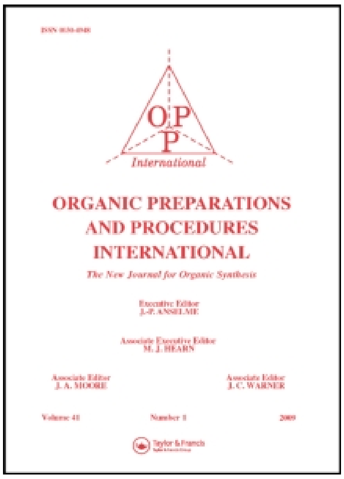


Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

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

Gretchen M. Rehberg[a]; Brian M. Glass[a]
[a] Department of Chemistry, Bucknell University, Lewisburg, PA

To cite this Article Rehberg, Gretchen M. and Glass, Brian M.(1995) 'IMPROVED SYNTHESIS OF 2H-1,3(3*H*)-OXAZINE-2,6-DIONE (OXAURACIL)', Organic Preparations and Procedures International, 27: 6, 651 — 652
To link to this Article: DOI: 10.1080/00304949509458523
URL: http://dx.doi.org/10.1080/00304949509458523

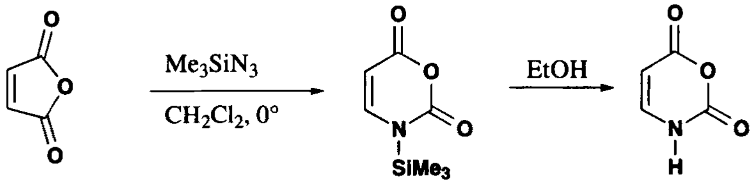
IMPROVED SYNTHESIS OF 2H-1,3(3*H*)-OXAZINE-2,6-DIONE (OXAURACIL)

Submitted by
(05/12/95)

Gretchen M. Rehberg* and Brian M. Glass[†]

Department of Chemistry
Bucknell University, Lewisburg, PA 17837

In our study of hetero Diels-Alder reactions, we had need of the 3-oxa derivative of uracil, 2H-1,3(3*H*)-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°.



1

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(3*H*)-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]

Acknowledgements.- Research support from Bucknell University gratefully acknowledged. BG thanks the Council on Undergraduate Research for a summer fellowship. The Bruker ARX 300 NMR was purchased by funds from the Keck Foundation and an NSF ILI grant.

REFERENCES

[†] Dow Chemical Company Fellow (1992-1996).

1. J. H. Macmillan, *Org. Prep. Proced. Int.*, **9**, 87 (1977).

2. J. D. Warren, J. H. MacMillan, and S. S. Washburne, *J. Org. Chem.*, **40**, 743 (1975).

****

DIBROMANTIN AS A REAGENT FOR THE AROMATIC BROMINATION OF POLYALKYLBENZENES

Submitted by
(08/25/95)

Xavier Herault, Pakorn Bovonsombat and Edward Mc Nelis*

Department of Chemistry, New York University, New York, NY 10003

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 dibromantin (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, dibromantin (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 dibromantin 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.