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CONVERSION OF AROMATIC KETONES, BENZYL ALCOHOLS, AND ALKYL ARYL ETHERS TO AROMATIC HYDROCARBONS WITH LITHIUM 4,4′-DI-*t*-BUTYLBIPHENYL RADICAL ANION

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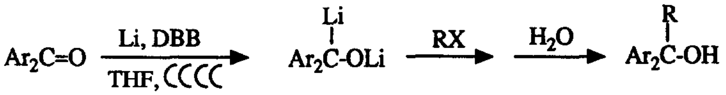
Summary: Treatment of tetrahydrofuran (THF) solutions of the title compounds with excess lithium (or potassium) metal under ultrasonic irradiation in the presence of catalytic amounts of the electron-transfer agent 4,4′-di-*t*-butylbiphenyl (DBB) caused conversions to aromatic hydrocarbons in good yields. Addition of 1 or 2 equiv of alkyl halides prior to aq ammonium chloride treatment during workup provided mono- or di-alkylated products.

We have recently shown that aromatic ketones, when dissolved in tetrahydrofuran (THF) and exposed to ultrasonic irradiation and an excess of lithium metal in the presence of catalytic amounts of 4,4′-di-*t*-butylbiphenyl (DBB), may undergo two successive single-electron transfers (SET) to form dilithium species that are reactive toward electrophiles (eq 1).[1] The substituted products resulting from these "umpolunged" carbonyls are sometimes very difficult to synthesize by conventional synthetic methods and may display interesting chemical behavior.[1b,2] We have continued to study the effects of the strong reducing conditions produced by the combination of lithium, DBB, and ultrasonic irradiation on various substrates.[3] A particular observation made during this work has led to the present report.



$$Ar_2C{=}O \xrightarrow[\text{THF, ((((}]{\text{Li, DBB}} Ar_2\overset{\overset{\text{Li}}{|}}{C}\text{-OLi} \xrightarrow{RX} \xrightarrow{H_2O} Ar_2\overset{\overset{R}{|}}{C}\text{-OH} \qquad (1)$$

In order to extend the technique summarized in eq 1 to include triarylcarbinol products, we attempted the synthesis of 9-phenylxanthen-9-ol by reacting the dilithium derivative of xanthone with iodobenzene following the previously described method.[1,4,5] Surprisingly, the product contained only 5% of the expected 9-phenylxanthen-9-ol. The major product (90%) was the hydrocarbon 9-phenyl-9*H*-xanthene. The experiment was repeated and, as time passed, aliquots were withdrawn, quenched with aq ammonium chloride solution, and analyzed by GC/MS and ^1H NMR methods. It was thus possible to observe the slow intermediate formation of 9-phenylxanthen-9-ol which then underwent gradual reduction to 9-phenyl-9*H*-xanthene. Treatment of a known sample of 9-phenylxanthen-9-ol to the reaction conditions led to formation of the same hydrocarbon. In contrast, several 9-alkylxanthen-9-ols subjected to the same conditions resisted reduction unless the reaction times were extended. Reduction and alkylation of several aryl carbinols as well as the reduction of some ethers were observed. Monitoring of the reaction of 1,1-diphenyl-1-methoxyethane, as above, indicated the intermediate formation of corresponding alcohol which then underwent conversion to the hydrocarbon.[6] The results of these experiments are summarized in the Table.

Table. Reduction/Alkylation of Aromatic Ketones, Alkyl Aryl Ethers, and Benzyl Alcohols with Lithium Metal and DBB in THF with Ultrasonication[a]

entry	substrate	time, h	product	yield, %[b]
1	9-phenylfluoren-9-ol	24	9-phenyl-9*H*-fluorene	80
2	"	80	"	90[c]
3	1,1-diphenylethanol	24	1,1-diphenylethane	76
4	"	72	"	98[c]
5	"	72	"	13[d]
6	9-phenylxanthen-9-ol	24	9-phenyl-9*H*-xanthene	80
7	9-methylxanthen-9-ol	24	9-methyl-9*H*-xanthene	53
8	9-methylfluoren-9-ol	24	9-methyl-9*H*-fluorene	88
9	triphenylmethanol	48	triphenylmethane	41
10	benzyl alcohol	48	1-phenylpropane	91[e]
11	benzhydrol	48	diphenylmethane	72
12	"	48	1,1-diphenylethane	72[f]
13	9-methoxy-9-methylfluorene	120	9-methyl-9*H*-fluorene	88
14	1,1-diphenyl-1-methoxyethane	72	1,1-diphenylethane	92
15	9-fluorenone	24	9-methyl-9*H*-fluorene	95[f]
16	"	24	9,9-dimethylfluorene	98[g]
17	"	24	9-ethyl-9-methylfluorene	96[h]
18	9-xanthone	24	9-methyl-9*H*-xanthene	48[f]
19	"	24	9-phenyl-9*H*-xanthene	90[i]
20	benzophenone	24	2,2-diphenylpropane	75[g]
21	"	24	1,1-diphenylethane	74[f]

[a] Unless otherwise indicated, reactions were conducted using 6 equiv of metal and 0.1 equiv of DBB. [b] Yields estimated by ^{1}H-NMR analysis. [c] Potassium metal used in place of lithium. [d] No DBB added. [e] Treated with 1.1 equiv of ethyl iodide before workup. [f] Treated with 1.1 equiv of methyl iodide before workup. [g] Treated with 2.2 equiv of methyl iodide before workup. [h] Treated first with 1.1 equiv of methyl iodide and then with 1.1 equiv of ethyl iodide before workup. [i] Treated with 1.1 equiv of iodobenzene before workup. Also obtained was a 5% yield of 9-phenylxanthen-9-ol.

These reactions resemble to a certain extent the reduction[7] or substitution[5,8] reactions of aromatic ketones and secondary alcohols upon treatment with lithium or sodium in liquid ammonia or in aprotic ethers. A significant difference here is that use of a large excess of metal with ultrasonic irradiation in aprotic THF in conjunction with the powerfully catalytic electron-transfer agent DBB[9] allows the occurrence of both reduction and substitution processes to take place. This permits deoxidation to accompany substitution.

Several points derived from these experiments deserve comment. First, the reactions proceed slowly or not at all in the absence of the DBB and ultrasonic irradiation. Second, potassium, but not sodium, may be used in place of lithium, but the reactions are somewhat slower. This is very likely related both to the effective oxidation potentials of the metals under the reaction conditions and to their relative abilities to bind to oxygen centers.[2] Finally, attempts to reduce alcohols lacking an aromatic ring failed. Starting material was recovered. This is no doubt related to the necessity of the substrate to have a reduction potential less than the oxidation potential of the DBB radical anion. An aromatic ring in the substrate permits that requirement to be met.

A mechanism to explain the present results that is also consistent with previous work[1,3,5,7,8] is shown in the Scheme. The use of this approach ought to provide the basis of some novel, useful techniques to complement existing synthetic methods. We are continuing our investigations in this area.

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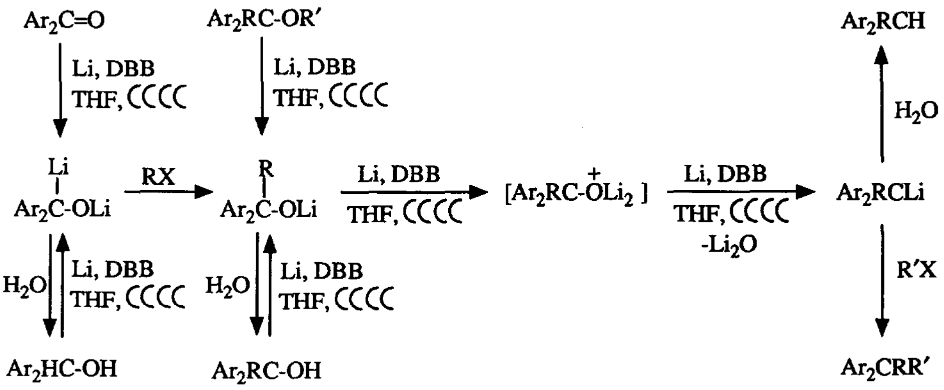

Scheme. Suggested Reaction Pathways

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4. The substrate (ca. 10 millimol) was dissolved in anhydrous THF under Ar with 6 equiv of metal and 0.1 equiv of DBB. The flask containing the reactants was placed in a common laboratory ultrasonic bath. In the case of the reductions of alcohols and ethers, sonication continued for the indicated times prior to workup with aq ammonium chloride to destroy excess metal. In the case of the reactions of ketones, sonication was continued for 2 h, then the flask was placed in a dry-ice bath and 1.1 equiv of electrophilic species was added with magnetic stirring. The reaction flask was allowed to warm to room temperature ($\leq$2 h), then returned to the ultrasonic bath for the indicated time. If a second 1.1 equiv of electrophile was to be added, the reaction flask was first cooled to -78 °C and then allowed to warm to room temperature as before, otherwise final workup with aq ammonium chloride proceeded directly.
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6. Quenching of the final stage of the alcohol reduction with D_2O instead of H_2O gave 1,1-diphenylethane-1-d_1, whereas quenching with CO_2 before aqueous workup provided 2,2-diphenylpropionic acid.
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