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Selective Hydroboration of Unconjugated Alkynyl Ketones and Aldehydes

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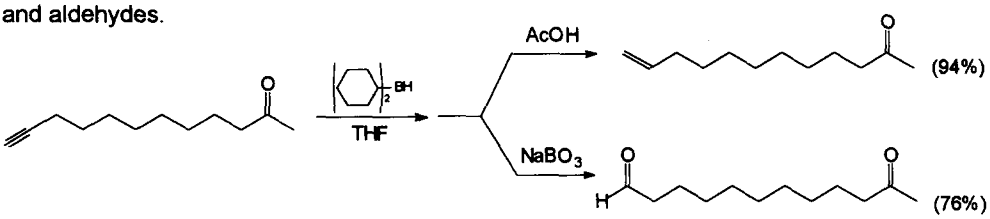
Abstract: Unconjugated alkynyl ketones and aldehydes are selectively hydroborated to give the corresponding olefinic carbonyl compounds after protonation, or dicarbonyl compounds after oxidation.

Hydroboration of alkenes and alkynes has been utilized extensively in organic synthesis.[1] The hydroboration of substrates containing carbonyl groups is often carried out by either converting the carbonyl group to a less reactive functionality[2] or modifying the hydroborating agent[3] to avoid reduction of the carbonyl group[4] even though kinetic studies involving disiamylborane suggested that these approaches might not be necessary.[5] Recently, we reported that terminal alkenes could be selectively hydroborated in the presence of ketones and aldehydes.[6] We now wish to report the selective hydroboration of unconjugated alkynyl ketones and aldehydes.



A variety of unconjugated alkynyl carbonyl compounds were hydroborated with dicyclohexylborane. The results are summarized in the Table. Both terminal and internal alkynyl carbonyl compounds could be selectively hydroboroated in the presence of the carbonyl group. The reaction affords the corresponding olefins in high yields (71-94%) after protonation, or the dicarbonyl compounds in good yields (50-76%) after oxidation with sodium perborate.[7]

The hydroboration of 11-dodecyn-2-one is representative: BH_3•THF (2.0 mmol, 2.0 mL of a 1.0*M* solution in THF) was placed in a dry, argon-flushed flask which was then immersed in an ice-water bath. Cyclohexene (4.0 mmol, 0.33g, 0.41 mL) was added dropwise and the mixture stirred at 0 °C for 1 hour. 11-Dodecyn-2-one (2.0 mmol, 0.36 g) was then added to the slurry of dicyclohexylborane in THF. The cooling bath was removed and the mixture stirred for 1 hour at room temperature. Protonation was achieved by adding glacial acetic acid (1 mL) and stirring

Table. Preparation of Olefinic Carbonyl Compounds and Dicarbonyl Compounds

Entry	Substrate	Work-up	Product[a]	Yield (%)[b]
1	$CH_3C\equiv C(CH_2)_8\ C(O)C_6H_5$	protonation	$(Z)\text{-}CH_3CH{=}(CH_2)_8C(O)C_6H_5$	92
2	$CH_3C\equiv C(CH_2)_8\ C(O)CH_3$	protonation	$(Z)\text{-}CH_3CH{=}(CH_2)_8C(O)CH_3$	88
3	$CH_3C\equiv C(CH_2)_8\ CHO$	protonation	$(Z)\text{-}CH_3CH{=}(CH_2)_8\ CHO$	71
4	$HC\equiv C(CH_2)_8\ C(O)CH_3$	protonation	$CH_2{=}CH(CH_2)_8C(O)CH_3$	94
5	$HC\equiv C(CH_2)_8\ C(O)CH_3$	oxidation	$HC(O)(CH_2)_9C(O)CH_3$	76
6	$HC\equiv C(CH_2)_8\ C(O)CH_2CH_3$	protonation	$CH_2{=}CH(CH_2)_8C(O)CH_2CH_3$	83
7	$HC\equiv C(CH_2)_8\ C(O)CH_2CH_3$	oxidation	$HC(O)(CH_2)_9\ C(O)CH_2CH_3$	68
8	$HC\equiv C(CH_2)_8\ CHO$	protonation	$CH_2{=}CH(CH_2)_8\ CHO$	90
9	$HC\equiv C(CH_2)_8\ CHO$	oxidation	$HC(O)(CH_2)_9\ CHO$	50
10	$HC\equiv C(CH_2)_3\ C(O)ph$	protonation	$CH_2{=}CH(CH_2)_3\ C(O)ph$	85
11	$HC\equiv C(CH_2)_3\ C(O)ph$	oxidation	$HC(O)(CH_2)_4\ C(O)ph$	66

[a] Products exhibited physical and spectral characteristics in accord with literature values or gave acceptable elemental analyses. [b] Isolated yield.

the mixture at room temperature for 1 hour. 11-Dodecen-2-one (0.34 g, 94% yield) was isolated after work up. Alternatively, oxidation could be achieved by adding of $NaBO_3\cdot 4H_2O$ (6.0 mmol, 0.92 g) and water (2 mL) and stirring the mixture at room temperature for 2 hours. 11-Keto-dodecanal (0.30 g, 76% yield) was isolated after workup.

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