This new method can also be applied to the synthesis of cyclopropenones although in the case of the dimethyl derivative the yields obtained so far *via* 7 have been very poor (<2%). On the other hand, treatment of 8[4] with a 1:1

$CH_3CBr_2COCBr_2CH_3$
7

$C_6H_5CBr_2COCHBrC_6H_5$
8

mixture of tris(dimethylamino)phosphine and triethylamine gave diphenylcyclopropenone in 60% yield. Optimizing the yields in the dialkyl cases would make this a valuable route to the otherwise difficultly accessible aliphatic cyclopropenones.[6] Sample experimental procedures follow.

Preparation of $CH_3CBr_2SO_2CBr_2CH_3$. A solution of 16.6 g of $(MeO)_3P$ in 30 ml of dry benzene was added dropwise (15 min) to a stirred solution of 37.9 g of $CBr_3SO_2CBr_3$ in 125 ml of benzene. The temperature rose to 80°. After 1 hr at room temperature the solution was washed with water and 10% $NaHCO_3$, dried ($MgSO_4$), and concentrated to 50 ml *in vacuo*. Dilution with 300 ml of cold hexane (0°) and recrystallization of the precipitated solid from benzene–hexane (1:2) gave 20 g (70%) of the sulfone, mp 142–143°, nmr ($CDCl_3$) δ 3.15 (s, CH_3).

Preparation of Dimethylthiirene Dioxide. A solution of 8.76 g of 3 (R = Me) in 150 ml of dry CH_2Cl_2 was treated (15 min) at −40 to −30° with 10.48 g of triphenylphosphine in 50 ml of CH_2Cl_2. The solution was warmed to 0° for 1 hr and cooled to −10°; 1.44 g of H_2O was added with stirring. The mixture was allowed to warm to room temperature, the solvent evaporated, and the white solid extracted with six 15-ml portions of H_2O. The combined water extracts were added to 300 ml of CH_2Cl_2; the solution was cooled to 0° and solid $NaHCO_3$ added until gas evolution ceased. Anhydrous $MgSO_4$ was then added (keeping the temperature below 10°) until the drying agent formed a solid mass. The CH_2Cl_2 was decanted and a fresh portion of CH_2Cl_2 (300 ml) used to extract the residue. Evaporation of the combined CH_2Cl_2 solutions gave 1.2 g (50%) of the vinylene sulfone, mp 100.5–101.5° dec (lit.[1] mp 101–101.5° dec).

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(2) Compare (a) F. G. Bordwell, B. B. Jarvis, and P. W. R. Corfield, *J. Amer. Chem. Soc.*, **90**, 5298 (1968); (b) B. B. Jarvis, S. D. Dutky, and H. L. Ammon, *ibid.*, **94**, 2136 (1972).

(3) K. Szabo, U. S. Patent 3,106,585; *Chem. Abstr.*, **60**, 2841b (1964); U. S. Patent 3,294,845; *Chem. Abstr.*, **67**, 11210c (1967). See also C. J. Kelly, Ph.D. Dissertation, Indiana University, Bloomington, Ind., 1969.

(4) The compound reported in the literature[5] as $\alpha,\alpha,\alpha',\alpha'$-tetrabromodibenzyl ketone may in fact be the tribromo derivative **8**. In our hands all attempts to prepare the tetrabromo ketone gave only the tribromo derivative.

(5) (a) E. Bourcart, *Ber.*, **22**, 1369 (1889); (b) A. Schönberg and E. Frese, *ibid.*, **103**, 3885 (1970).

(6) R. Breslow and L. J. Altman, *J. Amer. Chem. Soc.*, **88**, 504 (1966).

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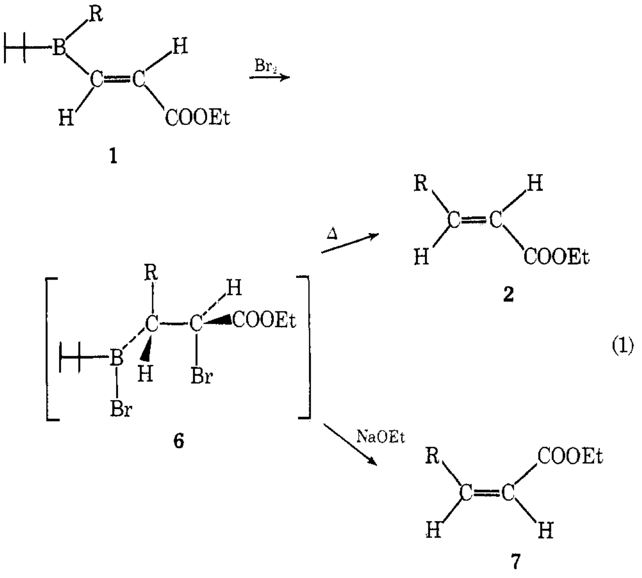
A Novel Stereoselective Synthesis of (*E*)- and (*Z*)-α,β-Unsaturated Carboxylic Esters *via* Hydroboration

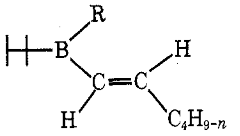
Summary: Treatment of thexylalkyl(β-carbethoxyethenyl)boranes (1) with 1 equiv of bromine followed by refluxing produces the ethyl esters of (*E*)-3-alkylpropenoic acids (2) in good yields, whereas the bromination of 1 followed by the addition of sodium ethoxide provides the *Z* isomers of 2.

Sir: We wish to report unique results of the bromination of 2,3-dimethyl-2-butylalkylalkenylboranes (thexylalkylalkenylboranes, 1), which permit a convenient stereoselective synthesis of either (*E*)- or (*Z*)-α,β-unsaturated carboxylic esters with the possibility of incorporating stereochemically defined groups in the β position.



We have recently found that the hydroboration of ethyl propiolate, with 2,3-dimethyl-2-butylmonoalkylboranes (thexylmonoalkylboranes)[1] cleanly produces **1**.[2] Treatment of 1 with 1 equiv of bromine followed by refluxing permits coupling of the alkyl group (R) and the β-carbethoxyethenyl group to form (*E*)-α,β-unsaturated carboxylic acid esters (2) in a highly stereoselective manner (>95%). The experimental results are summarized in Table I.

The results are unexpected, since the bromination of alkenylboranes are known to produce the corresponding alkenyl bromides.[3] Indeed, the bromination of 3 produces predominantly a mixture of (*E*)- and (*Z*)-alkenyl bromides. Therefore, the presence of the β-carbethoxy group must be responsible for diverting the course of the reaction.



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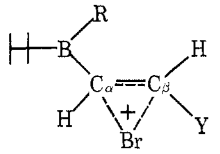

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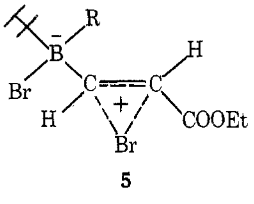


5

Y = C_4H_9-*n* or COOEt

Table I
The Preparation of (*E*)- and (*Z*)-α,β-Unsaturated Carboxylic Esters[a]

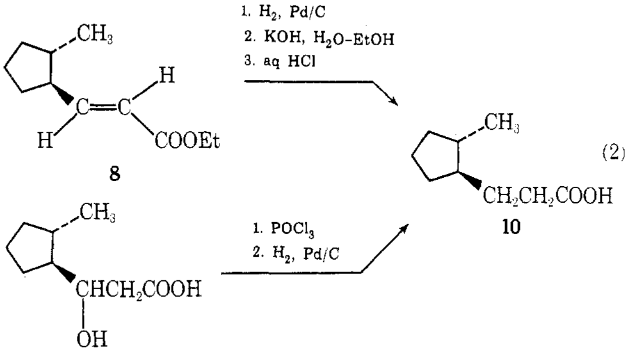
Alkyl group (R)	(*E*)-RCH=CHCOOEt Yield,[b] %	(*E*)-RCH=CHCOOEt Stereo-isomeric purity, %	(*Z*)-RCH=CHCOOEt Yield,[b] %	(*Z*)-RCH=CHCOOEt Stereo-isomeric purity, %
Cyclohexyl	65	99	73	94
Norbornyl	68 (58)	99	76 (60)	90
(*E*)-2-Methylcyclopentyl	52 (45)	95	57 (53)	91
1,2-Dimethylpropyl	55 (46)	99	65	93

[a] The products yielded satisfactory pmr and ir data. [b] By glpc (SE-30). The numbers in parentheses are isolated yields.

The contrasting behaviors presented above may be interpreted as follows. The bromination of alkenylboranes presumably proceeds through the formation of the bromonium ion **4**.[3] In the bromination of **1**, the presence of the dialkylboryl and carbethoxy groups, both of which destabilize the adjacent positive charge, effectively prevents the attack at either the α- or β-carbon atom by the bromide anion, thus directing the anion to the boron atom. Formation of **5** followed by the alkyl migration would produce **6**. In the bromination of **3**, however, **4** (Y = C_4H_9-*n*) is preferentially converted to the corresponding α,β-dibromo derivative.[3,4] Based on the previous results,[3] thermal decomposition of **6** should proceed in a syn fashion, whereas the base-assisted elimination in an anti fashion. Indeed, treatment of **1** with bromine at −78° followed by addition of sodium ethoxide at this temperature and warming the mixture results in the clean formation of the *Z* isomer **7** (Table I). In no case was either the alkenyl bromide or the thexyl-migrated product formed to any appreciable extent (≤2–3%).

Other reagents tested so far, such as iodine and cyanogen bromide,[5] are not nearly so effective as bromine. It is somewhat disappointing that the hydroboration of conjugated alkynyl ketones, such as 3-butyn-2-one, with thexylmonoalkylboranes has not produced clean hydroboration products.[6]

That the stereochemistry of the migrating alkyl group is retained has been demonstrated by converting **8** and **9**, the stereochemistry of which was established earlier,[2] to **10** as shown by eq 2 and comparing the glpc (trimethylsilyl ester and spectral behaviors of the two samples of **10**.



The following procedure for the preparation of the ethyl esters of 3-*exo*-norbornylpropenoic acid is representative. To a dry 300-ml flask equipped with a septum inlet, a reflux condenser, and a magnetic stirring bar was placed 23.0 ml (50 mmol) of 2.17 *M* thexylborane[1] in THF after the system was flushed with nitrogen. To this were added in sequence 4.71 g (50 mmol) of norbornene in 10 ml of THF (1 hr at −25 to −30°) and 5.33 ml (50 mmol) of 96% ethyl propiolate (1 hr at −25 to −30°). The resultant mixture was cooled to −78°, and 2.56 ml (50 mmol) of bromine was added within 1 min. The bromine color disappeared immediately. The mixture was warmed to 25° over 1–2 hr and then refluxed for 1 hr.[7] After oxidation[8] with 17 ml each of 3 *N* sodium acetate and 30% hydrogen peroxide and the usual work-up, distillation provided 5.64 g (58%) of ethyl (*E*)-3-*exo*-norbornylpropenoate (isomeric purity 99%): bp 85–87° (0.2 mm); $n^{25.3}{}_D$ 1.4877; pmr (CCl_4, TMS) 0.9–2.0 (m with t centered at 1.25 ppm, 11 H), 2.0–2.4 (m, 3 H), 4.1 (q, *J* = 7 Hz, 2 H), 5.62 (d, *J* = 16 Hz, 1 H), 1650, 980 cm^{-1}. The preparation of the *Z* isomer (50-mmol scale) can be achieved as follows. After the addition of bromine at −78° the mixture was treated at −78° with sodium ethoxide (10.2 g, 150 mmol) in ethanol over 30 min and then warmed to 25° over 2 hr. The oxidation and work-up of the reaction mixture as described above for the *E* isomer provided a 60% yield of the *Z* isomer: pmr (CCl_4, TMS) 0.9–1.8 (m with t centered at 1.27 ppm, 11 H), 1.8–2.4 (m, 2 H), 3.1–3.6 (m, 1 H), 4.11 (q, *J* = 7 Hz, 2 H), 5.54 (d, of d, *J* = 11 and 1 Hz, 1 H), 6.05 (d of d, *J* = 11 and 9 Hz, 1 H) ppm; ir (neat) 1725, 1650, 1180, 1035 cm^{-1}.

Acknowledgment. Financial support by Syracuse University is gratefully acknowledged.

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(1) E. Negishi and H. C. Brown, *Synthesis*, 77 (1974).
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(3) H. C. Brown, D. H. Bowman, S. Misumi, and M. K. Unni, *J. Amer. Chem. Soc.*, **89**, 4531 (1967).
(4) Based on the proposed interpretation, it may be argued that it is the β-carbon atom of **4** which is attacked by the bromide anion in the bromination of **3**.
(5) G. Zweifel, R. P. Fisher, J. T. Snow, and C. C. Whitney, *J. Amer. Chem. Soc.*, **94**, 6560 (1972).
(6) A detailed pmr study of these reactions is in progress.
(7) We have found that refluxing is necessary to complete debromoboration. If it is incomplete, the undesirable *Z* isomer is produced during the oxidative work-up.
(8) If the oxidation step is omitted, the boron-containing by-products tend to complicate the distillation.

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