Tetrahedron Letters,Vol.24,No.49,pp 5551-5552,1983 0040-4039/83 $3.00 + .00
Printed in Great Britain

PHOTOCHEMICAL REACTIONS OF BENZOHYDROXAMIC ACIDS

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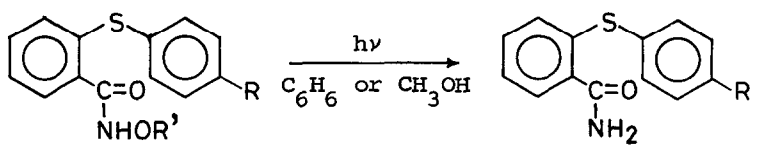
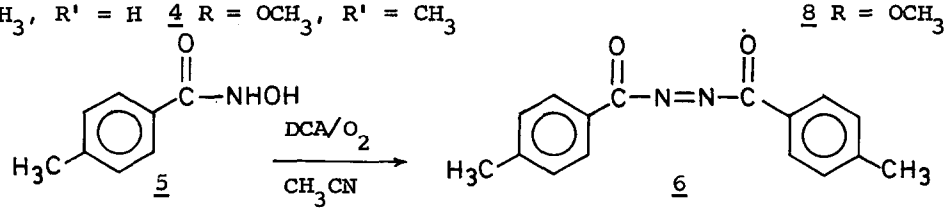
Summary: 2-(Arylthio)benzohydroxamic acids 1 & 2 undergo photodeoxygenation under unsensitised irradiations. DCA sensitized irradiation of a model benzohydroxamic acid (5), however, yields 1, 2-diacyldiazene (6).

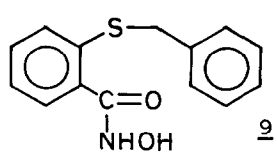
Photooxidation of sulfides to corresponding sulfoxides is known under unsensitized[1] conditions. However, studies on 2-(arylthio)benzohydroxamic acids 1 & 2 and their O-methyl derivatives 3 & 4 under unsensitized conditions of photooxidation reveal that neither the sulfoxides nor the oxygen transfer products viz. 2-(arylsulfinyl)benzamides[2] are formed. Instead, photodeoxygenation occurs. The photooxidation under 9, 10-dicyanoanthracene (DCA) sensitization[3],

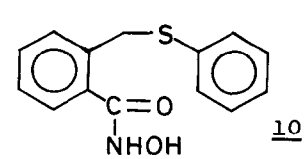


1 R = R' = H 3 R = H, R' = CH_3 7 R = H

2 R = OCH_3, R' = H 4 R = OCH_3, R' = CH_3 8 R = OCH_3







on the other hand, brings about deep seated transformation involving -CONHOH function, clearly seen in the photooxidation of benzohydroxamic acid 5 which gives 1, 2-diacyldiazene, (6).

Thus 2 Mmoles of 2-(phenylthio)benzohydroxamic acid m.p. 175°[4] (1) and O-methyl-2-(phenylthio)benzohydroxamic acid m.p. 105°[6] (3) were separately irradiated by high pressure Hg-lamp (USHIO-452) in benzene or methanol (50 ml) for 2 hrs to give 2-(phenylthio)benzamide m.p. 178°[4] (7). Under similar conditions 2-(4-methoxyphenylthio)benzohydroxamic acid m.p. 140°[5] (2) and O-methyl-2-(4-methoxyphenylthio)benzohydroxamic acid m.p. 125°[6] (4) afforded 2-(4-methoxyphenylthio) benzamide m.p. 201°[5] (8). The isolated yields in these reactions were 80-85%. Irradiation of 4-methylbenzohydroxamic acid m.p. 154°[7] (5), 2-(phenylmethylthio) benzohydroxamic acid 139°[8] (9) and 2-(phenylthiomethyl)benzohydroxamic acid m.p. 177°[8] (10) fails to bring about any change, indicating very effective cage-recombination processes, not possible in case of compounds 1 - 4 due to inherent geometry. Irradiation of 2Mmoles of 4-methylbenzohydroxamic acid (5) in presence of DCA (5 mg) in acetonitrile (50 ml) saturated with oxygen afforded 1, 2-bis(4-methylbenzoyl)diazene (6) m.p. 107° /m/e 266, IR 1775, 1685 cm^{-1}; PMR δ 2.4 (6H, s), δ 7.8 (4H, d, J=7Hz), δ 8.0 (4H, d, J=7Hz/.

The generation of R-CONH radical can account for the observed results and has been substantiated by both thermal and photochemical studies which will be the subject matter of a future communication.

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(Received in UK 11 October 1983)