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FUNGICIDES AND PHOTOCHEMISTRY
PHOTODEGRADATION OF THE DICARBOXIMIDE FUNGICIDE PROCYMIDONE

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ABSTRACT

The photoreactivity of the dicarboximide fungicide procymidone (1) (3-(3,5-dichlorophenyl)-1,5-dimethyl-3-azabicyclo[3.1.0]hexane-2,4-dione) on plant surfaces was studied by irradiation experiments in different organic solvents simulating the plant cuticle environment. Photodegradation ($\lambda > 280$ nm) increased in the order isopropanol, cyclohexane, cyclohexene. In the presence of isopropanol or cyclohexane, mainly photodehalogenation reactions were observed, which, to a minor extent, competed with substitutions by solvent molecules. In the presence of cyclohexene, however, substitution of a phenyl-Cl by the the solvent was strongly preferred and the monodehalogenated procymidone was only found in low percentages.

KEY WORDS

Dicarboximide fungicides, procymidone, photochemistry, photoproducts

INTRODUCTION

Procymidone (Sumisclex[R]) is one of the three dicarboximide fungicides commonly used for the protection of fruits and vegetables, especially to prevent grey mold in viniculture. After spray application, procymidone as a contact poison with low systemic activity [1] mainly remains on plant surfaces, slightly pentrates into the plant cuticle layers, and is exposed to sunlight. Since procymidone, and the two other dicarboximides vinclozolin and iprodione [2,3], also absorb UV-light up to 310 nm (Figure 1) photochemical breakdown caused by sunlight irradiations on fruits and leaves can be presumed.

So far there are only three papers on the photochemical reactivity of procymidone available in the literature [4-6]. Schwack et al. [4] reported that photodegradation of procymidone in isopropanol mainly occured by dehalogenation yielding the monodechloro derivate 2 as the main photoproduct. Nutahara et al. [5] proposed an accelerating effect of oleic acid on the photodecomposition of some pesticides including procymidone. This fungicide was mainly degraded by hydrolysis in destilled, river and sea waters while sunlight had a limited effect on photodecomposition as was pointed out by Mikami and associates [6].

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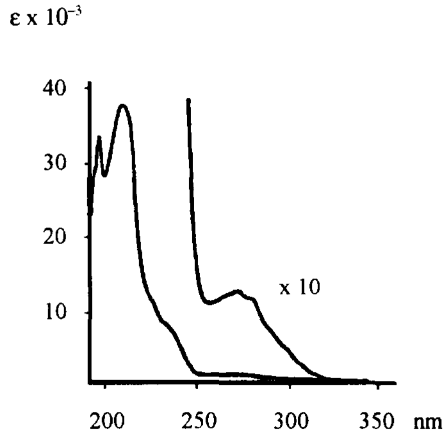

Figure 1: UV-absorption spectrum of procymidone (ethanol)

Continuing our work to study possible photoreactions of the dicarboximide fungicide group in the plant cuticle environment [3, 10] model reactions of procymidone in the presence of cyclohexene, cyclohexane and isopropanol as our proven model systems [4, 7, 8, 9] were performed.

EXPERIMENTAL SECTION

Materials. Procymidone was isolated by extraction of Sumisclex^R (Sumitomo Chem. Co., J) with CH_2Cl_2 and was further purified by repeated crystallisation from n-hexane. The solvents used for photolysis were of analytical grade (Merck, Darmstadt, FRG); cyclohexane and cyclohexene were rectified over P_2O_5.

Photolysis equipment and photolysis procedure. For kinetic experiments procymidone solutions (50 mg/50 ml) were irradiated in a quartz tube (120 mm x 28 mm) using a 150 W high pressure mercury lamp (TQ 150, Hanau Quarzlampen GmbH, FRG) equipped with a quartz glass watercooling jacket. The UV light was filtered by glass filters WG 295 ($\lambda > 280$ nm), WG 305 ($\lambda > 295$ nm), WG 320 ($\lambda > 300$ nm) (Schott Glaswerke, Mainz, FRG). For preparative product isolation procymidone was irradiated at concentrations of 150 mg/50 ml.

High performance liquid chromatography (hplc). Procymidone degradation rates were determined on a Knauer (Bad Homburg, FRG) hplc system equipped with a variable wavelength detector and a GAT (Bremerhaven, FRG) autosampler. For purity checkings and spectrum information a Shimadzu (Kyoto, J) photo diode array detector (SPD M6a) was adapted to the above mentioned system. A Nucleosil (Knauer) R 100, 5µm, C18 reversed phase column (4,6 i.d x 250 mm) was used and eluted with methanol/water (70/30) at a flow rate of 1 ml/min. Quantification was performed by external standard mode. 10 µl of the reaction mixtures were injected.

NMR-Spectroscopy. 250 MHz-^{1}H-nmr-spectroscopy was carried out with a Bruker Cryospec WM 250 (Karlsruhe, FRG), 400 MHz-^{1}H-nmr-spectroscopy and 100 MHz-^{13}C-nmr-spectroscopy with a Bruker WM 400 in $CDCl_3$ solution. Spectra are reported in ppm downfield from TMS as internal standard.

IR-spectroscopy was performed on a ir spectrometer model PE 882 (Perkin Elmer, Überlingen, FRG) using KBr pellets, CCl_4 as solvent.

High resolution mass spectrometry (hrms) was carried out on a Finnigan MAT 90 (Bremen, FRG);
r (resolution) = 60000.

Gaschromatography/Mass spectrometry (gc/ms) was carried out on a GC 6000 Vega Series (Carlo Erba, Mainz, FRG), equipped with a fused silica quartz capillary column (10 m, stat. phase: OV1), coupled to a Finnigan MAT, model ITD 800 (Bremen, FRG).
Temperature programm: 100°C (2 min) - 10°C/min - 280°C (5 min).

Product isolation. The reaction mixtures were evaporated to dryness under vacuum. The residue was redissolved in 2 ml of CH_2Cl_2 and chromatographed on silica gel (LOBAR B column filled with LiChroprep Si 60; Merck, Darmstadt, FRG) with petroleum ether/diethylether (70/30) (flow-rate: 8 ml/min) as eluent. For purity checkings 20 µl of these fractions were diluted with 200 µl methanol and subjected to analytical hplc.

Elemental analysis was performed with an Carlo Erba EA Model 1106 (Milano, I).

3-(3-Chlorophenyl)-1,5-dimethyl-3-azabicyclo-[3.1.0]hexane-2,4-dione (2); colourless crystals

ir (KBr): 3470, 3080, 2980, 2940, 2880, 1780, 1700, 1590, 1580, 1480, 1440, 1430, 1390, 1380, 1340, 1150, 1120, 1090, 1040 cm^{-1}.

ms (70 eV): m/z = 249 (51 %, M^+, Cl_1), 215 (10 %), 96 (100 %), 68 (37 %), 67 (41%), 53 (20 %), 41 (20 %).

^{1}H-nmr (250 MHz, $CDCl_3$): δ = 7,25 - 7,37 (3 H, m, phenyl-H); 7,10 - 7,17 (1 H, m, phenyl-H); 1,75 (1 H, d, J = 4,6 Hz); 1,49 (6 H, s, 2x CH_3); 1,17 (1 H, d, J = 4,6 Hz).

$C_{13}H_{12}NO_2Cl$: C: found 62,5 % (calculated 62,5 %); H: found 4,86 % (calculated 4,82 %); N: found 5,63 % (calculated 5,62 %); Cl: found 14,2 % (calculated 14,1 %).

3-Phenyl-1,5-dimethyl-3-azabicyclo-[3.1.0]hexane-2,4-dione (3)

ms (70 eV): m/z = 215 (100 %, M^+), 187 (5,0 %), 144 (5,8%), 96 (37,5 %), 68 (11,7 %), 67 (17,2 %), 53 (8,7 %).

^{1}H-nmr (250 MHz, $CDCl_3$): δ = 7,23 - 7,48 (5 H, m, phenyl-H); 1,75 (1 H, d, J = 4,6 Hz); 1,49 (6 H, s, 2x CH_3); 1,17 (1 H, d, J = 4,6 Hz).

$C_{13}H_{13}NO_2$: C: found 72,4 % (calculated 72,5 %); H: found 6,07 % (calculated 6,05); N: found 6,42 % (calculated 6,51 %).

3-[3-Chloro-5-(1-hydroxy-1-methylethyl)-phenyl]-1,5-dimethyl-3-azabicyclo-[3.1.0]hexane-2,4-dione (4)

ir (KBr): 3600, 3470, 3080, 2980, 2940, 2880, 1780, 1700, 1590, 1580, 1440, 1390, 1380, 1250, 1150, 1120, 1090, 1040 cm^{-1}.

ms (70 eV): m/z = 307 (10 %, M^+, Cl_1), 292 (100 %, Cl_1), 289 (16 %, Cl_1), 250 (10 %, Cl_1), 182 (10 %), 179 (18 %), 141 (18 %), 109 (35 %), 96 (23 %), 67 (38 %), 55 (33%).

^{1}H-nmr (400 MHz, $CDCl_3$): δ = 7,44 - 7,70 (1 H, t, phenyl-H, J_{meta} = 1,8 Hz); 7,26 (1 H, t, phenyl-H, J_{meta} = 1,8 Hz); 7,14 (1 H, t, phenyl-H, J_{meta} = 1,8 Hz); 1,94 (1 H, s, -OH, exchangeable with D_2O); 1,75 (1 H, d, J = 4,6 Hz); 1,55 (6 H, s, -C($\underline{CH_3}$)$_2$OH); 1,49 (6 H, s, 2x CH_3); 1,17 (1 H, d, J = 4,6 Hz).

$C_{16}H_{18}NO_3Cl$ (hrms): found 307,0976 (calculated 307,0975)

3-[3-(1-Hydroxy-1-methylethyl)-phenyl]-1,5-dimethyl-3-azabicyclo-[3.1.0]hexane-2,4-dione (5)

gc/ms: m/z = 273 (5 %, M^+), 258 (88 %), 216 (40 %), 188 (13 %), 96 (17 %), 67 (50 %), 53 (23 %), 43 (100 %).

3-(3-Chloro-4-cyclohexylphenyl)-1,5-dimethyl-3-azabicyclo-[3.1.0]hexane-2,4-dione (6); colourless crystals

ir (CCl_4): 3040, 2930, 2860, 1720, 1495, 1450, 1375, 1115 cm^{-1}.

ms (70 eV): m/z = 331 (100 %, M^+, Cl_1), 297 (21 %), 295 (15 %), 288 (24 %, Cl_1), 275 (19 %, Cl_1), 262 (26 %, Cl_1), 166 (10 %, Cl_1), 149 (19 %), 96 (25 %), 67 (37 %).

^{1}H-nmr (400 MHz, $CDCl_3$): δ = 7,31 (1 H, d, phenyl-H, J_{ortho} = 6 Hz); 7,24 (1 H, d, phenyl-H, J_{meta} = 1,7 Hz); 7,10 (1 H, dd, phenyl-H, J_{ortho} = 6 Hz, J_{meta} = 1,7 Hz); 1,75 (1 H, d, J = 4,6 Hz); 1,49 (6 H, s, 2x CH_3); 1,17 (1 H, d, J = 4,6 Hz); 1,15 - 1,90 (11 H, m, cyclohexyl-H).

$C_{19}H_{22}NO_2Cl$ (hrms): found 331,1321 (calculated 331,1339)

3-(3-Chloro-5-cyclohexenylphenyl)-1,5-dimethyl-3-azabicyclo-[3.1.0]hexane-2,4-dione (7/8)

gc/ms: m/z = 329 (100 %, M^+, Cl_1), 294 (44 %), 96 (30 %), 81 (42 %), 79 (42 %), 67 (93 %), 53 (49 %), 41 (88 %), 39 (91 %).

^{1}H-nmr (250 MHz, $CDCl_3$): δ = 7,12 (1H, t, phenyl-H, J_{meta} = 1,8 Hz); 7,08 (1 H, t, phenyl-H, J_{meta} = 1,8 Hz); 6,95 (1 H, t, phenyl-H, J_{meta} = 1,8 Hz); 1,75 (1 H, d, J = 4,6 Hz); 1,49 (6 H, s, 2x CH_3); 1,17 (1 H, d, J = 4,6 Hz).

RESULTS AND DISCUSSION

On UV-irradiation (λ > 280 nm) photodegradation of procymidone (1) was much more efficient in the isopropanol solution (61 % after 5 h) than in cyclohexane or cyclohexene, where degradation was only 10 % and 6 %, respectively (Figure 2). Comparative irradiations using different UV-filters increasingly cutting off the short wavelength UVB-spectrum of the light source showed the expected decreases in photodecomposition (Figure 2).

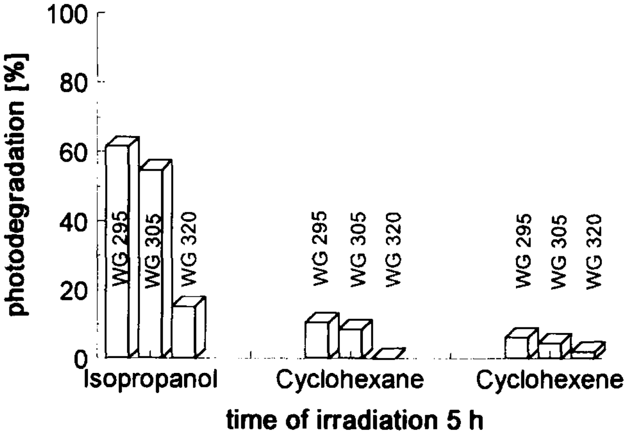

Figure 2: Photodegradation of procymidone in isopropanol, cyclohexane and cyclohexene using different UV-filters

After 5 hours of irradiation in the presence of isopropanol 72 %, 6 %, and 12 % of the degraded procymidone were converted to the photoproducts 2, 3, and 4, respectively (Figure 3), when 5 was detected as a trace compound which could not be quantified individually. Thus, the main reactions consist of successive dehalogenations of the parent compound leading to the photoproducts 2 and 3. To a minor extend substitution of a phenyl-Cl by a hydroxyisopropyl moiety occured yielding 4 and, by following dechlorination, 5. The obtained photoproducts in isopropanol may be derived as shown in figure 3. Homolytic or charge transfer induced cleavage of a C-Cl bond of 1 yields the radical 1a which offers two possible ways of stabilization reactions. More likely is the saturation by hydrogen transfer from the solvent yielding 2 as the monodechloro product of 1.

Alternatively 1a can combine with a hydroxyisopropyl radical B, intermediately resulting from the above mentioned hydrogen transfer, leading to 4 as a substitution product to a minor extend. Following the same mechanisms, both 2 and 4 were further dehalogenated yielding 3 and 5.

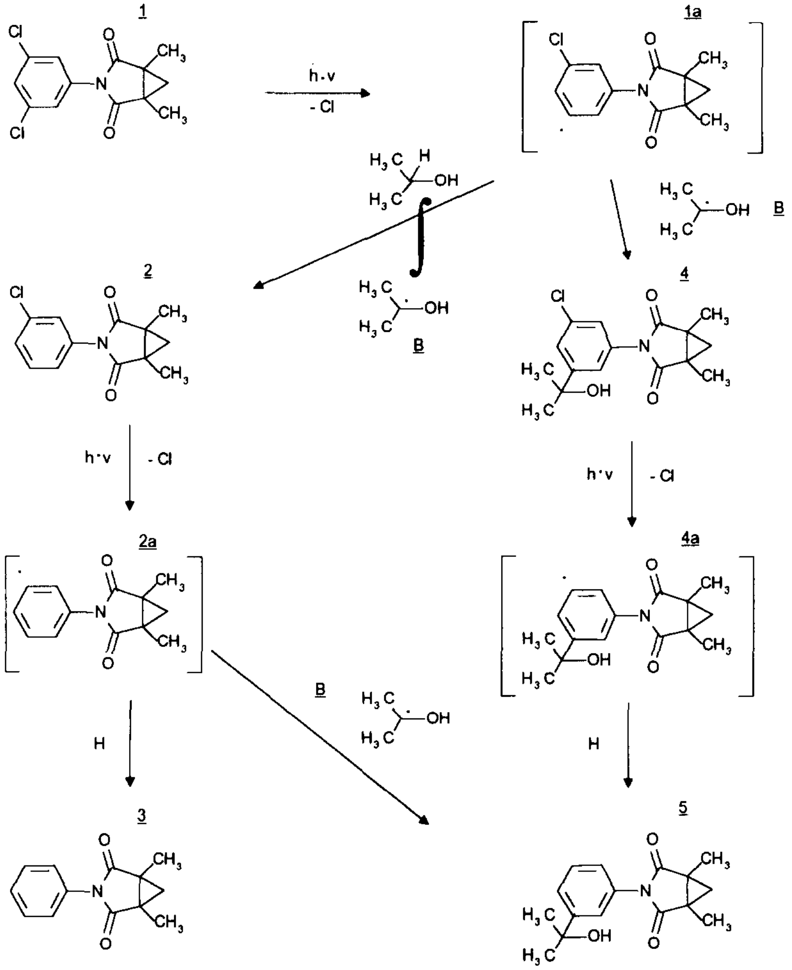

Figure 3: Photodegradation pathway of procymidone dissolved in isopropanol

However, 5 may also be seen as a combination product of the subsequently formed radical 2a and an intermediate hydroxyisopropyl radical B. The dehalogenation products 2 and 3 have also been synthesized individually to obtain pure reference materials [10].

On irradiation of procymidone dissolved in cyclohexane, photodechlorination was also the dominant pathway yielding 2 with an amount of 85 % based on the degraded procymidone (after 5 h), but 3 was never found even after 20 hours of irradiation. Additionally, 6 was isolated as a surprising photoaddition product at a 5 % level after 5 hours of irradiation. Here, the solvent addition took place at the C-4 position of the phenyl moiety (Figure 4).

The proton nmr-signals clearly indicate an ABC-pattern with coupling constants for a 1,2,4-substitution instead of the 1,3,5-trisubstitution of the parent compound or the solvent addition product 4 in figure 3. Because the isomerisation of the radical 1a (Figure 3) including a 1,2H-shift seems unlikely a substitution of the photodehalogenated product 2 by free cyclohexyl radicals is proposed. Such a reaction is strongly ortho/para directed and the ortho position C-4 is preferred, for the ortho C-2 and the para C-6 are sterically hindered by the imide group.

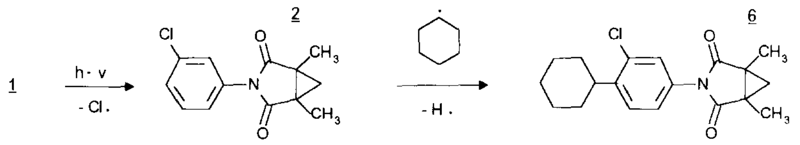

Figure 4: Proposed photoaddition pathway of procymidone to the solvent cyclohexane forming 6

When procymidone was irradiated in cyclohexene substitution of a phenyl-Cl by solvent molecules leading to the cyclohexenyl-substituted photoadditon products 7 and 8 (Figure 5) was observed mainly. The cyclohexyl-substituted photoproduct 9 as was also found on comparative irradiations of vinclozolin [3, 10] and iprodione [3, 10], could not be isolated from the irradiation mixture as a pure compound, but was undoubtedly found during GC/MS analyses by its molecular ion at m/z 331. In course of the good scavenging properties of olefinic environments for short-living free phenyl radicals [3, 10] the singly dehalogenated product 2 only was found with 10 % of the degraded procymidone after 5 hours of irradiation in the presence of cyclohexene.

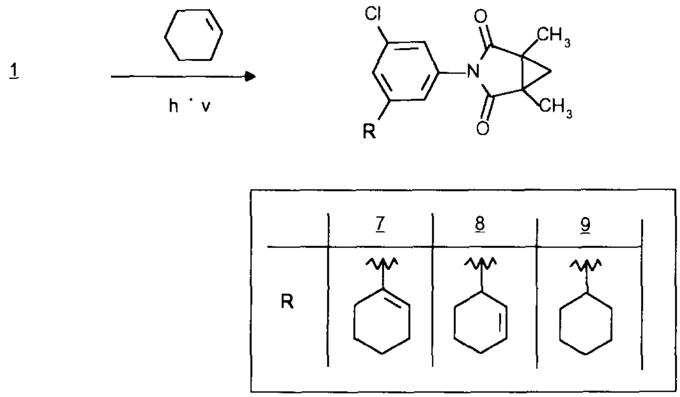

Figure 5: Photodegradation of procymidone in the presence of cyclohexene

Alicyclic imides are known to undergo photoaddition reactions with olefins mainly forming oxetanes beside of photoreductions leading to carbinols [7, 12]. However, corresponding photoproducts could not be detected after irradiation of procymidone in the presence of cyclohexene. The comparative low photodegradation may be a further indication that these types of reactions did not occur.

CONCLUSIONS

The present results show the definite potential of procymidone to undergo photoinduced reactions in the presence of various chemical environments especially in the presence of the secondary alcohol. Formation of the photosubstitution products containing the solvent moiety indicates the possible formation of bound residues in plant cuticles where solvent molecules are replaced by constituents of plant waxes and the cutin polymer in such reaction pathways. Experiments in model solvents are the first step to investigate the photochemistry of procymidone on plant surfaces [10, 11]. A detailed report of the results obtained on further cuticle model systems and on fruit surfaces will be the subject of a forthcoming publication.

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REFERENCES

[1] W. Perkow (1983/1988) Wirksubstanzen der Pflanzenschutz- und Schädlingsbekämpfungsmittel, Verlag Paul Parey, Berlin, Hamburg

[2] F. Matsumura, C. R. K. Murti, Biodegradation of Pesticides, p. 81, Plenum Press, New York, London (1982)

[3] B. Bourgeois, Ph. D. Thesis, University of Karlsruhe, FRG (1991)

[4] W. Schwack, B. Bourgeois, Z. Lebensm. Unters. Forsch. 188, 346-347 (1989)

[5] M. Nutahara, T. Murai, Nippon Noyako Gakkaishi 9, 667-674 (1984)

[6] N. Mikami, K. Imanishi, H. Yamada, J. Miyamoto, J. Pesticide Sci. 9, 223-228 (1984)

[7] W. Schwack, Z. Lebensm. Unters. Forsch. 190, 420-424 (1990)

[8] W. Schwack, Toxicol. Environ. Chem. 14, 63-72 (1987)

[9] W. Schwack, H. Flößer-Müller, Chemosphere 21, 905-912 (1990)

[10] F.Walker, Ph. D. Thesis, University of Karlsruhe, FRG (1994)

[11] W. Armbruster, F. Walker, W. Schwack, Eighth IUPAC Int. Congr. Pestic. Chem. (1994), Book of Abstracts, vol. I, p. 337

[12] W. Schwack, Tetrahedron Lett. 28, 1869-1872 (1987)