Photolysis of 4-Amino-3-methylthio-6-phenyl-1,2,4-triazin-5-one (Aglypt)

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The herbicide, 4-amino-3-methylthio-6-phenyl-1, 2, 4-triazin-5-one (I, BAY 79758, Aglypt) is currently under development at Farbenfabriken Bayer. We report here preliminary results of the photolysis of this material in aqueous solution.

Experimental

Aqueous solutions (40 ppm) of I, in stoppered Pyrex flasks, were exposed to sunlight in early November, early December and late December, 1970. The first exposure was for four hours, and the others for eight hours, all between 10 a. m. and 2 p. m. After irradiation, a 10 ml aliquot was analyzed by u. v. absorption spectroscopy and the remainder was extracted with ethyl acetate. The extract was separated into acidic and non-acidic fractions with 1M sodium hydroxide and the two fractions were analyzed by gas-liquid chromatography (4 ft. x 1/16 in. glass column containing 5% OV-210 on Ultrapak, 80-100 mesh, at a temperature of 235° C.) and thin-layer chromatography (20:1, benzene-acetic acid) on Eastman silica gel sheets with fluorescent indicator. Rf values were determined on the basis of a 10 cm. solvent front.

Inhibition of the Hill reaction was determined with isolated spinach chloroplasts; potassium ferricyanide being employed as the electron acceptor (1). The rate of oxygen evolution was measured polarographically with an oxygen electrode.

Synthesis of II. A solution of 902 mg I in 1-liter methyl alcohol and 100 ml distilled water was irradiated for 18 hours with a 450-watt Hanovia lamp through a Pyrex filter. Nitrogen gas was bubbled through the solution throughout the course of the irradiation. The methanol was evaporated under reduced pressure and the resulting aqueous suspension was treated with 200 ml ethyl acetate and two 50 ml portions of 1M sodium hydroxide. The combined alkaline layers were acidified with 2M hydrochloric acid and the resulting precipitate was filtered, washed, and dried. Recrystallization from ethyl acetate afforded 160 mg II (19% yield), m. p. 233-36° C.

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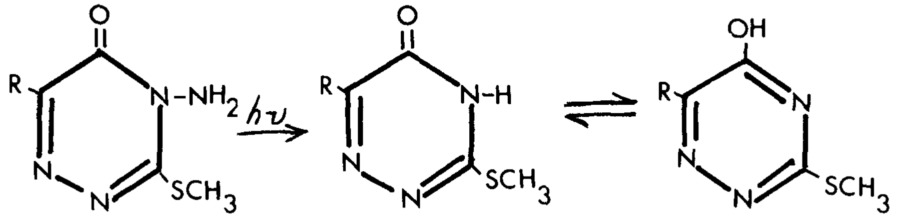

I, III, V, VII II, IV, VI, VIII

I, II : R=phenyl; III, IV : R=t-butyl; V, VI : R=isopropyl; VII, VIII : R=cyclohexyl

Results and Discussion

Thin-layer chromatography of a concentrated ethyl acetate extract of the sunlight-irradiated solution revealed three spots with Rf values of 0.13, 0.27 and 0.57. The latter two, which were very faint, were due to a trace of unidentified photoproduct and a small amount of starting material, respectively. The material at Rf 0.13 was identified as 3-methylthio-6-phenyl-1,2,4-triazin-5-one (II) by mass spectroscopy. Confirmation of the structure of II was obtained by comparison of its infrared spectrum to that of an authentic sample. The photochemistry of I is thus analogous to that of the 6-alkyl-substituted triazinones (III, V, VII) studied recently by Pape and Zabick (2). The base peak in each of the reported (2) mass spectra of the 6-alkyl-substituted photoproducts (IV, VI, VIII) occurs at m/e 69, due probably to the loss of methyl thiocyanate and the 6-substituent. The mass spectrum of II exhibits two base peaks of equal intensity, one at m/e 69 and another at m/e 104, the latter most probably indicating $[\emptyset\text{-C=NH}^{+}]$. Pape and Zabick also reported analogous peaks of lower intensity at m/e 84, 70, and 110 for IV, VI and VIII, respectively.

The rate of disappearance of I upon exposure to sunlight in aqueous solution was very rapid. Within four hours in early November, less than 10% I remained unphotolyzed as estimated by gas-liquid chromatography. Approximately one month later, two four-hour exposures on successive days resulted in about 50% photodegradation, while a similar exposure at the end of December led to no significant photodecomposition. The calculations of Forsythe and Christison (3) indicate that the amount of solar energy available per day in the spectral region in which I absorbs light at this latitude in early November is approximately 16% the daily solar energy available in early May. By late December, less than 3% of the May solar energy is available. It is thus reasonable to expect that I will be converted to II very rapidly during the Spring application season when applied as a wettable powder and when not incorporated into the soil.

We have also confirmed the reported conversion of III (BAY 94337) to IV in sunlight (2). Although IV was not formed on exposure to sunlight in the early November experiments, it was formed very slowly when exposed to a 20-watt "Vitalite" fluorescent lamp. Our previous experience has been that a material undergoing photodecomposition when irradiated with this lamp will also undergo photodecomposition in sunlight. The difference in the rate of photolysis between I and III is due, in part, to their different light absorption characteristics. The former has an absorption maximum at 3230 A^{o} (e=14,500) and the latter at 2930 A^{o} (e=8700). Both absorption maxima were measured in aqueous solution at pH 6.8.

Studies with spinach chloroplasts indicated that I, at a concentration of 7×10^{-8} mole/1, inhibited the Hill reaction 50%, while under identical conditions the value for II was 5.6×10^{-7} mole/1. Similarly, the reported (2) photolysis of III to IV resulted in only a four-fold increase in the 50% inhibition concentration, i.e. from 1.3×10^{-7} to 5.2×10^{-7} mole/1. The previously reported (4) value for both I and III is 2.34×10^{-7} mole/1, when measured manometrically. Although these results suggest that herbicidal effectiveness is not seriously diminished as a result of photolysis, field trials of II indicated that it was of no value either as a post- or pre-emergence herbicide (5).

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References

1. VISHNIAC, W., Methods in Enzymology, vol. IV, S.P. Colowich and N.O. Kaplan, eds., pp. 342-355 (1957), Academic Press, New York.

2. PAPE, B.E. and ZABIK, M.J., Division of Pesticide Chemistry, CIC-ACS Joint Conference, Toronto, May 1970.

3. FORSYTHE, W.F. and CHRISTISON, F., Gen. Elec. Rev. 32, 664 (1929).

4. DRABER, W., DICKORE, K., BUCHEL, K.H., TREBST, A., and PISTORIUS, E., Naturwissenschaften 55, 446 (1968).

5. EUE, L., Farbenfabriken Bayer, Leverkusen, private communication.

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