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METHALLYL ALCOHOL DIANION ADDITIONS AS THE SALIENT FEATURE IN A FACILE SYNTHESIS OF α-METHYLENE-γ-LACTONES

Robert M. Carlson
Department of Chemistry
University of Minnesota
Duluth, Minnesota 55812

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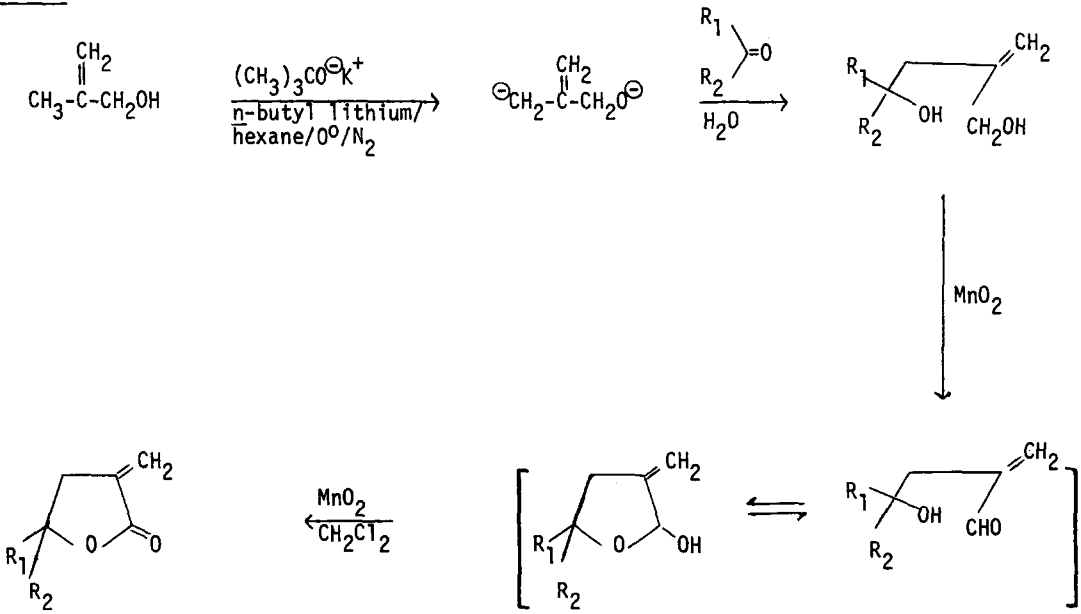
We wish to report the ability of the potassium t-butoxide/n-butyl lithium complex[1-3] to generate from methallyl alcohol a dianion in which an allylic proton has been selectively removed from the methyl carbon.[4] The synthetic applications of such dianions are manifold, but this preliminary report focuses on the addition reactions to aldehydes and ketones (Table 1). The diols produced from such additions are distinguished by the presence of an allylic alcohol that can be subsequently oxidized by activated manganese dioxide[5] to the α-methylene-γ-lactone *via* the presumed hemiacetal intermediate (Scheme I).

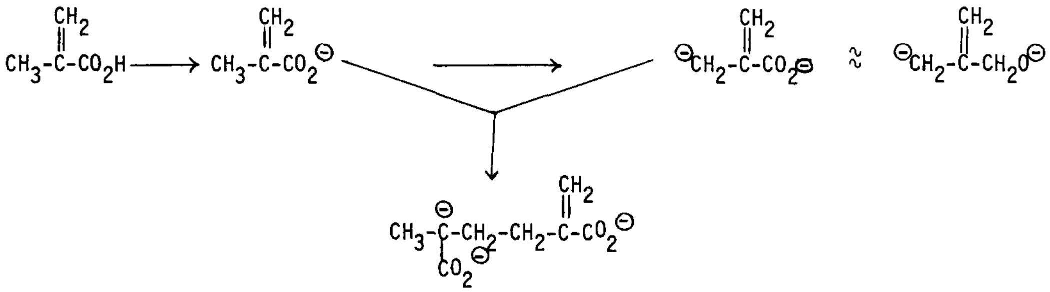
Scheme I



In this synthetic scheme, the methallyl alcohol dianion provides the structural equivalent of the methacrylic acid dianion (Scheme II). This parent acid dianion system has remained elusive during the course of our ongoing investigation into the use of substituted methacrylic acids as precursors to α-methylene lactones[6,7] due to diversive conjugate addition processes.[8]

The ready availability of reagents, the easy purification of the diol products, the high yield conversion of the diols to the lactone (Table 2), and the intrinsic interest of the α-methylene-γ-lactone system[9] mitigates the low (15%) to moderate (40%) yields observed in the addition step (Table 1).

Scheme II



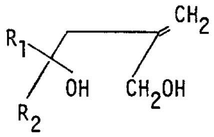
Typical Diol Synthesis Procedure:

To a suspension of commercial 95-99% potassium t-butoxide (2.37 g, 21 mmol, Ventron Corporation) in hexane (10 cc, 0°, N_2) was rapidly added via syringe a sample of methallyl alcohol (0.72 g, 0.84 cc, 10 mmol, Aldrich Chemical Company). n-Butyl lithium (21 mmol, in hexane, Aldrich Chemical Company) was likewise introduced into the remaining suspension over a 10-min period. After approximately one-half of the n-butyl lithium was added there was also noted the onset of the gold coloration characteristic of the suspension that was generated after the complete addition. The golden suspension was stirred for an additional 15 minutes at 0° whereupon the introduction of diethyl ketone (0.86 g, 1.05 cc, 10 mmol) in hexane (∿3 cc) produced a rapid loss of color. The isolation procedure consisted of the addition of water (10 cc), a two-fold extraction with ether (25 cc), the removal of water from the combined organic layers with sodium sulfate, and the evaporation of the hexane and ether in vacuo. The overall procedure resulted in the quantitative isolation of a crude product that contained 40-45% of the desired diol (nmr analysis). The pure diol was readily isolated in a 25% overall yield from the non-polar biproducts and starting materials by a chromatographic separation on silica gel (50x wt crude diol) using hexane to load the column and ether to elute the product.

General oxidation procedure

The diol could be converted to the lactone by the introduction of a pure sample into a methylene chloride suspension of active manganese dioxide (10X wt of diol)[10] and subsequently stirred at room temperature for 2 hrs.[11] Filtration and evaporation of the methylene chloride provides the desired lactone in high yield (Table 2).

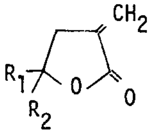
Table 1[12] Diols



R_1	R_2	Yield*	nmr (ppm, J in Hz)
$CH_3CH_2CH_2CH_2$-	$CH_3CH_2CH_2CH_2$-	35	0.95 (t, 6H, J = 3.5); 1.4 (m, 12H); 2.37 (s, 2H); 3.70 (s, 2H); 4.21 (s, 2H); 5.05 (m, 1H, J < 2); 5.30 (m, 1H, J < 2).
CH_3CH_2-	CH_3CH_2-	40	0.86 (t, 6H, J = 3.5); 1.52 (q, 4H, J = 3.5); 2.33 (s, 2H); 3.76 (s, 2H); 4.17 (s, 2H); 5.03 (m, 1H, J < 2); 5.27 (m, 1H, J < 2).
-$CH_2CH_2CH_2CH_2$-CH_2-		15	1.52 (m, 10H); 2.33 (s, 2H); 4.19 (s, 2H); 4.36 (s, 2H); 5.02 (m, 1H, J < 2); 5.25 (m, 1H, J < 2).
H	$CH_3(CH_2)_5$-	20	0.96 (t, 3H, J = 3.5); 1.3 (m, 10H); 2.3 (m, 2H); 3.8 (m, 1H); 4.19 (s, 2H); 4.47 (s, 2H); 5.06 (m, 1H, J < 2); 5.26 (m, 1H, J < 2).

* Yields derived from nmr spectra of isolated crude product.

Table 2[12] α-Methylene-γ-lactones



R_1	R_2	Yield	nmr (ppm, J in Hz)
$CH_3CH_2CH_2CH_2$-	$CH_3CH_2CH_2CH_2$-	91	0.93 (t, 6H, J = 2.0); 1.4 (m, 12H); 2.80 (t, 2H, J = 2.0); 5.77 (t, 1H, J = 2.0); 6.36 (t, 1H, J = 2.0).
CH_3CH_2-	CH_3CH_2-	86	0.92 (t, 6H, J = 3.5); 1.72 (q, 4H, J = 3.5); 2.80 (t, 2H, J = 1.5); 5.77 (t, 1H, J = 1.5); 6.34 (t, 1H, J = 1.5).
-$CH_2CH_2CH_2CH_2CH_2$-		85	1.68 (m, 10H); 2.83 (t, 2H, J = 1.5); 5.82 (t, 1H, J = 1.5); 6.38 (t, 1H, J = 1.5).
H	$CH_3(CH_2)_5$-	79[11]	0.93 (t, 3H, J = 2.0); 1.3 (m, 10H); 2.9 (m, 2H); 4.7 (m, 1H); 5.82 (t, 1H, J = 1.5); 6.40 (t, 1H, J = 1.5).

References and Notes

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11. The prolonged length of time (i.e., 18 hrs at room temperature) required for the oxidation of the aldehyde addition product is presumed to be due to a diminished tendency towards the formation of the requisite cyclic hemiacetal.
12. All new compounds gave satisfactory elemental or mass spectral analysis.