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PHOTOCHEMICAL DESULFURIZATION OF METHYLTHIO-S-TRIAZINES

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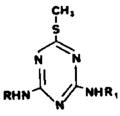
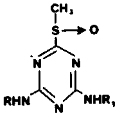
Methylthio-bis(alkylamino)-s-triazine herbicides (I) are converted to 2-hydroxy-bis-(alkylamino)-s-triazines by way of the intermediate sulfoxide (II) and sulfone (III) in plants (1). A sulfhydryl compound (IV) and the disulfide (V) have been identified as metabolites in rat urine (2). To determine whether the reaction sequence (I) to (III) could also occur by photooxidation, we have investigated the photolysis of the 2-methylthio-s-triazines. Oxidation of the methylthio group did not occur in air, but elimination occurred with hydrogen transfer. A similar phenomenon is observed in mass spectral fragmentation of methylthio-s-triazines.

Solid 2-methylthio-4,6-bis(ethylamino)-s-triazine (simetryne) (Ia) was irradiated for 72 hr in air with a sun lamp (output max. 310 nm). The products were examined by thin-layer chromatography on silica (solvent: benzene/acetone, 2:1). Only one compound was detected in low yield in addition to starting material. Its identity was indicated by comparison of R_f values with authentic 2,4-bis(ethylamino)-s-triazine (VIa). Structure (VIa) was confirmed by mass spectrometric analysis.

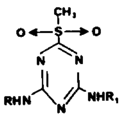
Irradiation of 2-methylthio-4,6-bis(isopropylamino)-s-triazine (prometryne) (Ib) gave similar results. The single photoproduct was examined by thin-layer chromatography. Comparison of R_f values with (II) and (III) revealed that these were not present. The mass spectral fragmentation pattern suggested that the product was 2,4-bis(isopropylamino)-s-triazine (VIb).



I

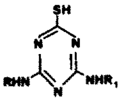


II

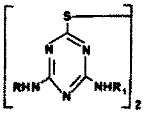


III

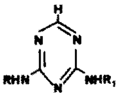
Ia $R = R_1 = C_2H_5$
Ib $R = R_1 = (CH_3)_2CH$



IV



V



VI

VIa $R = R_1 = C_2H_5$

VIb $R = R_1 = (CH_3)_2CH$

The mass spectra of some s-triazines have been reported (3). Authentic 2,4-bis-(ethylamino)-s-triazine had base peak m/e 43. A molecular ion was observed at m/e 167. Fragments at m/e 152, m/e 139, m/e 138, m/e 124 and m/e 111 arise by loss of alkyl groups. Fragments m/e 139 (M-28) and m/e 111 arise by double and single McLafferty rearrangements, respectively.

Simetryne showed an intense molecular ion at m/e 213 (base peak). Loss of alkyl groups afforded peaks at m/e 198 (29.6), m/e 185 (22.4), m/e 170 (58.4) and m/e 155 (56.0). McLafferty rearrangements give rise to fragments at m/e 185 (M-28) and m/e 170 (M-(28 + 15)). Loss of thiomethyl radical should afford an ion at m/e 166, and a small peak was observed (relative abundance 4.0%). A larger peak at m/e 167 (24.0) arises by loss of 46 mass units ($M-CH_2S$). We propose that this represents the loss of CH_2S, as substituted thioanisoles also fragment by loss of CH_2S. The fragment ion at m/e 180 (M-HS) is of low relative abundance (2.4%) in contrast to the aromatic thioethers (4). A formal analogy exists between fragmentation in the mass spectrometer and the process of photodecomposition of (Ia) (5). The nature of the volatile sulfur-containing compound evolved on photolysis is unknown.

Schultz *et al.* (6) have reported that photodesulfurization of a sulfoxide in the presence of benzophenone gives an oxidized product. We suggest that photooxidation of the methylthio-group to a sulfoxide or sulfone before elimination of the sulfur-containing fragment would afford a 2-hydroxy-s-triazine. The photochemistry of (II) and (III) is being studied.

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