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Direct Synthesis of Anilides from Nitroarenes

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Nitroaromatic compounds are readily reduced to arylamines by a number of reagents [e.g., Fe, Sn, Sn(II), Zn, Ti(III)]. However, only a few methods are available for their direct conversion to the anilides, e.g., catalytic hydrogenation in the presence of acid anhydrides, and reaction with acyl tetracarbonylferrates.[1] We wish to report a new method for this latter transformation.

Despite conspicuousness of the reducing ability of low-valent molybdenum, the property has, until recently, rarely been exploited in organic synthesis. Aside from our own effort,[2] we are aware of only one report[3] on the use of complex salts of molybdenum for deoxygenation of sulfoxides. As molybdenum(II) species[4] are conveniently prepared by heating $Mo(CO)_6$ with carboxylic acids, we considered it worthwhile to examine the synthetic utility of the system. From various experiments performed, it has been shown that nitroarenes are converted to anilides directly.

$$ArNO_2 \xrightarrow{Mo(CO)_6,\ RCOOH} RCONHAr$$

Since arylamines undergo acylation on heating with carboxylic acids, it can be inferred that the amines, either in the free or metalated state, are the intermediates of our reaction. Dimeric products such as azoarenes have neither been detected nor isolated. In fact, these compounds are convertible to anilides also.[5]

It should be emphasized that the reagent combination is a rather mild reducing system. For example, it can be used to reduce a nitro group in the presence of an olefinic linkage which cannot be achieved by catalytic hydrogenation. To illustrate this point, 4-nitrostilbene was subjected to our experimental conditions. 4-Acetaminostilbene[6] was isolated. Most other functional groups such as alcohols, ketones, esters, acids, amides, nitriles, and sulfones are stable toward the Mo(II) reagents.

Table I. Reductive Acylation of Nitroarenes

Nitroarene	Anilide	Yield, %
$PhNO_2$ 98-95-3	PhNHAc 103-84-4	55
	PhNHCOEt 620-71-3	62
	$PhNHCOPr^n$ 1129-50-6	63
m-$MeC_6H_4NO_2$ 99-08-1	m-MeC_6H_4NHAc 537-92-8	68
p-$MeOC_6H_4NO_2$ 100-17-4	p-$MeOC_6H_4NHAc$ 57-66-1	85
p-$AcC_6H_4NO_2$ 100-19-6	p-AcC_6H_4NHAc 2719-21-3	46
p-$O_2NC_6H_4CH{=}CHPh$ 4003-94-5	p-$AcNHC_6H_4CH{=}CHPh$ 18559-97-2	50

Experimental Section

General Procedure for Reductive Acylation of Nitroarenes. A mixture of a nitroarene (5 mmol) and molybdenum hexacarbonyl (2.64 g, 10 mmol) in a carboxylic acid (5 mL) was heated under nitrogen at 120 °C for 20 h. The sublimed $Mo(CO)_6$ was returned to the liquid phase during reaction by occasional swirling. The cooled reaction mixture was neutralized with dilute ammonia and extracted with ether (three 50-mL portions), and the extracts were dried and evaporated to give a solid product, which was recrystallized and identified by comparison with an authentic sample.

Registry No.—$Mo(CO)_6$, 13939-06-5; acetic acid, 64-19-7; propionic acid, 79-09-4; butyric acid, 107-92-6.

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Alkylation of 1,5-Dimethoxy-1,4-cyclohexadiene. A Convenient Synthesis of 2-Alkyl- and 2-Alkenyl-1,3-cyclohexanediones

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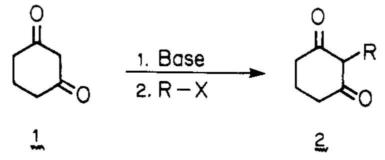
In connection with another research problem in our laboratory, we required a series of 2-alkyl- and 2-alkenyl-1,3-cyclohexanediones (**2**). The preparation of this type of compound via direct alkylation of the parent 1,3-cyclohexanedione (**1**) is reasonably efficient with reactive alkylating reagents such as methyl iodide[1] and allylic[2,3] or benzylic halides.[2] However , with less reactive alkylating agents, the reaction is generally sluggish. For example, alkylation of **1** with 1-bromobutane[3] and 4-iodo-1-butene[4] afforded the corresponding alkylated products **2** [R = $(CH_2)_3CH_3$ and $(CH_2)_2CH{=}CH_2$, respectively] in very poor yield (<11%).[5] We report herein an efficient and experimentally convenient method which avoids this problem. The method involves two simple steps: the alkylation of 1,5-dimethoxy-1,4-cyclohexadiene (**3**)[7,8] and the acid-catalyzed hydrolysis of the resultant products **5**.



The dimethoxy compound **3** was converted into the corresponding organolithium derivative by treatment with t-BuLi in THF at −78 °C. On the basis of competing inductive and