The Reductive Cross-Coupling of Ketones and Aldehydes to Olefins by Ditungsten Hexaalkoxides

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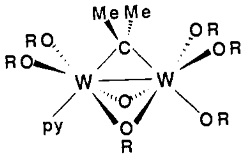
The McMurry reaction, that involves the use of a reagent prepared from the reduction of $TiCl_3$ with $LiAlH_4$, is a well-established procedure for the reductive coupling of organic carbonyl-containing compounds to olefins.[1] Another procedure, developed by Sharpless and coworkers, involves a reagent prepared by the reaction between WCl_6 and *n*-BuLi.[2] The latter works best for substrates containing one aryl substituent. Both the McMurry and Sharpless reactions appear to proceed by initial electron transfer and coupling to form a pinacolate that is then deoxygenated to liberate the olefin. Indeed, when the McMurry reaction is carried out at low temperature, hydrolysis yields the pinacol and not the olefin.[3] We describe here preliminary results of the reductive coupling of ketones to olefins by $W_2(OR)_6(py)_2$ compounds and evidence for a ditungsten alkylidene bridged intermediate. The latter which are stable below 0 °C, in certain cases, afford a reaction not heretofore realized, namely a selective reductive cross-coupling of two ketones or a ketone and an aldehyde to give olefins.

Following the discovery that $W_2(O\text{-}i\text{-}Pr)_6(py)_2$ and acetone react in hydrocarbon solutions to give $W_4O_2(O\text{-}i\text{-}Pr)_{12}$ and tetramethylethylene,[4] we have investigated both the course of the reaction and extensions to other alkoxides and ketones. Steric factors are apparently important since $W_2(O\text{-}t\text{-}Bu)_6$ and acetone fail to react under similar conditions. Similarly no reaction is observed between $W_2(O\text{-}i\text{-}Pr)_6(py)_2$ and $(t\text{-}Bu)_2CO$.

$W_2(OCH_2CMe_3)_6(py)_2$ and acetone (3 equiv) react in hydrocarbon solvents at 0 °C over a period of 48 h to give a compound of empirical formula $W_2(OCH_2CMe_3)_6(OCMe_2)(py)$ (**1**) that can be recrystallized at −78 °C from hexane (84% yield). The NMR spectroscopic characterization of the latter compound shows six types of OR ligands in the integral ratio 1:1:1:1:1:1, and each CH_2 group contains diastereotopic protons. The two methyl groups derived from acetone are inequivalent and when labeled $Me_2{}^{13}C{=}O$ is employed a resonance in the ^{13}C NMR spectrum at δ 163.7 is seen to be derived from the ketonic carbon atom. This signal is flanked by satellites of intensity 24% due to coupling to two ^{183}W nuclei: $^1J_{^{183}W-^{13}C} = 83$ Hz (^{183}W, $I = 1/2$, 14.5% natural abundance). The magnitude of the latter is typical of a W–Csp^3 one bond coupling.[5] Collectively the data lead us to propose that **1** has a binuclear alkylidene bridged structure such as A or B below.



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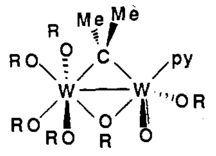

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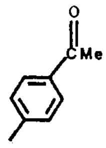
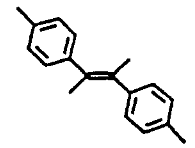
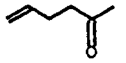
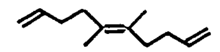
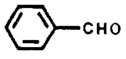
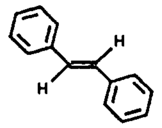
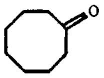
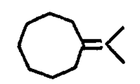
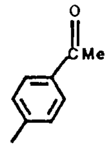
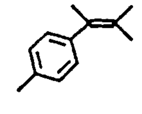
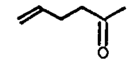
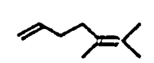
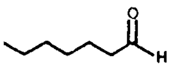
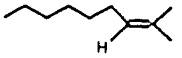
Clear evidence for alkylidene formation comes from the following: (1) Treatment of $W_2(OCH_2CMe_3)_6(O)(CMe_2)(py)$ with CF_3COOH in hexane or toluene leads to a crystalline compound $W_2(OCH_2CMe_3)_4\ (\eta^1\text{-}O_2CCF_3)_2(CMe_2)(O)(py)$ which has been structurally characterized and found to contain a μ-CMe_2 ligand. (2) Treatment of the analogue of **1** formed in the reaction between 9-fluorenone and $W_2(OCH_2CMe_3)_6(py)_2$, with CH_3COOH leads to the liberation of fluorene (^1H NMR and mp), consistent with protonolysis of a fluorenylidene ligand.

Table I. Alkenes Formed by Reductive Coupling or Cross-Coupling of Ketones/Aldehydes by $W_2(OCH_2\text{-}t\text{-}Bu)_6py_2$[a]

aldehyde/ketone	olefin		yield[a] (%)
		1	51
		2	21
		3	34
		b 4	44
		b 5	66
		b 6	36
		b 7	18

[a] Yields are unoptimized. [b] Olefins **4**–**7** were formed by cross-coupling reactions using $W_2(OCH_2\text{-}t\text{-}Bu)_6(O)(CMe_2)(py)$, **1**.

The compound **1** when dissolved in hydrocarbon solvents reacts further with acetone at 22 °C to give tetramethylethylene and an as yet uncharacterized tungsten-containing alkoxide.

When reactions between $W_2(OCH_2CMe_3)_6(py)_2$ and other ketones were carried out in toluene-d_8 at or below 0 °C, evidence from NMR spectroscopy for intermediates similar to **1** was obtained, but an intermediate has been isolated only in the reaction with 9-fluorenone. Nevertheless, olefinic products were formed from reactions involving dialkyl or alkyl/aryl ketones or aldehydes in the isolated yields shown in Table I. In a typical reaction, $W_2(OCH_2CMe_3)_6(py)_2$ (300 mg) was dissolved in hexane (5 mL) in a Schlenk flask, and the ketone (2.5 equiv) was added via syringe. After stirring at 22 °C for 12–24 h, water was added to destroy the tungsten alkoxide; the aqueous layer was extracted with ether, and the organic product was isolated by column chromatography (SiO_2, hexane/Et_2O). The olefinic products were identified by NMR spectroscopy and mass spectrometry.

The potential for the selective reductive cross-coupling of ketones is suggested by the fact that compound **1** may act as a propylidene source. When a toluene-d_8 solution of **1*** (containing $^{13}CMe_2$ from $Me_2{}^{13}C{=}O$) was treated with $Ph(Me)^{13}C{=}O$ at room temperature, the starting materials were consumed within 12 h as shown by NMR spectroscopy. The ^1H NMR spectrum contained resonances consistent with $Ph(Me)^{13}C{=}^{13}CMe_2$, but the solvent resonances obscured the olefinic region of the ^{13}C NMR spectrum. Therefore, the sample was filtered through silica gel, the volatile components were removed in vacuo, and the residue was dissolved in $CDCl_3$. The ^{13}C NMR spectrum now revealed a pair of doublets at 135.8 and 127.6 ppm with $^1J_{^{13}C-^{13}C} = 75.2$ Hz. This, together with mass spectrometry, confirmed the formation of $Ph(Me)C{=}CMe_2$. On a preparative scale **1** (300 mg) was allowed to react with *p*-Me-Ph(Me)C=O (1.1 equiv) in hexane (3 mL)

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to give the corresponding olefin in 66% isolated yield (Table I).

The dinuclear chemistry reported here combines two reactions known for mononuclear chemistry: (1) The reaction between an early transition-metal alkylidene and a ketone to give an alkene and a metal-oxo derivative, first noted by Schrock[6] and (2) the recently reported cleavage of the carbonyl bond in the reaction between ketones and $WCl_2(PMe_2Ph)_4$ to give W(6+)-oxo-alkylidene complexes.[7]

Further studies are in progress.[8]

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Multiple Reversible Electrochemical Reduction of Aromatic Hydrocarbons in Liquid Alkylamines

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The thermodynamic reduction potentials of many aromatic hydrocarbons have been known since the work of Hoytink.[1] Their values obtained either by polarographic or by voltammetric techniques have been reported several times in the literature.[2] Recently,[3,4] the further reduction of these species to their respective dianions or higher charged states has attracted increasing interest. The reason is that their electronic and spectroscopic behavior offers new insights into the unconventional properties of charged π-systems. Moreover, highly charged aromatics are interesting model compounds for the study of thermodynamics of charge storage.

Although chemical reduction of such systems is now easily achieved by the reaction with alkali metals, e.g., in dry THF,[3] electrochemical reduction experiments leading to stable higher redox states still demand skill and a sophisticated technique. Therefore, up to now, relatively few reduction potentials for the formation of aromatic diions have been given in the literature. Many are the result of irreversible processes due to protonation reactions induced by impurities in the solvent or by reactivity of the supporting electrolyte.[5] In these cases the desired thermodynamic information cannot be derived from the measured data. Therefore, we will report here on an easily accessible technique of measuring thermodynamic redox potentials of dianions and even higher charged anions of aromatic hydrocarbons using methylamine (MA) and dimethylamine (DMA) as solvents.

In the past, in order to minimize problems arising from coupled chemical reactions, so-called dipolar systems such as acetonitrile (ACN), propionitrile (PrCN), or dimethyl formamide (DMF) have been favored as solvents. Parker et al.[6] showed that by using these solvents and applying a special purification technique with alumina suspended in the cell several aromatic hydrocarbons can be reversibly reduced to their respective dianions within the time scale of slow sweep cyclic voltammetry. This becomes increasingly difficult the more negative the corresponding reduction step occurs on the potential scale. Obviously, the increasing basicity of the diionic or multiionic species as a function of more negative reduction potentials favors successive protonation reactions. In addition, the appearance of background currents normally limits the extension of the cathodic scan to values more positive than −3.0 V vs Ag/AgCl. Therefore, reversible reduction steps at extremely negative potentials around −3.0 V vs Ag/AgCl are exceptional.[7] Since then Heinze et al.[8] have successfully used highly purified and super-dry tetrahydrofuran (THF) with $NaBPh_4$ as supporting electrolyte for the reversible generation of highly charged anions.

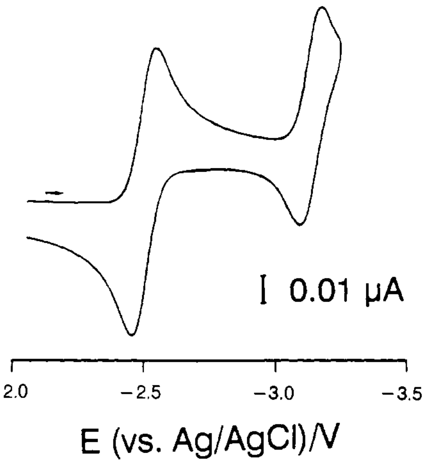

Figure 1. Cyclic voltammogram for the reduction of phenanthrene in DMA/0.1 M TBABr: scan rate = 500 mV s^{-1}; $T = -60$ °C.

In recent years Bard,[9] Savêant, and Thiêbault[10] independent of each other used liquid ammonia as solvent for electrochemical reduction experiments. Because of its extremely low electrophilicity it was possible to determine redox potentials as well as to study reaction mechanisms without side reactions. The cathodic limit of liquid ammonia is −3.0 V vs Ag/AgCl, but the relatively small temperature range of liquidity under normal pressure (mp −78 °C, bp −34 °C) and the insufficient solubility of nonpolar compounds in liquid ammonia limit its use in electrochemistry.

For this reason we used liquid MA and DMA as solvents in cyclic voltammetry for the first time. To our knowledge, only MA has been applied up to now in electrochemistry for electrochemical synthesis and the study of properties of solvated electrons.[11]

MA and DMA stabilize anions to the same extent as ammonia, but in contrast to it they can be used over a larger range of temperatures. The solubility of nonpolar compounds is better and,

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