# Reactivity of the Actinoid-Carbon Bond: Alkyluranium Compounds as Selective Nucleophilic Reagents in Organic Synthesis

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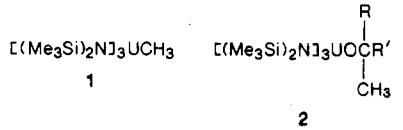
*Received July 10, 1987*

Stable tris[bis(trimethylsilyl)amido]methyluranium is a very highly selective nucleophilic Grignard-like reagent in chemo- and stereoselective alkylation reactions of carbonyl compounds. Related tris[bis(trimethylsilyl)amido]-, trichloro-, and cyclopentadienyldichloroalkyluranium complexes are less selective reagents.

In the past few years, attention of organic chemists has been focused on the question of how to achieve a high degree of selectivity in organic reactions using transition organometallic compounds. For this purpose, organotitanium compounds[1,2] and to a less extent organozirconium[2,3] or organohafnium[4] derivatives have been widely used. It is well-known that trialkoxyalkyltitaniums are highly selective nucleophilic alkylating reagents.[2,5] However, it is surprising that the related alkylorganouranium compounds, as well as organolanthanide alkyl derivatives,[6] have been poorly investigated.

In a previous paper,[7] we reported on reactions of the easily synthetized, thermally stable tris[bis(trimethylsilyl)amido]methyluranium (1).[8] This compound reacted with aldehydes or ketones affording quantitatively the tris[bis(trimethylsilyl)amido]alkoxyuranium or -(aryloxy)uranium **2**.



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After hydrolysis, the corresponding secondary or tertiary alcohols are obtained in high yields. We report here some examples of applications of 1 and related alkyluranium derivatives as very high selective nucleophilic Grignard-like reagents in chemo- and stereoselective alkylation reactions of carbonyl compounds.

## Results and Discussion

**Alkyluraniums.** The methyl derivative 1 is the only tris[bis(trimethylsilyl)amido]alkyluranium stable at room temperature. In hydrocarbon solutions, a slow $\gamma$-elimination reaction led to the metallacycle (eq 1).[8,9]

(1)

Completion of the cyclization reaction required 10–15 days at room temperature; at 60 °C, this reaction was complete within 1 h in benzene. Of course, this behavior precludes heating and all reactions must imperatively be performed at temperatures lower than 25 °C.

The alkyl homologues were synthesized from $(HMDS)_3UCl$ and corresponding alkyllithiums at −70 °C (eq 2) (for convenience, the ligand bis(trimethylsilyl)amido will be abbreviated as HMDS). An immediate reaction occurred and the pale pink-brown solution of $(HMDS)_3UCl$ turned yellow-brown with LiCl precipitating from the reaction mixture. These exceedingly thermally unstable compounds were stored for a short period of time (2–3 h) at low temperature (−70 °C) without noticeable decomposition. Upon raising the temperature, a quantitative and clean intramolecular cyclization reaction afforded the metallacycle $(HMDS)_2\overline{UCH_2SiMe_2NSiMe_3}$. In order to avoid this reaction, alkyl compounds **1a–c** were synthesized immediately before use.

$$(HMDS)_3UCl + RLi \xrightarrow[THF]{-70\ °C} \underset{\mathbf{1a-c}}{(HMDS)_3UR} \quad (2)$$

(**a**, R = $C_2H_5$; **b**, R = $CH(CH_3)_2$; **c**, R = $n$-$C_4H_9$)

The thermally unstable monoalkyltrichlorouraniums $UCl_3R$ **3** were never isolated. The reaction of $UCl_4$ and 1 equiv of alkyllithium quantitatively generated a reduced U(III) species upon warming at room temperature.[10,11] Two reasonable explanations of this reduction reaction can be put forward: the initial formation of the expected $UCl_3R$ was followed by a $\beta$-elimination reaction, affording the uranium(IV) hydride with subsequent reduction elimination of $H_2$ or RH to provide U(III) (eq 3).

$$\begin{gathered} UCl_4 + RLi \rightarrow UCl_3R + LiCl \\ UCl_3R \rightarrow UCl_3H + R(H) \\ 2UCl_3H \rightarrow 2UCl_3 + H_2 \qquad (3) \\ \text{or} \\ UCl_3H + UCl_3R \rightarrow 2UCl_3 + RH \end{gathered}$$

The formation of U(III) upon reaction of 1 equiv of RLi with $UCl_4$ may also result from a direct reduction of $UCl_4$ by an electron-transfer process (eq 4).

$$UCl_4 + RLi \xrightarrow[THF]{-70\ °C} UCl_3 + LiCl + R^{\bullet} \quad (4)$$

The experimental data did not allow to distinguish between these two pathways.

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**Table I. Chemoselective and Stereoselective Reactions of Thermally Unstable *n*-Butyluranium Derivatives with Carbonyls at −70 °C and at Room Temperature (in Pentane)**

| reagent | temp, °C | chemoselectvty[a] | stereoselectvty[b] |
|---|---|---|---|
| BuLi[c] | −70, +20 | 65/35[d] | 75/25[e] |
| $BuU(HMDS)_3$ | −70 | 90/10 | 90/10 |
| | +20 | no reaction[f] | |
| $BuUCl_3$ | −70 | 80/20 | 88/12 |
| | +20 | no reaction[f] | |
| $BuUCl_2Cp$ | −70 | 70/30 | 80/20 |
| | +20 | no reaction[f] | |

[a] Reaction of 1 molar equiv of butyl derivative with a 1/1 mixture of benzaldehyde/acetophenone. [b] Reaction 1/1 with hydratropic aldehyde. [c] Ethyl- and isopropyllithium give similar results. [d] Secondary alcohol/tertiary alcohol. [e] Major diastereoisomer/minor diastereoisomer. [f] Two series of experiments were performed: reaction of alkyllithium with $UCl_4$ in THF solution at −70 °C, raising at room temperature, addition of carbonyl compounds and workup; reaction at room temperature of $UCl_4$ in THF with alkyllithium, addition of carbonyl compound, and workup.

The high degree of selectivity observed in chemoselective or stereoselective reactions of carbonyl compounds when added to a cold freshly prepared mixture of $UCl_4$ and alkyllithium (Table I) established unambiguously the initial formation of $UCl_3R$ (eq 5) and indeed the predominance of the $\beta$-elimination rather than electron transfer to form U(III) species upon warming.

$$UCl_4 + RLi \xrightarrow[THF]{-70\ °C} \underset{\mathbf{3a-c}}{UCl_3R} + LiCl \qquad (5)$$

(**a**, R = $CH_3$; **b**, R = $C_2H_5$; **c**, R = $n$-$C_4H_9$)

It is noteworthy that when carbonyl compounds were added after raising at room temperature, no reaction occurred. On the other hand, no reaction occurred with the mixture $UCl_4$/*tert*-butyllithium (1/1) at low temperature. The electron-transfer reaction (eq 4) may be favored in that case; *tert*-butyllithium is indeed a stronger reducing agent than primary or secondary alkyllithiums.[12]

In the same way, monocyclopentadienyldichloroalkyluraniums **4** were synthesized in situ in two steps (eq 6): addition of 1 equiv of cyclopentadienylsodium to a THF solution of $UCl_4$ at 0 °C, cooling at −70 °C, and addition of 1 equiv of alkyllithium and storage at this temperature before reaction with carbonyl compounds.

$$UCl_4 + CpNa \xrightarrow[THF]{0\ °C} UCl_3Cp + RLi \xrightarrow{-70\ °C} \underset{\mathbf{4a-c}}{UCl_2CpR} \qquad (6)$$

(**a**, R = $CH_3$; **b**, R = $C_2H_5$; **c**, R = $n$-$C_4H_9$)

The low thermal stability of monocyclopentadienylalkyluraniums **4** precluded all attempts of isolation. However, the high selectivity observed after reaction with carbonyl compounds (see Table I) proves formally the formation and the relative stability of **4** at low temperature.

**Chemoselective Reactions.** The reaction with aliphatic aldehydes was performed very rapidly at room temperature and at reasonable rate (5–10 min) at −70 °C in chloroform. The reaction with ketones was monitored by NMR in $C_6D_6$ solution at room temperature. Aliphatic ketones or cyclohexanones reacted slowly: 30 min to 24 h. In the same way, only 30% of alkoxyuranium were obtained after 3 days with acetophenone and no reaction occurred with benzoylferrocene. Sterically hindered ketones, camphor and (−)-fenchone, were very poorly reactive,

**Table II. Reaction of 1 with Aldehydes and Ketones at Room Temperature**

| carbonyl derivative | 1, mol equiv | reactn time | alkoxy compd, %[a] | alcohol S or T[b] |
|---|---|---|---|---|
| propanol | 1.1 | 5 min | 100 | 95 |
| hexanal | 1.1 | 5 min | 100 | 90 |
| benzaldehyde | 1.1 | 10 min | 100 | 95 |
| ferrocenealdehyde | 1.1 | 2 min | 95 | 92 |
| propanone | 1.2 | 30 min | 100 | 90 |
| 3-pentanone | 1.2 | 5 h | 100 | 90 |
| 2-hexanone | 1.2 | 5 h | 100 | 95 |
| 4-heptanone | 1.2 | 12 h | 100 | 95 |
| acetophenone | 1.0 | 72 h | 30 | 25 |
| phenylpropanone | 1.2 | 6 h | 90 | 83 |
| acetylferrocene | 2 | 2 h | 100 | 86[c] |
| benzoylferrocene | 3 | 72 h | 0 | |
| 4-*tert*-butylcyclohexanone | 1.5 | 16 h | 100 | 95 |
| 2-methylcyclohexanone | 1.5 | 48 h | 100 | 95 |
| camphor | 3 | 60 h | <5 | |
| (*R*)-(−)-fenchone | 3 | 60 h | <5 | |

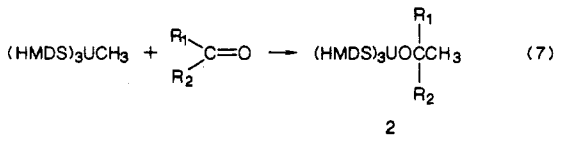
[a] By NMR: relative peaks areas of $N(SiMe_3)_2$ protons alkoxy compound/starting compound. [b] By GC: yields based on an internal standard. [c] By TLC: yields on isolated products.

**Table III. Results of the Addition of $CH_3M$ (M = Li, MgBr, $Ti(OiPr)_3$, $U(HMDS)_3$) in Pentane (1 mol equiv of $CH_3M$) to a 1:1 Mixture of Benzaldehyde and Acetophenone at Room Temperature**

| M | % benzald | % acetoph | % T | % S | % benzyl alcohol |
|---|---|---|---|---|---|
| Li | 15 | 7 | 39 | 33 | 6 |
| MgBr | 6 | 37 | 13 | 43 | 1 |
| $Ti(O\text{-}i\text{-}Pr)_3$ | 0 | 48 | 1 | 44 | 0 |
| $U(HMDS)_3$ | 0 | 48 | 0 | 46 | 0 |

giving about 5% yield after 3 days.

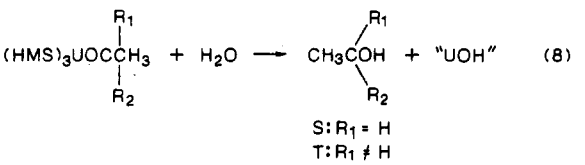
The intermediate alkoxyuraniums **2** (eq 7) were quantitatively formed and could be isolated in a pure state as microcrystalline brown powders after removal of the solvent.[13]




(7)

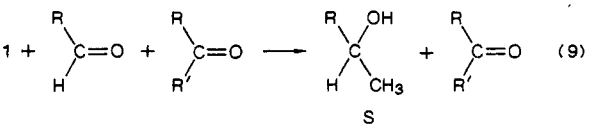
**2**

After hydrolysis of **2**, the pure secondary (S) or tertiary alcohols (T) were obtained in high yields (eq 8). Experimental results are summarized in Table II.




(8)

The high selectivity of **1** to the carbonyl group of aldehydes vs ketones was tested in intramolecular competition experiments. Treatment of a 1:1 mixture of benzaldehyde and acetophenone in benzene with 1 equiv of **1** afforded exclusively the secondary alcohols (S) and unreacted acetophenone was quantitatively recovered (eq 9).




(9)

**S**

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**Table IV. Results of the Addition of $(HMDS)_3UCH_3$ (1 mol equiv) to a 1:1 Mixture of Aliphatic Aldehydes and Ketones at Room Temperature**

| aldehyde | ketone | % S | % T |
|---|---|---|---|
| propanal | propanone | 81 (98)[a] | 2 (2) |
| hexanal | propanone | 85 (96) | 3 (4) |
| hexanal | 3-pentanone | 91 (99.8) | 0 (0.2) |
| heptanal | 4-heptanone | 92 (100) | 0 (0) |

[a] Ratios of $(HMDS)_3UOC(R_1R_2)CH_3$ calculated by NMR integration (relative peak areas of HMDS protons) in the reaction mixture before hydrolysis.

**Table V. Reaction of Alkyluranium: RM (M = $(HMDS)_3U$; $Cl_3U$; $CpCl_2U$), 1 mol equiv with a 1:1 Mixture of Heptanal and 4-Heptanone in Pentane at −70 °C; Reaction Time, 2 h; Relative Ratios, Secondary Alcohol/Tertiary Alcohols (S/T)**

| R | $(HMDS)_3UR$ | $Cl_3UR$ | $CpCl_2UR$ |
|---|---|---|---|
| $CH_3$ | 99/1 | 70/30 | 65/35 |
| $C_2H_5$ | 85/15 | 70/30 | 70/30 |
| $CH(CH_3)_2$ | 80/20 | | |
| $n$-$C_4H_9$ | 90/10 | 80/20 | 70/30 |

**Table VI. Diastereoselective Methylation of 2- and 4-Substituted Cyclohexanones with Methyluranium and Methyltitanium Reagents (2 mol equiv): Room Temperature; Relative Ratios, Axial Alcohol/Equatorial Alcohol (m/n)**

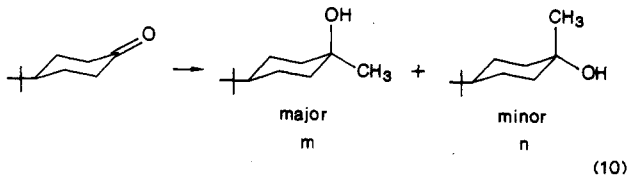
| subst | $(HMDS)_3UCH_3$ | $(O\text{-}i\text{-}Pr)_3TiCH_3$ |
|---|---|---|
| 4-*tert*-butyl | 85/15 | 94/6 |
| 4-methyl | 85/15 | 88/12 |
| 2-methyl | 89/11 | 94/6 |

Comparative results are reported in Table III. It is noteworthy that uranium compound **1** is at least as selective as titanium compounds (**2**).

Essentially complete chemoselectivity was also observed in reactions of **1** with mixtures of aliphatic aldehydes and ketones (Table IV). The reaction was performed in $C_6D_6$, and the products were analyzed by NMR, showing the high selectivity of the reaction even with $C_3$ carbonyls.

Thermally unstable alkyltris[bis(trimethylsilyl)amido]uraniums **1a–c** reacted at low temperature with an equimolecular mixture of heptanal and 4-heptanone. A much lower selectivity was observed (Table V). These results were not surprising if we compare the exceedingly reactive metal–carbon bond in these compounds to the relatively stable uranium–methyl bond of **1**. In the same way, an alkylation competitive reaction aldehyde vs ketone performed in THF solution at −70 °C showed the very low selectivity of alkyltrichlorouranium **3** and alkyldichlorocyclopentadienyluranium **4** (Table V).

**Diastereoselective Reactions.** 2- and 4-substituted cyclohexanones are known to react with organometallic reagents, with preferential equatorial attack, providing the major axial alcohol (eq 10).[14]




(10)

Table VI reports the ratios m/n obtained from **1** and substituted cyclohexanones. The reactions appear to be highly stereoselective. Nevertheless, better results were obtained starting from titanium reagents.

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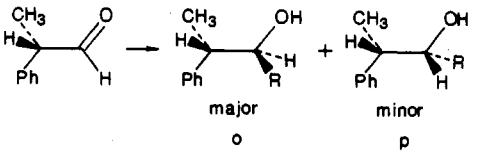
**Table VII. Diastereoselective Reaction of Alkyluranium or Alkyltitanium: RM (1 mol equiv) with 2-Phenylpropanal in Pentane at −70 °C; 2 h; Relatives Ratios, Major Alcohol/Minor Alcohol (o/p)**

| | M | | |
|---|---|---|---|
| R | $Cl_3UR$ | $(HMDS)_3UR$ | $(O\text{-}i\text{-}Pr)_3TiR$ |
| $CH_3$ | 90/10 | 88/12 | 93/7 |
| $C_2H_5$ | 84/16 | 80/20 | |
| $CH(CH_3)_2$ | 96/4 | 95/5 | |
| $n$-$C_4H_9$ | 88/12 | 90/10 | 89/11 |

A widely quoted example of asymmetric induction in the addition of organometallic compounds to carbonyls is the addition to 2-phenylpropanal (hydratropic aldehyde) to form the diastereoisomeric alcohols (eq 11). From Grignard or alkyllithium reagents, a ratio of about 2/1 is generally obtained. A much higher diastereoselectivity is observed when using organotitanium or organozirconium reagents, with the best ratios of Cram to anti-Cram product observed to be 93/7.[15] Alkyluraniums reacted readily with hydratropic aldehyde. Table VII reports the relative ratios o/p obtained from uranium and titanium compounds.




(11)

Alkyluranium derivatives appear to be potentially usable reagents in organic synthesis. In some cases, they could be used in preference to titanium reagents and we are pursuing investigations in this area.

## Experimental Section

All operations were performed with rigorous exclusion of oxygen and moisture (before hydrolysis!) in thoroughly dried Schlenk-type glassware under argon. Aliphatic hydrocarbon solvents were dried and stored on $LiCH_3$ and distilled directly in the reaction vessels. THF was stored on Na/benzophenone and distilled immediately before use. Proton NMR spectra were recorded on a JEOL FX 100 spectrometer in $C_6D_6$. Gas chromatographic (GC) analyses were performed on a CARLO ERBA instrument with appropriate columns and flame ionization detection.

$(HMDS)_3UCl$,[8] $(HMDS)_3UCH_3$,[8] and $(HMDS)_2UCH_2SiMe_2NSiMe_3$[16] were obtained as previously described.

**$UCl_3R$.** $UCl_4$ (1.9 g, 5 mmol) was dissolved in 45 mL of THF. After cooling at −70 °C, RLi (5 mmol) in 5 mL of THF (*n*-BuLi) was added dropwise and the yellow solution was stirred 1 h. The brown solution was divided in five parts of 10 mL (1 mmol) and used immediately (see below).

**$UCl_2CpR$.** $UCl_4$ (1.9 g, 5 mmol) was dissolved in 20 mL of THF and a solution of CpNa (0.44 g, 5 mmol) in 20 mL of THF was added dropwise. After 1 h of being stirred, the green mixture was cooled to −70 °C, and RLi (5 mmol) in 5 mL of THF was added slowly. The yellow brown solution was stored at −70 °C and used within 2 h.

**Typical Chemoselective Reactions. (A) Room Temperature.** To a solution of 1 mmol of benzaldehyde and 1 mmol of acetophenone in 10 mL of pentane was slowly added under stirring a solution of $(HMDS)_3UCH_3$ (0.735 g, 1 mmol) in 10 mL of pentane. After 1 h, the solution was quenched with 10 mL of saturated aqueous $NH_4F$. The organic layer was washed twice with water, dried over sodium sulfate, concentrated to 10 mL, and analyzed (GC, 5% XE 60 on Chromosorb 100–120 mesh).

**(B) Low Temperature.** To a cold (−70 °C) solution of 1 mmol of heptanal and 1 mmol of 2-heptanone in 10 mL of THF was

(15) Reetz, M. T. *Top. Curr. Chem.* **1982**, *106*, 1 and references cited therein.

(16) Dormond, A.; Elbouadili, A.; Moïse, C. *J. Organomet. Chem.* **1985**, *288*, C1.

slowly added a cold solution (−70 °C) of 1 mmol of $(HMDS)_3UR$ (from 5 mmol of $HMDS)_3UCl$ and 5 mmol of RLi, see above) in 10 mL of THF. After mixture was stirred for 2 h, 5 mL of 10% aqueous THF was added, and the reaction mixture was allowed to warm to room temperature. Water (100 mL) was added. THF was partially removed under vacuum, and the mixture was extracted with 3 × 10 mL of pentane. The organic phase was dried over sodium sulfate, concentrated to 10 mL, and analyzed (GC).

**Typical Stereoselective Reactions. (A) Hydratropic Aldehyde.** To a stirred solution of 1 mmol of 2-phenylpropanal in 10 mL of pentane was added dropwise a solution of $(HMDS)_3UCH_3$ (0.37 g, 0.5 mmol) in 10 mL of pentane. After 1 h, the solution was hydrolyzed with 10 mL of saturated aqueous $NH_4F$. The organic layer was washed twice with water, dried over sodium sulfate, concentrated to 5 mL, and analyzed (GC).

**(B) 4-*tert*-Butylcyclohexanone.** A solution of 1 mmol of 4-*tert*-butylcyclohexanone in 20 mL of pentane was poured onto solid $(HMDS)_3UCH_3$ (0.735 g; 1 mmol), and the solution was stirred 24 h at 20 °C. After hydrolysis and workup, the organic phase was concentrated to 10 mL and analyzed (GC).

**Registry No.** 1, 69517-44-8; **1a**, 112460-13-6; **1b**, 112460-14-7; **1c**, 112460-15-8; **2** ($R_1$ = H, $R_2$ = $C_2H_5$), 107145-73-3; **2** ($R_1$ = H, $R_2$ = $n$-$C_4H_9$), 107145-74-4; **2** ($R_1$ = H, $R_2$ = $C_6H_5$), 107164-07-8; **2** ($R_1$ = H, $R_2$ = $C_5H_5FeC_5H_4$), 107241-38-3; **2** ($R_1$ = $R_2$ = $CH_3$), 99646-25-0; **2** ($R_1$ = $R_2$ = $C_2H_5$), 107145-75-5; **2** ($R_1$ = $CH_3$, $R_2$ = $n$-$C_4H_9$), 112460-17-0; **2** ($R_1$ = $R_2$ = $n$-$C_3H_7$), 112460-18-1; **2** ($R_1$ = $CH_3$, $R_2$ = $C_6H_5$), 107164-08-9; **2** ($R_1$ = $CH_3$, $R_2$ = $C_6H_5CH_2$), 107145-76-6; **2** ($R_1$ = $CH_3$, $R_2$ = $C_5H_5FeC_5H_4$), 107222-01-5; **2** ($R_1$ = $C_6H_58$ $R_2$ = $C_5H_5FeC_5H_4$), 112460-24-9; **2** ($CR_1R_2$ = *cis*-4-*tert*-butylcyclohexyl), 112572-75-5; **2** ($CR_1R_2$ = *trans*-4-*tert*-butylcyclohexyl), 112460-25-0; **2** ($CR_1R_2$ = *cis*-2-methylcyclohexyl), 112460-26-1; **2** ($CR_1R_2$ = *trans*-2-methylcyclohexyl), 112530-32-2; **2** ($CR_1R_2$ = bornyl), 112460-19-2; **2** ($CR_1R_2$ = frenchyl), 112460-20-5; **3a**, 112460-08-9; **3b**, 112460-09-0; **3c**, 112460-10-3; **3** (R = $CH(CH_3)_2$), 112460-16-9; **3** (R = $t$-$C_4H_9$), 112460-11-4; **4a**, 112460-21-6; **4b**, 112460-22-7; **4c**, 112460-23-8; $UCl_4$, 10026-10-5; $U(HMDS)_3Cl$, 69517-42-6; $(HMDS)_2\overline{UCH_2SiMe_2NSiMe_3}$, 72472-77-6; $UCl_3Cp$, 112460-12-5; $C_2H_5CHO$, 123-38-6; $n$-$C_6H_{11}CHO$, 66-25-1; $C_6H_5CHO$, 100-52-7; $C_5H_5FeC_5H_4CHO$, 12093-10-6; $(CH_3)_2CO$, 67-64-1; $(C_2H_5)_2CO$, 96-22-0; $CH_3COC_4H_9$-$n$, 591-78-6; $(n$-$C_9H_7)_2CO$, 123-19-3; $C_6H_5COCH_3$, 98-86-2; $C_6H_5CH_2COCH_3$, 103-79-7; $C_5H_5FeC_5H_4COCH_3$, 1271-55-2; $C_5H_5FeC_5H_4COC_6H_5$, 1272-44-2; $C_2H_5CH(OH)CH_3$, 78-92-2; $n$-$C_5H_{11}CH(OH)CH_3$, 543-49-7; $C_6H_5CH(OH)CH_3$, 98-85-1; $C_5H_5FeC_5H_4CO(OH)CH_3$, 1277-49-2; $t$-$C_4H_9OH$, 75-65-0; $(C_2H_5)_2C(OH)CH_3$, 77-74-7; $n$-$C_4H_9C(CH_3)_2OH$, 625-23-0; $(n$-$C_3H_7)_2C(OH)CH_3$, 598-01-6; $C_6H_5C(CH_3)_2OH$, 617-94-7; $C_6H_5CH_2C(CH_3)_2OH$, 100-86-7; $C_5H_5FeC_5H_4C(CH_3)_2OH$, 12093-87-7; $C_6H_5CH(CH_3)CHO$, 93-53-8; (*R**,*R**)-$C_6H_5CH(CH_3)CH(OH)CH_3$, 1502-79-0; (*R**,*S**)-$C_6H_5CH(CH_3)CH(OH)CH_3$, 1502-80-3; (*R**,*R**)-$C_6H_5CH(CH_3)CH(OH)C_2H_5$, 1502-77-8; (*R**,*S**)-$C_6H_5CH(CH_3)CH(OH)C_2H_5$, 1502-78-9; (*R**,*R**)-$C_6H_5CH(CH_3)CH(OH)CH(CH_3)_2$, 1502-75-6; (*R**,*S**)-$C_6H_5CH(CH_3)CH(OH)CH(CH_3)_2$, 1502-76-7; (*R**,*R**)-$C_6H_5CH(CH_3)CH(OH)C_4H_9$-$n$, 96929-99-6; (*R**,*S**)-$C_6H_5CH(CH_3)CH(OH)C_4H_9$-$n$, 96930-05-1; 4-*tert*-butylcyclohexanone, 98-53-3; 2-methylcyclohexanone, 583-60-8; camphor, 76-22-2; (*R*)-(−)-fenchone, 7787-20-4; 4-methylcyclohexanone, 589-92-4; *cis*-4-*tert*-butyl-1-methylcyclohexanol, 16980-55-5; *trans*-4-*tert*-butyl-1-methylcyclohexanol, 16980-56-6; *cis*-1,2-dimethylcyclohexanol, 19879-11-9; *trans*-1,2-dimethylcyclohexanol, 19879-12-0; *cis*-1,4-dimethylcyclohexanol, 16980-61-3; *trans*-1,4-dimethylcyclohexanol, 16980-60-2.

# Generation of [α-(Alkoxycarbonyl)vinyl]aluminum and Aluminum Allenolates by the Hydroalumination of α,β-Acetylenic Carbonyl Compounds and Their Reaction with Carbonyl Compounds

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*Received July 16, 1987*

[α-(Alkoxycarbonyl)vinyl]aluminum and aluminum allenolate intermediates were generated by the hydroalumination of α,β-acetylenic ester and ketone, respectively, with DIBAH–HMPA. The [α-(methoxycarbonyl)vinyl]aluminum generated from methyl propynoate reacted with aldehydes and ketones to produce methyl α-(1-hydroxyalkyl)acrylates in good yields although its reaction with ketones required Lewis acid activation by $BF_3$·$Et_2O$. In contrast, the nucleophilic reactivity of the aluminum allenolate intermediates from α,β-acetylenic ketones was not high. Their reaction with aldehydes produced α-(1-hydroxyalkyl) α,β-enones in relatively low yield.

Very recently, we have reported the hydroalumination of α,β-acetylenic carbonyl compounds with diisobutylaluminum hydride (DIBAH) in the presence of the hexamethylphosphoric triamide (HMPA) ligand.[1] On hydrolysis, the organoaluminum intermediates generated afford α,β-olefinic carbonyl compounds, i.e., the conjugate reduction products of the α,β-acetylenic carbonyl compounds. The organoaluminum obtained from methyl propynoate (1) reacts with a variety of allylic bromides to give synthetically useful methyl α-allylacrylates. To expand the scope of the hydroalumination reaction of the α,β-acetylenic carbonyl compounds with DIBAH–HMPA, we have explored here the reaction of the organoaluminum intermediates with carbonyl compounds.

Another interesting problem concerns the structure of the organoaluminum intermediate. The possible structures of the organoaluminums from α,β-acetylenic ester 1 and ketones 4 are [α-(alkoxycarbonyl)vinyl]aluminum **2** and (α-acylvinyl)aluminum **5**, aluminum allenolates **3** and **6**, and their equilibrated mixtures (Scheme I). Here we have also investigated spectroscopically the structures of the organoaluminum intermediates, which are thermally stable at room temperature to permit the spectroscopic study.

In the spectroscopic study of the organoaluminum intermediates, methyl propynoate (1), 1-hexyn-3-one (**4a**), 2-methyl-4-nonyn-3-one (**4b**), and 1-phenyl-2-hexyn-1-one (**4c**) were used as α,β-acetylenic carbonyl compounds. The results are summarized in Table I. The [α-(alkoxycarbonyl)vinyl]- and (α-acylvinyl)aluminums **2** and **5** and

(1) Tsuda, T.; Yoshida, T.; Kawamoto, T.; Saegusa, T. *J. Org. Chem.* **1987**, *52*, 1624.

0022-3263/88/1953-1037$01.50/0 