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Photochemical Conversion of a Dicofol Impurity, α-Chloro-DDT, to DDE

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Dicofol or Kelthane® is a non-systemic acaricide used extensively for the control of mites on a wide range of crops. Structurally it can be considered as the α-hydroxy analog of DDT [1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane]. Prior to its restricted use, DDT was the major source of environmental DDE formed primarily by photochemical dehydrochlorination (Plimmer et al. 1970; Crosby and Moilanen 1977). DDT is also a contaminant in some preparations of technical dicofol, appearing in amounts up to 0.6% (Camoni et al. 1983). Another dicofol impurity, α-chloro-DDT (Cl-DDT), occurs at levels as high as 10% (Anonymous 1985). Continuing high levels of environmental DDE, e.g. as monitored in birds, may originate from the extensive use of technical dicofol and possibly from its Cl-DDT impurity (Hunt et al. 1986; Risebrough et al. 1986).

Exposure of dicofol as a thin film to direct sunlight yields 4,4'-dichlorobenzophenone (DCBP) as the only photoproduct whereas solution photolysis in a quartz vessel with a mercury vapor lamp produces not only DCBP but also dechlorodicofol (DCD) and a variety of solvent adducts and hydrolysis products (Vaidyanathaswamy et al. 1981). DCBP is also the only photoproduct detected on dicofol-treated almond hull meal and apple pomace exposed to ultraviolet light (Archer 1970, 1974). The present investigation examines the photochemical reactions of Cl-DDT and dicofol with particular attention to environmental sources of DDE and other DDT-related contaminants (Figure 1).

MATERIALS AND METHODS

Thin-layer chromatography (TLC) used silica gel 60 F-254 chromatoplates (20 X 20 cm; 0.25 mm for analysis and 0.5 mm for purification). Gas liquid chromatography (GLC) used a Hewlett Packard 5830A gas chromatograph equipped with a ^{63}Ni electron capture detector and a 2% OV-225 or 3% OV-101 glass column (1 m) operated isothermally at 175° or 190°C, respectively (30 ml N_2/-

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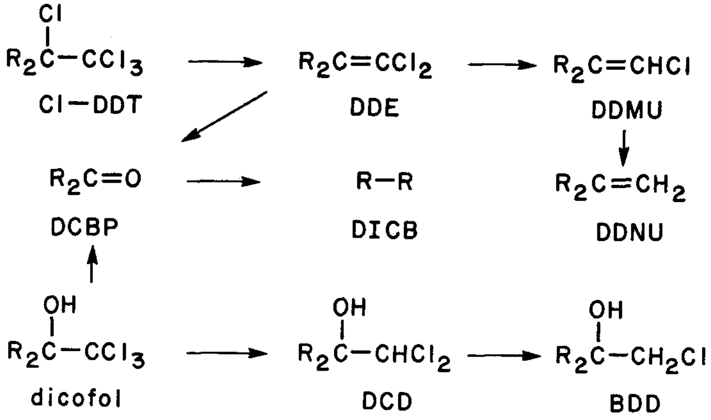

Figure 1. Structures and designations of the α-chloro-DDT and dicofol photoproducts considered. R = p-chlorophenyl

min). GLC-chemical ionization (CI)-mass spectrometry (MS) (230 eV) utilized a Hewlett Packard 5985B instrument equipped with a methyl silicone high performance capillary column (10 m) operated with temperature programming (120-240°C, 20°C/min, 1 ml He carrier/min) and methane (0.8 Torr) as the ionization gas. Samples were also introduced directly into the source of the mass spectrometer for both electron impact (EI)-MS (70 eV) and CI-MS. Nuclear magnetic resonance (NMR) spectroscopy utilized a Bruker WM 300 spectrometer operated at 300 MHz (^1H) or 75.5 MHz (^{13}C) for samples in 5-mm tubes, using $CDCl_3$ as the solvent and internal lock and standard (^1H 7.26 ppm; ^{13}C 77.0 ppm). For integration of peaks in ^1H NMR, 30° flip angle pulses were used, with 4 s delays between pulses. Data were acquired over 16 K data points, and Fourier transformed using 0.2 s (^1H) or 5 s (^{13}C) exponential multiplication.

Cl-DDT and [^{14}C]Cl-DDT were synthesized by photochlorination of DDT (Grummitt et al. 1945) and [^{14}C]DDT. Thus, a solution of [^{14}C-phenyl]DDT (26 mg, 1.5 mCi/mmol) and PCl_3 (4 µl) in CCl_4 (50 ml) with bubbling Cl_2 gas was refluxed for 1 h under a 60 watt incandescent lamp, and then washed with aqueous bicarbonate, dried ($MgSO_4$), filtered, the solvent evaporated, and the residue purified by TLC (hexane/ether 20:1) resulting in complete separation of Cl-DDT (R_f 0.9) (30 mg) from any residual DDT (R_f 0.8).

Unlabeled dicofol was purified by TLC (hexane/ether 5:1, 50 mg technical dicofol/plate) to completely remove DDT, Cl-DDT, DDE and other impurities. [^{14}C]Dicofol was prepared (Bergmann and Kaluszyner 1958) by treating [^{14}C]Cl-DDT as above with silver acetate (15 mg) in glacial acetic acid (15 ml) under reflux for 3 h, pouring the mixture into ice water, extracting into hexane, washing the hexane layer with aqueous bicarbonate, drying

($MgSO_4$), filtration, and solvent evaporation to give dicofol acetate. Hydrolysis of this acetate involved treatment for 3 h in a refluxing solution of water (4.5 ml), conc. H_2SO_4 (0.6 ml) and glacial acetic acid (15 ml) with workup as for dicofol acetate and TLC of the residue (hexane/ether 5:1) yielding pure [^{14}C]dicofol (14 mg) and recovered [^{14}C]Cl-DDT (15 mg).

DDMU was prepared by refluxing a solution of the corresponding dichloroethane (100 mg) and NaOH (80 mg) in ethanol (20 ml) for 1 min, followed by addition of water, extraction with hexane, drying the hexane layer ($MgSO_4$), filtration and evaporation to yield the desired product (67 mg) as a pale yellow oil. [^{14}C]-DCBP was obtained by treating [^{14}C]dicofol (1 mg) with KOH (10 mg) in ethanol (5 ml) followed by product isolation (~1 mg) as described for DDMU.

Cl-DDT (50 mM), DDE (5 mM), dicofol (50 mM), and DCBP (8 mM), as hexane solutions in Pyrex vessels, were individually irradiated at λ >290 nm in a Rayonette reactor (The Southern New England Ultraviolet Co., Middletown, CT) equipped with 16 RPR 3000 lamps. Photolysates were inspected by ^{1}H NMR, GLC-CI-MS and TLC at multiple intervals. Product yields were determined by integration of ^{1}H NMR signals and by comparisons of GLC peak areas with standards. [^{14}C]Cl-DDT, [^{14}C]dicofol and [^{14}C]DCBP were also subjected to photolysis on plant foliage exposed to direct sunlight for 48 h. Individual leaves of 3-week old bean plants (30 cm height) were treated with each labeled compound (3 µg in 10 µl hexane). The irradiated leaves were rinsed with hexane/acetone (4:1) and the recovered products were characterized by two-dimensional TLC cochromatography and quantitated by liquid scintillation counting.

RESULTS AND DISCUSSION

Chromatographic and spectroscopic properties of the starting materials and photoproducts are given in Table 1. The photoproducts from hexane irradiations are identified by isolation and NMR comparisons with standards (DDE, DDMU and DCBP), isolation and NMR and MS (DICB, DCD and BDD) or direct NMR of photolysates (DDNU). Photoproduct yields from irradiation of Cl-DDT, DDE, dicofol and DCBP in hexane solution at >290 nm and of Cl-DDT and dicofol on bean leaves exposed to sunlight are shown in Table 2. The reaction sequences in Figure 1 are based on experimental observations detailed below.

Photolysis of Cl-DDT in hexane yields DDE, DCBP, DDMU and DDNU whereas on bean leaves it gives DDE and DCBP. Irradiation of DDE in hexane also yields DDMU and DDNU, as previously reported under other conditions (Plimmer et al. 1977; Crosby and Moilanen 1977), suggesting that DDE serves as an intermediate in the conversion of Cl-DDT to DDMU and DDNU. Photodechlorination of Cl-DDT occurs by loss of Cl$^\cdot$ followed by proton abstraction to form HCl (as detected in the head space with moist litmus paper). Addition of 1% triethylamine to Cl-DDT greatly enhances

Table 1. Chromatographic and Spectroscopic Data for Photolysis Products and Standards

	TLC solvents and Rfs			GLC Rt (min)[a]		^{1}H NMR chemical shifts ($CDCl_3$)		
Compound	Hexane:ether		Hexane: CH_2Cl_2 3:1	OV-101	OV-225	AB quartet		Other, δ ppm
	99:1	6:1				δ ppm	J (Hz)	
Cl-DDT[b]	0.78	0.92		13.1	8.2	7.63, 7.29	9.0	
DDE	0.78	0.92		5.2	7.9	7.32, 7.21	8.0	
DDMU	0.72	0.89		4.1	6.6	7.38, 7.25	8.0	6.59 (s,1H)
						7.28, 7.12	9.0	
DICB[c]	0.72	0.89		1.7		7.47, 7.41	9.0	
Dicofol[bd]	0.22	0.48	0.34			7.63, 7.29	9.0	3.49 (s,1H)
DBCP	0.29	0.39	0.46		6.2	7.73, 7.48	8.5	
DCD[cd]	0.18	0.38	0.21			7.44, 7.31	9.0	6.51 (s,1H) 3.21 (s,1H)
BDD[e]	0.10	0.16	0.11			7.48, 7.06	9.0	4.87 (s,2H)

[a] OV-101 column gives some decomposition of Cl-DDT to DDE whereas OV-225 gives separation with no decomposition.

[b] UV absorption (300 nm): Cl-DDT ε 4.0; dicofol ε 14.0.

[c] CI-MS, *m*/*e* (rel. intensity): DICB 223 (M+1, 100), 251 (M+29, 32); DCD 335 (M+1, 13), 317 (M+1-H_2O, 33), 265 (M+1-2Cl, 100).

[d] ^{13}C NMR: dicofol 86.7, 105.4, 127.8, 130.7, 134.6, 138.7; DCD 78.4 ($CHCl_2$ by DEPT experiment), 81.1 (COH), 127.6 and 128.6 (CH, phenyl by DEPT experiment), 134.1 and 140.3 (CCCl and CC phenyl).

[e] EI-MS, *m*/*e* (rel. intensity): BDD 300 (M^+, 0.4), 250 ($M-CH_3Cl$, 0.5), 139 ($ClC_6H_4CO^+$, 100), 111 ($ClC_6H_4^+$, 32).

Table 2. Photoproducts of α-Chloro-DDT, DDE, Dicofol and Dichlorobenzophenone (DCBP) from Irradiation in Hexane Solution at >290 nm or on Bean Leaves with Sunlight

Starting material	Product recovery[a] (%)			
	Parent	DDE	DCBP	Others
<u>Hexane, >290 nM</u>				
Cl-DDT[b]	1	68	5	DDMU (21), DDNU (4)
DDE[c]	-	75	1	DDMU (18), DDNU (4)
Dicofol[d]	69	0	1	DCD (27), DICB (1), BDD (1)
DCBP	-	0	95	DICB (1), several unidentified
<u>Bean leaf, sunlight</u>				
Cl-DDT[e]	72	12	11	origin (5)
Dicofol[e]	93	0	1	DCD (1), origin (5)

[a] Irradiation times: 20 h for Cl-DDT, DDE and dicofol in hexane; 48 h for DCBP in hexane and Cl-DDT and dicofol on bean leaves.

[b] Product recoveries after 1 h irradiation with 1% triethylamine: 17% parent, 76% DDE and 6% DCBP.

[c] Photolysis rate and product distribution not altered by 1% triethylamine.

[d] Decomposition to DCBP greatly accelerated by 1% triethylamine even in the dark.

[e] Recoveries of parent compounds: 21% Cl-DDT, 29% dicofol and 36% DCBP.

its rate of photolysis, suggesting that photodechlorination under these conditions occurs in a concerted fashion with loss of Cl^-. The photolysis rate and product distribution on irradiation of DDE are not altered by 1% triethylamine.

Photolysis of dicofol in hexane at >290 nm or on bean leaves in sunlight does not produce any detectable DDE; the major photoproducts are DCD and DCBP. DICB is detected as a minor photoproduct of both dicofol and DCBP in hexane but not of either compound on bean leaves. Photolysis of DCBP to DICB in hexane suggests that this benzophenone serves as an intermediate in the conversion of dicofol to DICB, consistent with an earlier postulation (Plimmer <u>et al</u>. 1970). DCBP is slowly converted in vapor phase photolysis to a dichlorobiphenyl isomer, which is stable to further irradiation, perhaps originating from decarboxylation of an intermediate chlorinated fluorenone which would lead to the formation of 3,3'-dichlorobiphenyl (Crosby and

Moilanen 1977). However, in the present study, ^1H NMR unambiguously identifies the photoproduct of dicofol or DCBP in hexane as exclusively 4,4'-dichlorobiphenyl, indicating direct formation from DCBP by Norrish Type I cleavage followed by loss of CO.

This study establishes that dicofol photodecomposes to DCD, DCBP and DICB but not DDE whereas its impurity Cl-DDT undergoes facile photochemical dechlorination, thereby providing a probable source for environmental DDE.

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