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Preliminary communication

A novel reducing agent. The reduction of dicarbonyls, acyloins, alkynes, and alkenes with active uranium *

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Abstract

Active uranium, prepared in hydrocarbon solvents from UCl_4 and $[(TMEDA)Li]_2$[naphthalene] is a novel reducing agent. The unprecedented stepwise reduction of benzil and benzoin to bibenzyl has been shown to proceed via the unsaturated species diphenylacetylene, *cis*-stilbene, and *trans*-stilbene. Active uranium also effects oligomerizations of diphenylacetylene and *trans*-stilbene.

The use of transition metals [2–12], as well as lanthanides and actinides [12–15], in the reduction of organic compounds is widespread. These reductions generally are of two forms; removal of oxygen, and addition of hydrogen. The highly oxophilic early transition metals, lanthanides, and actinides, especially in low oxidation states have been commonly used for deoxygenation of organic species [2–4]. A variety of metal hydrides as well as catalytic late transition metal/H_2 systems are commonly used to hydrogenate organic species with unique specificities [3–11]. The combination of oxygen removal and hydrogen addition is extremely important in the formation of larger organic compounds from simple oxygenated substrates used in the widely studied Fischer–Tropsch catalytic systems [12–17].

We wish to report the use of active uranium as an extremely versatile reducing agent, capable of both oxygen removal, and hydrogen addition to simple organic systems. Furthermore, the unprecedented stepwise reduction of the α-diketone benzil or the α-hydroxy ketone benzoin to bibenzyl has been shown to proceed via the unsaturated species diphenylacetylene, *cis*-stilbene, and *trans*-stilbene.

The synthesis of alkynes from α-diketones is a very useful organic transformation which allows the synthesis of disubstituted alkynes. Alkyne synthesis from α-diketones usually proceeds indirectly by oxidation ($CuCl/O_2$/pyridine [18], $Pb(OAc)_4$ [19]; NiO_2 [20]; CF_3COOAg [21]; HgO [22,23]) of the corresponding bis-hydrazones.

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* Taken in part from the dissertation of B.E.K. [1].

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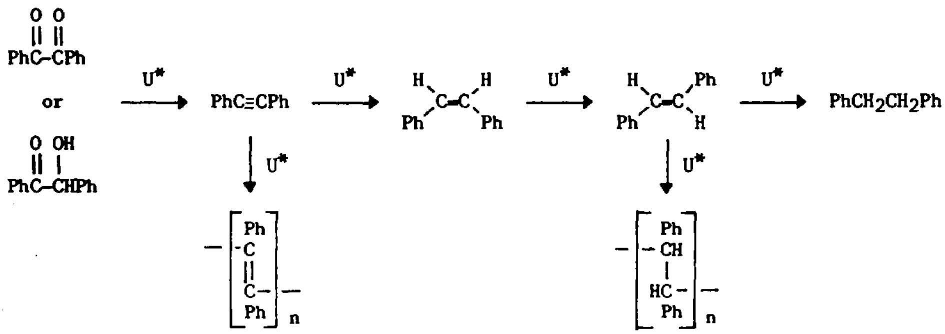

Scheme 1. Reactions of active uranium.

Other indirect methods used are reduction or thermolysis of cyclic enediol oxaphosphoranes [24], phosphates [25,26], thiocarbamates [27] or 1,3-dioxoles [28].

We thought that the high oxophilicity of active uranium and its demonstrated deoxygenation reactions of carbonyl compounds [29–31], as well as its large coordination capacity, would help effect the reduction of α-diketones to alkynes. The reduction of α-diketones to alkynes by activated forms of titanium has been attempted by two authors without success [27,32]. The only report of the use of a metal in the reductive deoxygenation of an α-diketone to an alkyne is the reduction of benzil to diphenylacetylene by $(C_6H_6)_2Ti$ in THF [33]. This complex has been prepared by metal atom vaporization [34], and is difficult to obtain.

The reduction of benzil or benzoin by active uranium [35] in refluxing xylenes proceeds initially to give diphenylacetylene [36,38]. The diphenylacetylene so generated, is rapidly hydrogenated under the deoxygenation conditions to give *cis*-stilbene, which rapidly isomerizes to *trans*-stilbene (Scheme 1). Since the hydrogenation of diphenylacetylene is much faster than the deoxygenation of benzil or benzoin (vide infra) the maximum yield of diphenylacetylene seen so far is 30% (GC, based on benzil). This reaction however, has not yet been optimized for the production of diphenylacetylene. Active uranium has been shown to activate C–H bonds of TMEDA (*N*,*N*,*N*′,*N*′-tetramethylethylenediamine) under these conditions giving hydridic uranium species [29–31]. The hydrogenation of diphenylacetylene under these conditions in the presence of uranium hydrides is not surprising, though the mechanism is not understood at this point.

Diphenylacetylene reacts with active uranium to give the same hydrogenated products as when benzil or benzoin are used as the starting material. Diphenylacetylene reacts with active uranium much faster than does benzil or benzoin. Diphenylacetylene (2 equiv.) was completely consumed by active uranium (1 equiv.) within 15 min in refluxing xylenes. Hydrogenation of diphenylacetylene can be observed even at room temperature. When diphenylacetylene (10 equiv.) was treated with active uranium (1 equiv.), the ultimate hydrogenated product was bibenzyl (3 equiv.). In addition to the hydrogenated products, diphenylacetylene oligomers were seen. Mass spectra (High Resolution–Electron Ionization (HREI)) of the resulting oligomers showed molecular ions corresponding to $[C_6H_5C{\equiv}CC_6H_5]_n$ ($n = 2$–4). In his study of polymerization catalysts, the uranium powder prepared by Chang et al. [39] (via thermal decomposition of U/Hg) did not polymerize diphenylacetylene at all. We have previously shown that active uranium prepared by Na/K reduction of

UCl_4 in 1,2-dimethoxyethane (DME) is much more reactive in the polymerization of 1,3-butadiene than is the uranium powder prepared by Chang et al. [29].

Active uranium isomerizes *cis*-stilbene to *trans*-stilbene extremely rapidly [40*]. The isomerization of *cis*-stilbene (1 equiv.) to *trans*-stilbene is 94% complete after 1 h at room temperature. The *trans*-stilbene produced can be reduced to bibenzyl in 4 h at 92° C. After cooling this reaction to room temperature, additional *cis*-stilbene (1 equiv.) was isomerized to *trans*-stilbene in 95% completion after 5 min at room temperature. This additional reactivity can be explained by surface activation of the active uranium powder, and has been demonstrated previously [29].

trans-Stilbene reacts with active uranium quite slowly to give bibenzyl. The hydrogenation of *trans*-stilbene (5 equiv.) was 50% complete after 15 h at 92° C. The remainder of the *trans*-stilbene reacted with active uranium upon reflux to give bibenzyl as well as many other products. Mass spectra showed peaks due to stilbene oligomers [41*].

Bibenzyl does not react with active uranium. After 43 days in refluxing xylenes, no other products were seen from the reaction of bibenzyl (2 equiv.) with active uranium (1 equiv.), and the bibenzyl could be recovered quantitatively.

In conclusion, the novel stepwise reduction of benzil and benzoin to bibenzyl has been demonstrated. The initial step is the deoxygenation of benzil or benzoin to diphenylacetylene, which has not been demonstrated for any other heterogeneous metal system. The success of active uranium in accomplishing this reaction, as opposed to that of titanium, is probably due to the fact that active uranium is capable of coordinating two oxygens per metal center. This has been shown previously in reactions of active uranium with aryl ketones [29]. The ability of actinide compounds to form large coordination numbers allows novel chemistry, not possible using transition metals, to be accomplished.

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41 HREI mass spectra showed $C_{21}H_{17}$ 269.1316, $C_{28}H_{24}$ 360.1874, and $C_{35}H_{29}$ 449.2293.