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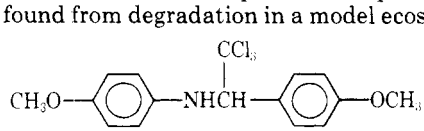
Photochemistry of *N*-(α-Trichloromethyl-*p*-methoxybenzyl)-*p*-methoxyaniline

Larry L. Miller,* Gerald D. Nordblom, and Gregory A. Yost

N-(α-Trichloromethyl-*p*-methoxybenzyl)-*p*-methoxyaniline was photolyzed in aqueous solution and on glass, silica gel, cellulose, and leaves. The major photolysis product was *N*,2-dianisyl-2-hydroxyacetamide. Anisaldehyde, anisic acid, anisidine, and *N*,2-dianisyl-2-oxoacetamide were also found in certain cases. In wet ether α,α-dichloroacetophenone and anisidine were formed as major products. A comparison with degradation products formed in a model ecosystem is made.

We have been interested in the feasibility of building a photodegradable pesticide. This study has utilized photosensitized decomposition of organic chlorides by aromatic amines (Miller and Narang, 1970) as a molecular test system. In this reaction the amine absorbs light in the solar region (>290 nm) and excited amine molecules attack the chloride. The reaction was previously shown to be applicable to chlorinated insecticides. DDT, for example, is readily degraded by diethylaniline using 310-nm light in aerated solutions (Miller *et al.*, 1973). Our approach then was to incorporate the sensitizer into a chlorinated molecule with insecticidal activity. In this way each molecule would have a propensity for self-destruction in sunlight, regardless of its chemical environment. Fortunately, Hirwe *et al.* (1972) recently synthesized a series of compounds with attributes desirable for our goal. One of these was *N*-(α-trichloromethyl-*p*-methoxybenzyl)-*p*-methoxyaniline (**1**). Compounds in this series have insecticidal activity comparable to DDT, degrade more readily than DDT, and apparently do not build up through the food chain. From our point of view these compounds seemed quite likely to photodegrade since they incorporated an aromatic amine into a chlorinated pesticide. The present study elucidates the photoproducts from **1** in media similar to those in nature and compares these photoproducts with those found from degradation in a model ecosystem.

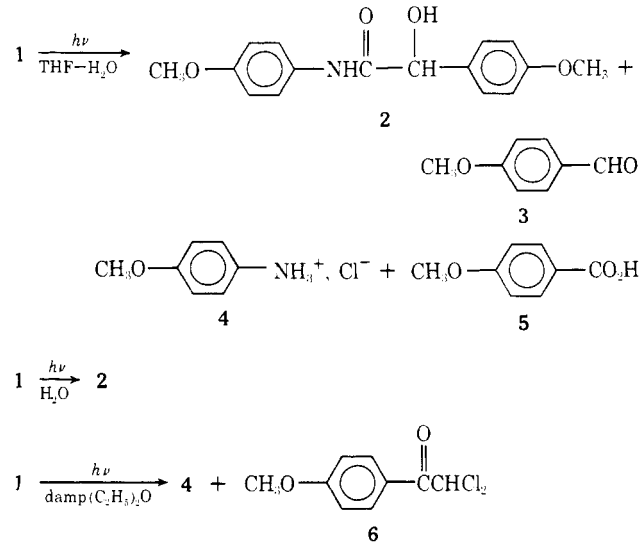


1

RESULTS

Photolysis in Solution. Compound **1** was photolyzed in a Rayonet reactor using 295–320-nm light. Initial product studies were facilitated by using a solvent mixture of 60% tetrahydrofuran (THF) and 40% water. A 3.5×10^{-2} *M* solution was allowed to react for 24 hr in air and worked up by vacuum evaporation and extraction. Chromatographic separation of the neutral products was accomplished on a silica gel column. The results are illustrated in Scheme I and detailed in Table I.

Scheme I



Photolysis of **1** in damp diethyl ether or damp THF gave α,α-dichloroacetophenone (**6**) and **4** as the major products. Small amounts (~1%) of water are necessary for the formation of **4** and **6**. In rigorously dry ether a complex, presently unresolved mixture of products was produced.

For further studies of this reaction it was desirable to have a rapid, quantitative analytical technique for the

Chemistry Department, Colorado State University, Fort Collins, Colorado 80521.

Table I. Products from Solution Photolysis of *N*-(α-Trichloromethyl-*p*-methoxybenzyl)-*p*-methoxyaniline[a]

Solvent	Time, hr	Products (% yield)
Ether (damp)	4	**4** (95), **6** (95)
Ether (dry)	8	**2** (1.0), **3** (0.38), **4** (0.21), **6** (−)[b]
60% THF–40% H_2O	24	**2** (63), **3** (16), **4** (26), **5** (5)
H_2O[c]	24	**2** (99)

[a] 5×10^{-2} *M*, 310-nm light. [b] Yields relative to **2**. [c] Saturated solution 20 ppm. **6** was present, but not quantified.

Table II. Products from Solid Phase Photolysis of *N*-(α-Trichloromethyl-*p*-methoxybenzyl)-*p*-methoxyaniline[a]

Medium	Time, hr	Products (yield relative to **2**)
Cellulose	25	**2** (1.0), **3** (0.64), **4** (0.09), **7** (−)[b]
Silica gel	18	**2** (1.0), **3** (0.03)
Glass	31	**2** (1.0), **3** (0.44), **4** (0.27), **7** (−)
Lettuce leaves	2	**2** (1.0), **3** (trace), **4** (trace), **7** (trace)
Bean leaves	5	**2** (1.0), **3** (trace), **6** (trace), **7** (−)

[a] 5×10^{-2} *M*, 310-nm light. [b] The yield of **7** was not measured.

products 2–6. Glc was not suitable because of the thermal instability of **1**. Although some separation of products was feasible using tlc on silica gel plates, a far superior method using high-pressure liquid chromatography was developed. Compounds 2–6 can be separated and assayed on a Porasil A column using isopropyl ether–hexane solvent. This analysis without gradient elution was, however, time consuming due to the long retention time of **2** and **4** under conditions suitable for separating **3**, **5**, and **6**. This aspect was obviated by silylation of the reaction mixture with bistrimethylsilylacetamide. The silylated amine and amides **2** and **7** were now much less polar and had correspondingly lower retention times. Liquid chromatography is advantageous because it allows ready quantification and products can be collected for identification.

Analysis of the photolysate from an aqueous solution of **1** was undertaken. From photolysis of a saturated solution (~20 ppm) the product was **2** in essentially quantitative yield. Liquid chromatography was also used to explore the rate of reaction in THF–water. It was found that photolysis was 50% complete in 1.3 hr and >90% conversion was observed in 4 hr. The product ratios were relatively insensitive to irradiation time and bubbling oxygen through the solution during photolysis did not substantially change the results. It was also established that **1** was not being thermalized in the photoreactor. The temperature in this reactor is 40°. Refluxing **1** in THF–H_2O for 24 hr gave no reaction.

Photolysis on Solid Surfaces. Because environmental photolyses could very well involve pesticides on surfaces we have investigated the products formed on glass, cellulose, silica gel, lettuce leaves, and bean leaves. As shown in Table II, the products were similar to those formed in solution. One new compound was formed on lettuce leaves and glass. It is **7** whose structure was proven spectroscopically. In general, however, the major product was **2**. Only relative yields of these products are cited because control of the amount photolyzed and its volatilization were not achieved.

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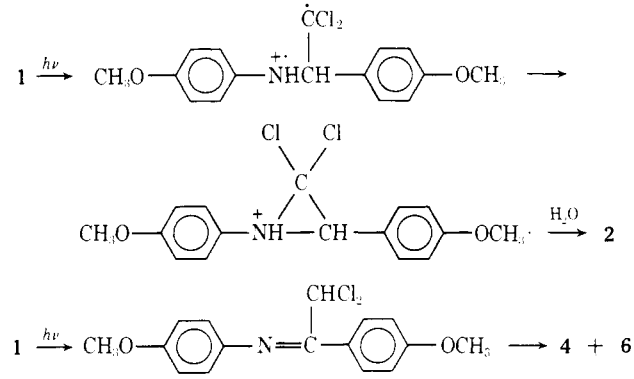
DISCUSSION

Compound **1** is photoreactive with light in the solar region as predicted. It is considerably more reactive than its carbon analog, DDT. Under identical photolysis conditions at 310 nm DDT shows no measurable decomposition after 4 hr, while **1** is completely degraded. This may be due, in part, to its greater (4×) absorptivity at 310 nm. The absorption spectrum of **1** shows λ_{max} (ε) 233 (18,800), 280 (2040), and 305 nm (1690). This indicates that it could degrade photochemically in the environment. Degradation of a diethoxy analog of **1** in a model ecosystem gave several products including those corresponding to **4**, **5**, and **6** (Hirwe *et al.*, 1972). A further unknown was present, but whether this corresponds to **2** remains to be elucidated. This result cannot be taken as evidence for or against the importance of photodegradation since these products are known from independent experiments to arise from animal metabolism as well as photolysis. Tests in a true field situation seem important. The model ecosystem minimizes exposure of the pesticide to light in order to study the impact on animals and *in vitro* photolysis is obviously an unrealistic model.

The mechanism of this photoreaction has not been studied. Feasible pathways to the products **2** and **6** are, however, shown in Scheme II. Initial photoinduced charge transfer is a reasonable first step based on literature analogies (Miller *et al.*, 1973, and references cited therein). Rapid loss of chloride ion and collapse to the dichloroaziridine would certainly be feasible and this provides a rational path to mandelic acid **2**. The aziridine was previously synthesized (Brooks *et al.*, 1966) and shown to decompose to **2** at 40° in water with a half-life of a few minutes. Similarly, the hydrolysis of the imine to produce **4** and **6** provides a logical route to these products. Compounds **5** and **7** are presumed to arise from photooxidation of **3** and **2**. Detailed speculation about the differences between the various solid surfaces and solutions and their effect on the reaction pathway seems unwarranted.

Scheme II



EXPERIMENTAL SECTION

Materials. *N*-(α-Trichloromethyl-*p*-methoxybenzyl)-*p*-methoxyaniline was prepared by the method of Hirwe *et al.* (1972). Reagent grade ether (anhydrous), tetrahydrofuran, and bistrimethylsilylacetamide (BSA) were used without further purification. Lettuce leaves were obtained from a local commercial source and bean leaves were cut from plants 2–3 weeks old. Analytical cellulose (20 × 20 cm) and silica gel (5 × 10 cm) tlc plates were obtained from Brinkmann Instruments.

Photolyses. A Rayonet photochemical reactor, equipped with a merry-go-round and 16 310-nm lamps, was used. All solutions were photolyzed in Pyrex containers.

High-Pressure Liquid Chromatography (HPLC). A Waters Associates ALC-202 liquid chromatograph with a

differential uv detector operating at 254 nm was used. The column was 2 mm i.d. × 3 ft packed with Porasil A. The eluting solvent was diisopropyl ether–hexane (1:1) (v/v). The column was operated at ambient temperature with a flow rate of 1.35 ml/min.

Spectra. Ir spectra were taken on a Perkin-Elmer Model 337 grating infrared spectrophotometer. Nmr spectra were taken on a Varian A-60A nmr spectrometer. Mass spectra were run on an AEI-MS12 mass spectrometer at 70 eV with a solid probe.

Solution Photolyses. All reactions were done on solutions of 1.00 g of 1/100 ml of solvent except for the photolysis in H_2O. In this case approximately 50 mg of 1 was added to 1 l. of H_2O; the mixture was brought to boiling with stirring for 15 min. This does not lead to decomposition. The hot solution was filtered and photolyzed in 250-ml erlenmeyer flasks open to the atmosphere. Once photolyzed, any organic solvent used was removed on a rotary evaporator, $CHCl_3$ was added, and sufficient 5% $NaHCO_3$ was added to make the solution basic. The $CHCl_3$ was separated and the aqueous solution reextracted with $CHCl_3$. The organic solution was then dried over Na_2SO_4 and the volume reduced *in vacuo* to 1 ml, 2–3 ml of BSA was added, and the solution was heated to 45° for 30 sec. The solution was then eluted through silica gel with diisopropyl ether adjusted to a volume of 5 ml and the resulting solution analyzed by HPLC. Although some variation in retention times was observed, the following are representative (retention times, minutes): 1 (6.5), 2 (19), 3 (4.5), 4 (23), 6 (3.5), 7 (13.5). Compound 5 was isolated by acidification of $NaHCO_3$ solution and reextraction with $CHCl_3$.

Solid Phase Photolyses. Dilute solutions of 1 in ether (66–700 mg/100 ml) were made and applied directly to the tlc plates with a pipet until the entire plate was covered. In the case of the leaves and glass plates, the solution was applied to the surface and blown dry with warm air from a heatgun. After photolysis the tlc plates were scraped and the adsorbent extracted with methanol and $CHCl_3$. The solution was evaporated to dryness and dissolved in $CHCl_3$, then worked up further as described in the solution photolyses, followed by HPLC analysis. The glass plates and leaves were washed with THF, the organic solution evaporated to dryness, and the residue dissolved in $CHCl_3$. The same work-up procedure followed and HPLC analysis was carried out.

***N*,2-Dianisyl-2-hydroxyacetamide (2).** 1 (2.00 g) was photolyzed in 200 ml of THF–H_2O (60:40) (v/v) for 24 hr. The solution was then placed on a rotary evaporator and the THF removed. The resulting mixture was extracted with $CHCl_3$ and the organic layer then extracted with 10% HCl, 5% $NaHCO_3$, and H_2O. After drying and evaporation the resulting oil was chromatographed on silica gel. After eluting with hexane, elution with CCl_4 gave a pale yellow solid which recrystallized from H_2O to give colorless crystals: mp 117–118°; ir (KBr) 3400, 3330, 1650 cm^{-1}; nmr ($CDCl_3$) δ 3.8 (s, 6 H), 5.0 (s, 1 H), 6.84 (d, 2 H), 6.86 (d, 2 H), 7.36 (d, 2 H), 7.38 (d, 2 H), 8.0 (s, 1 H). *Anal.* Calcd: C, 66.89; H, 5.96; N, 4.88. Found: C, 67.00; H, 6.10; N, 4.79.

***N*,2-Dianisyl-2-oxoacetamide (7).** Pesticide 1 was photolyzed for 24 hr on cellulose tlc plates. After scraping the plates and extracting with MeOH, the product mixture was worked up as described above for 2. The chromatography was done on silica gel. After eluting with hexane, hexane + 5% ether yielded a yellow solid: mp 114–115.5°; ir ($CHCl_3$) 3380, 1680, 1650, 1585, 1580 cm^{-1}; nmr ($CDCl_3$) δ 3.82 (s, 3 H), 3.90 (s, 3 H), 6.90 (d, 2 H), 6.92 (d, 2 H), 7.62 (d, 2 H), 8.50 (d, 2 H); mass spectrum *m/e* (rel intensity) 285 (100), 144 (5.3), 135 (100), 122 (7.9), 117 (13.1), 92 (21.0), 77 (29.9), 64 (14.4).

α,α-Dichloroacetophenone. Pesticide 1 (0.97 g, 2.5 mmol) was photolyzed as a solution in 100 ml of wet ether. After photolysis a solid had precipitated which was identified as *p*-anisidine hydrochloride. The filtrate was concentrated under reduced pressure yielding a yellow oil which was purified by kugelrohr distillation yielding a white solid that was identified as *p*-methoxy-α,α-dichloroacetophenone: mp 74–75°; lit. mp 75–76° (Johannssen, 1900). The nmr spectrum gave singlets at 6.72 (1 H) and 3.96 (3 H) and an AA′XX′ system (4 H), A 7.03, X 8.18 (J_{AX} = 4.2 Hz). The mass spectrum showed a parent peak with *m/e* equal to 218 with P, P + 2, and P + 4 in the ratio 1.00:0.68:0.15 indicating two chlorine atoms. Other prominent peaks were 184 (2.4%), 155 (7.4%), 135 (100%), 107 (8.5%), and 77 (28.5%).

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