Structural Reassignment of the Condensation Product of the 2-Phenylimidazole-4,5-dione Benzamidinium Salt

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It is shown by ^{13}C nmr spectroscopy that the thermolysis and dehydration of the 2-phenylimidazole-4,5-dione benzamidinium salt (**1**) yield 2-cyano-4,6-diphenyl-1,3,5-triazine (**7**) and not as postulated previously, 2,5-diphenylimidazo[4,5-*d*]imidazole (**3**) as the reaction product.

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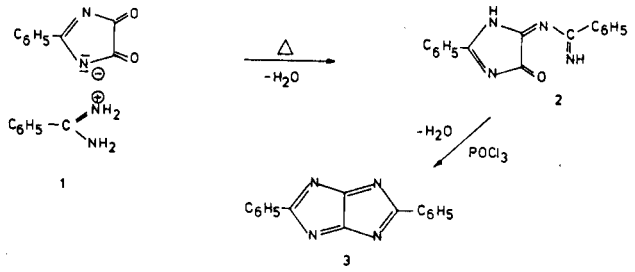
In the course of our studies of pentalenes (1) and azapentalenes (2) we were interested in the condensation product of the 2-phenylimidazole-4,5-dione benzamidinium salt (**1**), for which H. R. Kwasnik, J. E. Oliver and R. T. Brown (3) proposed the structure of a 2,5-diphenyl-1,3,4,6-tetraazapentalene (**3**). Since the described thermodynamic stability and colour of the product were unusual in view of the properties of azapentalenes prepared by us so far, we repeated the preparation of the alleged tetraazapentalene (**3**) and examined the structure by ^{13}C nmr spectroscopy. The product obtained exhibits all chemical and physical properties described by H. R. Kwasnik, *et al.* (3). Its ^{1}H-broad band decoupled ^{13}C nmr spectrum (Figure 1, Table I), however, shows seven signals which is not in agreement with structure **3** for which one would expect only six signals, four for the phenyl groups and two for the bicyclic system. A comparison of the ^{13}C nmr spectrum with those of the phenyl substituted *s*-triazines **4** and **5** (4) as well as the signal of a quaternary C



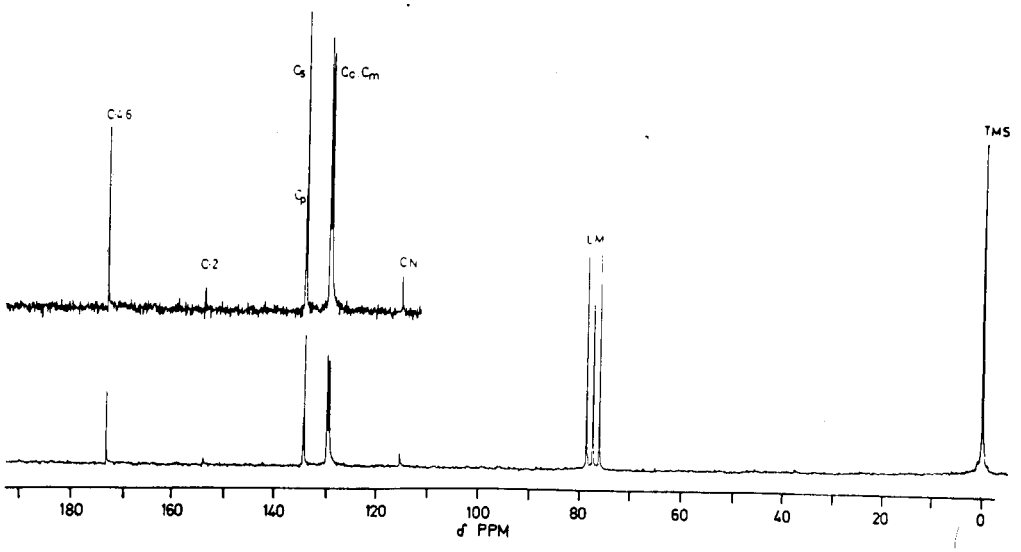


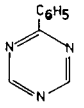
Figure 1: ^{13}C nmr spectrum of compound 7.

Table I

^{13}C nmr Data of 1,3,5-Triazines (ppm from TMS)

	C_2	C_4/C_6	C_s	$C_{o,m}$	C_p	CN	$CONH_2$
4(a)	171.2	166.3	135.0	128.9; 129.0	131.1	-----	-----
5(a)	171.7	171.7	136.4	128.6; 129.1	132.0	-----	-----
6	166.4(b)	171.7	134.7(c)	128.9	133.3(c)	-----	163.6(b)
7	153.6	172.6	133.9	129.0; 129.4	134.1	114.9	-----

(a) *Cf.* literature (4). (b), (c) Assignments may be interchanged.



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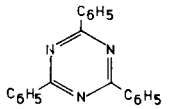

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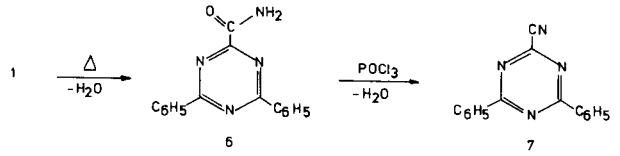
atom at δC = 114.9 ppm led to the conclusion that the compound described as tetraazapentalene **3** is in fact 2-cyano-4,6-diphenyl-1,3,5-triazine (**7**). The ^{13}C signal mentioned above is characteristic for a cyano group, and for the cyano substituted C-2 one observes a high field shift of 12 ppm, in accord with the α-effect of a CN group in benzonitril or 2-cyanopyridine (5,6).

The *s*-triazine structure **7** was ruled out by the authors, as they could not detect a CN absorption in the ir spectrum of the product. This absorption, however, can be observed at higher concentrations.

The intermediate in the synthesis of **7** for which structure **2** was suggested also has a symmetrical *s*-triazine structure with two equivalent phenyl groups, *i.e.* **6**, as shown by its ^{13}C nmr spectrum (Table I).



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Since it had been claimed by Kwasnik, *et al.* (3), that the mass spectral data of **7** "support the proposed structure", we looked thoroughly into the mass spectra of **6** and **7** and determined the elemental composition of most peaks by high resolution techniques. The measurements on **7** proved the assumption of the authors as far as the peaks m/e 258 ($C_{16}H_{10}N_4$), 155 ($C_9H_5N_3$), 103 (C_7H_5N) and 76 (C_6H_4) are concerned. The signal m/e 129, however, cannot be interpreted as $C_8H_5N_2^+$, but has to be assigned to the doubled charged molecular ion M^{2+}. Furthermore, the peak m/e 52 needs some comment. More than 90% of its intensity arise from $C_4H_4^+$ and $C_3{}^{13}CH_3^+$, the latter being related to m/e 51 with the elemental composition C_4H_3, whereas the intensity of the peak of $C_2N_2^+$ is so low (< 10%) that no conclusions could be drawn from it. The main fragmentation pathway, however, is not in contradiction to neither the tetraazapentalene structure proposed by the authors nor the *s*-triazine structure.

In the ir spectra of **4-7** appear bands near 840 cm^{-1} which might be due to the out-of-plane vibration of the *s*-triazine ring. However as results from assignments of the ir spectra of *s*-triazine itself and several derivatives, this vibration seems substituent dependent and therefore of limited diagnostic value (*cf.* (7) and references cited therein).

Our results clearly show, that contrary to the assumption of H. R. Kwasnik, *et al.* (3), the first condensation product of the amidinium salt **1** has the structure of the triazine **6**, which yields **7** by dehydration.

EXPERIMENTAL

The ir spectra were taken with a Perkin-Elmer 125 spectrophotometer, the mass spectra with a Varian MAT 311A instrument connected with a SS100 MS data system and the ^{13}C nmr spectra with a Varian XL-100 spectrometer equipped with a Pulse Fourier Transform Unit. For the ^{13}C nmr measurements, deuteriochloroform was used as solvent with the exception of **6**, which was measured in DMSO-d_6.

Compounds **6** and **7** were prepared according to the procedure of Kwasnik, *et al.* (3), and showed the data given by them in Table I and in the text (*cf.* the discussion given above).

Acknowledgement.

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