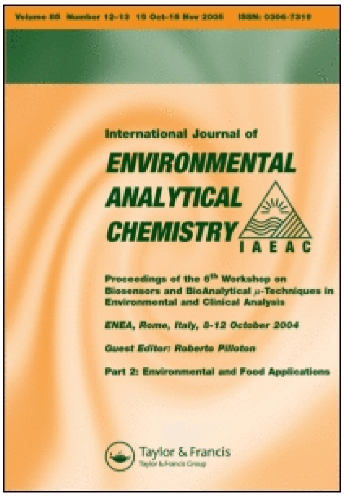

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The Photochemistry of Carbamates, I.

The photodecomposition of Zectran: 4-dimethylamino-3,5-xylyl-N-methyl carbamate

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The photodecomposition of 4-dimethylamino-3,5-xylyl-N-methyl carbamate (Zectran) in aerated and degassed solution has been carried out. Three major photoproducts were detected and characterized to be: 4-dimethylamino-3,5-dimethyl phenol, 4-hydroxy-2,6-dimethyl-N-methyl benzamide and 4-monomethylamino-3,5-xylyl-N-methyl carbamate. The phenol and benzamide products suggest that one of the pathways of photodecomposition of Zectran is via a photo-Fries rearrangement. The ortho-benzamide (5-dimethylamino-4,6-dimethyl-2-hydroxy-N-methyl benzamide) which could also be expected to occur in a photo-Fries reaction, was not observed. The excitation wavelength was > 296.7 nm, i.e. radiation available in the solar spectrum. Thus the products observed in this study may be expected to occur in the environment as a result of the action of sunlight on Zectran.

INTRODUCTION

The N-methyl carbamates are an important class of pesticides and although there exists a body of literature dealing with the trace analysis of these compounds,[1-4] very little work has been reported on the photochemical reactions of these molecules. It is known that the carbamates decompose following the absorption of radiation in the solar spectrum.[5] However, it is not known what the products of the photodecomposition are and techniques have not been developed to monitor the possible products arising from the solar decomposition of carbamates in the environment. Simultaneously, the carbamates should be of interest to the photochemist since they would be expected to undergo a photo-Fries rearrangement,[6] and indeed Trecker *et al.*[7] have reported such a reaction for *p*-tolyl-N-methyl carbamate. There is a good deal of controversy in the literature as to whether the photo-Fries reaction proceeds via a concerted or free radical mechanism.[8] The study of the photo-reactions of the N-methyl carbamates should help to elucidate this question.

EXPERIMENTAL

Chemicals

Zectran was obtained from the Dow Chemical Company, Midland Division, Midland, Michigan, as an analytical standard having a stated purity of 99%. This material was recrystallized twice in absolute ethanol and dried. TLC showed the resulting material to be pure to the limits of detection. VPC of this sample showed little, since decomposition of the molecule occurred during the analyses even though a variety of conditions and columns were tried. The spectral properties of Zectran are given below:

> m.p. 84.5°C (recrystallized product); ms, M^+ 222; n.m.r. ($CDCl_3$) τ 3.22 (s, 2H, aromatic protons), 7.18 (s, 6H, $-N(C\underline{H}_3)_2$), 7.17 (coincident d, 3H, 5Hz, $-CO-NH-C\underline{H}_3$), 7.71 (s, 6H, $-C{=}C-C\underline{H}_3$); infrared ($CHCl_3$) 1730 cm^{-1} (ν C=O)

Absolute ethanol, for solution photolyses, was obtained from Consolidated Alcohols Limited, Toronto, Ontario. Cyclohexane was obtained from Harleco, Philadelphia, Pa. 19143. Both solvents were used without further purification.

Instrumentation

Infrared spectra were recorded on a Perkin–Elmer grating spectrophotometer, Model 457. U.v. spectra were determined on a Perkin-Elmer 402 U.v.-visible spectrophotometer. N.m.r. spectra were recorded on a Varian T-60 n.m.r. spectrometer; tetramethysilane was used as an internal standard. Mass spectra were recorded using an Hitachi Perkin–Elmer RMU-6D mass spectrometer. Melting points were determined on a Kofler hot-stage apparatus and are uncorrected.

Photochemical Procedures

The irradiating source was a 1-kW Hanovia high-pressure Xenon-mercury lamp contained in a Schoeffel housing, air-cooled to a temperature of 110°C. Light emitted from the lamp was filtered using two Corning 0-54(0160) filters, each being 2.1 mm thick and with an exact wavelength cut-off at 300 nm. For other photolyses, the lamp radiation was passed through two 0.25-m Jarrell–Ash (Model 82-410) grating monochromators, in tandem, continuously flushed with dry nitrogen. The 296.7 or the 313 nm Hg bands were selected for photolyses, the band pass for both being ~ 2.5 nm. At all times, the infrared from the lamp was partially filtered using distilled water contained in a 10-cm cylindrical cell. Photolyses were carried out in either 1 × 4 cm fluorimetric quartz cuvettes fitted with a side arm (for work under degassed conditions) or 1 × 5 cm cylindrical quartz cells. Solution concentrations were typically 5 g/l in cyclohexane or absolute ethanol.

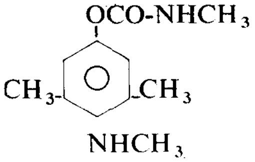
Analytical Techniques

Analytical and preparative TLC was performed on microscope slides or 20 × 20 cm glass plates. Silica-gel G (Merck) was used throughout at a layer thickness of 0.5 mm for the preparative plates. The plates were activated in an air-oven at 140°C for 6 hr. The best separations of the components of the photolysed mixtures were obtained by the following technique: Samples were placed on the plates, 1.5 cm from the bottom, using a 10-mcl microapplicator obtained from Applied Science Labs. Inc., State College, Pa. 16801. The samples were then eluted half-way up the plate, by the ascending technique, in a solvent consisting of $CHCl_3$ and MeOH (5% methanol) at tank saturation, and then carefully dried in a cool air-stream. The plates were then eluted to within 2 cm of the top using a $CHCl_3$/diethyl ether mixture (9:1). In this way, the unreacted Zectran was eluted almost to the top of the plate, well away from the well-separated and more polar products. Samples scraped from the plates were eluted with methanol, filtered, and the solvent evaporated. The residue was then dissolved in chloroform, filtered to remove silica gel followed by chloroform evaporation prior to spectral analysis. Initially, phenolic products were extracted from the photolysis mixtures using ^{2}N NaOH. The solutions were then neutralized carefully with HCl, and extracted into chloroform. Phenolic components were then separated by TLC ($CHCl_3$|MeOH 5%), removed and eluted for spectral analyses. The non-phenolic components resulting from this extraction were separated by TLC using the two-solvent system technique described above (R_f, Zectran 0.85; demethylated product 0.55).

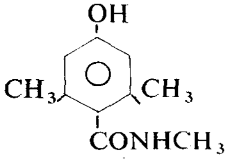
RESULTS AND DISCUSSION

Zectran exhibits a broad structureless absorption extending from approx. 240 to 320 nm with $\lambda_{max}(C_6H_{12}) = 267.0$ nm, $\lambda_{max}(EtOH) = 262.5$ nm. This hypsochromic shift suggests that the photochemical behaviour due to excitation in this region results from an n, π^* transition. The excitation wavelength was in all cases > 296.7 nm which corresponds to the cut-off of solar radiation. Experiments were carried out in degassed and aerated cyclohexane and ethanol solutions; the results are summarized in Table I.

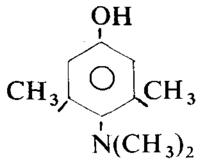
The reaction produces three major products:



, 4-monomethylamino-3,5-xylyl-N-methyl carbamate,



, 4-hydroxy-2,6-dimethyl-N-methyl benzamide, and



, 4-dimethylamino-3,5-dimethyl phenol.

These three molecules were observed to be the major products in both cyclohexane and ethanol solutions and in aerated as well as degassed solutions. The phenol product was found to be identical with the compound produced in the alkaline hydrolyses of Zectran. The products were identified from their spectral characteristics given below:

4-monomethylamino-3,5-xylyl-N-methyl carbamate

ms, M^+ 208; n.m.r. τ 3.24 (s, 2H, aromatic protons), 7.15 (d, 3H, 5Hz, $-\mathrm{CO}-\mathrm{NH}-\mathrm{C}\underline{\mathrm{H}}_3$), 7.27 (s, 3H, $-\mathrm{C}{=}\overset{|}{\mathrm{C}}-\mathrm{N}{<}^{\mathrm{H}}_{\mathrm{C}\underline{\mathrm{H}}_3}$), 7.73 (s, 6H, $-\underset{|}{\mathrm{C}}{=}\mathrm{C}-\mathrm{C}\underline{\mathrm{H}}_3$); infrared ($CHCl_3$) 1732 cm^{-1}, 1671 cm^{-1}, 3428 cm^{-1}.

4-hydroxy-2,6-dimethyl-N-methyl benzamide

ms, M^+ 179, (M—1) 178; n.m.r. ($CDCl_3$) τ 6.82 (s, 3H, $-\mathrm{CO}-\mathrm{NH}-\mathrm{C}\underline{\mathrm{H}}_3$), 7.76 (s, 6H, $-\mathrm{C}{=}\overset{|}{\mathrm{C}}-\mathrm{C}\underline{\mathrm{H}}_3$), 3.48 (s, 2H, aromatic protons); infrared ($CHCl_3$) 1668 cm^{-1}, 1600 cm^{-1}, phenolic-OH, 3600 cm^{-1} and H-bonding band $\bar{\nu}_{max} \sim 3300\ cm^{-1}$.

TABLE I

Typical photolyses, $\lambda_{ex} > 296.7$ nm

Solvent	Aerated and degassed	Photolysis time (hours)	Products			
			Para-benzamide	Phenol	Carbamate	Other
Ethanol	Air	2	—	—	+[a]	yellow "polymer" and other phenolic materials
Ethanol	Air	4	—	—	–	ditto
Ethanol	Air	8	traces	+	+	ditto
Ethanol	Air	24	+	+	+	ditto
C_6H_{12}	Air	6	–	+[b]	+	ditto
C_6H_{12}	Air	19	+	+[b]	+	ditto
Ethanol	degassed	5	traces	+	+	phenolic and different yields than in air
Ethanol	degassed	10	+	+	+	ditto
C_6H_{12}	degassed	5	traces	+	+	milky solution—oily droplets formed
		10	+	+	+	ditto

[a] + indicates present in amount sufficient to isolate from photolyzed solution.

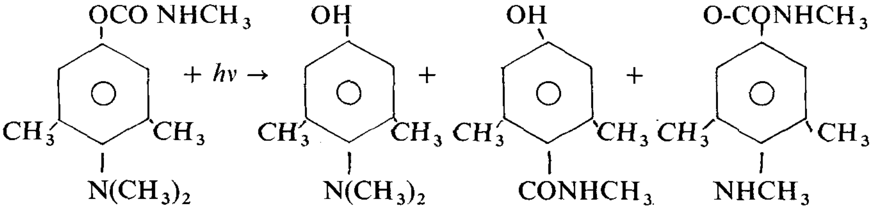
[b] Amount was sufficient to isolate from photolyzed solution; yield of phenol is higher in C_6H_{12} compared with ethanol.

4-dimethylamino-3,5-dimethyl phenol

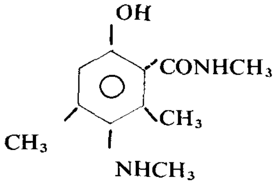
m.p. 92.5°C, ms, M^+ 165, (M-1) 164; n.m.r. ($CDCl_3$) τ 3,34 (s, 2H, aromatic protons), 7.22 (s, 6H, $-N(C\underline{H}_3)_2$), 7.76 (s, 6H, $-\overset{|}{C}=C-C\underline{H}_3$); infrared ($CHCl_3$) ~ 3600 cm^{-1}, 1600 cm^{-1}.

In addition to these products trace quantities of unidentified materials (most of which were phenolic in nature) were detected.[†] in aerated ethanol solutions a yellow polymeric material, which turned orange on standing, was also produced. Spectroscopic evidence indicates that this material was quinonoid in nature, resulting from phenol oxidation. In all instances, the 4-monomethylamino-3,5-xylyl-N-methyl carbamate was produced in larger quantity than either the phenol or benzamide products, although the yield of the phenol increases in cyclohexane compared to that in EtOH and the yield of the monomethyl compound is lower in degassed solutions. There was no evidence for any decarboxylation products, often encountered in photo-Fries reactions.[6]

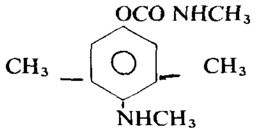
The photodecomposition of Zectran may be represented as:



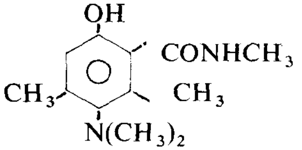
[†] These trace products are very likely due to the secondary photolysis of the major products, e.g. in experiments where the photolysis time exceeded 20 hr,



was detected. ms, M^+ 208; n.m.r. ($CDCl_3$) τ 3.25 (s, 1H, aromatic), 7.12 (d, 3H, 5Hz, $-CO-NHC\underline{H}_3$), 7.30 (s, 3H, $=\underset{|}{C}-NH-C\underline{H}_3$), 7.72 (s, 3H, $-\overset{|}{C}=\overset{|}{C}-C\underline{H}_3$), 7.82 (s, 3H, $-C=C-C\underline{H}_3$); infrared ($CHCl_3$ 3600 cm^{-1}; base soluble. This molecule is presumably due to the photo-Fries rearrangement of



Our results indicate that the photochemical dissociation proceeds through two primary steps. One pathway is a photo-Fries rearrangement yielding the phenol and benzamide products, while the other results in carbon-nitrogen bond cleavage in the dimethylamino moiety of Zectran, followed by hydrogen atom abstraction to produce the monomethylamino carbamate. The production of the benzamide product requires a simultaneous elimination of the $N(CH_3)_2$ group. This type of elimination is known to occur in photo-Fries reactions where the para position is substituted with $-I$, $+M$ substituents.[9] A photo-Fries rearrangement of Zectran would also be expected to yield the ortho-benzamide, i.e.,



as a product. This material was not detected even in photolyses of prolonged duration. If the photolysis of Zectran is similar to that of phenyl benzoate (which also proceeds via a photo-Fries rearrangement) this observation is not surprising, since in the photolysis of that molecule in cyclohexane[10] and ethanol,[11] the para-rearranged product is produced in far larger quantities than the ortho product. It is also interesting to note that an attempt to produce the ortho-benzamide from Zectran by the acid-catalyzed Fries rearrangement was unsuccessful. A study is currently underway in our laboratory on the photodecomposition of Landrin (3,4,5-trimethylphenyl-N-methyl carbamate). In this case alkyl elimination from the para position should not occur and the photo-Fries reaction should yield the phenol and ortho-benzamide.

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