

Table II. Conversion of Functionally Substituted Olefins into Aldehydes via Hydroboration with 9-BBN and Carbonylation in the Presence of Lithium Tri-*t*-butoxyaluminumhydride^a

Olefin	Product ^b	Yield, %		<i>n</i> _D ²⁰	Properties	
		Glpc	Isolated		Bp, °C (mm)	2,4-DNP mp, °C
Methyl 10-undecenoate	10-Carbomethoxyundecanal	99	85	1.4452	115–118 (1.5)	70–71.5
10-Undecenitrile	10-Cyanododecanal	99	83	1.4542	120–122 (1.2)	60–62
10-Undecen-1-yl acetate	12-Acetoxydodecanal	99	87	1.4460	110–112 (0.3)	75–77
Allyl benzoate	4-Benzoxybutanal	89	74	1.5243	116–118 (0.5)	76.5–77.5 ^c
Ethyl vinylacetate	4-Carbethoxybutanal	83	70	1.4259	68 (1.5)	69–70 ^d
Allyl cyanide	4-Cyanobutanal	85	72	1.4262	83.5 (2)	117–118 ^e
3-Buten-1-yl acetate	5-Acetoxypentanal	92	84	1.4284	66–67 (1.5)	99–100 ^f

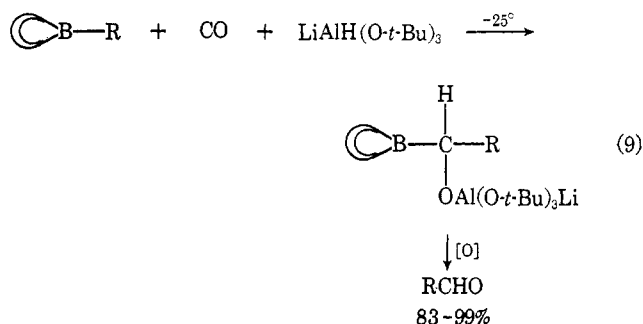
^a Procedure followed that described for methyl 10-undecenoate. ^b All spectroscopic data and elemental analyses were in agreement with the structure indicated. ^c Lit. mp 77.5°. ^d Lit. mp 70–70.5°. ^e Lit. mp 117–118°. ^f Lit. mp 100°.

with the reducible groups. Representative results are summarized in Table I.

The yields, while quite satisfactory for the longer chain derivative, dropped off seriously for the shorter chain derivatives. Evidently, in these derivatives reduction of the functional groups competes seriously with reduction of the carbonyl intermediate.

It appeared that this difficulty might be solved by use of a milder reducing agent. Lithium tri-*t*-butoxyaluminumhydride is such a mild reducing agent.⁹ Indeed, under standard conditions (0°, THF) it does not reduce esters or nitriles.⁹ Fortunately, it reduces nicely the postulated carbonyl intermediate from B-R-9BBN, even though it had previously failed to react with the intermediate from the usual trialkylborane.¹⁰ Evidently this is another indication of the much less hindered environment at the bridgehead position of B-R-9-BBN¹¹ and its carbonyl derivative.¹

In any event, the use of lithium tri-*t*-butoxyaluminumhydride solved the difficulties previously encountered and gave excellent yields for both short- and long-chain derivatives (eq 9). Representative results are summarized in Table II.



The following procedure describing the conversion of methyl 10-undecenoate into 11-carbomethoxyundecanal is representative. The dried reaction vessel of the automatic carbonylator⁸ was flushed with nitrogen and charged with 20 ml of THF and 9.9 g (50 mmoles) of methyl 10-undecenoate. Hydroboration was achieved by adding slowly (over 20 min) 100 ml of a 0.5 *M* solution of 9-BBN in THF. After 15 min,

reaction was initiated by flushing the system with carbon monoxide from the generator, cooling the flask to approximately –25 to –35°, and adding 50 ml of a 1.0 *M* solution of lithium tri-*t*-butoxyaluminumhydride over 45 min. Complete absorption of carbon monoxide required an additional 90 min. The reaction mixture was brought to room temperature, 120 ml of a buffer of pH 7 was added (a water solution 2.2 *M* in NaH₂PO₄ and K₂HPO₄), and oxidation was carried out by the dropwise addition of 21 ml of 30% hydrogen peroxide, keeping the temperature below 30°. The THF phase was twice washed with a saturated sodium chloride-water solution and then stirred for 1 hr with 100 ml of a saturated aqueous sodium bisulfite solution. The precipitated adduct was washed and then treated with 50 ml of a saturated aqueous magnesium sulfate solution, 50 ml of pentane, and 5 ml of a 40% solution of formaldehyde.¹³ After the bisulfite adduct had disappeared (30 min), the pentane layer was removed. Distillation yielded 9.7 g (85%) of 11-carbomethoxyundecanal, bp 115–118° (1 mm), *n*_D²⁰ 1.4452, 2,4-DNP mp 70–71.5°.

This study emphasized nitrile and ester derivatives as containing relatively easily reducible groups and thereby provided a severe test. There would appear to be no difficulty in extending the procedure to structures containing less readily reducible groups, such as halo, nitro, or sulfone.¹⁴ Consequently, this aldehyde synthesis appears to be both simple and of very wide generality and should find an important place in synthetic work.

(12) The carbonylation reaction had previously been carried out at 0°. However, we have since observed that at –25 to –35° the B-alkyl group of B-R-9-BBN migrates almost exclusively, to the practical exclusion of a cyclooctylboron migration, providing almost quantitative yields of the desired derivatives.

(13) This procedure for the regeneration of aldehyde from the bisulfite adduct proved to be the best of those examined. It is described by J. W. Cornforth, "Organic Syntheses," Coll. Vol. IV, John Wiley & Sons, Inc., New York, N. Y., 1963, p 757.

(14) We have successfully converted *m*-nitrostyrene into *m*-nitrohydrocinnamaldehyde.

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