Synthesis of ^{14}C-Labeled 2,4,6-Trichlorophenyl 4-Nitrophenyl Ether and 4-(Acetylamino)phenyl 2,4,6-Trichlorophenyl Ether

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The herbicide 2,4,6-trichlorophenyl 4-nitrophenyl ether (CNP) was synthesized with ^{14}C label in both the trichlorophenyl and the nitrophenyl rings. The synthesis of radioactive CNP with label in the trichlorophenyl ring was developed on a semimicroscale employing 24.5 mCi of [U-^{14}C]phenol as starting material. This synthesis gave a 39% overall yield of 2,4,6-trichloro[^{14}C]phenyl 4-nitrophenyl ether (specific activity of 0.94 mCi/mmol) with an estimated purity of 97 to 99%. CNP with the radiolabel located in the nitrophenyl ring was synthesized on a microscale with 0.97 mCi of [U-^{14}C]chlorobenzene. This synthesis gave a 44% overall yield of 2,4,6-trichlorophenyl 4-nitro[^{14}C]phenyl ether with a specific activity of 0.97 mCi/mmol. A large fraction (80%) of nitrophenyl labeled CNP was reduced to 4-amino[^{14}C]phenyl 2,4,6-trichlorophenyl ether (CNP-NH_2), and for stabilization and storage purposes, the CNP-NH_2 was acetylated to yield 4-(acetylamino)[^{14}C]phenyl 2,4,6-trichlorophenyl ether (acetamino-CNP). The acetamino-CNP was obtained in 63% yield based on CNP with a radiochemical purity of greater than 99%.

The diphenyl ether herbicide, 2,4,6-trichlorophenyl 4-nitrophenyl ether (CNP), was first synthesized and developed by Mitsui Toatsu Chemicals, Inc. In 1965, CNP became commerically available as a preemergence herbicide for paddy fields (Toyama and Takasawa, 1971). CNP is widely used for weed control in paddy fields in Japan and other Asian rice growing countries because of its low toxicity. For the last several years, CNP has been used in the largest quantity of all pesticides employed in Japan. Approximately 6000 metric tons of CNP as active ingredient was produced in 1975 (Kuwatsuka and Niki, 1976).

Degradation of CNP in flooded and upland soils has been studied (Niki and Kuwatsuka, 1976), and the rate of decomposition appears to be associated primarily with the soil redox potential. In the laboratory under simulated paddy field conditions, CNP was rapidly degraded to 4-aminophenyl 2,4,6-trichlorophenyl ether (CNP-NH_2) (Niki and Kuwatsuka, 1976; Kuwatsuka, 1972). As an environmental residue study, the rate of CNP disappearance from paddy fields was carefully monitored (Yamada and Nakamura, 1973). The transformation of CNP to CNP-NH_2 was examined in soil samples collected throughout Japan (Yamada, 1976a). This survey indicated that CNP-NH_2 was held as a soil bound residue, and the residues appeared to be accumulating in the paddy field soils.

Therefore, to study the metabolic fate of CNP (Yamada, 1976b; Kuwatsuka et al., 1976) and to determine the character and significance of the CNP-NH_2 bound residues in paddy field soils, it was necessary to prepare the two title compounds with ^{14}C label. Reactions were developed for the preparation of CNP with ^{14}C in both the trichlorophenyl and the nitrophenyl rings and CNP-NH_2 with the radiolabel in the aminophenyl ring. The reaction scheme given in Figure 1 was developed for the radiochemical preparation of CNP and CNP-NH_2 under semimicro- and microscale conditions. Since radiolabeled amino compounds readily degrade by self-radiolysis, the labeled CNP-NH_2 was immediately acetylated after synthesis to yield 4-(acetylamino)phenyl 2,4,6-trichlorophenyl ether (acetamino-CNP), a compound more resistant to self-radiolysis. Thus, the acetamino-CNP could be stored with minimum decomposition, and CNP-NH_2 would be readily available by hydrolysis of acetamino-CNP for environmental fate studies.

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EXPERIMENTAL SECTION

Materials. Analytical grade dimethylformamide (DMF) was distilled before use. Chlorine gas was washed and dried with concentrated sulfuric acid and passed through anhydrous calcium chloride to remove acidic aerosols before use. [U-^{14}C]Phenol (25 mCi) with a specific activity of 4.7 mCi/mmol (radiochemical purity, 98%) and [U-^{14}C]chlorobenzene (1 mCi) with a specific activity of 5.0 mCi/mmol (radiochemical purity, 97%) were purchased from the Radiochemical Centre (Amersham, U.K.) through the Japan Radioisotope Association.

Thin-Layer Chromatography (TLC). Preparative TLC was employed for the purification of the radioactive samples from the microscale synthesis. Purification was accomplished on 0.5-mm thick plates of Wakogel B-5F (Wako Chemical Co.). The developing solvent for purification of [^{14}C]CNP was hexane–acetone (10:1, v/v) and that for [^{14}C]acetamino-CNP was benzene–acetone (2:1, v/v). In each case, the radioactive band containing the desired product was removed from the TLC plate with the aid of vacuum into small glass columns. The product was then eluted from silica gel with acetone.

Gas–Liquid Chromatography (GLC). A Neva Model 1400 chromatograph with flame ionization detector was used for the analyses of reaction mixtures from semimicroscale CNP synthesis. A 3 m × 3 mm i.d. glass column packed with 3% DC-11 coated on 80 to 100 mesh Gas-Chrom Q was employed. Column temperature was programmed at a rate of 15 °C/min from 80 to 230 °C, and nitrogen was used as a carrier gas at a flow rate of 80 mL/min. Under these conditions, the retention times were: dichlorophenol, 3 min; trichlorophenol, 4.5 min; tetrachlorophenol, 6.3 min; and CNP, 11.6 min.

A Shimadzu Model GC-5A chromatograph with flame ionization detector was used for the analyses of reaction mixtures from microscale syntheses. Nitrogen was em-

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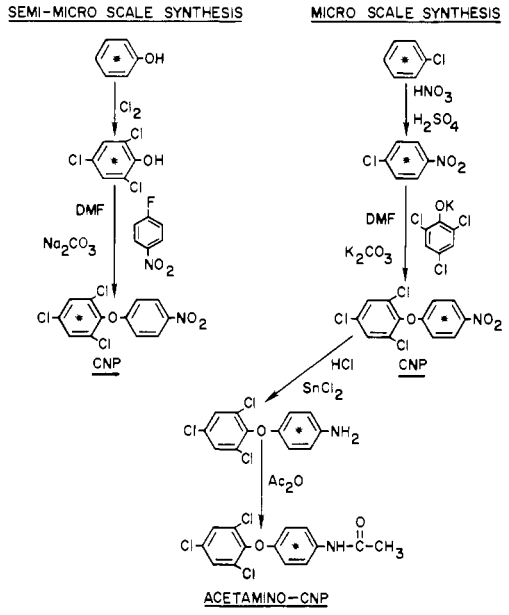

Figure 1. Scheme for the radiochemical synthesis of CNP and acetamino-CNP; asterisk indicates the aromatic ring with ^{14}C label.

ployed as carrier gas at 80 mL/min. A 2 m × 3 mm i.d. column of 5% OV-1 coated on 60 to 80 mesh Gas-Chrom Q was used for the analysis of *p*-chloronitrobenzene and CNP. At a column temperature of 140 °C, the retention time of chloronitrobenzene (ortho and para) was 1.5 min, and at 220 °C, the retention time of CNP was 7 min. A 1-m column containing 5% DC-11 coated on 60 to 80 mesh Gas-Chrom Q was operated at 220 °C for the analysis of acetamino-CNP. Under these conditions, the retention time for CNP was 2.8 min and that for acetamino-CNP was 7 min.

Assay of Radioactivity. A Packard Model 574 liquid scintillation spectrometer with automatic external standard was employed for radioactivity measurements. The fluor solution consisted of 2.5 g/L of 2,5-diphenyl-1,3-oxazole and 0.15 g/L 1,4-bis[2-(4-methyl-5-phenyloxazolyl)]-benzene dissolved in toluene. Radiochemical purity of the products from the microscale synthesis was estimated by TLC on precoated plates of silica gel 60 F_{254} of 0.25 mm thickness followed by autoradiography employing Fuji no-screen X-ray film.

Synthesis of 2,4,6-Trichloro[^{14}C]phenol (TCP). The radioactive phenol (0.49 g, 24.5 mCi) was diluted with 2.0 g of nonradioactive phenol and transferred with 5 mL of carbon tetrachloride into the chlorination apparatus (Figure 2). After transfer the carbon tetrachloride was removed under reduced pressure, and the phenol was chlorinated at 60 to 80 °C for 10 h with dry chlorine gas introduced at the bottom of the reaction vessel at a rate of 10 mL/min (total chlorine: 2.4 L at 20 °C and 1 atm; 1.34 times theoretical). After chlorination, nitrogen gas was introduced into the reaction mixture for 10 min at a flow rate of about 20 mL/min to remove hydrogen chloride gas and excess chlorine. Then 15 mL of 0.25 M aqueous sodium sulfite was added to the residue in the chlorination vessel, and the mixture was agitated for 20 min at 70 °C to eliminate reducible impurities. After allowing the reaction to cool to ambient temperature, the trichlorophenol was extracted with 15 mL of carbon tetrachloride (yield of crude TCP was 4.9 g; 95%, 23.3 mCi). The crude TCP extract was washed with 10 mL of distilled water and dried by passage through an anhydrous sodium sulfate (30 g) column. The column was washed with an additional 10 mL of carbon tetrachloride. The eluates were combined

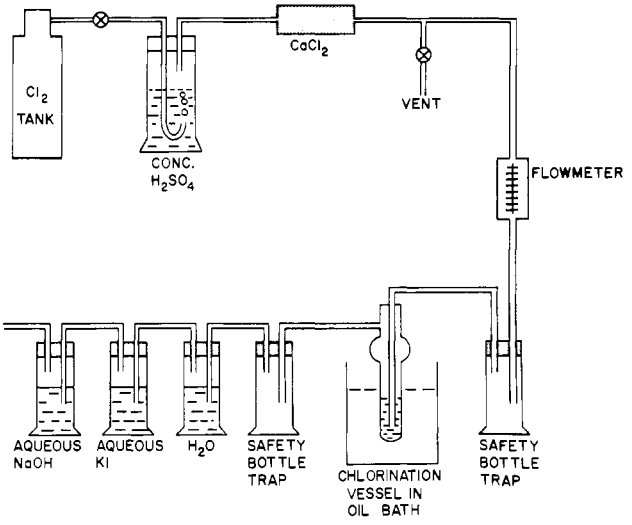

Figure 2. Chlorination apparatus.

and reduced to dryness under reduced pressure. Yield of 2,4,6-trichloro[^{14}C]phenol with a chemical purity of 99.5% (GLC) was 82% (4.2 g; 20 mCi).

Synthesis of 2,4,6-Trichloro[^{14}C]phenyl 4-Nitrophenyl Ether (CNP). A 100-mL three-necked flask was fitted with air condenser, immersion thermometer, and glass stopper. Into the flask was added 4.2 g (21.3 mmol) of radioactive 2,4,6-trichlorophenol, 2.7 g (19.1 mmol) of 1-fluoro-4-nitrobenzene (*p*-FNB), 2.3 g (21.7 mmol) of anhydrous sodium carbonate, and 35 mL of DMF. The contents in the flask were carefully mixed with a magnetic stirrer. After thoroughly mixing, the reaction was heated at 150 °C in an oil bath with stirring for 11 h. The reaction mixture was cooled to ambient temperature, and 30 mL of distilled water was added with stirring. The CNP was allowed to crystallize from the mixture, and the crude product was isolated by filtration. The product was purified by washing with 60 mL of distilled water (40 °C) followed by 100 mL of 50% (v/v) aqueous ethanol. The purified CNP was dissolved in 30 mL of benzene (category I carcinogen) and passed through a column of anhydrous sodium sulfate (30 g). An additional 10 mL of benzene was used to thoroughly wash the column. The combined benzene eluates were reduced to dryness under reduced pressure, yielding pale-yellow crystals of CNP. Yield of radioactive CNP with a chemical purity of 97 to 99% (GLC) was 48% (3.25 g; 9.55 mCi) based on trichlorophenol. Overall yield of CNP based on phenol as starting material was 39% with a final specific activity of 0.94 mCi/mmol.

Synthesis of 1-Chloro-4-nitro[^{14}C]benzene (*p*-CNB). The sealed ampule of radioactive chlorobenzene (21.8 mg, 0.97 mCi) was cooled in a dry ice–acetone bath and the break-seal was carefully opened. Then 90.35 mg (81.6 μL) of nonradioactive chlorobenzene was added. Nitration was accomplished by addition of 0.32 mL (5 mmol) of concentrated nitric acid and 0.32 mL (5.7 mmol) of concentrated sulfuric acid. The ampule was resealed, and the reaction mixture was allowed to stand at ambient temperature (ca. 25 °C) with occasional agitation for 4 days. After reaction, ice–water was slowly added, and the product was extracted with aliquots of diethyl ether. The combined ether extract was dried over anhydrous sodium sulfate and then filtered through glass wool.

The ethereal solution for chloronitro[^{14}C]benzene was transferred into a 25-mL eggplant-shaped flask to concentrate the solution. A 40 cm × 1 cm i.d. air condenser with two loosely packed balls of glass wool located 5 cm

and 12 cm from the top of the column was used to prevent volatilization of the product and to allow evaporation of the ether solvent (a 2-ball micro Snyder column could also be employed). To prevent loss of labeled *p*-CNB during solution concentration, 2 mL of nitrobenzene was added to the ethereal chloronitrobenzene. The solution was heated at approximately 65 °C in a water bath until the diethyl ether was removed by volatilization.

Product yield from this reaction, which included both ortho and para isomers, was 83%. Isomer ratio for this reaction was reported as 70% para and 30% ortho (Fieser and Fieser, 1957). Therefore, the product yield for the para isomer was 58% (564 μCi).

Preparation of Purified 2,4,6-Trichlorophenol (TCP). Trace quantities of impurities in trichlorophenol such as 2,4,4,6-tetrachloro-2,5-cyclohexadien-1-one were reported to interfere with CNP synthesis (Inoue et al., 1966; Toyama and Takasawa, 1971). Therefore, 80 mL of distilled water and 2 g of sodium bisulfite were added into a 200-mL flask and heated to approximately 75 °C. Then 40.5 g of TCP (greater than 99% purity) was slowly added to the hot bisulfite solution with vigorous stirring. After addition, the TCP was vigorously stirred for 10 min at 75 °C. The aqueous layer was removed, and the organic layer was washed two times with 40-mL aliquots of distilled water (75 °C).

Preparation of the Potassium Salt of TCP (TCP-K). Purified TCP (22 g, 0.1 mol) was placed in a reaction vessel and heated at 90 °C in an oil bath. Then 10 mL of 40% aqueous potassium hydroxide (6.7 g, 0.12 mol) was slowly added with stirring. Heating was continued and the temperature was allowed to rise very slowly to a maximum internal solution temperature of 120 °C. As the temperature increased, the water was allowed to evaporate; heating was stopped when the temperature of the salt solution reached 120 °C. Most of the water was removed by this technique, and the TCP-K was easily reduced to a dry solid by storage in a vacuum dessicator over anhydrous calcium chloride. The dried TCP-K was dissolved in diethyl ether and filtered to remove excess potassium hydroxide. Then hexane was added to the ethereal solution to allow precipitation of the purified product. The purified TCP-K was filtered, dried, and pulverized into a fine powder for use in CNP synthesis.

Synthesis of 2,4,6-Trichlorophenyl 4-Nitro[^{14}C]phenyl Ether (CNP). To 91.35 mg (0.58 mmol) of 1-chloro-4-nitro[^{14}C]benzene contained in 2 mL of nitrobenzene were added 4 mL of DMF, 472 mg (2 mmol) of TCP-K, and 200 mg (1.44 mmol) of finely pulverized potassium carbonate. The reaction mixture was vigorously flushed with a fine stream of nitrogen for approximately 5 min to remove dissolved oxygen (Lappin and Zannucci, 1971). The flask was stoppered, and the glass stopper was fixed into position with plastic tape. The sealed sample was heated in an oil bath at approximately 150 °C for 5 days. The solution at the beginning of the heating period was a deep wine-red color, and this solution should not darken during the heating period. When the reaction was complete, the sample was cooled, 25 mL of 4 N aqueous sodium chloride was added, and the product was extracted with aliquots of diethyl ether. The combined ether extract was concentrated, and the [^{14}C]CNP was purified by preparative TLC. Yield of purified [^{14}C]CNP was 76% (428 μCi) based on [^{14}C]*p*-CNB. Twenty percent (85.6 μCi, 28 mg) of [^{14}C]CNP was stored for experimental use, and the remainder was used for the preparation of CNP-NH_2.

Synthesis of 4-Amino[^{14}C]phenyl 2,4,6-Trichlorophenyl Ether and the Acetamino-CNP Derivative. Into a 30-mL Erlenmeyer flask containing 112 mg (0.35 mmol) of [^{14}C]CNP were added 5 mL of absolute ethanol, 2 mL of concentrated hydrochloric acid, and 600 mg (2.66 mmol) of stannous chloride dihydrate. The reaction mixture was heated in a water bath at 90 °C and stirred magnetically for a period of 1.5 h. The mixture was cooled and made basic with 40% (w/w) aqueous potassium hydroxide (ca. 3.5 mL; added slowly with stirring). Diethyl ether was employed for the extraction of CNP-NH_2 from the reaction mixture. Then 2 mL (20 mmol) of acetic anhydride was added to the ethereal solution of CNP-NH_2 to prepare acetamino-CNP. Excess acetic anhydride and solvent were removed by warming the solution and allowing the volatile material to evaporate.

The radioactive acetamino-CNP was purified by preparative TLC, and the purified product yield was 63.4% (217 μCi). The specific activity was verified as 0.97 mCi/mmol by measuring the radioactivity of the product by liquid scintillation counting and the amount of material by quantitative GLC analysis. TLC followed by autoradiography indicated a radiochemical purity of greater than 99%. For storage purposes, the [^{14}C]acetamino-CNP was divided equally into 10 amber ampules, reduced to dryness with nitrogen, flame sealed, and stored below freezing temperature.

DISCUSSION

^{14}C Synthesis on the Semimicroscale. The chlorination of phenol to TCP was carefully studied to determine optimum reaction conditions. Reactions were first examined with carbon tetrachloride as solvent. For these reactions, however, a significant quantity of tetrachlorophenol was produced even though greater than 20% of the original phenol remained in solution as dichlorophenol. Time course studies for the chlorination reaction with carbon tetrachloride indicated that reaction rates for chlorination of the mono-, di-, and trichlorophenols were approximately the same. Hence, trichlorophenol was being chlorinated to tetrachlorophenol at approximately the same rate as dichlorophenol was being converted to trichlorophenol. Chlorination with solvent was not suitable for TCP synthesis; therefore, chlorination was then examined without solvent. Neat reactions showed that tetrachlorophenol was not produced after 6 h of reaction time while dichlorophenol was essentially consumed during the same period. As the reaction time was increased to 12 h, however, tetrachlorophenol was produced at the 2% level. Time course studies with nonsolvent chlorination indicated that the less-substituted phenols were chlorinated at a faster rate; thus successive chlorination of phenol was accomplished. A comparison of the chlorination reaction with and without solvent revealed that the neat reaction produced higher yields with fewer byproducts, and reaction time was less than half that required for solvent chlorination. Therefore, after optimization of the neat reaction, a good reproducible yield of TCP was obtained.

Inoue et al. (1968) and Toyama and Takasawa (1971) reported that reducible substances were formed during the chlorination of phenol, and these byproducts in trace quantities were responsible for the inhibition of the coupling reaction of TCP with *p*-CNB in CNP synthesis. These reducible impurities were characterized as chlorinated cyclohexadienones. Treatment of TCP with sodium sulfite (bisulfite and thiosulfate) was very effective for removal of the inhibitory chlorinated cyclohexadienones. If sulfite treatment was not employed, yields for CNP synthesis were less than 10% and large quantities of starting material were recovered. With the sulfite

treatment, however, satisfactory yields of CNP were obtained.

By use of dimethyl sulfoxide as solvent or sodium or potassium hydroxide as base, dark-colored reactions with considerable decomposition of reactants and very low yields of CNP were obtained. With potassium carbonate as base, reaction rates with *p*-FNB and *p*-CNB were examined. CNP formation progressed at the fastest rate when *p*-FNB was employed. The reaction rate with *p*-CNB was considerably slower; but the yield of undesired products was much lower. In time course studies with different mole ratios of TCP and *p*-FNB for 8-h periods, as unknown byproduct was observed in significant quantity. The relative yield of this byproduct was directly related to the time allowed for the diphenyl ether reaction. The unknown product was not identified, but retention time by GLC indicated that the material was bis(4-nitrophenyl) ether. Also, if the mole ratio of TCP to *p*-FNB was changed from 1:0.9 to 1:1.3, the yield of this byproduct was approximately doubled. If sodium carbonate was used as base, formation of the byproduct was not observed during the first 7 h of reaction. If potassium carbonate was used as base, the byproduct was observed within 1 h of reaction time. Therefore, for the radiochemical synthesis a mole ratio of 1:0.9 (TCP:*p*-FNB) was employed, and sodium carbonate was used as base to reduce the apparent bis(4-nitrophenyl) ether formation to less than 1%. Reaction time was increased to 11 h because reaction rate was slower with sodium carbonate than with potassium carbonate. In the CNP synthesis, *p*-FNB rather than *p*-CNB was employed because the fluoro group is known to be a better leaving group than the chloro group in aromatic nucleophilic substitution reactions (Buehler and Pearson, 1970). Another advantage of *p*-FNB was the fact that unreacted *p*-FNB was easily removed from CNP by washing first with water and then with ethanol–water. Thus, CNP of high purity was obtained without employing column chromatography or recrystallization techniques.

Crystallization of CNP from the crude reaction mixture required the addition of an exact volume of water. With insufficient water CNP would not crystallize from the reaction mixture as desired, and with excess water *p*-FNB would coprecipitate with CNP to produce a highly contaminated product.

^{14}C Synthesis on the Microscale. Synthesis with ^{14}C label in the nitrophenyl ring of CNP was carried out with radioactive chlorobenzene as starting material. Chlorobenzene was selected over fluorobenzene because this material was readily available from a commercial source.

Nitration of chlorobenzene with nitric acid to yield *p*-CNB appeared to be the most suitable choice of reactions even though 30% of the nitrated product was the ortho isomer. This reaction was selected because it was very clean, reliable, and simple, and time was not available for development of a higher yielding reaction. Working at the milligram level, nitration proceeded best at ambient temperature (25 °C). If reactions were heated at approximately 60 °C for 1 or 3 h, the chloronitrobenzene yield was reduced by about 10%.

Separation of the ortho and para isomers of chloronitrobenzene was not necessary prior to synthesis of CNP. Owing to the steric interaction of the ortho nitro group of chloronitrobenzene with the two ortho-substituted chlorine groups of TCP, the diphenyl ether synthesis strongly favored formation of only the para nitro isomer. Furthermore, it was possible during purification of [^{14}C]CNP by TLC to easily separate CNP from its ortho isomer using the hexane–acetone solvent system (Kanazawa and Tomizawa, 1978). Therefore, the synthesis and purification of CNP was accomplished without interference from the ortho isomer even though the two isomeric forms of chloronitrobenzene were present.

When the ethereal chloronitro[^{14}C]benzene extract was concentrated, nitrobenzene was added to retain the radioactive product while diethyl ether was allowed to evaporate. Nitrobenzene was selected because this material was initially believed to be the solvent that was to be used in the [^{14}C]CNP synthesis. Nitrobenzene, however, proved unsuitable for CNP synthesis on the microscale even though this material was reported as the reaction solvent for the commercial preparation of CNP (Inoue et al., 1966). Only trace quantities of CNP were produced with nitrobenzene as solvent. Dimethyl sulfoxide or diglyme were also ineffective for this diphenyl ether synthesis even though these solvents were very effective for other ether syntheses (Smith et al., 1969; Tanaka et al., 1976). Dimethylformamide proved to be the best solvent for CNP synthesis giving reliable results and high yields.

Purified TCP-K was prepared for the microsynthesis because Inoue et al. (1966, 1968) reported that the potassium salt of TCP gave higher yields of CNP than the sodium salt. Preliminary studies revealed that reactions containing dissolved oxygen quickly darkened, and only trace quantities of CNP were formed due to rapid reactant decomposition. If samples were vigorously flushed with nitrogen, decomposition of reactants was largely reduced, but the reaction would still become dark brown. With nitrogen flushing, a 35% yield of CNP was achieved after heating for 2 days. Upon addition of a small quantity of potassium carbonate, however, decomposition of the reactants was essentially eliminated. Potassium carbonate addition was necessary for the prevention of reactant decomposition even though TCP was added as a completely neutralized salt. Potassium carbonate appeared to act as a buffer in the reaction media to control the pH of the reaction mixture. Thus, a critical pH was apparently achieved which prevented decomposition of the reactants. With potassium carbonate and deoxygenated samples, time course studies were performed to optimize yields. A 70% yield of CNP was obtained after heating for 3 days, and a maximum yield of 76% was achieved after heating for 5 days. Even when the heating period was extended to 9 days, there was no apparent decrease in CNP yield. A comparison of the reaction with and without nitrobenzene addition showed that nitrobenzene had no effect on the CNP yield. Therefore, a very reliable reaction was developed for CNP synthesis.

Nearly quantitative yields were obtained for the reduction of CNP to CNP-NH_2 during trial studies. When the amine hydrochloride was neutralized in the preliminary experiments, aqueous potassium hydroxide was added dropwise to the reaction mixture. Frequent tests of the reaction mixture were taken with pH paper to determine the point where a basic solution was achieved. Consequently, with very slow addition of potassium hydroxide, a 99% yield of CNP-NH_2 was obtained during reaction development. For the radiochemical synthesis, however, the required amount of potassium hydroxide (estimated from trial studies) was rather quickly added to the reaction to neutralize the amine hydrochloride. This technique avoided the constant testing of the radioactive solution pH; hence, for the radioactive solution only one pH measurement was required after the addition of base. With this method, however, the yield of CNP-NH_2 was reduced by about 35%. The CNP-NH_2 was transformed into another product that migrated just above acetamino-CNP

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.

ACKNOWLEDGMENT

F.S.T. wishes to thank the National Institute of Agricultural Sciences and Mitsui Toatsu Chemicals, Inc., for their kind cooperation during the course of the research program.

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Received for review June 2, 1978. Accepted August 24, 1978. Financial support for F.S.T. was provided by the Science and Technology Agency of Japan through the Japanese Government Research Award for Foreign Specialists. Mention of a trademark, proprietary product, or vendor does not constitute a guarantee or warranty of the product by the U.S. Department of Agriculture and does not imply its approval to the exclusion of other products that may also be suitable.

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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0021-8561/79/1427-0079$01.00/0