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A NEW ELECTROGENERATED BASE. CONDENSATION OF CHLOROFORM WITH ALIPHATIC ALDEHYDES[1)]

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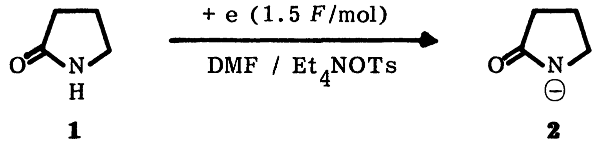
A novel base was generated by electrochemical reduction of 2-pyrrolidone in DMF, and this electrogenerated base (EGB) was effective to promote the condensation of chloroform with aliphatic aldehydes in good yields.

Bases promote a variety of useful organic reactions, whereas almost all of the base-catalyzed reactions never take place without the addition of bases to the reaction systems. The electrogenerated bases (EGB), namely, anionic species formed from probasic compounds (PB) under the conditions of cathodic reduction have been suggested to behave as bases, though only limited examples have been reported so far.[2-7)]

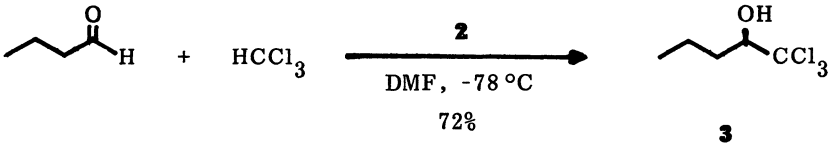
In this letter we wish to report that a novel EGB **2** is generated by the electrochemical reduction of 2-pyrrolidone (**1**) in DMF (Scheme 1), and the EGB **2** is effective to promote the condensation of chloroform with aliphatic aldehydes, though this condensation reaction is not always easy under the conditions of using usual bases.[8,9)]

Scheme 1.



As shown in Scheme 2, the addition of **2** into a mixture of chloroform and *n*-butyraldehyde in DMF afforded the corresponding trichloromethyl carbinol **3** in good yield. This method can be applied to a variety of aliphatic and aromatic aldehydes as the other examples are summarized in Table 1.

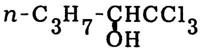
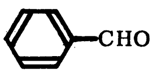
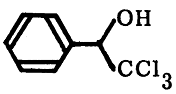
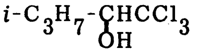
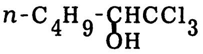
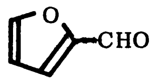
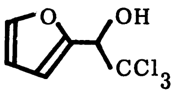
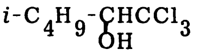
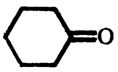
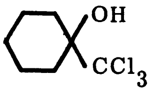
Scheme 2.



The typical procedure is as follows. The electrochemical reduction of **1** was carried out in a divided cell equipped with platinum electrodes. The cathodic solution was 20 ml of DMF containing 0.01 mol of **1** and Et_4NOTs (0.01 mol) as a supporting electrolyte. After 1.5 *F*/mol of electricity was passed, the catholyte was added to a mixture of butyraldehyde (0.01 mol) and chloroform (0.01 mol) in 10 ml of DMF at -78 °C, and the mixture was stirred for 1 h. The usual working up gave **3** in 72% yield.

Under the conditions of using usual bases, the reaction of aliphatic aldehydes with chloroform is often accompanied by the aldol condensation of the aldehydes[10)] resulting in low yields of the corre-

Table 1. Synthesis of Trichloromethyl Carbinols

Carbonyl Compound	Product[a]	Yield (%)[b]	Carbonyl Compound	Product[a]	Yield (%)[b]
$n\text{-}C_3H_7\text{-}CHO$	 $n\text{-}C_3H_7\text{-}\underset{OH}{C}HCCl_3$	80			70
$i\text{-}C_3H_7\text{-}CHO$	 $i\text{-}C_3H_7\text{-}\underset{OH}{C}HCCl_3$	56			
$n\text{-}C_4H_9\text{-}CHO$	 $n\text{-}C_4H_9\text{-}\underset{OH}{C}HCCl_3$	72			49
$i\text{-}C_4H_9\text{-}CHO$	 $i\text{-}C_4H_9\text{-}\underset{OH}{C}HCCl_3$	72			69

[a] All the products gave satisfactory spectroscopic values for the assigned structures.
[b] Isolated.

sponding trichloromethyl carbinols. On the contrary, the fact that side reactions such as aldol condensation were not observed in this new reaction system suggests that the EGB **2** is sufficiently basic to deprotonate chloroform even at -78 °C and it does not initiate the aldol condensation at this low temperature.[11]

The present method possesses high potentiality in organic synthesis since trichloromethyl carbinols are important key intermediates for the synthesis of α-substituted carboxylic acids,[12,13] carbohydrates,[14] and α-haloketones.[15]

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