3.56 (3 H, br m, $w/2$ = 27 Hz, THP and 24-H), 3.68 (2 H, d, J = 7 Hz, 26-CH_2OH), 3.90 (1 H, br m, $w/2$ = 18 Hz, 3-H), 4.74 (1 H, m, $w/2$ = 8 Hz, THP). Anal. Calcd for $C_{32}H_{56}O_4$: C, 76.14; H, 11.18. Found: C, 76.13; H, 11.21.

Diol **9** (89 mg, 0.18 mmol) was treated with sodium metaperiodate (50 mg, 0.23 mmol) by a procedure similar to that for diol **8**. Worked up as described above, there was obtained the aldehyde **10** [68 mg (72%)] as an oil: IR ν 2700, 1720 (CHO), 1030, 980 (THP ether) cm^{-1}; ^{1}H NMR δ 0.65 (3 H, s, 18-CH_3), 0.93 (3 H, s, 19-CH_3), 0.94 (3 H, d, J = 7 Hz, 21-CH_3), 1.10 (3 H, d, J = 7 Hz, 24-CH_3), 3.53 (2 H, br m, $w/2$ = 20 Hz, THP - H), 3.90 (1 H, br m, $w/2$ = 14 Hz, 3-H), 4.73 (1 H, m, $w/2$ = 14 Hz, 3-H), 4.73 (1 H, m, $w/2$ = 9 Hz, THP-H). Anal. Calcd for $C_{31}H_{52}O_3$: C, 78.76; H, 11.09. Found: C, 78.80; H, 11.13.

(24*R*,25*S*)-5β-Cholestane-3α,24-26-triol (11). Diol **8** (95 mg, 0.19 mmol) was suspended in methanol (20 mL) followed by the addition of p-toluenesulfonic acid (36 mg, 0.20 mmol). The reaction was allowed to proceed at room temperature for 2 h, while progress was followed by TLC. It was then worked up by concentrating the reaction mixture in vacuo, maintaining the bath temperature below 40 °C. Dilution with methylene chloride (100 mL) washing successively with 5% sodium bicarbonate, water, and brine, and drying over anhydrous sodium sulfate followed by evaporation of solvents yielded a crude white solid material. This was purified on preparative TLC (2 × 10% methanol/methylene chloride). Extraction of the product from the silica gel yielded the triol **11** [63.4 mg (80%)] as white crystals: mp 169–170 °C (ethyl acetate); $[\alpha]^{25}{}_D$ +40 ± 2° (c 0.27, methanol); IR ν 3400 (OH) cm^{-1}; ^{1}H NMR δ 0.67 (3 H, s, 18-CH_3), 0.87 (3 H, d, J = 7 Hz, 27-CH_3), 0.93 (3 H, s, 19-CH_3), 0.93 (3 H, d, J = 7 Hz, 21-CH_3), 3.50 (4 H, br m, $w/2$ = 21 Hz, 3-H, 24-H, 26-H). Anal. Calcd for $C_{27}H_{48}O_3$: C, 77.09; H, 11.50. Found: C, 77.08; H, 11.54.

Uranium-Mediated Methylenation of Carbonyl Compounds

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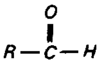
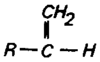
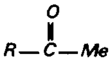
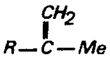
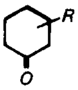
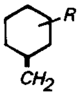
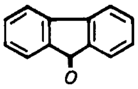
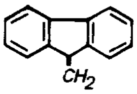
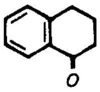
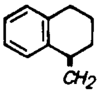
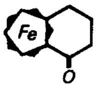
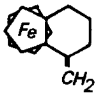
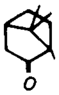
The direct methylenation of carbonyl compounds via phosphorus ylides[1] shows some limitations: as an example, poor yields were obtained from cyclic or sterically hindered ketones.[2] A major advance in this area occurred when new techniques using alkyltitanium,[3] zinc–alkylidene-aluminium,[4] zinc–alkylidenetitanium,[5] or titanium–alkylidenealuminium (Tebbe reactif)[6] were used. Moreover, several papers reported Wittig-like reactions with both group 4[7] and 5[8] alkylidenes and group 6 alkylidenes complexes.[9] We report here a rapid, clean, and high-yield methylenation reaction of a wide range of both aldehydes and ketones using an uranium metallacycle: $((Me_3Si)_2N)_2\overline{UCH_2SiMe_2N}SiMe_3$ (**1**).[10]

Table I. Representative Reactions of Aldehydes and Ketones with $[(Me_3Si)_2N]_2\overline{UCH_2SiMe_2N}SiMe_3$ (1)

entry	substrate		product^a	yield,^{b} %
A	 $R-\overset{\overset{O}{\Vert}}{C}-H$	R = Ph; Fc;^{c} n-C_8H_{17}	 $R-\overset{\overset{CH_2}{\Vert}}{C}-H$	75; 92, 90
B	 $R-\overset{\overset{O}{\Vert}}{C}-Me$	R = Ph; Fc;^{c} n-C_8H_{17}	 $R-\overset{\overset{CH_2}{\Vert}}{C}-Me$	85; 90; 70
C		R = 4-t-Bu		90
D		R = 3,3,5,5-Me_4		90
E				85
F				88
G				90
H				85

^{a} All products afforded satisfactory NMR and analytical data. ^{b} Yields cited were on isolated olefinic products. ^{c} Fc = $C_5H_5FeC_5H_4$.

Experimental Section

All operations using the air- and moisture-sensitive metallacycle **1** were carried out in Schlenk-type vessels under purified argon. The solvents were thoroughly dried and deoxygenated and distilled under argon prior to use.

NMR spectra were obtained on JEOL FX 100 or BRUCKER 400-W spectrometers in C_6D_6 at 25 °C. Chemical shifts are reported in ppm from the external standard tetramethylsilane.

General Procedure for the Methylenation Reaction. A solution of 1 mmol of the carbonyl compound in 2 mmL of pentane was added dropwise (1 min) at room temperature to 1.1 mmol of **1** (0.25 M) in pentane.

(a) The reaction was immediately quenched by addition of 2 mL of diluted (1 M) HCl.[12] The organic layer was washed twice with 1 mL of water, diluted with 10 mL of pentane, and dried on sodium sulfate. After removal of the solvent, the crude vinyl compound was purified by chromatography on a short column of neutral alumina (pentane as eluant): 75–90% yield.

(b) After removal of the solvent, the brown powder was washed twice with 1 mL of pentane at −70 °C, affording the metallacycle **2** in good yield (80–90%). Analysis by NMR revealed the product to be >95% pure. After redissolution in pentane, **2** can be hydrolyzed as described above.

Results and Discussion

The crystalline metallacycle **1** was synthesized in high yield (>95%) in an one-step synthesis according to our

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[1] Maercker, A. *Org. React. (N.Y.)* **1965**; *14*, 270. Johnson, A. W. In *Ylid Chemistry*; Academic: New York, 1966.

[2] Sowerby, R. L.; Coastes, R. M. *J. Am. Chem. Soc.* **1972**, *94*, 4758.

[3] Kaufmann, T.; König, R.; Pahde, C.; Tannert, A. *Tetrahedron Lett.* **1981**, *22*, 5031.

[4] Takai, K.; Hotta, Y.; Oshima, K.; Nozaki, H. *Tetrahedron Lett.* **1978**, *27*, 2417.

[5] Eisch, J. J.; Piotrowski, A. *Tetrahedron Lett.* **1983**, *24*, 2043.

[6] Tebbe, N.; Parshall, G. W.; Reddy, G. S. *J. Am. Chem. Soc.* **1978**, *100*, 3611. Pine, S. H.; Zahler, R.; Evans, D. A.; Grubbs, R. H. *Ibid.* **1980**, *102*, 3270. For a review, see: Brown-Wensley, K. A.; Buchwald, S. L.; Cannizzo, L.; Clawson, L.; Ho, S.; Meinhardt, D.; Stille, J. R.; Straus, D.; Grubbs, R. H. *Pure Appl. Chem.* **1978**, *55*, 1733.

[7] Clift, S. M.; Schwartz, J. *J. Am. Chem. Soc.* **1984**, *106*, 8301.

[8] Schrock, R. R. *J. Am. Chem. Soc.* **1976**, *98*, 5399.

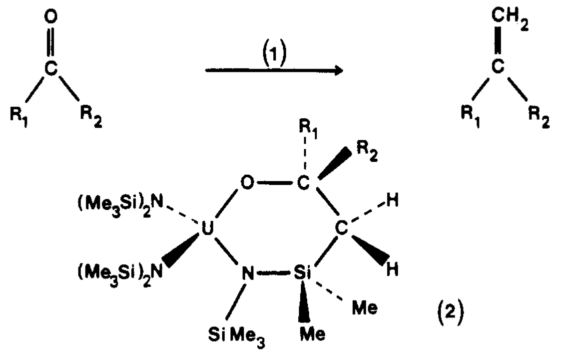
[9] Freudenberger, J. H.; Schrock, R. R. *Organometallics* **1986**, *5*, 398.

[10] Simpson, S. J.; Turner, H. W.; Andersen, R. A. *Inorg. Chem.* **1981**, *20*, 2991.

[11] Dormond, A.; El Bouadili, A.; Moïse, C. *J. Organomet. Chem.* **1985**, *288*, C1.

[12] Workup with water or 10% aqueous Na_2CO_3 afforded similar yields. Nevertheless, free $HN(SiMe_3)_2$ and the remaining "UOH" products were best eliminated with aqueous HCl.

Scheme I



(2)

R_1, R_2 = acyclic (**2A,B**) or cyclic moieties (**2C–H**)

Table II. ^{1}H NMR Chemical Shifts (δ) of Significant Protons[a] for 2C–H Spiro Compounds

	CH_2	$SiMe_2$	$NSiMe_3$	$[N(SiMe_3)_2]_2$
2C$_\alpha$[b]	3.72	0.50	−12.62	−4.79[c]
2C$_\beta$	6.85	2.10	−13.41	−5.03[c]
2D	11.85	2.82	−11.24	−13.12
2E	16.75[c,d]	−0.30[c]	−22.37[c]	−4.80[c]
2F	16.03[c,d]	4.06[c]		−3.10[c]
	5.51[c]	−2.90[c]		−8.49[c]
2G$_\alpha$	28.66[c,d]	−2.01[c]	−12.35	−6.04[c]
	14.79	−2.91[c]		−7.30[c]
2H$_\alpha$	32.35[c]	−4.07[c]	−10.82	−8.37[c]
	18.76	−4.15[c]		−10.23[c]
2H$_\beta$	21.4[c,d]	−4.10[c]	−13.02	−2.85[c]
	16.1[c,d]	−3.25[c]		−1.03[c]

[a] Other protons were omitted for clarity. [b] α, major isomer; β, minor isomer. [c] Broadened signal at room temperature. [d] Recorded at 60 °C; all signals sharpened upon raising the temperature.

procedure.[11] Handling of this air- and moisture-sensitive complex was facilitated by employing standardized solutions in organic solvents (aromatic or aliphatics, 0.2–0.5 M); these solutions can be stored under argon at room temperature during several months without loss of reactivity. The reactions with carbonyl compounds were very clean and rapid (1–2 min) (Scheme I). After workup, the methylenation product is the only compound observed and can be isolated in high yields. The list of representative carbonyl compounds employed in this study is illustrated in Table I.

Inspection of Table I reveals that the reaction of the uranium metallacycle 1 with a variety of aliphatic, aromatic, and cyclic carbonyl compounds is a general high yield operation. Entries C, D, and F–H illustrate the important point that no olefin isomerization occurs in any of these reactions. Entries F and G show that the reaction can be extended to easily enolizable ketones without noticeable formation of intermediate enol addition compound,[13] and entries E and H establish the superiority of this method on the Wittig reaction.[14]

The intermediate metallacycles 2 were almost quantitatively formed[15] and can be isolated in good yields. ^{1}H NMR affords interesting information on their geometry and on the stereoselectivity of the insertion reaction. Table II summarizes relevant spectral data of spiro compounds **2C–H**.[16] The $N(SiMe_3)_2$, $SiMe_2$, and CH_2 protons of **2D**, **2E**, and both **2C**α and **2C**β were equivalent, the six-membered ring containing the tetrahedral uranium atom appeared also to be quite planar at room temperature, and the broadening of these signals in **2E–H** spectra could be due to a dramatic increase of the steric crowding around the nitrogen atom.[11]

2C and **2H** were, in fact, mixtures of the two expected diastereoisomers in the ratio α/β, 2/1 and 20/1, respectively, whereas only one diastereoisomer was obtained for the bimetallic compound **2G**. The stereochemistry of this insertion reaction is under investigation and will be discussed elsewhere.

Acknowledgment. We thank D. Arnoult for his technical assistance.

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(13) About 3% of the **F** and **G** starting ketones were recovered after workup even if a large excess of **1** was used. ^{1}H NMR monitoring of the reaction showed the complete consumption of the ketone whereas an additional broad singlet appeared near the $N(SiMe_3)_2$ signals of **2F** (δ 2.51) and **2G** (δ 3.96). This singlet could be attributed to the 54 equiv of $N(SiMe_3)_2$ protons of the enol addition compounds (yields determined by comparison of intensities of signals of the $N(SiMe_3)_2$ protons: 3–5 %).

(14) Greenwald, R.; Chaykovsky, M.; Corey, E. J. *J. Org. Chem.* **1963**, *28*, 1128.

(15) Based on ^{1}H NMR analysis of the crude product.

(16) Cyclanic protons of **2F** and **2G** appeared as poorly resolved multiplets. All other signals of cyclanic, cyclopentadienyl, aromatic, and alkyl protons were well resolved, and the chemical shift dispersion (40–50 ppm) allowed observation and assignment of every resonance even at 100 MHz.

Synthesis of Diacids and Keto Acids by Ruthenium Tetraoxide Catalyzed Oxidation of Cyclic Allylic Alcohols and α,β-Unsaturated Ketones

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In the course of synthesizing both enantiomers of the pheromone grandisol,[1] we needed to oxidatively cleave tertiary, allylic alcohol 1 to the known keto acid 2. This transformation has been reported by Zurflüh et al.,[2] who employed osmium tetraoxide and sodium periodate in a two-phase system of ether and water[3] to obtain a 51% isolated yield of keto acid 2. In our hands, the reaction gave erratic results with yields as low as 30%. In 1981, the Sharpless group reported a much improved method for cleaving simple olefins with a catalytic amount of ruthenium tetraoxide and a stoichiometric amount of sodium periodate.[4] Before Sharpless reported his results, catalytic ruthenium oxidations were troublesome and erratic.[5] As an extension of his work, we report the oxidative cleavage of cyclic allylic alcohols and α,β-unsaturated ketones.

In all of the reactions reported here, one or more carbon atoms are excised from a mono- or bicyclic compound, leaving either a keto acid or a diacid. There are many possible paths from the starting compound to the final, isolated product, and indeed there may be no one predominant path. In any event, the following reactions are probably occurring. First, any lower valence forms of ruthenium are oxidized to the tetraoxide. The initial olefin

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(1) Webster, F. X.; Silverstein, R. M. *J. Org. Chem.*, in press.

(2) Zurflüh, R.; Dunham, L. L.; Spain, V. L.; Siddall, J. B. *J. Am. Chem. Soc.* **1970**, *92*, 425.

(3) Pappo, R.; Allen, D. S., Jr.; Lemieux, R. U.; Johnson, W. S. *J. Org. Chem.* **1956**, *21*, 478.

(4) Carlsen, Per H. J.; Katsuki, T.; Martin, V. S.; Sharpless, K. B. *J. Org. Chem.* **1981**, *46*, 3936.

(5) Berkowitz, L. M.; Rylanders, P. M. *J. Am. Chem. Soc.* **1958**, *80*, 1261.