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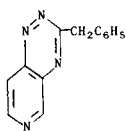
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The thermal degradation of 3-phenylmethylpyrido[3,4-*e*]-1,2,4-triazine (I) leads to a large number of compounds. The isolation and identification of two of these is described.

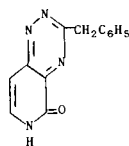
*J. Heterocyclic Chem.*, **19**, 1533 (1982).

As part of our interest in 3-phenylmethylpyrido[3,4-*e*]-1,2,4-triazine (I) (I), forced degradation studies were undertaken. A sample of the orange, crystalline compound after storage in an oven at 60° for 5 weeks had changed to a brittle black solid. Examination of the residue by gc showed only 10-12% of I remaining. Examination of the portion soluble in acetonitrile by tlc on silica gel plates using a solvent of 80 parts methylene chloride to 20 parts acetonitrile showed, in addition to considerable material remaining at the origin, at least seven spots. One of the spots running at  $R_f$  0.25 compared to I ( $R_f$  0.65), was yellow under white light, nonfluorescent under long wavelength uv and visible by quenching under short wavelength uv. Another spot at  $R_f$  0.9 was orange, nonfluorescent and less visible by quenching. In between these two spots of widely different polarity were several spots purple in color, nonfluorescent and visible by quenching. This report is concerned with identification studies carried out on the yellow and orange compounds which have been designated products A and B, respectively.

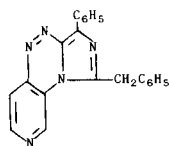
## STRUCTURES



I

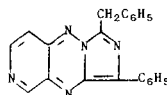


II



IIIa

or



IIIb

## EXPERIMENTAL

The ir spectra were determined as potassium bromide discs on a Perkin-Elmer 137 spectrophotometer. Proton nmr were taken on a Bruker WP-80 80 MHz using TMS as an internal standard. The uv spectra were recorded on a Perkin-Elmer 554 spectrophotometer. Mass spectra were obtained on an AEI MS902 spectrophotometer at Cornell University.

## Isolation of Degradants.

Early isolations of the two compounds was by tlc-elution and resulted in quantities up to about 1 mg. These samples were used primarily for ms studies. In order to obtain larger quantities, preparative lc based on the above tlc system was used. A solution of the soluble portion of 8 g of I that had been degraded at 60° for 5 weeks was subjected to preparative chromatography on a Prep Pak-500 silica cartridge using a Waters Prep LC 500. Step-wise elution with mixtures of acetonitrile and methylene chloride increasingly rich in acetonitrile was carried out at 250 ml/minute. Monitoring of the effluent stream was by refractive index detector. In all, 62 fractions ranging in volume from 50 to 250 ml were collected. Various fractions were examined by tlc to determine which contained the highest concentrations of products A and B.

Product A. 3-(Phenylmethyl)pyrido[3,4-*e*]-1,2,4-triazine-5(6H)-one (II).

The three cuts containing the majority of II were combined, evaporated to dryness, then subjected to preparative tlc in a somewhat more polar system - 5 parts methanol to 10 parts acetonitrile to 85 parts methylene chloride. II recovered from the plates showed a single spot in three solvent systems of widely different polarity. The isolated compound was finally recrystallized twice from acetonitrile to give 24 mg of purified yellow crystals; ir (potassium bromide): 1630  $\text{cm}^{-1}$  (C=O); nmr (acetonitrile- $d_3$ ):  $\delta$  4.63 (s, CH<sub>2</sub>, 2H), 6.90 (d, H-7, 1H, J 7.5 Hz), 7.2-7.4 (m, aromatics and NH, 7H); ms (CI): 239 (M+1, 100), 210 (M-N<sub>2</sub>, 24), 91 (tropylium, 10).

Anal. Calcd. for C<sub>13</sub>H<sub>10</sub>N<sub>4</sub>O: C, 65.53; H, 4.25; N, 23.52. Found: C, 66.01; H, 4.17; N, 23.73.

Product B. 3-Phenyl-1-(phenylmethyl)imidazo[3,4-*b*]pyrido[3,4-*e*]-1,2,4-triazine (IIIb).

From the preparative lc described above, the four cuts richest in III were selected. These cuts were found by tlc to contain a small amount of compound I. The combined cuts were evaporated to obtain orange crystals which on recrystallization from acetonitrile afforded 32 mg of fine orange needles that showed no contaminants by tlc; ir (potassium bromide): no functional groups; nmr (DMSO- $d_6$ ):  $\delta$  4.96 (s, CH<sub>2</sub>, 2H), 7.30 (s, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>, 5H), 7.66 and 8.53 (m, C<sub>6</sub>H<sub>5</sub>, 5H), 8.29 (d, H-8, 1H, J 5.25 Hz), 8.87 (d, H-7, 1H, J 5.25 Hz), 9.35 (s, H-5, 1H); ms (EI): 377 (M<sup>+</sup>, 94), 91 (tropylium, 100).

Anal. Calcd. for C<sub>21</sub>H<sub>15</sub>N<sub>5</sub>: C, 74.76; H, 4.48; N, 20.76. Found: C, 74.44; H, 4.49; N, 20.49.

A comparison of the uv-visible absorption spectra of the 3 compounds in acetonitrile is given below.

Compound	$\lambda$ max (nm)	$\epsilon$ ( $l^2/\text{mole-cm}$ )
I	232	29,860
	340	3,110
	476	265
II	251	10,125
	295	9,770
	385	2,810
III (a or b)	284	19,550
	447	8,930

Discussion.

#### Product A (II).

The ms obtained on this material showed a  $M + 1$  peak at 239, corresponding to the addition of one oxygen atom to I, a peak at 210 resulting from loss of nitrogen and a peak at 91, attributed to the tropylium ion formed by cleavage of the benzyl group. There was no peak at 223, the  $M + 1$  ion obtained from I. The loss of nitrogen from the triazine ring while still retaining the added oxygen atom shows that product A is not an *N*-oxide of one of the adjacent nitrogens in the triazine ring. Likewise, the presence of the tropylium ion shows that the oxygen is not on the benzyl group of I. The lack of a peak corresponding to I indicates that the oxygen is not present as an *N*-oxide of either the pyridine ring nitrogen or the single nitrogen of the triazine ring, since these would be expected to lose the oxygen and give rise to peaks corresponding to I. Product A is thus indicated to be a hydroxyl derivative of I with the hydroxyl on one of the three available positions on the pyridine ring. The strong band at  $1630\text{ cm}^{-1}$  in the ir favors one of the two possible  $\alpha$ -pyridone structures. Finally the pmr spectrum provided conclusive evidence that product A is 3-(phenylmethyl)pyrido[3,4-*e*]-1,2,4-triazine-5(6*H*)-one (II). This evidence is based on the presence of the doublet at  $\delta$  6.90 showing ortho splitting ( $J$  7.5 Hz). This doublet would not be present in the alternate pyridone structure.

#### Product B. (IIIb).

The ms indicated a molecular weight of 337 for this compound. This molecular weight is 115 higher than I and hence must represent a combination of fragments

resulting from the degradation of I. A high resolution ms gave an empirical formula of  $C_{21}H_{15}N_5$  for product B, which was confirmed by the elemental analysis. The lack of oxygen in the molecule is in agreement with the fragment-combination theory and with the similarity in polarity of I and product B found by tlc. No peak at 222 corresponding to I is present in the ms, nor is there one at 194 (I-nitrogen), which is prominent in the spectrum of I. Thus, it may be concluded that splitting to I does not occur.

Subtracting the empirical formula for I ( $C_{13}H_{10}N_4$ ) from that obtained for product B leaves  $C_8H_5N$  which is only 2 hydrogen atoms less than phenylacetonitrile. This compound is a likely degradant of I, produced by loss of nitrogen from the adjacent nitrogens of the triazine ring followed by cleavage of the remainder of this ring. Attack of phenylacetonitrile on another molecule of I, followed by aromatization leads to proposed structures IIIa or IIIb for product B. The lack of any functional groups in the ir is in agreement with the proposed structure.

The linear structure IIIb for degradation product B is preferred over the angular structure IIIa based primarily on the fact that loss of nitrogen is not observed in the ms.

#### Acknowledgements.

The author is indebted to Dr. Jerrold Meinwald of Cornell University for helpful discussions and mass spectral interpretations.

#### REFERENCES AND NOTES

- (1) G. C. Wright, A. V. Bayless and J. E. Gray, U. S. Patent 3,883,526; *Chem. Abstr.*, **82**, 171087f (1975).