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IMPROVED SYNTHESIS OF 2H-1,3(3H)-OXAZINE-2,6-DIONE (OXAUACIL)

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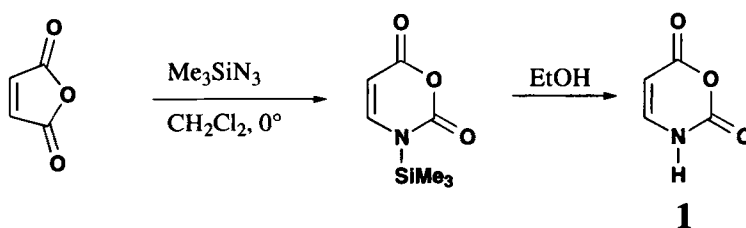
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IMPROVED SYNTHESIS OF 2H-1,3(3H)-OXAZINE-2,6-DIONE (OXAURACIL)

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(05/12/95)

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In our study of hetero Diels-Alder reactions, we had need of the 3-oxa derivative of uracil, 2H-1,3(3H)-oxazine-2,6-dione (**1**). The reaction of trimethylsilyl azide with maleic anhydride in the absence of solvent has been reported to provide **1**.¹ In our hands, however, the published approach resulted in a violent, exothermic reaction, little product, and much polymeric residue. We now present a modified procedure for the synthesis of **1** in 70-90% yields. Control of the reaction temperature is essential and was easily accomplished by running the reaction in methylene chloride at 0°.



EXPERIMENTAL SECTION

All glassware was washed with dilute acid, rinsed with distilled water, and then dried in an oven. NMR spectra taken on a Bruker ARX 300 spectrophotometer, IR spectrum taken on a Nicolet 5DXC FTIR spectrophotometer.

2H-1,3(3H)-Oxazine-2,6-dione (1).- A solution of maleic anhydride (3.0 g, 31 mmol) in methylene chloride (15 mL) in a dry flask under nitrogen was cooled to 0°. Trimethylsilyl azide (4.5 mL, 34 mmol) was then added dropwise. The mixture was kept at 0° for 2 hrs and then allowed to warm to room temperature overnight. Absolute ethanol (100 mL) was added and copious white crystals of **1** formed immediately. The product was collected, dried and recrystallized from ethanol to give 2.9 g (83 %) of single-crystal x-ray quality crystals, mp 156-157°, lit.² mp. 158-159°. The IR and NMR spectra are identical to those reported.²

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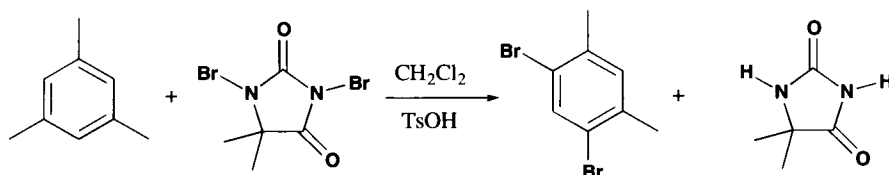
DIBROMANTIN AS A REAGENT FOR THE AROMATIC BROMINATION OF POLYALKYLBENZENES

Submitted by
(08/25/95)

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For the past several years, we have explored reagents useful for electrophilic aromatic halogenation.¹ Normally NBS is associated with allylic and benzylic free radical bromination and to a lesser extent as a source of bromonium ions. The same is true for the less expensive dibromantoin (1,3-dibromo-5,5-dimethylhydantoin or 1,3-dibromo-5,5-dimethyl-2,4-imidazolidinedione) which, in contrast to NBS, delivers *two* bromines and has been used for allylic bromination in commercial applications.² As with NBS, dibromantoin (DBH) brominates electron-rich aromatic compounds on



extended reflux in CCl_4 with or without free-radical initiators. Orazi and colleagues observed such brominations of aromatic ethers, acetanilides and thiophene by DBH as well as of phenanthrene and related polynuclear aromatics;³ under such conditions, DBH did not brominate benzene, bromobenzene or naphthalene.⁴ The aromatic bromination of activated benzoic acids such as 2,6-dimethoxybenzoic acid with DBH in aqueous base has been accomplished on a pilot plant scale.⁵ The present report describes the utility of dibromantoin for electrophilic aromatic bromination in combination with moderately acidic catalysts. It complements a recent note that such brominations can be carried out with DBH and very strong acids such as triflic acid and sulfuric acid.⁶ In order to determine the optimum conditions for the preparative uses of DBH for aromatic bromination of polyalkylbenzenes, a number of variables were examined at the one millimolar level. Such data (Tables 1-3) served to guide the selections of preparative variables without excessive losses of reagents and solvents.