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PHOTOISOMERIZATION OF BENTAZONE

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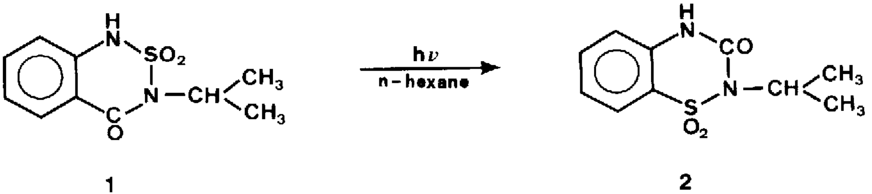
ABSTRACT: Photolysis of bentazone 1 in non-polar solvents e.g. n-hexane yields the unexpected photoproduct 2. On irradiation in methanol and in water 1-methylbentazone and anthranilic acid isopropylamide as a degradation product are observed.

3-Isopropyl-1H-2,1,3-benzothiadiazin-4(3H)-one 2,2-dioxide 1 is a widely used contact herbicide marketed as bentazone[1]. The UV spectrum of this compound shows strong absorption at 224 nm and a weak band at 328 nm. On irradiation with a high-pressure mercury lamp bentazone in non-polar solvents like n-hexane, toluene or dichloromethane is converted to an isomer[2], 2-isopropyl-2H-1,2,4-benzothiadiazin-3(4H)-one 1,1-dioxide 2. This compound was previously prepared by Vernin and Hurmer through condensation of o-aminobenzenesulfonic acid isopropylamide with phosgene and has tranquilizing and hypnotic activity[3].



1

2

The structure of 2 is confirmed by ^{1}H-nmr-, ^{13}C-nmr- and MS-data[4]. The mass spectrum of bentazone 1 shows a base peak at m/e 119 corresponding to $M^+-(SO_2-N-C_3H_7)$, whereas 2 has a base peak at m/e 91 (C_6H_4NH) and a fragment m/e 155 which can be explained as $M^+-(CO-N-C_3H_7)$. The ^{1}H-nmr spectra of 1 and 2 are similar except for small differences in the aromatic region resulting from the changed substitution on the benzene ring. The carbonyl carbon of 1 has a chemical shift of 162.6 ppm, appropriate for an aromatic amide, whereas the shift of δ = 151.48 ppm in 2 is typical of the urea type carbonyls of such compounds as uracil. Further proof of the structure of photoproduct 2 is the formation of o-aminobenzenesulfonic acid isopropylamide on alkaline hydrolysis[5]. The yield of the photorearrangement of bentazone is not high because of the formation of o-aminobenzenesulfonic acid isopropylamide as a degradation product; some polymeric material is formed as well.

It can be assumed that the rearrangement proceeds either intra- or intermolecularly by a radical mechanism e.g. after a sulphamide bond is broken by UV-irradiation the sulphur radical formed can attack the aromatic ring and a new carboxamide bond is developed between carbonyl and amino group. The details of this process need clarification. In polar solvents like methanol and water the photorearrangement of bentazone cannot be observed. Under these conditions 1-methylbentazone and anthranilic acid isopropylamide as a degradation product as well as dimers are formed[6].

ACKNOWLEDGEMENT

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REFERENCES AND NOTES

1. The Pesticide Manual, 8th ed., ed. by C. R. Worthing, The British Crop Protection Council, 1987, 63
2. Bentazone (50 mg) in 600 ml n-hexane/toluene (5:1) was irradiated through pyrex for 40 minutes. The product was purified by column chromatography on silica gel with dichloromethane/ethyl acetate (1:1); colorless prisms, yield ca. 15 %, R_F = 0.79, mp 175 °C
3. J. Vernin, R. Hurmer, Fr. M. 4279, 1967 (Chem. Abstr., 68: P 39659 a)
4. ^{1}H-nmr (90 MHz, $CDCl_3$) δ 1.6 (6H, d), 4.9 (1H, m), 7.2 (2H, m), 7.55 (1H, m), 7.8 (1H, m)
   ^{13}C-nmr (20 MHz, $CDCl_3$) δ 151.48, 134.51, 134.21, 123.53, 123.38, 122.50, 116.65, 48.83, 21.30
   MS (m/e) 240 (M^+); ν_{max} (KBr) cm^{-1} 1685, 1600
5. Colorless oil, mp 166 °C (as N-acetyl derivative), ^{13}C-nmr (20 MHz, $CDCl_3$) δ 144.93, 134.0, 129.55, 123.08, 117.96, 117.71, 46.18, 23.60, MS (m/e) 214 (M^+)
6. G. P. Nilles, M. J. Zabik, J. Agric. Food Chem. 23 (3), 410 (1975)

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