Photochemistry of Bioactive Compounds. Multiphase Photodegradation and Mass Spectral Analysis of Basagran

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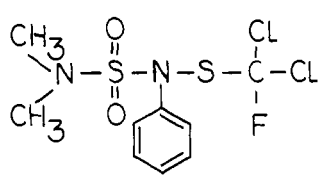
The natural sunlight and simulated sunlight photolyses of basagran (3-isopropyl-1*H*-2,1,3-benzothiadiazin-(4)-3*H*-one 2,2-dioxide) have been studied in aqueous solution, as a thin film, and on soil. The mass spectra of the major photoproducts are interpreted in terms of their structures. The major routes of photoalteration of this new herbicide were found to be oxidative dimerization and nonconcerted loss of sulfur dioxide. A new formation of the quinazolin-3*H*-4-one ring system is reported as well as the use of "neutralized" Caro's acid in the oxidation of an aromatic amine to the corresponding nitroso compound.

Sulfur in its various oxidation states and concatenations is widely encountered in many pesticides. However, the sulfamide group ($-NHSO_2NH-$) is represented only by one presently used pesticide compound, euparen (1). Recently, basagran (2) or bentazon (3-isopropyl-1*H*-2,1,3-benzothiadiazin-(4)-3*H*-one 2,2-dioxide) has come under development by BASF-Wyandotte Corp. as an experimental postemergence herbicide. It has shown considerable usefullness in controlling a wide range of broad leaf weeds.



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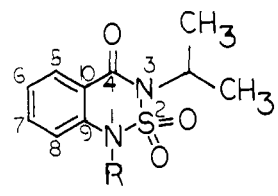

2 R=H
3 R=CH_3

An examination of its ultraviolet spectrum revealed fairly strong absorption in the sunlight region with a λ_{max} of 302 nm (ϵ 2210) and an extinction coefficient of at least 100 out to 360 nm. Thus, the possibility existed that basagran could be photochemically transformed under field conditions. In addition, we were unable to find any report dealing with the photochemistry of compounds containing the sulfamide group. Since such compounds can be readily and economically synthesized, they may come to be extensively used in the agrochemical area. Accordingly, the study we present herein, on the phototransformation of basagran, should be of interest from both the environmental and purely photochemical viewpoints.

EXPERIMENTAL SECTION

Equipment and Reagents. Mass spectra were determined on a DuPont 21-490 instrument, with the samples introduced through an interfaced Beckman GC-65 gas chromatograph. Masses and intensities were assigned via an on-line Digital Equipment Corporation PDP 12/LDP computer. All spectra were determined at 70 eV with the source temperature at ambient. Gas chromatography employed two columns: column A was a 6 ft × ⅛ in. i.d. glass column packed with 4% SE-30 on 80–100 mesh Gas-Chrom Q at 40-ml flow rate of 99.997% helium with the oven programmed at 160° for 15 min, then 7.5°/min to 250°; column B was a 6 ft × ⅛ in. i.d. glass column packed with 10% DC-200 on 80–100 mesh Gas-Chrom Q at 30 ml flow rate of 99.997% helium with the oven programmed at 120° for 10 min, then 2.5°/min to 250°. The injector was at 265° and the flame ionization detector was at 290°. Integration was performed by the cut and weigh method. NMR spectra were determined on a Varian T-60 instrument in deuteriochloroform with Me_4Si as the internal standard. Ultraviolet spectra were run on a Unicam SP800 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 2,5-diphenyloxazole and 300 mg of 1,4-bis[2-(5-phenyloxazolyl)]benzene/l. of toluene). Quench correction was by the internal standard method. Thin-layer chromatography used Analtech 250-μ, 5 × 20 cm silica G plates. The eluting solvent was a 3:7 mixture of methanol–chloroform. The irradiation apparatus was the same as described earlier (Nilles and Zabik, 1974). All solvents were of pesticide grade quality except ethyl acetate which was analytical reagent grade. The solvents were used without further purification.

Dideuteriodiazomethane was prepared by the method of Campbell (1972) but using methanol-*d* in place of carbitol-*d*. A 20-fold molar excess of 30% NaOD in D_2O was used to ensure complete exchange of deuterium for protium.

o-Nitro-*N*-isopropylbenzamide (8) was prepared by the method of Partridge and Stevens (1964). It was recrystallized from ethanol–water and melted at the reported 138–139°.

o-Nitroso-*N*-isopropylbenzamide (7) was prepared as follows. A suspension of 10 g of potassium persulfate in 7 ml of ice-cold concentrated sulfuric acid was stirred until a thick paste formed ((about 45 min). The paste was transferred to 100 g of ice and stirred until the ice dissolved. The solution was adjusted to pH 2 (Accutint paper #40) with solid potassium carbonate. This was filtered and the insoluble salts washed with enough water to bring the volume of the filtrate to 75 ml. This solution was cooled to 10° and a solution of 0.534 g (3.00 mmol) of 4 in 75 ml of boiling water (some starting material remained undissolved) was added in one portion with vigorous stirring. The reaction mixture was allowed to stir at room temperature for 1 hr and filtered. The solid consisted of pure (by GC) 7 weighing 0.43 g (2.24 mmol, 74.8%), mp 154–156° dec. Solutions of this material are pale green. While the use of "neutralized" Caro's acid in oxidations of this type has been reported before (Atkinson et al., 1954), exact details concerning the preparation and use of this reagent appear to be lacking. In the same manner we were also able to oxidize anthranilimide to the previously reported (Ibne-Rasa and Koubek, 1963) *o*-nitrosobenzamide in 95% yield.

N-(*o*-*N*-Isopropylbenzamidyl)nitrone (14) was prepared by treating 100 mg (0.522 mmol) of 7 with an excess of diazomethane in 5 ml of ethyl acetate. The initial green

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color of the nitroso compound was immediately discharged with a vigorous evolution of nitrogen. The solution was washed twice with 10 ml of 0.5% HCl and dried and the solvent removed by rotary evaporator to give 88 mg (0.43 mmol, 82%) of **14**, mp 146–147° dec. The NMR spectrum showed τ 2.1–3.2 (m, 6 H), 5.7–6.1 (m, 1 H), 8.8 (d, J = 6 Hz, 6 H). The nitrone protons are undoubtedly overlapped by the aromatic proton absorption (Baldwin et al., 1969).

Experimental Procedures. The photolysis apparatus consisted of a typical Rayonet reactor equipped with 3000- and 3500-Å lamps. This apparatus along with much of the general procedure has been described earlier (Nilles and Zabik, 1974). Specific differences are noted below.

(*A*) *In Solution.* The kinetic studies were performed on 5 l. of a 5.00-ppm solution of **2** in distilled water (pH 5.6). Two 500-ml aliquots of this solution were set aside as the dark control and the t = 0 sample. The remaining 4 l. of solution was transferred to the photolysis vessel, kept darkened, and cooled to 15°. The lamps were then switched on and 500-ml aliquots were withdrawn at 30 min, 1, 2, 4, 8, 24, and 48 hr. A given aliquot was half-saturated with sodium chloride and extracted with four 50-ml portions of ethyl acetate. The combined extracts were treated with 1.00 ml of standard lindane and then with 20 g of anhydrous sodium sulfate. After removing about 150 ml of solvent on a rotary evaporator, a ca. five-fold excess of ethereal diazomethane was added. This solution was allowed to stand at room temperature for 5 min and the aliquot was then concentrated to 0.5 ml and analyzed by GC. Since photolysis at 5 ppm did not provide a sufficient sample for mass spectral analysis of the less abundant photoproducts, photolyses were also run at 500 ppm in pure water (saturated solution) and at 2000 ppm in 14 mol % aqueous methanol. The photolysis solution was always maintained in equilibrium with the atmosphere. The 500- and 2000-ppm solutions were photolyzed for 115 hr, extracted, and analyzed by GC and mass spectrometer as above. The compounds eluting before methylbentazon were best separated on GC by column B and those eluting after methylbentazon by column A. In all cases where percent of products is given, this refers to integrated areas which are not corrected by detector response factors.

Two 5.00-ppm solutions of **2** in 1 l. of distilled water in stoppered Pyrex volumetric flasks were subjected to natural sunlight, out of doors at a height of 25 ft, from Oct 31 to Nov 19, 1973, inclusive. During this time the percent available sunlight was 23%, according to United States Weather Service records. The solutions were then analyzed for photoproducts and starting material as described for the kinetic runs.

(*B*) *On Soil.* For the soil studies, 5 × 20 cm thin layer plates of 500-μ 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 photoreactor for 24, 72, and 120 hr. The soil was extracted with three 20-ml portions of methanol, which was then concentrated to 0.5 ml, and 10 ml of ethyl acetate was added. This was concentrated to 0.5 ml and analyzed by GC.

(*C*) *On Silica Plates.* The procedure used by Ivie and Casida (1971) was followed using a 25-μg sample of bentazon-^{14}C (labeled at position 10). The plates were exposed to sunlight, out of doors at ground level. The ground level temperature was about 60°F, and all runs were made in triplicate. No photoproducts were noted in either the sensitized (anthraquinone) or unsensitized runs. The loss in radioactivity after 8-hr sunlight exposure amounted to 8.5% and after 20-hr exposure was 18.4% due to volatility of **2**. The dark controls were unaffected.

(*D*) *Thin Films.* Irradiation of bentazon in the solid state was carried out as thin films on Pyrex plates as described in our earlier paper. The irradiation times in the photoreactor were 24, 72, and 120 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 uncovered down to the 0.1% level of detection. No change in pH of any of the solution photolyses was noted, and separate photolyses of bentazon-^{14}C in solution indicated that no material was lost from solution by volatilization. No olfactory detection of sulfur dioxide was noted during any of the photolyses.

DISCUSSION

The irradiation of a saturated solution of basagran (500 ppm) in water for 115 hr produced extensive degradation as seen in Figure 1. Table I gives the product distribution as percentages of the total peak area from this GC tracing. Of the total area, only 1.3% represents unidentified photoproducts (indicated by the letter P). Impurities in the solvent system are indicated by the letter S. The best separation of the photolysis mixture components was achieved on GC column B (DC-200) although the 3-hr retention time of **13** slowed analysis considerably. It may be noted that column B has separated the components in order of increasing molecular weight.

Naturally, the easiest photoproducts to identify were those for which authentic standards were available, i.e. **4**, **7**, and **8**. Their GC retention times, by cochromatography, and GC–mass spectra confirmed their identities. In a similar manner, anthranilic acid (**5**) and *N*-(*N'*-isopropyl)sulfamoylanthranilic acid (**6**) were shown not to be photoproducts down to the 0.1% level of detection. With the exception of **9**, the remaining photoproducts (**10**, **19–21**) are postulated ones whose structures, we feel, are best consistent with all of the experimental data.

The identification of all of the photoproducts relied heavily on GC-MS spectrometry. A complication in the interpretation of data from this type of analysis arose from the necessity of treating the photolysis reaction mixture extract with diazomethane. Without this methylation step, basagran thermally degraded to several products whose GC retention times interfered with GC–MS analysis. Presumably, something similar happened to the higher molecular weight photoproducts **19–21** since they would not elute through any GC column tried, and only lower molecular weight compounds of shorter retention time were noted. The structures of these thermal degradation products of **19–21** were not investigated.

Fortunately, basagran is quite acidic (pK_a = 3.4) and it is quantitatively methylated by diazomethane at N-1 to give **3**. Similarly, **9** is readily dimethylated at N-1 and N-3 (Cohen and Klarberg, 1962). Photoproducts **19–21** were methylated only once, as will be described later. Compounds **5** and **6** were methylated once, on the carboxylic acid function, as confirmed by MS and NMR. The increase in acidity of the benzothiadiazine compounds relative to an acyclic sulfamide is probably due to an increase in aromaticity of the conjugate base of the cyclic system. As a result, the cyclic sulfamides in this study were methylated on nitrogen by diazomethane, while the acyclic sulfamides were not so methylated.

Since the nitrobenzamide (**8**) was identified as a photoproduct, it seemed reasonable that the corresponding nitroso compound **7** might be an intermediate in its formation. To confirm this, the nitroso compound was synthesized by monopersulfuric acid oxidation of the amine **4**. The GC retention time of this nitrosobenzamide was 31 min on column B. When the photolysis reaction mixture extract was injected on column B without diazomethane treatment, a GC peak was noted at 31 min retention time.

Table I. Distribution and Molecular Ions of the Photoproducts of Basagran

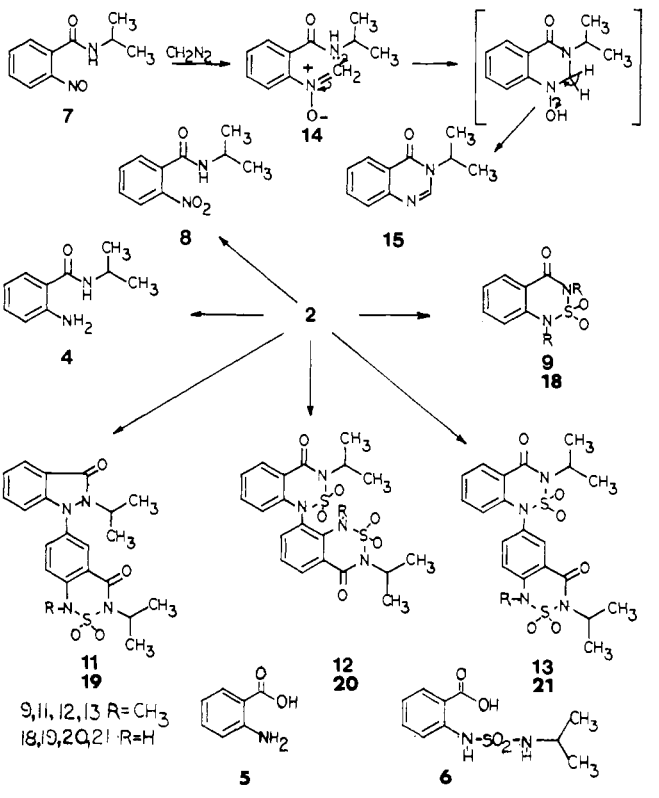
	Compound								
	2	4	7	8	9	10	11	12	13
% of total area in Fig. 1	63.8	3.86	1.11	0.25	0.04	0.90	3.43	3.18	22.1
Retention time,[a] min									
Col A	19	7.4	11.4	9.0		25.2	42	50	71.2
Col B	44.6	10.9	36.2[b]	39	40.4	60	103	126	180
Molecular ion (calcd)	240	178	192[c]	208	198	312	414	478	478
Molecular ion found after treatment with CH_2N_2	254	178	188[b]	208	226	312	428	492	492
Molecular ion found after treatment with CD_2N_2	256	178	189[b]	208	230	312	430	494	494

[a] After either CH_2N_2 or CD_2N_2 treatment. [b] Of the quinazolinone (see text). The retention time of 7 was 24.2 min on column B. [c] Of the nitroso compound.

Unfortunately, it was not well separated from other components. Repetitive scan GC–mass spectra taken from 30 to 32 min following sample injection (24 spectra, mass range 50–250) showed cleanly two mass spectra identical with the mass spectra of synthesized **7**. Although this result serves to confirm the presence of the nitrosobenzamide as a photolysis product, we will digress to report an interesting difficulty in the analysis of this compound when the photolysis mixture extract was treated with diazomethane.

A GC–MS analysis of all GC peaks shown in Figure 1 (post-diazomethane treatment) yielded no evidence for any compound with a mass of 192. Now it is well documented that nitroso compounds react with diazoalkanes to give nitrones (Boyer, 1969). However, an M^+ of 206, the mass of the proposed nitrone **14**, was not found among the parent ions from the total GC–MS scan. A new compound having a mass of 188 was detected, which suggested that if the nitrone had formed from **7**, it may have lost water. This could have happened during the initial treatment of **7** with diazomethane (unlikely) or in the mass spectrometer source or somewhere in the gas chromatograph. To answer this question, the nitrone **14** was prepared independently by the reaction of synthesized **7** with diazomethane. Its structure was confirmed by NMR. An examination of the mass spectrum of this material (direct probe, 150°) showed peaks at *m/e* 206 (100%) and 188 (88%). Increasing the inlet temperature increased the size of the 188 peak relative to the 206 peak. When a solution of this material was injected into the GC (GC conditions as for column B) a single peak with a retention time the same as the "188" peak (**15** in Figure 1) was noted. Clearly, the initially formed nitrone dehydrated in the GC to give **15**. The mass spectra of this "188" product obtained from the diazomethane-treated photolysis reaction mixture extract and the synthetic material were identical, when either was analyzed via the GC inlet. The most useful diagnostic ions in the mass spectrum of **15** were found at *m/e* 188 (67%, M^-) and at *m/e* 146 (100%, M^+ = 42). From *m/e* 146 on down, the mass spectrum was identical with that reported by Batterham et al. (1967) for quinazolin-3*H*-4-one. The facile loss of propene from the parent ion of **15** is probably a consequence of the resultant aromaticity of the 146 ion. Scheme I shows the reaction of **7** with diazomethane and a postulated mechanism for the formation of **15**. The nitrosobenzamide was usually analyzed as this quinazoline "derivative."

Scheme I



Compound **18**, the Norrish type II product, has been prepared previously and the mass spectrum of its dimethyl derivative reported (Bancroft et al., 1972). The mass spectrum obtained for peak 9 in Figure 1 was identical with that reported by these authors. The meager amount of this compound is in accord with the known reluctance of amides to undergo type II fragmentation (Nicholls and Leermakers, 1970).

The structural analysis of the photoproducts whose masses were greater than basagran was more difficult. One of the most useful diagnostic features in the mass spectrum of these compounds was the McLafferty loss of propene (*m/e* 42) via the SO_2 group. Basagran shows an M^+ ion of 45% intensity relative to the base peak at *m/e* 198 (M^+ − 42, loss of propene) while the isopropylbenza-

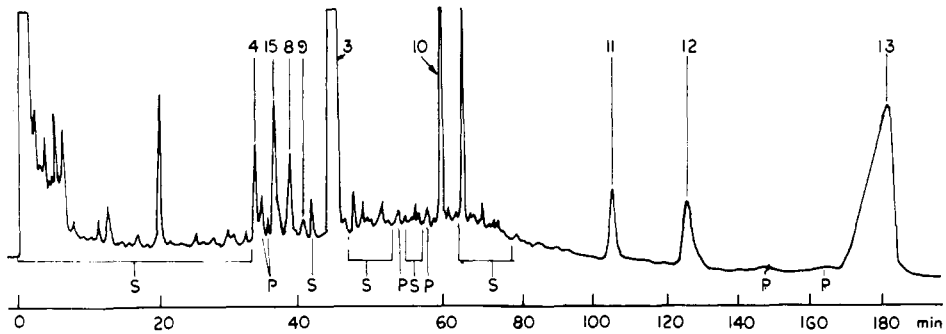
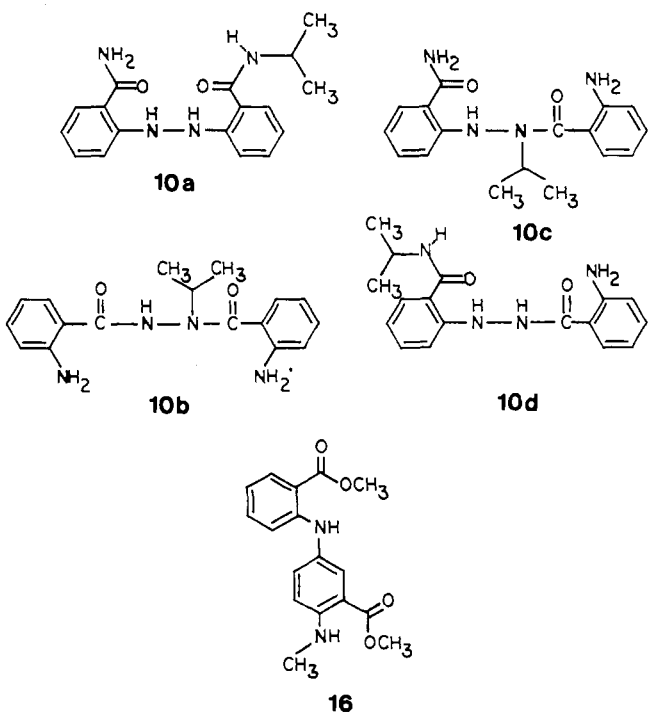


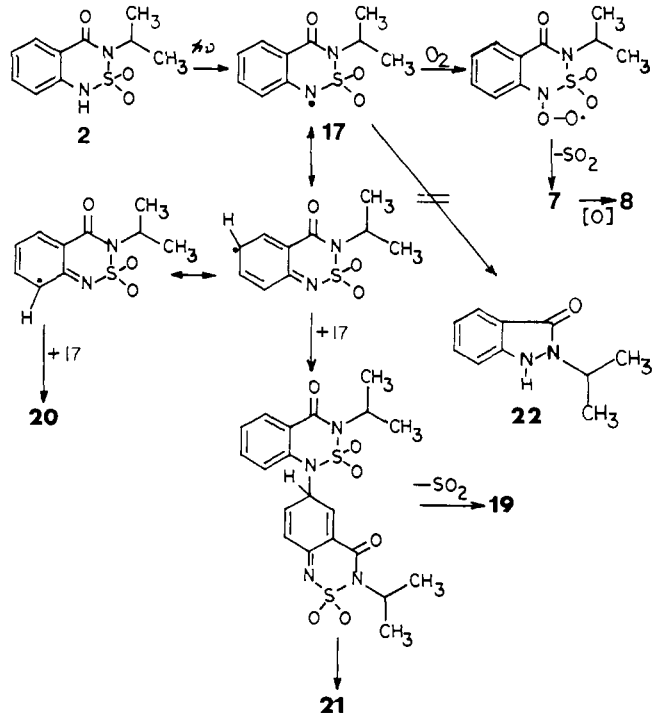
Figure 1. GC trace of basagran photolysis mixture extract after treatment with diazomethane using column B. The numbers above the peaks refer to the structures in Scheme I.

mide (4) shows an M^+ ion at m/e 178 (91%) and no $M^+ - 42$ peak. Thus, loss of propene must involve one of the sulfur-oxygen bonds in the transition state of the McLafferty rearrangement and not the carbonyl group. The SO_2 group must also be part of a cyclic sulfamide system. The mass spectrum of the methyl ester of 6 shows a parent ion of 11% intensity relative to the base peak at m/e 119 but no detectable $M^+ - 42$ peak. Thus, the presence of a strong $M^+ - 42$ peak usually indicated an intact 3-isopropyl-1*H*-2,1,3-benzothiadiazin-(4)-3*H*-one 2,2-dioxide system. Two exceptions to this rule were found: the quinazoline system 15 described above and the hydrazo system discussed below (**10a–d**).



Compound 13 derived from photoproduct 21 showed ions at m/e 492 (M^+, 100%), 450 ($M^+ - 42$, 33%), and 408 ($M^+ - 84$, 52%) as well as SO_2 extrusion from the McLafferty fragments at m/e 386 (7.2%) and 344 (25%). This implies a basagran "dimer," although the true dimer of methylbasagran has a mass of 508. If the photolysis reaction mixture extract was treated with dideuteriodiazomethane, the parent ion of 13 moved to 494. This increase of two mass units clearly indicates that only 1 equiv of diazomethane was used in the methylation. Therefore, 21 must have only one acidic proton. We wish to postulate that basagran has undergone oxidative photodimerization in which a bond has formed between the N-1 nitrogen of one basagran moiety and the benzene ring of another. There seems to be some precedent for this type of reaction. Forster et al. (1971) found that benzothiadiazole 2,2-dioxide coupled with itself when treated with sodium hypochlorite. Although they postulate the intermediacy of a nitrenium ion in the coupling, Weinstein and Chang (1974) believe a nitrogen radical could be involved in this reaction, as evidenced in their study of the reaction of the sulfamide group under similar conditions. Whether the ionic mechanism or the radical mechanism is operative in the present study, either would explain the formation of the coupled products (19–21) according to Scheme II.

Scheme II



Further evidence for the structure of 21 comes from isolation of its methyl derivative 13 by silicic acid chromatography. The NMR spectrum of 13 showed a multiplet at τ 1.6–3.2 (7–8 H), a multiplet at 4.7–5.2 (2 H), a singlet at 6.5 (3 H, N-CH_3), and overlapping doublets at 8.2–8.7 (11–12 H), all of which are in accord with the proposed structure. Upon treatment of 13 with Claisen's alkali and further methylation with diazomethane, a compound was formed whose parent ion at m/e 314 matched the expected structure 16 for this degradation product. In addition, peaks in the mass spectrum of 16 at $M^+ - 32$ (21%) and at $M^+ - 64$ (20%) establish the presence of two methyl ester functions.

The mass spectrum of 11, formed by methylation of 19,

Table II. Percentage Distribution of the Photoproducts from Basagran When Irradiated as a 5.00-ppm Solution in Water through Pyrex Using the Rayonet Reactor

	hr of irradiation			
Compd	1	4	8	24
Basagran	93	90	76	19
4	7	6.3	7.7	27
8	0	0.90	2.6	27
20	0	1.4	7.2	14
21	0	1.4	6.5	14

Table III. Percentage Distribution of the Photoproducts from Basagran When Irradiated as a 5.00-ppm Solution in Water by Natural Sunlight for 19 Days through Pyrex

	Compound						
	Basagran	4	8	10	19	20	21
% distribution	34.2	15	4.6	18	4.6	3.3	20

Table IV. Percentage Distribution of the Photoproducts from Basagran When Irradiated on Montcalm Sandy Loam

	hr of irradiation		
Compd	24	72	120
Basagran	71	58	56
7	22	8.1	5.7
8	7.0	8.1	3.1
10	0	8.1	13
19	0	4.7	5.3
20	0	9.4	4.2
21	0	4.2	8.8

Table V. Percentage Distribution of the Photoproducts from Basagran When Irradiated as a Thin Film on Pyrex

	hr of irradiation		
Compd	24	72	120
Basagran	85	60	63
4	4.5	4.4	3.3
7	3.6	26	20
8	6.4	11	13

showed diagnostic mass spectral ions at m/e 428 (M^+, 100%), 386 (59%), 322 (11%), and a weak peak at 344 (7.8%). The difference in mass between **11** and **13** together with the relatively weak loss of the second McLafferty fragment probably indicates simple photoextrusion of sulfur dioxide from higher weight product. That is, **21** is the precursor of **19**. Photoproduct **19** could also have been formed by coupling of an indazolone group with a basagran group, but then one might have expected to find simple indazolone photoproducts such as **22**. No such products were detected. Since monomethylation did occur with diazomethane (Table I), the photochemical loss of SO_2 had to be from the upper ring system. Although analogous studies have shown that extrusion of sulfur dioxide is a facile photochemical process (Block, 1969) only **19** among all the photoproducts appears to have resulted from the loss of SO_2.

The basagranyl radical **17** in Scheme II could have three other fates. These are reduction by hydrogen abstraction leading to **4**, air oxidation leading to **7** and **8**, and nitrogen to nitrogen coupling leading to **10a–d**.

The structure of this remaining compound (**10a–d**) is still tentative. The mass spectrum shows ions at m/e 312 (M^+, 48%) and 270 (100%). There was no $M^+ - 106$ ion (loss of SO_2 and propene) and no increase in the mass of the parent ion whether the photolysis reaction mixture extract was treated with diazomethane or dideuteriodiazomethane. This seems to rule out a basagranyl group in this photoproduct. The mass of the parent ion is not large enough to postulate a quinazoline ring either.

However, if one considers homolytic cleavage of the N-3 to sulfur bond in basagran this would give rise to a radical that might dimerize "head-to-head." If this were followed by loss of SO_2, reduction of the radicals at the N-1 nitrogens, and loss of one of the isopropyls due to steric compression, the result would be structure **10b**. The $M^+ - 42$ ion in the mass spectrum could form readily since it would be stabilized by the adjacent nitrogen in the hydrazido bridge. We must emphasize, however, that the other structures, particularly **10c**, must be considered as reasonable alternatives.

Irradiation of a higher concentration of basagran (2000 ppm) in 14 mol % methanol in water produced the same photoproducts in virtually the same relative quantities. If the photolysis of basagran was carried out at 5.00 ppm, however, only **4**, **8**, **20**, and **21** could be detected at various time intervals as shown in Table II. A plot of the basagran remaining as a function of time is linear (zero-order kinetics obeyed) to 24 hr. The half-life of the starting material is 15.0 hr and the rate constant for disappearance of basagran is 1.33×10^{-8} mol/(l. min).

The failure to find any evidence for the formation of the nitroso compound **7** from the 5.00-ppm photolysis may be due to atmospheric oxidation of this compound. It is possible that only at the lower concentration was a stoichiometrically sufficient amount of oxygen present to oxidize all of **7** to the nitro compound **8**.

The photolysis of basagran in sunlight as a 5.00-ppm solution in water in a sealed Pyrex vessel for 19 days gave the product distribution seen in Table III. In contrast to the laboratory photolysis at this concentration, all photoproducts were formed except, once again, the nitroso compound. Here again we feel that photooxidation may explain its absence.

The remaining photolysis studies were carried out in the solid state. The results of exposure of basagran, deposited on 0.25-mm silica gel plates in the manner of Ivie and Casida (1971), are given in Table IV. Only basagran was recovered after exposures of 8, 14, and 20 hr during cloud free days. Simultaneous sunlight irradiation of basagran-^{14}C, labeled at the 10 position, showed an average loss in radioactivity of 8.5% after 8 hr and 18.4% after 20 hr. An attempt to sensitize photodecomposition with anthraquinone was unsuccessful.

When basagran was irradiated on Montcalm sandy loam using the preparation of Helling and Turner (1968), the products shown in Table IV were formed under laboratory conditions. It may be noted that the nitroso compound **7** disappears with time; whether it is due to volatility or further photolysis is uncertain. The amine **4**, which requires reduction of the initially formed radical postulated in Scheme II, did not form at all.

Finally none of the higher molecular weight compounds were formed when basagran was photolyzed as a thin film on Pyrex glass. As seen in Table V, only the amine **4**, the nitroso compound **7**, and the nitro compound **8** were detected.

The presence of the dimer products from basagran when irradiated on soil is interesting from both the environmental aspect and the theoretical viewpoint, particularly since they did not form in the thin film study. It may be that the dimers form on soil because the soil contains certain transition metals which could coordinate with two basagran molecules and hold them in the correct proximity for coupling. For example, Jennings and Hill (1970) and Salomon et al. (1974) have shown that chromium and copper, respectively, facilitate photodimerization and photocoupling of certain olefins. Further studies on the role of soil transition metal chemistry relative to environmental photolysis may provide such answers.

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Esters of Sulfonic Acids as Derivatives for the Gas Chromatographic Analysis of Carbamate Pesticides

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Esters of sulfonic acids (sulfonates) may be readily prepared on a micro scale by reacting benzenesulfonyl chlorides with carbamate pesticides. The sulfonates are easily gas chromatographed and detected by a tritium electron capture detector at the 1-pg level. Flame photometric detection may also be employed at the 10-ng level. A simple analytical procedure for the analysis of carbamates on lettuce and cabbage is described; it can be adapted to other materials, such as soils. A sensitivity of 0.05 ppm is easily achieved.

The apparent thermal instability of carbamate pesticides has presented the pesticide chemist who chooses gas chromatography with a difficult problem. Degradation of the carbamate within the gas chromatograph usually occurs and results in small peaks or no peaks at all. Some success has been achieved using short columns and relatively low temperatures (Cook et al., 1969; Riva and Carisano, 1969) for the chromatography of the intact carbamate. Improving the thermal stability and chromatographic characteristics by derivatization has also produced some success.

Derivatives of the methylamine portion of the carbamate have been made (Crosby and Bowers, 1968; Holden et al., 1969; Moye, 1971); however, these suffer from nonspecificity since they do not distinguish between carbamates. Making a derivative of the phenolic portion obviates this problem but frequently requires lengthy reaction times (Argauer, 1969; Butler and McDonough, 1968; Bowman and Beroza, 1967) or results in an incomplete reaction.

Recently, Seiber (1971) and Khalifa and Mumma (1972) formed a carbamate derivative by replacing the amine portion hydrogen with a perfluoro acetate, propionate, or butyrate group.

The work described here concerns itself with the preparation of esters of sulfonyl chlorides (sulfonates) by the reaction of carbamate pesticides with halogenated benzenesulfonyl chlorides. These derivatives are easily prepared on a micro scale, are easily gas chromatographed, and respond well to electron capture detection. A somewhat reduced response is obtained with sulfur mode flame photometric detection. Analyses of spiked lettuce, cabbage, and weathered soil samples are illustrated.

EXPERIMENTAL SECTION

A Varian Model 1520B with a tritium electron capture detector was used except when otherwise noted. The column was glass, 6 ft × 0.25 in. o.d. × 2 mm i.d., packed with either 5% LSX-3-0295 or UCW98 on 100–120 Hi-Performance Chromosorb W. Column carrier, N_2, was 60 ml/min, at a temperature of 220°.

The *p*-bromo-, 2,5-dichloro-, and 3,4-dichlorobenzenesulfonyl chlorides were obtained in 99%+ form from Eastman Organic Chemicals, Rochester, N.Y. The pentafluorobenzenesulfonyl chloride was obtained in 99%+ form from Peninsula Chemical Research, Gainesville, Fla.

Preparation of Sulfonates. Four sulfonyl chlorides were allowed to react separately with 1-naphthol to produce 1-napththyl-2,5-dichloro-, -3,4-dichloro-, -*p*-bromo-,

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