m.p. 221–223°: ν (cm.$^{-1}$) 3490, 1696 in $CHCl_3$; 3410, 1692 in Nujol; λ_{max} in 95% EtOH 224 (4.80), 283 (4.07), 291 (4.00); *Anal.* Calcd. for $C_{21}H_{20}N_2O$: 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.

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[7] Research Corporation research assistant, 1956–1957. We are indebted to the Research Corp. for a Frederick Gardner Cottrell grant in support of this research.

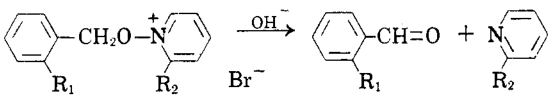
Alkaline Decomposition of Quaternary Salts of Amine Oxides[1]

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 colleagues[4] 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*-benzyloxypyridinium 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 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%.



I, R_1 and R_2 = H
II, R_1 = H, R_2 = CH_3
III, R_1 = NO_2, R_2 = H
IV, R_1 = H
V, R_1 = NO_2
VI, R_2 = H
VII, R_2 = CH_3

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]

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[1] Aided by a grant from the National Science Foundation.

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[8] Hass and Bender, *J. Am. Chem. Soc.*, **71**, 1767 (1949); *Org. Syntheses*, **30**, 99 (1950).

[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-

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ing agent, might exhibit markedly different selectivity than the saline borohydrides, as basic-type reducing agents, led us to explore the reducing potentialities of diborane. Ample data on the reducing properties of the borohydrides are now available for comparison.[3]

Diborane was prepared by adding a solution of sodium borohydride in diglyme to a solution of boron trifluoride etherate in the same solvent, and the gas was passed into a solution in diglyme or tetrahydrofuran of the compound under examination. After an appropriate interval of time, the residual hydride was determined by analysis. In cases where the group under study was one which is not reduced by sodium borohydride itself, the diborane could be conveniently generated within the reaction mixture by adding boron trifluoride etherate in diglyme to a solution of sodium borohydride and the compound in the same solvent.

Similar results were obtained in both procedures. The following data summarize typical observations using these procedures (the first figure in parenthesis gives the reaction time in hours, the second the moles of hydride utilized per mole of compound). All reactions were studied at room temperature.

Rapid Reduction	Slow or Negligible Reduction
Benzaldehyde (1.0, 1.0)	Benzoyl chloride (2.0, 0.4)
Benzophenone (1.0, 1.0)	Isobutyryl chloride (2.0, 0.4)
γ-Butyrolactone (1.0, 2.0)	Ethyl benzoate (2.0, 0.4)
Styrene oxide (1.0, 1.2)	Nitrobenzene (2.0, 0.1)
Azobenzene (1.0, 1.9)	1-Nitropropane (2.0, 0.1)
Benzoic acid (0.5, 2.8)	Naphthalene (2.0, 0.0)
p-Nitrobenzoic acid (0.5, 2.5)	
Benzonitrile (0.5, 2.0)	
n-Butyronitrile (1.0, 2.0)	

These results reveal remarkable differences in the reducing properties of diborane and the alkali metal borohydrides. Thus, in diglyme solution borohydride reduces acid chloride groups more readily than aldehyde or ketone groups,[4] whereas the reverse is true with diborane. Similarly, lithium borohydride reacts more readily with ester than with nitrile groups,[5] whereas diborane reacts far more rapidly with the nitrile than with the ester grouping. Finally, the rapid reduction of the carboxylic acid group is in marked contrast to its usual stability and inertness. These results suggest that a judicious application of diborane and the alkali metal borohydride would make possible a truly remarkable selectivity in organic reductions.

The following preparations are typical of the two procedures utilized.

The diborane generator consisted of a 250-ml. flask containing a dropping funnel, an inlet for nitrogen, and an outlet for the diborane. In the flask was placed 28.5 g. (0.20 mole) of boron trifluoride etherate in 50 ml. of diglyme; in the dropping funnel, a solution of 5.1 g. (0.135 mole) of sodium borohydride in 125 ml. of diglyme. The flask was connected to the reaction flask containing 29.6 g. (0.20 mole) of *m*-nitrobenzonitrile in 150 ml. of tetrahydrofuran. The system was flushed out with nitrogen. The diborane (0.08 mole) was generated at an even rate over a period of an hour by dropping the sodium borohydride solution into the boron trifluoride etherate and passed into the flask containing the nitrile. (The exit gases were passed through a wash bottle containing acetone to catch and destroy unreacted diborane.) The reaction mixture was permitted to stand at room temperature for a second hour, ethanol was added to destroy excess diborane, followed by dry hydrogen chloride to convert the amine to the hydrochloride. After removal of solvent under reduced pressure, the reaction mixture was allowed to cool, the solid hydrochloride was collected on a filter, washed with ethanol, and dried. There was obtained 33.2 g., 88%, of the crude amine hydrochloride, m.p. 223–225°. Recrystallization from ethanol yielded pure *m*-nitrobenzylamine hydrochloride, m.p. 225–227°, in 79% yield.

p-Nitrobenzoic acid, 0.20 mole, was slowly added and dissolved in 0.18 mole of sodium borohydride in 150 ml. of diglyme (nitrogen atmosphere). Hydrogen was evolved. The flask was cooled in a water bath, stirred, and 0.22 mole of freshly distilled boron trifluoride etherate was added over a period of 1 hr. After a second hour, the contents were hydrolyzed, and the solid product was collected. There was obtained 24.1 g., 79% yield, of *p*-nitrobenzyl alcohol, m.p. 91–93°.

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Hydroboration of Olefins. A Remarkably Fast Room-Temperature Addition of Diborane to Olefins

Sir:

Diborane has been reported to react very slowly with simple aliphatic olefins at elevated temperatures[1,2] and with styrene at room temperature[3] to form the corresponding organoboron compounds.

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