

m.p. 221–223°: ν (cm.⁻¹) 3490, 1696 in CHCl₃; 3410, 1692 in Nujol; λ_{\max} in 95% EtOH 224 (4.80), 283 (4.07), 291 (4.00); *Anal.* Calcd. for C₂₁H₂₀N₂O: C, 79.71; H, 6.37; N, 8.85; Found: C, 79.73; H, 6.43; N, 8.72. The differentiation between vinylindole and bisindole formation appears to be the result of a combination of electronic and steric effects on the relative rates with which the probable intermediate, the indolenine I, undergoes tautomerization to a vinylindole or alkylation by an indole to yield a bisindole.

SCHOOL OF CHEMISTRY WAYLAND E. NOLAND
UNIVERSITY OF MINNESOTA DONALD N. ROBINSON⁷
MINNEAPOLIS 14, MINN.

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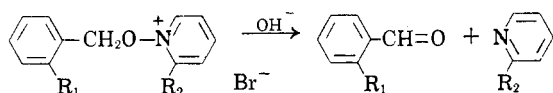
Alkaline Decomposition of Quaternary Salts of Amine Oxides¹

Sir:

Since the time of Meisenheimer's classic experiments on quaternary salts of amine oxides,² numerous reports have been made of the alkaline decomposition of such salts to tertiary amine and aldehyde.³ Ochiai and his colleagues⁴ have applied the reaction to salts of pyridine-*N*-oxide and observed the formation of formaldehyde and acetaldehyde. Recently, Katritsky studied this reaction as a method of deoxygenating pyridine-*N*-oxides under nonreducing conditions and reported the formation of the corresponding bases in fair yield.⁵

In view of this new application and the general lack of quantitative data on these reactions, we would like to report our experience with *N*-benzyl-oxypyridinium salts which demonstrates that this is both an excellent method for preparing aromatic aldehydes and a convenient way of deoxygenating pyridine-*N*-oxides.

The formation of quaternary salts, such as I, proceeded in high yield by heating the appropriate pyridine-*N*-oxide with benzyl bromide or a similar halide in acetonitrile (I, 95%, m.p. 94–96°, Found: C, 54.15, H, 4.55; II, 92%, m.p. 113–115°, Found: C, 55.81, N, 5.08; III, 67%, m.p. 97–98°, Found: C, 40.32, H, 3, 47). When either I or II was treated with dilute



I, R₁ and R₂ = H IV, R₁ = H VI, R₂ = H
II, R₁ = H, R₂ = CH₃ V, R₁ = NO₂ VII, R₂ = CH₃
III, R₁ = NO₂, R₂ = H

aqueous sodium hydroxide, benzaldehyde could be isolated in 90–92% yield by extraction of the acidified solution with chloroform followed by concentration and distillation. In the case of I and II, work-up of the basic fraction in the usual way gave pyridine and α -picoline in 78 and 84% yields, respectively, after distillation. The decomposition of III was studied to provide a comparison of our procedure with other standard aldehyde syntheses,⁶ and gave pure *o* nitrobenzaldehyde, m.p. 42–43°, after chromatography over alumina, in 60% yield. The crude yield of brown crystals was 97%.

When *m*-xylyl dibromide was treated with pyridine-*N*-oxide, the di-salt (m.p. 121–122°, Found: C, 45.54, H, 4.51) formed in 97% yield. Decomposition of this di-salt with base gave isophthalaldehyde as pure crystals, m.p. 88–89°, in 62% yield. Other applications of the method are being investigated. It is apparent that there is a formal analogy between these alkaline decompositions and the formation of aldehydes by the alkaline cleavage of nitronic esters.^{7,8}

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF ROCHESTER
ROCHESTER, N. Y.

W. FEELY
W. L. LEHN⁹
V. BOEKELHEIDE

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(9) Predoctoral Fellow, National Institutes of Health, 1956–57.

Selective Reductions with Diborane, an Acidic-Type Reducing Agent

Sir:

Alkali metal borohydrides and aluminohydrides are now widely utilized for the selective reduction of functional groups. Such reductions are believed to involve a transfer of a hydride unit from the complex anion to an electron-deficient center in the organic reactant.¹

Diborane has long been known to reduce aldehydes and ketones rapidly. In these reactions it is believed to function through an attack on an electron-rich center in the functional group.² The possibility that diborane, as an acidic-type reduc-

(1) Aided by a grant from the National Science Foundation.

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