

REASSIGNMENT OF STRUCTURES OF THE DIHYDRO- ν -TETRAZINES.-III

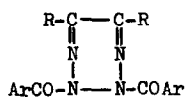
MASS SPECTRAL STUDY

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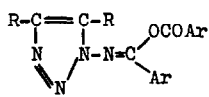
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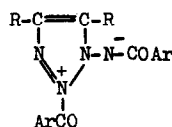
The oxidation product of bis-benzoylhydrazone of 1,2-dicarbonyl compounds was previously believed (1) to be a dihydro- ν -tetrazine, I. This structure has been revised (2) to the ν -triazole imino anhydride (isoimide), II, with the zwitterion structure III proposed as an alternative.



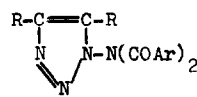
I



II



III



IV

- IIA R=-CH₃, Ar=-C₆H₅
IIB R=-CH₃, Ar=-C₆H₄OCH₃-p
IIC R=-C₆H₅, Ar=-C₆H₅
IID R=-C₆H₅, Ar=-C₆H₄OCH₃-p

- IVA R=-CH₃, Ar=-C₆H₅

In this paper additional evidence for the isoimide structure II are provided by means of mass spectrometry. The mass spectra of the compounds IIA, IIB, IIC and IID showed similar fragmentation pattern. They all gave a low intensity peak for the molecular ion M⁺, which then gives rise to a prominent M-28 ion corresponding to loss of N₂. The formation of this peak is readily explained by the structure II, but not by III; it is well known (3) that several analogously to II substituted ν -triazoles release N₂ from the ν -triazole ring on pyrolysis. However, the M-28 peak could be also attributed to loss of CO from the enol ester group (4), but the ratio of intensities of

The intensity of the peak at m/e 121 is very low, since the cleavage of oxygen-to-carbon in the aromatic esters (5) is generally less important, whereas the cleavage at the carbonyl group, the aroyl ion, is the most abundant peak in the spectra studied. However, in *p*-methoxy derivative (Table I, IID) a remarkable increase of intensity of the ions 151 and 152 ($P+1$), formed by oxygen-to-carbon cleavage, is observed.

TABLE I

Mass spectra of *v*-triazole derivatives II and IV

IIA:	320(1.8), 293(1.8), 292(8.5), 225(0.2), 224(N), 187(0.6), 172(1), 145(1), 122(0.4), 121(0.2), 105(100), 104(1), 103(0.3), 77(29), 68(6), 54(0.4), 51(6), m^* 266.2(320 \rightarrow 292), 56.5(105 \rightarrow 77), 37.8(292 \rightarrow 105).
IIB:	380(0.8), 353(1.8), 352(6.5), 285(0.5), 217(0.5), 152(0.4), 151(0.2), 135(100), 134(1.5), 107(4), 77(9), 76(1), 68(1), 54(0.2), 51(0.5), m^* 326(380 \rightarrow 352), 51.5(352 \rightarrow 135), 44.4(135 \rightarrow 77).
IIC:	445(0.2), 444(0.5), 417(2.2), 416(6.85), 313(1.8), 311(2), 225(0.3), 224(N), 208(2.6), 192(9.5), 178(6.5), 165(2.6), 122(0.5), 121(0.1), 105(100), 103(7.8), 89(2.7), 77(28), 51(5.8), m^* 389(444 \rightarrow 416), 233(416 \rightarrow 311), 56.5(105 \rightarrow 77), 26.3(416 \rightarrow 105).
IID:	504(0.2), 477(0.9), 476(2.2), 341(1), 339(10), 285(3.3), 284(0.4), 221(2), 192(6.2), 178(73), 152(7.7), 151(2.7), 135(100), 133(4.2), 107(5.6), 105(3.4), 103(6.6), 102(1.4), 77(12.7), 64(4), 51(3.3), m^* 85(135 \rightarrow 107), 55.5(107 \rightarrow 77), 39.5(151 \rightarrow 77).
IIV:	321(0.15), 320(0.15), 293(2.7), 292(11.2), 187(0.4), 172(0.5), 145(0.6), 122(N, \sim 0.02), 121(N, \sim 0.04), 105(100), 104(1), 103(0.2), 77(47), 68(5), 51(12.5), m^* 267.5(321 \rightarrow 293), 56.5(105 \rightarrow 77), 37.8(292 \rightarrow 105).

The values in parenthesis represent the relative intensities.

N = Negligible, m^* = metastable peak.

Several transformations of this scheme are confirmed by metastable peaks and analogous fragmentation processes show the spectra of the rest compounds, which are presented in the Table I.

It is of interest to note that the above discussed fragmentation pattern,

especially the formation of the ions V, VII and IX cannot be explained by the structure III, unless a rearrangement of the zwitterion III to isoimide II on the electron impact is assumed. In this case, however, the fragmentation pattern should be different, the spectra should also exhibit additional peaks (e.g. M-105 etc.) which have not been observed, and furthermore no such rearrangement is known to take place chemically, thermally or photochemically. It should be emphasised that the compounds in question, II, undergo thermal rearrangement (2) forming diacyl-aminotriazoles IV. The mass spectrum of IVA, as expected, showed a similar fragmentation pattern to that of IIA. However, there are several characteristic differences between them: The intensity of the molecular ion in IVA is less than one tenth of that in IIA; the ratio of intensities M/M-28 in IIA is equal to 0.21, whereas in IVA is 0.013 and this fact suggests a more rapid loss of N₂ from the molecular ion in the last compound. The peaks at 225 and 224 are absent in IVA and the intensity of the ion at m/e 121 and 122 (P+1), which may come by a rearrangement reaction, is negligible (the sum of intensities of these ions in IVA is only one tenth of that in IIA). On the basis of these facts we consider that in the mass spectrometer only a small amount of IIA isomerizes to IVA.

The new compounds IIB and IID, prepared by standard procedures (2), gave correct analyses and had m.p. 123-124^o and 163-164^o respectively. The mass spectra were obtained at the Noyes Chemical Laboratory of the University of Illinois, with an Atlas CH4 mass spectrometer; the ionization energy was maintained at 70 eV.

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