N, 4.56. Found: C, 81.87; H, 8.23; N, 4.84.

5-Cyano-2-(3′,5′-di-*tert*-butyl-4′-hydroxyphenyl)pyridine: mp 149.5 °C; ^{1}H NMR δ 1.51 (s, 18 H), 5.57 (s, 1 phenolic H), 7.77 (dd, J = 8.4, 0.8 Hz, 1 H), 7.89 (s, 2 H), 7.91 (dd, J = 8.4, 2 Hz, 1 H), 8.87 (dd, J = 2, 0.8 Hz, 1 H); IR 3500, 2950, 2250, 1600, 1350 cm^{-1}. Anal. Calcd for $C_{20}H_{24}N_2O$: C, 77.88; H, 7.82; N, 9.06. Found: C, 78.33; H, 7.89; N, 9.01.

Acknowledgment. This work was partially supported by CNRS (UA 1110: "Activations Moléculaires" and UA 429). Partial support from MRES, and from SNPE (Ref 14/89) and EDF (Contrat 4L 7343) is also acknowledged.

Registry No. 2-Chloropyridine, 109-09-1; 3-chloropyridine, 626-60-8; 4-chloropyridine, 626-61-9; 2,5-dichloropyridine, 16110-09-1; 2-chloro-5-cyanopyridine, 33252-28-7; 2-chlorobenzonitrile, 873-32-5; 3-chlorobenzonitrile, 766-84-7; 4-chlorobenzonitrile, 623-03-0; 4-chloro(trifluoromethyl)benzene, 98-56-6; 2,4-difluorobromobenzene, 348-57-2; potassium 2,6-di-*tert*-butylphenoxide, 24676-69-5; 2,2′-bipyridine, 366-18-7; 4,4′-bipyridine, 553-26-4; phthalonitrile, 91-15-6; 4-cyanopyridine, 100-48-1; 2-cyanopyridine, 100-70-9; 2,4′-bipyridine, 581-47-5; 3,3′-bipyridine, 581-46-4; 2,3′-bipyridine, 581-50-0; pyridazine, 289-80-5; 3-(3′,5′-di-*tert*-butyl-4′-hyroxyphenyl)pyridine, 129708-80-1; 4-(3′,5′-di-*tert*-butyl-4′-hydroxyphenyl)pyridine, 129708-81-2; 2-cyano-3′,5′-di-*tert*-butyl-4′-hydroxy-1,1′-biphenyl, 118720-23-3; 3-cyano-3′,5′-di-*tert*-butyl-4′-hydroxy-1,1′-biphenyl, 129708-82-3; 4-cyano-3′,5′-di-*tert*-butyl-4′-hydroxy-1,1′-biphenyl, 114460-19-4; 5-cyano-2-(3′,5′-di-*tert*-butyl-4′-hydroxyphenyl)pyridine, 114460-18-3; 2,6-di-*tert*-butylphenol, 128-39-2.

Direct Synthesis of Carboxylic Acids from Organoboranes[1]

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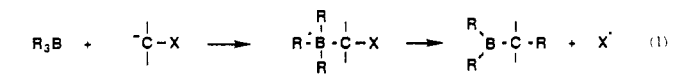
Direct synthesis of carboxylic acids through a two carbon atom homologation from organoboranes has been achieved, by the reaction with the dianion of phenoxyacetic acid. It is now possible to synthesize alkanoic, alkenoic, or alkynoic acids, from the corresponding alkenes, dienes, or enynes, respectively, via hydroboration. The reaction is tolerant of various functional groups present in alkenes, thus giving the corresponding carboxylic acids with chloro, sulfide, ether, acetal, and thioacetal functionalities in good yields.

Introduction

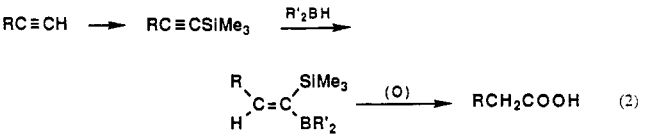
Since the discovery of the hydroboration reaction, the chemistry of organoboranes has been rapidly developed. Many fascinating features have been discovered and applied to the syntheses[2] of a wide variety of organic molecules. The use of organoboranes for carbon–carbon bond formation is well documented.[3] Most of these reactions involve the formation of tetracoordinate organoborates ("ate" complexes) between the electron-deficient boron and a nucleophilic carbon atom.[4] The complex formation is followed by the 1,2-intramolecular migration of an alkyl group from the boron atom to the adjacent carbon atom. These anionic rearrangements occur either with substitution of leaving group (eq 1) or by addition to a carbon–carbon or carbon–heteroatom multiple bond activated by an electrophile.



(1)

A wide variety of functional derivatives like aldehydes, ketones, esters, nitriles, etc.[5,6] have been synthesized, via this methodology. However, there was no successful report of the direct synthesis of carboxylic acids via carbon homologation from organoboranes. In our continued efforts to achieve this feat, we reported[1] the first direct synthesis of carboxylic acids by the reaction of organoboranes with the dianion of phenoxyacetic acid. We now describe, in full, the results of our systematic investigations.

Carboxylic acids are important biological molecules and synthetic materials. Zweifel and Backlund[7] have reported the conversion of alkynes to monosubstituted acetic acids via silylation, hydroboration, and oxidation (eq 2). With



(2)

this method, the alkyl groups of organoboranes are not used as the alkyl source. From the same laboratory, the high yield method illustrated in eq 3 has been published.[8a] Although this is a very useful reaction, it does not offer homologation capability.

Brown et al.[5] and Hooz and Morrison[6] have reported the synthesis of esters by a carbon–carbon homologation se-

(1) Preliminary accounts of this work have appeared: (a) Dhillon, R. S.; Hara, S.; Suzuki, A. Abstracts of the 46th Annual Meeting of the Chemical Society of Japan, Part II, 1982, p 674. (b) Hara, S.; Kishimura, K.; Suzuki, A. *Tetrahedron Lett.* **1978**, 2891.

(2) Brown, H. C. *Hydroboration*; Benjamin: New York, 1962. Second printing with Nobel Lecture, Benjamin/Cummings: Reading, MA, 1980.

(3) For example, Pelter, A.; Smith, K.; Brown, H. C. *Borane Reagents*; Academic Press: London, 1988.

(4) (a) Suzuki, A. *Top. Curr. Chem.* **1983**, *112*, 67. (b) Negishi, E. *J. Organomet. Chem.* **1976**, *108*, 281.

(5) (a) Brown, H. C.; Rogic, M. M.; Rathke, M. W.; Kabalka, G. W. *J. Am. Chem. Soc.* **1968**, *90*, 818. (b) Weill-Raynal, J. *Synthesis* **1976**, 633.

(6) Hooz, J.; Morrison, G. F. *Can. J. Chem.* **1970**, *48*, 868 and references cited therein.

(7) Zweifel, G.; Backlund, S. J. *J. Am. Chem. Soc.* **1977**, *99*, 3184.

(8) (a) Zweifel, G.; Arzoumanian, H. *J. Am. Chem. Soc.* **1967**, *89*, 291. (b) Brown, H. C.; Imai, T. *J. Org. Chem.* **1984**, *49*, 892. (c) Periasamy, M.; Narayana, C.; Anitha, N. *Indian J. Chem.* **1986**, *25B*, 844.

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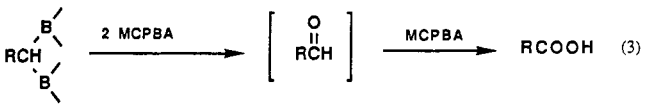
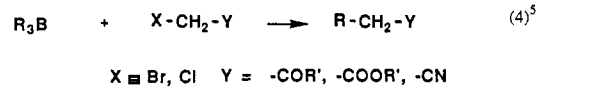
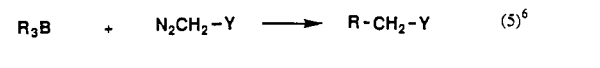


(3)

quence from olefins, via hydroboration (eqs 4 and 5).



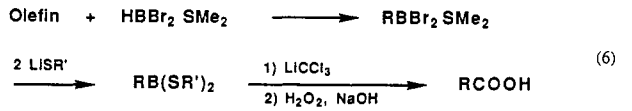
(4)[5]



(5)[6]

Though the hydrolysis of a resulting ester would lead to a carboxylic acid, this methodology does not represent a direct acid synthesis from organoboranes.

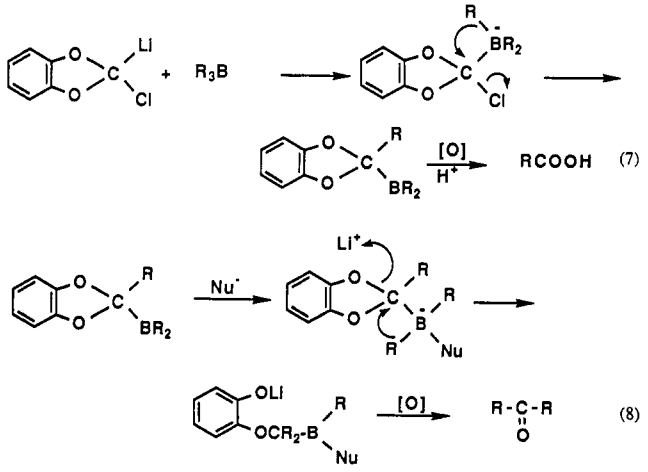
After the publication of our preliminary results, Brown and Imai[8b] reported the reaction of alkylthioboronic esters with trichloromethyllithium to afford in good yields one-carbon homologated carboxylic acids from alkenes via hydroboration (eq 6). The method is multistep however and requires the prior formation of alkylthioboronic esters.



(6)

Results and Discussion

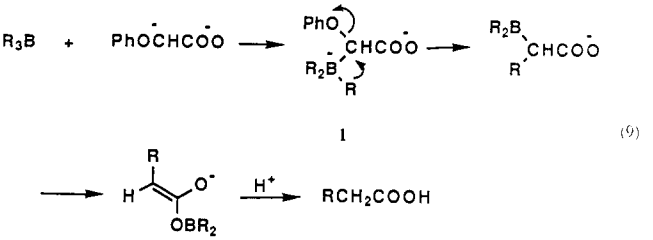
At the outset, in an effort to find a suitable dianion of a carboxylic acid with a proper leaving group, we initiated our work with chloro- and bromoacetic acids. These acids were allowed to react with trialkylboranes under different reaction conditions. The expected acids were only found in trace amounts. Addition of hexamethylphosphoric triamide (HMPA), in the lithiation stage before the addition of trialkylboranes, did not result in any improvement of the yields. The dianions of these halo carboxylic acids seem to be unstable under the conditions of their formation. In the course of our studies, we tried the reactions of trialkylboranes with catechol dichloromethylene ether,[9] in the presence of methyllithium with the hope of producing carboxylic acid (eq 7). However, the products obtained were not the expected carboxylic acids, but the corresponding ketones.[10] This result can be explained by the depicted reaction in eq 8.



(7) (8)

These results suggested that a phenoxy group on the carbon adjacent to the boron atom of organoborane is a good leaving group under such reaction conditions. Actually, we found that the dianion of phenoxyacetic acid, prepared by treatment with 2 equiv of lithium diisopropylamide in THF at 0 °C, upon reaction with the organoboranes at 66 °C for several hours resulted in the successful synthesis of the corresponding carboxylic acids. The dianion is fortunately soluble in THF at 0 °C and can be prepared without the addition of any polar solvents such as HMPA[11] and without heating the system.[12,13]

The reaction is exceedingly simple and provides acids in good yields, from olefins, by a two-carbon homologation. The reaction involves the formation of "ate" complex (1) followed by migration of the alkyl group from boron with simultaneous elimination of the phenoxy group (eq 9).



(9)

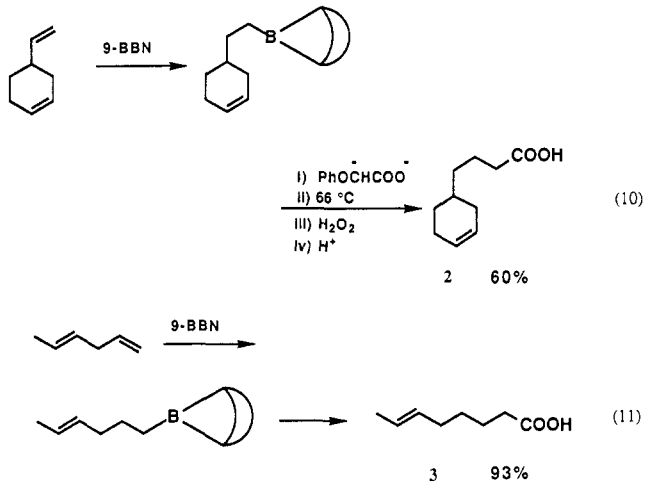
Table I shows that carboxylic acids can be obtained in excellent yields when diborane is employed as the hydroborating agent for simple alkenes. However, the yield drops gradually when the bulkiness of the migratory alkyl group on the boron is increased (Table I). Brown overcame this steric problem in the reaction of α-halo esters with hindered trialkylboranes by using 9-BBN derivatives.[14] We also used 9-BBN derivatives in the cases of introducing hindered alkyl groups, but only partially succeeded in improving the yield (Table I).

The use of diborane has the obvious disadvantage of leading to the loss of two valuable alkyl groups. In an attempt to avoid this, the use of dialkylborane derivatives such as dicyclohexylborane and disiamylborane was investigated. They caused steric problems and a serious decrease in the product yield. Dichloroborane ether complex also afforded poor results under different reaction conditions.

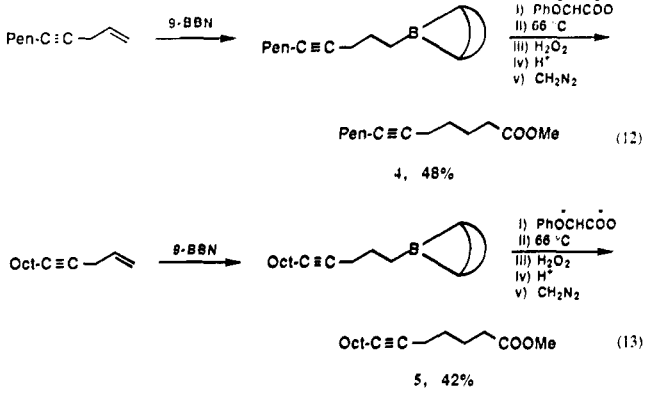
9-BBN exhibits high regioselectively for terminal bonds in the hydroboration of dienes.[15-17] Consequently, we intended to extend this methodology for the synthesis of unsaturated carboxylic acids. Accordingly, the conversion of 4-vinylcyclohexene and 1,4-hexadiene to the corresponding carboxylic acids (2 and 3) has been achieved in good yields (eqs 10 and 11).

Recently, 9-BBN has been demonstrated to discriminate in preference for a terminal bond in the presence of an internal triple bond.[18] In order to extend the present reaction for the synthesis of alkynoic acids, we hydroborated 1-decen-4-yne and 1-tridecen-4-yne. The corresponding alkynylboranes on treatment with the dianion of phenoxyacetic acid at 66 °C for 4 h resulted in the

(9) Gross, H.; Rusche, J.; Mirsch, M. *Chem. Ber.* **1963**, *96*, 1382.
(10) Kawaguchi, T.; Ishidoya, M.: Suzuki, A. *Heterocycles* **1982**, *18*, 113.
(11) Pfeffer, P. E.; Kinsel, E.; Silbert, L. S. *J. Org. Chem.* **1972**, *37*, 1256.
(12) Krapcho, A. P.; Jahnger, E. G. E., Jr. *J. Org. Chem.* **1974**, *39*, 1332 and 1650.
(13) For a review, see: Petragnani, N.; Yanashiro, M. *Synthesis* **1982**, 521.
(14) Brown, H. C.; Rogic, M. M. *J. Am. Chem. Soc.* **1969**, *91*, 2146.
(15) Miyaura, N.; Tagami, H.; Itoh, M.; Suzuki, A. *Chem. Lett.* **1974**, 1411.
(16) Levy, A. B.; Angelastro, R.; Marinelli, E. R. *Synthesis* **1980**, 945.
(17) Liotta, R.; Brown, H. C. *J. Org. Chem.* **1977**, *42*, 2836.
(18) Brown, C. A.; Coleman, R. A. *J. Org. Chem.* **1979**, *44*, 2328.

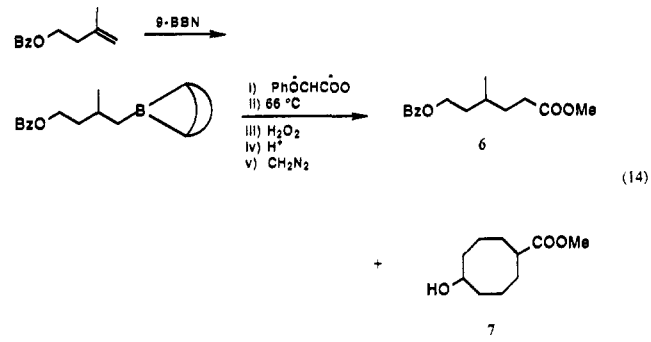


synthesis of the desired carboxylic acids (4 and 5) (eqs 12 and 13) in moderate yields.



The above results prompted us to apply this reaction to the synthesis of carboxylic acids with various functional groups. Brown and co-workers have examined the hydroboration of alkenes containing functional groups by using 9-BBN[19] and diborane.[20-22] However, diborane has been reported to reduce a number of functional groups.[23] On the other hand, 9-BBN has shown to be an unusual dialkylborane with valuable properties.[24,25] Consequently, we attempted to utilize 9-BBN as a hydroborating agent. To start with, we chose the benzyl ether of 3-methyl-3-buten-1-ol, which upon hydroboration with 9-BBN and subsequent treatment with the dianion of phenoxyacetic acid resulted in the synthesis of the corresponding carboxylic acid. The crude mixture was esterified with diazomethane for GLPC analysis, and the desired carboxylic acid ester (6) was isolated and characterized by IR, NMR, and mass spectrometry. However, the yield of the expected product was very low and the main product isolated and characterized was the hydroxy ester (7) derived from the cyclooctyl moiety of 9-BBN (eq 14).

We are unable to suggest a reason for the selective migration of the cyclooctyl group in this case as opposed to former cases. But all attempts to prevent the migration



of the cyclooctyl group under different reaction conditions proved fruitless. Considering that the methyl group adjacent to the migratory terminus might be posing a hindrance to the sole migration of the desired B–C bond, we changed to the benzyl ether of 3-buten-1-ol with the hope of getting only the desired carboxylic acid. Again we failed to prevent the migration of the cyclooctyl moiety of 9-BBN.[26] Attempts to carry out the rection at reduced temperatures, varying from 0 to 25 °C for 2–12 h, afforded the desired carboxylic acid, but in very poor yield. These results forced us to settle on the conventional hydroboration agent "diborane".

The trialkylboranes obtained after hydroboration with diborane in THF, followed by their reaction with 2 equiv of the dianion of phenoxyacetic acid at 66 °C (reaction time indicated in the tables), resulted in the formation of the corresponding carboxylic acids in good yields. The acids were esterified with diazomethane for characterization and GLPC analysis. These results are summarized in Table II. It is noteworthy that the chloro group (entry 6, Table II) can withstand the reaction conditions, thus leading to the desired carboxylic acid in a good yield. The acetal group (entry 4, Table II) is cleaved to the parent ketone during acidification of the aqueous layer.

Conclusion

This new methodology provides a convenient procedure for the two carbon atom homologation of an olefin to a carboxylic acid. The simple means by which carboxylic acid functional groups can be converted to other functionalities like aldehydes or alcohols further enhance the synthetic application of this reaction. The present reaction has distinguished advantages. For example, it is possible to synthesize directly a variety of saturated and unsaturated carboxylic acids starting from alkenes, dienes, or enynes. This reaction can tolerate the presence of a variety of functional groups in the alkene and is exceedingly simple to perform.

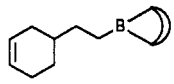
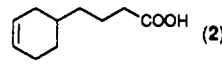
Experimental Section

General. Infrared spectra were recorded on a Hitachi 260-10 IR spectrophotometer. ^{1}H NMR spectra were recorded on a R-22 Hitach high-resolution NMR spectrometer and reported in δ units using tetramethylsilane as an internal standard. Elemental analyses and high-resolution mass spectra were recorded by the Analytical Center of Hokkaido University.

Analytical gas–liquid chromatography was carried on a Hitachi 164 gas chromatograph equipped with flame ionization detector. Columns refer to 2 m × 4 mm stainless steel column packed with 15% carbowax 20M on 60–80-mesh Chromosorb W-AW and using 2 m × 4 mm stainless steel column packed with 15% silicon SE 30 on Chromosorb W-AW. Carboxylic acids were analyzed using a 1 m × 4 mm stainless steel column with EGS–3% H_3PO_4 supported on 60–80-mesh Uniport-B. Preparative gas–liquid

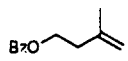
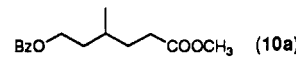
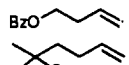
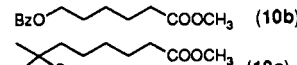
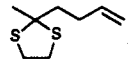
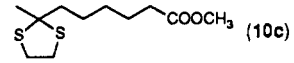
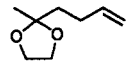
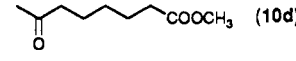
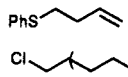
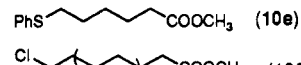
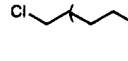
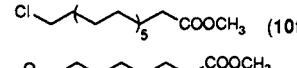
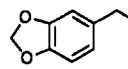
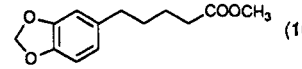
(19) Brown, H. C.; Chem, J. C. *J. Org. Chem.* **1981**, *46*, 3978 and references cited therein.
(20) Brown, H. C.; Unni, M. K. *J. Am. Chem. Soc.* **1968**, *90*, 2902.
(21) Brown, H. C.; Gallivan, R. M. *J. Am. Chem. Soc.* **1968**, *90*, 2906.
(22) Brown, H. C.; Sharp, R. L. *J. Am. Chem. Soc.* **1968**, *90*, 2915.
(23) (a) Lane, C. F. *Chem. Rev.* **1976**, *76*, 773. (b) Lane, C. F. *Aldrichimica Acta* **1977**, *10*, 41.
(24) Lane, C. F.; Brown, H. C. *Heterocycles* **1977**, *7*, 453.
(25) Brown, H. C.; Knights, E. F.; Scouten, C. G. *J. Am. Chem. Soc.* **1974**, *96*, 7765.
(26) For relative migratory aptitude of alkyl groups, see: Slayden, S. W. *J. Org. Chem.* **1981**, *46*, 2311.

Table I. Synthesis of Carboxylic Acids via Reaction of Organoboranes with the Dianion of Phenoxyacetic Acid[a]

entry	organoborane R_3B or B-R-9-BBN	product[b]	reaction time at 66 °C, h	yield,[c] %
1	tripropylborane	pentanoic acid (**8a**)	2	81
2	tributylborane	hexanoic acid (**8b**)	2	100
3	triisobutylborane	4-methylpentanoic acid (**8c**)	4	67
4	tri-*sec*-butylborane	3-methylpentanoic acid (**8d**)	6	17
5	*B*-*sec*-butyl-9-BBN	3-methylpentanoic acid (**8d**)	6	39
6	trihexylborane	octanoic acid (**8e**)	2	77
7	tricyclopentylborane	cyclopentylacetic acid (**8f**)	6	97
8	*B*-cyclohexyl-9-BBN	cyclohexylacetic acid (**8g**)	6	36
9	tris(2-phenylpropyl)borane	4-phenylpentanoic acid (**8h**)	6	65
10	*B*-(4-hexenyl)-9-BBN	6-octenoic acid (**3**)	6	93
11	trioctylborane	*decanoic acid* (**8i**)	4	90
12		 (**2**)	6	60

[a] A 50% excess of the dianion was used. [b] Satisfactory IR and ^{1}NMR spectra were obtained for all compounds. [c] Yield by GLPC analysis based on the organoborane used.

Table II. Synthesis of Functionalized Carboxylic Acids via the Reaction of Organoboranes[a] with the Dianion of Phenoxyacetic Acid[b]

entry	alkenes	product[c]	reaction time at 66 °C, h	yield,[d] %
1	 (**9a**)	 (**10a**)	18	75
2	 (**9b**)	 (**10b**)	12	86
3	 (**9c**)	 (**10c**)	12	53
4	 (**9d**)	 (**10d**)	12	83
5	 (**9e**)	 (**10e**)	12	69
6	 (**9f**)	 (**10f**)	12	73
7	 (**9g**)	 (**10g**)	12	90

[a] Synthesized by hydroboration with diborane. [b] Two equivalents of the dianion was used. [c] Satisfactory data were obtained for all the compounds. [d] Yields by GPLC analysis based on organoboranes used.

chromatography was performed on Varian Aerograph Autoprep 700 gas chromatograph using 2 m × 6 mm copper column packed with 10% SE 30 on 40–60-mesh Chromosorb W.

Reagents and Solvents. Tetrahydrofuran was distilled from benzophenone ketyl. Alkenes used as starting material and alkanes used as internal standard were purchased from Tokyo Kasei Kogyo Co., Ltd., Japan. Phenoxyacetic acid was purchased from Wako Chemical Industries, Ltd., Japan.

A stock solution of diborane in THF, prepared according to the reported procedure,[3c] was used and the concentration was determined prior to use.[3c] The 9-BBN was prepared according to the literature method[3c] and was used as a THF solution. A stock solution of BuLi in hexane purchased from Aldrich Chemical Co. was used and was titrated by the procedure of Watson and Eastham.[27]

Starting Materials. The alkenes having functionalities such as benzyl ether (**9a,b**),[28] thioacetal (**9c**),[29] acetal (**9d**),[30] phenyl sulfide (9e),[31] and chloride (**9f**)[32] were prepared according to the published procedures. Copper acetylides[33] prepared from alkynes were converted to the corresponding enynes by treatment with allyl bromide.[34] All other materials were obtained commercially and were of analytical reagent quality.

General Procedure for the Preparation of Organoboranes. With Diborane. A flame-dried 25-mL flask with an injection port was equipped with a magnetic stirring bar and a gas inlet tube attached to a low-pressure nitrogen supply. The cooled flask was flushed with nitrogen. The injection port was capped with a rubber serum stopple and the flask was immersed in an ice–water bath. The flask was charged via syringe with 4 mL of anhydrous THF and 2.49 mmol of an alkene. To the flask was added BH_3–THF solution (10% less, 0.747 mmol, 0.70 mL of 1.06 M) slowly via a syringe. The ice bath was removed, and the solution was stirred for 3 h at room temperature (25 °C).

With 9-BBN. A flame-dried 25-mL, N_2-flushed (as previously described), round-bottomed flask equipped with a magnetic stirring bar and septum inlet was charged with 4 mL of dry THF at 0 °C followed by the addition of an appropriate enyne (2.23 mmol). To this cooled solution at 0 °C was added a solution of 9-BBN in THF (2.23 mmol, 3.81 mL of 0.585 M) slowly via a syringe. The solution was then stirred at room temperature for 3 h. This procedure is typical for the hydroboration of dienes, with 9-BBN, as well. All reactions involving organoboranes were carried out under the atmosphere of nitrogen until oxidation.

Preparation of the Dianion of Phenoxyacetic Acid. A 50-mL flask equipped with a magnetic stirring bar, septum inlet, and reflux condenser was flame-dried and cooled under the atmosphere of nitrogen as reported above. The flask was lowered in an ice bath and was charged under N_2 with 0.42 mL (4 equiv, corresponding to organoborane, 3 mmol) of diisopropylamine and 5 mL of dry THF. Butyllithium (3 mmol, 1.36 mL of a 2.20 M

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solution in hexane) was added to form lithium diisopropylamide. After the mixture was stirred for 15 min at 0 °C, 228 mg (1.5 mmol) of phenoxyacetic acid in 2 mL of dry THF was added slowly via a syringe. The reaction mixture was stirred for 2 h at 0 °C to complete the formation of the dianion of phenoxyacetic acid.

Reaction of Trialkylboranes with the Dianion of Phenoxyacetic Acid. The procedure described below is typical for each class of the organoboranes.

Trialkylborane was added to a solution of the dianion of phenoxyacetic acid via a double ended needle technique at 0 °C. The ice bath was replaced by an oil bath, and the reaction mixture was stirred at 66 °C for a period specified in the tables. After the specific period, the mixture was cooled to 0 °C and 2 mL of 3 M NaOH solution was added slowly, followed by the dropwise addition of 2 mL of 30% H_2O_2 at 0 °C. The reaction mixture was stirred for 2 h at 0 °C, and 10 mL of ether was added. To the separated aqueous layer was added 10 mL of ether, and the solution was acidified by the slow addition of 3 M HCl at room temperature, saturated with sodium chloride, and extracted with ether (3 × 10 mL). After evaporation of most of the solvent in vacuo, the crude mixture was treated with ethereal solution of diazomethane (prepared from *p*-tolysulfonylmethylnitrosamide). The yellow solution was stirred overnight, dried over anhydrous sodium sulfate, and concentrated in vacuo. The crude product was purified by column chromatography (silica gel, hexane/ether gradient) to afford the desired methyl ester of carboxylic acids, which were characterized by IR, ^{1}H NMR, combustion analysis, and/or high-resolution mass spectra. The corresponding yields of esters were determined by GLPC analysis using alkanes as internal standards.

In the case of carboxylic acids prepared from unfunctionalized alkenes or dienes, the corresponding products were identified and characterized without esterification. The GLPC yields were determined with suitable carboxylic acids as internal standards. Pentanoic acid (**8a**), hexanoic acid (**8b**), 4-methylpentanoic acid (**8c**), octanoic acid (**8e**), cyclohexylacetic acid (**8g**), and decanoic acid (**8i**) were identified and characterized, after isolation, by the comparison of the ^{1}H NMR and IR spectra and retention time of GLPC with the commercially available authentic samples. 3-Methylpentanoic acid (**8d**), cyclopentylacetic acid (**8f**), 4-phenylpentanoic acid (**8h**), 6-octenoic acid (**3**) and 4-(3-cyclohexenyl)butanoic acid (**2**) were synthesized by the saponification of the corresponding esters obtained by the Brown's method[5a,35] for spectral and GLPC comparison.

Spectral Data. 4-Phenylacetic acid (8h): n^{25}_D 1.5140 [lit.[36] n^{25}_D 1.5129]; IR (neat) 3600, 1700, 760, 690 cm^{-1}; ^{1}H NMR (CCl_4) δ 10.64 (s, 1 H), 7.13 (s, 5 H), 2.49–2.82 (m, 2 H), 1.81–2.22 (m, 2 H), 1.26 (d, J = 6.5 Hz, 3 H).

6-Octenoic acid (3): n^{25}_D 1.4511 [lit.[37] n^{25}_D 1.4555]; IR (Neat), 3600, 1715, 1415, 1280, 980 cm^{-1}; ^{1}H NMR (CCl_4) δ 11.13 (s, 1 H), 5.36 (m, 2 H), 2.30 (t, J = 7 Hz, 2 H), 1.84–2.11 (m, 2 H), 1.22–1.84 (m, 7 H).

4-(3-Cyclohexenyl)butanoic acid (2): n^{25}_D 1.4762 [lit.[38] n^{25}_D 1.4785]; IR (neat) 3600, 1710, 1440, 1290, 920 cm^{-1}; ^{1}H NMR (CCl_4) δ 10.51 (s, 1 H), 5.53 (m, 2 H), 2.29 (t, J = 8 Hz, 2 H), 1.88–2.11 (m, 4 H), 1.21–1.88 (m, 7 H).

Methyl 6-(benzyloxy)-4-methylhexanoate (10a): n^{20}_D 1.4928; IR (neat) 1745, 1610, 1458, 1205, 1170, 1110, 738, 700 cm^{-1}; ^{1}H NMR (CCl_4) δ 7.18 (m, 5 H), 4.38 (s, 2 H), 3.57 (s, 3 H), 3.42 (t, J = 6 Hz, 2 H), 2.44 (t, J = 6 Hz, 2 H), 1.55 (m, 4 H), 0.92 (d, J = 6 Hz, 3 H). Anal. Calcd for $C_{15}H_{22}O_3$: C, 71.97, H, 8.86. Found: C, 71.93; H, 8.93.

Methyl 6-(benzyloxy)hexanoate (10b): n^{20}_D 1.4923; IR (neat) 1745, 1605, 1458, 1205, 1170, 1105, 735, 695 cm^{-1}; ^{1}H NMR (CCl_4) δ 7.32 (m, 5 H), 4.49 (s, 2 H), 3.65 (s, 3 H), 3.47 (t, J = 6 Hz, 2 H), 2.31 (t, J = 7 Hz, 2 H), 1.63 (m, 4 H), 1.42 (m, 2 H). Anal. Calcd for $C_{14}H_{20}O_3$: C, 71.15; H, 8.53. Found: C, 71.07; H, 8.55.

Methyl 7,7-(ethylenedithio)octanoate (10c): n^{20}_D 1.5164; IR (neat) 1745, 1438, 1278, 1195, 1155, 735, 685 cm^{-1}; ^{1}H NMR δ (CCl_4) 3.58 (s, 3 H), 3.24 (s, 4 H), 2.20 (t, J = 7 Hz, 2 H), 1.69 (s, 3 H), 1.10–1.98 (m, 8 H). Anal. Calcd for $C_{11}H_{20}S_2O_2$: C, 53.18; H, 8.11; S, 25.81. Found: C, 53.28; H, 7.94; S, 25.80.

Methyl 7-oxooctanoate (10d): n^{20}_D 1.4395; IR (neat) 1740, 1718, 1428, 1360, 1205, 1175, 1085 cm^{-1}; ^{1}H NMR (CCl_4) δ 3.66 (s, 3 H), 2.43 (t, J = 8 Hz, 2 H), 2.31 (t, J = 8 Hz, 2 H), 2.13 (s, 3 H), 1.61 (m, 4 H), 1.33 (m, 2 H). Anal. Calcd for $C_9H_{16}O_3$: C, 62.76; H, 9.36. Found: C, 62.65; H, 9.37.

Methyl 6-(phenylthio)hexanoate (10e): n^{20}_D 1.5335; IR (neat) 1742, 1595, 1440, 1205, 1175, 742, 695 cm^{-1}; ^{1}H NMR (CCl_4) δ 7.20 (m, 5 H), 3.60 (s, 3 H), 2.84 (t, J = 7 Hz, 2 H), 2.20 (t, J = 6 Hz, 2 H), 1.16–1.92 (m, 6 H). Anal. Calcd for $C_{13}H_{18}SO_2$: C, 65.51; H, 7.61; S, 13.45. Found: C, 65.37; H, 7.61; S, 13.22.

Methyl 13-chlorotridecanoate (10f): n^{20}_D 1.4517; IR (neat) 1750, 1440, 1200, 1175, 720, 650 cm^{-1}; ^{1}H NMR (CCl_4) δ 3.56 (s, 3 H), 3.41 (t, J = 7 Hz, 2 H), 2.15 (t, J = 7 Hz, 2 H), 0.88–1.88 (m, 20 H). Anal. Calcd for $C_{14}H_{27}ClO_2$: C, 63.98; H, 10.35; Cl 13.48. Found: C, 63.93; H, 10.16; Cl, 13.69.

Methyl 5-(3,4-(methylenedioxy)phenyl)pentanoate (10g): n^{20}_D 1.5150; IR (neat) 1745, 1615, 1445, 1247, 1105, 1045, 778, 735 cm^{-1}; ^{1}H NMR (CCl_4) δ 6.55 (m, 3 H), 5.88 (s, 2 H), 3.60 (s, 3 H), 2.48 (m, 2 H), 2.19 (m, 2 H), 1.45–1.73 (m, 4 H). Anal. Calcd for $C_{13}H_{16}O_4$: C, 66.08; H, 6.82. Found: C, 65.83; H, 6.75.

Methyl 6-dodecynoate (4): n^{20}_D 1.4510; IR (neat) 1747, 1435, 1210, 1170 cm^{-1}; ^{1}H NMR (CCl_4) δ 3.60 (s, 3 H), 1.89–2.38 (m, 6 H), 0.70–1.89 (m, 10 H). Anal. Calcd for $C_{13}H_{22}O_2$: C, 74.24; H, 10.54. Found: C, 74.01; H, 10.43.

Methyl 6-pentadecynoate (5): n^{20}_D 1.4602; IR (neat) 1745, 1435, 1205, 1175 cm^{-1}; ^{1}H NMR (CCl_4) δ 3.62 (s, 3 H), 1.90–2.40 (m, 6 H), 0.70–1.90 (m, 16 H); high-resolution MS m/z calcd for $C_{16}H_{28}O_2$ 252.2090, found 252.2101.

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