Uv Irradiation of 6-Methyl-2,3-Quinoxalinedithiol Cyclic Carbonate (Morestan®)

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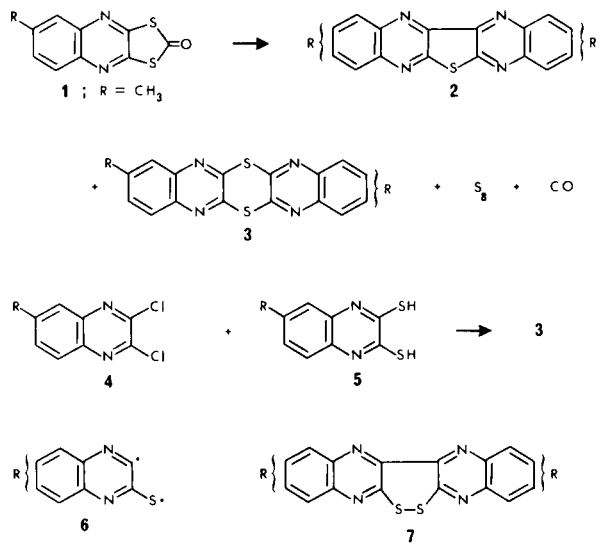
Received February 7, 1972

Quinoxaline-2,3-diol carbonates are a relatively new class of pesticides (1,2), the photochemistry of which has not yet been reported. Since it was recently reported that field workers using Morestan® experienced severe skin irritation on body areas exposed to sunlight (3), and since photochemical reactions are important transformation pathways for chemicals in the environment, we undertook an investigation of the irradiation of Morestan (**1**).

The irradiation of a dilute benzene solution of Morestan (**1**) by long wavelength (above approximately 280 nm) uv light gives, in addition to unreacted starting material, mainly the dimethylthieno[2,3-*b*:4,5-*b*′]diquinoxaline (**2**), the dimethyl-*p*-dithiino[2,3-*b*:5,6-*b*′]diquinoxaline (**3**), and elemental sulfur; evidence has also been obtained for the evolution of carbon monoxide (4).



The structure of compound **2**, which appears to be a member of a new class of thiophene derivatives, was assigned on the basis of consideration of its mass spectrum and comparison of the latter with those of compounds **1** and **3**. Figure 1 shows the partial mass spectra of these compounds. The peaks at m/e 174, 148, 142, and 116 are presumed to be due to $[C_9H_6N_2S]^+$ and other logical aromatic fragments (5). The similarity of the spectra indicates that the quinoxaline moiety is intact in each of the photoproducts, and the absence of a peak at m/e 206 (corresponding to $[C_9H_6N_2S_2]^+$) in the spectrum of compound **2** argues against the presence of two sulfur atoms. The structure of compound **3** was established by its independent synthesis by the condensation (6) of 6-methyl-2,3-dichloroquinoxaline **4** with 6-methyl-2,3-quinoxalinedithiol (**5**).

Since sulfides and sulfoxides can be photooxidized (7), sometimes very readily (8), and since photolytic desulfurization of some sulfoxides and sulfones is possible (9,10), we investigated the possibility that **3** was an intermediate in the formation of **2**. That this is unlikely, however, is shown by the finding that **2** was not produced in detectable amounts when **3** was irradiated. Production of **2**, therefore, seems difficult to rationalize. One might speculate, however, that if **3** and **7** were formed initially, perhaps through some intermediate such as **6**, then **2** could be accounted for by the loss of elemental sulfur from **7**; 1,2-dithiins have been reported to be unstable materials which readily lose sulfur thermally or photolytically to yield thiophenes (11).

EXPERIMENTAL

Technical grade 6-methyl-2,3-dichloroquinoxaline (m.p. 113-115°, cloudy melt) and 6-methyl-2,3-dimercaptoquinoxaline (m.p. 270-280° dec.) were supplied by Chemagro (12), exhibited consistent mass spectra, and were used as received. Morestan (manufacturer's standard) was also supplied by Chemagro; that the Morestan was pure was indicated by its m.p. (m.p. 168.8-169.3°; reported (1) m.p. 172°), by the observation of only a single spot on tlc after development in several different solvents, by the lack of change in its ir spectrum after vacuum sublimation, and by the homogeneity shown as the sample was deliberately fractionated from the inlet probe of the mass spectrometer. Yellow technical-grade Morestan could be purified as described below.

A Hanovia 450 W "high pressure" mercury vapor lamp (No. 679 A) and a pyrex filter (which passes light above approximately 280 nm) were used for the irradiation; this is a medium-pressure lamp, most of whose output is at the various mercury emission lines. There was no dark reaction. Analtech precoated Silica Gel

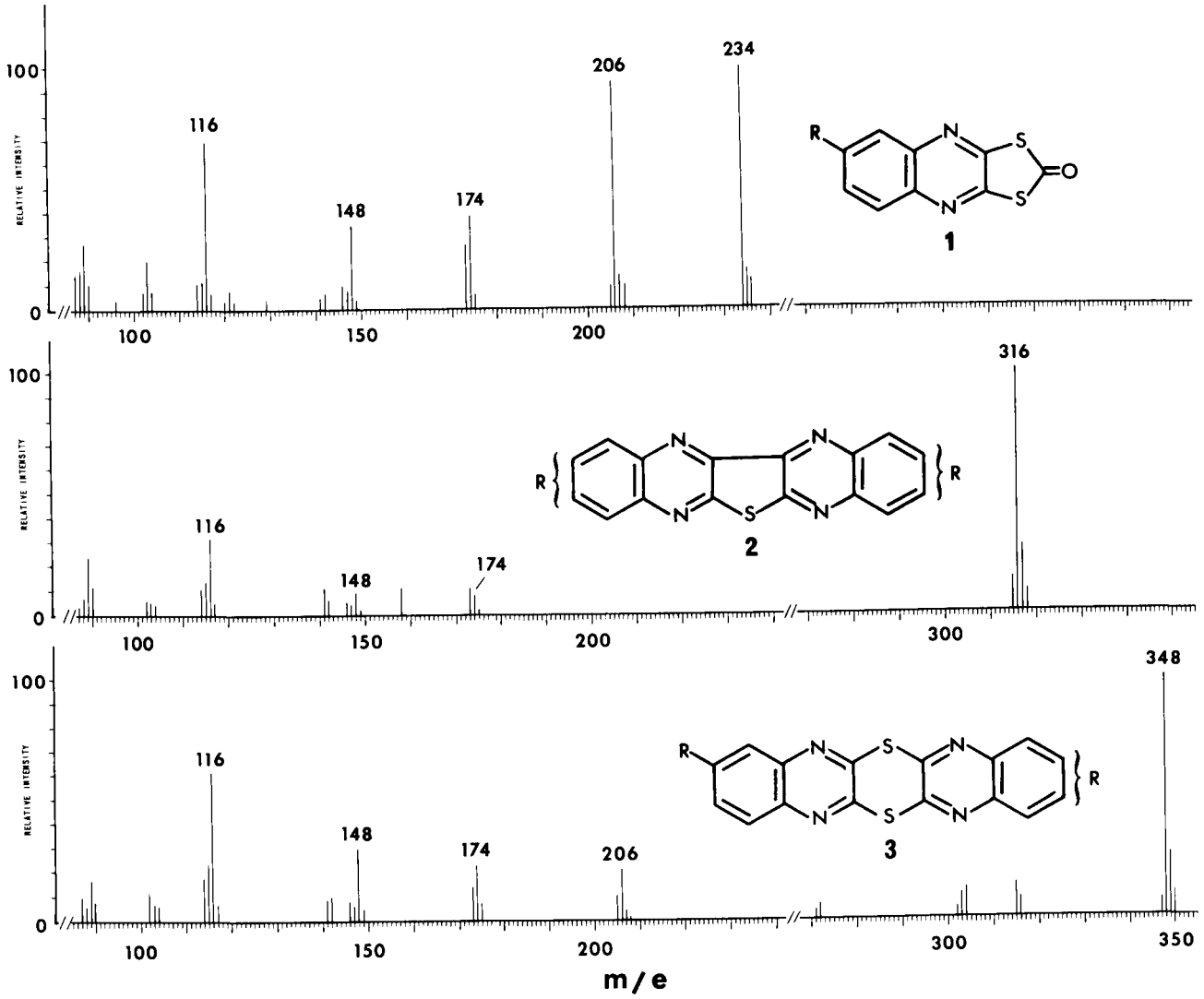


Figure 1. Mass spectra of Morestan (**1**) and photoproducts **2** and **3**. R = Methyl.

G plates were developed approximately 13 cm. in Burdick and Jackson glass-distilled solvents for the thin layer chromatography; all spots were detected by long-wavelength uv light, except for sulfur, which was located by iodine vapor. Differences in R_f values are due to the use of different lots of plates and different loadings. Thin layer plates were examined in fluorescence mode on a Schoefel Model SD 3000 spectrofluorodensitometer. Products were weighed on a Cahn gram electrobalance, and melting points were determined on a Mettler FP2 hot stage or a Thomas Hoover capillary melting point apparatus and are uncorrected. Infrared spectra (presented in Figure 2) were obtained in potassium bromide matrices on a Beckman IR-10 or Perkin-Elmer model 621 spectrophotometer equipped with a 6x beam condenser (13). Mass spectra (direct probe) were obtained by using an Atlas CH-4B mass spectrometer (14). Ultraviolet spectra were recorded on a Cary Model 14 spectrophotometer.

Irradiation of Morestan (**1**).

A solution of Morestan (29.5 mg., 0.126 mmole) in 325 ml. of reagent benzene was magnetically stirred, and irradiated at 25° for 7.5 hours (15) while being agitated by bubbling nitrogen. After irradiation, the reaction mixture was concentrated and the brown residue was washed several times with chloroform, yielding approximately 4 mg. of chloroform-insoluble (residue A) and 27 mg. of chloroform-soluble (residue B) brown residues. Residue A was insoluble in any of the common solvents, and we could not obtain an ir or Raman spectrum by the usual techniques.

Residue B was preparatively chromatographed (methylene chloride) on Silica Gel G tlc plates; visualization showed three fluorescent bands. The plates were scraped into six fractions: 1) from the origin to the bottom of a green-fluorescing band; 2) the green-fluorescing band at R_f = 0.17; 3) a blue-white fluorescing band at R_f = 0.24; 4) the area between fractions 3 and 5;

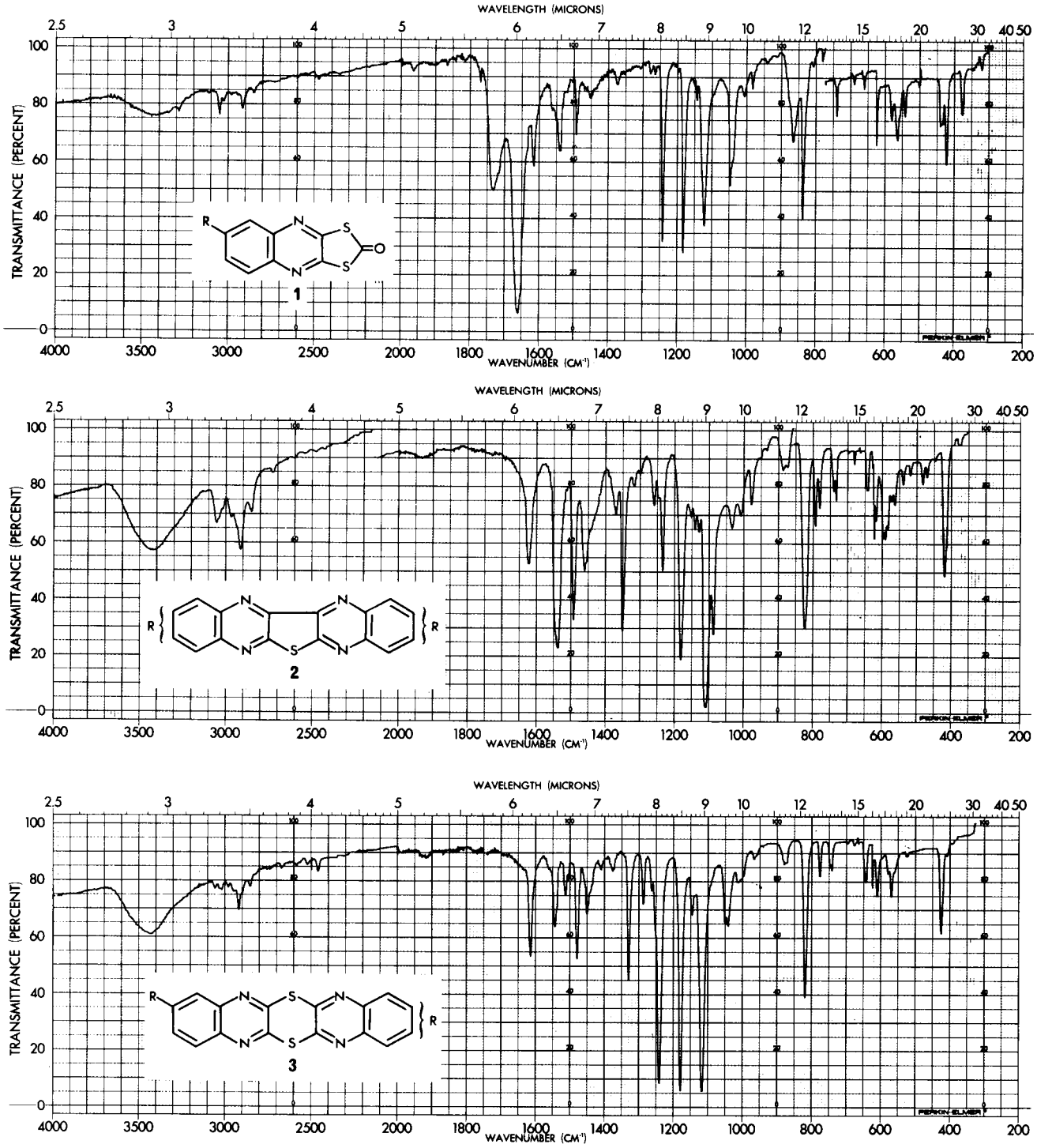


Figure 2. Infrared spectra of Morestan (**1**) and photoproducts **2** and **3**. R = Methyl.

5) a well-separated purple-fluorescing band at R_f = 0.55; (6) the area from fraction 5 to the solvent front. The collected fractions were extracted with chloroform to yield crude products which were further purified as described below. The extract from fraction 1 consisted of only a small amount of dark red residue which was not further investigated. The extract from fraction 2 (the green-fluorescing band) was rechromatographed on the thin layer silica gel plates; this time the plates were developed twice with methylene chloride. This treatment removed several faint bands of low R_f (approximately 0.1) as well as some contamina-

tion from fraction 3 from the main band. The product was again collected, eluted from the adsorbent with chloroform, and finally sublimed at 180° (0.2 torr). After collection of the product from the cold finger (chloroform) and removal of solvent, there remained 5.1 mg. of yellow material, hot stage m.p. 275-300° with sublimation (product A, **2**). Despite its giving a "single" spot on tlc (see below), the product appears to consist of several materials (isomers?), since the tlc scanner shows an unsymmetrical fluorescence (at least two peaks) across the spot when run in fluorescence mode with 360 nm incident light and the filter set to pass 450 nm (or longer wavelength) light. The extract from fraction 3 (the blue-white fluorescing band) was further purified by tlc (methylene chloride); the single product band was scraped off the plates, eluted with chloroform, and finally sublimed at 180° (0.2 torr) to yield 0.58 mg. of yellow material, hot stage m.p. 292-300° with sublimation (product B, **3**). Fraction 4 yielded only a bit of scum, and was discarded. The material from fraction 5 (the purple-fluorescing band) was sublimed twice at 100° (0.2 torr), and after recovery from the cold finger consisted of 1.63 mg. of nearly white material (product C, Morestan). The crude product from fraction 6 was sublimed at 100° (0.2 torr) to yield 2.98 mg. of very light yellow solid (product D, S_8) and some brownish oily residue.

Products A-C were characterized by their mass, ir, and uv spectra. The mass and ir spectra have been presented in Figures 1 and 2 above. The uv data are presented below (for each λ, ϵ x 10^{-4} values are given in parentheses): Product A (1% chloroform in hexane) λ max 247 (3.26), 266 (5.05), 308 (2.59), 363 (2.76, shoulder), 377 (2.98); λ min 233 (2.52), 253 (2.37), 278 (0.99), 328 (0.76) nm. Product B (5% chloroform in hexane) λ max 257 (7.30), 283 (2.80), 395 (2.48); λ min 232 (2.36), 271 (2.28), 333 (0.49) nm. Product C (1% chloroform in hexane) λ max 257 (3.33), 262 (4.21), 330 (0.79), 338 (1.01), 346 (1.58), 355 (1.54), 363 (2.29); λ min 259 (3.00), 275-295 (0.24), 333 (0.71), 341 (0.95), 350 (1.03), 358 (1.11) nm. Product D: This material was shown to be impure elemental sulfur by its mass spectrum (70 ev), which exhibited major peaks at m/e 256, 224, 192, 160, 128, 96, 64, and 32. Their isotopic distributions correspond well with those calculated by Beynon (16). In addition to these sulfur peaks, the spectrum also exhibited a number of peaks (among them m/e 41, 43, 55, 57, 66, and 69) that correspond very well with the mass spectrum of the sublimation residue, which does not contain elemental sulfur.

On two-dimensional tlc of products A, B, and D (chloroform, then 5% ether in toluene), the materials each showed a single spot. Below are listed the R_f values in methylene chloride, followed by those in ether-toluene: product A 0.18, 0.25; product B 0.30, 0.47; product D 0.89, 0.81. When the Morestan fraction was similarly checked it showed two spots: Morestan with R_f values of 0.56 and 0.67 and a new yellow-fluorescing spot at R_f values of 0.51 and 0.56. Evidently the Morestan fraction decomposed or became contaminated after it was collected.

Preparation of Dimethyl-*p*-dithiino[2,3-*b*:5,6-*b*′]diquinoxaline (**3**).

A solution of 2,3-dichloro-6-methylquinoxaline (**4**, 100 mg., 0.47 mmole) in 2 ml. of dimethylformamide was added to a solution of 6-methylquinoxaline-2,3-dithiol (**5**, 106 mg., 0.51 mmole) in 5 ml. of DMF and 5 ml. of concentrated ammonium hydroxide. A yellow precipitate formed immediately, but the mixture was stirred at room temperature for an additional hour. The precipitate was collected, washed twice with water, dried, and found to consist of 113 mg. (65% crude yield) of yellow material. Further fractions were not collected. On tlc (methylene chloride), the product showed 3 minor impurities as well as the major blue-white-fluorescing band at R_f = 0.32. The material could be recrystallized from toluene or chloroform, then sublimed at 180° (0.2 torr) to give yellow material whose chromatography, ir, uv, and mass spectra match those of **3** isolated from the Morestan irradiation.

Irradiation of Dimethyl-*p*-dithiino[2,3-*b*:5,6-*b*′]diquinoxaline (**3**).

Compound **3** (18.9 mg., 0.054 mmole) in 325 ml. of benzene was irradiated as in the Morestan irradiation. After solvent removal, the residue consisted of 18.8 mg. of brown material whose tlc (methylene chloride) showed no spot corresponding to product A in the Morestan photolysis. The major spot corresponded to the starting material, R_f = 0.32; in addition, several minor spots in the R_f 0.0-0.2 region were observed. A control test showed that approximately 0.3 μg of **2** could have been easily detected in the presence of 1.2 μg of residue spotted. However, it does not fluoresce strongly.

Irradiation of Dimethyl-*p*-dithiino[2,3-*b*:5,6-*b*′]diquinoxaline (**3**) under Oxygen.

Compound **3** (50 mg., 0.143 mmole) in 325 ml. of benzene was irradiated as in the Morestan photolysis, but under oxygen. After standing overnight, the reaction mixture was filtered to remove a fine precipitate, which weighed 33 mg. when dry. The solution was concentrated to yield 33 mg. of chloroform-soluble yellow residue whose behavior on tlc (methylene chloride) matched that of the starting material (R_f = 0.32, blue-white fluorescence). Several other minor spots were also observed. No spot corresponding to **2** could be observed; a control test showed that approximately 0.3 μg of **2** could have been easily detected in the presence of the 1.1 μg of chloroform-soluble residue spotted.

Purification of Technical Morestan.

Solid technical-grade Morestan (yellow, 600 mg.) was placed on top of a 5 x 0.75 inch column of silicic acid, capped with a layer of sand, and eluted with benzene:hexane (3:1). Nearly white Morestan (547 mg.) eluted first; then chloroform was used to elute a yellow material (18.3 mg.); a brown band remained at the top of the column. The Morestan was recrystallized from chloroform-hexane (using activated carbon) to yield white material, m.p. 169.0-169.2° (Hoover, uncorrected), whose ir spectrum matched that of the standard Morestan reported above. The ir and uv spectra of the yellow material isolated from the chloroform fraction essentially matched those of **3** synthesized above. On tlc (methylene chloride), the Morestan exhibited a single purple-fluorescing spot at R_f = 0.63; the **3** showed a major blue-white-fluorescing spot at R_f = 0.33 and several minor spots below R_f = 0.2.

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(13) We would like to thank Dr. J. Y. T. Chen for providing some of the ir spectra.

(14) We would like to thank Mr. J. Damico for obtaining these spectra.

(15) A glc monitor (at 195° on a 6 foot column of DC-200 coated 10% on Chromosorb W-HP, E. C. detector) indicated that approximately 20% of the Morestan remained unreacted after this time. No other products chromatographed.

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