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A Convenient Reagent for the Intermolecular Coupling of Aldehydes and Ketones to Form Olefins

Anthony R. Carroll and Walter C. Taylor

Department of Organic Chemistry, University of Sydney, N.S.W. 2006.

Abstract

When aldehydes or ketones are treated with titanium tetrachloride and amalgamated magnesium turnings in tetrahydrofuran at 0° for 2 h and subsequently under reflux for 24 h, reductive coupling occurs to give olefin in high yield. The optimum ratio of carbonyl substrate to titanium reagent was found to be 1 : 4. Examples of symmetrical and mixed couplings are given. Intramolecular coupling was not successful.

The reductive coupling of carbonyl compounds with low-valent titanium reagents, the so-called McMurry reaction, is an attractive method for the formation of carbon–carbon bonds which has found considerable application in synthesis.[1–3] It is now generally recognized that the active species is titanium(0), normally produced *in situ* by reduction of $TiCl_3$. Some systems which have been used are $TiCL_3$/K or Li, $TiCl_3$/Mg, $TiCl_3/LiAlH_4$ and $TiCl_3$/Zn–Cu; the last combination is particularly useful, being effective in a wide variety of situations.

In addition to the $TiCl_3$-based systems there are some limited examples of the use of $TiCl_4$. For example, $TiCl_4$/Zn was shown first[4] to couple diaryl and alkyl aryl ketones and benzaldehyde, and later it was reported[5] that $TiCl_4$/Zn (in refluxing tetrahydrofuran) reductively coupled aliphatic ketones in reasonable yields. Corey introduced $TiCl_4$/amalgamated magnesium mesh (at 0°) as a reagent for coupling carbonyl compounds to produce pinacols, which are the intermediate products in the olefin-forming reactions,[6] in high yield. It was believed that a titanium(II) species is involved in this reaction; a well-defined titanium(II) species prepared from aluminium, aluminium trichloride, $TiCl_4$ and hexamethylbenzene was also found to effect pinacolic coupling in high

[1] McMurry, J. E., Fleming, M. P., Kees, K. L., and Krepsi, L. R., *J. Org. Chem.*, 1978, **43**, 3255.
[2] McMurry, J. E., *Acc. Chem. Res.*, 1983, **16**, 405.
[3] Lenoir, D., *Synthesis*, 1989, 883.
[4] Mukaiyama, T., Sato, T., and Hanna, J., *Chem. Lett.*, 1973, 1041.
[5] Lenoir, D., *Synthesis*, 1977, 553.
[6] Corey, E. J., Danheiser, R. L., and Chandrasekaran, S., *J. Org. Chem.*, 1976, **41**, 260.

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yield. $TiCl_4$/Zn–Cu in refluxing tetrahydrofuran causes intramolecular pinacolic coupling of dodecanedial.[7]

In connection with other work we have confirmed the effectiveness of the Corey method for preparing pinacols, but we have also found that when aldehydes or ketones are treated with $TiCl_4$/Hg/Mg (turnings) in tetrahydrofuran

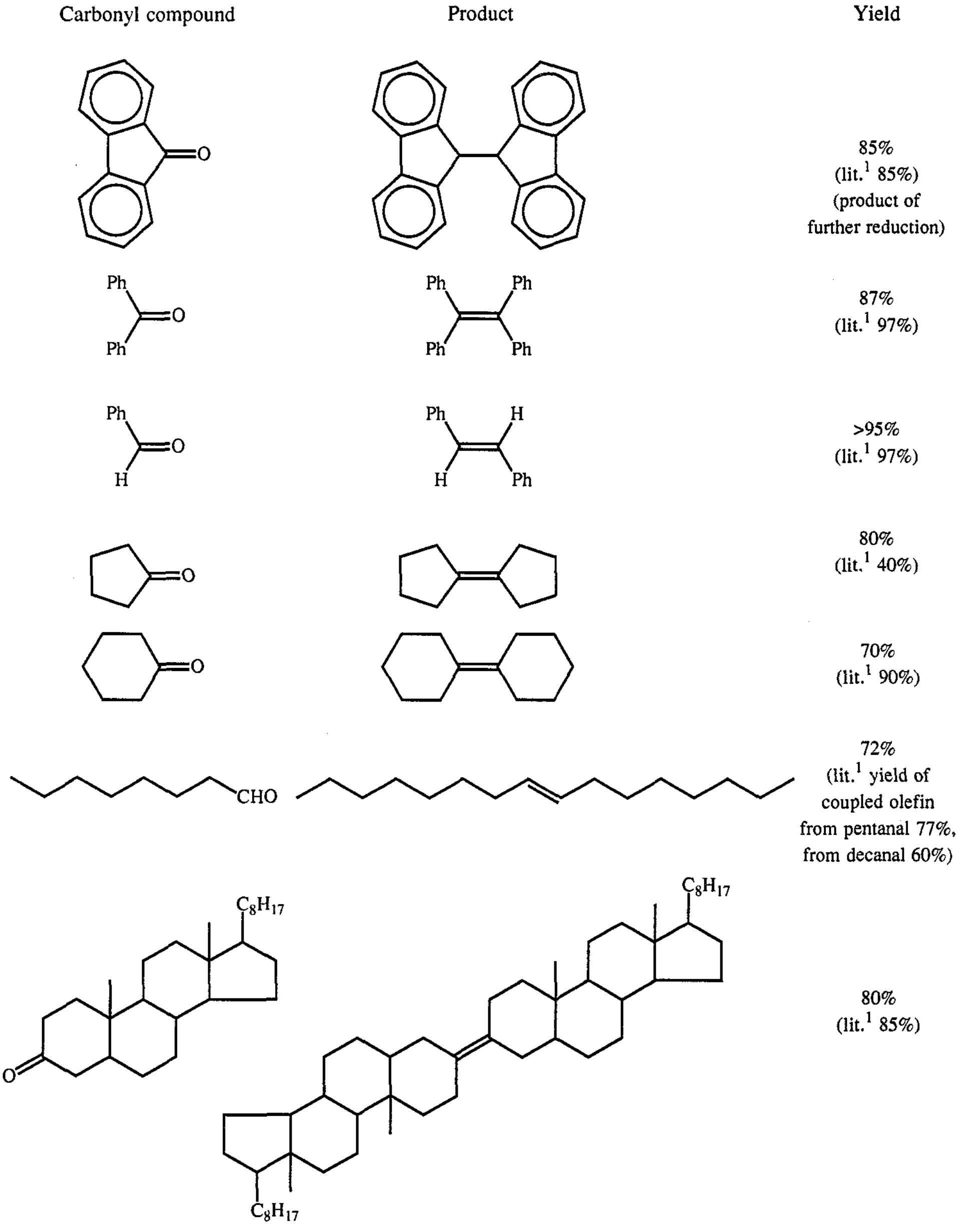

Fig. 1. Reductive coupling of carbonyl compounds with $TiCl_4$/Mg/Hg.

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[7] Ghiringhelli, D., *Tetrahedron Lett.*, 1983, 287.

at 0° for 2 h and subsequently under reflux for 24 h, olefins are produced in high yield. The optimum ratio of ketone/titanium reagent was found to be 1:4 rather than 2:3 as used by Corey. The reaction is quite general for intermolecular coupling (Fig. 1), and yields are comparable with those reported from using $TiCl_3$ reagents; in the case of cyclopentanone the yield of coupled product is much higher than previously found. Mixed coupling is also possible (Fig. 2). Intramolecular coupling was not successful in two aliphatic systems examined (dodecanedial and tetradecane-2,13-dione). In view of the greater convenience of handling $TiCl_4$ compared with $TiCl_3$, we believe the conditions reported here represent an attractive alternative for effecting the McMurry reaction.

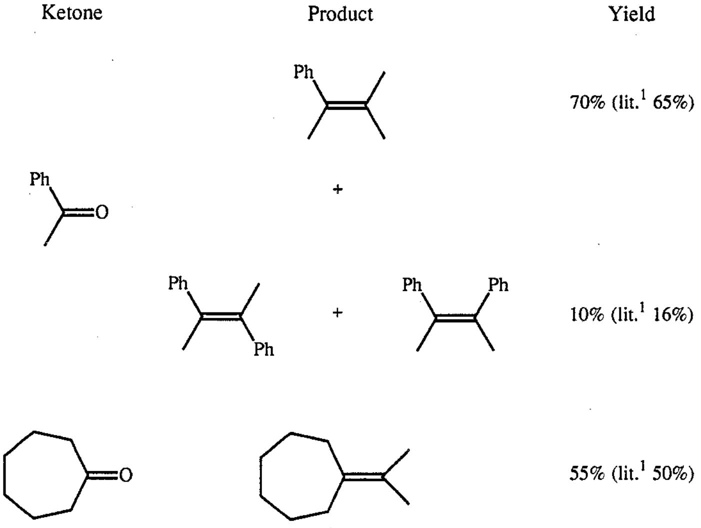

Fig. 2. Mixed carbonyl coupling between acetone and other ketones (acetone/ketone = 4 : 1).

Experimental

Melting points were determined on a Kofler hot-stage microscope and are uncorrected. ^1H n.m.r. spectra of $CDCl_3$ solutions were recorded with a Varian 390 90 MHz spectrometer. All reagents were of commercial quality from freshly opened containers. Magnesium turnings (Grignard grade) from E. Merck were used. Light petroleum had b.p. 60–70°.

General Procedure for Intermolecular Coupling

To a solution of mercuric chloride (0·55 g, 2·0 mmol) in tetrahydrofuran (20 ml) was added magnesium turnings (1·8 g, 8·0 mmol) and the resulting mixture was stirred at room temperature under nitrogen for 30 min. The turbid supernatant liquid was withdrawn by syringe and the remaining amalgam was washed with tetrahydrofuran (3×10 ml). The resulting amalgam was covered with tetrahydrofuran (50 ml), cooled to −10° in an ice/salt bath, and treated dropwise with titanium tetrachloride (4·4 ml, 7·6 g, 40 mmol) to give a yellow-green mixture. A solution of the carbonyl compound (10 mmol) in tetrahydrofuran (25 ml) was added. The solution gradually darkened and was stirred at 0° for 2 h. The solution was allowed to warm to room temperature and then brought to reflux. The black solution was refluxed for 24 h. The reaction mixture was then cooled to room temperature and quenched with saturated potassium carbonate (5 ml) and stirred vigorously for 30 min. The resulting black mixture was diluted with ether and filtered with the aid of Celite. The filtrate was concentrated and the resulting residue redissolved in ether and washed with brine, dried over anhydrous magnesium sulfate and concentrated. The alkenes were generally purified by column chromatography on silica gel (Merck 80–120 mesh) usually being eluted with light petroleum/ether mixtures. In each case the product was characterized by m.p. and/or n.m.r. and mass spectra.

9,9′-Bifluorene from Fluorenone

9,9′-Bifluorene (85% yield) was isolated by column chromatography (light petroleum/ether, 4:1), m.p. 240–242° (ethanol/benzene).

Tetraphenylethylene from Benzophenone

Tetraphenylethylene (87% yield) was isolated by column chromatography (light petroleum/ether, 9:1), m.p. 222–224° (ethanol/benzene).

*(*E*)-Stilbene from Benzaldehyde*

A 95% yield of (*E*)-stilbene was obtained after column chromatography (light petroleum/ether, 9:1), m.p. 124–125° (ethanol).

Cyclopentylidenecyclopentane from Cyclopentanone

Cyclopentylidenecyclopentane (80% yield) was isolated as an oil by column chromatography (light petroleum/ether, 9:1). ^{1}H n.m.r. δ 1·62, m, 8H; 2·10, m, 8H.

Cyclohexylidenecyclohexane from Cyclohexanone

Cyclohexylidenecyclohexane (70% yield) was isolated by column chromatography (light petroleum/ether, 9:1), m.p. 53–55° (methanol).

Hexadec-8-ene from Octanal

A 72% yield of hexadec-8-ene was obtained after column chromatography (light petroleum). The product was an oil. ^{1}H n.m.r. δ 0·88, m, 6H; 1·29, m, 20H; 1·95, m, 4H; 5·30, m, 2H.

3-(5α-Cholestan-3-ylidene)-5α-cholestane from 5α-Cholestan-3-one

An 82% yield of 3-(5α-cholestan-3-ylidene)-5α-cholestane was obtained by column chromatography (light petroleum/ether, 3:1), m.p. 317° (dec.) (ethanol).

General Procedure for the Mixed Carbonyl Coupling

The same general procedure as above was employed for mixed coupling except that the two carbonyl components (10 mmol in total) were added in the ratio 4:1 acetone/ketone.

Acetophenone with Acetone

The residue obtained after treatment of acetophenone and 4 equiv. of acetone with the titanium reagent was chromatographed (elution with light petroleum/ether, 95:5) to yield 2-methyl-3-phenylbut-2-ene as an oil (70%), ^{1}H n.m.r. δ 1·56, s, Me; 1·80, s, Me; 1·97, s, Me; 7·16, m, Ph; and a mixture of (*E*)- and (*Z*)-2,3-diphenylbut-2-ene as an oil (10%), δ_H (*E*) 2·14, s, 2×Me; 7·29, m, 2×Ph; δ_H (*Z*) 1·87, s, 2×Me; 7·23, m, 2×Ph.

Cycloheptanone with Acetone

Treatment of cycloheptanone and 4 equiv. of acetone yielded isopropylidenecycloheptane as an oil (55%) after column chromatography (light petroleum/ether, 9:1). ^{1}H n.m.r. δ 1·52, m, 8H; 1·65, m, 6H; 2·20, s, 2×Me.

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