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Thermal decomposition of alkyl *N*-(*o*-nitrophenyl)carbamates: A novel synthesis of benzofurazan

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Several alkyl *N*-(*o*-nitrophenyl)carbamates have been shown to undergo thermal breakdown to give benzofurazan with the methyl derivative giving the optimum results.

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During an investigation into the mechanism of the breakdown of nitrourethanes, it was found that alkyl *N*-(*o*-nitrophenyl)carbamates could be converted into benzo-2,1,3-oxadiazole (benzofurazan) by heating the carbamates to 250–270°.

Gaughran *et al.* (1) have prepared benzofurazan by the reduction of benzofurazan *N*-oxide with alkaline hydroxylamine. The benzofurazan *N*-oxide can be obtained by the oxidation of *o*-nitroaniline (1, 2) or by the pyrolysis of *o*-nitrophenyl azide (3). The method used in our laboratory involved the pyrolysis of alkyl *N*-(*o*-nitrophenyl)carbamates and afforded a ready source of pure benzofurazan in yields up to 53% in the case of the methyl carbamate.

The alkyl *N*-(*o*-nitrophenyl)carbamates were made using the method outlined by Synerholm *et al.* (4). Table I indicates the carbamates synthesized and used in the preparation of benzofurazan.

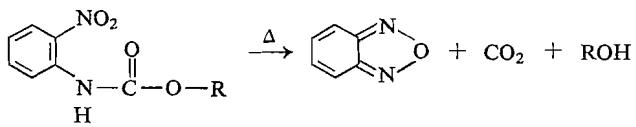
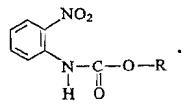


TABLE I

Preparation and decomposition of alkyl *N*-(*o*-nitrophenyl)carbamates*

R	Melting point (°C)	% Composition Calculated C	Calculated H	Calculated N	Found C	Found H	Found N	% Yield benzofurazan
CH_3—	51–52†	48.98	4.11	14.28	48.89	4.01	14.28	53
CH_3CH_2—	55–56‡	51.43	4.79	13.33	51.10	4.65	13.54	25
CH_2=CH—CH_2—	20–21	54.05	4.54	12.61	54.16	4.79	12.65	25
Me—O-C$_6$H$_4$-CH_2—	99.5–100.5	59.60	4.67	9.27	59.79	4.66	9.52	9
C$_6$H$_5$-CH_2—	64.5–66.0§	61.76	4.44	10.29	61.57	4.31	10.06	12
O_2N-C$_6$H$_4$-CH_2—	143–145	53.00	3.49	13.24	52.90	3.33	13.06	27

*General formula:  .

†Reported m.p. 53 °C (5).
‡Reported m.p. 57 °C (5).
§Reported m.p. 61–62 °C (6).

Undoubtedly an intermediate reaction that had to be considered was the formation of isocyanate (7, 8). The carbamates could be decomposing into the *o*-nitrophenyl isocyanate which then could lead to the formation of benzofurazan. However, when the *o*-nitrophenyl isocyanate was subjected to the same conditions as the carbamates, only a very small amount of benzofurazan (5%) was obtained, the major portion being a black tar. Thus the benzofurazan formation from the carbamate does not seem to include preliminary isocyanate formation.

The rate at which decomposition temperature was reached played an important part in the yield of benzofurazan. When the flask contents were brought to decomposition temperature slowly, the yield of benzofurazan was quite low (10%). However, if the flask contents were brought to the decomposition temperature rapidly, the yield of benzofurazan was greatly increased. This could be due to a decrease in the competing isocyanate reaction.

Thus thermal decomposition of methyl *N*-(*o*-nitrophenyl)carbamate has been shown to afford a quick method of preparing pure benzofurazan in good yields. Further investigation on this reaction is in progress.

Experimental

All melting points were determined on the Fisher–Johns melting point apparatus and are uncorrected. Analyses were performed by Organic Microanalyses, 5757 Decelles Avenue, Montreal, Quebec.

The preparation of the carbamates and their decomposition can be outlined by describing the general procedure used for the methyl *N*-(*o*-nitrophenyl)carbamate.

Preparation of Methyl N-(o-nitrophenyl)carbamate

o-Nitrophenyl isocyanate (16.4 g, 0.10 mole) was added over a period of 10 min to a solution of 3.5 g (0.11 mole) methanol in 150 ml of dry benzene. The reaction mixture was refluxed for a period of 2 h. The benzene was removed *in vacuo* and the resultant oil was taken up in hot hexane. After filtration, the solution was cooled and the resultant crystals were recovered by filtration, m.p. 51–52°. The yields for the different carbamates varied from 60–90%.

Thermal Decomposition of Methyl N-(o-nitrophenyl)-carbamate

Using a simple distillation set-up, 30 g (0.15 mole) of the carbamate were placed in a 50 ml distilling flask. The flask contents were heated quickly to 250–270 °C by means of a heating mantle. The gas evolved was allowed to escape into the atmosphere and the alcohol which distilled off was collected. The benzofurazan then began to distil over (distilling head temperature 190°) and solidified in the condenser. The crude product (11.40 g) was collected and purified by sublimation to give 9.70 g of pure benzofurazan, m.p. 51.5–53.0° in a 53% yield.

By comparison of physical properties and infrared spectra this compound was shown to be identical with

benzofurazan prepared by the method of Gaughran *et al.* (1). In all cases, the remainder of the flask contents was unidentified.

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Anodic addition of hydroxy and benzoyloxy groups to stilbenes[1]

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The anodic reaction of benzoic acid in acetonitrile has been carried out in the presence of *trans*- and *cis*-stilbenes using platinum electrodes. The reaction with added *trans*-stilbene gave meso-hydrobenzoin dibenzoate together with *threo*-2-benzoyloxy-1,2-diphenylethanol. Under similar conditions, *cis*-stilbene also gave these products. No evidence for the isomerization of *cis*-stilbene to the *trans*-isomer during the electrolysis was found. Stereoisomeric *dl*-hydrobenzoin dibenzoate and erythro-2-benzoyloxy-1,2-diphenylethanol were not obtained from either stilbene. For comparison, the "wet" Prévost reaction of *cis*-stilbene with silver acetate and iodine was studied. These results are discussed on the basis of a stepwise oxidation mechanism which involves a cyclic 1,2-benzoxonium ion intermediate.

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Over the last decade, considerable attention has been devoted to electrochemical addition reactions. An example of such reactions is the polymerization of vinyl monomers during the Kolbe electrolysis (1, 2). The free radicals produced by the Kolbe electrolysis are capable of attacking 1,3-dienes present, giving rise to the additive dimers (3–5). Smith *et al.* (6) have investigated the stereochemistry of the addition of free radicals to dienes in the anodic oxidation of carboxylic anions.

A previous communication (7) from this laboratory indicated that the electrolysis of sodium methoxide in methanol in the presence of *trans*- and *cis*-stilbenes afforded a mixture of meso- and *dl*-hydrobenzoin dimethyl ethers. More *cis*-adduct than *trans*-adduct was formed in each case. These results seem to be consistent with simultaneous addition of two methoxy radicals to a carbon–carbon double bond of an adsorbed stilbene from one side of the double bond, analogous to the catalytic hydrogenation of unsaturated compounds. An alternative mechanism involves a benzylic cation intermediate formed from stilbene during a stepwise two-electron transfer to the anode (8).

Recently, Mango and Bonner (9) found that electrolysis of sodium acetate in acetic acid in the presence of *trans*-stilbene yielded mainly meso-hydrobenzoin diacetate under anhydrous conditions, and *threo*-2-acetoxy-1,2-diphenylethanol together with a mixture of epimers of 1,2-diphenyl-1-propyl acetate under moist conditions. The stereoisomeric *erythro*-hydroxyacetate was not obtained from either experiment with added *trans*-stilbene. They concluded that the mechanism involved a cyclic acetoxonium ion intermediate **1** which was formed stereoselectively on the surface of an anode. Although the details of the formation of the cyclic intermediate ion, **1**, in this mechanism were not completely clear from their work, they suggested two possibilities; one-step and two-step oxidation mechanisms, as illustrated in Schemes 1 and 2, respectively.

The present study deals with the mechanism of

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