

plication in both frequency domains to give 512×512 real data points, the final data matrix symmetrized²³ prior to plotting. Total data acquisition time for the COSY spectrum was 6 h. The proton double quantum spectrum was acquired by using the following pulse sequence:

$$\pi/2-\tau-\pi/2, \pi, \pi/2-\tau-\pi/2-t_1-\pi/4-t_2$$

with the transmitter located downfield of the H6 resonance and with data collection conducted using a 32-step phase cycle.²⁴ The spectrum was collected as $512 \times 2K$ data points and was processed by using 0.1-Hz sinusoidal multiplication in both frequency domains with zero filling prior to the second Fourier transform to give 512×512 real data points in the quadrant of the spectrum finally plotted as a ten-level contour plot (Figure 2). Total acquisition time for the proton double quantum spectrum was 14 h. Finally, the heteronuclear chemical shift correlation spectrum was acquired overnight by using the modified pulse sequence described by Bax and Morris.¹⁵ The spectrum was collected as $256 \times 2K$ data points and was processed by using double exponential apodization prior to both Fourier transformations with zero filling prior to the second to give the final data matrix containing $512 \times 1K$ data points which is presented as a six-level contour plot in Figure 3.

The proton reference spectrum shown in all of the two-dimensional NMR spectra was obtained by using 32K data points which was processed by using an 0.03-Hz exponential line broadening. The long-range couplings initially identified from the proton double quantum spectrum were confirmed by using a 64K data file which was processed with double exponential apodization followed by 0.02-Hz sinusoidal multiplication, the observed couplings reported in Table I.

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Registry No. 1, 77-16-7.

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(24) The experiment was performed with the delay $\tau = 1/4J_{HH}$. An average vicinal coupling constant of 7 Hz was assumed, giving $\tau = 35.7$ ms. Complete details of the 32-step phase cycling scheme employed in the performance of the proton double quantum experiment are available from the authors upon request.

In Situ Preparation of (μ -Chloro)(μ -methylene)bis(cyclopentadienyl)(dimethylaluminum)titanium (Tebbe's Reagent)[†]

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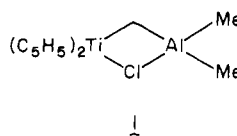
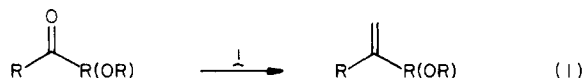
The titanium alkylidene 1 (Tebbe's reagent) is a versatile methylenation agent for the conversion of ketones to olefins and esters to vinyl ethers (eq 1).¹ Unfortunately, this commercially available reagent (Strem, Alfa) is ex-

Table I. Equivalents of 1 Produced under Different Reaction Conditions^a

runs	prep	equiv of 1 produced
1	68 °C, 11 h	0.40
2	72 °C, 11 h	0.47
3	87 °C, 11 h	0.23
4	60 °C, 11.5 h	0.30
5	50 °C, 18.5 h	0.55
6	rt, 72 h	0.65

^a See Experimental Section for preparation of 1 and determination of equivalents produced.

pensive for large scale reactions, and currently one needs to employ vacuum line and Schlenk techniques for its synthesis.²

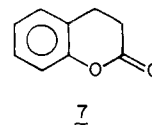


We felt there was a need to develop a facile method for the in situ generation of 1 (utilizing only an inert gas manifold and standard synthetic organic techniques) which could also be applied to large scale synthesis.

It was found that the crude reaction mixture formed by the combination of titanocene dichloride and 2 equiv of $AlMe_3$ (2.0 M in PhMe) could be used directly to effect methylene transfer. Optimization of reaction conditions were performed by allowing the crude mixture, containing 1 and ~1 equiv of $AlMe_2Cl$ in PhMe, to react with a THF solution of 2-*tert*-butylcyclohexanone (2). Workup afforded a combined quantitative yield of starting ketone and the methylenation product 3 as an oil upon which ¹H NMR analysis gave the equivalents of 1 consumed by the ketone (Table I).

On a 50-mmol scale performed using the parameters of run no. 6 (Table I) under slightly modified conditions, 1.3 equiv of 4-phenylcyclohexanone (4) were methylenated by the in situ Tebbe's reagent 1 derived from 1 equiv of titanocene dichloride to give an 82% isolated yield (94% crude yield) of the olefin 5.³

In addition, 1.0 equiv of the ester dihydrocoumarin (7) was converted to the vinyl ether 8^{1b} in 76% isolated yield upon treatment with 1 generated as above while use of 1.3 equiv of ester gave unreacted ester upon workup.



(1) (a) Clawson, L. E.; Buchwald, S. L.; Grubbs, R. H. *Tetrahedron Lett.* 1984, 5733. (b) Pine, S. H.; Zahler, R.; Evans, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* 1980, 102, 3270.

(2) Lee, J. B.; Ott, K. C.; Grubbs, R. H. *J. Am. Chem. Soc.* 1982, 104, 7491.

(3) This may result from regeneration of 1 during the reaction. Conversion of the methylenation byproduct $[Cp_2Ti=O]$ (Cp = cyclopentadienyl) to $Cp_2TiMeCl$ by $AlMe_2Cl$ and its reaction with $AlMe_3$ could yield 1.^{5a} Alternatively, $AlMe_2Cl$ may react with $Cp_2TiMeCl$ to give $Cp_2TiCH_2-AlMe_2Cl$ (6),^{5a} a less reactive methylenation agent.^{5b} The existence and potential use of these proposed catalytic pathways are currently being explored. Standard Wittig procedure gave 34% isolated yield of 5. Barrett, A. G. M.; Betts, M. J.; Fenwick, A. J. *J. Org. Chem.* 1985, 50, 169.

(4) Howard, T. R.; Grubbs, R. H., unpublished results.

(5) (a) Ott, K. C.; deBoer, E. J. M.; Grubbs, R. H. *Organometallics* 1984, 3, 223. (b) Howard, T.; Pine, S.; Grubbs, R. H., unpublished results.

[†] Contribution No. 7126.

The procedures listed in the Experimental Section for methylenation of 4 and 7 may be used as general guides for ketones and esters, respectively. One potential side reaction of ketones is the formation of $\text{Cp}_2\text{TiCH}_2\text{CR}_2\text{CH}_2$ (9) by the combination of the olefin produced and excess 1. These compounds serve as good methylenation agents when heated above their decomposition point⁶ and normally react with ketone present to form 2 equiv of olefin and $(\text{Cp}_2\text{Ti}=\text{O})$.⁷ If unquenched by ketone, 9 will be hydrolyzed upon workup to give the *gem*-dimethyl product 10.⁸ Therefore, use of a slight excess of ketone or warming the reaction above $\sim 60^\circ\text{C}$ before quenching is advised. Conversely, metallacycle formation with vinyl ethers has never been observed and should present no problem in reacting in situ 1 with esters. Potential side reactions of carbonyl starting materials and methylenation products with organoaluminum species present during these reactions does not appear to proceed to a significant degree.

Experimental Section

General Procedures. ^1H and ^{13}C NMR spectra were recorded on a JEOL FX-90Q (89.60 MHz ^1H , 22.53 MHz ^{13}C). Chemical shifts are referenced to residual protiosolvent residues. Elemental analysis was performed by L. Henling at the analytical facilities of the California Institute of Technology.

Materials. Titanocene dichloride (Boulder) was purified by Soxhlet extraction with CH_2Cl_2 before use. AlMe_3 (2.0 M in PhMe) was purchased from Aldrich (packaged under nitrogen in Sure/Seal bottles). 2-*tert*-Butylcyclohexanone (2), 4-phenylcyclohexanone (4), and dihydrocoumarin (7) were also purchased from Aldrich and used as received. Dry THF was previously distilled from sodium benzophenone ketyl and stored in solvent flasks equipped with Teflon screw-type valves. Solvents listed as reagent or technical were used as received. Silica gel (60, 230-400 mesh ATM) was purchased from EM reagents.

"Titration" of in Situ Solutions of 1. Solutions of 1 were prepared as below by using titanocene dichloride (2.49 g, 10.0 mmol) and AlMe_3 (2.0 M in PhMe, 10 mL, 20.0 mmol of AlMe_3). After the solution was stirred as described in Table I, 2-*tert*-butylcyclohexanone (2) (1.54 g, 10.0 mmol) in 30 mL of THF was treated with the prepared solution of 1 as below with stirring continued 0.5 h at -40°C and an additional 15 min at room temperature. Workup as below gave quantitative crude yields of organic products as a mixture of ketone and olefin. ^1H NMR integration of the *tert*-butyl resonances of 2 and 3 were used to calculate equivalents of 1 produced.

Preparation of (4-Methylenecyclohex-1-yl)benzene (5). A three-neck 250-mL round-bottom flask equipped with a magnetic stir bar and oil bubbler was charged with titanocene dichloride (12.45 g, 50.0 mmol) and flushed with argon, and AlMe_3 (2.0 M in PhMe, 55 mL total, 110 mmol of AlMe_3) was added by cannula from a graduated cylinder (the graduated cylinder was previously flushed with argon, capped with a rubber septum and charged by cannula from an Aldrich Sure/Seal bottle). The resulting dark red mixture was stirred at room temperature with initial evolution of CH_4 through the bubbler. After 72 h of stirring, additional AlMe_3 (2.0 M in PhMe, 20 mL total, 40 mmol of AlMe_3) was added by the above method and stirring continued for 12 h.

A 500-mL round-bottom flask equipped with magnetic stir bar and charged with 4-phenylcyclohexanone (4) (11.32 g, 65.0 mmol) was flushed with argon and capped with a rubber septum. A 80-mL sample of dry THF was added by syringe and the resulting solution stirred and cooled to -40°C . The previously prepared solution of 1 was added via cannula over a 10-min period while the resulting mixture was maintained at or below -40°C . Stirring was continued for 0.5 h at -40°C , 1.5 h at -40 to 0°C , and finally 1 h at room temperature.

The resulting dark red mixture was diluted with 50 mL of reagent THF added by syringe, vigorously stirred, and cooled to -10°C . A 40-mL sample of 15% NaOH (aqueous) was added initially in 0.2-0.3-mL portions by syringe with vigorous evolution of CH_4 , while the mixture was maintained at -10°C or below. When the mixture became too viscous for magnetic stirring, the flask was swirled by hand with frequent cooling and the remainder of the NaOH solution was added in much larger portions to the open flask. Additional stirring at room temperature produced a mixture containing a pale orange supernatant with a large amount of slightly bluish precipitate which turned white upon standing. The aluminosilicate polymer formed serves as an excellent drying agent, and no further drying was required.

The mixture was filtered through a Celite pad on a coarse frit with suction and the precipitate and pad liberally washed with technical Et_2O . The combined filtrate and washings were evaporated under reduced pressure to afford a clear orange toluene solution of crude product which was diluted with 300 mL of reagent pentane to precipitate a large amount of orange solid. After filtration through a silica gel pad (on a coarse frit with suction) with liberally washing of the precipitate with reagent pentane, the combined washing and filtrate were evaporated under reduced pressure to give 10.57 g (94% yield) of product as a yellow oil. Vacuum distillation (bp 88°C (2 torr)) afforded 9.21 g (82% yield) of pure 5 as a colorless oil: ^1H NMR (CD_2Cl_2) δ 7.26 (m, 5 H), 4.72 (m, 2 H), 2.89-1.45 (m, 9 H); ^{13}C NMR (CD_2Cl_2) δ 149.4, 147.5, 128.8, 127.3, 126.4, 107.6, 44.6, 36.1, 35.7. Anal. Calcd for $\text{C}_{13}\text{H}_{16}$: C, 90.64; H, 9.36. Found: C, 90.66; H, 9.50.

Preparation of 3,4-Dihydro-2-methylene-2H-1-benzopyran (8). Dihydrocoumarin (7) (7.41 g, 50.0 mmol) was treated as above to give a toluene solution of crude 8. Due to the insolubility of 8 in pentane, an alternative method of purification was employed. This consisted of evaporation of the toluene under reduced pressure at 50°C to give a deep orange oil containing significant quantities of titanocene compounds (^1H NMR), followed by vacuum distillation to afford 5.56 g (76% yield) of 8^{1b} as a slightly yellow oil: ^1H NMR (CD_2Cl_2) δ 7.04 (m, 4 H), 4.54 (s, 1 H), 4.17 (m, 1 H), 2.74 (m, 2 H), 2.64 (m, 2 H); ^{13}C NMR (CD_2Cl_2) δ 156.8, 153.6, 129.2, 128.1, 123.5, 121.6, 116.3, 89.5, 27.0, 25.7. Anal. Calcd for $\text{C}_{10}\text{H}_{10}\text{O}$: C, 82.16; H, 6.89. Found: C, 81.77; H, 6.98.

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Registry No. 1, 67719-69-1; 2, 1728-46-7; 3, 1728-46-7; 4, 4894-75-1; 5, 87143-17-7; 6, 77933-59-6; 7, 119-84-6; 8, 74104-13-5; Cp_2TiCl_2 , 1271-19-8; $\text{Cp}_2\text{Ti}=\text{O}$, 59487-89-7; Cp_2TiMeCl , 1278-83-7; AlMe_3 , 75-24-1; AlMe_2Cl , 1184-58-3.

Liquid-Phase Radical Reactions of Octanal and *tert*-Butyl Hydroperoxide

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Introduction

The reaction of alkyl hydroperoxides with aldehydes has received little attention in the literature despite the practical significance this process holds in the autoxidation of such diverse materials as edible oils and distillate fuels.¹⁻⁵ Much of what has been reported is characterized

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