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THE CLEAVAGE OF FORMYL GROUPS BY SODIUM HYDRIDE

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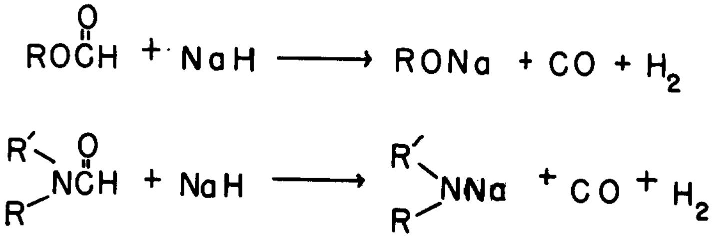
We report herein a new method of cleaving the formyl group in formates and formamides which has obvious advantages over the aqueous acidic or basic conditions sometimes employed.[2] The reagent employed is sodium hydride, and the overall reaction may be summarized by the equations



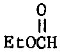
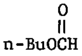
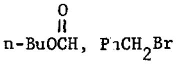
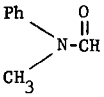
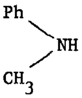
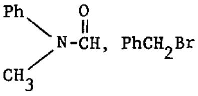
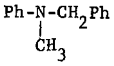
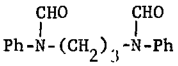
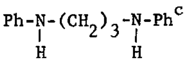
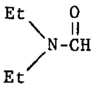
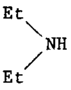
$$\mathrm{RO\overset{O}{\overset{\|}{C}}H + NaH \longrightarrow RONa + CO + H_2}$$

$$\mathrm{R'RN\overset{O}{\overset{\|}{C}}H + NaH \longrightarrow R'RNNa + CO + H_2}$$

This method should find utility in systems containing easily hydrolyzable or reducible functional groups. Illustrative results are given in Table I.

A typical reaction was carried out by adding 10.2 g. (0.1 mole) of n-butyl formate to 2.4 g. (0.1 mole) of sodium hydride in refluxing 1,2-dimethoxyethane. The progress of the reaction was followed by measuring gas evolution. The reaction had stopped after 20 minutes and the evolution of 0.19 moles of gas. The cooled reaction mixture was poured into water and the organic components separated by extraction with ether. Fractional distillation of this mixture through a 40 cm. spinning band column yielded

TABLE I

Reactant(s)	Product[a]	Yield[b]
 $\mathrm{EtO}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{H}$	EtOH	70%
 $\mathrm{n\text{-}BuO}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{H}$	nBuOH	68%
 $\mathrm{n\text{-}BuO}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{H}$, $\mathrm{PhCH_2Br}$	$\mathrm{nBuOCH_2Ph}$	43%
 $(\mathrm{Ph})(\mathrm{CH_3})\mathrm{N\text{-}}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{H}$	 $(\mathrm{Ph})(\mathrm{CH_3})\mathrm{NH}$	70%
 $(\mathrm{Ph})(\mathrm{CH_3})\mathrm{N\text{-}}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{H}$, $\mathrm{PhCH_2Br}$	 $\mathrm{Ph\text{-}}\underset{\underset{\mathrm{CH_3}}{\vert}}{\mathrm{N}}\mathrm{\text{-}CH_2Ph}$	30%
 $\mathrm{Ph\text{-}}\overset{\overset{\mathrm{CHO}}{\vert}}{\mathrm{N}}\mathrm{\text{-}(CH_2)_3\text{-}}\overset{\overset{\mathrm{CHO}}{\vert}}{\mathrm{N}}\mathrm{\text{-}Ph}$	 $\mathrm{Ph\text{-}}\underset{\underset{\mathrm{H}}{\vert}}{\mathrm{N}}\mathrm{\text{-}(CH_2)_3\text{-}}\underset{\underset{\mathrm{H}}{\vert}}{\mathrm{N}}\mathrm{\text{-}Ph}$[c]	79%
 $(\mathrm{Et})(\mathrm{Et})\mathrm{N\text{-}}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{H}$	 $(\mathrm{Et})(\mathrm{Et})\mathrm{NH}$	40%

a. Products were characterized by comparison of their infrared spectra and v.p.c. retention times with those of authentic samples.

b. Yield of pure isolated product. Product purity was determined by vapor phase chromatography.

c. Shown to be identical with an authentic sample prepared by the reaction of aniline with 1,3-dibromopropane.

5.0 g. of a fraction with b.p. 116-118. The gas chromatogram of this fraction showed a single peak with a retention time identical with that of an authentic sample of n-butanol.

Diethyl ether, dimethylsulfoxide, benzene and 1,2-dimethoxyethane have been used thus far as solvents for this reaction. Formates are readily cleaved by bases other than sodium hydride. Triphenylmethyl sodium and potassium t-butoxide are equally effective. Formamides on the other hand are only cleaved by sodium hydride. Formates and formanilides react quite rapidly, the reaction being over in 20-60 minutes. Simple alkyl formamides were quite stable and required refluxing overnight.

The intermediate alkoxides and amide ions can easily be trapped by performing the reaction in the presence of an alkylating agent. For example, cleavage of n-butyl formate in the presence of benzyl bromide gave benzyl n-butylether in 43% yield. No products arising from any intermediate carbanion could be detected even when the reaction was carried out under an atmosphere (1500 p.s.i.) of carbon monoxide.[3]

This reaction probably proceeds by a concerted mechanism in which hydride abstracts the formyl proton as carbon monoxide is being formed[4] (two moles of gas evolved per mole of formate used). Significant driving force for the reaction must be supplied by stability of carbon monoxide. When the cleavage of n-butyl formate was carried to 80% completion using potassium t-butoxide in dimethylsulfoxide-d_6, the recovered n-butyl formate was enriched (1.5%) with deuterium. The mass spectrum clearly showed all the deuterium to be located at the formyl position, demonstrating that some exchange had occurred. Further studies are in progress to delineate the scope and mechanism of this reaction.[5]

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References

(1) 1964 National Science Foundation Undergraduate Research Participant.

(2) R. A. Boissonnas in "Advances in Organic Chemistry," Vol. 3, p. 178, Interscience, New York, 1963; J. F. W. Mcomie, *ibid.*, p. 219.

(3) H. Scheibler, *Ber.*, **67B**, 312-17 (1934) and earlier papers has suggested that formates react with sodium alkoxides and triphenylmethylsodium at low temperatures to give the sodium salts $RO_2C^-Na^+$. We were unable to repeat these results. At low temperatures no reaction occurred; at high temperature cleavage to alkoxides and carbon monoxide took place.

(4) This reaction is in essence the reverse of the base catalyzed reaction of alcohols with carbon monoxide to yield formates. B. S. Lacy, R. G. Dunning and H. H. Storch, *J. Am. Chem. Soc.*, **52**, 926 (1930); A. Staher, *Ber.*, **47**, 580 (1914); J. C. Gjaldback, *Acta Chem. Scand.*, **2**, 683 (1948). However, we observed no reaction between alkyl formates and sodium alkoxides in alcoholic solution.

(5) For other examples of base catalyzed decomposition of formate esters see: H. J. Ringold, B. Löken, G. Rosenkranz and F. Sondheimer, *J. Am. Chem. Soc.*, **78**, 816 (1956) and F. Adickes and G. Schäfer, *Ber.*, **65**, 953 (1932).