thesis of [^{14}C]fenvalerate, E. J. Silveira for the GC–mass spectral analysis, and Gerri Solano for the preparation of this manuscript.

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Novel Photoreactions of an Insecticidal Nitromethylene Heterocycle

Daniel Kleier, Ian Holden, John E. Casida, and Luis O. Ruzo*

Tetrahydro-2-(nitromethylene)-2H-1,3-thiazine, a remarkably potent insecticide, undergoes facile photoreaction by processes including conversion to the nitrile, reduction to the nitroso derivative and dimerization, oxidative cleavage of the nitromethylene group, and exchange of the vinylic hydrogen in protic solvents. The very efficient exchange reaction is essentially complete before degradation products are evident in the photolysate. Three possible mechanisms for photoexchange at the nitrovinyl group are α,β-addition of the solvent followed by elimination, hydrogen abstraction similar to that in Norrish type II photoreaction, and formation of an excited state with enhanced acidity of the vinylic proton.

The nitromethylene heterocycles are a unique insecticide class including compounds with very high insecticidal activity coupled with low mammalian toxicity (Soloway et al., 1978). Tetrahydro-2-(nitromethylene)-2H-1,3-thiazine (1, Shell Development Co.) (Figure 1) is one of the most active compounds but its high photolability is a serious drawback in practical applications. It is therefore of interest and importance to define the principal photoprocesses in the facile decomposition of 1 and the possible involvement of the toxophoric nitromethylene substituent in these reactions.

MATERIALS AND METHODS

Chemicals. Compounds 1, 4, and 5 (Figure 1) were synthetic standards prepared by Shell Development Co. The sensitizers and deuterated solvents were from Aldrich Chemical Co. (Milwaukee, WI).

Photolysis Procedures. 1 at 0.01 M in water, sodium dodecyl sulfate (SDS) (0.03 M) micellar solutions, methanol, dichloromethane, or toluene was irradiated to <10 or ∼30% conversion at 360 nm in a Rayonette reactor (The Southern New England Ultraviolet Co., Middletown, CT). Alternatively, for mechanistic studies, 1 at 0.06 M in D_2O or CH_3OD was irradiated to <1% conversion with a low-pressure Hanovia lamp (Pyrex filter) at −80 °C. Benzophenone, biphenyl, and naphthalene were used as sensitizers at 0.1 M in dichloromethane. Solutions were

either oxygenated or degassed by flushing (1 h) with oxygen or argon, respectively.

Chromatography and Spectroscopy. Ultraviolet spectra were recorded in hexane, methanol, water, or 0.03 M SDS aqueous micellar solution. Thin-layer chromatography (TLC) employed silica gel F-254 chromatoplates (0.25 mm, EM Reagents) with carbon tetrachloride–ether (3:1) for isolation of 2 and chloroform–methanol (10:1) for other analyses. High performance liquid chromatography (HPLC) utilized a Beckman 344 instrument equipped with a C_{18} μBondapak reverse-phase column eluted with methanol–water gradients. Photoproducts were isolated by combinations of TLC and HPLC, but only 2 was obtained in high purity due to decomposition of others during workup. Nuclear magnetic resonance (NMR) spectra were obtained on a Bruker spectrometer at 300 MHz (^{1}H), 47 MHz (^{2}H), and 75.5 MHz (^{13}C). ^{2}H spectra were recorded in the unlocked mode with reference to external deuteriochloroform. Samples were dissolved in protio- or deuteriomethanol, acetone, chloroform, or water as appropriate and chemical shifts are reported as ppm down field from tetramethylsilane.

Mass spectrometry (MS) utilized a Hewlett Packard 5985B system with ionization by electron impact (EI, 70 eV) or chemical ionization (CI, 230 eV) with methane as the reactant gas (0.8 torr). Fast atom (xenon) bombardment (FAB) spectra were obtained on a ZAB-2F mass spectrometer with samples in glycerol matrix. Masses and relative intensities are given for molecular (M$^+$) or quasi-molecular [(M + 1)$^+$] ions and other important fragments. Samples introduced via direct inlet were heated (60–200 °C) as necessary. Benzoic acid from irradiation of 1 in toluene was identified by gas chromatography–mass

Pesticide Chemistry and Toxicology Laboratory, Department of Entomological Sciences, University of California, Berkeley, California 94720 (I.H., J.E.C., and L.O.R.), and Shell Development Company, Modesto, California 95352 (D.K.).

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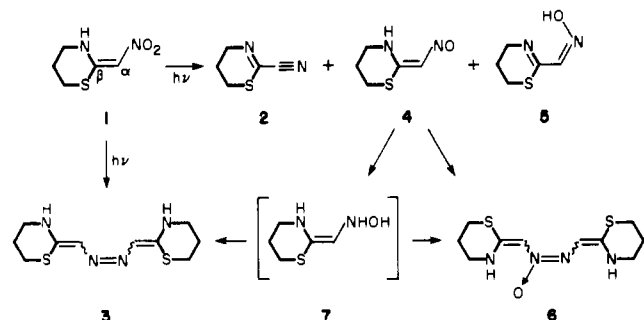
Figure 1. Major pathways for photodecomposition of nitromethylene heterocycle 1.
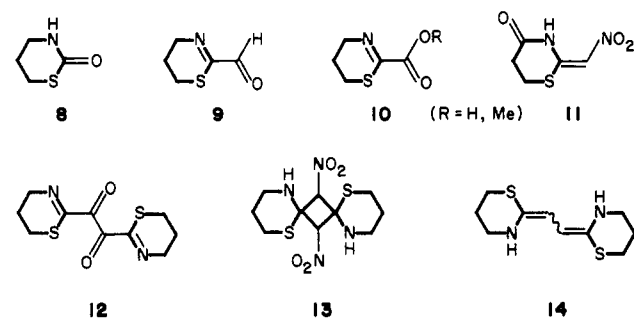
Figure 2. Photoproducts of 1 resulting from oxidation and dimerization in protic solvents.

spectrometry (GC–MS) using a high performance cross-linked methyl silicone column (12 m) operated at 100 °C and 1 mL/min helium carrier gas.

RESULTS AND DISCUSSION

Nitromethylene 1 exhibits strong absorption in water and methanol ($\epsilon \sim 40\,000$) at 365 nm and a bathochromic shift of ~ 40 nm on transfer from hexane to water, consistent with a transition in which the dipole moment of the excited state is larger and generally in the same direction as that of the ground state (Reichardt, 1979). This shift and electronic structure calculations (described later) suggest that the transition responsible for the long wavelength band involves the transfer of π electron density from the enamine portion of the molecule to the nitro group. The UV spectrum of 1 is essentially the same in water and aqueous SDS solutions.

Direct irradiation of 1 (360 nm) in water, methanol, or dichloromethane results in loss of insecticidal activity yielding complex photoproduct mixtures of up to 43 components (HPLC, TLC), some of which are indicated in Figures 1 and 2 and many of which are unstable on attempted concentration or isolation. Similar product distributions are obtained in the three solvents with significant differences in rates and yields as discussed below.

The major photoproduct obtained in dichloromethane ($\sim 22\%$ yield at 30% conversion) is the nitrile (2), identified by CI-MS (127 [M + 1]+, 100, and corresponding [M + 29]+ and [M + 41]+ signals, 100 [M – CN]+, 82), high resolution (HR) EI-MS (calcd 126.1758, found 126.1749 [M+], $C_5H_6N_2S$), and NMR (^{1}H [acetone-d_6] δ 1.94 [2 H, m], 3.28 [2 H, t], 3.85 [2 H, t]; ^{13}C δ 179.9, 128.3 [CN], 47.4, 25.0, 18.7). Azo dimer 3 (EI-MS 256 [M]+, CI-MS 257 [M + 1]+, 100; 285 [M + 29]+, 16; HR-EI-MS (calcd for C_{10}-$H_{16}N_4S_2$ 256.3832, found 256.3667 [M+]) is also a major photoproduct in dichloromethane ($\sim 10\%$).

Nitroso (4, CI-MS 145 [M + 1]+, 100; 115 [M – NO]+, 65), oxime (5, EI-MS 144 [M]+, 100; 127 [M – OH]+, 48), and azoxy (6, FAB 273 [M + 1]+) derivatives are formed in <5% yield and are tentatively characterized by MS.

The presence of 4 and 5 was further confirmed by co-chromatography (HPLC) with authentic standards.

It is as yet unclear how 2 is formed. A possible intermediate is oxime 5 which could dehydrate to the nitrile. However, photolysis of dilute solutions of 5 in dichloromethane yielded only trace amounts of 2 and an intractable mixture of polar products.

Photolysis of 1 in water or methanol to 30% conversion yields 3 as the major product (15–20%) with 2 and 4–6 in small amounts (<5%). Several additional minor products (<1%) (8–14) form exclusively in protic media. Structure assignments are based on molecular and quasi-molecular ions obtained on EI- and CI-MS and for 12 additionally on HR-EI-MS (calcd for $C_{10}H_{12}N_2O_2S_2$ 256.3362, found 256.3349 [M+]) which differentiates it from 3. The geometry of the dimers is not determined.

Photodecomposition initially proceeds 10-fold faster in dichloromethane (1.7 mM h^{-1}) than in water, however, at greater than 10% conversion the reaction rates are considerably increased in both solvents by secondary reactions, i.e., dimerizations and interactions with the products. On concentration of the reaction mixture, product yields are affected with a decrease in 4 relative to 6.

Addition of a variety of photoactive substances (benzophenone, biphenyl, and naphthalene) to solutions of 1 did not retard reaction (except to the extent explainable by competitive light absorption), however, use of SDS micellar solutions was successful in decreasing the rate by $\sim 50\%$. This may be due to seclusion of 1 making it unavailable for secondary reactions.

The well recognized (Morrison, 1969; Chow, 1982) photoreduction pathway $NO_2 \rightarrow NO \rightarrow NHOH \rightarrow NH_2$ is an important degradation route for 1 as indicated by the presence of dimers 3 and 6 and of benzoic acid (GC–MS) in irradiated toluene solutions (Chow, 1982). In general, similarities in the photochemistry of 1 and nitroaromatics may be expected based on MS characteristics, i.e., loss of 30 amu corresponding to NO, a process absent in aliphatic nitro compounds (Budzikiewicz et al., 1967). Oxidation products 8–10 (Figure 2) are probably not the result of nitro–nitrite rearrangement, since they are present in oxygenated but not in degassed solutions, and on degassing the reaction rate is substantially decreased.

In order to establish the earliest photoprocesses of 1, D_2O solutions were irradiated and monitored by ^{1}H and ^{13}C NMR leading to unexpected and novel (to our knowledge) results. ^{13}C NMR of 1 exhibits δ 157.0, 98.1, 31.2, 16.5, 10.1. The singlet at 98.1 becomes a 1:1:1 triplet in the deuteriovinyl product. ^{1}H NMR: δ 2.39 (2 H, m), 3.41 (2 H, t), 3.87 (2 H, t), 7.09 (1 H, s). The photoexchange was monitored by the disappearance of the vinylic proton. At irradiation times when <1% reaction of 1 could be detected the C-α proton was completely exchanged with deuterium. ^{2}H NMR and CI-MS confirmed the incorporation of deuterium in samples irradiated in D_2O or CD_3OD but not $CDCl_3$. The reaction did not take place in the dark.

Three possible mechanisms are envisaged for the vinylic proton photoexchange process. In one, α,β-addition of the solvent is followed by elimination, presumably due to thermal instability of the intermediate (Figure 3 part a). Irradiation of 1 in methanol at −80 °C and inspection of ^{1}H NMR spectra at that temperature revealed two very small (<1% of scale) new signals at δ 3.25 (C–OCH$_3$) and 4.50 (CH$_2$NO$_2$) which disappear on warming to 25 °C. By ^{13}C NMR only one new signal was detected at δ 125.5 (CH$_2$NO$_2$) (OCH$_3$ group obscured). These may indicate formation of an unstable α,β-adduct of methanol or con-

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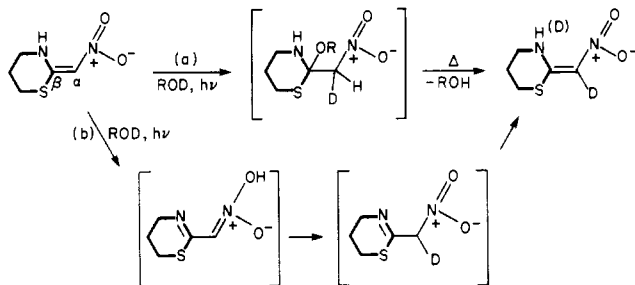
Figure 3. Possible mechanisms for photoexchange reaction of the vinylic proton of **1** in D$_2$O or CH$_3$OD.
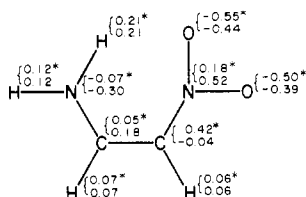
Figure 4. Mulliken charges in electrons for ground and excited (*) states of *cis*-nitrovinylamine as calculated by CNDO/S.

ceivably of another transient product.

A second possibility involves hydrogen abstraction similar to that in Norrish type II photoreaction (Figure 3 part b). In this case deuterium would also be incorporated at the amine and in fact the exchange gives ~30% dideuterio-**1** detected by MS.

A third and better supported mechanism involves proton exchange from an excited state more acidic than ground state **1**. This mechanism is suggested by an analysis of the charge distribution within the excited state of a model system. CNDO/S calculations (Jaffe, 1976) on the excited states of *cis*-nitrovinylamine support the charge-transfer nature of the lowest $\pi\pi^*$ excited state as indicated in Figure 4. Specifically the calculations predict that about 0.56 e are transferred from the vinylamine to the nitro group during the transition. This transfer of charge is expected to enhance the acidity of the C-α proton. The pK_a of the exocyclic carbon is expected to be 10 or less in the ground state. Excitation will change the pK_a (Jaffe and Orchin, 1962) to a lower value and this should be

accompanied by enhanced exchange rates.

This study establishes that the photochemistry of **1** involves a variety of processes and results in a complex product distribution but it does not firmly establish the nature of the excited state or intermediate leading to facile vinylic proton exchange. It is evident that the nitrovinyl chromophore, essential for insecticidal activity (Soloway et al., 1978), is destroyed by photoreaction. Thus, photostabilization of the nitromethylene class may ultimately require the use of external additives.

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