in the benzene–acetone solvent used for TLC purification. The addition of potassium hydroxide at a moderately rapid rate was believed to have no effect on CNP-NH_2 yield because concentrated potassium hydroxide was previously employed in the extraction procedures for isolation of CNP-NH_2 from soil bound residues (Yamada, 1976a; Tatsukawa et al., 1973). From our results, however, the rate of potassium hydroxide addition appears to be critical. Therefore, to obtain maximum yields of CNP-NH_2, the aqueous potassium hydroxide for neutralization of the amine hydrochloride salt must be added very slowly with stirring.

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Photodecomposition of a Formulated Mixed Butyl Ester of 2,4-Dichlorophenoxyacetic Acid in Aqueous and Hexane Solutions

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Aqueous and hexane solutions of a commercial chemically defined formulation containing mixed butyl esters of 2,4-dichlorophenoxyacetic acid (2,4-D) were irradiated by ultraviolet light of around 300- and 350-nm wavelengths, and the results were compared with those for hexane solutions of the pure *n*-butyl ester and for dark controls. Photodecomposition in all solvents was negligible at 350 nm (ca. 2%), but reductive dechlorination at the ortho position preferentially occurred at 300 nm independent of solvent or whether Pyrex or quartz reactor cells were utilized. Thus, the (*p*-chlorophenoxy)acetic esters, which are still quite phytotoxic, were the major products, and these could pose a threat to nontarget plants because of their volatility. In the studies dealing with commercial emulsion concentrates, a complete mass balance with respect to 2,4-D was obtained by using ^{14}C acid labeled separately in the carboxyl, methylene, and ring (uniformly labeled) positions. The existence of micelles in aqueous solutions was postulated to explain the photoproducts formed in aqueous solution. No chlorinated *p*-dibenzodioxins were found.

The photodecomposition of the esters of 2,4-dichlorophenoxyacetic acid (2,4-D) in organic solvents has been reported by various researchers (Binkley and Oakes, 1974a,b; Que Hee and Sutherland, 1973a, 1974a). The photolysis products are the corresponding esters of the dechlorinated parent acid resulting from reductive dechlorination. In contrast, hydroxylation occurs after dechlorination when aqueous solutions of the sodium salt are irradiated, thus producing chlorophenols and polymeric humic acids (Crosby and Tutass, 1966).

Since commercial-formulated emulsion concentrates of most herbicides contain surfactants, sequestering agents, and "inert" compounds in addition to the active ingredients, these other agents may also affect the photolytic pathway or the rates of decomposition.

Thus, a commercial formulation of the mixed butyl

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esters of 2,4-D was irradiated to evaluate the influence of some of the above factors.

EXPERIMENTAL SECTION

Reagents. A 1-gal can of "mixed butyl ester formulation of 2,4-D" (Chipman 2,4-D 128) was utilized. It was shown to contain 860 ± 40 mg/mL of acid equivalent 2,4-D by the method of Henshaw et al. (1975). This figure compares well with the nominal acid equivalent of 800 mg/mL. The isobutyl and normal butyl esters were present in an approximately 1:1 ratio. The formulation also contained butyl esters of (2,4,6-trichlorophenoxy)acetic acid (1%), (*p*- and *o*-chlorophenoxy)acetic acids (1.5%), phenoxyacetic acid (0.1%), and also chlorophenols (0.5%). These substances were also quantitated by the method of Henshaw et al. (1975). The "inert" components, a kerosene fuel oil, constituted 8.9% by weight of the formulation and comprised at least 40 volatile compounds. The surfactant (5.08% by weight of the formulation) was a blend of oil-soluble amine sulfonates and polyoxyethylene ethers based on "Sponto" types of emulsifiers (Types N710, N712, and N714 in McCutcheon's "Detergents and Emulsifiers". The actual final composition of the surfactant is classified information.

[^{14}C]2,4-D samples labeled in the ring (uniformly labeled; sp act., 9.46 mCi/mmol), methylene (sp act., 4.25 mCi/mmol), and carboxyl (sp act., 3.30 mCi/mmol) positions were obtained from Mallinckrodt Nuclear. These were shown to be 99% pure by TLC.

Preparation of Pure *n*-Butyl Ester of 2,4-D. Two grams of reagent grade 2,4-D (Aldrich) was esterified with BF_3/1-BuOH according to the procedure of Horner et al. (1974). After distillation of the excess hexane and 1-butanol, the ester was distilled at 0.1 mmHg. Purity was confirmed by mass spectroscopy and gas chromatography.

Esterification of Labeled Compounds. The labeled free acids were also *n*-butylated, the excess butanol and hexane were distilled at 0.1 mmHg at a temperature below 50 °C, and the radioactive residue was diluted to 100 mL with reagent hexane in each case. On fortification of an aliquot with pure unlabeled ester and subsequent thermal conductivity gas–liquid chromatography, all the radioactivity eluted with the *n*-butyl ester peak. The radioactivity was counted using the scintillation cocktail utilized by Que Hee and Sutherland (1973b).

Irradiation of Pure *n*-Butyl Ester in Hexane. A 10-μL volume of pure *n*-butyl ester was irradiated in 30 mL of hexane contained in cylindrical Vitreosil or Pyrex tubes 2.54 cm i.d. which also contained a Pyrex cold finger to provide thermostating at 27 °C. The solution was stirred magnetically. All solutions in the above cell were irradiated inside a Rayonet Srinivason photoreactor equipped with lamps producing rated UV radiation around 300 nm (1.2×10^{16} photons s^{-1} mL^{-1}) and 350 nm (3.3×10^{16} photons s^{-1} mL^{-1}). For the Pyrex cuvette, the intensity for the 300-nm lamps was approximately 6×10^{15} photons s^{-1} mL^{-1}.

The formation and decomposition of the volatile products were monitored by subjecting 1-μL samples of the irradiated solution to gas–liquid chromatography using a ^{63}Ni electron-capture detector. The column was a 6 ft (1.83 m) long, 3.5 mm i.d. Pyrex U-tube packed with 10% SE-30 on 60/80 mesh Chromosorb W (AW-DMCS). The temperatures of the injector, column, and detector were 232, 190, and 222 °C, respectively. The flow of 19:1 argon/methane gas was 27 ± 1 mL/min. Calibration curves were done for the *n*-butyl esters of 2,4-D and of (*p*-chlorophenoxy)acetic acid and (*o*-chlorophenoxy)acetic acid (Henshaw et al., 1975).

GC–MS was also done utilizing the same packing within a 6 ft (1.83 m) × 2 mm i.d. stainless steel tube. The temperatures of the injector and flame ionization detector were 232 and 350 °C, respectively. The temperature program consisted of holding the column at 70 °C for 8 min and then heating at 4 °C/min to a temperature of 250 °C, which was then maintained until all peaks had eluted. The flow rates of compressed air, hydrogen, and helium were 500, 35, and 20 mL/min, respectively. A single-focusing MS-12 mass spectrometer recorded the mass spectra of the separated compounds.

After the irradiation was completed, the hexane solvent was evaporated and the residue butylated again with BF_3/1-BuOH reagent, and the amount of total esters were compared with that obtained by direct means when the irradiation was completed.

Irradiation of Solutions of Formulations. One milliliter of labeled material (ca. 8×10^5 dpm) was added to the reaction cell described above, the hexane solvent was gently evaporated, 0.1 mL of the formulation was added, and the volume was made up to 30 mL with solvent (hexane or deionized water). The magnetically stirred solutions were irradiated in the Rayonet Reactor for 3 days (350-nm lamps) or for 8 h (300-nm lamps) under the same conditions as described above. The experiments using hexane as solvent were monitored directly in the same manner as for the irradiation of the pure *n*-butyl ester. The irradiations were carried out in Pyrex and in Vitreosil cells at 300 nm. The radioactivity was estimated before and after irradiation. Dark controls were also prepared and left in the dark for as long as the corresponding irradiations.

After the irradiation, in the case of the aqueous solutions, enough salt was added to make the solutions saturated. For hexane solutions, 10 mL of saturated saline solution was added, and the hexane layer was evaporated off under reduced pressure at room temperature. The following procedure was then utilized for both solutions.

The saline solution was extracted with acetonitrile of equal volume (five times), 10% NaOH (10 mL) added to the combined extracts, and the excess acetonitrile evaporated. The alkaline residue was refluxed for 30 min, cooled, and then extracted with hexane (3 × 20 mL). The aqueous alkaline solution was acidified to pH 2 with HCl and then extracted with ether (3 × 10 mL). One milliliter of 1-butanol was added to the combined ether extracts, the excess ether evaporated, and 1-butanol (10 mL) further added together with 3 mL of BF_3/1-BuOH reagent (0.2 g/mL). The solution was then refluxed for 30 min and cooled, distilled water (10 mL) was added, and the solution was extracted with hexane (3 × 10 mL). Aliquots of the organic extracts were injected into a flame ionization gas chromatograph which utilized a 1.83 m × 3.5 mm i.d. Pyrex U-tube packed with 10% SE-30 on 60/80 mesh Chromosorb W (AW-DMCS) with flow rates of compressed air, helium carrier, and hydrogen being 350, 30, and 50 mL/min, respectively. The temperatures of the injector and detector were 232 and 222 °C, respectively. The column temperature was held at 75 °C for 8 min, then increased at 10 °C/min to 222 °C, and thereafter held at this latter temperature until all peaks eluted. Aliquots of the organic extracts were also counted. The efficiency of the procedure for *n*-butyl ester was 90.3 ± 8.6% at an initial level of 1 μg.

The pH of the saline residue remaining after the acetonitrile extractions was adjusted with HCl to pH 2 and the solution was extracted with ether (3 × 10 mL), the combined extracts were then concentrated, and aliquots

Table I. Decomposition of Pure *n*-Butyl and of *n*-Butyl and Isobutyl Esters of 2,4-D Contained in a Mixed Butyl Ester Formulation Irradiated in 30 mL of Hexane in Pyrex (P) and Quartz (Q) Reactors at 300 nm and 27 °C

origin of substrate	substrate	vessel	first-order rate constant, h^{-1}	initial rate of degradation, $\mu g\ h^{-1}\ mL^{-1}$
vacuum distillation	*n*-butyl ester of 2,4-D	P	(I) 0.491 ± 0.025 (initially)	119 ± 6
			(II) 0.177 ± 0.008 (steady-state)	196 ± 9
	n-butyl of (*p*-chlorophenoxy)acetate	Q	0.138 ± 0.012	28.5 ± 2.5
formulation	isobutyl ester of 2,4-D	P	0.101 ± 0.007	91.3 ± 6.3
		Q	0.675 ± 0.058	605 ± 52
	n-butyl ester of 2,4-D	P	0.104 ± 0.007	92.7 ± 6.2
		Q	0.675 ± 0.042	605 ± 38

were injected into the gas chromatograph and also counted. All three aqueous residues were evaporated to dryness at room temperature under vacuum. The residual sodium chloride was washed with methanol (5 × 10 mL) under suction, the washings were combined, and aliquots of the concentrate were quantitated as above.

The above procedure was repeated also on the dark controls. All experiments were done in triplicate. GC–MS was carried out on appropriate samples under the same conditions as for the pure *n*-butyl ester.

RESULTS

Nearly all the irradiations followed simple first-order kinetics with respect to the degrading species. The rate constants and the initial rates of decomposition are presented in Table I. These are dependent on the geometry and conditions but since these were held constant, all runs are comparable. As expected, photolysis in the Pyrex vessel at 300 nm was much slower than in the quartz vessel. The 300-nm lamps produce ca. 1% 254-nm light, but since the 300-nm emission is almost symmetrically distributed between 270 to 340 nm, the cut-off of 1-mm Pyrex halves the intensity of the latter and virtually eliminates all radiation below 290 nm (<0.1%). The relative errors in the rate constants and decomposition rates were of the order of 4 to 10%.

Irradiation of Pure *n*-Butyl Ester. The major product was the butyl (*p*-chlorophenoxy)acetate as shown by its retention time and mass spectrum. The rate of formation of the dechlorinated ester was the same as the rate of decomposition of the parent ester, and its production in the quartz reactor was complete within 1 h. Negligible amounts of *o*-chloro derivative (<1%) were formed. The butyl (*p*-chlorophenoxy)acetate then, in turn, quickly decomposed in the quartz vessel but very slowly in the Pyrex cell (Table I) to form butyl phenoxyacetate. Final product analysis showed that after 8 h of irradiation at 300 nm in the Pyrex cell at 27 °C, the solution contained 10% free 2,4-D, 20% *n*-butyl (*p*-chlorophenoxy)acetate, and 5% *n*-butyl phenoxyacetate in addition to unreacted 2,4-D ester. Negligible photolysis (ca. 1.5%) occurred at 350 nm.

Irradiation of Solutions of the Butyl Ester Formulation. For the dark controls, nearly all the label recovered (90 to 96%) was contained in the hexane extract after *n*-butylation, regardless of label position or solvent. In fact, no matter what the wavelength of irradiation, the position of the label, or the solvent, >80% of the label was always found in this extract. Thus, at 350 nm, the latter contained 84 to 98% of the recovered label from the aqueous solutions with the ring-labeled material consistently showing the lowest recoveries. At 300 nm, the extract contained 88 to 99% of the recovered label. This extract always contained butylated esters and free phenols, and analysis showed that production of the monochloro ester was essentially complete after 8 h of 300-nm irradiation of the quartz cell.

At 350 nm, the hexane extract after alkaline hydrolysis contained seven times more ring label than the corresponding dark control. All other extracts showed the same amount of label as the dark control. GC–MS revealed that no chloroinated *p*-dibenzodioxins were present (<100 ng).

At 300 nm, slightly more (two times) ring label was found in the acidified saline extract after ether extraction than in the dark controls, independent of the original solvent. However, the methylene label was present seven times in excess of its dark control.

GC–MS of the hexane extracts after *n*-butylation showed that after 350-nm irradiation of either aqueous or hexane solutions, a small amount of dechlorination (ca. 2%) occurred compared with dark control. However, the levels of (2,4,6-trichlorophenoxy)acetic acid and chlorophenols were not significantly higher than in the dark controls. Some other compounds not in the dark control were detected, e.g., nonan-5-one (0.5%; M_r 142), (2-oxopropyl)-2-pentenoate (0.3%; M_r 156), and the Photo-Fries product of butyl phenoxyacetate, butyl 2-hydroxyphenylacetate (0.5%). The latter showed a pronounced (p-1) peak in its mass spectrum in contrast to the butyl phenoxyacetate. More 2,4-dichlorophenol was detected in aqueous irradiations than in the hexane ones, but never exceeded 5% in yield.

Direct GLC analysis of the hexane irradiations at 300 nm showed that the isobutyl and *n*-butyl esters of (*p*-chlorophenoxy)acetic acid were formed from the corresponding esters of 2,4-D (Table I). Both iso and normal esters photolyzed at approximately the same rate. The rates cited here were much lower than the corresponding rates for the *n*-butyl ester in hexane at the same conditions. This was probably due to other UV absorbing compounds, e.g., the amino sulfonates in the surfactant, siphoning off some of the incident radiation since the UV absorbance at 300 nm of the formulation in hexane was greater than the absorbance of a pure *n*-butyl ester solution of the same nominal concentration.

The hexane extract after alkaline hydrolysis contained no detectable volatile chlorinated residues (GC–MS, or EC GC), and hence no chlorinated *p*-dibenzodioxins.

DISCUSSION

The results confirm that reductive dechlorination is the major pathway in the 300-nm photolysis of a mixed butyl ester formulation in aqueous or hexane solution. This agrees with the pathways previously elucidated by Binkley and Oakes (1974a,b) and Que Hee et al. (1973a, 1974a). Formation of 2,4-dichlorophenol and humic acid polymers as observed by Crosby and Tutass (1966) for the photodecomposition of the sodium salts of 2,4-D was shown to be minor in either solvent. This implies that the ester molecules exist in micelles with the hydrophobic phenyl moiety being immersed in a hydrocarbon-like environment. Of necessity, the hydrophilic portions of the surfactants should be in intimate contact with water molecules in these mixed micelles, and the photochemistry within such en-

tities might be expected to favor the "organic" reductive route rather than the hydroxylation characteristic of the aqueous system. The reduction process appears to occur by a radical pathway since radical recombination products such as the Photo-Fries product, and nonan-5-one, (2-oxopropyl)-2-pentenoate, and the expected Norrish Type II product (the free acid) were detected. The presence of the Photo-Fries product in the formulation study but not in the irradiation of the pure ester implies that the mixed micelles must constitute fairly "tight" radical cages to allow the Photo-Fries to occur (Kelly et al., 1969). This is further evidence for the existence of micellar aggregates.

In addition, the results indicate that the photoproducts expected from sprayed mixed ester emulsion concentrates should be the same whether or not the water carrier evaporates from the impinged droplets.

The major photoproduct, the ester of (*p*-chlorophenoxy)acetic acid, is much more volatile than the parent ester, since its retention time on the same GC column is about half that of the parent ester. As the chlorophenoxyacetate is still quite phytotoxic (Thompson et al., 1946), this could pose a possible threat to nontarget plants. This threat would not be appreciably diminished by use of such "nonvolatile" active ingredients as the isooctyl or butoxyethanol esters since, on dechlorination, volatile phytotoxic photoproducts would also be produced. To minimize environmental pollution from this source, amine salt formulations should be used whenever possible (Que Hee and Sutherland, 1974b).

An interesting effect is demonstrated by the difference in decomposition rates observed in Pyrex and quartz vessels. Although photodegradation was negligible at 350 nm, it was quite appreciable at 300 nm using Pyrex vessels to produce nearly 40% conversion for the pure *n*-butyl ester in 8 h. This situation simulates the sunlight photolysis of sprayed droplets from which all the water carrier has been evaporated so that the 2,4-D ester is in an excess of volatile "inert" components.

This study is one of the first published on the photochemistry of a commercially produced formulation for which the constituent chemicals have been stated and for which a complete mass balance with respect to the active ingredient (in this case the free acid) has been demonstrated by utilizing ^{14}C radiolabel at all its carbon atoms.

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1-[(5,9-Dimethyl-3,8-decadienyl)oxy]benzene and Derivatives: Vinylogues of Aryl Citronellyl Ethers Highly Effective as Juvenile Hormone Mimics

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Twenty-two 5,9-dimethyl-3,8-decadienyl aryl ethers and the corresponding 8,9-epoxy, 9-methoxy, and 9-ethoxy analogues were synthesized as well as eight 6,10-dimethyl-4,9-undecadienyl aryl ethers plus the corresponding 9,10-epoxy analogues. Bioassay data on the large milkweed bug (*Oncopeltus fasciatus*) and the yellow mealworm (*Tenebrio molitor*) are given. Most of the epoxide derivatives showed outstanding activity against *O. fasciatus*, and the meta-substituted derivatives were generally much more active than the corresponding para-substituted isomers. The *Z* configuration of the disubstituted double bond at the 3-position of the side chain is not detrimental to exceptional activity. The *Z* isomer generally showed a substantial increase in biological activity against both *O. fasciatus* and *T. molitor* over that of the *E* isomers in the comparisons made. In no case was the *E* isomer more active than the *Z* isomer.

Over the past decade, numerous chemicals exhibiting juvenile hormone (JH) activity against a variety of insects were discovered and are described in the literature. Several review articles adequately cover much of this work (Menn and Beroza, 1972; Slama et al., 1974; Henrick et al., 1976).

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One particular group of chemicals that has received extensive investigation is the aryl terpenoid type of JH mimic. Most of these chemicals were aryl terpenoid ethers, amines, carbamates, or hydrocarbons derived from the appropriate geranyl, "ethylgeranyl" (3,7-dimethyl-2,6-nonadienyl), citronellyl, or farnesyl moiety. While much work has been reported on changes in biological activity associated with the aryl substitution, derivatization of the 6,7 (or terminal) double bond of the terpenoid arm, and manipulations with the methyl branches on the side chain, relatively little information has been reported on biological effects associated with terpenoid side chains other than