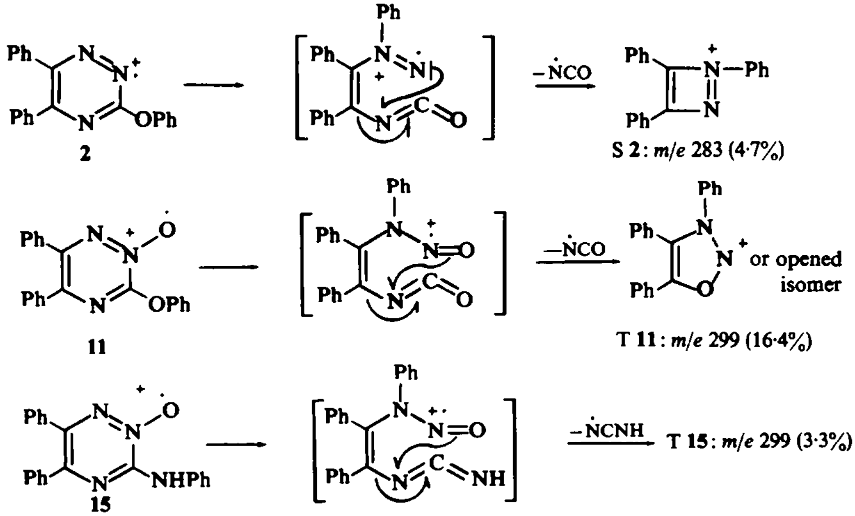
SCHEME VI



III *Phenyl migrations in* 3-*phenoxy and* 3-*anilino compounds*

The spectra of compounds **2** and **11** are characterized by occurrence of distinct (M − 42) peaks at mass 283 (4·7%) and 299 (16·4%), respectively, the former was shown to be $C_{20}H_{15}N_2$ by high-resolution measurement. 2·55% of the *m/e* 283 ion was also recognized in the spectrum of **11**. Concerning the *m/e* 299 ion, it is difficult to ascribe its origin to the (M − 16), (M − 17) or (M − 30) ion in the spectrum of **11**. Thus, the lost 42 mass unit should be attributed to NCO but not to N_3 in either case. We believe that here a 1,4-transfer of the ether-Ph group to nitrogen-1 is involved prior to fragmentation of each molecular ion. This process is visualized in Scheme VII.

SCHEME VII



This electron impact induced O → N transfer of a Ph group has not been recorded, although another type of 1,4-migration of an aryl group involving ether-O → carbonyl-O transfer has been reported.[11]

The *m/e* 283 ion in the spectrum of **11** seems to owe its origin to the (M − 16) ion because the intensity ratio of the former to the latter ion (0·23) bears a close resemblance to the value (0·26 = *m/e* 283/M^+) calculated for the case of 2.

Furthermore, the *m/e* 299 ion peak occurs also in the spectrum of 3-anilino compound **15** and corresponds to (M − 41) ion. This ion can be analogously interpreted in terms of 1,4-Ph migration followed by loss of an N=C=NH unit as indicated in the scheme.

EXPERIMENTAL

The mass spectra and high-resolution mass measurements were obtained on a Hitachi RMU-D double focusing mass spectrometer operating at ionization potential of 80 eV and ionizing current of 50 μa. The solid samples were ionized by electron bombardment after sublimation directly into the electron beam at 150–200°.

3-*Anilino-5,6-diphenyl-as-triazine* (**4**). 3-Chloro-5,6-diphenyl-*as*-triazine[12] (2.0 g), aniline (0·77 g) and Et_3N (0·76 g) were combined in benzene (10 ml) and the mixture was refluxed for 5 hr. After cooling, additional benzene (20 ml) was added and the soln washed with water. The organic layer was dried with Na_2SO_4 and evaporated to dryness *in vacuo*. Recrystallization of the residue from a mixture of alcohol and chloroform gave 1·5 g of yellow needles; m.p. 230–232°. (Found: C, 77·51; H, 4·51; N, 17·01. $C_{21}H_{16}N_4$ required: C, 77·75; H, 4·97; N, 17·27%).

3-*Anilino-5,6-diphenyl-as-triazine 1-oxide* (**14**). A soln of **4** (0·6 g) in AcOH (15 ml) was added to 30% H_2O_2 (0·3 ml) and the mixture was kept at 70° for 2 hr. Additional 30% H_2O_2 (0·3 ml) was added and the mixture was again warmed at the same temp for 4 hr. After cooling, the mixture was poured into a large amount of water and the separating solid was filtered off by suction and dissolved in chloroform. The chloroform soln was dried with Na_2SO_4, condensed to a small bulk and chromatographed in chloroform on a silica gel column (100 mesh). Recrystallization of the main fraction from a mixture of MeOH and $CHCl_3$ gave 0·4 g of yellow needles, m.p. 224–226°. (Found: C, 73·65; H, 4·34; N, 16·07. $C_{21}H_{16}N_4O$ required: C, 74·10; H, 4·74; N, 16·46%).

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APPENDIX

The structure of compound **14** was established to be 1-N-oxide principally on the basis that the (M − 16) ion peak in its mass spectrum is much stronger than the (M − 17) ion peak (Table 2), and also since its fragmentation pattern is similar to that of **12** (Scheme V-2). Furthermore, the absence of any of the irregular peaks due to Ph migration is evidence of the 1-oxide structure of this compound.

This may be further supported by the fact that 3-anilino-5,6-diphenyl-*as*-triazine (**4**) is a chemical analogue of the 3-amino compound (**3**) and that compound **14** is derived from compound **4** by oxidation with peracetic acid similar to the preparation of 1-oxide **12**.[4]