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Reaction of Saturated Ketones with a Trivalent Uranium Complex. Isolation and Characterization of the Alcoholate and Enolate Products

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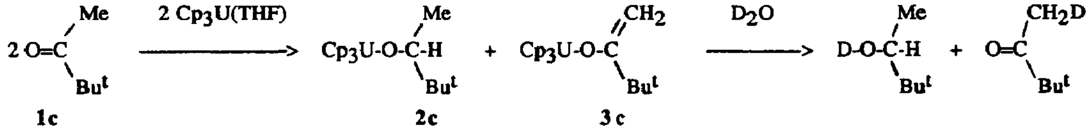
Abstract : The uranium (III) complex $Cp_3U(THF)$ ($Cp = \eta - C_5H_5$, THF = tetrahydrofuran) reacted with saturated ketones $RCOCH_2R'$ to give equimolar mixtures of the compounds $Cp_3U\text{-}OCHR(CH_2R')$ and $Cp_3U\text{-}OCR(=CHR')$.

The ketyls resulting from the reduction of saturated ketones by means of alkali metals in aprotic solvents were found to undergo rapid disproportionation into the corresponding alcoholates and enolates; these latter were evidenced by their treatment with H_2O, MeI or MeCOCl [1]. Even in the presence of an excess of alcohol, this disproportionation of the ketyls is in strong competition with their protonation, the key step of the mechanism proposed by House for the dissolving metal reduction of ketones [2]. It is surprising that such transformations of ketones with other metals or low valent metal species have been overlooked, whereas reduction and coupling reactions of carbonyl compounds have been extensively studied [3]. In this context, we decided to examine the reactivity of ketones towards uranium (III) complexes [4].

Treatment of the ketone $RCOCH_2R'$ 1 in toluene (a = acetone; b = cyclohexanone; c = pinacolone, Scheme 1) with 1 mol. equiv. of the triscyclopentadienyl uranium compound $Cp_3U(THF)$ ($Cp = \eta - C_5H_5$, THF = tetrahydrofuran) gave an equimolar mixture of the complexes $Cp_3U\text{-}OCHR(CH_2R')$ 2 and $Cp_3U\text{-}OCR(=CHR')$ 3 in almost quantitative yield; these could be directly observed and characterized by ^1H NMR spectroscopy [5].



1c 2c 3c

Scheme 1. Reaction of pinacolone with $Cp_3U(THF)$

Compounds 2, which belong to the family of the alkoxides Cp_3UOR, have been prepared as previously described, by treatment of Cp_3UCl with the corresponding NaOR reagent [6] or by reaction of $Cp_3U(THF)$ with ROH [7].

Products 3 are unique examples of uranium enolate complexes. The derivatives 3b and 3c were unequivocally synthesized by treating Cp_3UCl with the lithium enolate of cyclohexanone [8] or pinacolone [9], respectively; after crystallization from hexane, 3c was isolated in 45 % yield, as a yellow microcrystalline powder [10]. Not surprisingly, hydrolysis of 2c and 3c with deuterium oxide afforded respectively the O-deuteriated pinacolyl alcohol and the pinacolone, monodeuteriated in the α position (quantitative yield and total deuteriation by NMR, Scheme 1).

The uranium (III) complex $Cp_3U(THF)$ has been shown to be capable of acting as an efficient electron transfer reagent towards a variety of organic, inorganic and organometallic compounds [11]. It seems likely that the radical $Cp_3U - OCR(CH_2R')$, the canonical form of the adduct $Cp_3U \leftarrow O{=}CR(CH_2R')$ [12], is the key intermediate in these reactions of $Cp_3U(THF)$ with ketones; this latter would readily disproportionate into the final products 2 and 3.

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5. 1 equiv. of the ketone was added to a solution of $Cp_3U(THF)$ (ca 10 mg) in toluene d_8 (0.4 ml); the brown solution turned yellow (immediately for **1a** and **1b**, after 1 h for **1c**). The ^1H NMR spectra showed the quantitative formation of 2 and 3, in a 1:1 ratio. δ ppm (toluene, 30°C, 60 MHz). **2a** : 60.88 (1H, OCH), 17.31 (6H, Me), -18.42 (15H, Cp); **3a** : 2.5 - 1.5 (m, masked by the THF and toluene resonances), -9.89 (15H, Cp); **2b** : 60.59 (1H, OCH), 18.12 and 16.58 (2H + 2H, 2,6-H), 10.12 and 9.31 (2H + 2H, 3,5-H), 5.66 (2H, 4-H), -18.38 (15H, Cp); **3b** : 2.5 - 1.5 (m, masked by the THF and toluene resonances), -11.60 (15H, Cp); **2c** : 60.64 (1H, OCH), 16.78 (3H, Me), 8.09 (9H, Bu^t), -17.82 (15H, Cp); **3c** (crystalline powder [10]): 3.86 and 2.60 (1H + 1H, CH_2), -3.86 (9H, Bu^t), -9.76 (15H, Cp). When not specified, the signals are singlets with half - heigth widths between 10 and 25 Hz.
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10. A 50 ml round bottom flask was charged with Cp_3UCl (100 mg, 0.21 mmol) and the lithium enolate of pinacolone [9] (22.3 mg, 0.21 mmol) and THF (20 ml) was condensed under vacuum at -78°C. The reaction mixture was stirred for 1 h at 20°C. After filtration, the solution was evaporated to dryness and the residue extracted with hexane (20 ml). Evaporation of hexane afforded a yellow powder of 3c (50.7 mg, 45%). Analysis. Found : C, 47.37; H, 4.89. $C_{21}H_{26}OU$ requires: C, 47.20; H, 5.00 %.
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12. Ketones without hydrogens in α position (2,2,4,4-tetramethyl-3-pentanone or 2,2,6,6-tetramethylcyclohexanone) form labile adducts with $Cp_3U(THF)$.

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