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DEOXIDATION/REDUCTION OF AROMATIC ESTERS, α-DIKETONES, ACYLOINS, AND EPOXIDES TO THE CORRESPONDING BIBENZYL PRODUCTS WITH LITHIUM 4,4′-DI-*T*-BUTYLBIPHENYL RADICAL ANION

Rafik Karaman and James L. Fry
Bowman-Oddy Laboratories, Department of Chemistry
The University of Toledo, Toledo, OH 43606-3390

Summary: Sonication of aromatic esters, benzil, benzoin, *cis*- and *trans*-stilbene, and *trans*-stilbene oxide with excess lithium in the presence of catalytic amounts of 4,4′-di-*t*-butylbiphenyl (DBB) in dry THF afforded bibenzyl derivatives in high yields.

The reactions of esters with alkali metals (Na and K) have been studied for a long time. Alkyl and aryl benzoates, for example, react with sodium to give radical anions which can couple and then suffer spontaneous loss of alkoxide to give benzil which in turn undergoes reduction to yield benzoin as a final product.[1-5] This procedure has been improved by adding trimethylchlorosilane to the reaction mixture of sodium and ester.[6]

Surprisingly, although the reductions of esters[7,8] and related carbonyl compounds such as ketones[9,10] and aldehydes[11] with lithium metal in liquid ammonia have been reported, there appears to be no information on the reaction of esters with lithium in inert solvents. Continuing our investigation of the umpolung reactions of carbonyl compounds,[12] we have found that aromatic esters undergo facile reductive elimination to form bibenzyl derivatives when they are subjected to ultrasonic irradiation with an excess of metallic lithium and a catalytic amount of 4,4′-di-*t*-butylbiphenyl (DBB)[13] in dry THF under a dry nitrogen atmosphere for 6 h.

In order to gain further information on these transformations, a reaction mixture of 1 equiv of methyl benzoate, 4.5 equiv of lithium and 0.1 equiv of DBB in THF was sonicated at room temperature for two hours. Workup was accomplished by quenching with saturated aqueous ammonium chloride, extraction with dichloromethane, and evaporation. Examination of the reaction product mixture by GC/MS and ^{1}H NMR spectral analyses indicated the presence of benzil, benzoin, benzyl phenyl ketone, *trans*-stilbene, 1,2-diphenylethane-1,2-diol, and bibenzyl.[14] Extension of the reaction time to five hours afforded bibenzyl as the only reaction product. Repeating the same experiment beginning with known samples of benzil, benzoin, *cis*-stilbene, *trans*-stilbene and *trans*-stilbene oxide in each case afforded bibenzyl in high yields (see Table).

Table. Reductions with Lithium/DBB in THF

Substrate	% Yield of Bibenzyl[a]
Methyl benzoate	68[b]
Ethyl benzoate	74[c]
Benzyl benzoate	52[c]
Methyl *p*-toluate	49[c,d]
Benzil	76[c]
Benzoin	82[b]
cis-Stilbene	95[b]
trans-Stilbene	92[b]
trans-Stilbene oxide	95[b]

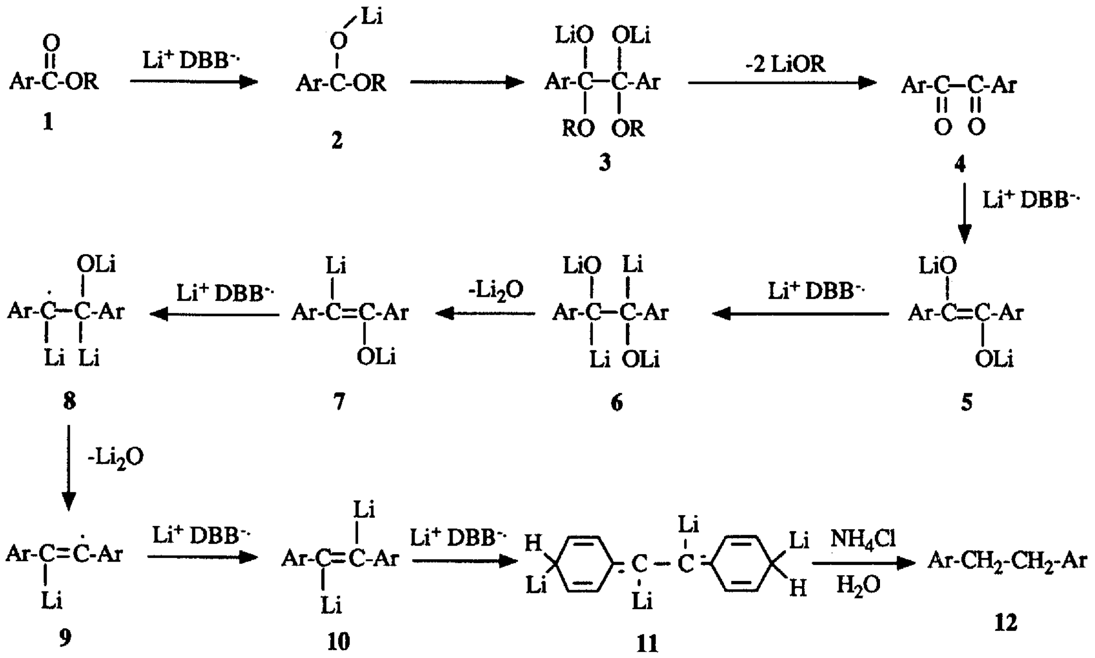
[a] The substrate (10 mmol) was sonicated with 45 mmol of Li and 1 mmol of DBB in 30 mL of dry THF under N_2 for 6 h. [b] Isolated yields. [c] The yields were estimated from the 400-MHz ^{1}H NMR spectra. [d] The corresponding bibenzyl was formed.

A mechanistic explanation for the results presented is summarized in the Scheme. We suggest that an aromatic ester (**1**) reacts with lithium DBB radical anion to form, in the first step, a radical anion, **2**, which then dimerizes to **3**. This species then expels two equiv of lithium alkoxide to form **4**. Through the further steps shown, this gives bibenzyl (**12**).[15] The sequence from **6** to **12** can be understood on the basis of the behavior of benzoin under the same conditions.[16,17]

In the absence of DBB, the reaction is very slow. This indicates that DBB served as an electron-transfer reagent from the lithium metal onto the carbonyl compound.[18] When reductions of methyl benzoate, benzil, and benzoin were attempted using sodium instead of lithium metal, no bibenzyl was obtained. This illustrates the markedly greater ability of lithium to form covalent bonds (or, possibly, tighter ion pairs) to oxygen or carbon than sodium.[19,20] There seems little doubt that the relative thermodynamic stabilities of lithium oxide and lithium alkoxide species make them good leaving groups in these reactions.

It seems clear that these factors must be keys to understanding the unique reducing properties of lithium/DBB toward aromatic esters under these reaction conditions. In accord with predictions based on the reaction mechanism proposed in the Scheme, preliminary studies involving the reduction of benzoic *acid* by the Li/DBB method indicate that the reaction stops at a stage which yields benzil after workup. Finally, it must be emphasized that the behavior of aliphatic esters differs from that of the aromatic esters reported here. This seems to be due to the different stability and reaction behavior of the aliphatic analog of radical species **2**.[21]

This reducing system holds promise of being useful for effecting a number of synthetic transformations. Further work is underway to define the scope and limitations of this method of reduction and to further investigate the mechanistic basis for its efficacy.



1
Li⁺ DBB⁻·
2
3
-2 LiOR
4
Li⁺ DBB⁻·
5
Li⁺ DBB⁻·
6
-Li₂O
7
Li⁺ DBB⁻·
8
-Li₂O
9
Li⁺ DBB⁻·
10
Li⁺ DBB⁻·
11
NH₄Cl
H₂O
12

Scheme

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