Photochemistry of Bioactive Compounds. Multiphase Photodegradation of Basalin

George P. Nilles and Matthew J. Zabik *

The photolysis of basalin (N-(2-chloroethyl)-2,6-dinitro-N-propyl-4-trifluoromethylbenzenamine) has been studied, in solution, as a thin film and on soil. The structures of the major photoproducts have been determined and a comparison has been made between laboratory photolysis and natural sunlight photolysis for this compound.

It is now accepted that laboratory studies of the photochemistry of pesticides have broad significance in regard to formulating environmental usage and persistence parameters. Such studies should, of course, be conducted either in natural sunlight or with the use of irradiation devices which simulate sunlight as closely as possible in regard to spectral distribution.

The trifluralin (1) type herbicides were introduced in the early 1960's and have met with widespread acceptance and use. However, only recently has the detailed photochemistry of 1 (Crosby and Leitus, 1973) or similar compounds such as dinitramine (Newson and Woods, 1973) been explored.

Basalin (2, Fluchloralin, BAS-392, N-(2-chloroethyl)-2,6-dinitro-N-propyl-4-(trifluoromethyl)benzenamine) is an experimental herbicide under development by BASF Wyandotte Corp. Its ultraviolet spectrum shows a continuous extinction coefficient of at least 475 throughout the 290-450-nm region with a maximum at 364 nm (e 2060). A study of the photoproducts from this molecule should be conducted in order to confirm earlier findings in regard to the generality of the formation of benzimidazoles from this type of compound. In addition, the presence of the chlorinated side chain could well lead to reactions giving products more diverse than the normally substituted anilines.

EXPERIMENTAL SECTION

Equipment and Reagents. Gas chromatography (gc) employed a Beckmann GC-65 instrument equipped with a 6 ft x ½ in. i.d. glass column packed with either 3% XE-60 or 5% SE-30 on 80-100 mesh Gas Chrom Q. The oven was programmed as follows: 8 min at 105° and then heated to 175° at 2.5°/min and held at 175°. The injector temperature was 265° and the flame ionization detector was heated at 280°. The carrier gas was 99.996% pure helium at 20 ml/min. Mass spectra were run on a DuPont 21-490 instrument interfaced to the above gc. All samples were introduced via the gc inlet and spectra were determined at 70 eV with the source temperature at ambient. Integration was performed electronically (Houston Instruments “Omniscribe” Integrator) or by the cut and weigh method. Nmr spectra were determined on a Varian T-60 machine in carbon tetrachloride with TMS as the internal standard. Ultraviolet spectra were run on a Unicam SP 800 spectrometer in 95% ethanol. Liquid scintillation counting employed a Nuclear-Chicago “unilux” counter. Samples were counted in 10 ml of scintillation cocktail (5 g of PPO and 300 mg of POPOP/l. of toluene). Quench correction was by the internal standard method. Thin-layer chromatography used either (A) “Analtech” 250-μ, 5 × 20 cm silica G plates, (B) E. Merck 250-μ, 20 × 20 cm silica GF-254 plates, or (C) a 500-μ coating of E. Merck silica GF-254 on a 20 × 20 cm plate. All elutions were performed with chloroform. A Rayonet Srinivasan-Griffin photoreactor employing eight RPR 3000-A and eight RPR 3500-A lamps in an alternate configuration was used for all photolyses involving artificial sunlight. The spectral distribution of the photoreactor is shown in Figure 1. The photolysis vessel consisted of a 30 × 160 mm Pyrex vessel fitted with an air inlet and cold finger condenser which was immersed in the photolysis solution and connected to an external constant temperature bath by which means the photolysis solution was maintained at 15°. The solution was magnetically stirred during photolysis. For the kinetic studies in solution, the above vessel was replaced with a 4.5-l. Pyrex bottle. The solution was cooled and stirred in the same manner as above. The energy output of the photolamps in either vessel was measured by a YSI

Pesticide Research Center and the Departments of Entomology and Chemistry, Michigan State University, East Lansing, Michigan 48824.

*Department of Entomology.
Kettering Model 65 radiometer and determined to be 2–4 \times 10^4 \text{ ergs/(cm}^2 \text{ sec)}. For comparison, the sunlight on Sept 10, 1973 (100% clear sky) at 11:30 a.m., East Lansing, Mich., at the ground level was 6–8 \times 10^5 \text{ ergs/(cm}^2 \text{ sec)}, while on a 100% overcast day (Oct 4, 1973) the sunlight energy at the ground was 2 \times 10^4 \text{ ergs/(cm}^2 \text{ sec)}.

All solid phase irradiations which were performed in the photoreactor were done with the aid of a typical merry-go-round apparatus in order to ensure that all samples received uniform radiation.

All solvents were of pesticide grade quality and were used without further purification. We express our appreciation to Dr. Duane Ferrell, BASF-Wyandotte Corp., for analytical samples of basalin (2), 2,6-dinitro-4-trifluoromethyl-N-propyylaniline (5), 2,6-dinitro-4-trifluoromethyl-N-(2-chloroethyl)aniline (12), 2,6-dinitro-4-trifluoromethylaniline (11), 2,6-dinitro-4-trifluoromethyl-N-(2-hydroxyethyl)aniline (14), and uniformly ring-labeled basalin-^{14}C.

![Chemical Structures](image)

**Procedures.** (A) In Solution. The kinetic studies were performed on a 5.0-ppm solution of 2 made by dissolving 25.0 mg of 2 in 50 ml of methanol and adding 4950 ml of water. After thorough mixing, two 500-ml aliquots were removed to serve as a dark reaction control and as the \( t = \) 0 sample. The remaining 4 l. of solution was transferred to the photolysis vessel, kept darkened, and cooled to 15\(^\circ\)C. The lamps were then switched on and 500-ml aliquots were withdrawn at intervals of 5, 15, 30, 60, 90, and 120 min. A given aliquot was extracted under darkened conditions with four 50-ml portions of methylene chloride. The combined extracts were treated with 1.00 ml of standard biphenyl solution and then with 5 g of anhydrous sodium sulfate. After removal of the drying agent and concentration to 0.5 ml, the sample was analyzed by gc. Since photolysis at the 5-ppm level did not provide sufficient material for convenient mass spectral, nmr, and tlc procedures, a solution at the 1200-ppm level was photolyzed. This solution was prepared by dissolving 120 mg of 2 in 65 ml of methanol and adding 35 ml of water. This was irradiated as described above. The pH of the photolysis solution remained unchanged (5.6) during all irradiation periods. In all cases the irradiation vessel was kept exposed to the atmosphere, except as noted below, and no attempt was made to remove naturally dissolved gases from the solution before photolysis. At intervals of 4, 16, 40, and 60 hr (~80% loss of starting material) a 10-ml aliquot was withdrawn. The alcohol was removed by rotary evaporator at a bath temperature of 40\(^\circ\)C. The oily residue was treated with 25 ml more water and extracted with 3 \times 25 ml portions of methylene chloride. After concentrating to about 1 ml, the sample was analyzed by gc and mass spectra were taken for each peak. Both the XE-60 and SE-30 columns were used to facilitate analysis when overlapping peaks occurred. In all cases where the per cent of products is given, this refers to integrated areas which are not corrected by detector response factors.

A 5.0-ppm solution of 2 in a 1-l. stoppered Pyrex volumetric flask was subjected to natural sunlight out of doors, at a height of 25 ft from Aug 23 to Oct 9, 1973 and from Aug 23 to Sept 6, 1973 inclusive. During this time the available sunlight was 56 and 68%, respectively, according to United States Weather Service records. The solution was analyzed for photoproducts in the same manner as described for the kinetic runs.

(B) On Soil. For the soil studies, 5 \times 20 cm thin layer plates of 500-\(\mu\) thick Montcalm sandy loam were prepared (cf. Helling and Turner, 1968). The plates were treated with a solution of 2 in methylene chloride. The surface concentration was 0.1 mg/cm\(^2\). The plates were placed in the Rayonet reactor for 24 and 48 hr. The soil was extracted with 3 \times 20 ml portions of methanol and the solvent concentrated and analyzed for photoproducts by gc.

(C) On Silica Plates. A 25-\(\mu\)g sample of basalin-^{14}C (sp act. 14.0 mCi/mmol) was subjected to natural sunlight in a manner similar to that of Ivie and Casida (1971) using tlc system A. Simultaneously, a 500-\(\mu\)g sample of 2 was exposed on similar plates. Both runs were conducted in the presence and absence of anthraquinone, a known triplet sensitizer \( (E_\alpha = 62 \text{ kcal/mol}) \). At the end of the run the silica plates containing the basalin-^{14}C were scrapped into scintillation cocktail and counted. At least 99% of the

Figure 1. Spectral energy distribution for one RPR 3000-Å lamp and one RPR 3500-Å lamp.
DISCUSSION

Irradiation of a 1200-ppm solution of 2 in methanol-water produced eight major photoproducts, 3-10, as shown in Table I. The aniline products 4 and 11 were identified by cochromatography of the photolysis reaction mixture spiked with authentic samples, as well as by comparison of their mass spectra. In the same manner 12 and 14 were shown not to be isolable photoproducts under any conditions down to the 1% level of detection. They could not be detected after photolysis periods of 5 min to 80 hr.

In all cases a dark control experiment was used to ensure that a given product arose from photochemical processes and was not thermally initiated. The dark control was always the last sample to be analyzed. All dark control analyses in this study gave only starting material. No evidence of any other products was detectable down to the 0.5% level.

During separate runs of the thin film and 1200-ppm solution photolyses, nitrogen gas was passed through the reaction vessels in an effort to remove any possible aldehyde. Propionaldehyde could be detected by this method. All photoproducts and standards (2, 5, 11, 12, 14) gave well-defined parent peaks and exhibited a weak peak at m/e 69 and at m/e (M-19) indicating that the trifluoromethyl group was preserved during photolysis.

The presence of the chloroethyl side chain was always indicated by the appearance of a peak at m/e (M-49) and the absence of a peak at m/e (M-29). These two fragments are postulated to arise by β cleavage to give the resonance stabilized ion. Loss of 29 should be unfavorable in 7 compared to the loss of 49 mass units since the former would result in the formation of a heteroaryl cation which can only be resonance stabilized by placing a positive charge at the N-1 position. Whether photodealkylation of the chloroethyl side chain occurs before or after benzimidazole formation has not been determined.

The presence of the chloroethyl side chain was always indicated by the weak appearance of peaks at 63 and at 65 with intensities in the proper isotopic abundance. Loss of 21 mass units from 9 indicated that either a loss of methoxy or hydroxymethylene had occurred from the parent ion. Since 9 could be formed from 7 by either ground-state or photonucleophilic displacement of the chlorine, 9 appears to be the preferred structure. In addition, the alcohol was indicated by the peak at m/e (M-17). Since 14 could not be detected in the photolysis mixture at any time, it is probably not the precursor to 9 although a slow formation of 14 followed by a rapid conversion to 9 cannot be ruled out. The nitroso compound 4 eluted on the gc just before the corresponding nitro compound 5. Its mass spectrum showed a parent peak 16 mass units less than 5 as well as an m/e (M-30) peak. This compound was not found during the photolysis of 2 at the 5-ppm level or in any solid-phase photolyses. These other studies were conducted in the presence of a stoichiometric abundance of atmospheric oxygen which may have oxidized the nitroso group to the nitro, i.e., 5 to 4. Some evidence of this is gained from the observance that if the photolysis mixture is allowed to stand in the presence of a stoichiometric abundance of atmospheric oxygen which may have oxidized the nitroso group to the nitro, i.e., 5 to 4. Some evidence of this is gained from the observance that if the photolysis mixture is allowed to stand in the presence of a stoichiometric abundance of atmospheric oxygen which may have oxidized the nitroso group to the nitro, i.e., 5 to 4.

All photoproducts and standards (2, 5, 11, 12, 14) gave well-defined parent peaks and exhibited a weak peak at m/e 69 and at m/e (M-19) indicating that the trifluoromethyl group was preserved during photolysis.

The formation of the benzimidazole products was not unexpected. Previous studies have shown that N-alkyl-o-nitroanilines are readily converted to benzimidazoles and benzimidazole N-oxides upon irradiation at 2537 Å (Neadle and Pollitt, 1967) and upon irradiation through Pyrex (Fielden et al., 1970, and references therein). The entire aspect of o-nitroaniline interactions has been the subject of a recent review by Preston and Tennant (1972).

Product 6 was readily identified by comparison with the mass spectrum of this compound reported by Kearney et al. (1973). In particular, the peaks at m/e M-1 and M-47 characteristic of a 3-unsubstituted nitrobenzimidazole were noted. Since these authors had found in their study of the metabolism of trifluralin (1) that the 3-substituted nitrobenzimidazole was formed, we were encouraged to look for the corresponding photoproduct from basalin in which N-3 would be substituted by either an n-propyl or 2-chloroethyl group. That ring closure had occurred to give 7 was indicated by the appearance of a peak at m/e (M-49) and the absence of a peak at m/e (M-29). These two fragments are postulated to arise by β cleavage to give the resonance stabilized ion. Loss of 29 should be unfavorable in 7 compared to the loss of 49 mass units since the former would result in the formation of a heteroaryl cation which can only be resonance stabilized by placing a positive charge at the N-1 position. Whether photodealkylation of the chloroethyl side chain occurs before or after benzimidazole formation has not been determined.

The presence of the chloroethyl side chain was always indicated by the weak appearance of peaks at 63 and at 65 with intensities in the proper isotopic abundance. Loss of 21 mass units from 9 indicated that either a loss of methoxy or hydroxymethylene had occurred from the parent ion. Since 9 could be formed from 7 by either ground-state or photonucleophilic displacement of the chlorine, 9 appears to be the preferred structure. In addition, the alcohol was indicated by the peak at m/e (M-17). Since 14 could not be detected in the photolysis mixture at any time, it is probably not the precursor to 9 although a slow formation of 14 followed by a rapid conversion to 9 cannot be ruled out. The nitroso compound 4 eluted on the gc just before the corresponding nitro compound 5. Its mass spectrum showed a parent peak 16 mass units less than 5 as well as an m/e (M-30) peak. This compound was not found during the photolysis of 2 at the 5-ppm level or in any solid-phase photolyses. These other studies were conducted in the presence of a stoichiometric abundance of atmospheric oxygen which may have oxidized the nitroso group to the nitro, i.e., 5 to 4. Some evidence of this is gained from the observance that if the photolysis mixture is al-

<table>
<thead>
<tr>
<th>Compd</th>
<th>Gc reten. time, min</th>
<th>% integrated area</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>31.5</td>
<td>18.5</td>
</tr>
<tr>
<td>3</td>
<td>22.0</td>
<td>16.4</td>
</tr>
<tr>
<td>4</td>
<td>25.5</td>
<td>6.2</td>
</tr>
<tr>
<td>5</td>
<td>28.6</td>
<td>22.2</td>
</tr>
<tr>
<td>6</td>
<td>32.7</td>
<td>5.2</td>
</tr>
<tr>
<td>7</td>
<td>36.4</td>
<td>14.0</td>
</tr>
<tr>
<td>8</td>
<td>37.0</td>
<td>3.7</td>
</tr>
<tr>
<td>9</td>
<td>51.0</td>
<td>2.6</td>
</tr>
<tr>
<td>10</td>
<td>52.5</td>
<td>5.3</td>
</tr>
<tr>
<td>11</td>
<td>22.8</td>
<td>1.4</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>95.8</td>
</tr>
</tbody>
</table>

* The remaining 4.4% was divided among eight other peaks with none more than 1%.
lowed to stand several weeks in the dark in the presence of air, the peak in the gc corresponding to 4 disappears. The nitroso compound probably arises in the manner suggested by McMahon (1966) which would result in the formation of the labile chloroacetaldehyde. Efforts to trap either chloroacetaldehyde or propionaldehyde as their 2,4-dinitrophenylhydrazine derivatives were unsuccessful. Just as it was not possible to detect 12 it was not possible to detect its nitroso analog 13.

Fielden et al. (1970) have postulated an ionic mechanism for the formation of benzimidazoles and benzimidazole N-oxides from the photolysis of o-nitro-tert-anilines in the presence of acid. Since our photolyses were conducted in the absence of added acid and since the pH of the reaction mixture remained constant, we propose an alternate mechanism to account for the formation of benzimidazole and its N-oxide (Scheme I).

Scheme I

\[
\begin{align*}
2 & \rightarrow 2^+ \\
& \text{(H)}
\end{align*}
\]

\[
\begin{align*}
15 & \rightarrow 10 \\
& \text{(CF}_3)\text{CF}_2
\end{align*}
\]

\[
\begin{align*}
4 & \rightarrow 4^+ \\
& \text{(CF}_3)\text{CF}_2
\end{align*}
\]

\[
\begin{align*}
\text{N} & \text{H} \\
\text{N} & \text{O}_\text{N}_\text{O}
\end{align*}
\]

\[
\begin{align*}
16 & \rightarrow 6 \\
& \text{CF}_3
\end{align*}
\]

Intermediates of type 15 have been trapped by Chachaty and Forchioni (1968). If the chloroethyl side chain in 10 was photodealkylated, this would lead to the N-1 oxide of 6. However, this compound could not be detected, which might imply that 4 is the precursor of 6. It must be pointed out, however, that reduction of one of the nitro groups of 2 to a nitroso group (the hypothetical precursor of 7) could not be detected either.

The structure of the benzimidazole N-oxide (10) was deduced from its mass spectrum which showed characteristic peaks for M+, M – 15 (loss of methyl), M – 17 (loss of hydroxyl), and M – 49 (loss of chloromethylene). In contrast to N-3-unsubstituted benzimidazole N-oxides (Tatematsu et al., 1967) 10 shows only an M – 17 rather than an M – 16 (loss of oxygen) peak. This is probably a function of the "ortho effect" of the adjacent 2-ethyl group and/or the source temperature of the mass spectrometer. Thus Duffield and Buchardt (1972) found that in heterocyclic N-oxides the M – 17 peak largely predominated and became weaker compared to M+ as the source temperature was lowered. That ring closure has occurred to give 10 and not 5-(2-chloroethyl)-5-ethyl-4-nitro-6-trifluoromethylbenzimidazole N-oxide is shown by the M – 49 peak and absence of the M – 29 peak for the reasons cited above in regard to the formation of 7.

The structure of compound 8 is not clear. Having a mass at 319 and M + 2 peak at 321 (relative intensity, 40%) and an M – 49 peak would indicate a chloroethyl compound possibly derived by a 1,4 loss of water from 10. However, benzimidazole N-oxide appears to be photocleavable, both from this study, and from earlier work by Fielden et al. (1970). Isomeric with 8 in structure is the benz diazipin compound 17 which could arise via hydrogen abstraction and ring closure in a scheme analogous to the formation of 16. This would, however, involve a nine-membered transition state.

Finally, photoproduct 3, the rather unusual quinoxaline, was deduced by mass spectra and nmr. The only peaks in the mass spectrum which were of diagnostic value came at 243 (M+) at M – 19, M – 46, and at m/e 69. Assuming the trifluoromethyl group, one nitro group, and the benzene ring remained intact and that the benzene ring is still tetrasubstituted, one must account for a mass of 54. Further assuming a total of three nitrogens (two being excluded on the basis of the odd mass parent ion) leaves a mass of 26 which can only reasonably be accommodated by a vinyl bridge. That the bridge is attached 1,2 rather than 1,1 is indicated by the nmr spectrum which shows only aromatic protons at r 1.75 (1 H), 1.40 (1 H), and 0.90 (2 H).

The photolysis of 2 as a 5.0-ppm solution in water-methanol (100:1) in natural sunlight for 13 days and 48 days produced the products shown in Table III. They were identified by cochromatography with the 60-hr photolysis reaction mixture. No other products were detected. Of interest is the buildup of the unsubstituted aniline 11 and the benzimidazole 6 which appear to be photostable. The relative percentage of the quinoxaline 3 increases with time and then apparently degrades to unascertained products.

Ivie and Casida's procedure (1971) was used to ascertain the nature of the photoproducts resulting from direct sunlight irradiation of solid basalin. In addition, this allowed us to determine the overall volatility of the products plus starting material by simultaneous sunlight exposure of ring-labeled 2-14C. Counting of the silica scrapped from the plates showed a loss of 5% after sunlight exposure of 4 hr. It may be noted that 2 has a vapor pressure of 2.5 x 10^-5 Torr at 30°. The products produced in this study were 11, 5, 6, and 7, with 5 and 7 accounting for at least 80% of the products. Exposure of 2 to sunlight in the presence of anthraquinone, a known triplet sensitizer, resulted only in the quenching of the formation of 6 and 11 and the only photoproducts detected were 5 and 7.

On a sandy loam soil, the irradiation of 2 for 48 hr with the photoreactor produced 3 (26%), 5 (13%), 6 (35%), 7 (21%), and 8 (5%). At this point exactly 80% of the basalin remained. No other photoproducts were detected.

A thin film (6 μ) of 2 was irradiated through Pyrex in the photoreactor. Individual samples were examined by gc at 3, 6, 24, and 48 hr. The results are shown in terms of relative percentages of photoproducts and unreacted 2 in Table IV.

From an overview of the above results, one might be tempted to postulate which compounds are precursors to others further down the photodegradation pathway. This would be rather naive, since the multiplicities of pathways indicate more than one, independent product formation route.

Thus, 10 is probably a directly formed stable product from 2. Clearly, diverse products such as 10, 6, 3, and 11 arise via different pathways and may or may not have common intermediates. For example, 3 might arise via...
Table IV. Formation of Photoproducts from a Thin Film of Basalin

<table>
<thead>
<tr>
<th>Compd</th>
<th>0</th>
<th>3</th>
<th>6</th>
<th>24</th>
<th>48</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>100</td>
<td>84</td>
<td>83</td>
<td>74</td>
<td>48</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>8</td>
<td>4</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>8</td>
<td>3</td>
<td>4</td>
<td>7</td>
</tr>
<tr>
<td>6</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>3</td>
<td>5</td>
</tr>
<tr>
<td>7</td>
<td>0</td>
<td>0</td>
<td>6</td>
<td>8</td>
<td>7</td>
</tr>
<tr>
<td>8</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>11</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>4</td>
</tr>
</tbody>
</table>

Figure 2. Concentration of 2 as a function of irradiation time.

nitro to nitroso reduction with concomitant photodepropylation to give 13, air oxidation to give 12, homolytic cleavage of the carbon–chlorine bond, pairing of the resultant radical with the triplet state of the nitro group, hydrogen abstraction from the solvent, and finally 1,2 and 1,4 loss of two molecules of water. These intermediates are quite different than those expected in the formation of 6 or 11.

Thus, simple observation of the increase and decrease of various compounds cannot be interpreted in terms of products and their precursors.

One thing is certain, namely, the photodestruction of 2 at potential environmental concentrations is rapid. Under laboratory conditions, a 5.0-ppm solution of basalin has a half-life of 27 min, exhibits zero-order kinetics, to 60% conversion, and has a rate constant of disappearance of $2.6 \times 10^{-7}$ mol/(l.min) (Figure 2). The deviation from linearity in the kinetic plot is apparently caused by the quite visible shift in the absorption spectrum of the photolysis mixture, the initially bright yellow solution becoming deep red-brown. The only major photostable products, whether natural or artificial light is used, appear to be the benzimidazole 6 and the aniline 11. Indeed, unless high concentrations of 2 are encountered, products 4, 8, 9, and 10 do not form at all.

Both Newsom and Woods (1973) and Crosby and Leitus (1973) have isolated unstable dihydroxybenzimidazolines as intermediates in the formation of the benzimidazole photoproducts. That a compound of this type could not be isolated in the present work probably is indicative of the unstable nature of these compounds which in our case may have degraded on the gc column. Beyond this, basalin appears to undergo the same general types of photoreactions as the other similar nitroaniline herbicides. The presence of the chlorinated side chain has certainly led to more diverse products such as 3 and 14 which are probably unique to the photochemistry of basalin.

**Supplementary Material Available.** A listing of mass spectral m/e values will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JAFC-74-6&1.

**LITERATURE CITED**

Preston, P. N., Tennant, G., Chem. Rev. 72, 627 (1972).

Received for review November 23, 1973. Accepted March 6, 1974. This research was supported in part by grants from BASF-Wyandotte Corporation and the Michigan Agriculture Experiment Station, Michigan Agricultural Experiment Station Journal Article No. 6839.