The Photochemical Reactions of Carbamates II. The Solution Photochemistry of *Matacil* (4-dimethyl-amino-m-tolyl-N-methyl carbamate) and *Landrin* (3,4,5-trimethylphenyl-N-methyl carbamate)

by

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The N-methyl carbamates form an important and interesting class of pesticides. The majority of these molecules, unlike many of the common organochlorine pesticides, absorb radiation available in the solar region ($\lambda > 300$ nm) and hence would be expected to undergo photochemical as well as metabolic degradation when introduced into the environment. CASIDA and collaborators (1966, 1967, 1970) have studied the fate of various N-methyl carbamates when the solutions of the above were sprayed on bean foliage and exposed to sunlight or artificial light ($\lambda = 254$ nm). It is not entirely clear from the work of CASIDA et al. whether the products they observed are due solely to photochemical reaction or to absorption followed by enzymatic attack.

This work describes the photochemical behavior of Matacil (4-dimethylamino-m-tolyl-N-methyl-carbamate) and Landrin (3,4,5-trimethylphenyl-N-methyl-carbamate) when these molecules are irradiated with $\lambda > 300$ nm in ethanol and cyclohexane solution. The products observed may be expected to occur in the environment as a result of photochemical decomposition of these molecules.

EXPERIMENTAL

Chemicals

Matacil was obtained from the Chemagro Corporation, Kansas City, Missouri, as an analytical standard (> 99% pure). This material was recrystallized in cyclohexane (decolourized with charcoal) and carefully dried under vacuum. TLC showed the resulting white, "fluffy" crystals to be pure to the limits of detection.

Landrin was obtained from the Shell Chemical Company (Agricultural Division, San Ramon, Calif.) as an analytical standard (99.8% pure). This material was the 3,4,5-isomer and was used without further purification. The spectral properties of the insecticides are given below:

Matacil

mp 92°C; ms, M^+ 208; n.m.r. ($CDCl_3$) τ 7.62 (s, 3H, -CH=C-CH_3), 7.28 (s, 6H, -N(CH_3)$_2$), 7.05 (d, 4Hz, 3H, -CO-NH-CH_3), 3.12-2.92 (unresolved, 3H, aromatic protons); ir ($CHCl_3$) $\bar{\nu}_{max.}$ (C=O) 1738 cm^{-1}, 3460 cm^{-1} (N-H); uv (ethanol) $\lambda_{max.}$ = 248.5 nm, $\varepsilon = 6.67 \times 10^4$ liters/mole.cm, ε (300 nm) = 7.32×10^3 liters/mole.cm.

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Landrin

mp 118°C; ms, M^+ 193; n.m.r. ($CDCl_3$) τ 7.88 (s, 3H, 4-methyl), 7.71 (s, 6H, 3,5-methyls), 7.12 (d, 4Hz, 3H,-CO-$NHCH_3$), 3.20 (s, 2H, aromatic protons); ir($CHCH_3$) $\bar{\upsilon}_{max}$ (C=O) 1740 cm^{-1}, 3460 cm^{-1}(N-H); uv(ethanol) λ_{max}=269.0nm, $\varepsilon = 4.01 \times 10^3$ liters/mole.cm ε (300nm) $\simeq 1 \times 10^2$ liters/mole.cm

Absolute ethanol, for solution photolyses, was obtained from Consolidated Alcohols Limited, Toronto, Ontario. Cyclohexane was obtained from Harleco, Philadelphia, Pa., 19143, as fluorometric grade; both solvents were used without further purification. Chloroform, used as a general solvent, was distilled and stored over molecular sieve.

Instrumentation

Infrared spectra were recorded on a Perkin-Elmer grating spectrophotometer, Model 457. The cells, with KBr windows, had a window-thickness of 0.09 cm. U.V. spectra were determined either on a Perkin-Elmer, 402, U.V. -visible spectrophotometer or an Hitachi EPS-3T spectrophotometer. N.m.r. spectra were recorded on a Varian T-60 n.m.r. spectrometer; tetramethylsilane was used as an internal standard. Mass spectra were recorded on an Hitachi Perkin-Elmer RMU-6D mass spectrometer. Melting points were recorded on a Kofler hot-stage apparatus and are uncorrected.

Photochemical Procedures

An Hanovia high-pressure 1000 Watt Xenon-mercury lamp, contained in an air-cooled Schoeffel housing, was used as the irradiating source. 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, operating in tandem, continuously flushed with dry nitrogen gas. At all times, the infrared radiation from the lamp was partially filtered using a distilled water "sink" contained in a 10 cm cylindrical cell placed directly in front of the lamp lens aperture. Photolyses at 253.7 nm were carried out using a low-pressure mercury resonance lamp manufactured by Hanovia. Radiation from the lamp was filtered using two Corning filters (cat. No. 7910) to ensure complete removal of the strong resonance line at 184.9 mn. Photolyses were carried out in either 1 x 4 cm fluorometric quartz cuvettes fitted with a side-arm (for work under degassed conditions) or 1 x 5 cm cylindrical quartz cells. Solution concentration was typically 5g/l in ethanol or cyclohexane.

Analytical Techniques

Analytical and preparative TLC was performed on microscope slides or 20x20 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 by heating in an air-oven to 140°C for six hours. Samples were placed on the plates, 1.5 cm from the bottom using a 10 µl microapplicator obtained from Applied Science Labs., Inc., State College, Pa. 16801. Elution was achieved, by the ascending technique, using chloroform/ether (9:1) Samples, scraped from the plates, were eluted from the silica-gel with methanol, filtered, and the solvent evaporated. The residue was then dissolved in chloroform, filtered to remove traces of silica gel, followed by solvent evaporated prior to spectral analysis. Phenolic products were also extracted from photolysed solutions using 1N sodium hydroxide solution followed by neutralization with HCl and extraction into chloroform. Ninhydrin was used as a visualization reagent throughout along with U.V. detection aided by "phosphor" incorporation into the silica-gel layers.

VPC was performed on a Perkin-Elmer 990 gas chromatograph equipped with a flame ionization detector. Helium was used as a carrier gas (∿ 70 ml/min). The column was 120 cm in length, 4 mm I.D., stainless steel packed with 3% OV-17 on Chromosorb Q. Column temperatures were 145°C for Landrin samples and 170°C for Matacil samples. Injection-port and detector temperatures were 220°C and 240°C respectively. Samples were dissolved in chloroform prior to injection.

Results and Discussion

The photodecomposition of Matacil (λ excitation > 300nm) was examined in both aerated and degassed ethanol and cyclohexane solutions; the results are summarized in the table. The major product under all conditions is 4-dimethylamino-3-methyl phenol. Trace quantities of other products were also observed. For one of the photolysis runs, the excitation wavelength was 253.7 nm, where again the major product was found to be the phenol. The spectral characteristics of the phenol are given below:

ms, M^+151, $(M-1)^+$150; n.m.r. ($CDCl_3$) τ 7.73 (s, 3H, -CH=C-CH_3), 7.35 (s, 6H,-N(CH_3)$_2$), 2.95-3.47 (3H, aromatic protons); ir ($CHCl_3$) $\bar{\upsilon}_{max.}$ 3600cm^{-1}(O-H), 1608 cm^{-1}.

The photolysis of Landrin was carried out under a similar set of conditions as that of Matacil, λ excitation > 300nm. The major product was 3,4,5,-trimethyl phenol. Its spectral characteristics are:

ms, M^+136, $(M-1)^+$135; n.m.r. ($CDCl_3$) τ 7.90 (s,3H,4-methyl), 7.75(s, 6H, 3,5-methyls), 3.45(s,2H, aromatic protons); ir ($CHCl_3$) $\bar{\upsilon}_{max.}$ 3580 cm^{-1}(O-H), 1600cm^{-1}.

Authentic samples of 4-dimethylamino-3-methyl phenol and 3,4,5-trimethyl phenol were synthesized by the alkaline hydrolysis of the corresponding carbamates. In each case, identical spectra were obtained for these products compared to the phenols extracted and/or separated from photolysed solutions.

The photoproduct of Matacil found here does not correspond to any of the degradation products observed when Matacil is sprayed on bean foliage [CASIDA et al. 1967] and exposed to ultraviolet light. 3,4,5-trimethyl phenol, the photoproduct of Landrin, is detected as a metabolite in living mice [SLADE and CASIDA 1970] but is not found as a photoproduct on growing bean foliage.

It is interesting to note that the photodegradation of Matacil and Landrin does not yield similar products to that found in the prodegradation of Zectran, 4-dimethylamino-3,5-xylyl-N-methyl carbamate [SILK and UNGER 1973], where the major photoproducts were 4-dimethylamino-3,5-dimethylphenol, 4-monomethylamino-3,5-xylyl-N-methyl carbamate, and 4-hydroxy-2,6-dimethyl-N-methyl benzamide. The photolysis of carbamates likely proceeds via a photo-Fries mechanism [BELLUS 1971; OSBORN et al 1968] and should yield a phenol and ortho as well as para-benzamides depending largely on the nature and position of ring substituents. In Zectran, the phenol and para-benzamide are indeed observed, although the ortho-product is absent, indicating perhaps, a steric effect of the two ring methyl groups. Instead, N-demethylation occurs in Zectran and the mono-methylamino carbamate is the major product. It is possible that photo-Fries products in Zectran, i.e., the phenol and para-benzamide, arise from the usual $\Pi - \Pi^*$ transition [KALMUS and HERCULES 1972] and the N-demethylation is due to an overlapping $n-\Pi^*$ band, resulting from the presence of the dimethylamino moiety. This band extends into the sunlight region of the ultraviolet. The $\Pi - \Pi^*$ transition in Matacil would be expected to be relatively stronger than that in Zectran due to the difference in ring-symmetry of the two molecules and hence would result in a far greater production of the phenol than the monomethylamino carbamate. This would explain the absence of the latter molecule in the photolysis of Matacil at these wavelengths.

In Landrin, the dimethylamino group is absent and hence ring-absorption is due to a $\Pi - \Pi^*$ transition. Since alkyl elimination in photo-Fries rearrangements does not occur [BELLUS 1971], the para position in Landrin, is in effect, blocked. At the same time, the photoproduction of the ortho benzamide in Landrin is not favoured for the following reasons: (a) steric factors probably hinder its formation [SILK and UNGER 1973]; (b) in general, para-rearrangement is far more preferable than ortho [FINNEGAN and MATTICE 1965; ANDERSON and REESE 1963]; thus, only phenol would be expected and this is observed experimentally.

TABLE I

Typical Photolyses of Matacil Solutions

λ(nm)	Solvent	Aerated or Degassed	Photolysis Time (Hours)	Products % Phenol	Products Others	Comments
> 300 nm	Ethanol	Aerated	2	trace, 1%	traces of	phenol--major product
"	"	"	10	4%	other products	3 product spots on TLC
"	"	"	16	11%	on TLC	(2 minor) unidentified.
"	"	"	40	38%	"	R_f(phenol)=0.34
"	Cyclohexane	"	2	4%	"	Product(s) at R_f=0.0
"	"	"	10	8%	"	Yield of phenol increased in
"	Ethanol	Degassed	15	8%	"	cyclohexane solution.
"	Cychohexane	"	10	7%	"	In degassed solutions, large
253.7	Ethanol	Aerated	140	10%	traces of others	decrease in R_f=0.0 products Phenol remains as major product

Typical Photolyses of Landrin Solutions

> 300 nm	Ethanol	Aerated	2	traces	--	R_f(Landrin) =0.70
"	"	"	10	"	--	R_f(phenol) = 0.43
"	"	"	16	1%	--	
"	"	"	22	2%	--	
"	Cyclohexane	"	12	1%	--	No products of R_f= 0.0
"	Ethanol	Degassed	24	2%	--	

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