chlorinated aromatic compounds in paddy soil. Pentachlorophenol was reported to be rapidly degraded in laboratory-stored paddy soil with the formation of all three possible isomeric tetrachlorophenols, 2,4,5- and 2,3,5-trichlorophenols, 3,4- and 3,5-dichlorophenols, and 3-chlorophenol (Ide et al., 1972). In paddy field soil, residues of nitrofen (2,4-dichloro-4′-nitrodiphenyl ether) were detected in fields treated 10 months previously with 4′-nitro-2,4,6-trichlorodiphenyl ether (Yamada, 1976). In view of the results obtained with pentachlorophenol, it is perhaps surprising that significant further dechlorination of techlofthalam was not observed. However, it has been shown (Alexander and Aleem, 1961) that the rate of decomposition of various chlorinated phenols and phenoxyalkanoic acids by soil microbial cultures is very dependent on the positioning of chlorine substituents on the aromatic nucleus.

Most of the radioactivity applied to the leaves of rice plants could be recovered by washing with acetone for samples collected up to 30 days after the application. Techlofthalam was the major component in these washes, but the proportion of techlofthalam imide increased to about 20% of the radioactivity at 30 days. The same two components were also detected in solvent extracts of the same leaves sampled up to 15 days, although by 30 days techlofthalam was only a minor component. Formation of the imide appears to be the major initial transformation which could be a chemical process on the leaf surface or an enzymic reaction within the leaf. However, at least some penetration of the applied techlofthalam probably occurs since this compound was detected in the solvent extracts of washed leaves.

LITERATURE CITED

Alexander, M.; Aleem, M. I. H. *J. Agric. Food Chem.* **1961**, *9*, 44.
Ide, A.; Niki, Y.; Sakamoto, F.; Watanabe, I.; Watanabe, H. *Agric. Biol. Chem.* **1972**, *36*, 1937.
Ishida, M., Sankyo Co. Ltd., unpublished results, 1975.
Kirkpatrick, D., Finn, C. M.; Conway, B.; Hawkins, D. R.; Honda, T.; Ishida, M.; Powell, G. P. *J. Agric. Food Chem.* **1981**, *29*, 608.
Nakagami, K.; Tanaka, H.; Ishida, M.; Koremura, M.; Honda, T.; Yamazaki, T. *Nippon Noyaku Gakkaishi* **1980**, *5*, 237.
Yamada, T. *Proc. Asian-Pac. Weed Sci. Soc. Conf., 5th, 1975* **1976**, 217.

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Biphenyl Formation in the Photolysis of 3-(4-Chlorophenyl)-1,1-dimethylurea (Monuron) in Aqueous Solution

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In the photolysis of dilute aqueous solutions of monuron, a photoproduct with a mass spectral molecular ion at m/e 360 was isolated and partially characterized. Initial data suggested that the unknown product was a substituted diphenylamine, and this material was apparently being formed by photocoupling of two monuron molecules with concomitant elimination of hydrogen chloride. Upon further examination, however, the photoproduct was characterized as a substituted biphenyl compound. After hydrolysis and acetylation of the unknown, high-performance liquid chromatography revealed that the photoproduct was a mixture of two isomeric compounds. When synthetic and spectroscopic methods were employed, the isomeric biphenyl photoproducts were identified as the 2-chloro-4′,5-bis(*N*′,*N*′-dimethylureido)biphenyl and the 5-chloro-2,4′-bis(*N*′,*N*′-dimethylureido)biphenyl. The 5-chloro isomer represented 92% of the isomeric mixture, and the 2-chloro isomer represented the remaining 8%.

During the investigation of the photolysis of monuron in dilute aqueous solution, a photoproduct with a molecular mass equivalent to the coupling of two monuron molecules minus the mass of hydrogen chloride was isolated and partially characterized (Tanaka et al., 1977). This compound was the second most abundant photoproduct isolated and was observed in 2% yield after a 45-min exposure period in a Rayonet reactor equipped with sunlight lamps. During this exposure period, about 29% of the monuron was decomposed; therefore, approximately 7% of the decomposed monuron was transformed into this unknown photoproduct. The identity of the unknown photoproduct was of considerable interest because Rosen and Strusz (1968) detected a photoproduct of similar nature from natural sunlight photolysis of metrobromuron.

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Since hydrogen chloride was the only product eliminated from the coupling of two monuron molecules, the results suggested that a substituted diphenylamine was probably being produced. There was some question, however, as to the position of aromatic coupling (Tanaka et al., 1977). Consequently, further study was necessary to determine complete identification of the coupled photoproduct.

EXPERIMENTAL METHODS

Materials and Equipment. The 2-chloro-5-nitroaniline and 5-chloro-2-nitrobenzoic acid were purchased from Aldrich Chemical Co. The 1,5-naphthalenedisulfonic acid (sodium salt) was obtained from Eastman Kodak Co. [*ring*-^{14}C]Monuron was prepared in the laboratory (Tanaka, 1970).

Sample preparation, photolysis with the Rayonet photoreactor, and photoproduct isolation were conducted as previously described (Tanaka et al., 1977). Infrared (IR) spectra were taken on a Perkin-Elmer Model 399 spectrophotometer equipped with the Model 3500 data handling station. Mass spectra were obtained on a Varian

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CH-5DF spectrometer, and data were processed with a PDP-11 computer. Nuclear magnetic resonance (NMR) spectra were recorded on a JEOL FX90Q Fourier transform spectrometer. Tetramethylsilane was used as the internal reference, and spectra were taken in both 1.8 and 5 mm o.d. tubes. Melting points were measured with a Thomas-Hoover apparatus, and the observed melting points were reported uncorrected. Catalytic reductions were performed with a Parr series 3910 low pressure hydrogenation apparatus. High-performance liquid chromatography (HPLC) was conducted with the Waters Associates radial compression unit (Model RCM-100) containing 8-mm Radial-Pak cartridges of 10-μm spherical particles of C_{18}, CN, and silica gel. The isocratic elution solvent was 18% acetonitrile in water, and flow rate was 3 mL/min unless specified otherwise. Quantitation by HPLC was performed with a Chromatronix ultraviolet (254 nm) detector and a Shimadzu Chromatopac-E1A digital integrator. Thin-layer chromatography (TLC) was generally performed on 0.25 mm thick plates of Anasil HF (Analabs), and the developing solvent was benzene–acetone (2:1) unless specified otherwise.

Sodium 4-Nitrophenylsulfonylcyanamide (1). To a solution of 1.68 g (40 mmol) of cyanamide in 10 mL of water was added 4.4 g (20 mmol) of 4-nitrobenzenesulfonyl chloride (Moed, 1947). The reaction was initiated with 10 mL of 3 N NaOH (15 mmol), and the mixture was stirred at ambient temperature. As the solution became acidic, a second portion (10 mL) of 3 N NaOH was added to maintain the reaction under strongly alkaline conditions. After being stirred for 3 h, the turbid liquid was filtered and the precipitate was washed with 25 mL of water. The filtrate was acidified with dilute HCl and concentrated by flash evaporation. The precipitated 4-nitrophenylsulfonylcyanamide was isolated, titrated with base, and reduced to dryness. Then 1 was redissolved in acetone, filtered, and dried. Final purification was accomplished by recrystallizing from water and drying in vacuo.

***N*-(4-Nitrophenylsulfonyl)-*N'*-(4-chlorophenyl)-guanidine (2).** This material was prepared by dissolving 1 g (4 mmol) of 1 and 0.55 g (4.4 mmol) of 4-chloroaniline in 5 mL of glacial acetic acid (Backer and Wadman, 1949). The mixture was heated at boiling temperature for 10 min, and upon cooling the product crystallized from solution. Without further purification, 2 gave a melting point of 170 °C with decomposition to an orange liquid (lit. mp 175.5 °C; Backer and Wadman, 1949).

4-Chloro-4'-nitrodiphenylamine (3). By use of the method of Backer and Wadman (1949), 1 g of 2 was added to 10 mL of 2 N NaOH and 10 mL of ethanol. The mixture was heated at boiling temperature for about 10 min and then allowed to cool. The product that crystallized from solution was filtered, washed with water, and then recrystallized from methanol: mp 179 °C (lit. mp 181 °C; Backer and Wadman, 1949); ^{1}H NMR (acetone-d_6) δ 7.19 and 8.16 (2 d, 4 H, A_2X_2, J = 9.6 Hz), 7.33 and 7.47 (2 d, 4 H, A_2B_2, J = 9.5 Hz), 8.48 (br s, H, NH); ^{13}C NMR (Me_2SO-d_6) δ 112.8 (2 C atoms), 120.9 (2 C atoms), 124.9 (2 C atoms), 125.7, 128.1 (2 C atoms), 137.3, 138.0, 148.9.

4-Chloro-4'-aminodiphenylamine Dihydrochloride (4). Reduction was accomplished by placing 2 g (8 mmol) of 3, 100 mL of ethanol, 6 mL of 12 N HCl, and 6.7 g of stannous chloride dihydrate into a 500-mL flask. The reaction was heated at approximately 80 °C and stirred for 1.5 h. Water (100 mL) was added and the solution was rendered alkaline with dilute base. The product was extracted with benzene, and the extract was dried over anhydrous potassium carbonate and filtered. The benzene filtrate was sparged with dry HCl to precipitate 4 from solution. The product was filtered and dried in vacuo. Mass spectrum m/e (rel intensity) 218 (molecular ion, 100), 182 (20), 107 (36).

4-Chloro-4'-(*N',N'*-dimethylureido)-*N*-[*N,N*-(dimethylamino)carbonyl]diphenylamine (5). (Dimethylamino)carbonyl groups were attached by reaction with phosgene followed by dimethylamine (Searle and Cupery, 1958). Dimethylcarbamyl chloride reactions (Elder and Koch, 1977) were unsuccessful owing to the ease of oxidation of 4. By use of the apparatus of Shriner et al. (1943), 1 g (3.4 mmol) of 4 dissolved in peroxide-free dioxane (Fieser and Fieser, 1967) was treated with phosgene for 2 h at 75 °C. Excess phosgene and HCl were removed by distilling a portion of the solvent. When the mixture was cooled to 10 °C, an excess of dimethylamine was added. After the mixture was heated for a short period at 55 °C, the solvent was removed and the product was partitioned with water. The aqueous layer was decanted and the tarry brown material was dissolved in acetone. The acetone solution was passed through a 2 × 18 cm column of silica gel (60–200 mesh) with additional acetone until about 150 mL of eluate was collected. Water was added to the eluate until a cloudy solution was obtained. The mixture was allowed to stand at 5 °C and brown tarry material separated from solution. This tarry material was removed and additional water was added. After several repetitions of the above procedure to remove tarry byproducts, only a white flocculant precipitate was observed. This material was isolated by filtration and dried: mp of 5 98 °C; ^{1}H NMR (acetone-d_6) δ 2.79 (s, 6 H, 2 Me), 3.00 (s, 6 H, 2 Me), 6.92 (d, 4 H, J = 9 Hz), 7.27 (d, 2 H, J = 9 Hz), 7.54 (d, 2 H, J = 9 Hz), 7.73 (br s, H, NH); ^{13}C NMR (Me_2SO-d_6) δ 35.76 (2 Me), 36.84 (2 Me), 119.4 (2 C atoms), 123.9 (2 C atoms), 124.1 (2 C atoms), 126.2, 127.6 (2 C atoms), 136.0, 136.4, 143.1, 157.9 (2 C=O); mass spectrum m/e (rel intensity) 360 (molecular ion, 99), 315 (55), 288 (24), 271 (16), 244 (7), 111 (13), 72 (100), 44 (17).

5-Chloro-2-nitroaniline (7b). The synthesis was based on a procedure reported by Vogel (1956). Into a 250-mL three-necked flask fitted with reflux condenser, addition funnel, and immersion thermometer was added 10 g (50 mmol) of 5-chloro-2-nitrobenzoic acid, 6. By use of the additional funnel, a mixture of 30 mL of fuming sulfuric acid and 5 mL of concentrated sulfuric acid was slowly added with stirring. Then 75 mL of chloroform was added as the mixture was rapidly stirred. The temperature was increased to 45 °C, and 5 g (59 mmol) of sodium azide was slowly added. The reaction mixture was refluxed for 3 h and then allowed to cool. The chloroform was removed by flash evaporation, and the mixture was poured onto crushed ice. The precipitated product was isolated, washed with water, and recrystallized from aqueous ethanol: mass spectrum m/e 172 (molecular ion).

2-Chloro-5-nitrophenyl Diazonium (8a) and 5-Chloro-2-nitrophenyl Diazonium (8b) Salts of 1,5-Naphthalenedisulfonic Acid. Into a beaker held in an ice bath was added 20 mL of concentrated hydrochloric acid and 10 mL of concentrated sulfuric acid. At a temperature of about 8 °C, 1 g of sodium nitrite was slowly added with stirring. While a reaction temperature of less than 15 °C was maintained, 2 g (11.6 mmol) of 2-chloro-5-nitroaniline (or 5-chloro-2-nitroaniline) dissolved in 20 mL of glacial acetic acid was added. The temperature was reduced to 5 °C, and an additional 1 g of sodium nitrite was added. After the mixture was stirred for 30 min, the excess nitrous acid was destroyed with urea. So that the stabilized diazonium salt could be prepared (Bachmann

and Hoffman, 1944), 4 g (12 mmol) of disodium 1,5-naphthalenedisulfonate was added. The reaction was stirred for about 1 h, and the precipitated product was filtered, washed with acetone, and dried.

2-Chloro-4′,5-dinitrobiphenyl (9a) and 5-Chloro-2,4′-dinitrobiphenyl (9b). Into a 100-mL flask was added 0.5 g (1.1 mmol) of the stabilized diazonium salt (**8a** or **8b**), 50 mL of dry nitrobenzene, 0.5 g of anhydrous sodium acetate, and 1 mL of acetic anhydride. The flask was fitted with a reflux condenser with drying tube, and the reaction was magnetically stirred at room temperature for 24 h. The mixture was then heated at 125 °C for 1 h. Following completion of reaction, nitrobenzene and other volatile materials were removed by introducing a stream of air into the sample (in a fume hood). The solid material remaining was slurried in acetone, and the insoluble byproducts were removed by filtration. The filtrate was reduced to dryness and redissolved in benzene. Initial purification was accomplished by loading the material onto a 2 × 15 cm column packed with dry silica gel, and 200 mL of benzene–hexane (1:1) was used for product elution. The eluate was taken to dryness, redissolved in a small amount of acetone, streaked onto 0.5 mm thick silica gel HF plates, and developed in a solvent of benzene–hexane (2:1). Standard techniques were used to isolate the product from the TLC plates: mass spectrum m/e 278 (molecular ion) for both **9a** and **9b**.

2-Chloro-4′,5-diaminobiphenyl (10a) and 5-Chloro-2,4′-diaminobiphenyl (10b). The method reported by Adams and Cohen (1941) for the catalytic reduction of ethyl 4-nitrobenzoate was used. Low-pressure hydrogenation of 1 g (3.6 mmol) of **9a** or **9b** was accomplished with 15 mg of platinum oxide catalyst in absolute ethanol. Reduction was carried out at about 40 psi of pressure until the hydrogen pressure ceased to fall (1 h). Catalyst and solvent were removed, and **10a** and **10b** were used without storage.

2-Chloro-4′,5-diacetaminobiphenyl (11a) and 5-Chloro-2,4′-diacetaminobiphenyl (11b). After low-pressure hydrogenation, **10a** or **10b** was dissolved in 10 mL of ethyl acetate and 1 mL of acetic anhydride. The reaction was heated at gentle reflux for 30 min, and then the ethyl acetate and excess acetic anhydride were removed by flash evaporation. The product was purified by TLC and C_{18} reversed-phase HPLC.

Data for **11a** are as follows: IR (KBr) 3455 (NH), 1674 (C=O), 1604, 1538, 1474, 1380 br, 1320, 1084, 1032, 840 cm^{-1}; mass spectrum m/e (rel intensity) 302 (molecular ion, 15), 260 (30), 218 (24), 182 (13), 154 (7), 43 (100); ^1H NMR (acetone-d_6) δ 2.05 (s, 3 H, Me), 2.07 (s, 3 H, Me), 7.32 (s, H), 7.43 (d, H, J = 5.3 Hz), 7.38 and 7.75 (2 d, 4 H, J = 7.0 Hz, A_2B_2), 7.66 (d, H, J = 5.3 Hz), 9.29 (br s, 2 H, 2 NH, exchangeable with D_2O).

Data for **11b** are as follows: IR (KBr) 3290 (NH), 1655 (C=O), 1600, 1525, 1385 (d), 1315 (d), 1288, 1120, 1042 (d), 840, 630 cm^{-1}; mass spectrum m/e 302 (molecular ion), fragmentation pattern same as **11a**; ^1H NMR (acetone-d_6) δ 1.29 (d, 3 H, J = 1.8 Hz), 2.08 (d, 3 H, J = 1.8 Hz), 7.26 (s, H), 7.30 (d, 2 H, J = 8.0 Hz), 7.28 and 7.74 (2 d, 4 H, J = 8.6 Hz, A_2B_2), 8.03 (d, H, J = 8.0 Hz), 8.37 (br s, H, NH, exchangeable with D_2O), 9.26 (br s, H, NH, exchangeable with D_2O); ^{13}C NMR (Me_2SO-d_6) δ 23.79 (Me), 24.28 (Me), 120.23 (2 C atoms), 126.38, 128.13 (2 C atoms), 130.23, 130.28 (2 C atoms), 130.47, 133.0, 135.44, 140.42, 169.09 (2 C=O).

2-Chloro-4′,5-bis(*N′,N′*-dimethylureido)biphenyl (12a) and 5-Chloro-2,4′-bis(*N′,N′*-dimethylureido)biphenyl (12b). The catalytic reduction step with 150 mg (0.54 mmol) of **9a** or **9b** was performed to yield about 117 mg of **10a** or **10b**. The catalyst and solvent were removed, and the chlorodiaminobiphenyl was treated with 50 mL of acetonitrile, 10 mL of pyridine, and 15 mL of dimethylcarbamyl chloride (Elder and Koch, 1977). The mixture was heated at reflux for 1 h. The product was purified first by preparative TLC and finally by HPLC.

Data for **12a** are as follows: ^1H NMR (Me_2SO-d_6) δ 2.90 (s, 6 H, 2 Me), 2.92 (s, 6 H, 2 Me), 7.21–7.49 (m, 7 H, Ph–Ph), 8.39 (s, 2 H, 2 NH); ^{13}C NMR (Me_2SO-d_6) δ 36.18 (2 Me), 36.77 (2 Me), 119.07 (2 C atoms), 119.36, 122.0, 123.2, 128.92 (2 C atoms), 129.41, 132.04, 139.26, 139.84, 140.23, 155.44 (C=O), 155.64 (C=O); mass spectrum m/e 360 (molecular ion), same fragmentation pattern as **12b**. Product was very slightly soluble in acetone.

Data for **12b** are as follows: ^1H NMR (acetone-d_6) δ 2.81 (s, 6 H, 2 Me), 3.03 (s, 6 H, 2 Me), 6.98 (br s, H, NH, exchangeable with D_2O), 7.23 (s, H), 7.28 (d, H, J = 8.6 Hz), 7.33 and 7.64 (2 d, 4 H, J = 8.6 Hz, A_2B_2), 7.9 (br s, H, NH, exchangeable with D_2O), 8.16 (d, H, J = 8.6 Hz); ^{13}C NMR (Me_2SO-d_6) δ 35.89 (2 Me), 36.18 (2 Me), 119.36 (2 C atoms), 126.87 (2 C atoms), 128.04, 128.63 (2 C atoms), 129.02, 130.58, 135.65, 137.12, 140.33, 155.73 (2 C atoms, C=O); mass spectrum m/e (rel intensity) 360 (molecular ion, 20), 315 (99), 270 (63), 244 (13), 72 (100), 45 (48), 44 (65). Chlorine isotopic cluster indicated one chlorine was present. Product was moderately soluble in acetone.

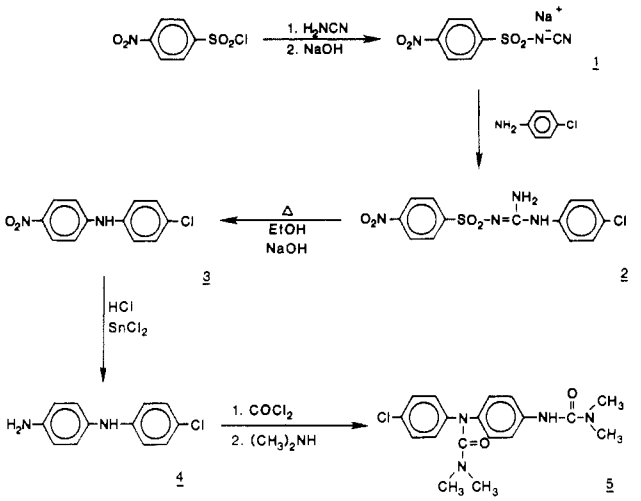
One-Step Synthesis of 9a and 9b. Into a 100-mL flask was added 1.57 g (10 mmol) of 4-chloronitrobenzene, 50 mL of acetic anhydride, 2 g of sodium acetate, and 2.37 g (10 mmol) of 4-nitrobenzenediazonium tetrafluoroborate. The reaction mixture was stirred for 24 h at room temperature. The dissolved products were separated from the precipitated salts, and then purification was conducted as described earlier. The separation of **9a** from **9b** was accomplished by HPLC using a Radial-Pak silica gel column with dichloromethane–isooctane (2:8) as the developing solvent.

Hydrolysis of the Coupled Unknown Photoproduct of Monuron. This reaction was carried out according to the procedure described for the hydrolysis of diuron (Tanaka and Wien, 1971). To approximately 300 mg of the unknown material was added 7 mL of methyl cellosolve and 10 mL of 6 N sodium hydroxide. Under an atmosphere of nitrogen, the mixture was heated at 130 °C for 3.5 h. The product was extracted with hexane, and the hexane fraction was dried over anhydrous sodium sulfate, filtered, and treated with acetic anhydride. The acetylated derivative of the hydrolyzed photoproduct was purified by TLC and C_{18} reversed-phase HPLC.

RESULTS AND DISCUSSION

Mass spectrometry of the unknown photoproduct gave a molecular ion at m/e 360 to establish the molecular mass as being equivalent to the sum of two monuron molecules minus hydrogen chloride. NMR data taken with a Varian A60A spectrometer (Tanaka et al., 1977) showed an unresolved multiplet of eight protons in the aromatic region and two singlet peaks corresponding to the methyl protons of two different dimethylamino moieties in the aliphatic region. The FMN-sensitized photolysis of 4-chloroaniline to afford 4-chloro-4′-(4-chloroanilino)azobenzene (Rosen et al., 1970) gave precedence for the displacement of chlorine by a 4-chloroanilino moiety at the para position of an aromatic ring. On the basis of the above information, a substituted diphenylamine was proposed as the structure of the unknown photoproduct. Photocoupling of the anilino nitrogen of monuron at the para position of a second molecule of monuron would afford a substituted di-

Scheme I



phenylamine (structure 5, Scheme I).

By use of the reaction sequence of Scheme I, 5 was synthesized, and the NMR data verified that rearrangement of 2 to 3 afforded a para-substituted isomer as reported by Backer and Wadman (1949). The mass spectral fragmentation pattern and the NMR spectrum of 5 did not, however, agree with the spectral data of the unknown. Hence, it was positively established by synthesis that 5 was not the structure of the unknown photoproduct even though coupling reactions of this nature were reported by Rosen et al. (1970).

With increased sensitivity and resolution provided by the JEOL FX90Q Fourier transform NMR spectrometer, a para pattern (A_2B_2) was observed in the aromatic region, and two broad peaks, exchangeable with deuterated water, were observed to suggest the presence of two different NH groups. Since 5 was not the structure of the unknown and two different NH groups were apparently present, it now appeared that a Fries type of rearrangement similar to that reported by Mazzocchi and Rao (1972) for the photolysis of monuron in methanol may have occurred. If a (dimethylamino)carbonyl moiety had migrated during the coupling process to a ring position ortho to the central diphenylamine nitrogen, this structure would then allow for two successive losses of m/e 45 by mass spectral analysis to afford an ion fragment of m/e 270 as was observed with the unknown. Rather than synthesize this suggested structure, however, it appeared easier to simplify the photoproduct structure by hydrolyzing the side chains and stabilizing the freed amino groups by acetylation.

After hydrolysis and acetylation, the derivatized unknown photoproduct gave a mass spectral molecular ion at m/e 302 to indicate the removal of two (dimethylamino)carbonyl groups. Consequently, the photo-Fries rearrangement of a (dimethylamino)carbonyl group to a ring position during coupling could be ruled out. The NMR spectrum of the derivatized product gave an A_2B_2 pattern in the aromatic region, and two different NH groups were still observed after diacetylation. Therefore, the two phenyl groups were not attached to nitrogen to afford a diphenylamine structure, but rather ring coupling had apparently occurred to yield a biphenyl structure (Tanaka et al., 1980). However, the exact positions of dimethylurea substitution on the aromatic ring were not clearly established.

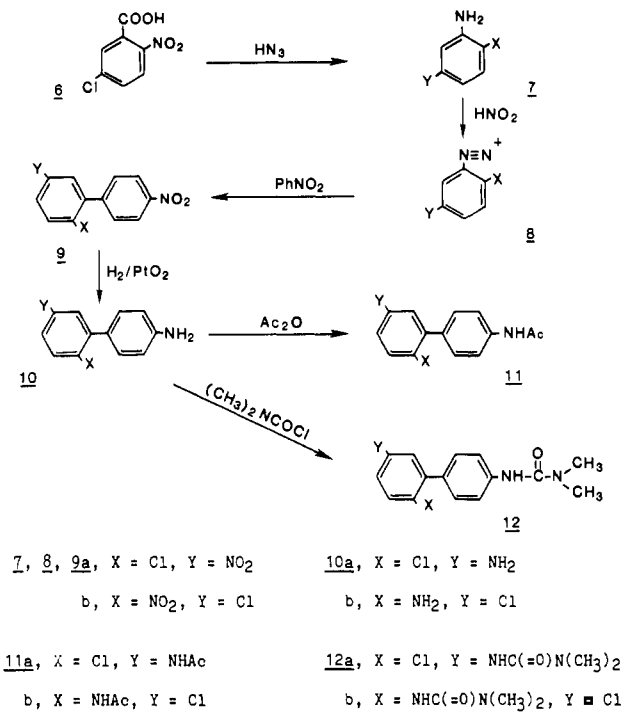
By use of C_{18} reversed-phase HPLC for purification of the derivatized photoproduct, two major peaks were observed. Upon spectral examination, the two peaks gave identical mass spectra but different NMR spectra.

Table I. HPLC Separation of the Isomeric Biphenyls

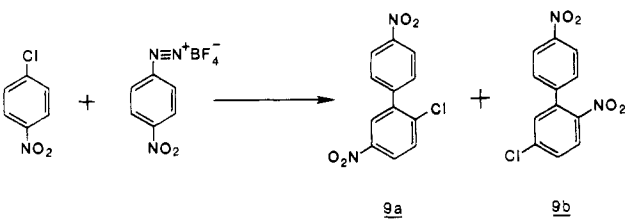
Radial-Pak	compound	retention time,[a] min
C_{18}	11a	12.0
	11b	14.0
C_{18}	12a	15.9
	12b	16.0[b]
CN	12a	6.2
	12b	8.1

[a] Isocratic solvent was 18% acetonitrile in water, and the flow rate was 3 mL/min. [b] Peak for 12b was a small shoulder on 12a.

Scheme II



Scheme III



Therefore, the unknown biphenyl photoproduct was actually two unresolved isomeric compounds with 92% contained in the larger peak and 8% in the smaller peak. This ratio was later verified by measurement of the isomer ratio of the intact photoproducts which were separable by HPLC using a nitrile column (Table I).

Generally, biphenyls are prepared by free radical coupling reactions (Bachmann and Hoffman, 1944). Since photoreactions are a good source of free radicals, some type of radical process was apparently occurring to afford the two substituted biphenyls. If radical addition of excited monuron with a second molecule of monuron was occurring, only two biphenyl structures would be produced owing to the symmetry of para substitution. Starting with **7a** and **7b** with known substitution patterns, we prepared a small amount of **11a** and **11b** by Scheme II. The synthetic materials were quickly compared with the derivatized unknowns by using HPLC retention times (Table I)

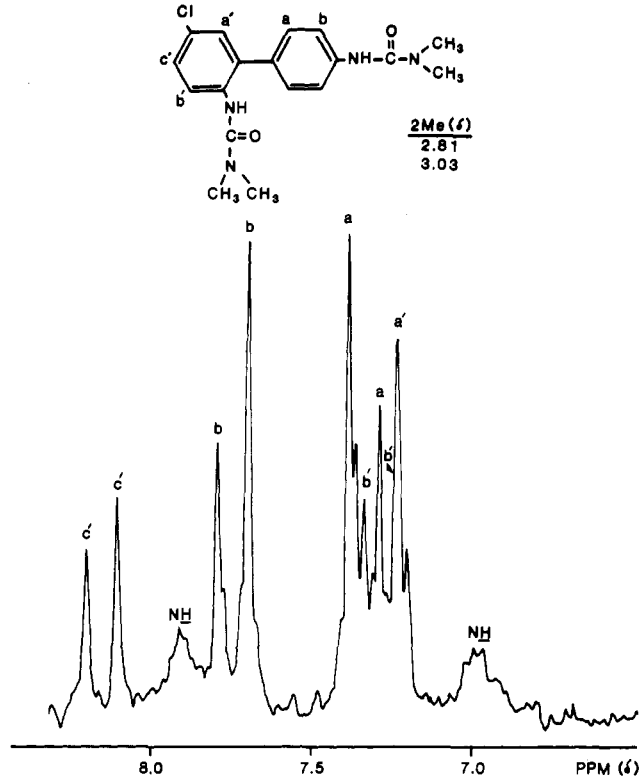


Figure 1. NMR spectrum of the aromatic region of the 5-chloro isomer (**12b**) of the unknown biphenyl photoproduct.

and mass spectral analysis. For confirmation that the HPLC and mass spectral data were in agreement with the unknowns, larger amounts of **9a** and **9b** were prepared as a mixture using the one-step reaction shown in Scheme III. The identities of the two positional isomers afforded by Scheme III were determined with the synthetic standards prepared by Scheme II. When **9a** and **9b** from Scheme III were employed as starting material, sufficient quantities of **11a**, **11b**, **12a**, and **12b** were prepared by Scheme II for spectral comparison with the unknown products.

The isomer observed as 92% of the unknown photoproduct was identified as 5-chloro-2,4′-bis(*N′*,*N′*-dimethylureido)biphenyl. The derivatized unknown was compared with synthetic **11b** by ^{1}H NMR, ^{13}C NMR, IR, and mass spectrometry. In addition, for verification that no changes had occurred during hydrolysis, the intact unknown photoproduct was compared with synthetic **12b** by ^{1}H NMR (Figure 1), ^{13}C NMR, and mass spectrometry. By spectral comparison, in all cases, the synthetic and unknown materials were identical.

The isomer observed as 8% of the unknown photoproduct was identified as 2-chloro-4′,5-bis(*N′*,*N′*-dimethylureido)biphenyl. The derivatized unknown was compared with synthetic **11a** by ^{1}H NMR (Figure 2), IR, and mass spectrometry. The intact photoproduct was compared with synthetic **12a** by ^{1}H NMR and mass spectral analysis. The synthetic and unknown materials were identical.

With the identification of **12** as a mixture of biphenyls, there may be some concern that an accumulation of these materials might occur in the environment. Time–course studies with ultraviolet lamps (Tanaka et al., 1977) have shown that an approximate steady-state concentration of **12** was reached when approximately 40% of the monuron was decomposed. At steady state levels, the yield of **12** was about 1.5% based on monuron. When aqueous monuron was photolyzed to completion, **12** was also completely degraded. Therefore, an environmental buildup

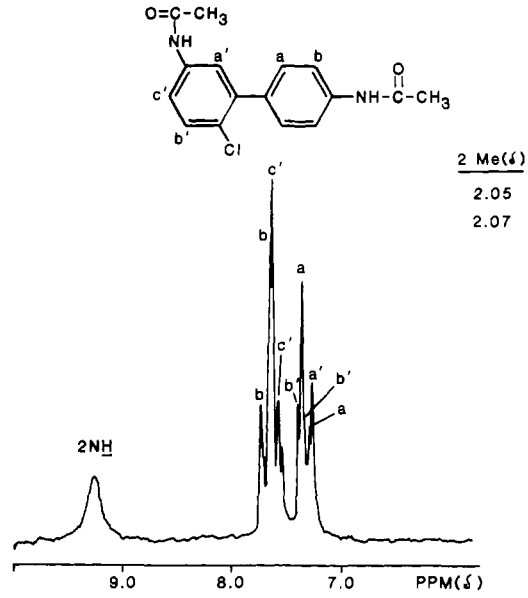


Figure 2. NMR spectrum of the aromatic region of the 2-chloro isomer (**11a**) of the unknown biphenyl photoproduct after hydrolysis and diacetylation.

of these biphenyls would not normally be expected.

According to recent legal action (*Chem. Eng. News*, 1980), monochlorosubstituted biphenyls are now being classified as polychlorinated biphenyls (PCB's); thus, **12a** and **12b** would be classified as PCB's. Furthermore, **12** and its photobyproducts may be part of a group of compounds which may be of concern because some aminobiphenyls have been previously reported as carcinogens (Weisburger and Weisburger, 1966). In our studies, photoproducts with free amino groups have not been identified, and the biological activity of the dimethylcarbamylated aminobiphenyls has not been established.

In this study the unknown monuron photoproduct was determined to be a mixture of two isomeric compounds that were clearly identified as substituted biphenyls. Therefore, the results suggest that biphenyl compounds could be formed photolytically in aqueous solution from pesticidal materials that are currently being applied to environmental systems.

Further studies are being conducted to survey a series of substituted phenylurea herbicides to determine if biphenyl formation is a general reaction during photolysis. Materials are being examined under laboratory conditions to determine if biphenyls can be produced, and the compounds that do give positive results are then examined by photolysis with natural sunlight. The results of this investigation may give some insight as to the possibility for photolytic biphenyl formation under naturally occurring environmental conditions.

LITERATURE CITED

Adams, R.; Cohen, F. L. "Organic Syntheses"; Gilman, H.; Blatt, A. H., Eds.; Wiley: New York, 1941; Collect. Vol. I, p 240.

Bachmann, W. E.; Hoffman, R. A. "Organic Reactions"; Adams, R.; Bachmann, W. E.; Fieser, L. F.; Johnson, J. R.; Snyder, H. R., Eds.; Wiley: New York, 1944; Vol. II, p 248.

Backer, H. J.; Wadman, S. K. *Recl. Trav. Chim. Pays-Bas* **1949**, *68*, 595.

Chem. Eng. News **1980**, *58* (41), 13.

Elder, V. A.; Koch, B. L. *J. Agric. Food Chem.* **1977**, *25*, 973.

Fieser, L. F.; Fieser, M. "Reagents for Organic Synthesis"; Wiley: New York, 1967; Vol. I, p 333.

Mazzocchi, P. H.; Rao, M. P. *J. Agric. Food Chem.* **1972**, *20*, 957.

Moed, H. D. Thesis, Groningen, 1947, p 70.

Rosen, J. D.; Siewierski, M.; Winnet, G. *J. Agric. Food Chem.* **1970**, *18*, 494.

Rosen, J. D.; Strusz, R. F. *J. Agric. Food Chem.* **1968**, *16*, 568.
Searle, N. E.; Cupery, H. E. "Organic Syntheses with Isotopes"; Murray, A., III; Williams, D. L., Eds.; Interscience: New York, 1958; Part I, pp 599–601.
Shriner, R. L.; Horne, W. H.; Cox, R. F. B. "Organic Syntheses"; Blatt, A. H., Ed.; Wiley: New York, 1943; Collect. Vol. II, p 453.
Tanaka, F. S. *J. Agric. Food Chem.* **1970**, *18*, 213.
Tanaka, F. S.; Wien, R. G. *J. Labelled Compd.* **1971**, *7*, 459.
Tanaka, F. S.; Wien, R. G.; Hoffer, B. L. "Abstracts of Papers", Second Chemical Congress of the North American Continent, Las Vegas, NV, Aug 1980; American Chemical Society: Washington, DC, 1980; PEST 7.
Tanaka, F. S.; Wien, R. G.; Zaylskie, R. G. *J. Agric. Food Chem.* **1977**, *25*, 1068.
Vogel, A. I. "A Textbook of Practical Organic Chemistry", 3rd ed.; Wiley: New York, 1956; p 919.
Weisburger, J. H.; Weisburger, E. K. *Chem. Eng. News* **1966**, *44* (6), 124.

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Chemical Quality, in Vitro Cellulose Digestion, and Yield of Tall Fescue Forage Affected by Mefluidide

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Tall fescue (*Festuca arundinacea* Schreb. "Ky 31") was treated with mefluidide at 0 and 0.28 kg/ha on April 1, April 15, April 29, or May 13 in 1976. Forage was sampled through Aug 9, and dry matter yields were obtained 2 weeks after application and on Sept 15. The April 29 and May 13 treatments had lowered cellulose content through July 8 and Aug 9, respectively. All treatments of mefluidide except the April 1 treatment increased crude protein content on Aug 9. In vitro cellulose digestion was increased ($P < 0.05$) and may be related to increased crude protein and decreased cellulose content. Dry matter yield was reduced ($P < 0.05$) only at 2 weeks after the April 1 and April 15 applications. Mefluidide treatments made between April 1 and May 13 enhanced forage quality. Data indicate that mefluidide affects tall fescue quality longer than previous considered.

Tall fescue (*Festuca arundinacea* Schreb.) is the predominant cool-season pasture species in the transition zone that separates the northern and southern regions in the eastern half of the United States. Kentucky 31 is the predominant cultivar. Tall fescue quality is often inadequate to produce maximum lean meat by ruminants. Forage quality decreases from the onset of reproductive growth until maturity (Blazer, 1964; Norman and Richardson, 1937). Total sugar and digestible energy decrease (Sullivan, 1969) and cellulose content increases (Phillips et al., 1954) as tall fescue matures. Burrus (1957) found that inhibition of the maturation process of tall fescue with frequent clippings (14-day intervals) produced a high-quality forage.

Mefluidide [*N*-[2,4-dimethyl-5-[[(trifluoromethyl)-sulfonyl]amino]phenyl]acetamide] is a plant growth regulator that inhibits seed head production of many cool-season grasses. Glenn et al. (1980) found that mefluidide applied on April 29 enhanced total water-soluble carbohydrate and crude protein concentration of tall fescue and decreased cellulose content through mid-May in 1975 and mid-June in 1976. The effect of mefluidide on quality later in the summer was not determined. Dry matter yield of tall fescue was decreased 21 days after treatment with 0.28 and 0.56 kg/ha mefluidide in 1975 and 0.56 kg/ha in 1976. However, there was no effect of mefluidide on dry matter yield by the second harvest.

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The objectives of this study were to examine cellulose content, crude protein content, and in vitro cellulose digestion of tall fescue through Aug 9 after treatment with mefluidide at several different dates. Dry matter yield of mefluidide-treated tall fescue was examined through Sept 15.

MATERIALS AND METHODS

Kentucky 31 tall fescue was mowed and fertilized with 330 kg/ha 16–16–16 on March 23, 1976. Mefluidide was applied to the tall fescue at 0 or 0.28 kg/ha on April 1, April 15, April 29, or May 13. The tall fescue sward was young and vegetative on April 1 and in the late boot to early bloom stage on May 13. The plots were 2 by 7.6 m and were distributed in a randomized complete block design with four replications. The study was conducted at Lexington, KY, and with Maury silt loam (Typic Paleudalfs). Dry matter yields were obtained from a 0.9 by 6.7 m area through the middle of each plot 14 days after treatment and again on Sept 15. Immediately after harvest for yield determination the remaining portion of each plot was harvested. Grab samples were obtained from each plot on the day of but prior to treatment, May 13, July 11, July 8, and Aug 9. Precautions were taken to sample an area from each plot other than the area from which yields were obtained.

The samples were analyzed for cellulose and crude protein content and in vitro cellulose digestion was determined. The cellulose component of tall fescue was analyzed by the acetic–nitric acid (10:1) (v/v) method (Crampton and Maynard, 1938). Crude protein was calculated from total nitrogen determined by the Kjeldahl

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