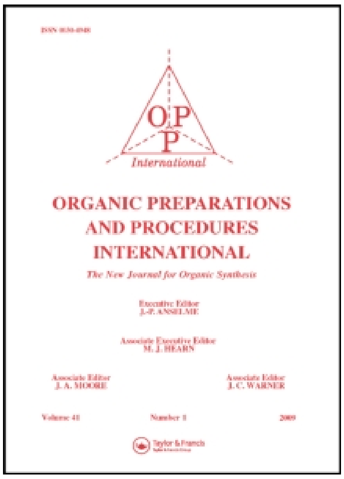


Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

A CONVENIENT PREPARATION OF ALKYL- AND ARYLSULFONYLPYRIDINES

C. S. Giam[a]; K. Kikukawa[a]; D. A. Trujillo[a]
[a] Department of Chemistry, Texas A & M University, College Station, Texas

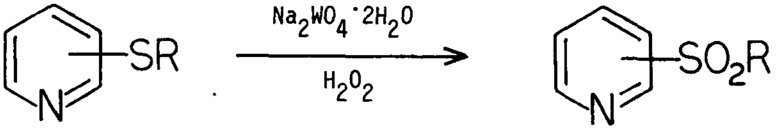
To cite this Article Giam, C. S. , Kikukawa, K. and Trujillo, D. A.(1981) 'A CONVENIENT PREPARATION OF ALKYL-AND ARYLSULFONYLPYRIDINES', Organic Preparations and Procedures International, 13: 2, 137 — 140
To link to this Article: DOI: 10.1080/00304948109356112
URL: http://dx.doi.org/10.1080/00304948109356112

A CONVENIENT PREPARATION OF ALKYL- AND ARYLSULFONYLPYRIDINES

Submitted by C. S. Giam*, K. Kikukawa and D. A. Trujillo
(5/21/80)
Department of Chemistry
Texas A & M University
College Station, Texas 77843

The oxidation of alkylthiopyridines to the corresponding alkylsulfonylpyridines has been reported in the literature,[1-4] but the procedure of choice involved the use of potassium permanganate[5,6] and a rather cumbersome procedure for the isolation of products. As alkylphenyl sulfides have reportedly been converted to arylsulfones in the presence of tungstinic acid,[7] we investigated a similar procedure for the alkylthiopyridine systems. The pyridylalkyl sulfides and sulfones are commercially desirable as they have exhibited antibacterial, herbicidal and fungicidal activity.[8,9]

We now report the successful oxidation of alkyl- and arylthiopyridines[10] to the corresponding alkyl- or arylsulfonylpyridines by the action of hydrogen peroxide and sodium tungstate. The procedure is particularly convenient since the reaction is carried out in a heterogeneous aqueous mixture and only a simple extraction is required to obtain the sulfonylpyridine. The additional advantages of this reaction are that it utilizes 1/15 of the solvent used in the potassium perman-



ganate reaction and also tolerates an excess of hydrogen peroxide without producing the N-oxide. The table illustrates the yields obtained.

Table

R	Yield II (%)	mp. (bp.)	Lit.
a) 2-methyl	76	(136-139°/2.5 torr)	(325°/1 atm)[11]
b) 3-methyl	99	54-55°[a]	55-56°[12]
c) 4-methyl	36	79-80°[a]	83°[13]
d) 3-phenyl	95	102.5-103°[2]	106-107°†[14]

[a] Recrystalized from benzene-petroleum ether. † Uncorrected.

EXPERIMENTAL

Melting points were measured in a Buchi melting point apparatus and are corrected. NMR spectra were recorded on a Varian T-60 spectrometer in deuterochloroform with chemical shifts reported in δ units downfield from internal tetramethylsilane. The following procedure is representative of the various sulfonylpyridines prepared.

<u>3-Methylsulfonylpyridine</u>. <u>General Procedure</u>.- A mixture of 14 mg of sodium tungstate, 4 ml of distilled water and one drop of acetic acid was warmed to 65° with stirring and 4.010 g (0.032 mol) of 3-methylthiopyridine[10] was added to give a heterogeneous mixture. Hydrogen peroxide, 6.5 ml (0.065 mol), was added dropwise at a rate of one drop every 15 sec (addition time of 25-30 min.). After addition the temperature was increased to and held at 75-80° for 20 min. The solution was cooled to room temperature and 5 drops of ammonium hydroxide were added, followed by a sufficient amount of sodium bisulfite to neutralize the excess hydrogen peroxide (effervescence ceases). The aqueous solution was extracted with chloroform to yield

5.00 g (99% yield) of 3-methylsulfonylpyridine, mp. 54-55°. A sample was recrystallized from petroleum ether for elemental analysis.

Anal. Calcd for $C_6H_7NO_2S$: C, 45.84; H, 4.49; N, 8.91.
Found: C, 46.06; H, 4.49; N, 8.85.

Acknowledgement.- We wish to thank the Robert A. Welch Foundation for the support of this research.

REFERENCES

1. S. P. Acharya and K. S. Nargund, J. Sci. Ind. Res., 21B, 483 (1962).
2. H. Johnston, U.S. Patent 3,296,272; Chem. Abstr., 66, 104903a (1967).
3. H. C. Van der Plas and H. J. den Hertog, Rec. Trav. Chim. Pays-Bas., 81, 841 (1962).
4. E. Profft and W. Rolle, Wiss. Z. Tech. Hochsch. Chem. Leuna-Merseburg, 2, 187 (1959-1960).
5. D. E. Ames and B. T. Warren, J. Chem. Soc., Suppl. No. 1, 5518 (1964).
6. A. Albert and G. B. Barlin, J. Chem. Soc., (C), 2389 (1959).
7. H. S. Schultz, H. B. Freyermuth, and S. R. Buc, J. Org. Chem., 28, 1140 (1963).
8. J. Dekker and P. A. Ark, Physiol. Plant., 12, 888 (1959).
9. D. R. Grassetti, M. E. Brokke and J. F. Murray, Jr., J. Med. Chem., 8, 753 (1965).
10. C. S. Giam and K. Kikukawa, presented at the 176th Annual Meeting of the American Chemical Society, Miami, Florida, September (1978).

11. E. C. Taylor and S. F. Martin, J. Am. Chem. Soc., 96, 8095 (1974).

12. G. B. Barlin and J. A. Benbow, J. Chem. Soc., Perkin Trans., 2, (7), 790 (1974).

13. H. King and L. L. Ware, J. Chem. Soc., 873 (1939).

14. C. S. Muth, R. S. Darlak and J. C. Patton, J. Heterocycl. Chem., 9 (5), 1003 (1972).

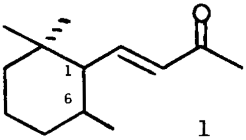
A CONVENIENT PREPARATION OF *cis*-DIHYDROIONONE

Submitted (5/14/80)

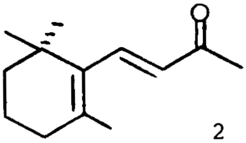
by Crist N. Filer*, James C. Pugliese, John C. Morrison and David G. Ahern

Ligands Group
New England Nuclear
Boston, Massachusetts 02118

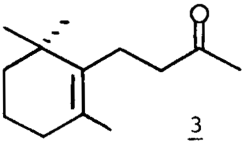
The recent, increased attention in the chemopreventive role of retinoids in the development of cancers of the epithelial tissues,[1] has prompted interest in syntheses of radiolabelled retinoic acid, its analogues and metabolites. For a synthesis of *cis*-5,6-dihydroretinoic acid [10-^{3}H], large quantities of a precursor, *cis*-dihydroionone (1), were required. An obvious and inviting approach from the standpoint of simplicity and cost appeared to be the selective reduction of the



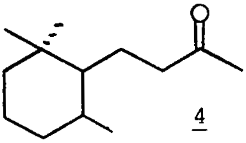
1



2



3



4