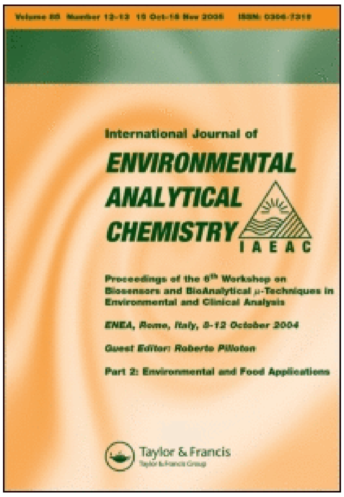

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# The Photochemistry of Carbamates V: The Photodecomposition of Sevin (1-naphthyl-N-methyl carbamate) and of Phenmec (phenyl-N-methyl carbamate)

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# The Photochemistry of Carbamates V

## The Photodecomposition of Sevin (1-naphthyl-N-methyl carbamate) and of Phenmec (phenyl-N-methyl carbamate)

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The photodecomposition of Sevin (1-naphthyl-N-methyl carbamate) and of Phenmec (phenyl-N-methyl carbamate) in aerated and degassed solutions has been examined.

The solvents were ethanol, cyclohexane, isopropyl alcohol and *t*-butanol; the exciting wavelength was $> 265$ nm. In the case of Sevin the major products are $\alpha$-naphthol and naphthalene. Traces of $\beta$-naphthyl-1-naphthol and of photo Fries products were also detected for long irradiation times. In the case of Phenmec the products are: phenol, 2-hydroxy-N-methylbenzamide, 4-hydroxy-N-methyl benzamide and benzene. For both molecules, photodecomposition proceeds via $\alpha$ and $\beta$ cleavage.

## INTRODUCTION

In 1968, Trecker, Foote and Osborn[1] showed that carbamates undergo the photo-Fries reaction[2]. Most of the ring substituted members of this class of compounds are pesticidal and have come into increasing usage as one of the substitutes for the organochlorine pesticides. In addition, most of the pesticidal carbamates absorb radiation available in the solar region and, as a result of this, undergo photodissociation.[3,4] Thus the study of the photoreactions of the carbamates allows one to examine the mechanistic details of the photo-Fries reaction, about which there has been considerable discussion,[5,6] and to determine the photodegradation products which may result due to the use of these materials in the environment. In this paper we report the results of the phototransformations of Sevin, one of the most commonly used insecticidal carbamates, and of Phenmec, which is not known to be pesticidal, but which may be considered structurally as the parent of all the carbamates.

## EXPERIMENTAL

Sevin (1-naphthyl-N-methyl carbamate) and Phenmec (phenyl-N-methyl carbamate) were synthesized by a general method[7] involving the condensation of methyl isocyanate with 1-naphthol and phenol, respectively. The following general procedure was employed:

The pure phenol (1-naphthol or phenol; 0.16 moles) was dissolved in 50 ml of dry methylene chloride in a 250 ml round-bottomed flask. Five ml of triethylamine was then added and the mixture was stirred for ten minutes. Methyl isocyanate (0.16 moles) was added dropwise to the mixture over a period of twenty minutes. A condenser was then fitted to the flask and the mixture was stirred at room temperature for twenty-four hours. The solvent was then stripped from the solution in a rotary evaporator and the crystals were collected. These crystals were dissolved in chloroform and the solution was shaken with small aliquots of 1N sodium hydroxide solution to remove any traces of unreacted phenol. The chloroform solution was then washed with distilled water, dried over magnesium sulphate, and the solvent evaporated. The compounds were then recrystallized from cyclohexane (with decolourising charcoal) and the crystals dried under vacuum. Crude yields of both products were ~ 95%. TLC and VPC pure to the limits of detection; mp's Sevin 142°C; Phenmec, 75°C. The spectral properties of these compounds were determined to be:

### Phenmec

ms, $M^+$, 151; ir ($CHCl_3$) 3475 $cm^{-1}$ (N—H) 1730 $cm^{-1}$ (C=O), 1595 $cm^{-1}$ (benzene); uv (ethanol) $\lambda_{max.}$ 261 nm ($\varepsilon$ = 327 liters/mol-cm), 266.5 nm ($\varepsilon$ = 277 liters/mole-cm); uv ($C_6H_{12}$) $\lambda_{max.}$ 263.5 nm ($\varepsilon$ = 280 liters/mole-cm), 270 nm ($\varepsilon$ = 258 liters/mole-cm).

### Sevin

ms, $M^+$, 201; ir ($CHCl_3$) 3460 $cm^{-1}$ (N—H), 1730 $cm^{-1}$ (C = O), 1595 $cm^{-1}$ (benzene); n.m.r. ($CDCl_3$) $\tau$ 7.08 (d, 3H, 5H, NH*Me*), 2.65–1.95 (multiplet, 7H, aromatic protons); uv(ethanol) $\lambda_{max.}$ 272 nm ($\varepsilon = 5.33 \times 10^3$ liters/

mole-cm); 281 nm ($\varepsilon = 6.5\times10^3$ liters/mole-cm); uv(cyclohexane) $\lambda_{max.}$ 281 nm ($\varepsilon = 5.65\times10^3$ liters/mole-cm.

Absolute ethanol, for solution photolyses, was obtained from Consolidated Alcohols Ltd., Toronto, Ontario. Cyclohexane was obtained from Harleco Co., Philadelphia, Pa., as fluorometric grade; both solvents were used without further purification.

Details of the instrumentation, photochemical procedures and TLC techniques have been described elsewhere.[8]

VPC analysis of photolysed solutions was performed on a Perkin–Elmer 990 gas chromatograph equipped with a flame ionization detector. The photoproducts were mostly phenolic in nature making direct VPC analysis difficult. These products were converted, quantitatively, to their more volatile trimethyl silyl ethers using bis(trimethylsilyl)acetamide (BSA) as reagent.[6] The column used for both systems was 6′ long, stainless-steel (1/8″OD) packed with 10% w/w UCW-98 on Chromosorb-W. Temperature programming was employed in order to achieve satisfactory separations for Phenmec solutions. Helium was used as carrier gas throughout. Samples were dissolved in chloroform prior to injection.

## RESULTS AND DISCUSSION

### A: Sevin

The photolysis of Sevin was examined in aerated and degassed ethanol, cyclohexane, iso-propyl alcohol and *t*-butanol solutions. Typical results, and TLC parameters, are listed in Table 1. Under all conditions α-naphthol is the major product and in cyclohexane solution it is the only product. This solvent effect, i.e., formation of phenol only in non polar solvents, has been documented[2] and is consistent with our findings on the photolysis of other carbamates[8–10]. In polar solvents in addition to the phenol, small amounts of naphthamides and naphthalene were produced. α-naphthol and naphthalene, isolated from photolysed solutions, were spectroscopically identical to authentic samples of these materials. The general scheme for the photo-Fries rearrangement in carbamates is given below:

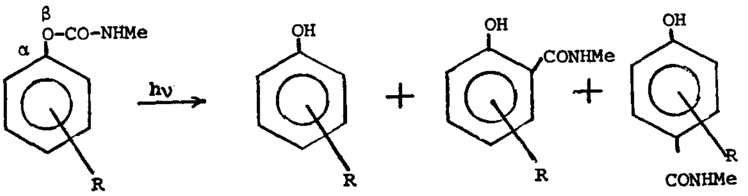

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TABLE I

Typical photolyses of Sevin and Phenmec at $\lambda > 265$*nm

| Solvent | Aerated or degassed | Photolysis time (hours) | % Decomposition | %Products | | | |
|---|---|---|---|---|---|---|---|
| | | | | Phenol | Ortho | Para | α-cleavage |
| | | | Sevin | | | | |
| Ethanol | Aerated | 2 | 1.75 | 95 | — | — | 0.8 |
| Ethanol | Aerated | 4 | 6.2 | 95 | — | — | 1.5 |
| Ethanol | Aerated | 6 | 11.0 | 83 | — | — | 7.5 |
| Ethanol | Aerated | 12 | 29 | 80 | — | — | 12.8 |
| Ethanol | Degassed | 12 | 30 | 70 | — | — | 15 |
| Cyclohexane | Aerated | 12 | 28 | 90 | — | — | — |
| Cyclohexane | Degassed | 12 | 28 | 95 | — | — | — |
| | | | Phenmec | | | | |
| Ethanol | Aerated | 2 | ~8 | 60 | 20 | 15 | ~0.1 |
| Ethanol | Aerated | 20 | 49 | 48 | 30 | 7 | ~1 |
| Ethanol | Aerated | 30 | 54 | 50 | 31.3 | 6.4 | ~1 |
| Ethanol | Degassed | 30 | ~50 | 50 | 16 | 8 | ~1 |
| Cyclohexane | Aerated | 30 | 38 | ~95 | — | — | — |

* Irradiation of Sevin solutions at 313nm resulted in light absorption but not detectable decomposition even after prolonged photolyses. Instead a bright-blue emission was observed.

TLC Parameters

Sevin

$R_f$(Naphthalene, $C_6H_{12}$) = 0.43
$R_f$($CHCl_3$/ether 8:2)
α-naphthol = 0.81)
Sevin = 0.68)
naphthalene = 1.00)

Phenmec

$R_f$(Chloroform/ether, 6:4)
phenol = 0.82
Phenmec = 0.75
ortho-product = 0.59
para-product = 0.17

The photo-Fries products are due to $\beta$ cleavage and their production, as well as the relative amounts of the ortho and para benzamides, is dependent on solvent polarity, nature and position of ring substituents. In Sevin geometric factors probably preclude significant formation of ortho and para Fries products. Carbamate photolysis may also proceed via $\alpha$ cleavage,[11] leading to phenyl radicals. Consequently the major product arising from $\alpha$ cleavage is the corresponding aromatic hydrocarbon. For Sevin, if $\alpha$ cleavage occurs, naphthalene would be expected as one of the products, and was indeed found. Thus both $\alpha$ and $\beta$ cleavage occurs in the photolysis of Sevin under the conditions employed in this study.† This is not surprising since simple Huckel calculations for the ground states of Sevin indicate that the bond orders for O-aryl and O-acyl are approximately the same but considerably smaller than those of any other bond in the molecule (the same being true for Phenmec.)

## B. Phenmec

In aerated and degassed ethanol the products are phenol, ortho and para hydroxy benzamides and small quantitites of benzene. (See Table 1). The spectral characteristics of the ortho and para hydroxy benzamides as determined by us are listed below:

*2-hydroxy-N-methyl-benzamide*

ms, $M^+$, 151; n.m.r. ($CDCl_3$) $\tau$ 7.01 (d,3H,5Hz, N-*Me*), 2.80–3.20 (multiplet, 4H, aromatic protons); ir ($CHCl_3$) $\bar{\nu}_{max.}$ 3620 $cm^{-1}$ (O—H), 3480 $cm^{-1}$ (N—H), 1645 $cm^{-1}$ (C=O), 1600 $cm^{-1}$ (benzene); uv (ethanol)$\lambda_{max.}$ 238 nm, 303 nm.

*4-hydroxy-N-methyl benzamide*

ms, $M^+$, 151; n.m.r. ($CDCl_3$) $\tau$ 7.00 (d,3H, 5Hz, N-*Me*), 2.32 and 3.10 (pair of doublets, 4H, 8Hz, apparent AB system, aromatic protons); ir($CHCl_3$). $\bar{\nu}_{max.}$ 3580 $cm^{-1}$ (O—H), 3460 $cm^{-1}$ (N—H), 1640 $cm^{-1}$ (C=O), 1600 $cm^{-1}$ (benzene) uv(ethanol) $\lambda_{max.}$ 253 nm.

The spectralcharacteristics of the phenol and benzene extracted from photolysed solutions of Phenmec were identical to those of authentic samples of these materials.

The photolysis of Phenmec, in ethanol, should yield all three possible photo-Fries products since there are no ring substituents. These products were indeed observed. The formation of benzene indicates that in this molecule $\alpha$ cleavage also occurs, but only to a very small extent.[11] In cyclohexane, as expected, only phenol was observed even for very large percentage decomposition.

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† The photolysis of Sevin in aqueous solution has been reported to yield $\alpha$-naphthol[12]. However, it is not clear whether any attempt was made to look for any other products.

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