

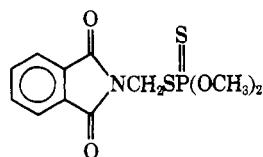
The Photochemistry of Imidan in Diethyl Ether

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The photolysis of imidan, *O,O*-dimethyl *S*-phthalimidomethyl phosphorodithioate, in diethyl ether has produced two isolable products in

low yield, *N*-methylphthalimide and *N*-methoxymethylphthalimide.

Concern about the widespread use of pesticides and the ultimate fate of these compounds in the environment has led to extensive studies of their photolytic reactions. We wish to report some observations made on the photolysis of imidan, *O,O*-dimethyl *S*-phthalimidomethyl phosphorodithioate (1). It is a nonsystemic acaricide and insecticide



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used for the control of codling moths, alfalfa weevils, and spider mites. It is rapidly hydrolyzed in base and at pH 7 it has a half-life of less than 12 hr. However, it is fairly stable to acid, with a half-life of 13 days at pH 4.5 (Spencer, 1968). Since imidan is rapidly hydrolyzed under neutral and alkaline conditions, it was decided to conduct the photolyses under laboratory conditions such that a maximum of photoproducts and not hydrolysis products could be observed.

The photolytic degradation of *N*-methylphthalimide, one of the isolable photoproducts of imidan, was also performed to see if this contributed significantly to the formation of the large number of minor photoproducts observed.

MATERIALS AND METHODS

Imidan was obtained from Stauffer Chemical Co. and was recrystallized from methanol prior to its use. The recrystallized imidan was homogeneous by thin-layer chromatography. All solvents used were of analytical grade and not treated further. All photochemical reactions were done in a quartz immersion well apparatus using a Hanovia 450-W ultraviolet lamp. The solutions were magnetically stirred and cooled to maintain a temperature of 20–25°.

Thin-layer chromatography (tlc) was carried out on Silica gel G-F plates using HCCl_3 as the development solvent. Visualization was by uv light or iodine absorption. Column chromatography was done on silicic acid, 90–200 mesh, using hexane, benzene, chloroform, and ethyl acetate as eluants. Gas-liquid partition chromatography (glpc) analyses were done using an Aerograph A-90-P instrument on 5 ft 5% DC-200 liquid phase column on Chromosorb P, with an isothermal temperature range of 185–200°.

All melting points are uncorrected. Infrared (ir) and ultraviolet (uv) spectra were taken on Perkin-Elmer infrared and Perkin-Elmer 202 spectrometer, respectively. Nuclear magnetic resonance (nmr) spectra were obtained on Varian T-60 and HA 100 instruments. Chloroform- d_1

with a tetramethylsilane internal standard was the solvent for all nmr spectra. Mass spectra were obtained on a CEC 121 spectrometer.

PHOTOLYSES REACTIONS

In a typical experiment, 5.0 g of imidan in 1.3 l. of diethyl ether was irradiated for 72 hr. At this time tlc and glpc indicated there were several photoproducts as well as unreacted imidan present. The ether solution was concentrated to 200 ml, extracted with 3×25 ml 10% NaOH, dried over anhydrous MgSO_4 , and evaporated to give 2.2 g of dark red oil with a foul odor.

The NaOH solution was acidified with 6 *N* HCl and extracted with ether. The ether solution was dried (MgSO_4) and evaporated to give 1.8 g of acidic material. This material, when triturated with ethyl acetate, gave a small quantity of white solid which was recrystallized from ethyl acetate to give 0.21 g of phthalic acid. This assignment is made on comparison of the ir spectra with that of an authentic sample of phthalic acid. Since phthalic acid was observed only in one run, its occurrence may be an artifact. The remainder of the acidic fraction from this experiment and the total acid fraction from other runs proved intractable.

The 2.2 g of neutral red oil was chromatographed on 100 g of silica gel. Elution was begun with benzene and gradually changed to HCCl_3 . Several minor malodorous components were eluted with benzene and the mixed benzene-chloroform solvents. Elution with 1000 ml of mixed solvent going from 60 to 100% v/v HCCl_3 in benzene yielded approximately 200 mg of material, which was shown to be starting imidan, a small amount of *N*-methylphthalimide, and a second photoproduct by glpc and tlc. Elution with 500 ml of HCCl_3 gave 200 mg of material, which was primarily *N*-methylphthalimide. The next fraction, 650 mg, was eluted with an additional 500 ml of HCCl_3 . This fraction was shown by glpc to be *N*-methylphthalimide and the second photoproduct with a trace of imidan. The tlc showed several minor components also. Further elution of the column with HCCl_3 and ethyl acetate gave small amounts of several additional components.

This 650-mg fraction was sublimed at 90° at 1 mm for 18 hr to give 292 mg of colorless crystals which tlc indicated was free of the minor components. The glpc indicated the sublimate was primarily the second photoproduct contaminated with *N*-methylphthalimide and imidan.

The second photoproduct was finally obtained in pure form by thick-layer chromatography and recrystallization from ethanol to give 68 mg, mp 116–118°.

Spectral data: ir (imide) 5.65 and 5.82 μ ; nmr δ 7.92 (4 H multiplet), 5.06 (2 H singlet), and 3.43 (3 H singlet); mass spectrum m/e 191, molecular ion (M^+ , $\text{C}_{10}\text{H}_9\text{NO}_3$), 176 ($M - \text{CH}_3$), 160 ($M - \text{OCH}_3$).

Elemental analysis: found for C, 62.82; for H, 4.74; for N, 7.33. $\text{C}_{10}\text{H}_9\text{NO}_3$ requires: C, 62.48; H, 4.94; N, 7.53. All these data are consistent with the assignment of *N*-methoxymethylphthalimide (5) to this photoproduct. This compound is reported to melt at 121.5–122° (Kato *et al.*, 1965).

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Repeating this experiment using a Pyrex filter which filters all radiation <286 nm produced the same two major photoproducts but the rate was much slower. Substantial amounts, over 2 g, of unreacted imidan were recovered after the 72-hr photolysis. Performing the photolysis under air or nitrogen gave identical results.

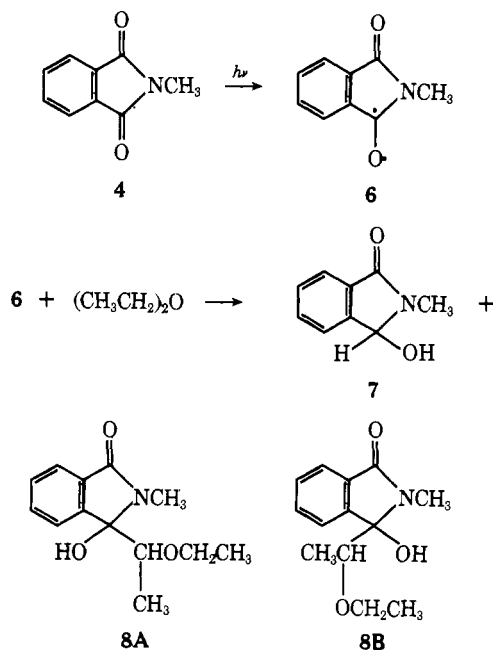
PHOTOLYSIS OF *N*-METHYLPHthalimide

In a manner analogous to the photolysis of imidan, 5.0 g of *N*-methylphthalimide was irradiated for 72 hr in ether under N_2 . The ether was concentrated and extracted with 100 ml of 1 *N* HCl followed by 100 ml of 1 *N* NaOH, dried, and evaporated to a white solid. This white solid was recrystallized from ethanol to give 2.12 g of starting *N*-methylphthalimide. Evaporation of the mother liquors gave an additional 1.82 g, for a total of 3.94 g. Tlc (C_6H_6) shows the material from the mother liquors contains only a trace of more polar material.

The NaOH extract was made acidic and extracted with CCl_4 to give, after drying and removal of solvent, 787 mg of an amber oil which by tlc (CCl_4 -EtOAc 2:1) showed three major components and three minor components. Only the major components were investigated further.

Photolyses run in air gave the same results as when under a nitrogen atmosphere. Increasing the reaction time to 113 hr proportionally increased the production of base-soluble products to 1.33 g, which indicates they are stable under the photolysis conditions (see Scheme I).

Scheme I



Isolation of *N*-Methylphthalimide Photoproducts.

The 1.33 g of base-soluble oil from the 113-hr irradiation was chromatographed on 12 16-in. silica gel H thick-layer plates. The developing solvent was 14% EtOAc in CCl_4 and the plates were developed three times. The photoproducts were located by uv light and the major bands were scraped off. The more polar one was clearly resolved and, after elution from the silica with EtOAc, was recrystallized from benzene-hexane to give 32 mg of homogeneous material later shown to be 7. The two less polar compounds were not clearly separated. This band was divided in half and eluted from the silica, and the two fractions were recrystallized from benzene-hexane until homogeneous samples were obtained. In this manner 339 mg of the faster moving component 8A and 178 mg of its slower

moving isomer 8B were obtained. These compounds are represented as 8A and 8B for convenience; no conformational or stereochemical relationships for these isomers were determined.

3-Hydroxy-2-methylphthalimidine (7). The slowest moving major band material was identified as 3-hydroxy-2-methylphthalimidine from the following data: mp 124–125° [lit. 129° (Dunet and Willemart, 1948) and 130° (Horii *et al.*, 1961)]; analysis found for: C, 66.15; H, 5.75; N, 8.34; $C_9H_9NO_2$ requires: C, 66.25; H, 5.56; N, 8.58. It shows an OH absorption at 3 μ and an amide at 5.9 μ . The mass spectrum shows a parent peak at m/e 163, a $p - 1$ peak at 162, and a $p - 17$ peak at 146. The nmr spectrum shows a 3-proton singlet at δ 2.93 (NCH₃), a broad proton singlet at δ 5.31 (the methine proton), and a 4-proton multiplet between δ 7.2 and 7.3 (the aromatic protons).

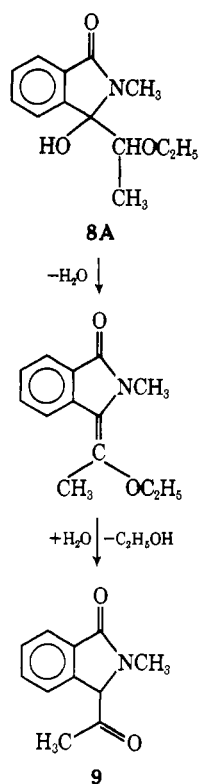
3-(1'-Ethoxyethyl)-3-hydroxy-2-methylphthalimidine Diastereomers 8A and 8B. The faster moving component 8A crystallized as rosettes from benzene-hexane with a mp of 113–115°. Analysis found for: C, 66.45; H, 7.43; N, 6.17. $C_{13}H_{17}NO_3$ requires: C, 66.36; H, 7.28; N, 5.95. The ir spectrum shows an OH at 3 μ and an amide at 5.9 μ . The mass spectrum shows a $p - 17$ peak at 218 (loss of OH), and a $p - 73$ peak at 162 (loss of $CH_3CHOCH_2CH_3$). The nmr spectrum in $CDCl_3$ shows a 3-proton doublet at δ 0.81 ($J = 6$ Hz), a 3-proton triplet at δ 1.26 ($J = 7$ Hz), and a 3-proton multiplet between δ 3.3 and 4.1, which comprises the ethyl ether moiety ($CH_3CHOCH_2CH_3$); there is a 3-proton singlet at δ 2.99 (NCH₃), a 1-proton singlet at δ 2.64 (OH, exchanges with D_2O), and a 4-proton multiplet between δ 7.4 and 7.85 (aromatic).

The slower moving component, 8B, crystallized from benzene-hexane as short prism with a mp of 115.5–116°. Analysis found for: C, 66.68; H, 7.46; N, 6.12. $C_{13}H_{17}NO_3$ requires: C, 66.36; H, 7.28; N, 5.95. The ir spectrum shows OH at 3.05 μ and amide at 6.0 μ . The mass spectrum shows prominent peaks at m/e of 217, 188, and 162. Formulas derived from the high-resolution mass spectrum for these peaks are $C_{13}H_{15}NO_2$, $C_{11}H_{10}NO_2$, and $C_9H_8NO_2$, respectively. The nmr spectrum in $CDCl_3$ shows a 3-proton doublet ($J = 6$ Hz) at δ 0.69, a 3-proton triplet ($J = 6$ Hz) at δ 1.28, and a 3-proton multiplet between δ 3.58 and 3.96, which comprise the ethyl ether grouping $CH_3CHOCH_2CH_3$; the NCH₃ shows a singlet 3-proton signal at δ 2.79, the OH shows a singlet at δ 4.07, which exchanges with D_2O , and the aromatics give a 4-proton multiplet between δ 7.24 and 7.77. Irradiation of the doublet at δ 0.69 located the methine proton at δ 3.89 and irradiation of the triplet at δ 1.28 located the methylene at δ 3.73.

Compound 8A is readily isomerized into a mixture of 8A and 8B by dissolving in 5% NaOH, acidification, and extraction into CCl_4 .

Methyl 2-Methylphthalimidine-3-yl Ketone 9. A solution of 91 mg of 8A in 4 ml of 6 *N* HCl and 1 ml of 95% ethanol was refluxed for 2 hr. The solution was extracted with CCl_4 . The CCl_4 was dried (Na_2SO_4) and evaporated to dryness to give 79 mg of solid which was crystallized from benzene-hexane to give 32 mg of an orange-tinted solid with a mp of 91–92°. Although the analysis was not satisfactory, the best fit gave a formula of $C_{11}H_{11}NO_2$. The ir spectrum showed no OH but greatly enhanced carbonyl absorptions. The mass spectrum showed only a small parent peak at $m/e = 189$, with a much larger $p + 1$ peak. The most intense peak was $m/e = 146$ or the parent molecule minus $-COCH_3$. The nmr spectrum in $CDCl_3$ was very simple and showed a 3-proton singlet at δ 1.90 ($-COCH_3$), a 3-proton singlet at δ 3.13 (NCH₃), a 1-proton singlet at δ 4.89 (the methine), and 4 aromatic protons between δ 7.30 and 8.0.

Scheme II

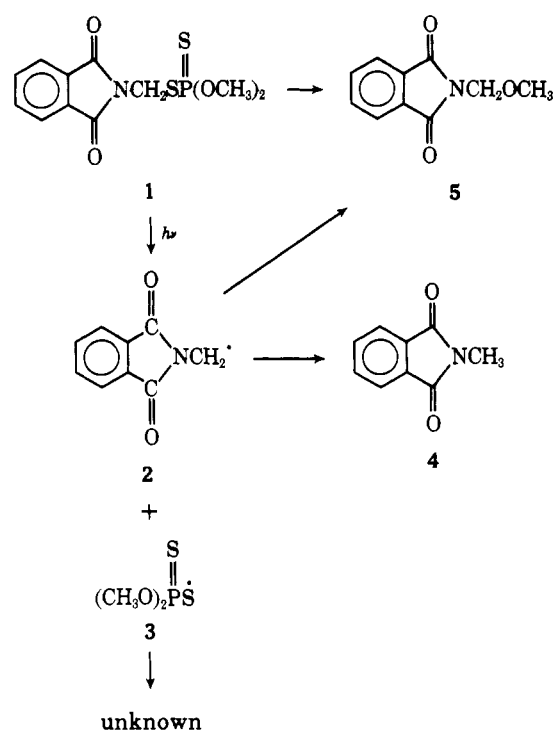


RESULTS AND DISCUSSION

A reaction pathway is outlined in Scheme III which can account for the two observed photoproducts from imidan. The scission of the sulfur carbon bond of imidan to give the dithiophosphate radical, 3, and the phthalimidomethylene radical, 2, is not unreasonable due to the stability one would expect of 3 with its unpaired electron spread over two sulfur atoms (Neckers, 1967; Walling and Huysler, 1964). The radical 2 abstracts a proton from the solvent (Elad, 1967; Walling, 1957) to give *N*-methylphthalimide (4). The *N*-methoxymethylphthalimide, 5, is formed either by an intramolecular reaction or by a transfer of the methoxyl group from 1 or 3 to the phthalimidomethylene radical, 2. McBain and Menn (1973) have found imidan to produce *N*-methoxymethylphthalimide, 5, as the major product when irradiated with sunlight in dilute aqueous solutions or as thin films on silica chromatoplates. From their experiments in water at low imidan concentrations, these workers favor an intramolecular transfer of the methoxyl group from phosphorous to carbon. The ultimate fate of 3 is unknown; all attempts to isolate a homogeneous compound containing phosphorous and sulfur other than the starting imidan failed.

Kanaoka and Koyama (1972) and Kanaoka *et al.* (1973) have shown that imides undergo photoreduction, addition, and cyclization. In this manner the imide carbonyl behaves similarly to the ketone carbonyl. These authors have also shown that 5, a photoproduct from imidan, is cyclized to give a cyclopentanol. Although no photoproducts from *N*-methylphthalimide (4) or *N*-methoxymethylphthalimide (5) were isolated from the imidan photolyses, they undoubtedly contribute to the many minor products observed in both the base-soluble and neutral fractions. Because of the potential for radical recombination of these many species and the possibility of the imide carbonyls of imidan behaving similarly, the large number of minor products is not at all surprising.

Scheme III



CONCLUSIONS

Photolysis of imidan in diethyl ether under laboratory conditions led to only two isolable products. These two photoproducts are *N*-methylphthalimide and *N*-methoxymethylphthalimide, which are inactive as insecticides. Photolysis of one of the photoproducts, *N*-methylphthalimide, demonstrated the occurrence of photoreduction and photoaddition to the imide system which, in part, may contribute to the complex mixture of minor photoproducts observed in the imidan photolyses. No photoproduct containing phosphorous or sulfur could be isolated from the many minor components and the effect of these minor photoproducts on the environment remains unknown. No field studies or natural sunlight studies were undertaken.

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Received for review June 21, 1973. Accepted October 18, 1973. This work was generously supported by a grant from the Environmental Protection Agency, R-801841.