

FORMIC ACID REDUCTION XXV. A SELECTIVE REDUCTION OF  
CARBON-CARBON DOUBLE BONDS CONJUGATED WITH NITRO, CYANO,  
OR SULFONYL GROUP

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It has been found that the carbon-carbon double bonds conjugated with nitro, cyano, or sulfonyl group were selectively reduced by heating with the azeotrope, composed of formic acid and triethylamine, in N,N-dimethylformamide.

In the previous papers<sup>1)</sup> we reported that the selective reduction of carbon-carbon double bonds adjacent to carbonyl was effected on heating with the azeotrope<sup>2)</sup> (abbreviated as TEAF)<sup>3)</sup>, bp 102°C/20mmHg, composed of formic acid and triethylamine in ca. 5/2 molar proportion. Despite these works, development of methods applicable for the selective reductions of carbon-carbon double bonds conjugated with nitro, cyano, or sulfonyl group has been a synthetic subject. Although several reports have appeared describing performance of the selective reductions by the catalytic hydrogenation over palladium-on-charcoal<sup>4,5)</sup> and tris(triphenylphosphine)chlororhodium(I)<sup>6)</sup> and by sodium borohydride reduction<sup>7)</sup>, virtually no generally applicable methods are known.

The present publication describes an establishment of selective formic acid reductions of carbon-carbon double bonds conjugated with nitro, cyano, or sulfonyl groups. Preliminary experimental data using benzylidenemalononitrile as a substrate are shown in Table 1. The selective reduction of the carbon-carbon double bond of the substrate was easily affected by formic acid in basic media. It was found that the reduction with TEAF was highly accelerated by the use of N,N-dimethylformamide (DMF) as a solvent.

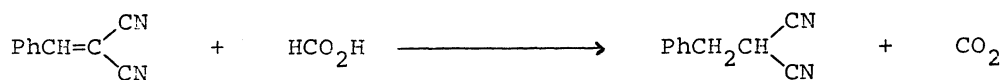


Table 1. Formic Acid Reduction of Benzylidenemalononitrile

	Reagent	Solvent <sup>a)</sup>	Reaction Temp. (°C)	Reaction Time (h)	Yield (%)
1.	99% $\text{HCO}_2\text{H}$	99% $\text{HCO}_2\text{H}$	100-105	5	0
2.	99% $\text{HCO}_2\text{H}$ <sup>b)</sup>	DMF	120-130 <sup>c)</sup>	12	81
3.	TEAF	TEAF	60 <sup>c)</sup>	2.5	90
4.	TEAF <sup>b)</sup>	DMF	25-30 <sup>c)</sup>	2	91

a) 40 ml for 0.02 mol of benzylidenemalononitrile

b) benzylidenemalononitrile(0.02 mol)/reagent=1/3

c) At this temperature considerable evolution of carbon dioxide is observed.

The procedures are as follows; to a solution of 5.2 g of TEAF in 40 ml of N,N-dimethylformamide 3.1 g (0.02 mol) of benzylidenemalononitrile was added in small portions and the mixture was stirred at room temperature until evolution of carbon dioxide almost ceased. The reaction mixture was poured into an ice water and a liberated oily material was extracted with benzene. The benzene solution was dried over anhydrous  $\text{MgSO}_4$  and evaporated. The resulting solid residue was recrystallized from ethanol to give benzylmalononitrile as colorless prisms, mp 87-88°C, in a 91% yield.

Efficiencies of TEAF in DMF toward the carbon-carbon double bonds conjugated with nitro, cyano, or sulfonyl groups were then examined with a variety of the compounds. Results are summarized in Table 2. Although yields of the desired reduction products were lowered in certain cases by undefined side reactions, reductions of nitro, cyano, carbonyl and sulfonyl groups were not observed. From these successful data, it is emphasized that the method is practically applicable for the selective reduction of such conjugated carbon-carbon double bonds. Except the  $\alpha,\beta$ -unsaturated nitro compounds, the double bonds which are able to undergo the reduction should be conjugated doubly with cyano, sulfonyl, carbonyl, or ethoxycarbonyl groups. The nature of the adjacent electron-withdrawing group is responsible for reactivities of the carbon-carbon double bonds. Effects of the electron-withdrawing groups are supposed to be in the following order;  $\text{NO}_2 > \text{CN} > \text{SO}_2\text{Ph} > \text{COPh}$ .

Although the above base-catalyzed formic acid reduction is supposed mechanistically to be familiar with the previously reported reduction<sup>8)</sup> of  $\alpha,\beta$ -unsaturated carbonyl compounds, the exhibited characteristics of the reaction

deserve a mechanistic investigation, which is now under way.

Table 2. Formic Acid Reduction of Carbon-Carbon Double Bonds Conjugated with Nitro, Cyano, or Sulfonyl Group.

No.	Substrate	Reaction Temp. (°C)	Reaction Time (h)	Yield (%)
1.	$\begin{array}{c} \text{Ph} \\ \diagdown \\ \text{C}=\text{C} \\ \diagup \\ \text{H} \end{array} \begin{array}{c} \text{NO}_2 \\ \diagup \\ \text{C} \\ \diagdown \\ \text{Ph} \end{array}$	120-125	5.5	47
2.	$\begin{array}{c} \text{Ph} \\ \diagdown \\ \text{C}=\text{C} \\ \diagup \\ \text{H} \end{array} \begin{array}{c} \text{NO}_2 \\ \diagup \\ \text{C} \\ \diagdown \\ \text{Et} \end{array}$	115-120	14.0	83
3.	$\begin{array}{c} \text{Ph} \\ \diagdown \\ \text{C}=\text{C} \\ \diagup \\ \text{Ph} \end{array} \begin{array}{c} \text{NO}_2 \\ \diagup \\ \text{C} \\ \diagdown \\ \text{H} \end{array}$	120-125	5.0	57
4.	$\begin{array}{c} \text{Ph} \\ \diagdown \\ \text{C}=\text{C} \\ \diagup \\ \text{H} \end{array} \begin{array}{c} \text{CN} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{CO}_2\text{Et} \end{array}$	50-55	2.0	84
5.	$\begin{array}{c} \text{Ph} \\ \diagdown \\ \text{C}=\text{C} \\ \diagup \\ \text{Et} \end{array} \begin{array}{c} \text{CN} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{CN} \end{array}$	75-80	5.0	77
6.	$\begin{array}{c} \text{Ph} \\ \diagdown \\ \text{C}=\text{C} \\ \diagup \\ \text{PhCH}_2 \end{array} \begin{array}{c} \text{CN} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{CN} \end{array}$	65-70	2.0	90
7.	$\begin{array}{c} \text{Ph} \\ \diagdown \\ \text{C}=\text{C} \\ \diagup \\ \text{H} \end{array} \begin{array}{c} \text{CN} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{Ph} \end{array}$	146-148	3.0	0
8.	$\begin{array}{c} \text{Ph} \\ \diagdown \\ \text{C}=\text{C} \\ \diagup \\ \text{H} \end{array} \begin{array}{c} \text{SO}_2\text{Ph} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{CN} \end{array}$	45-50	1.5	93
9.	$\begin{array}{c} \text{Ph} \\ \diagdown \\ \text{C}=\text{C} \\ \diagup \\ \text{H} \end{array} \begin{array}{c} \text{SO}_2\text{Ph} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{COPh} \end{array}$	118-120	4.0	72
10.	$\begin{array}{c} \text{Ph} \\ \diagdown \\ \text{C}=\text{C} \\ \diagup \\ \text{H} \end{array} \begin{array}{c} \text{SO}_2\text{Ph} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{H} \end{array}$	146-147	4.0	0

Substrate; 0.02 mol, TEAF; 5.2 g (0.06 mol as  $\text{HCO}_2\text{H}$ ), DMF; 40 ml

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