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Photodegradation of O,O-Diethyl-S(3,4-dihydro-4-oxobenzo[d][1,2,3]triazin-3-yl-methyl)phosphorodithioate (Azinphos-ethyl)

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The photodegradation of Azinphos-ethyl (**1**) in chloroform and methanol solution has been studied. 3,4-Dihydro-3-methyl-4-oxobenzo[d][1,2,3]triazine (**3**), 3,4-dihydro-4-oxo-benzo[d]-[1,2,3]triazine (**5**), O,O-diethyl-O(3-methylbenzo[d][1,2,3]triazine-4-yl)phosphate (**8**), N-methyl-anthranilic acid (**11**) (in methanol: methyl ester **12**), and sulfur have been isolated and characterized as photoproducts. The decay mechanism is discussed.

Introduction

In the course of our investigations on the photochemistry of pesticides, we have recently [1, 3] cast our attention on photolysis studies of heterocyclic pesticides carrying phosphate and thiophosphate rests. Organophosphates and -thiophosphates possess high insecticidal activity and are widely applied [4–6]. Photochemical studies on these compounds offer valuable knowledge about the role displayed by the solar UV irradiation on insolation (exposure to sunlight) of these pesticides.

In the present investigation, we have studied the photolysis of O,O-diethyl-S(3,4-dihydro-4-oxobenzo[d][1,2,3]triazin-3-yl-methyl)phosphorodithioate (azinphos-ethyl) (**1**), marketed under the names Bayer 16259, ENT 22014, Gusathion A®, Ethyl Gusathion® [7]. Azinphos-ethyl (**1**) and its methyl ester analogue azinphos-methyl have found broad application as insecticides in the widest sense [4, 7].

As early as 1959, the first qualitative investigations have been undertaken to study the influence of light and breakdown of azinphos [8], and later on, the effect of light, temperature, and pH has been investigated on the degradation of azinphos-methyl [9]. The latter study has been carried out in micro scale on ¹⁴C-labelled azinphos-methyl in water and on glass surfaces to form CHCl₃- and water soluble breakdown products. Some of the compounds identified

have been benzazimide, anthranilic acid, N-methylbenzazimide sulfide, and N-methylbenzazimide. Traces of mercaptomethylbenzazimide and of the oxygen analogue of azinphos-methyl have been also claimed to be found. This easy photodegradation, even in sunlight, of azinphos-methyl, a kind of 3-alkyl substituted 4-oxo-benzo[d][1,2,3]triazine is surprising, after it is known from several photochemical investigations that 3-alkyl-4-oxobenzo[d]-[1,2,3]triazines are in general stable to irradiation with UV light, while the 3-aryl analogues lose nitrogen to form 1-aryl-benzazetionones and subsequent products [10–12].

Results and Discussions

In our present systematic study, we have irradiated an 1% chloroform solution of azinphos-ethyl **1** for 200 h in a Pyrex photoreactor using a high pressure mercury lamp ($\lambda > 313$ nm). The photolyate was separated by chromatography on silica gel whereby besides elemental sulfur, four crystalline products were isolated, namely: 3,4-dihydro-3-methyl-4-oxobenzo[d][1,2,3]triazine (**3**) (3-methylbenzazimide), 3,4-dihydro-4-oxobenzo[d][1,2,3]triazine (**5**) (benzazimide), N-methyl anthranilic acid (**11**), and O,O-diethyl-O(3-methylbenzo[d][1,2,3]triazol-4-yl)phosphate (**8**). Thus, with respect to **3** and **5** we were able to isolate products identical with those of Liang and Lichtenstein [9], but with **8** and **11** we have got different breakdown products.

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Scheme 1.

The first three compounds **3**, **5**, and **11** were characterized by comparison with authentic samples (*cf.* experimental part). The fourth product, **8**, which is unequivocally different from an "oxygen analogue of azinphos [9]" is assigned to be phosphate **8** basing upon the following evidences: (a) Elemental analysis and MS agree with formula C₁₂H₁₈N₃O₄P (299.2). (b) The IR spectrum does not exhibit any carbonyl band in the 1650–1800 cm⁻¹ region (for comparison, **1**: $\nu_{C=O}$ = 1690 cm⁻¹); however, characteristic absorption bands are observed at 3450 (NH) and 1625 (ring vibration), as well as at 1280 ($\rightarrow$ P=O, free) and at 1030 cm⁻¹ ($\rightarrow$ P-O-C₂H₅) [13]. (c) The ¹H NMR spectrum of **8** discloses signals at δ = 1.42 (t, P(O) O-CH₂-CH₃), 4.28 (q, P(O) O-CH₂-CH₃), each with J = 8.5 Hz, while a methyl group appears as singlet at 3.06 ppm. Moreover, a NH proton is found at δ = 13.35 ppm (exchangeable with D₂O). (d) The ³¹P NMR spectrum shows a resonance signal at δ =

–4.91 ppm, which lends as additional support to the assigned phosphate constitution and rules out alternative phosphonate constitutions [14].

Upon changing the solvent from chloroform to methanol (with improving the yield) the photodegradation of **1** results in the formation of elemental sulfur, **3**, **5**, **8**, and methyl N-methylantranilate **12**.

The formation of the benzo[d][1,2,3]triazinones **3** and **5** during the photoreaction of **1** in chloroform or methanol can be rationalized by a pathway "A" (*cf.* Scheme 1) involving homolytic cleavage of the side chain, either of the N-CH₂- or of the -CH₂-S bond; the triazinone radicals formed by this way, **2** and/or **4** furnish products **3** and **5** *via* hydrogen abstraction; **3** and **5** can be considered to be stable against further UV irradiation according to literature reports [10, 11].

The formation of the phosphate **8** can be explained by path "B" in terms of initial desulfuration leading

to intermediate **6**. Photochemical extrusion of sulfur from **1** meets a well documented analogy in the photolysis of various organic sulfides (and sulf-oxides) leading, *e.g.* to the corresponding alkanes [15]; similarly, 2-methylmercapto-1,3,5-triazine herbicides ("triatynes") are known to be cleaved homolytically at the C–S bond [16]. Intramolecular rearrangement of **6** followed by or concurrent with its oxidation, then gives product **8**. Photooxidations of the type $\text{>P=S} \rightarrow \text{>P=O}$ are well documented for thiophosphates during insolation [4] or photo-reactions [1, 5]. An alternative pathway for the production of **8** involving initial formation of **3** and **5** along with subsequent attack of trimethyl phosphorodithioate to the 4-carbonyl group seems to be unlikely for several reasons.

Photogeneration of **11** or **12** (dependent of the solvent used) can be reasonably interpreted by path "C" which is in accordance with the mechanisms previously reported by Ege, and by Burgess and Milne [10–12].

Experimental

Melting points: uncorrected. – Elemental analyses: Mikroanalytisches Laboratorium Dr. F. Pascher, Bonn. – IR spectra: Perkin-Elmer 157-G. – ^1H NMR spectra: Bruker WH-90 (δ -values, TMS as internal standard). – ^{31}P NMR: Varian CFT-20 (*vs.* 85% H_3PO_4). – MS: MS-50 of Kratos (A. E. I.). – T. L. C. system: toluene-ethylacetate-ethanol (6:3:1. v/v/v). The photolyses were carried out in a Pyrex photoreactor equipped with a mercury high pressure lamp (Philips HPK 125).

Azinphos ethyl (**1**) was supplied by the Bayer AG, D-5090 Leverkusen.

Photolysis of *azinphos ethyl* (**1**)

a) Irradiation in chloroform

A solution of *azinphos ethyl* (**1**, 3.4 g, 10 mmol) in chloroform (350 ml) was irradiated for 200 h. Then, the reaction mixture was evaporated *in vacuo*. The residue obtained (yellow oil) was chromatographed on silica gel; system: toluene, then with toluene containing increasing amounts of ethyl acetate.

Fraction (100% toluene) gave 780 mg (23%) of unchanged **1**, m.p. 52–54 °C (petroleum ether 60–80; lit. m.p. 52–54 °C [17]); MS: m/z 346 (M^+).

Fraction (9:1, 500 ml) gave 272 mg (17%) of a yellow product; recrystallization from cyclohexane

furnished yellow leaflets of m.p. 122 °C, and identified as 3,4-dihydro-3-methyl-4-oxo-benzo[d]-[1,2,3]triazine (**3**) (lit. m.p. 123–124 °C [18]); MS: m/z 161 (M^+).

Fraction (9:1, further 800 ml) provided another yellow crysalline material: 255 mg (8%); recrystallized from acetone to give pale yellow crystals of m.p. 162 °C, and identified as the phosphate **8**.

Analysis for $\text{C}_{12}\text{H}_{18}\text{N}_3\text{O}_4\text{P}$ (299.2)

Calcd	C 48.81	H 5.76	N 13.82	P 9.99,
Found	C 48.16	H 6.06	N 14.04	P 10.35.

MS: m/z 299 (M^+).

IR (KBr): 3450 (NH), 1625, 1600, 1570 ($\text{C}=\text{C}$, $\text{C}=\text{N}$ ring vibrations), 1280 ($\text{P}=\text{O}$, free), 1030 cm^{-1} ($-\text{P}-\text{O}-\text{C}_2\text{H}_5$).

^1H NMR ($\text{DMSO}-d_6$): δ 1.42 (dt, POCH_2CH_3 , $J = 8.5$ Hz, $J = 0.8$ Hz), 3.06 (s, $\text{N}-\text{CH}_3$), 4.28 (dq, POCH_2CH_3 , $J = 8.5$ Hz, $J = 10.2$ Hz), 7.15–7.78 (m, H_{ar}), 13.35 (s, NH, exchangeable with D_2O).

^{31}P NMR ($\text{DMSO}-d_6/\text{CDCl}_3$): δ –4.91 ppm.

Fraction (8:2, 500 ml) contained 120 mg (37.5%) of yellow crystals of m.p. 119–122 °C, identified as sulfur (T. L. C., MS).

Fraction (up to 6:4) gave 398 mg (28%) of a yellow material, recrystallized from ethanol/ether (4:1, v/v) of m.p. 210–212 °C, shown to be 3,4-dihydrobenzol[d][1,2,3]triazine-4-one (**5**), mixed m.p. with authentic probe (lit. m.p. 210 °C [19]); MS: m/z 147 (M^+).

Fraction (5:5, 1 l) afforded a colorless crystalline product 74 mg (5%) which proved to be N-methyl anthranilic acid (**11**) of m.p. 170 °C; lit. m.p. 168–170 °C [20]. Characterization by comparison with an authentic specimen.

b) Irradiation in methanol

A solution of *azinphos ethyl* (**1**, 3.4 g, 10 mmol) in methanol (340 ml) was irradiated for 200 h under the conditions described above a). Working up the photolysate in the usual manner resulted in isolation and identification of methyl N-methylantranilate **12** (114 mg, 7%), unchanged *azinphos ethyl* **1** (510 mg, 15%), 3,4-dihydro-3-methyl-4-oxo-benzo[d]-[1,2,3]triazine (**3**) (352 mg, 22%), the phosphate **8** (320 mg, 11%), sulfur (125 mg, 38%), and 3,4-dihydro-4-oxobenzo[d][1,2,3]triazine (**5**) (472 mg, 33%), respectively.

c) Irradiation of **3** and/or **5** in methanol

3,4-Dihydro-3-methyl-4-oxobenzo[d][1,2,3]triazine (**3**) (1 g, 6 mmol) and/or 3,4-dihydro-4-oxo-

benzo[d][1,2,3]triazine (**5**) (1 g, 6 mmol) in methanol (100 ml) were irradiated like under a) for 150 h. T.L.C. analysis did not reveal any trace of products formed, and only starting material was recovered in quantitative yield.

During the working up of the reaction mixture obtained from the photolysis of **1** in chloroform or

methanol, minor constituents and traces could also be isolated, but an identification failed.

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