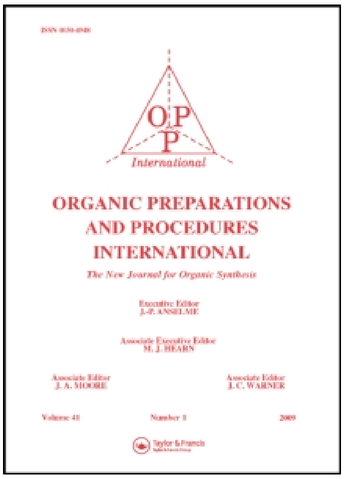

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TEREPHTHALOHYDROXIMOYL CHLORIDE

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"anisaldehyde-sulfuric acid" reagent[7] and heated gently for 1-2 min at 75-80°. The 5α-epimer eluted first and gave a yellow spot on TLC. This separated well from the 5β-epimer which eluted next and gave an orange spot. They further recrystallized from acetone-petroleum ether to afford pure products.

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TEREPHTHALOHYDROXIMOYL CHLORIDE

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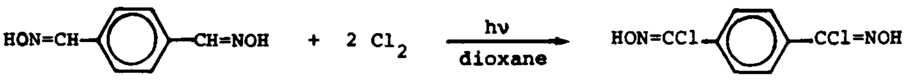
Terephthalohydroximoyl chloride, which is used as bactericide and mould killer in the textile industry,[1] has been synthesized by several workers,[2-7] in yields between 48-78% with reported melting points of 140°, 177.5°, 183° and 189°. In this work, it was prepared by chlorination of



terephthalaldoxime under UV radiation (or direct sunlight), in a higher yield (87%) than previously reported and in shorter reaction time. Thus, this method is more convenient even on a industrial scale.

EXPERIMENTAL SECTION

Terephthalohydroximoyl Chloride.- In a 100 ml round bottom flask, equipped with a reflux condenser and a gas inlet tube, a solution of 2 g (12.2 mmol) terephthalaldoxime[2,8,9] in 35 ml of dioxane was introduced and the apparatus placed in a thermostated bath at 10°; the experiment was performed under irradiation by a UV lamp (λ 366 nm). The chlorine stream was then started. The yellow color of the solution faded within a few minutes, then began to turn green. After 0.5 hr, the color was dark green and the chlorine stream was stopped. Upon standing, the color turned bluish and terephthalohydroximoyl chloride began to precipitate and within 0.5 hr precipitation was completed. The colorless neddles, mp. 165-167° were collected and recrystallized from ethanol-water (1:2) or dioxane-chloroform (1:2) to give 2.48 g (87%) of product, mp. 187-189°; lit. mps. are variable.[2-7] The product is soluble in ethanol, acetone, ether, ethyl acetate, DMF and THF, slightly soluble in dioxane, nearly insoluble in boiling benzene or chloroform. IR (KBr): 3300-3200, 3080, 1620, 1520, 1120, 1000, 940, 650 cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 7.9 (s, 4H, aromatic), 12.45 (s, 2H, hydroxyl).

Anal. Calcd. for $C_8H_6Cl_2N_2O_2$: C, 41.23; H, 2.60; Cl, 30.42; N, 12.02
Found : C, 41.02; H, 2.68; Cl, 30.76; N, 12.17

It is possible to carry out the reaction under direct sunlight. Although the various stages of the reaction are the same, the reaction required 2 hrs and the mp. of crude product was 178-185°; after recrystallization, it rose to the same melting point as above; the yield is slightly lower.

The variable mps.[2-7] and of terephthalaldoxime[2,8,9] reported in the literature, could be attributed to the syn- $\rightleftharpoons$ anti- isomerization. There are two C=N double bond in these compounds and three geometrical isomers, e.g. syn- syn-; anti- anti- and syn- anti- are possible.

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