Communications TO THE EDITOR

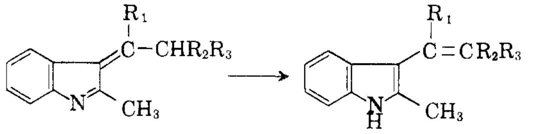
Synthesis of 3-Vinylindoles

Sir:

The recent disclosure[1] that the 2-methylindole adduct of methyl vinyl ketone can be converted to 2-methylcarbazole prompts us to report on some of our studies with 3-vinylindoles, since it has seemed likely to us that carbonyl-containing 2-methyl-3-vinylindoles, such as IIa–IId, may also serve as carbazole precursors.

The colorless 1:1 condensation product, m.p. 124–125°, from 2-methylindole and ethyl acetoacetate with hydrochloric acid, to which Scholtz[2] and later Cook and Majer[3] assigned the indolenine structure Ia, is now assigned the 3-vinylindole structure IIa since it has NH and conjugated carbonyl absorption in the infrared [ν(cm.$^{-1}$) 3440, 3330, 1684, 1608 in $CHCl_3$; 3350, 3150, 1670, and 1652 (doublet), 1617 in Nujol] and conjugated absorption in the ultraviolet [λ_{max} in 95% EtOH, with intensities in log ϵ in parentheses, 224 (4.65), 266[4] (3.79), 283 (3.94), 289 (3.93), 331 (3.93)]. Similarly, the yellow condensation product, m.p. 121–123°, from refluxing 2-methylindole with acetylacetone in acetic acid solution, to which Scholtz[5] assigned the bisindole structure IIIb on the basis of apparently erroneous analytical data, is now assigned the 3-vinylindole structure IIb: ν (cm.$^{-1}$) 3440, 3310, 1657 in $CHCl_3$; 3230, 1649 in Nujol; λ_{max} in 95% EtOH 224 (4.48), 281 (3.92), 285[4] (3.91), 358 (4.09). *Anal.* Calcd. for $C_{14}H_{15}NO$: C, 78.84; H, 7.09; N, 6.57; Mol. wt. 213.27. Found: C, 79.06; H, 7.01; N, 6.64; Mol. wt. 220 (Rast).

Condensations in refluxing acetic acid solution of 2-methylindole with carbonyl compounds containing a readily enolizable α-hydrogen appear to represent a quite general route to 3-vinylindoles. By this method we have obtained, in addition to IIa and IIb, IIc (from benzoylacetone), yellow, m.p. 157–158°: ν (cm.$^{-1}$) 3440, 1643 in $CHCl_3$; 3230, 1631 in Nujol; λ_{max} in 95% EtOH 222 (4.49), 263 (4.27), 279[4] (4.15), 286[4] (4.06), 391 (4.15); *Anal.* Calcd. for $C_{19}H_{17}NO$: C, 82.88; H, 6.22; N, 5.09; Found: C, 82.64; H, 6.32; N, 5.14; IId (from dibenzoylmethane), orange, m.p. 193–195°: ν (cm.$^{-1}$) 3440, 1633 in $CHCl_3$; 3240, 1627 in Nujol; λ_{max} in 95% EtOH 221 (4.58), 282 (4.28), 406 (3.70); *Anal.* Calcd. for $C_{24}H_{19}NO$: C, 85.43; H, 5.68; N, 4.15; Found: C, 85.52; H, 5.81; N, 4.22; IIe (from α-phenylacetoacetonitrile), pale yellow, m.p. 193–194°: ν (cm.$^{-1}$) 3440, 3310, 2200 in $CHCl_3$; 3340, 2190 in Nujol; λ_{max} in 95% EtOH 224 (4.54), 279 (3.98), 288 (3.92), 352 (3.86); *Anal.* Calcd. for $C_{19}H_{16}N_2$: C, 83.79; H, 5.92; N, 10.29; Found: C, 83.95; H, 6.21; N, 10.38; IIf (from desoxybenzoin), colorless, m.p. 163–164°: ν (cm.$^{-1}$) 3450 in $CHCl_3$; 3400 in Nujol; λ_{max} in 95% EtOH 226 (4.56), 279 (4.37), 353 (3.90); *Anal.* Calcd. for $C_{23}H_{19}N$: C, 89.28; H, 6.19; N, 4.53; Found: C, 89.53; H, 6.44; N, 4.81.



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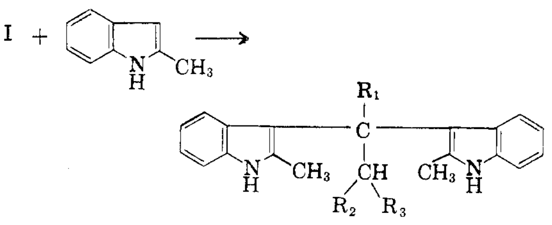

III

Ia–IIa: R_1 = CH_3, R_2 = $COOC_2H_5$, R_3 = H
IIb–IIIb: R_1 = CH_3, R_2 = $COCH_3$, R_3 = H
IIc: R_1 = CH_3, R_2 = COC_6H_5, R_3 = H
IId: R_1 = C_6H_5, R_2 = COC_6H_5, R_3 = H
IIe: R_1 = CH_3, R_2 = CN, R_3 = C_6H_5
IIf: R_1 = R_2 = C_6H_5, R_3 = H
IIIg: R_1 = CH_3, R_2 = C_6H_5, R_3 = H

Some of the limits to the 3-vinylindole synthesis are suggested by the facts that under analogous conditions acetone and acetophenone give bisindoles (like III)[6] and phenylacetone (in contrast to desoxybenzoin) with 2-methylindole gives a bisindole (IIIg), colorless, m.p. 269–271°: ν (cm.$^{-1}$) 3460 in $CHCl_3$; 3380 in Nujol; λ_{max} in 95% EtOH 229 (4.79), 285 (4.11), 292 (4.09); *Anal.* Calcd. for $C_{27}H_{26}N_2$: C, 85.67: H, 6.92; N, 7.40; Found: C, 85.30; H, 6.93; N, 7.64; as does indole (in contrast to 2-methylindole) with acetylacetone: colorless,

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(1) J. Szmuszkovicz, *J. Am. Chem. Soc.*, **79**, 2819 (1957).

(2) M. Scholtz, *Ber.*, **46**, 1082 (1913).

(3) A. H. Cook and J. R. Majer, *J. Chem. Soc.*, **1944**, 486. Although it has not been experimentally verified by us, it seems likely that other 1:1 condensation products of indoles with β-ketoesters described in this reference should also be formulated as 3-vinylindoles (like II), and not as indolenines (like I), since they were not obtained as salts, even though prepared in the presence of hydrochloric acid.

(4) Inflection.

(5) M. Scholtz, *Arch. Pharm.*, **253**, 629 (1915).

(6) W. E. Noland, M. H. Fischer, D. N. Robinson, and H. Sorger-Domenigg, Paper 39 presented before The Organic Division at the 131st National Meeting of The American Chemical Society, Miami, Fla., April 9, 1957, Abstracts, p. 24-O.

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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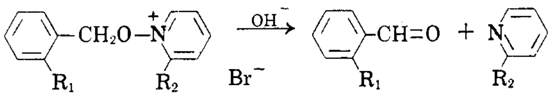
Alkaline Decomposition of Quaternary Salts of Amine Oxides[1]

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.

[2] Meisenheimer, *Ann.*, **397**, 273 (1913).

[3] *Cf.* Culvenor, *Rev. Pure. Applied Chem. (Australia)*, **3**, 83 (1953); Katritsky, *Quart. Rev.*, **10**, 395 (1956).

[4] Ochiai, Katada and Naita, *J. Pharm. Soc. Japan*, **64**, 210 (1944); *Chem. Abstr.*, **45**, 5154 (1951).

[5] Katritsky, *J. Chem. Soc.*, 2404 (1956).

[6] *Org. Syntheses*, **Coll. Vol. 3**, 641 (1955).

[7] Weisler and Helmkamp, *J. Am. Chem. Soc.*, **67**, 1167 (1945).

[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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[1] L. W. Trevoy and W. G. Brown, *J. Am. Chem. Soc.*, **71**, 1675 (1949). H. C. Brown, E. J. Mead, and B. C. Subba Rao, *J. Am. Chem. Soc.*, **77**, 6209 (1955).

[2] H. C. Brown, H. I. Schlesinger, and A. B. Burg, *J. Am. Chem. Soc.*, **61**, 673 (1939).