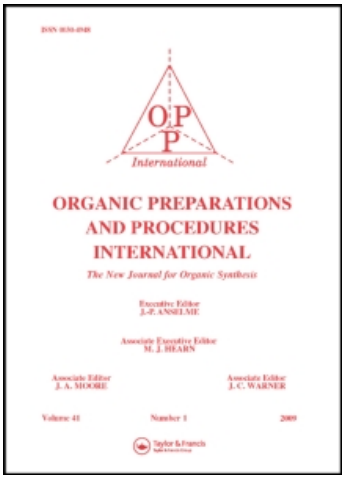

Organic Preparations and Procedures International

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

A HIGH YIELDING PREPARATION OF 2,2'-BIPYRIDINE-1-OXIDE

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To cite this Article Demnitz, F. W. Joachim and D'heni, Maria Betânia(1998) 'A HIGH YIELDING PREPARATION OF 2,2'-BIPYRIDINE-1-OXIDE', Organic Preparations and Procedures International, 30: 4, 467 — 469
To link to this Article: DOI: 10.1080/00304949809355313
URL: http://dx.doi.org/10.1080/00304949809355313

A HIGH YIELDING PREPARATION OF 2,2'-BIPYRIDINE-1-OXIDE

Submitted by (12/01/97)

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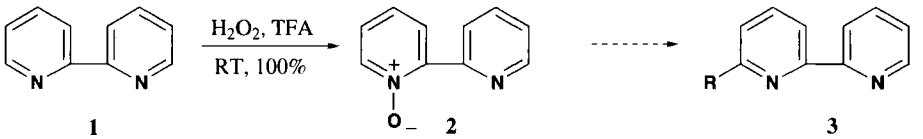
The bipyridyl moiety **1** continues to be widely used as a complexation agent in both organic and inorganic complex chemistry.[1] For example, the use of the bipyridyl function as an *antenna*[2,3] attached to some other ligand (**3**) has been considered in light conversion devices. As such, one can envisage the bipyridyl function as a component of luminescent lanthanoid complexes,[3,4] some of which are currently being used in immunoassay kits.[5] Typically bi- (and higher) pyridine systems can be synthesized by diverse methods involving coupling of individual monomeric pyridine units[6] or by manipulation of existing bipyridines. In the many cases involving the use of unsymmetrical bipyridine moieties,[6,7] an attractive starting compound for the preparation of requisite materials is 2,2'-bipyridin-1-oxide (**2**) which, with the aid of relevant protocols, can be transformed into 6-substituted-2,2'-bipyridine derivatives **3**.



1 **2** **3**

Compound **2** has been previously synthesized by the oxidation of 2,2'-bipyridyl **1** with 30% hydrogen peroxide in glacial acetic acid[8] or by *m*-CPBA in chloroform[9] in poor and moderate-to-good yields respectively. The work-up and purification involved in these methods is lengthy (cf. ref. 8) and provided only moderate yields of the mono-N-oxide **2** at best in our hands. We now report an efficient, mild, rapid and high-yielding method for the synthesis of 2,2'-bipyridine-1-oxide **2**, which constitutes a significant improvement in terms of yield, reaction time and ease of work-up over hitherto used procedures as well as avoiding chromatographic purification of the product. Namely stirring of 2,2'-bipyridyl **1** with 30% hydrogen peroxide in trifluoroacetic acid for one to two hours at room temperature provided after work-up a quantitative yield of the desired 1-oxide **2**. Neither unreacted starting material[9] nor over-oxidized 1,1'-dioxide (even after prolonged reaction times) were isolated. The crude oily product solidified *in vacuo* to a hygroscopic solid which was pure by tlc, MS and ^{13}C- and ^{1}H NMR. In practice it could be used as such for further transformations. We believe this to be the method of choice for the preparation of this useful intermediate.

EXPERIMENTAL SECTION

Reagents were used as supplied by Aldrich. NMR, IR and Mass spectra were recorded on Varian Unity Plus 300MHz, Brüker IF566 and Finnigan MAT GCQ intruments respectively.

2,2'-Bipyridine-1-oxide.- To a solution of 2,2'-bipyridyl (624 mg, 4 mmol) in trifluoroacetic acid (3 mL, 40 mmol, 10 equiv.) was added 30% hydrogen peroxide (0.6 mL, ≈6 mmol, ≈1.5 equiv.). After stirring at room temperature for 2 h, the solution was transferred to a separatory funnel with chloroform and washed with 6N NaOH (3 x 5 mL). The aqueous washes were back-extracted with chloroform (4 x 10 mL) and the combined organic phases dried (Na_2SO_4), filtered and concentrated *in vacuo* to afford a clear yellow oil, which solidified *in vacuo* (50 mm Hg) to a gray-brown solid (688 mg, 100%), mp. 51-52°, lit.: 58.5-59.5°,[8a] 59°,[9a] 54-56°,[9b] 59-61°.[9c] We attribute the lower melting point of the material obtained by us to the effect of the very high atmospheric humidity (≈100%) in this part of Brazil upon this hygroscopic[9a] product. All spectroscopic data were fully consistent with those reported:[9b] ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.82 (d, *J* = 8 Hz, 1H), 8.66 (br d, *J* = 4.5 Hz, 1H), 8.26 (br d, *J* = 7 Hz, 1H), 8.11 (dd, *J* = 8, 2.5 Hz, 1H), 7.77 (ddd, *J* = 8, 8, 2 Hz, 1H), 7.38-7.16 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 149.4, 149.2, 147.1, 140.5, 136.1, 127.7, 125.8, 125.4, 125.1, 124.2; IR (KBr): 1584, 1248 cm^{-1}; MS (EI): 172 (M^+), 156.

REFERENCES

1. J. Reedijk in *Comprehensive Coordination Chemistry*, G. Wilkinson Ed., Vol. 2, pp 73, Pergamon Press, 1987; C. Bolm, M. Zehnder and D. Bur, *Angew. Chem., Int. Ed. Engl.*, **29**, 205 (1990); A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser and A. V. Zelewsky, *Coord. Chem. Rev.*, **84**, 85 (1988); E. C. Constable, *Adv. Inorg. Chem.*, **1**, 34, (1989).

2. B. Alpha, J.-M. Lehn and G. Mathis, *Angew. Chem., Int. Ed. Engl.*, **26**, 266 (1987); J.-M. Lehn, *Angew. Chem., Int. Ed. Engl.*, **29**, 1304 (1990).

3. L. Prodi, M. Maestri, R. Ziessel and V. Balzani, *Inorg. Chem.*, **30**, 3798 (1991).

4. M. Murru, D. Parker, G. Williams and A. Beeby, *Chem. Commun.*, 1116 (**1993**); M. Balzani, J.-M. Lehn, J. van de Loosdrecht, A. Mecati, N. Sabbatini and R. Ziessel, *Angew. Chem., Int. Ed. Engl.*, **30**, 190 (1991); V.-M. Mukkala, C. Sund, M. Kwiatkowski, P. Pasanen, M. Hogberg, J. Kankare and H. Takalo, *Helv. Chim. Acta*, **75**, 1621 (1992).

5. E. Soini and I. Hemmila, *Clin. Chem.*, **25**, 353 (1979); E. Soini, I. Hemmila and P. Dahlen, *Ann. Biol. Clin.*, **48**, 567 (1990); R. A. Evangelista, A. Pollak, B. Allore, E. F. Templeton, R. C. Morton and E. P. Diamandis, *Clin. Biochem.*, **21**, 173 (1988).

6. D. J. Cardenas and J. P. Sauvage, *Synlett.*, 916 (**1996**) and references therein.

7. For some examples see: A. Downard, G. E. Honey and P. J. Steel, *Inorg. Chem.*, **30**, 3733 (1991); J. Uenishi, T. Tanaka, S. Wakabayashi and S. Oae, *Tetrahedron Lett.*, **31**, 4625 (1990); J. Uenishi, T. Tanaka, K. Nishiwaki, S. Wakabayashi, S. Oae and H. Tsukube, *J. Org. Chem.*, **58**, 4382 (1993); J. Uenishi, K. Nishiwaki, S. Hata and K. Nakamura, *Tetrahedron Lett.*, **35**, 7973 (1994); J. S. Field, R. J. Haines, J. P. Campbell and H. S. Sadesh, *S. Afr. J. Chem.*, **46**, 70 (1993).

8. a) I. Murase, *Nippon Kagaku Zasshi*, **77**, 682 (1956); b) I. Antonini, F. Claudi, G. Cristalli, P. Franchetti, M. Grifantini and S. Martelli, *J. Med. Chem.*, **24**, 1181 (1981); c) D. B. Moran, G. O.

Morton and J. D. Albright, *J. Heterocyclic Chem.*, **23**, 1071 (1986).

9. a) D. Wenkert and R. B. Woodward, *J. Org. Chem.*, **48**, 283 (1983); b) J.-C. Plaquevent and I. Chichaoui, *Bull. Soc. Chim. Fr.*, **133**, 369 (1996); c) W. Sont and H. Alper, *Org. Prep. Proced. Int.*, **12**, 243 (1980).

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SURFACE MEDIATED SYNTHESIS OF O-PHOSPHOROTHIOATES

Submitted by (10/27/97) K. Ramadas*, N. Janarthanan and D. Meera Rani

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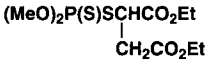
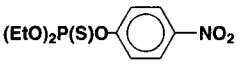
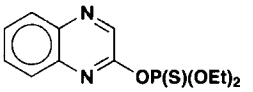
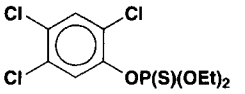
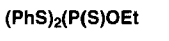
Malathion, *parathion*, *quinalphos*, *chlorpyrifos*, *edifenphos*, *monocrotophos*, *phosphamidon*, and *phorate* are widely used organophosphorus compounds for pest control in India. *Parathion* is manufactured industrially by a laborious procedure involving the treatment of O,O-diethyl thiophosphoryl chloride with *p*-nitrophenol at 10° in a 20% solution of sodium ethoxide in ethanol.[1]

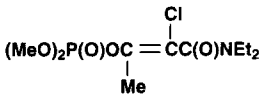
Malathion 

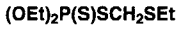
Parathion 

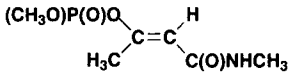
Quinalphos 

Chlorpyrifos 

Edifenphos 

Phosphamidan 

Phorate 

Monocrotophos 

Distillation of solvent, followed by dilution with water, filtration and subsequent steam distillation provides the product. Finally the product is dried by heating at 110° under vacuum. Similar aqueous work-up and vacuum distillation are necessary to manufacture *chlorpyrifos*[2] *monocrotophos*, *phosphamidon* and *malathion*.

The general method of reacting a hydroxy compound with thiophosphoryl chloride at elevated temperatures in the presence of an acid binder in ketones suffers from disadvantages such as (a) liberation of hydrogen chloride gas which leads to corrosion in industrial production, (b) formation of side-products at high temperatures, and (c) hydrolysis of the organophosphorus compounds during