

Photochemistry of *N*-*sec*-Butyl-4-*tert*-butyl-2,6-dinitroanilineJack R. Plimmer* and Ute I. Klingebiel¹

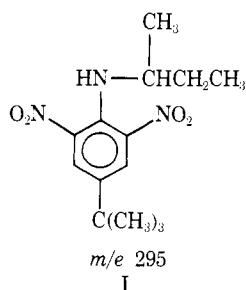
The herbicide *N*-*sec*-butyl-4-*tert*-butyl-2,6-dinitroaniline photodecomposed in water or methanol. Irradiation in sunlight or light from a mercury arc gave the dealkylated nitroso compound (4-*tert*-butyl-2-nitro-6-nitrosoaniline) as the major product together with a mixture of minor photoproducts, including 4-*tert*-butyl-2,6-dinitroaniline. The structures of the minor products were investigated by mass spectrometry and pro-

vide evidence for the proposed mechanism of photochemical reaction. Two pathways may operate simultaneously. One involves excitation and subsequent reduction of the nitro group coupled with oxidation of other reactant molecules or solvent. The other minor pathway requires a displacement of the nitro group in either a radical or a photonucleophilic reaction.

The 2,6-dinitroaniline herbicides absorb light strongly in the visible (350–450 nm) region of the spectrum. Field-applied herbicides of this class might therefore be expected to undergo photochemical reaction. The practical consequences of photodecomposition have been demonstrated for trifluralin (α,α,α -trifluoro-2,6-dinitro-*N,N*-dipropyl-*p*-toluidine) which shows enhanced herbicidal activity when it is incorporated in soil as compared with surface application. Loss by volatilization or by photodecomposition may decrease its effectiveness. Loss by both pathways has been considered and, under certain conditions, either factor may contribute to this reduction (Pieczarka *et al.*, 1962; Wright and Warren, 1965).

Several studies of the photochemistry of *N*-alkylated nitroanilines have been concerned with the mechanism of *N*-dealkylation (Russell, 1964; Meth-Cohn, 1970; Davidson *et al.*, 1971). Photochemical dealkylation of trifluralin occurred but many unidentified products were obtained on irradiation (Day, 1969; McMahon, 1966). Recently, benzimidazole derivatives have been obtained as products of vapor-phase photolysis of trifluralin (Crosby and Moilanen, 1972) and as photoproducts of dinitramine (*N,N*-diethyl- α,α,α -trifluoro-3,5-dinitrotoluene-2,4-diamine) (Newsom and Woods, 1973).

The dinitroaniline herbicide, *N*-*sec*-butyl-4-*tert*-butyl-2,6-dinitroaniline (I), may be useful for controlling a range



of broadleaf weeds and annual grasses in some agronomic and horticultural crops. It is a brilliant orange crystalline solid (λ_{\max} 432 nm) and is only slightly soluble in water (ca. 1 ppm at 20°). Although it appears to be less readily photodecomposed than trifluralin, I is altered on exposure to sunlight. In this paper, structures postulated for several photoproducts of I (Plimmer and Klingebiel, 1972) are discussed in relation to mechanisms for the photoreduction of nitrobenzenes.

Agriculture Research Center, Agricultural Research Service, U. S. Department of Agriculture, Beltsville, Maryland 20705.

¹ Agricultural Environmental Quality Institute, Agricultural Research Service, U. S. Department of Agriculture, Beltsville, Md. 20705.

MATERIALS AND METHODS

Chemicals and Instrumental Techniques. Purified I, supplied by Amchem Products Inc., Ambler, Pa., mp 61.5–62°, was homogeneous on thin-layer chromatography (tlc), gas chromatography (gc), and high-pressure liquid chromatography. 4-*tert*-Butyl-2,6-dinitroaniline, mp 134°, was also supplied by Amchem Products Inc.

Low-resolution spectra were obtained on a Perkin-Elmer Model GC 270 combination gas chromatograph-mass spectrometer using direct or gc inlet systems. High-resolution mass spectra were determined on an AEI-MS 9 mass spectrometer by Professor R. C. Dougherty at Florida State University, Tallahassee, Fla. Infrared spectra were recorded in KBr on a Perkin-Elmer Model 621 infrared spectrophotometer. Ultraviolet spectra were determined on a Carey Model 15 instrument. The high-pressure liquid chromatograph used was a DuPont Model 830 fitted with an ultraviolet photometric detector and equipped with a 1 m × 2.1 mm i.d. column packed with "Permaphase" ODS using methanol-water mixtures as the mobile phase.

Irradiation Experiments. (1) *Natural Sunlight.* I (90 mg) dissolved in ethanol (10 ml) was added to distilled water (11 l.) contained in six 2-l. borosilicate glass erlenmeyer flasks. The mouths of the flasks were covered to prevent contamination. The suspension was exposed to sunlight for 14 days outdoors. Similar mixtures were maintained in the dark as controls in all experiments. Products were extracted by shaking with ether. The extract was dried (MgSO_4) and evaporated to a brown syrup. Column chromatography on silica gel (Merck, silica gel 60) was used to separate fractions. Fractions were eluted from the column with hexane, benzene, and ethyl acetate successively and were further purified by TLC.

(2) *Sunlamp.* A similar experiment was performed using a 40-W GE sunlamp (maximum output ca. 310 nm) as a source of illumination. Products were examined after 1 week as described in method 1. In a related experiment, 2 g of I was irradiated in methanol (1 l.) for 23 hr to examine the influence of solvent on the products of the reaction.

(3) *Mercury Vapor Lamp.* A mercury vapor lamp (Hannovia Catalog No. 679-A-36) housed in a double-walled water-cooled quartz well was immersed in a solution of I in methanol contained in the reaction vessel. Nitrogen was bubbled through the solution during the irradiation. A borosilicate glass filter sleeve was used to exclude light of wavelength less than 280 nm. Similar sleeves of Corex or Vycor excluded light of wavelength less than 260 or 220 nm, respectively.

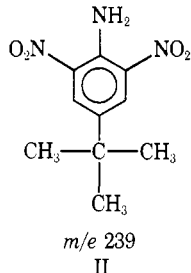
In a typical experiment, I (1.25 g) in methanol (250 ml) was irradiated (Corex filter) for 5.25 hr. The solution was evaporated and the residual syrup was fractionated by column chromatography on silica gel.

(4) *Comparison of Photolysis Rates of I with Those of Other Dinitroaniline Herbicides and a Dinitrophenylenediamine.* I, trifluralin, dinitramine, and CGA 10832 [*N*-(cyclopropylmethyl)- α,α,α -trifluoro-2,6-dinitro-*N*-propyl-*m*-toluidine] were dissolved in methanol (2 g/l.). Samples of each solution (5 ml) were sealed into borosilicate glass ampoules and exposed to sunlight for 8 hr. The amount of unchanged herbicide remaining was determined by gas chromatography.

(5) *Irradiation of I in the Solid State.* I was applied as a streak to a silica-coated glass plate. This was covered with a quartz plate and exposed to laboratory illumination. Similar plates were exposed to a sunlamp (>310 nm) and to natural sunlight. In a second experiment pure I was dissolved in acetone and the solvent was allowed to evaporate from the inside surface of an irradiation reaction vessel. The solid was exposed to a mercury lamp (Corex filter). Products were examined by tlc.

RESULTS AND DISCUSSION

I was decomposed by sunlight more slowly than the dinitroaniline herbicide, trifluralin, or the dinitrophenylenediamine, dinitramine. After 8 hr exposure to sunlight in methanolic solution, 75% of I could be recovered unchanged. Corresponding recoveries were, for trifluralin, 40%, for dinitramine, 25%, and for CGA 10832, 50%. In a relatively short period of irradiation at longer wavelengths (sunlight or sunlamp) a major product in methanol or water was 4-*tert*-butyl-2-nitro-6-nitrosoaniline (III). This compound accounted for approximately 76% of the total I consumed in a 5.25-hr irradiation in methanol with a Corex filter. Most experiments also afforded a small amount of 4-*tert*-butyl-2,6-dinitroaniline (II).



The first fraction eluted by benzene-hexane (1:1) from a silica gel column contained unchanged I (1.1 g). The second fraction (6 mg) crystallized as an orange-yellow solid; purified by vacuum sublimation it had mp 131.5°. The third fraction (86 mg) crystallized to give an orange-brown solid (needles) with a greenish luster.

The second fraction was identified as 4-*tert*-butyl-2,6-dinitroaniline by comparison of its spectral properties (ir, uv, and mass) and chromatographic mobility with those of an authentic sample. The third fraction was the major photolysis product.

The remaining fractions 4-11 were separated as discrete bands on the column but required further purification by tlc. Several milligrams of each of the crude fractions 4-7 were obtained. Later fractions were isolated in smaller quantities. Mass spectrometry was the primary technique used for structural identification.

The remaining photoproducts were present in small or trace quantities and the greater complexity of the product mixture with increased irradiation periods presumably resulted from the photolability of the products. These ranged in color from orange to violet. Examination by mass spectrometry (solids inlet) showed no evidence of dimeric products.

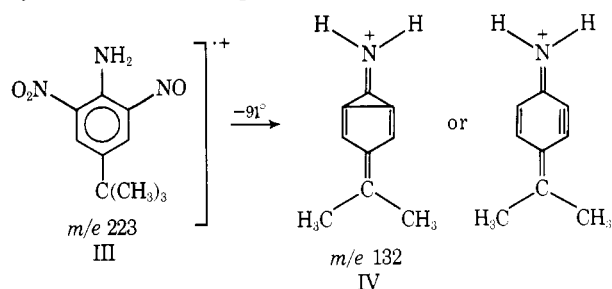
After I on a silica gel coated plate had been exposed to laboratory illumination for 1 month, no photoproducts could be detected when the plate was developed with benzene. Samples of solid I exposed to light of wavelengths

greater than 260 nm for 3.5 hr showed only small amounts of photoproducts. Fractionation of the mixture on a silica gel column gave I and the dealkylated product II on elution with hexane-benzene (1:1). Ethyl acetate eluted the polar fractions, one of which had $M = 277$, with m/e 262 ($M - 15$), 261 ($M - 16$), 260 ($M - 17$), 249 ($M - 28$), 246 ($M - 31$), and 234 ($M - 43$). Similar results were observed when the plate was exposed to natural sunlight for 8 hr.

Qualitatively similar results were obtained in water and in methanol after sunlamp or sunlight irradiation. In each case, the first three fractions were as reported above and as many as 16 products could be separated by tlc in one instance. Irradiation of I in methanol at shorter wavelengths produced similar mixtures of products and the solution darkened during the initial irradiation period. Longer periods of irradiation modified the photoproducts and the solution became lighter in color.

The dealkylated photoproduct of I, 4-*tert*-butyl-2,6-dinitroaniline, has the same maximum as the parent compound (λ_{max} 432 nm) in ethanol (ir 3370, 3480 cm^{-1} (NH_2)).

Modification of the 2,6-dinitroaniline chromophore in the products was indicated by a shift in absorption maximum. The formation of α,α,α -trifluoro-2-nitro-6-nitroso-*p*-toluidine from trifluralin was accompanied by a long-wavelength shift in absorption maximum from 376 to 434 nm. The major photolysis product III of I showed an analogous long-wavelength shift of the absorption maximum to 457 nm. On tlc its mobility was similar to that of II. The compound had ir bands at 3380 and 3495 cm^{-1} assigned to NH_2 . Other ir bands in the 3300-3500- cm^{-1} region may be accounted for by the existence of internally hydrogen-bonded structures or an iminohydroxylamine tautomer. The empirical formula was obtained by high-resolution mass spectrometry. The molecular ion was at m/e 223 and had the composition $C_{10}H_{13}N_3O_3$. Fragment ions at m/e 208 ($M - 15$), 178 ($M - 45$), and 132 (base peak) corresponded to the molecular compositions $C_9H_{10}N_3O_3$, $C_9H_{10}N_2O_2$, and $C_9H_{10}N$, respectively. These fragments represent the loss of CH_3 , ($CH_3 + NO$), and ($CH_3 + NO + NO_2$), respectively, and provide evidence for the allotted structure. The ion at m/e 132 (base peak) may be stabilized through a quinoid form IV.



Some discussion of the mass spectrometric fragmentation patterns of the minor photoproducts is relevant, since their structures are significant in the discussion of photochemical pathways and postulated mechanisms. Their molecular ions are shown in Table I. In a number of cases, structures have been postulated. The mass spectrometric fragmentation of a range of model compounds related to the dinitroaniline herbicides has been investigated to provide background information (Plimmer and Klingebiel, 1973).

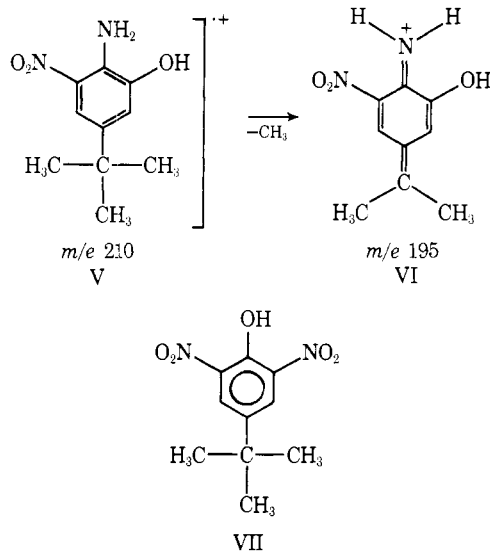
Most products had an odd mass number, indicating that no nitrogen had been lost. However, two compounds had $M = 210$ and $M = 266$. We postulate that these are phenolic derivatives in which a nitro group has been replaced by a hydroxyl in either a radical or photonucleophilic process (Calvert and Pitts, 1966; Crosby and Wong, 1970). The compound $M = 210$ (V) showed fragment ions

Table I. Photolysis Products of I^a

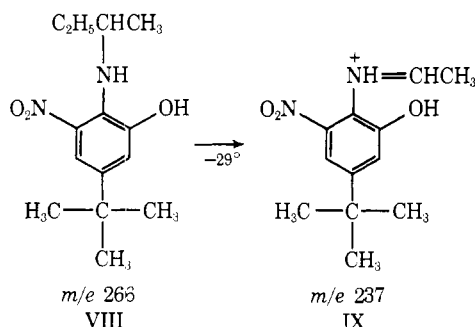
1	2	3
295 (I)	295	220
210 (XII)	223	240
223 (III)	239	247
239 (II)	266	267
251 (IX)	277	269
266 (VII)	293	273
279 (VIII)		275
		282
		287

^a 1, molecular ions for which structures have been postulated; 2, molecular ions most frequently observed under all photolytic conditions; 3, other molecular ions detected.

at m/e 195 ($M - 15$), 179, 177, 167 ($M - 43$), and 149 ($M - 61$). The base peak at m/e 195 may be ascribed to a stable quinoid structure VI. Stabilization of such a structure by localization of the charge at the nitrogen atom should afford an abundant ion; an alternative structure having the hydroxyl function at C-1 is unlikely, since the model compound VII did not show an abundant ion at $M - 15$. Losses of 28 (CO) or 46 (NO_2) from the base peak indicated the presence of phenolic and nitro substituents in the molecule.

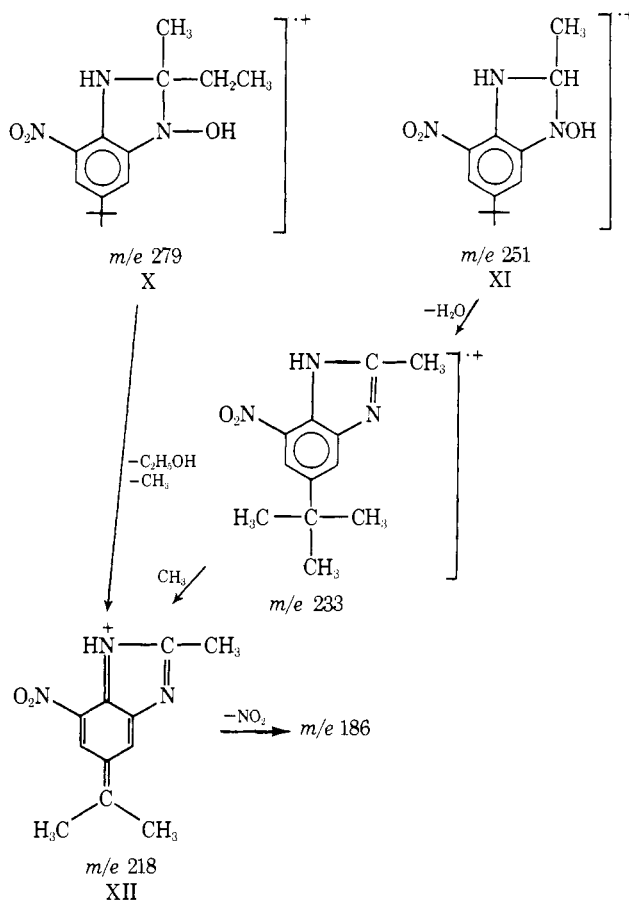


Structure VIII may be postulated for the compound $M = 266$. The replacement of one nitro substituent in I has occurred to give a phenol. The base peak at m/e 237 ($M - 29$) (IX) represents the formation of a stable ion by a fragmentation pattern frequently observed in alkylamines (McLafferty, 1966).



Among the photolysis products the only evidence for cyclization lies in the detection of two compounds having postulated structures X and XI with $M = 279$ and $M = 251$, respectively. Their fragmentation patterns are similar. The former compound showed a peak at m/e 233 (M

- 46) and an intense peak at m/e 218. The latter also has base peak at m/e 218 and loses CH_3 and H_2O from the parent ion to give fragments at m/e 236 and 233. The fragment ion at m/e 218 has an extremely high relative abundance, suggesting a heterocyclic (benzimidazole) structure such as XII. The compositions of this ion, $\text{C}_{11}\text{H}_{12}\text{N}_3\text{O}_2$, and other fragment ions were established by high-resolution measurements.



Studies of trifluralin revealed that *N*-alkyldinitroanilines are reduced and dealkylated by light. Of ten photo-products obtained by irradiation of trifluralin in hexane or methanol solution at 253.7 nm, only two compounds, α,α,α -trifluoro-2,6-dinitro-*N*-propyl-*p*-toluidine and α,α,α -trifluoro-2,6-dinitro-*p*-toluidine, were identified. The concentration of the former diminished rapidly after 1 hr, whereas the latter remained at a high level for up to 5 hr (Day, 1969).

McMahon (1966) further investigated the reaction, since photochemical dealkylation provided a possible model system for microsomal dealkylation reactions. Irradiation of the monomethyl analog of trifluralin, α,α,α -trifluoro-*N*-methyl-2,6-dinitro-*p*-toluidine, in methanol or *n*-heptane solution (10^{-3} M) under nitrogen for 3 hr with a 450-W mercury lamp gave α,α,α -trifluoro-2-nitro-6-nitroso-*p*-toluidine and formaldehyde. The former compound was also obtained from the mono-*N*-propyl analog of trifluralin, together with propionaldehyde. *N*-Dealkylation might involve the transfer of an oxygen atom from the nitro group to the carbon atom directly attached to the anilino nitrogen atom analogous to the photochemical rearrangement of *o*-nitrobenzaldehyde to *o*-nitrosobenzoic acid (Calvert and Pitts, 1966). However, in the latter case oxygen is donated to the carbon atom attached directly to an aromatic ring.

The mechanism of dealkylation must depend on the sequence of reactions that follows the photoexcitation of the aromatic nitro group. Nitrobenzene itself undergoes pho-

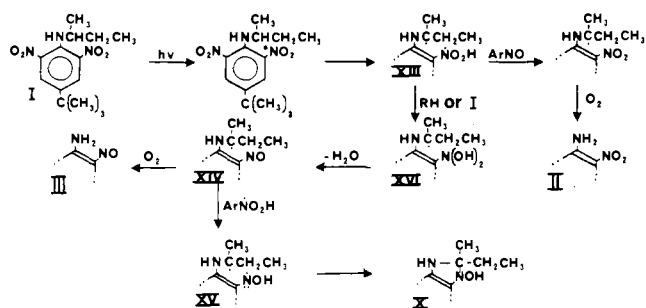


Figure 1. Photolysis of I in water; postulated reaction scheme.

tochemical reduction to give aniline, 2-hydroxyazobenzene, and other reduction products. Barltrop and Bunce (1968) investigated the mechanism of this reaction and found that short-wavelength ultraviolet light led predominantly to complete reduction, whereas ultraviolet light of longer wavelengths (>290 nm) favored the production of azoxybenzene and other bimolecular products. Detailed studies elucidated the nature of the intermediates in the sequence of reactions. Phenylhydroxylamine and nitrosobenzene were shown to be intermediates, but the reduction of nitrosobenzene to phenylhydroxylamine was considered to take place in a dark reaction. The reducing agent most likely to be capable of performing this reaction is the radical anion of nitrobenzene ($\text{PhNO}_2\cdot^-$) or its conjugate acid ($\text{PhNO}_2\text{H}\cdot$). This radical can act as either a dehydrogenating agent or a reducing agent and both roles are indicated in Figure 1.

The presence of readily abstractable hydrogen atoms in the solvent molecule was a necessary prerequisite for reaction. Oxygen transfer to solvent might also have been implicated in reduction, but the reaction was shown to proceed through a triplet [$^3(\pi-\pi^*)$] excited state, whereas the well-known intramolecular oxygen insertion reactions of *o*-nitrotoluene and *o*-nitrobenzaldehyde appear to involve a singlet state of the excited nitro compound.

More recently, the irradiation of 1,4-di-*tert*-butyl-2-nitrobenzene was shown to produce an indole *N*-oxide (Doepf, 1971). It was postulated that a nitron radical intermediate was formed by intramolecular hydrogen abstraction. The radical subsequently cyclized by eliminating a molecule of water. The analogous cyclization of *N,N*-dialkyl-*o*-nitroanilines to form benzimidazoles takes place under a variety of reaction conditions, including photochemical reaction in solutions of low pH (Fielden *et al.*, 1970; Preston and Tennant, 1972). A benzimidazole or benzimidazole *N*-oxide is produced depending on the structure of the reacting molecule. A complex mechanism has been proposed in which a furoxan is suggested as a key intermediate in the formation of the benzimidazole (Meth-Cohn, 1970; Fielden *et al.*, 1970). However, the reaction scheme can equally well be accounted for by a radical mechanism or a radical ion mechanism (Preston and Tennant, 1972); such a mechanism would also account for the photolysis products of I. These products include 4-*tert*-butyl-2,6-dinitroaniline (II), 4-*tert*-butyl-2-nitro-6-nitrosoaniline (III), and cyclic products X and XI. Mechanistically, the formation of these compounds could be explained by a reaction scheme (Figure 1) similar to that of Barltrop and Bunce (1968) (Figure 2). Facile intramolecular abstraction of hydrogen provides a pathway for radical formation and ultimately dealkylation. Solvent may participate in the reaction (Barltrop and Bunce, 1968; Hoshino *et al.*, 1971), but it seems equally possible that the reaction could proceed by an alternative intermolecular reaction (Davidson *et al.*, 1971). Therefore, it is likely that the oxidation of unreacted I or hydrogen donor solvent is coupled with the reduction of the nitro group.

The conjugate acid of the nitrobenzene radical XIII may be formed from I in an intramolecular reaction by hydro-

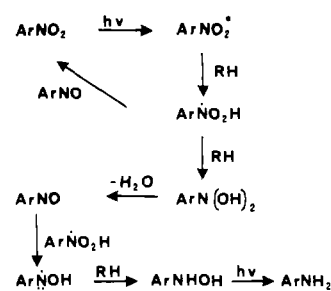


Figure 2. Reduction of nitroanilines. Scheme proposed for photoreduction of nitroaniline (Barltrop and Bunce, 1968).

gen abstraction. The radical thus formed may act as a reducing agent and react with a nitrosoaniline XIV to yield a phenylhydroxylamine derivative XV. Alternatively the radical XIII may react with I or solvent to give III.

An alternative mechanism for the formation of the dealkylated nitroso derivative III from the radical XIII could involve transfer of a hydroxyl radical from the nitronium group to the radical site on the alkyl side chain. Hydrolytic fission of the product thus formed would give III together with methyl ethyl ketone.

Formation of a benzimidazole from I is blocked by branching in the *N*-*sec*-butyl residue. Benzimidazoles are formed by photolysis of dinitramine in methanol by a reductive pathway *via* a 1,2-dihydroxybenzimidazoline intermediate (Newsom and Woods, 1973). If a five-membered cyclic compound were to be formed from I, it could not be a 1,2-dihydroxybenzimidazoline. A 1-hydroxybenzimidazoline structure is plausible, however, and structures of this type (X and XI) are suggested for the two products with molecular ions $M = 279$ and $M = 251$, respectively, obtained by photolysis in aqueous solution. The photolysis of I in the solid state gave two products with molecular ions $M = 239$ and $M = 277$, the former being the dealkylated compound II. The fragmentation pattern of the latter suggested a relationship to a purple compound $M = 293$ (differing by one oxygen atom), obtained in the majority of photolyses in water or methanol.

The replacement of NO₂ by OH can be explained either by a radical process or by photonucleophilic displacement (Havinga and Kronenberg, 1968). In the latter case, the course of the photochemical reaction will be influenced by the solvent and the concentration of nucleophiles such as OH⁻. If a nitro group is lost by a photonucleophilic reaction, this factor may be significant in determining the fate of a nitroaniline herbicide in an aquatic environment (Crosby and Wong, 1970).

An increasing number of dinitroaniline derivatives are being introduced as herbicides, and they are of potential agricultural importance. These molecules are photolabile, and it is anticipated that their photolysis pathways will be similar. Trifluralin and dinitramine give complex mixtures of photoproducts, and it is noteworthy that photochemical processes such as dealkylation, reduction, and benzimidazole formation have their parallels in metabolic reactions that occur in soil or on incubation with microorganisms (Funderburk *et al.*, 1967; Day, 1969; Laanio *et al.*, 1973; Newsom and Woods, 1973; Smith *et al.*, 1973).

In summary, we conclude that I is less readily photodecomposed than some closely related dinitroaniline herbicides, and that an aqueous suspension exposed to sunlight gives similar photoproducts to those obtained at lower wavelengths. Similar pathways are operative in water and methanol. The major product is 4-*tert*-butyl-2-nitro-6-nitrosoaniline, and cyclization does not occur to an appreciable extent. In the solid phase or on a silica gel plate, I appeared stable under normal laboratory illumination; however, photodecomposition occurred on a silica gel plate exposed to sunlight or sunlamp.

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Secondary Products from the Radiolysis of Tricaproin

Paul R. LeTellier and Wassef W. Nawar*

Tricaproin has been used as a model system to study the radiolysis of simple triglycerides. In addition to the primary radiolytic fragments and the recombination products reported earlier, certain compounds believed to result from more than one cleavage in the same parent molecule,

or from the decomposition of some primary intermediates, were classified as "secondary radiolytic products." In the present report, the identification and mode of formation of these compounds are discussed.

In our studies on the effects of high-energy radiation on fats, we selected tricaproin as a model system to investigate the mechanisms of radiolysis in saturated simple triglycerides. The use of this low molecular weight substrate permitted the separation and detection of both the short-chain radiolytic fragments and the higher molecular weight products. Among the radiolytic products 29 compounds, classified as "primary fragments," were found to result from scission of only one bond in the parent molecule. This group included hydrocarbons, aldehydes, methyl esters, ethanediol diesters, propane and propenediol diesters, diglycerides, and triglycerides (LeTellier and Nawar, 1972a). Quantitative analysis of these components indicated that cleavage of the ester bond (acyloxy-methylene) is the most predominant point of cleavage, while the acyl-oxy bond was the second most radiolabile linkage. More recently, we reported on the identification of 22 additional compounds which were classified as "recombination products," and believed to be produced by the combination of primary radicals, *i.e.* radicals formed by the cleavage of one bond in the parent molecule (LeTellier and Nawar, 1972b). These compounds consisted of longer chain hydrocarbons, ketones, esters, alkanediol diesters, and glyceryl ether diesters. In the present paper, the identification of certain other radiolytic products which could not be classified in the above two categories is discussed. Since these compounds are believed to result from more than one cleavage in the same molecule or from the decomposition of some primary intermediates, they are classified as "secondary products."

*Department of Food Science and Nutrition, University of Massachusetts, Amherst, Massachusetts 01002.

EXPERIMENTAL SECTION

Five-gram samples of purified tricaproin were irradiated under vacuum (10^{-2} Torr) at 6 megarads and 17° . The methods used for irradiation of the samples and for the isolation and identification of the radiolytic products were described in detail previously (Nawar *et al.*, 1969; LeTellier and Nawar, 1972a). The compounds identified as secondary products are listed in Table I. With the exception of acetylene and hexanol, reference standards were synthesized in the laboratory and their structure verified by gc-mass spectrometry and infrared analysis.

Isopropyl and heptyl hexanoate were prepared by the reaction of hexanoyl chloride with the appropriate alcohol according to Mattson and Volpenhein (1962).

2-Oxopropyl hexanoate was synthesized by the reaction of the sodium salt of hexanoic acid with chloro-2-propanone according to Hann *et al.* (1930). The sodium salt of the acid was prepared by reacting equimolar amounts of sodium hydroxide and hexanoic acid in water. The water was then removed under vacuum, the anhydrous salt placed in *N,N'*-dimethylformamide, and an equimolar amount of chloro-2-propanone added. The reaction was allowed to proceed for 2 hr at 80° . A few milliliters of a saturated solution of NaHCO_3 was added and chloroform was used to extract the ester from this solution. The ester was then purified by gas chromatography on a 10% Se-30 column. The mass and ir spectra of 2-oxopropyl hexanoate are shown in Figure 1. The molecular ion is of very low intensity (0.6%). The spectrum exhibits many ions which are characteristic of the fragmentation pattern of straight-chain aliphatic esters (Sharkey *et al.*, 1959)—an alkyl ion derived from the acid moiety (m/e 71), an intense acylium ion (m/e