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SOLUTION PHOTOCHEMISTRY OF THE POTENT PYRETHROID INSECTICIDE α-CYANO-3-PHENOXYBENZYL <u>cis</u>-2,2-DIMETHYL-3-(2,2-DIBROMOVINYL)CYCLOPROPANECARBOXYLATE

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The solution and thin layer photochemistry of pyrethrin I, related pyrethroids, and other chrysanthemates has received considerable attention in recent years[1,2], due in part to the need for pyrethroid insecticides of enhanced potency and photostability. We now wish to report the photoproducts from the most potent pyrethroid insecticide, [S]-α-cyano-3-phenoxybenzyl <u>cis</u>-[1R,3R]-2,2-dimethyl-3-(2,2-dibromovinyl)cyclopropanecarboxylate (1)[3]. Ester photochemistry generally involves decarboxylation[4], decarbonylation[5], and other types of cleavage while photochemical modifications of cyclopropanecarboxylates lead to epimerized and ring-open products[2]. The n-π^* and π-π^* mixed transition of 1 (λ_{max} 278 nm) extends to λ >290 nm and thus presents the possibility of extensive environmental decomposition <u>via</u> photoreactions of the various functional groups present.

Photolysis of 1 (8×10^{-3}M) in methanol, hexane, or 40% water-acetonitrile was carried out through Pyrex in a Rayonet reactor equipped with RPR 3000 lamps (peak output λ 290-320 nm). The products (Scheme 1) were isolated by preparative TLC and GLC and identified by comparison with authentic standards using various combinations of GLC, TLC, IR, NMR and CI-MS (1, 2, 4-8, 11 and 15-18)[6,7] or by GLC-CI-MS only (3, 9, 10 and 12-14). They were quantitated by GLC (Dexil on Varaport-30) with a flame ionization detector.

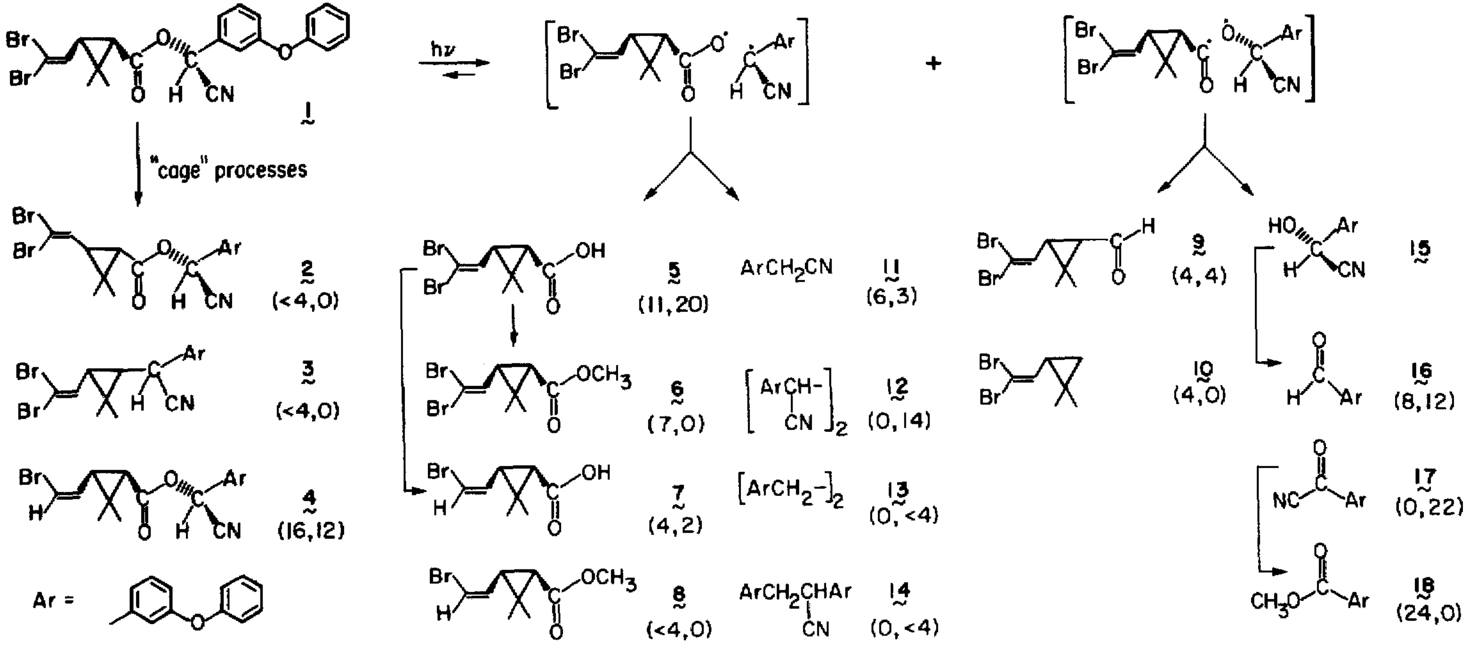
A simpler product mixture is obtained in hexane than in methanol (Scheme 1). Compound 1 undergoes isomerization, decarboxylation, and debromination to yield 2, 3, and 4, respectively. Although the principal compound (4) that retains the original ester linkage is formed by <u>trans</u>-debromination of 1, small amounts of the <u>cis</u>-debromo- and didebromo-derivatives of 1 are also observed. A vinylic radical intermediate is probably involved in the formation of compound 4 since one atom of deuterium is incorporated at the vinyl position when the photolysis is carried out in CD_3OD.

Major products from the acid moiety in methanol and hexane are the dibromovinyl (5) and monobromovinyl (7) acids and, in methanol, their methyl esters (6 and 8). Photolysis of 1 in aqueous acetonitrile yields only 5 from the acid moiety. Formation of 6 and 8 in methanol does not proceed <u>via</u> a ketene intermediate since on photolysis of 1 (10^{-3}M) in CD_3OD they incorporate only three deuterium atoms (GLC-CI-MS). Further, direct photolysis of 5 (10^{-3}M) in methanol yields non-isomerized 5 and 7 and their methyl esters (6 and 8) in a manner similar to that reported in the photolysis of other carboxylic acids[8]. In contrast to the predominant *trans*-debromination of **1** in methanol, direct photolysis of **6** (10^{-3}M) in methanol yields products arising from *cis*- and *trans*-debromination in approximately equal amounts. The alcohol moiety may sterically hinder *cis*-debromination in **1** but not in **6**. Vinylic free radicals are probable intermediates in these photoreductions since dimeric material appears upon photolysis of **6** in concentrated (10^{-1}M) solutions and by analogy with studies on other vinyl bromides[9]. Compounds **9** and **10** are minor products from the acid moiety[10].

The alcohol moiety yields the nitrile (**11**), dimers (**12** and **13**), compound **14**, the cyanohydrin (**15**), and the aldehyde (**16**) upon photolysis of **1** in methanol or hexane. An authentic sample of **15** yields **16** upon photolysis in methanol. The major product of **1** in hexane, absent in methanol, is the benzoyl cyanide (**17**). In contrast, the methyl benzoate (**18**) is the major product in methanol and on photolysis in CD_3OD the trideutero compound is formed. Authentic benzoyl cyanide (**17**) in methanol is readily converted to the methyl ester (**18**) upon heating at 50° or on photolysis. In aqueous acetonitrile, the aldehyde (**16**) and 3-phenoxybenzoic acid are the only major products from the alcohol moiety. Thus, the benzoyl cyanide observed in hexane is proposed as a novel intermediate leading to methyl 3-phenoxybenzoate in methanol and the corresponding acid in aqueous acetonitrile.

Products not retaining the original ester linkage (**5**-**18**) can be explained by homolytic cleavage of the carboxyl-carbon[11] or acyl-oxygen bonds[12], yielding the hypothetical intermediates shown in Scheme 1. No photoepimerization is apparent at the benzylic carbon so recombination of the radical intermediates must occur in stereospecific manner, as shown previously for aryl methyl esters[13]. Decarboxylation (**3**) and decarbonylation (**10**) products form in other systems *via* radical intermediates, and in some cases "cage" processes have been implied[13]. Since the relative rates of disappearance of **1** in various solvents decrease with increasing solvent viscosity (hexane > cyclohexane, methanol > ethanol > 2-propanol), the major degradative processes do not appear to involve "cage"-type intermediates. "Cage" processes appear to be involved to a greater extent, however, in the photolysis of **1** in 2-propanol where the major products (*e.g.*, **2**-**4**) are formed without extensive fragmentation of the molecule.

Several results with **1** support previous findings of excited triplet state intermediates in ester photolysis[11]. Thus, sensitized photolysis of **1** is observed in deoxygenated methanol with benzophenone or **16** (10^{-2}M) and in acetone solution; the reaction, however, is not as efficient as that obtained by direct irradiation of **1** and it gives an increased amount of isomerized material. Isobutyrophenone (10^{-2}M) sensitized photolysis of **6** (10^{-3}M) in benzene yields the *trans* isomer as the only major product. This presumably involves diradical formation *via* a triplet excited state followed by ring closure to the preferred *trans* configuration as shown previously in other cyclopropanecarboxylates[2]. When photolysis of **1** is carried out in hexane solutions of piperylene, styrene or 1,3-cyclohexadiene (10^{-2}M) or in oxygen saturated hexane, the rate of disappearance is considerably decreased and no new products are detected. The photochemical pathways of **1** must then include at least partial



Scheme 1

Photochemical pathways for 1 at 30% conversion showing compound designations. The yield of each product in methanol and hexane, respectively, is given in parenthesis as percent of total product formation. The following six products were tentatively identified (GLC-CI-MS, isobutane) by their "quasi" molecular ions or ion clusters (Br = 79) which were > 85% relative intensity in all cases: 3, 460: 9, 281: 10, 253: 12, 417: 13, 367: 14, 392. All other compounds were identified by spectral and cochromatographic comparisons with authentic standards.

intersystem crossing to the triplet and reaction from that excited state.

The variety of chromophores and possible reactive sites in **1** make further study of its photochemistry necessary to determine in more detail the excited states from which various products originate and the fate of products arising from the acidic component.

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References and Notes

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