## Novel Carbon Catalysis: Oxidation in Basic Solution

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Catalytic oxidations of hydrocarbons by molecular oxygen are of considerable biological and industrial importance. One hydrocarbon oxidation which has been extensively investigated is the oxidation of fluorene to fluorenone in basic solution[1] (eq 1). Fluorene is oxidized by molecular oxygen in the

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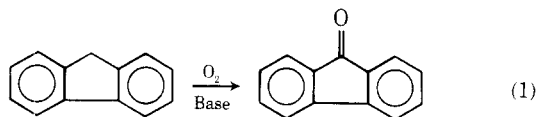
presence of potassium *tert*-butoxide in *tert*-butyl alcohol solution. The reaction is improved by the presence of benzene, dioxane, morpholine, piperidine, pyridine, hexamethylphosphoramide, dimethylformamide, or dimethyl sulfoxide (Me_2SO).[1] Also, the oxidation of solid fluorene is known to be catalyzed by ordinary or sodium methoxide treated alumina.[2]

The present note describes the strong catalysis by carbon of the fluorene oxidation in basic solutions of *tert*-butyl alcohol and ethanol. The addition of 5% charcoal in *tert*-butyl alcohol 0.2 M in potassium *tert*-butoxide increases initial reaction rate tenfold (see Figure 1). In refluxing ethanolic sodium hydroxide, autoxidation proceeds to the extent of <1%
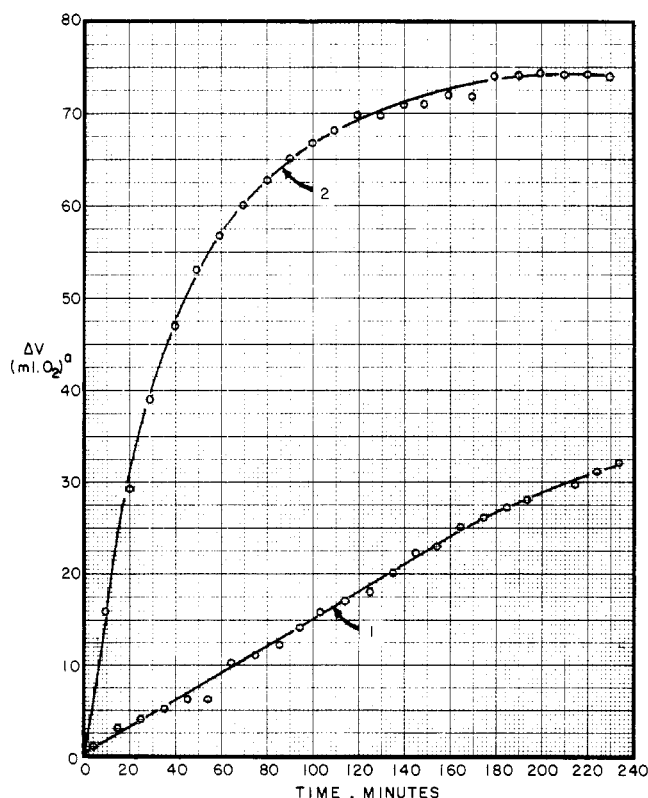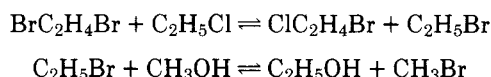

Figure 1. Autoxidation of fluorene (0.14 M) in the presence of 0.2 M potassium *tert*-butoxide: (1) *tert*-butyl alcohol; (2) with 5% by weight activated charcoal.[b] (a) No correction made for vapor pressure of water. (b) Theoretical consumption of O_2 is 75 mL.

in 2 h. With the addition of 5% charcoal, reaction is virtually complete in 2 h.

The present catalysis may be due to the fact that OH^- ions adsorbed on carbon are more basic than OH^- in solution. The adsorption of OH^- has been postulated before to explain the catalysis of H_2O_2 decomposition.[3] Carbon is known to catalyze exchange reactions of the type:[4,5]

$$BrC_2H_4Br + C_2H_5Cl \rightleftharpoons ClC_2H_4Br + C_2H_5Br$$

$$C_2H_5Br + CH_3OH \rightleftharpoons C_2H_5OH + CH_3Br$$

Here again, the occurrence of some interaction between negatively charged groups and the carbon surface is indicated. The OH^- activation may also occur through the adsorption of cations, similar to the case of anion activation by cation complexing observed in the crown ether–potassium hydroxide system.[6] In the catalysis by alumina mentioned earlier, an important role is played by adsorbed oxygen.[2] This may also be the case here. It is evident that the elucidation of mechanistic detail requires further investigation.

Reaction with charcoal in the common solvents has several advantages over reactions using catalysts previously described: (1) Charcoal is a relatively cheap material. (2) It is stable to acid, base, heat, and chemical reaction. In autoxidation it is not oxidized, as are some of the aprotic dipolar solvents.[7] It is not consumed in the reaction by complex formation as is, for example, Me_2SO.[1] (3) As a solid it can be used in a bed reactor for continuous flow processes.[8] (4) Finally, we have shown that charcoal catalyzes basic oxidation of fluorene in a solvent system not useful for oxidation without charcoal. Sodium hydroxide as base is superior to potassium *tert*-butoxide, pyridine,[9] or other common bases on economic grounds, as well as in simplicity of the chemical process, i.e., there is less chance for side products.

Experimental Section

Potassium *tert*-Butoxide–Butyl Alcohol. To a round-bottom flask fitted through a $CaCl_2$ drying tube[9] with oxygen inlet connected to a gas buret was added 25 mL of *tert*-butyl alcohol, 0.55 g of potassium *tert*-butoxide (5 mmol), and 0.56 g of fluorene (3.4 mmol). The flask was thoroughly flushed with oxygen, and reaction was allowed to proceed with vigorous stirring. The reactor was kept in a water bath at 27–30 °C. Oxygen pressure was maintained at the prevailing atmospheric pressure by means of a leveling bulb. After 4 h reaction time, the reaction mixture was quenched with water, products were extracted with carbon tetrachloride, and the organic solution was thoroughly washed with water, dried over Na_2SO_4, and then evaporated. The solid residue was analyzed by GC and NMR. Product conversion was 38% fluorenone (see Figure 1).

The above experiment was repeated with the addition of 1.0 g of Burrell charcoal (1135 m²/g; 95%, 50 mesh) to the solution. Product conversion was 94% fluorene (see Figure 1).

Sodium Hydroxide–Ethanol. The reactor described above was fitted with a reflux condenser; 25 mL of ethanol, 0.45 g of fluorene (2.7 mmol), and 0.20 g of sodium hydroxide (5 mequiv) were stirred at reflux temperature under an oxygen atmosphere for 2 h. Analysis by GC and NMR indicated <1% conversion to fluorenone.

The above procedure, with the addition of 1.0 g of charcoal, gave a bright yellow product which was pure fluorenone by GC analysis; NMR analysis indicated mostly fluorenone with some polymeric materials as impurity, but no fluorene.

Registry No.—Fluorene, 86-73-7; fluorenone, 486-25-9.

References and Notes

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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.

$$ArNO_2 \xrightarrow{Mo(CO)_6, RCOOH} RCONHAr$$
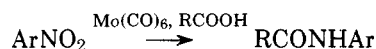
Since arylamines undergo acylation on heating with carboxylic acids, it can be inferred that the amines, either in the free or metalated state, are the intermediates of our reaction. Dimeric products such as azoarenes have neither been detected nor isolated. In fact, these compounds are convertible to 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.

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.

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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
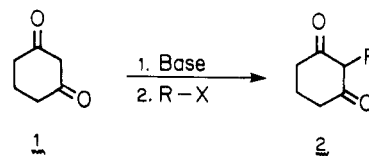
such as methyl iodide[1] and allylic[2,3] or benzylic halides.[2] However, with less reactive alkylating agents, the reaction is generally sluggish. For example, alkylation of 1 with 1-bromobutane[3] and 4-iodo-1-butene[4] afforded the corresponding alkylated products 2 [R = $(CH_2)_3CH_3$ and $(CH_2)_2CH=CH_2$, 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

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