Table II. Influence of the Catalyst on the Transformation 1f → 3f

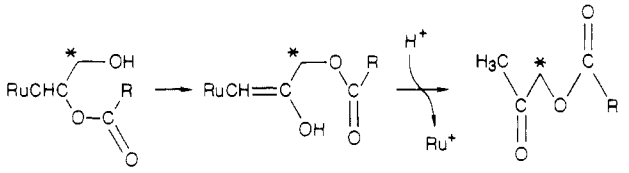
Ru catalyst	3f (% yield)
$RuCl_3 \cdot 3H_2O$	7
$RuCl_3 \cdot 3H_2O/2PBu_3$	43
$Ru_3(CO)_{12}$	33
$RuCl_2(PMe_3)(p\text{-cymene})$	62
$RuCl_2(PPh_3)(p\text{-cymene})$	64
$RuCl_2(P(OPh)_3)(p\text{-cymene})$	6
$RuCl_2(PMe_3)(C_6Me_6)$	61

similar way (Table I). They were isolated and purified by crystallization (**3f**, **8**, **9**) by reduced pressure distillation (**3a**, **3b**, **3c**), or by silica gel chromatography with ether (**3d**, **3e**, **10**).

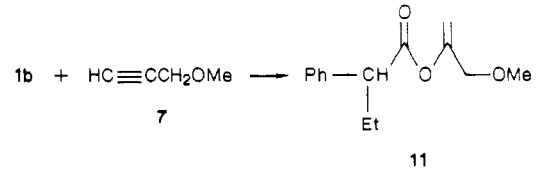
The addition of saturated (**1b**) and unsaturated (**1a**,**c**) carboxylic acids to propargyl alcohol (**2**) takes place under mild conditions (60 °C, 6 h) but mainly in the presence of ruthenium(II) catalysts. Amino acids do not add to **2** under similar conditions. However, N-protected amino acids give the corresponding esters (**3d-f**, **8**) in rather good yields (Table I). The ester formation takes place without deprotection of the amino group and the chiral esters **3d**, **3e**, and **10** retain optical activity.[7] Diacids such as **4** and **5** always yield a mixture of esters. However, when an excess of **2** was used, diesters **9** and **10** were isolated (Table I). The efficiency of the addition appears to be related to the steric hindrance of the acid (e.g. **3a** and **3b**; **3d** and **3e**).

The formation of esters **3** is catalyzed by a variety of ruthenium complexes. Thus, the ester **3f** was obtained from **1f**, under the above conditions, in yields which critically depended upon the nature of the Ru catalyst (Table II). The more efficient catalysts are the $RuCl_2(PR_3)$(arene) complexes containing basic phosphines (PPh_3, PMe_3).[8]

The formation of esters **3** may be similar to the addition of ammonium carbamates to propargyl alcohol:[9] initial addition of the carboxylate to the coordinated alkyne bond of **2** followed by intramolecular transesterification.



Indeed, when **1b** was treated with methyl propargyl ether (**7**), the addition occurred only under more drastic conditions (120 °C, 15 h, 44%) and gave the enol ester **11** corresponding to the expected addition product.[5]



The intramolecular transesterification is also supported by the reaction of **1f** with the dimethyl disubstituted propargyl alcohol $HC{\equiv}CC(CH_3)_2OH$ (**6**) which gave the ester **8** (Table I).

(7) $(\alpha)^{20}_D$ (*c* 2, EtOH): -67° (**3d**); -70° (**3e**); +14° (**10**). The optical purity has not been determined.

(8) One example of similar addition involving acetic acid and propargyl alcohol has just been reported, but using as a catalyst the three component system $Ru(\eta^5\text{-}C_8H_{11})_2/2PBu_3$/(maleic anhydride)$_2$. Mitsudo, T. A.; Hori, Y.; Yamakawa, Y.; Watanabe, Y. *J. Org. Chem.* **1987**, *52*, 2330.

(9) Bruneau, C.; Dixneuf, P. H. *Tetrahedron. Lett.* **1987**, *28*, 2005.

The facile one-step formation of β-oxopropyl esters **3**, particularly from chiral acids and N-protected amino acids, allows the use of these compounds as synthesis intermediates.

Acknowledgment. We are grateful to Dr. S. Lecolier for helpful discussions and to CNRS and SNPE for support of this work.

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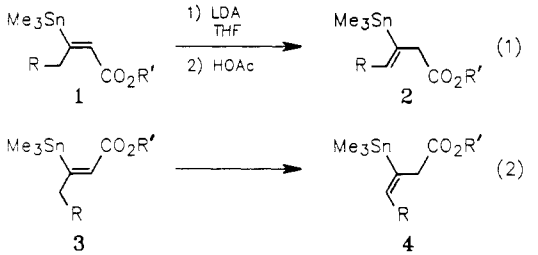
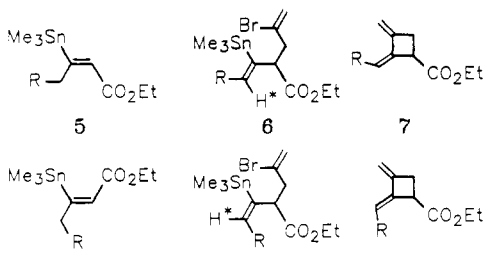
Deconjugation-Alkylation of Ethyl 3-(Trimethylstannyl)-2-alkenoates. Stereocontrolled Synthesis of Ethyl 2-Alkylidene-3-methylenecyclobutanecarboxylates

Summary: Alkylation of ethyl (*E*)- and (*Z*)-3-(trimethylstannyl)-2-alkenoates with 2,3-dibromopropene, followed by $(Ph_3P)_4Pd$-catalyzed cyclization of the resultant products, provides ethyl (*Z*)- and (*E*)-2-alkylidene-3-methylenecyclobutanecarboxylates, respectively, in good yields (60-79%).

Sir: Recently, we reported[1] that alkyl 3-(trimethylstannyl)-2-alkenoates **1** and **3** can be deconjugated stereospecifically to provide excellent yields of the corresponding alkyl 3-(trimethylstannyl)-3-alkenoates **2** and **4**, respectively (eq 1 and 2). We have subsequently found,



not surprisingly, that alkylative deconjugation of ethyl (*E*)- and (*Z*)-3-(trimethylstannyl)-2-alkenoates **5** and **8**, respectively, can also be accomplished readily. More importantly, we report herein that the products **6** and **9**, respectively, derived from alkylation of **5** and **8** with 2,3-dibromopropene cyclize smoothly in the presence of a palladium(0) catalyst to afford, stereospecifically, ethyl (*Z*)- and (*E*)-2-alkylidene-3-methylenecyclobutanecarboxylates **7** and **10**, respectively. It may be noted that 1,2-di-



a R=Me b R=$(CH_2)_2OCH_2OMe$
c R=$(CH_2)_3OSiMe_2Bu^t$ d R=OCH_2OMe e R=H

(1) Piers, E.; Gavai, A. V. *J. Chem. Soc., Chem. Commun.* **1985**, 1241.

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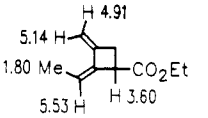
methylenecyclobutane and some of its "simple" alkyl-substituted derivatives have been known for some time and have been studied quite extensively, particularly from a physical organic viewpoint.[2] However, the methods that have been employed to prepare these materials are generally cumbersome, inefficient, and stereochemically ambiguous. Furthermore, the synthetic utility of 1,2-dialkylidenecyclobutane systems has not been investigated. The methodology outlined here provides substances of general structures **7** and **10** efficiently and in a completely stereocontrolled fashion.

Alkylation (lithium diisopropylamide, tetrahydrofuran–hexamethylphosphoramide, −78 → 0 °C; 2,3-dibromopropene, −78 °C, 1 h) of the ester **5a**[3] provided (72%) the β,γ-unsaturated ester **6a**[5] as a single product. In similar fashion, **5b–d**[3] were converted smoothly and exclusively into **6b–d** (78%, 95%, 91%), while **5e**[3] was transformed into **6e** (69%). On the other hand, alkylation of the (*Z*)-3-(trimethylstannyl)-2-alkenoates **8**[3] afforded only the *E* alkylation products **9**, in yields varying from 74% to 89%. In all cases, the conversions **5a–d** → **6a–d** and **8** → **9** were completely stereoselective.

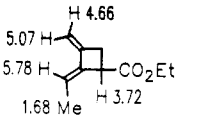
Since it is well established[6] that couplings between the ^{117}Sn and ^{119}Sn isotopes and a vicinal olefinic proton are much stronger when the R_3Sn group and the proton are trans than when they are cis, the stereochemistry of compounds **6** and **9** was readily established by ^{1}H NMR spectroscopy. Thus, the coupling constants $^3J_{Sn-H^*}$ in the ^{1}H NMR spectra of **6a–c** and **9a–c** are 128–131 and 72–74 Hz, respectively. The corresponding values for **6d** and **9d** are 88 and 36 Hz, respectively.

Treatment of each of the substances **6a–c,e** and **9a–c** with 5 mol % of $(Ph_3P)_4Pd$[7] in dry *N,N*-dimethylformamide at 80 °C for 1 h provided the corresponding cyclobutane derivatives **7a–c,e** and **10a–c**, respectively. In each case, the reaction was clean and efficient; the isolated yields of purified products ranged from 70% to 95%. Attempted ring closure of **6d** and **9d** under the conditions given above gave none of the desired products. However, when the reactions were carried out with 10 mol % of $(Ph_3P)_4Pd$ in the presence of 1 equiv of Et_3N and the crude products were purified by column chromatography on silica gel (elution with 1:8 ether–petroleum ether containing 1% Et_3N), the products **7d** and **10d** were obtained in yields of 71% and 68%, respectively. Structurally, the latter substances are particularly interesting, since they contain at C-2 a "hidden" aldehyde (enol ether) function.

The expectation that compounds **7a–d** and **10** possessed the indicated stereochemistry was readily verified by ^{1}H NMR spectroscopy. For example, in a NOE difference experiment, irradiation at δ 1.80 in the ^{1}H NMR spectrum of **7a** caused enhancement of the signals at δ 5.53 and 5.14.



7a



10a

On the other hand, in the ^{1}H NMR spectrum of **10a**, separate irradiations at δ 1.68 and 5.78 increased the intensity of the resonances at δ 5.78 and 3.72 and at δ 1.68 and 5.07, respectively.

Since β-trimethylstannyl α,β-unsaturated esters **5** and **8** containing many different (functionalized) R groups are readily available,[4b,c] it is clear that the methodology outlined above can potentially produce, in a stereospecific manner, a wide variety of functionalized alkyl 2,3-dimethylenecyclobutanecarboxylate derivatives. We are currently investigating further possibilities and are studying the chemistry of these novel substances.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada for financial support and to the University of British Columbia for a Graduate Fellowship (to Y.-F.L.).

Supplementary Material Available: Representative experimental procedures for the preparation of and spectral data for compounds **6a**, **7a**, **9a**, and **10a** (3 pages). Ordering information is given on any current masthead page.

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(2) See, for example: Heimbach, P.; Schimpf, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 206. Gajewski, J. J.; Shih, C. N. *J. Org. Chem.* **1972**, *37*, 64. Gajewski, J. J.; Shih, C. N. *J. Am. Chem. Soc.* **1972**, *94*, 1675. Berson, J. A.; Petrillo, E. W., Jr. *J. Am. Chem. Soc.* **1974**, *96*, 636. Gajewski, J. J. *J. Am. Chem. Soc.* **1975**, *97*, 3457. Kelso, P. A.; Yeshurun, A.; Shih, C. N.; Gajewski, J. J. *J. Am. Chem. Soc.* **1975**, *97*, 1513. Levek, T. J.; Kiefer, E. F. *J. Am. Chem. Soc.* **1976**, *98*, 1875. van Straten, J. W.; van Norden, J. J.; van Schaik, T. A. M.; Franke, G. Th.; de Wolf, W. H.; Bickelhaupt, F. *Recl. Trav. Chim. Pays-Bas* **1978**, *97*, 105. Pfeffer, H.-U.; Klessinger, M. *Chem. Ber.* **1979**, *112*, 890. Denis, J. M.; Niamayoua, R.; Vata, M.; Lablache-Combier, A. *Tetrahedron Lett.* **1980**, *21*, 515. Gajewski, J. J.; Benner, C. W.; Stahly, B. N.; Hall, R. F.; Sato, R. I. *Tetrahedron*, **1982**, *38*, 853. Dolbier, W. R., Jr.; Burkholder, C. R. *J. Org. Chem.* **1984**, *49*, 2381. Peelen, F. C.; Landheer, I. J.; de Wolf, W. H.; Bickelhaupt, F. *Recl.: J. R. Neth. Chem. Soc.* **1986**, *105*, 326. Roth, W. R.; Lennartz, H.-W.; Vogel, E.; Leiendecker, M.; Oda, M. *Chem. Ber.* **1986**, *119*, 837. Muller, P.; Rodriguez, D. *Helv. Chim. Acta* **1986**, *69*, 1546. Fukazawa, Y.; Fujihara, T.; Usui, S.; Shiobara, Y.; Kodama, M. *Tetrahedron Lett.* **1986**, *37*, 5621.

(3) Compounds **5** were prepared by reaction of the corresponding α,β-acetylenic esters with $[Me_3SnCuCN]Li$[4a] (THF, −78 °C; NH_4Cl–H_2O), while **8a–c** were derived by treatment of $RCH_2C{\equiv}CCO_2Et$ with $[Me_3SnCuSPh]Li$[4a] (THF, −48 °C; NH_4Cl–H_2O).[4b,c] Treatment of $MeOCH_2OCH_2C{\equiv}CCO_2Et$ with $[Me_3Sn(2\text{-thienyl})CuCN]Li_2$[4d] (THF, −78 °C; NH_4Cl–H_2O) provided **8d**.

(4) (a) Piers, E.; Morton, H. E.; Chong, J. M. *Can. J. Chem.* **1986**, *65*, 78. (b) Piers, E.; Morton, H. E. *J. Org. Chem.* **1980**, *45*, 4263. (c) Piers, E.; Chong, J. M.; Morton, H. E. *Tetrahedron Lett.* **1981**, *22*, 4905. (d) Piers, E.; Tillyer, R. D., unpublished work. See: Lipshutz, B. H.; Koerner, M.; Parker, D. A. *Tetrahedron Lett.* **1987**, *28*, 945 for corresponding alkyl higher order cuprates.

(5) All compounds reported herein exhibited spectra in full accord with structural assignments.

(6) Leusink, A. J.; Budding, H. A.; Marsman, J. W. *J. Organomet. Chem.* **1967**, *9*, 285.

(7) For a previous study on the Pd(0)-catalyzed cyclization of vinylstannane–enol triflates, see: Piers, E.; Friesen, R. W.; Keay, B. A. *J. Chem. Soc., Chem. Commun.* **1985**, 809. For the intermolecular coupling of vinylstannanes with vinyl halides, see: Stille, J. K.; Groh, B. L. *J. Am. Chem. Soc.* **1987**, *109*, 813.

Polymer-Bound Ephedrine as an Efficient Chiral Catalyst for the Enantioselective Addition of Dialkylzincs to Aldehydes

Summary: Polymer-bound ephedrine catalyzed the enantioselective addition of dialkylzincs to aldehydes. Optically active secondary alcohols in up to 89% ee were obtained.

Sir: Polymer supported catalysts have attracted increasing interest.[1] Their workup and recovery are easier than monomeric reagents. They are also analogous to biolog-

(1) For reviews: Mathur, N. K.; Narang, C. K.; Williams, R. E. *Polymers as Aids in Organic Chemistry*; Academic: New York, 1980. Pittman, C. U., Jr. "Polymer Supported Catalysts" In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon: Oxford, 1982; Chapter 55, pp 553–611.

0022-3263/88/1953-0927$01.50/0