flask equipped with a condenser whose top was connected by a Tygon tube to a 1000-mL graduated cylinder filled with water) was determined by heating a solution of $KMnO_4$ (25.3 mmol) in H_2O (250 mL) at reflux. The amides employed in the experiment are completely soluble in H_2O at the boiling temperature. A mixture of an amide (6.3 mmol) and $KMnO_4$ (25.3 mmol) was heated at boiling, and the volume of the evolved gas was measured at the predetermined time intervals. The evolution of the gas stopped after ca. 1 h from the beginning of boiling, and the volume of the gas reached to ca. 80% of the theoretical value. The rate constant was calculated graphically from the slope of a plot of time vs log $(V_t - V_0)$, where V_0 is the void volume.

Uranium Metallacycle [(Me₃Si)₂N]₂UCH₂SiMe₂NSiMe₃: A Mild Reagent for the Synthesis of Methyl Ketones from Nitriles

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The reaction of nitriles with Grignard reagents is a widely applicable synthetic route to ketimines, which by facile hydrolysis give ketones. However, this reaction suffers some limitations. With aliphatic nitriles, a serious complication arises due to the acidity of the α-hydrogen atom. If strongly basic solvents are used, they compete with the nitrile in formation of an organomagnesium complex. If organolithium reagents are used instead of Grignard reagents, the greater basicity of both lithium reagent and the product ketimine salt causes even more difficulty.

There is one report concerning the reaction of organotitanium reagents with benzonitrile to produce acetophenone;[1] however, it seems that the reaction of hydrocarbyl–metal compounds with nitriles has been little investigated.

In a previous paper, we described the specific reaction of tris(hexamethyldisilylamino)methyluranium with aliphatic nitriles to give azomethine complexes.[2] After hydrolysis, methyl ketones were isolated in high yield. Andersen et al. have also shown that *tert*-butyl cyanide inserted readily in the uranium–methylene bond of the metallacycle [(Me₃Si)₂N]₃UCH₂SiMe₂NSiMe₃ (1), affording the expected six-membered metallacycle in which the reduced *tert*-butyl cyanide group was structurally related to an azomethine.[3]

We report here a specific, rapid, clean, and high-yield reaction of nitriles to give the corresponding methyl ketones by using the uranium metallacycle 1 in nonbasic solvents.
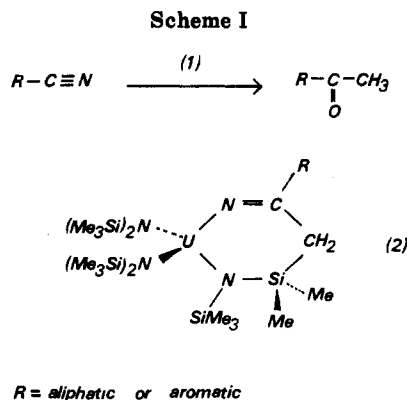
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Scheme I

R = aliphatic or aromatic

Table I. Representative Reactions of Nitriles RC≡N with [(Me₃Si)₂N]₂UCH₂SiMe₂NSiMe₃ To Give the Methyl Ketones RC(O)CH₃

entry	substrate R(RC≡N)	metallacycle 2 yield,[a] %	product RC(O)CH₃ yield,[b] %
A	CH₃	88	42
B	CH₃CH₂CH₂	86	47
C	(CH₃)₂CH	86	48
D	C₆H₅CH₂	85	66
E	(C₆H₅)₂CH	83	70
F	CH₂=CH	78	68
G	BrCH₂CH₂	80	70
H	C₆H₅	84	68
I	o-ClC₆H₄	75	72
J	N≡CCH₂CH₂	73	–

[a] On isolated compound. [b] By VPC after hydrolysis.

The stoichiometric reaction of 1 with aliphatic or aromatic nitriles was performed at room temperature (Scheme I). Pure and diluted nitriles were added dropwise to a stirred solution of 1 in pentane or toluene. After hydrolysis with dilute HCl, only the methylketones were obtained in the organic layer.[4] They can be isolated in high yield by TLC or VPC. Results obtained with some representative nitriles are summarized in Table I.

Uranium metallacycle 1 reacts with a variety of nitriles to produce metallacycles 2, which are isolated in 73–88% yields.[5] Methyl ketones are produced in 42–72% yield after hydrolysis. Entries A–E and H illustrate the very important point that the metallacycle 1 reacts exclusively with the C≡N group of aliphatic or aromatic nitriles, even in the case of acetonitrile and diphenylacetonitrile, which give very poor yields of ketone with Grignard reagents. The reaction gives also high yields with acrylonitrile (entry F). Entries G and I establish that the reaction can be extended to halogenated nitriles without a concurrent uranium–halogen substitution reaction. Unfortunately, it was impossible to isolate well-defined products from dinitriles (entry J). However a NMR-monitored reaction showed the quantitative formation of the monoinserted compound. The second cyano group was unreactive, even when an excess of metallacycle 1 was added.

The structures of metallacycles 2 were easily established by IR and NMR spectroscopy. The IR spectra showed an intense peak at ca. 1620 cm⁻¹ attributable to the C=N

(4) In fact, HN(SiMe₃)₂ and probably an aminosilanol were formed after hydrolysis of 2. These amino compounds form ammonium salts with HCl and are dissolved in the aqueous layer.
(5) ¹H NMR monitored reactions (in C₆D₆) show the complete consumption of 1 and the quantitative insertion of the nitriles to give 2; no additional peaks that could be attributed to the 54 N(SiMe₃)₂ protons of the reaction products between the nitrile anion and 1: [(SiMe₃)₂N]₃UCH(R)C≡N were detected.

Table II. Spectral Data (IR, ¹H NMR) of Metallacycles 2

	IR (νC≡N), cm^{-1}	N-(SiMe₃)₂ (54 H, s)	NSiMe₃ (9 H, s)	SiMe₂ (6 H, s)	CH₂ (2 H, br s)	R
		¹H NMR (δ, C_6D_6, 25 °C)				
2A	1615	-5.94	-18.30	6.01	25.21	-38.29 (3 H, s)
2B	1646	-6.37	-19.60	6.58	37.00	-37.18 (2 H, t), -19.17 (2 H, m), -9.95 (3 H, t)
2C	1643	-6.38	-16.59	7.33	36.73	-23.72 (1 H, hept), -13.65 (6 H, d)
2D	1627	-7.57	-20.73	7.63	47.15	-20.61 (2 H, s), -2.65 (2 H, d), 2.18 (2 H, t), 3.62 (1 H, t)
2E	1620	-7.57	-20.26	7.73	45.81	-20.38 (1 H, s), -2.42 (4 H, d), -2.18 (4 H, t), 3.62 (2 H, t)
2F	1618	-5.69	-17.29	7.27	18.29	-29.51 (1 H, dd), 12.0 (1 H, d), 11.6 (1 H, d)
2G	1640	-6.10	-21.25	7.08	34.98	-34.30 (2 H, t), -23.69 (2 H, t)
2H	1610	-6.08	-18.16	8.55	24.19	-11.26 (2 H, d), -2.52 (2 H, t), 6.61 (1 H, t)
2I	1630	-5.67	-19.50	7.47	22.45	-20.69 (1 H, d), -3.49 (1 H, t), 1.04 (1 H, d), 3.19 (1 H, t)
2J	1637	-8.50	-21.20	2.71	29.08	-50.30 (2 H, t), -6.15 (2 H, t)

bond stretching of azomethines. It is noteworthy that the stretching frequency of the unreacted C≡N group of 2J (2080 cm⁻¹) was significantly lower than that of the free ligand (2150 cm⁻¹). This decrease in frequency might be attributable to the internal coordination of the cyano group on the coordinatively unsaturated uranium atom.[6]

¹H NMR spectra of compounds 2 (Table II) were remarkably simple. (NSiMe₃)₂ and SiMe₃ protons exhibit very sharp singlets at high fields whereas CH₂ protons appear as broad, dramatically deshielded signals.[7] Each set of protons on the inserted azomethines showed very good resolved signals that were easily assigned to the corresponding hydrogens.[8]

Experimental Section

All operations on the air- and moisture-sensitive metallacycle 1 were performed under argon atmosphere in Schlenk-type vessels.

The solvents were distilled from sodium benzophenone ketyl under argon just prior to use. ¹H NMR spectra were recorded on Bruker 400W spectrometer in C_6D_6. Chemical shifts are reported in ppm from external TMS. Gas chromatographic analyses of ketones were performed on XE60, 5% on Chromosorb NAW 100-120. Metallacycle 1 was easily synthetized from UCl₄ and Na N(SiMe₃)₂ in nearly quantitative yields according to a published procedure.[9] It was stored in the crystalline state or as standardized solutions in toluene or pentane (1-2 mol L⁻¹).

General Procedure for the Synthesis of the Metallacycles 2. To a stirred solution of 1 (1.8 mmol) in 10 mL of toluene was added slowly (2 min) at room temperature 1.8 mmol of nitrile in 10 mL of toluene. After 5 min, the solvent was removed under vacuum and the brown residue was extracted twice with 10 mL of pentane. The solution was filtered and evaporated to give satisfactorily pure 2 (more than 95%) as a brown microcrystalline powder. Yields on isolated product were reported in Table I.

General Procedure for Direct Synthesis of the Methyl Ketones. To a stirred solution of 1 (1.2 mmol) in 2 mL of pentane was added 1.2 mmol of nitrile within 5 min. After 5 min, the mixture was quenched with 2 mL of HCl (1 M). The organic layer was separated, washed with 1 mL of water, dried over sodium sulfate, diluted to 10 mL with pentane, and analyzed by VPC.

Redissolution of 2 in pentane followed by hydrolysis as described above afforded methyl ketones in similar yields.

Registry No. 1, 72472-77-6; 2 (R = CH₃), 113765-70-1; 2 (R = CH₃CH₂CH₂), 113765-71-2; 2 (R = (CH₃)₂CH), 121029-64-9; 2 (R = C₆H₅CH₂), 121029-65-0; 2 (R = (C₆H₅)₂CH), 121029-66-1; 2 (R = CH₂ = CH), 121029-67-2; 2 (R = BrCH₂CH₂), 121029-68-3; 2 (R = C₆H₅), 113765-72-3; 2 (R = o-ClC₆H₄), 121029-69-4; 2 (R = N≡CCH₂CH₂), 121029-70-7; CH₃CN, 75-05-8; CH₃CH₂CH₂CN, 109-74-0; (CH₃)₂CHCN, 78-82-0; C₈H₅CH₂CN, 140-29-4; (C₆H₅)₂CHCN, 86-29-3; CH₂=CHCN, 107-13-1; BrCH₂CH₂CN, 2417-90-5; C₆H₅CN, 100-47-0; o-ClC₆H₅CN, 873-32-5; NCCH₂CH₂CN, 110-61-2; CH₃C(O)CH₃, 67-64-1; CH₃CH₂CH₂C(O)CH₃, 107-87-9; (CH₃)₂CHC(O)CH₃, 563-80-4; C₆H₅CH₂C(O)CH₃, 103-79-7; (C₆H₅)₂CHC(O)CH₃, 781-35-1; CH₂=CHC(O)CH₃, 78-94-4; BrCH₂CH₂C(O)CH₃, 28509-46-8; C₆H₅C(O)CH₃, 98-86-2; o-ClC₆H₄C(O)CH₃, 2142-68-9; NCCH₂CH₂C(O)CH₃, 927-56-0.


An Optimized Procedure for Titanium-Induced Carbonyl Coupling

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Fifteen years have passed since the discovery[1-3] that ketones and aldehydes undergo deoxygenative coupling to yield olefins on treatment with low-valent titanium. The reaction takes place equally well on all manner of substrates, be they saturated or unsaturated, aliphatic or aromatic, ketone or aldehyde. Furthermore, the reaction occurs both in an intermolecular sense on monocarbonyl compounds to yield acyclic alkenes and in an intramolecular sense on dicarbonyl compounds to yield cycloalkenes.[4]
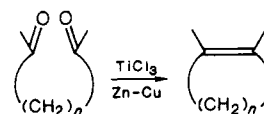
Although our initial work[1] involved preparation of the low-valent titanium reagent by reduction of TiCl₃ with LiAlH₄ in tetrahydrofuran (THF), we soon found that

(6) The lack of reactivity observed for the second cyano group, even if an excess of uranium reagent was added, is in good accordance with the internal coordination of this group on the uranium atom.

(7) The methylene singlet of 1 was strongly shielded (-118 ppm, C₆D₆, 25 °C) whereas the deshielding of the same protons in the metallacycles obtained after insertion of polar molecules into the U-C bond was a general feature (see ref 2, 3, 9 and also: Dormond, A.; Elbouadili, A.; Moise, C. J. Less. Com. Met. 1986, 122, 159).

(8) The considerable splitting and the good resolution of signals in ¹H NMR spectra of the metallacycles obtained after insertion in the uranium-methylene bond of 1 is a general feature for a wide range of organic molecules. Therefore, the utilization of the uranium metallacycle 1 as a shift reagent instead lanthanides complexes is under investigation.

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