

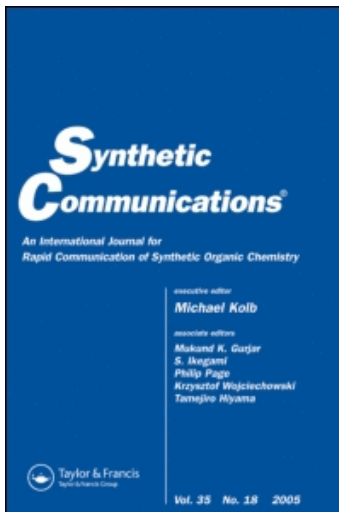
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A FACILE REDUCTIVE CLEAVAGE OF ALLYLIC AND BENZYLIC
ESTERS WITH LOW VALENT TITANIUM REAGENTS

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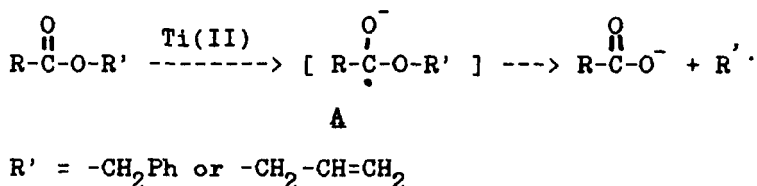
The reductive cleavage of allylic and benzylic esters 1a-g with titanium(II) reagent derived from Mg/Hg-TiCl₄ yielded the corresponding acids 3a-g and dimeric hydro⁴carbons 2a-g under mild reaction conditions.

Allylic and benzylic esters are often used as protective groups for carboxylic acids. There are a few methods available for the non-saponicative hydrolysis of these esters. Reported methods include the specific deblocking of cinnamyl esters by Corey and Tius using successive methoxymercuration and demercuriocarboxylation procedure,¹ and cleavage of allylic esters with lithium dimethylcuprate.² Cleavage of benzylic esters have been achieved with nitrosonium hexafluorophosphate,³ palladium on carbon,⁴ sodium in liquid ammonia⁵

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and chromium trioxide and chlorotrimethylsilane.⁶ Barton⁷ has reported the deoxygenation of sterically hindered esters with lithium/ethylamine.

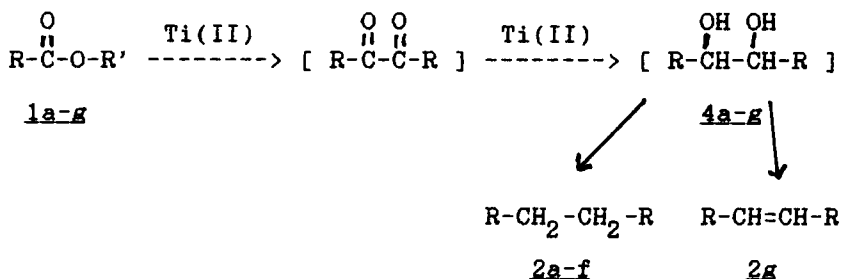
Earlier work from our laboratories has shown that the low valent titanium reagent generated by the reduction of titanium tetrachloride with amalgamated magnesium is very useful in the reductive coupling of carbonyl compounds⁸ and in the selective reduction of nitro compounds.⁹ We anticipated that the allylic and benzylic esters of carboxylic acids on treatment with low valent titanium reagents would form the radical anionic intermediate A which would readily undergo cleavage of the C-O bond with the formation of carboxylate anion and a stable allyl/benzyl radical (Scheme 1):



Hence it appeared reasonable to study this method for the deblocking of allylic and benzylic esters under mild reaction conditions.

Herein we report our results on the reductive cleavage of allylic and benzylic esters with Ti(II)

reagents generated by the reduction of $TiCl_4$ with amalgamated magnesium and they are summarised in the Table. Esters 1a-f (Table) on treatment with Ti(II) reagents at 0-20 °C for 2 h yielded the corresponding carboxylic acids 3a-f and the dimeric hydrocarbons 2a-f. In the case of 1a apart from the above products, 2-phenylacetophenone 5 (14%) was also formed. Formation of ketones like 5 from benzylbenzoates have been reported earlier in the reaction with lithium naphthalenide.¹⁰ It is possible that the dimeric hydrocarbons 2a-f are formed from diols 4a-g by hydrogenolysis under the reaction conditions whereas the diol 4g derived from alicyclic ester 1g undergoes deoxygenation to yield the olefin 2g.¹¹ (Scheme 2):



Another pathway for the formation of the dimeric hydrocarbons 2a-f could be by further reduction of carboxylic acids 3a-f with low valent titanium reagents. This is based on the observation that benzoic acid 3a on

TABLE : Reductive Cleavage of Allylic and Benzylic Esters with $\text{TiCl}_4/\text{Mg-Hg}$

Entry	Substrate	Dimeric hydrocarbon ^a (Yield %) ^b	Acid ^a (Yield %) ^b
1	$\text{Ph}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{CH}_2\text{Ph}$ <u>1a</u>	$\text{PhCH}_2-\text{CH}_2\text{Ph}$ <u>2a</u> (18%) + $\text{PhCH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{Ph}$ <u>5</u> (14%)	$\text{Ph}-\text{COOH}$ <u>3a</u> (64%)
2	$\text{Ph}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OCH}_2-\text{CH}=\text{CH}_2$ <u>1b</u>	<u>2a</u> (23%)	<u>3a</u> (57%)
3	$4\text{-}^t\text{Bu}-\text{C}_6\text{H}_4-\overset{\text{O}}{\parallel}{\text{C}}\text{OCH}_2-\text{CH}=\text{CH}_2$ <u>1c</u>	$4\text{-}^t\text{Bu}-\text{C}_6\text{H}_4-\text{COOH}$ <u>2c</u> (19%)	$4\text{-}^t\text{Bu}-\text{C}_6\text{H}_4\text{COOH}$ <u>3c</u> (48%)
4	$4\text{-Me}-\text{C}_6\text{H}_4-\overset{\text{O}}{\parallel}{\text{C}}\text{OCH}_2-\text{CH}=\text{CH}_2$ <u>1d</u>	$4\text{-Me}-\text{C}_6\text{H}_4-\text{CH}_2\text{-})_2$ <u>2d</u> (18%)	$4\text{-Me}-\text{C}_6\text{H}_4-\text{COOH}$ <u>3d</u> (67%)
5	$4\text{-Cl}-\text{C}_6\text{H}_4-\overset{\text{O}}{\parallel}{\text{C}}\text{OCH}_2-\text{CH}=\text{CH}_2$ <u>1e</u>	$4\text{-Cl}-\text{C}_6\text{H}_4-\text{CH}_2\text{-})_2$ <u>2e</u> (20%)	$4\text{-Cl}-\text{C}_6\text{H}_4-\text{COOH}$ <u>3e</u> (43%)

Table (contd.)

6	$3\text{-Cl-C}_6\text{H}_4\text{-}\overset{\text{O}}{\parallel}\text{COCH}_2\text{-}$ CH=CH_2 <p style="text-align: center;"><u>1f</u></p>	$3\text{-Cl-C}_6\text{H}_4\text{-CH}_2\text{-})_2$ <p style="text-align: center;"><u>2f</u> (17%)</p>	$3\text{-Cl-C}_6\text{H}_4\text{-COOH}$ <p style="text-align: center;"><u>3f</u> (42%)</p>
7	$\text{C}_6\text{H}_{11}\text{-COOCH}_2\text{-}$ CH=CH_2 <p style="text-align: center;"><u>1g</u></p>	$\text{C}_6\text{H}_{11}\text{CH=CHC}_6\text{H}_{11}$ <p style="text-align: center;"><u>cis</u></p> <p style="text-align: center;"><u>2g</u> (17%)</p>	$\text{C}_6\text{H}_{11}\text{-COOH}$ <p style="text-align: center;"><u>3g</u> (38%)</p>
8	$4\text{-Me-C}_6\text{H}_4\text{-COOMe}$ <p style="text-align: center;"><u>1h</u></p>	<p style="text-align: center;"><u>2d</u> (31%)</p>	-
9	Ph-COOH <p style="text-align: center;"><u>3a</u></p>	<p style="text-align: center;"><u>2a</u> (15%)</p>	<p style="text-align: center;"><u>3a</u> (70%)</p>

a) All the products gave satisfactory spectral data and were compared with authentic samples. b) Yield refers to pure isolated products.

treatment with $\text{TiCl}_4/\text{Mg-Hg}$ under the same reaction conditions yielded the dimeric hydrocarbon 2a (15%) along with recovered starting material (70%).

In order to show that only allylic and benzylic esters undergo this reductive cleavage with facility to yield the corresponding carboxylic acids, methyl toluate 1h was subjected to the same reaction conditions with $\text{TiCl}_4/\text{Mg-Hg}$. The only products that could be isolated in the reaction were the dimeric hydrocarbon

2d (30%) and benzil (12%) along with recovered starting material 1h (41%).

Experimental

Titanium tetrachloride was obtained from Riedel-de Haën, Germany and was used as such. M.ps. were determined with a Uni-melt capillary melting point apparatus and are uncorrected. Infrared spectra were recorded on Perkin-Elmer model 1320 and 580 spectrometers. Proton magnetic resonance spectra were recorded at 90 MHz on a Varian EM-390 instrument and at 80 MHz on a Bruker WP-80 instrument.

General method for the cleavage of allylic and benzylic esters. Reductive cleavage of benzylbenzoate:

To a solution of mercuric chloride (0.243 g, 0.9 mmol) in anhydrous tetrahydrofuran (10 ml), magnesium powder (0.72 g, 30 mg atom) was added and the resulting mixture was stirred at room temp. under nitrogen atmosphere, for 0.25 h. The turbid supernatant liquid was withdrawn and the amalgam was washed with three-5 ml portions of THF. 20 ml THF was added to the amalgam, cooled to 0 °C and titanium tetrachloride (2.267 g, 12 mmol, 1.31 ml) was added slowly, followed by the addition of benzylbenzoate 1a (1.272 g, 6 mmol) in 5 ml THF. The reaction mixture was stirred for 2 h by which time the temperature was allowed to raise to 20 °C. 10%

aq. K_2CO_3 solution (10 ml) was added and stirred for 10 min. Chloroform (25 ml) was added and the reaction mixture was filtered over a pad of Celite and sand. The filtrate was thoroughly washed with saturated aqueous bicarbonate solution and the organic layer was separated. The bicarbonate layer was neutralised with 10% HCl solution at 0 °C and was extracted with chloroform. The chloroform layer was washed with brine and dried over anhyd. sodium sulphate. Evaporation of the solvent afforded benzoic acid 3a (0.472 g, 64%). M.p. 120-122 °C (lit.¹² M.p. 120-122 °C).

The neutral portion on purification by flash chromatography on silica gel yielded dibenzyl 2a (0.2 g, 18%), m.p. 50-52 °C (lit.¹² m.p. 52 °C). IR (KBr): 3060, 2920, 1600 cm^{-1} . 1H NMR ($CDCl_3$): δ 2.83 (s, 4 H), 7.19 (s, 10 H) and 2-phenylacetophenone 5 (0.165 g, 14%), m.p. 58-59 °C (lit.¹³ m.p. 60 °C). IR (KBr): 3080, 3060, 1690, 1610 cm^{-1} . NMR ($CDCl_3$): δ 4.1 (s, 2 H), 7.2 (s, 5 H), 7.4 (m, 3 H), 7.9 (m, 2 H).

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