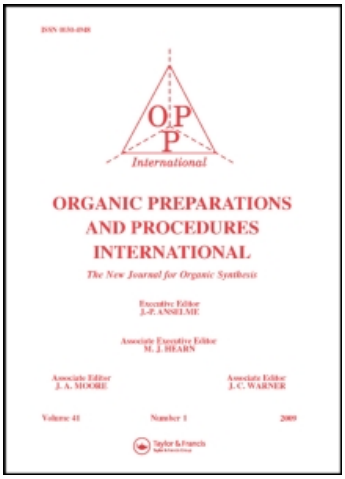

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SYNTHESIS OF ALDIMINES BY DEOXYGENATION OF NITRONES

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SYNTHESIS OF ALDIMINES BY DEOXYGENATION OF NITRONES

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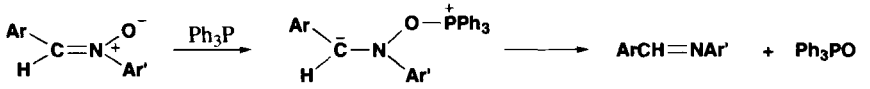
Aldimines are an important class of organic compounds[1] and perusal of the literature reveals that the preferred route for the synthesis of aldimines involves the condensation of aldehydes with ammonia or amines. However, this method is sensitive to the pH of the reaction medium and substituent effects. For example, it is difficult to obtain aldimines from the condensation of 4-methoxybenzaldehyde with amines or 4-nitroanilines with aldehydes. Hence, any method that does not depend upon these factors is worthy of examination. As a continuation of our work on the chemistry of nitrones,[2] it was proposed to synthesize the aldimines through the deoxygenation of α,N-diaryl nitrones. Perusal of the literature reveals that the selective deoxygenation of nitrones and heteroaromatic N-oxides has been the subject of considerable interest and several methods are available on the reduction of the N-O bond in these systems.[3] Triphenylphosphine has been used to reduce the N-O bond of the aldonitrones to yield the aldimines in 90% yield;[3c] the promised detailed procedures never appeared.[4] Related material supplied by Prof. Horner reported that attempts to deoxygenate α-(4-methoxyphenyl)-N-phenylnitrone with an equimolar quantity of triphenylphosphine by

boiling in petroleum ether (40-70°) failed. When the same reaction was repeated with petroleum ether (110-140°), the desired aldimine was obtained in 74% yield. However, several of our attempts to prepare the aldimine by this method did not give the expected products. Hence modification of the above procedure was sought.

In our procedure, equimolar quantities of a α,N-diaryl nitrone and triphenylphosphine were mixed in a flask dried in a hot air oven at 100°, fitted with an air condenser and heated in an oil bath gently and then refluxed for about 2.5 hrs at about 200°; lower temperatures and shorter times resulted either in the recovery of starting materials or a mixture of starting materials and the product. In order to generalize this method, this procedure was used with a number of differently substituted α,N-diaryl nitrones (Table). It must be noted that in this procedure, the aldimine was isolated by pouring petroleum ether into the reaction mixture while it was still hot (trituration of the solid obtained after cooling was rather difficult and resulted in poor yields), allowing it to cool and then decanting the petroleum ether solution. The removal of solvents gave in aldimines, purified by recrystallization from anhydrous ether and identified through their ^{1}H NMR spectra. The mechanism of the deoxygenation may be visualized as shown below.



a) Ar = Ar' = C_6H_5 b) Ar = 4-MeC_6H_4, Ar' = C_6H_5
c) Ar = 4-MeOC_6H_4, Ar' = C_6H_5 d) Ar = 4-ClC_6H_4, Ar' = C_6H_5
e) Ar = 4-FOC_6H_4, Ar' = C_6H_5 f) Ar = 4-$NO_2C_6H_4$, Ar' = C_6H_5
g) Ar = C_6H_5, Ar' = 4-MeC_6H_4 h) Ar = C_6H_5, Ar' = 4-ClC_6H_4
i) Ar = C_6H_5, Ar' = 4-FC_6H_4 j) Ar = C_6H_5, Ar' = 4-$EtO_2C_6H_4$

TABLE. Deoxygenation of Nitrones to Aldimines

Compd	Yield (%)	mp/bp (lit./°C)	^{1}H NMR ($CDCl_3$,δ) CH=	aromatic	others
2a	83	52-53[6]	8.40	7.0-8.0	–
2b	82	320/747mm[7]	8.30	7.0-7.9	2.20 (Me)
2c	80	63-64[8]	8.40	7.0-8.0	3.90 (MeO)
2d	85	64-65[7]	8.35	7.1-8.0	–
2e	79	176/5mm[a]	8.30	7.0-7.9	–
2f	87	93-94[9]	8.60	7.3-8.4	–
2g	85	150/4mm[10]	8.40	7.1-8.0	2.30 (Me)
2h	81	62-63[10]	8.40	7.0-7.9	–
2i	87	56-58[10]	8.40	7.0-8.0	–
2j	85	205/7mm[10]	8.40	7.2-8.1	4.56 (CH_2) 1.43 (CH_3)

a) *Anal.* Calcd. for $C_{13}H_{10}FN$: C, 78.37; H, 5.06; N, 7.03. Found: C, 78.35; H, 5.12; N, 6.98.

EXPERIMENTAL SECTION

Melting points were uncorrected. IR spectra were recorded on a Perkin-Elmer C577 spectrometer. ^1H nmr were recorded in $CDCl_3$ using a 90 MHz Perkin-Elmer spectrometer with TMS as the internal standard. The differently substituted diaryl nitrones (**1**) were prepared by condensing the corresponding substituted benzaldehydes with various phenyl hydroxylamines.[5]

Aldimines from Nitrones. Typical Procedure.- The α,N-diarylnitrone (**1**) mixed with an equimolar quantity of triphenylphosphine in a dried flask fitted with an air condenser was heated in an oil bath at 200° for about 2-2.5 hrs. Petroleum ether (30-40 mL) was added when the mixture was still hot (~50-60°), triturated well and cooled. The petroleum ether solution of aldimine was separated from the insoluble phosphine oxide by filtration. The solid was triturated further with petroleum ether (4-5x10 mL portions). The combined petroleum ether filtrates were decolorized with charcoal, filtered and the solvent was evaporated to yield the aldimines which were purified by recrystallization from anhydrous ether or distillation.

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IMPROVED PREPARATIONS OF SYMMETRIC PORPHYRINS

Submitted by (12/08/93)

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Symmetric porphyrins such as octaethylpocphyrin (**4a**), octamethylporphyrin and tetraphenylporphyrin have been synthesized via monopyrrole procedures.[1] The precursor of **4a**, ethyl 5-methyl-3,4-diethylpyrrole-2-carboxylate (**2a**), is usually obtained by diborane reduction of ethyl 4-acetyl-3-ethyl-5-methylpyrrole-2-carboxylate (**1a**). Other symmetric porphyrins, such as etioporphyrin I (**4b**), coproporphyrin I and uroporphyrin I, are reported to be synthesized *via* dipyrrylmethane or dipyrrylmethene procedures,[2] since they cannot be synthesized from monopyrroles because of the isomerization of the porphyrinogen in the strong mineral acid media used for the cyclization.[3] In our study of porphyrins, we have found that **2a** could be obtained in higher yield by zinc/hydrochloric acid reduction of **1a** in ethanol. Ethyl 4-acetyl-3-ethyl-5-methylpyrrole-2-carboxylate (**1a**) was obtained by the method of Paine *et al.*[4]

Although the porphyrinogen undergoes isomerization in strong mineral acid media, the type I porphyrins[5] can be formed under milder conditions from monopyrroles. The 5-methylpyrrole-2-carboxylates (**2**) were converted to pyrrylmethylamines (**3**) by bromination followed by diethylamination. The pyrrylmethylamines (**3**) which are amorphous solids or undistillable liquids, were saponified with ethanolic potash and then treated *in situ* with excess acetic acid and a stream of oxygen, the porphyrins (**4**) recrystallized after workup. Fine needles of **4** can be obtained by recrystallization. For porphyrins bearing carboxylic acid groups, such as coproporphyrin I, esterification in sulfuric acid/alcohol and then recrystallization yields better results. The precursor of etioporphyrin I (**4b**) in this study, ethyl 4-ethyl-3,5-dimethylpyrrole-2-carboxylate (**2b**), was also obtained by zinc/hydrochloric acid reduction of the corresponding acetylpyrrole **1b**[6,7] in ethanolic solution. This is a relatively shorter route for the porphyrin synthesis and thus the overall yields of the porphyrins are improved considerably. For example, the overall yield of **4b** is 15% by this method starting from **1b** (obtained from 2,4-pentanedione and ethyl acetoacetate)[7] based on ethyl acetoacetate, while the highest yield