

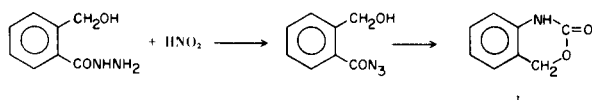
Aminimides X. Synthesis of 4*H*-1,3-Benzoxazin-2(1*H*)one by Thermolysis of Trimethylammonium, β -(2-hydroxymethylbenzoyl)imine (2) (1)

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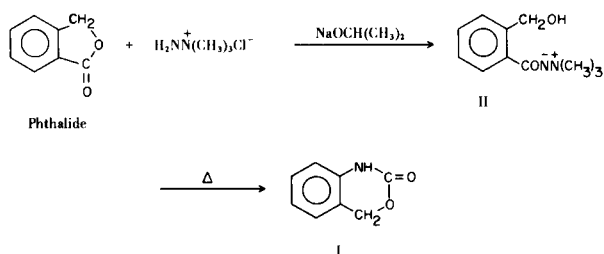
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Continuing the exploration of aminimide intermediates in the synthesis of potentially useful compounds (3), we considered next the synthesis of 4*H*-3,1-benzoxazin-2(1*H*)one (I). Compound I was originally prepared (4) by the following sequence of reactions:



The acid azide was a very unstable compound which decomposed slowly at room temperature and rapidly at 75°.

We proposed to synthesize I in the following manner:

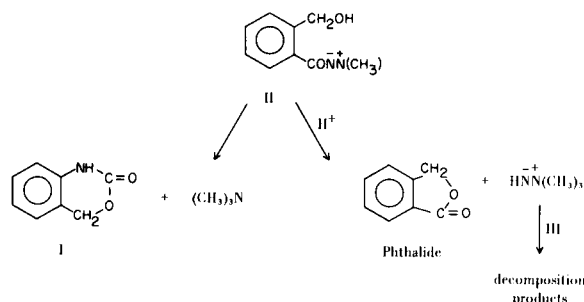


Formation of II was readily accomplished in a 90% yield. Thermolyses of II to I, however, resulted to a large extent in the formation of phthalide until thermolyses at lower concentrations of II in thermolyzing media were tried. When concentrations used successfully in thermolyzing trimethylammonium *N*-(alkyl- β -aminopropionyl)imines to the imidazolidinones (5) were applied to the thermolysis of II, very poor yields of I were obtained. Only when thermolyses at high dilutions were tried, satisfactory yields of I were obtained as is shown in Table I and in Figure I. The yields of I varied from 32.9% to 83.3% as the ratio of mesitylene volume per gram of II increased from 25 to 400 ml.

It was assumed at first that the yield of I depended only on the concentration of II. It was thought that as II is consumed additional amounts of II could be added to the thermolysis flask without adversely affecting the yield of I. However, a considerable lowering of the yield of I

resulted when such a procedure was used. This indicated that it is I which is somehow instrumental in the lowering of the yield of I in the thermolysis of II. Moreover, when large amounts of I or phthalide were added to the thermolysis medium before the addition of the aminimide, the yield of I was largely suppressed and phthalide was formed in substantial amounts. Presence of bases, like trimethylamine or Dabco, however, had no influence on the yield of I.

Thermolysis of II may proceed in two directions depending on whether the leaving group is trimethylamine or trimethylammonium imine as shown below.



The following mechanism for the formation of phthalide in the thermolysis of II was proposed by Professor Shalom Sarel of the Hebrew University in a private discussion with one of us and is outlined below.

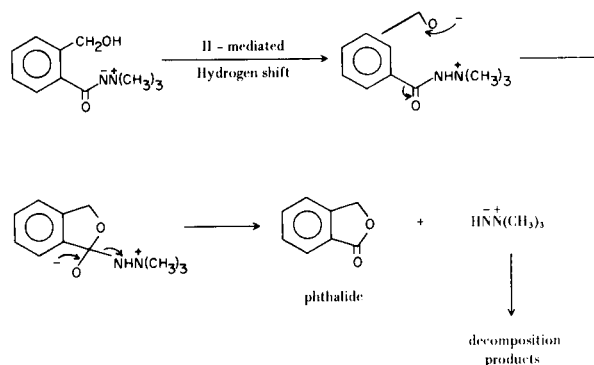
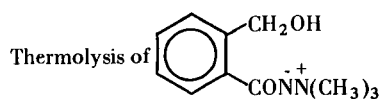


TABLE I



ml. Solvent 1 g. of II	Solvent	Reflux Temp.	Duration of Reflux	Yield of Crystalline (I)
25	Mesitylene	165°	2 hrs	32.9
50	Mesitylene	165°	2 hrs	53.1
50 (a)	Mesitylene	165°	2 hrs	50.3
75	Mesitylene	165°	2 hrs	59.4
100	Mesitylene	165°	2 hrs	70.6
100	Diethylbenzene	183°	1 hr	69.2
150	Mesitylene	165°	2 hrs	74.8
200 (b)	Mesitylene	165°	1/2 hr	75.5
200	Mesitylene	165°	2 hrs	80.4
200 (c)	Mesitylene	165°	1 hr	1.4
200 (d)	Mesitylene	165°	1 hr	4.8
250 (e)	Mesitylene	165°	2/3 hr	56.0
400	Mesitylene	165°	2 hrs	83.3

(a) Twelve g. of Dabco was added to 20 g. of II. (b) Thermolysis was not complete in 30 minutes. (c) Twenty g. of I was added to the thermolysis medium (10 g. of II was used). (d) Twenty g. of phthalimide was added to the thermolysis medium (10 g. of II was used). (e) Four successive batches of aminimide were used after 40 minute intervals.

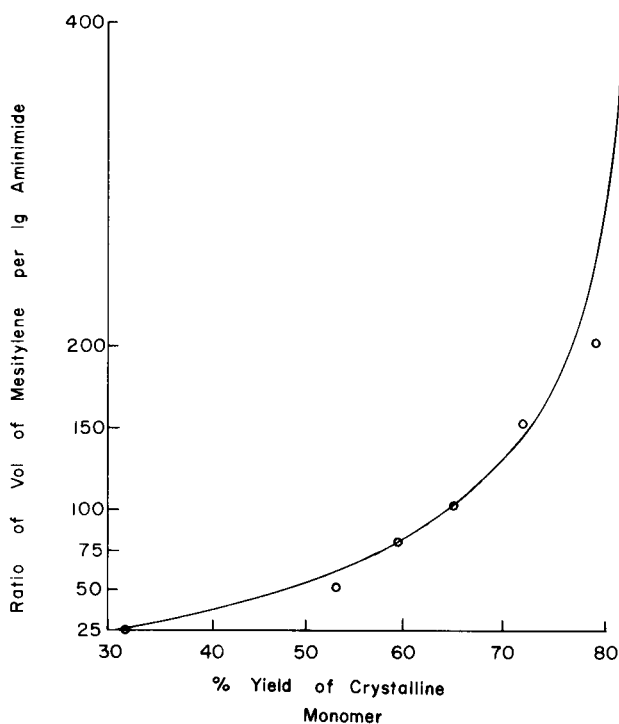


Figure I

At 165° the unstable trimethylammonium imine spontaneously decomposes into a number of gaseous products.

Results of thermolyses of II at different concentrations and the effect of adding bases, I and phthalimide are summarized in Table I.

EXPERIMENTAL

Trimethylammonium-2-(2-hydroxymethylbenzoyl)imine (II).

Sodium (23 g.) was dissolved in a refluxing solution of 40 ml. of methanol in 960 ml. of 2-propanol. The solution was cooled to 55°. Trimethylhydrazinium chloride (110.5 g., 1 mole) was added followed by phthalide (134 g., 1 mole). The mixture was agitated at 55° for 6 hours and it was allowed to stand overnight. The product was filtered and the salt was washed with 2-propanol. The combined filtrates were evaporated *in vacuo* at below 60°. The residue was extracted with boiling acetone. The acetone solution was cooled to 0°, filtered and the precipitate was dried. Successive crops were obtained by partial evaporation and cooling. The following fractions were obtained: (1) weighed 65.1 g., m.p. 126-127°; (2) weighed 91.2 g., m.p. 124-126.5°; (3) weighed 18.7 g., m.p. 125-127°; (4) weighed 12.6 g., m.p. 112-126°; (5) weighed 4.6 g., m.p. 107-126°. The liquid residue weighed 7.9 g. On the basis of the first four fractions, the yield was 90%. The aminimide was hygroscopic.

Anal. Calcd. for C₁₁H₁₆N₂O₂: C, 63.46; H, 7.69; N, 13.46. Found: C, 63.43; H, 7.71; N, 13.48.

Thermolysis of Trimethylammonium-(2-hydroxymethylbenzoyl)-imine (I).

Four liters of mesitylene were refluxed over a Stark and Dean tube for 30 minutes. The temperature was lowered to 140° and 20 g. of II was introduced at once with good agitation. The solution was refluxed for 2 hours. Fifty ml. samples were removed at 30 minute intervals, evaporated and subjected to ir scanning. There was no indication of residual aminimide (1585 cm^{-1}) after 30 minutes refluxing in mesitylene. The hot mesitylene solution was filtered, evaporated *in vacuo* and the residue (including those from the withdrawn samples) were dissolved in 150 ml. of boiling benzene, allowed to cool and 5°, filtered and dried at 100° at 0.3 mm. Fraction I weighed 10.4 g. m.p. 118.5°. The mother liquor was evaporated to 25 ml., cooled and yielded fraction 2 which weighed 1.1 g. m.p. 112-115°; the evaporated mother liquor weighed 2.9 g. On the basis of the two fractions, the yield was 80.4%.

Conclusions.

The yield of I from II is dilution dependent. The yield of I was increased from 32.9 to 83.3% as the ratio of the milliliters of mesitylene per gram of II increased from 25 to 400. The presence

of mild bases, such as Dabco or trimethylamine does not influence the yield of I, while I and phthalimide inhibit the formation of I and promote the formation of phthalide.

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- (3) Presented at the ACS Second Regional Meeting, Columbus, Ohio, June 1970.
- (4) H. Lindemann and W. Schultheis, *Am. Chem.*, **464**, 246 (1928).