It has been shown[11,12] that for dipole–dipole reactions in solution the Arrehenius activation energies give a measure of the electron densities at the reaction centers. The constancy of k_2 and Ea values for the reactions involving methyl, ethyl, *n*-propyl, and *n*-butyl alcohols (Table I) indicates that the electron-releasing inductive effect of the alkyl group in these four alcohols has little effect, as expected, on the electron density on the oxygen atom. In contrast to these alcohols, the activation energies for the reactions involving allyl alcohol and methoxyethanol are definitely higher by about 2 kcal mol^{-1}, and this is clearly due to the electron-attracting nature of the allyl and methoxy groups, as a consequence of which the electron density on the oxygen atom is reduced.

The dipole–dipole type of mechanism proposed in Scheme I was further confirmed by the following additional experimental observations. When chloro- or bromo-substituted ethyl alcohol was used as the reactant there was no reaction at 40 °C even after 6 h. The powerful electron-attracting capacity of the halogen atoms diminishes the electron density on the oxygen atom of the alcohol and drastically reduces the rate by increasing the activation energy Ea. The activated complex in the reaction is more polar than the reactants and hence an increase in the polarity of the solvent should increase the rate. It is found to be true since in chlorobenzene (ϵ = 5.6) the reaction proceeds at a faster rate than in benzene (ϵ = 2.2). For the *n*-butyl alcohol–phenyl isocyanate reaction in chlorobenzene, the value of 10^4k_2 was 5.9 M^{-1} s^{-1} at 30 °C and the corresponding Ea value was 7.3 kcal/mol (compare with values in Table I).

Acknowledgment. S.S. thanks the Council of Scientific and Industrial Research for the award of a Research Fellowship.

Registry No. C_6H_5NCO, 103-71-9; CH_3OH, 67-56-1; *n*-BuOH, 71-36-3; ethyl alcohol, 64-17-5; *n*-propyl alcohol, 71-23-8; allyl alcohol, 107-18-6; methoxyethanol, 109-86-4.

(11) Laidler, K. J. "Chemical Kinetics"; McGraw Hill: New York, 1965; p 241.
(12) Hinshelwood, C. N.; Laidler, K. J.; Timm, E. W. *J. Chem. Soc.* **1938**, 848.

The Ester Enolate Carroll Rearrangement

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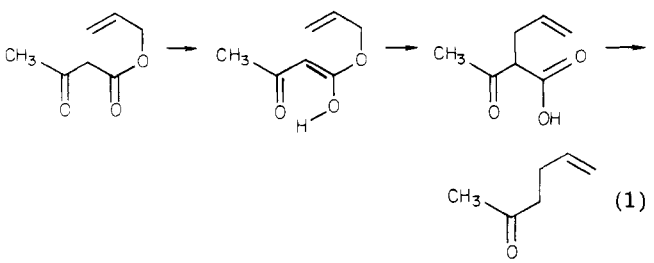
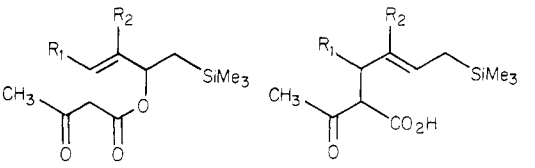
The Carroll rearrangement[1,2] is an old and well-established thermal rearrangement (eq 1) that involves the rearrangement of allylic esters to β-keto acids followed by decarboxylation. The reaction, while in principle a versatile complement to the Claisen rearrangement,[3] has not found widespread use. This is probably for two reasons: (1) the lack of a convenient high-yield method for the formation of β-keto esters[4] and (2) the harsh conditions required to effect rearrangement.[5,6]



(1)

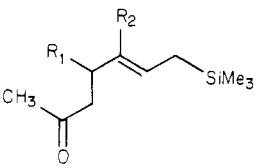
We report a mild and high-yield synthesis of allylic acetoacetates[7] and conditions for their rearrangement at room temperature or in refluxing THF. Although several reports[8] on the Carroll rearrangement allude to the fact that the reaction seems to be accelerated by base, there has been no specific study of the ester enolate[9] version of this reaction.

We have discovered that dianions[10] of allylic acetoacetates, generated by treatment of the acetoacetates with 2 equiv of LDA at −78 °C in THF, rearrange at room temperature or at reflux and *the resulting β-keto acids can be readily isolated.* For example, acetoacetates **1** and **2**



1, $R_1 = CH_3$; $R_2 = H$
2, $R_1 = H$; $R_2 = CH_3$

3, $R_1 = CH_3$; $R_2 = H$
4, $R_1 = H$; $R_2 = CH_3$



5, $R_1 = CH_3$; $R_2 = H$
6, $R_1 = H$; $R_2 = CH_3$

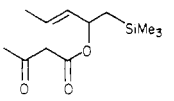
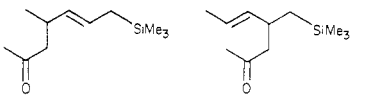
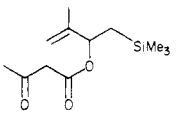
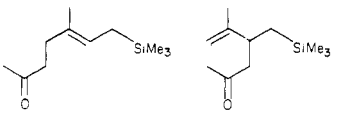
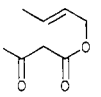
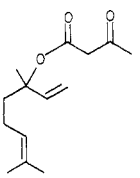
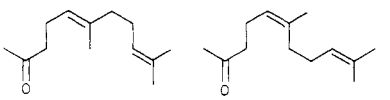
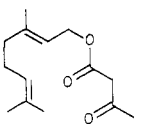
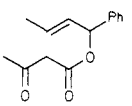
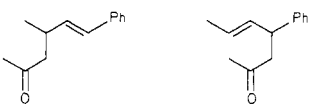
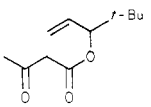
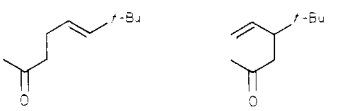
could be isomerized to β-keto acids **3** and **4** in 84% and 40% yields, respectively.[11] Heating the β-keto acids in CCl_4 solution for 1 h at 77 °C leads to decarboxylation. A number of examples are collected in Table I. Where possible the yield and product ratios have been compared to the pyrolysis method.

The acetoacetates used in this study were prepared in high yield by treatment of allylic alcohols[12] in ether at −20 °C with diketene and a catalytic amount of 4-(dimethylamino)pyridine (DMAP)[13] followed by stirring at room temperature. A number of examples are given in Table II. This method represents a significant improvement

(1) Carroll, M. F. *J. Chem. Soc.* **1940**, 1226.
(2) Kimel, W.; Cope, A. C. *J. Am. Chem. Soc.* **1943**, *65*, 1992.
(3) Ziegler, F. E., *Acc. Chem. Res.* **1977**, *10*, 227.
(4) A promising new method involves the reaction of 5-acyl Meldrum's acid with allylic alcohols: Oikawa, Y.; Sugano, K.; Yonemitsu, O. *J. Org. Chem.* **1978**, *43*, 2087.
(5) Rearrangement is normally carried out at temperatures of 130–220 °C by heating the β-keto ester neat or in a high-boiling solvent (xylene, diphenyl ether), usually after in situ preparation of the β-keto ester.
(6) An interesting report of the low-temperature Pd(0)-catalyzed rearrangement of allylic β-keto esters has appeared: Shimizu, I.; Yamada, T.; Tsuji, J. *Tetrahedron Lett.* **1980**, *21*, 3199.
(7) Acetoacetic esters of other types of alcohols have been prepared by this procedure.
(8) Bases include the following. (a) Al(*i*-PrO)$_3$: Cookson, R. C.; Parsons, D. J. *J. Chem. Soc., Chem. Commun.* **1976**, 990. Kimel, W.; Sax, N. W.; Kaiser, S.; Eichmann, G. G.; Chase, G. O.; Ofner, A. *J. Org. Chem.* **1958**, *23*, 153. (b) *s*-Collidine: Narwid, T. A.; Cooney, K. E.; Uskokovic, M. R. *Helv. Chim. Acta* **1974**, *57*, 771. (c) NaOAc: Camps, F.; Canela, R.; Coll, J.; Messeguer, A.; Roca, A. *Tetrahedron* **1978** *34*, 2179. (d) NaH: Tanabe, M.; Hayashi, K. *J. Org. Chem.* **1980**, *102*, 862.
(9) Ireland, R. E.; Mueller, R. *J. Am. Chem. Soc.* **1972**, *94*, 5897.
(10) Harris, T. M.; Murray, T. P.; Harris, C. M.; Gumulka, M. *J. Chem. Soc., Chem. Commun.* **1974**, 362.
(11) All new compounds possessed spectral and analytical data in accord with their structures.
(12) Wilson, S. R.; Price, M. F. *J. Am. Chem. Soc.* **1982**, *104*, 1124.
(13) Steglich, W.; Hofle, G. *Angew. Chem., Int. Ed. Engl.* **1969**, 981.

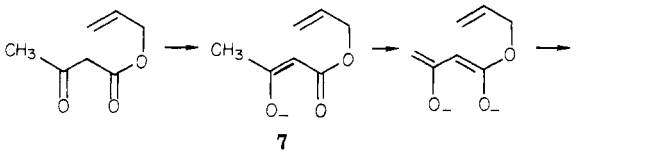
0022-3263/84/1949-0722$01.50/0

Table I. Ester Enolate Carroll Rearrangement

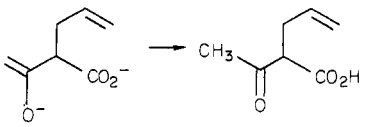
entry	substrate	condns[a]	products	yield, %
1				
		A	67:33	50
		B	56:44	50
		C	100:0	84
2				
		A	83:17	40
		C	100:0	40
		D	no reaction	
		E	no reaction	
3				
		F	100:0	37
		D	no reaction	
		C	100:0	95
4				
		F	54:46	67
		C	58:42	83
5				
		F	complex mixture	67
		C	no reaction	
6				
		B	36:64	70
		D	no reaction	
		C	complex mixture	
7				
		B	100:0	58
		C	100:0	80

[a] Conditions: (A) 170 °C/2 h/neat; (B) 200 °C/2 h/neat; (C) a, 2 equiv of LDA/THF/-70 to 65 °C (β-keto acid), b, 1 h/77 °C/CCl_4; (D) 1 equiv of LDA/THF/-70 to 65 °C; (E) KH/THF/65 °C; (F) 190-220 °C/18 h/diphenyl ether.

over other routes[14] and provides pure acetoacetates in high yield.



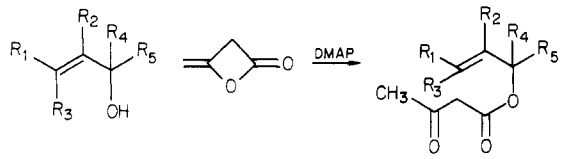
7



Several interesting observations concerning the Carroll rearrangement have been made. Formation of the monoanion using 1 equiv of LDA or KH gave only recovered starting material after refluxing in THF for several hours. Thus, we believe that the higher electron density at the reacting carbon favors the rearrangement. This observation is consistent with those of Denmark[15] and is in accord

(14) Acetoacetate formation has previously been carried out by using the following. (a) Et_3N: Kato, T.; Chita, T. *Chem. Pharm. Bull.* **1975**, *23*, 2263. (b) NaOR: Kimel, W.; Cope, A. C. *J. Am. Chem. Soc.* **1943**, *65*, 1992. (c) *p*-TsOH: Boese, A. B., Jr. *Ind. Eng. Chem.* **1940**, *32*, 16.

Table II. DMAP-Catalyzed Formation of β-Keto Esters

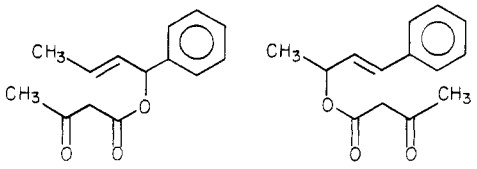


entry	R_1	R_2	R_3	R_4	R_5	time, h	yield, %
1	CH_3	H	H	H	$CH_2Si(CH_3)_3$	13	93
2	H	CH_3	H	H	$CH_2Si(CH_3)_3$	13	80
3	CH_3	H	H	H	H	2	96
4	H	H	H	H	*t*-Bu	15	92
5	CH_3	H	H	H	Ph	18	98
6	H	H	H	CH_3	C_7H_{13}[a]	4	87
7	C_7H_{13}[a]	CH_3	H	H	H	4	95

[a] $CH_2CH_2CH_2CH=C(CH_3)_2$.

with theoretical calculations of Carpenter,[16] where electron-withdrawing substituents at the 1-position increase the energy of activation for rearrangement.

Whereas pyrolysis occasionally gives allylic regioisomers (cf. entries 1, 2, and 6, Table I) formally representing [3,3] and [1,3] rearrangements,[17] the rearrangement of the dianions gives exclusively the expected [3,3] products. Evidence[18] suggests that the unexpected regioisomers are actually the result of allylic rearrangement of the β-keto esters followed by the normal [3,3] rearrangement. In fact, acetoacetate **8** isomerizes slowly to **9** at room temperature, which may account for the inability to effect its clean conversion to the γ,δ-unsaturated ketone.[19]



8 **9**

The geometry of the double bond in the products in all cases was shown to be >90% *E* by ^1H NMR and capillary GC. As has been found with other analogues of the Claisen rearrangement, we have observed dependence of the reaction rate on the substitution pattern of the allylic portion.[16] Acetoacetic esters derived from primary alcohols (entry 3, Table I) rearrange more slowly than those derived from secondary or tertiary alcohols. For example, whereas **1** (entry 1) rearranged at room temperature, the primary acetoacetate (entry 3) required several hours at reflux. In the case of geranyl acetoacetate (entry 5), only fragmentation was observed. When R^5 was a cation-stabilizing substituent (entries 1, 2, and 6), the reaction rate markedly increased, an observation that is consistent with a mechanism involving substantial polarization of the C(1)–oxygen bond in the transition state.[20]

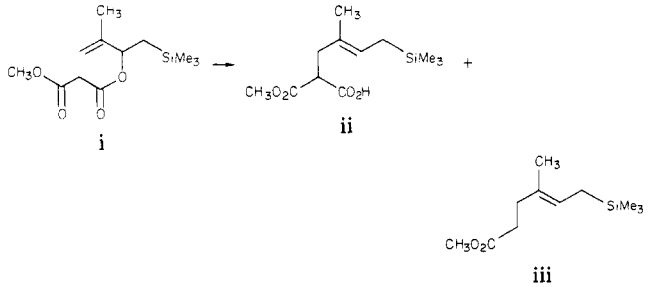
In conclusion, the ester enolate Carroll rearrangement is a mild procedure for the preparation of γ,δ-unsaturated ketones (or allyl-substituted acetoacetic acids). Isolation of the acetoacetic acids makes purification much simpler than the pyrolysis method.

Experimental Section

Preparation of Compound 1. 4-(Dimethylamino)pyridine (5 mg, 0.04 mmol) was added to a solution of 1-(trimethylsilyl)-2-hydroxy-3-methyl-3-butene[12] (1.53 g, 9.68 mmol) and diketene (920 mg, 11.0 mmol) in anhydrous ether (30 mL) cooled to −20 °C under N_2. After 30 min the yellow-orange solution was allowed to warm to room temperature. After being stirred overnight (generally the reaction is complete within 2 h), a 0.1% solution of NaOH was added and the layers were separated. The organic phase was washed twice with 0.1% NaOH and the volatiles were evaporated, leaving a yellow liquid, 2.02 g. Distillation by evacuating to 0.2 mm and rapid heating to 200 °C gave acetoacetic ester **1** as a colorless liquid, 1.88 g (80%).

Rearrangement of Compound 1. A solution of LDA (1.8 mL, 2.3 mmol) in THF was added dropwise to a solution of acetoacetic ester **1** (256 mg, 1.1 mmol) in anhydrous THF (5 mL) cooled to −78 °C under N_2. After 30 min at −78 °C the solution as allowed to warm to room temperature. After being stirred at room temperature for 4 h the mixture was heated at reflux for 1 h and then cooled. The volatiles were evaporated at reduced pressure *without heating*, and ether (20 mL) was added to the residue. Water was added and the layers were separated. The organic phase was washed with 0.1% NaOH (2 × 10 mL). The combined aqueous layers were then extracted twice with ether. Ether (15 mL) was added to the aqueous phase, which was carefully acidified with 10% HCl while stirring vigorously. The layers were quickly separated when the aqueous solution had reached pH 2, and the aqueous phase was extracted twice with ether. The combined organic phases were dried ($MgSO_4$) and the volatiles evaporated at reduced pressure without heating to give a pale yellow liquid, 211 mg (84%) of β-keto acid **3**. Decarboxylation was effected by

(15) Denmark, S. E.; Harata, M. A. *J. Am. Chem. Soc.* **1982**, *104*, 4972. We have observed that although the monoanion derived from the mixed malonate **i** is recovered unchanged after 1 h of refluxing in THF, at 120 °C in benzene (sealed tube) for 1 h a mixture of esters **ii** (55%) and **iii** (37%) could be isolated. That **iii** was the result of decarboxylation of the intermediate carboxylate and not from decarboxylation during workup was shown by the recovery of **ii** unchanged after 1 h of reflux in benzene containing *p*-TsOH.



i **ii** **iii**

(16) For the dependence of the reaction rate on the structure of the allyl vinyl ether system, see: (a) Claisen: Burrows, C. J.; Carpenter, B. K. *J. Am. Chem. Soc.* **1981**, *103*, 6983, 6984. (b) Ester–enolate Claisen: Ireland, R. E.; Mueller, R. H.; Willard, A. K. *Ibid.* **1976**, *98*, 2868.

(17) Competing [3,3] and [1,3] shifts in the ester enolate Claisen rearrangement have been studied: Arnold, R. T.; Kulenovic, S. T. *J. Org. Chem.* **1980**, *45*, 891.

(18) (a) Tessiere, P. *Recherches* **1957**, *7*, 29. (b) McAndrews, B. A.; Riezebos, G. *J. Chem. Soc., Perkin Trans 1* **1972**, 367. (c) Bohlman, F.; Lonitz, M. *Chem. Ber.* **1980**, *113*, 2410.

(19) Attempts to purify **8** by chromatography on silica gel led to complete isomerization to acetoacetic ester **9**.

(20) Smith, E. H.; Tyrrell, N. D. *J. Chem. Soc., Chem. Commun.* **1983**, 285.

dissolving in CCl_4 (5 mL) and heating at reflux for 1 h to produce **5** in quantitative yield from **3**.

Registry No. 1, 88343-77-5; 2, 88343-78-6; 5, 88343-82-2; 6, 88343-84-4; 8, 88390-10-7; (*E*)-2-butenyl acetoacetate, 82259-92-5; 3,7-dimethylocta-1,6-dien-3-yl acetoacetate, 25456-03-5; (*E*)-1-phenyl-2-butenyl acetoacetate, 88343-79-7; 4,4-dimethylpent-1-en-3-ol, 88357-95-3; geranyl acetoacetate, 10032-00-5; (*E*)-1-(trimethylsilyl)-3-penten-2-ol, 80993-48-2; 3-methyl-1-(trimethylsilyl)-3-buten-2-ol, 80399-29-7; (*E*)-2-buten-1-ol, 504-61-0; 4,4-dimethyl-1-penten-3-ol, 24580-44-7; 3,8-dimethyl-1,7-nonadien-3-ol, 88343-80-0; (*E*)-2,8-dimethyl-2,7-nonadien-1-ol, 88343-81-1; diketene, 674-82-8; (E)-4-[(trimethylsilyl)methyl]-5-hepten-2-one, 88343-83-3; 5-methyl-4-[(trimethylsilyl)methyl]-5-hexen-2-one, 88343-85-5; 4-methyl-5-hexen-2-one, 61675-14-7; (*E*)-6,10-dimethyl-5,9-undecadien-2-one, 3796-70-1; (*Z*)-6,10-dimethyl-5,9-undecadien-2-one, 3879-26-3; (*E*)-4-methyl-6-phenyl-5-hexen-2-one, 88343-86-6; (*E*)-4-phenyl-5-hepten-2-one, 88343-87-7; (*E*)-7,7-dimethyl-5-octen-2-one, 61478-31-7; 4-(dimethylamino)-pyridine, 1122-58-3; 4,8-dimethylnona-1,7-dien-3-yl acetoacetate, 88343-88-8; (*E*)-2,8-dimethylnona-2,7-dien-2-yl acetoacetate, 88343-89-9.

A Highly Stereoselective Synthesis of 1-Halo-1-(trimethylsilyl)-2,2-dialkyl Olefins

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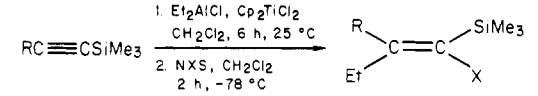
Department of Chemistry, University of California, Davis, California 95616

Received July 6, 1983

Isomerically pure 1-halo-1-(trimethylsilyl)-2,2-dialkyl olefins have the potential for serving as key intermediates in the stereospecific synthesis of tetrasubstituted olefins.[1] Unfortunately, attempts to synthesize these (halovinyl)-silanes in a highly stereoselective manner have proven to be difficult. In 1977, Seyferth et al.[2] reported the synthesis of $R_2C{=}CBrSiMe_3$ compounds, but the procedure is limited to having the 2,2-dialkyl groups the same. In 1978, Snider et al.[3] reported the Ni-catalyzed addition of methylmagnesium bromide to silylacetylenes followed by reaction with excess iodine to give a stereoselective synthesis of vinyliodosilanes; however, use of ethylmagnesium bromide did not give similar results. Also in 1978, Eisch et al.[4] reported that the carbotitanation of alkynylsilanes may or may not be stereoselective, depending upon the nature of the alkylaluminum chloride used; this work did not attempt to trap the vinyl metallic intermediate with halogens. In 1979, Snider and Karras[5] reported the most successful approach; they observed that carbotitanation of alkynylsilanes was highly stereoselective using dialkylaluminum chloride–titanocene dichloride (1:1). Although they were able to cleave the carbon–metal bond with aqueous sodium hydroxide in a highly stereoselective manner to give trisubstituted olefins, when cleavage was attempted with a large excess of iodine considerable loss of stereochemical control in and yield of the 1-iodo-1-(trimethylsilyl)-2,2-dialkyl olefin product was observed. We describe in this paper a modification of Snider's approach that allows the synthesis of the 1-halo-1-(trimethylsilyl)-2,2-dialkyl olefins in good yield and a highly stereoselective manner (>95:5 ratio).

Table I

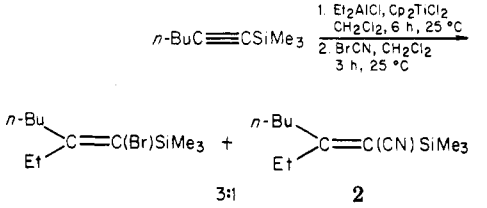


4

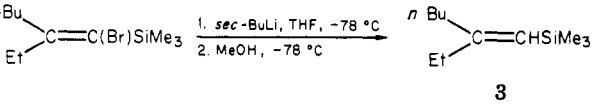
R	X	% yield of 4[a]	E:Z[b]
n-Bu	Br	90	97:3
n-Bu	Cl	85	
n-Bu	I	86	99:1
C_6H_{11}	Br	80	95:5

[a] Isolated yields. [b] Determined by capillary GLC on the corresponding trisubstituted olefin.

Our initial approach to this problem sought to use bromine to cleave the product of carbometalation in analogy to the preparation of 1-bromo-1-(trimethylsilyl)-2-alkyl olefins.[1,6] Thus 1-(trimethylsilyl)-1-hexyne[7] was reacted at room temperature with a solution derived from diethylaluminum chloride and titanocene dichloride (1:1) in dichloromethane solvent followed by treatment with bromine in dichloromethane at −78 °C. Unfortunately, a complex mixture of products was obtained with significant loss of the trimethylsilyl group. Next, cyanogen bromide was used as the electrophile, and it was found that indeed a good yield of cleavage products was obtained. Unfortunately, the products were a mixture of the desired 1-bromo-2-ethyl-1-(trimethylsilyl)-1-hexene (1) and 3-ethyl-2-(trimethylsilyl)-2-heptenenitrile (2) from which a 70% isolated yield of 1 could be obtained by silica gel chromatography. Attempts to determine the *E*/*Z* ratio



of (bromovinyl)silane 1 directly even on capillary GLC proved unsuccessful. Therefore compound 1 was subjected to halogen–metal exchange with *sec*-butyllithium at −78 °C followed by quenching with methanol at −78 °C to give 2-ethyl-1-(trimethylsilyl)-1-hexene 3.[8] Examination of this trisubstituted olefin by capillary GLC (30-m SE-54) showed 3 to be a 1:1 mixture of *E*:*Z* isomers.



3

The carbometalated intermediate was reacted with *N*-bromosuccinimide in dichloromethane at −78 °C in order to eliminate the nitrile side product and lower the temperature at which the cleavage reaction could be carried out. This procedure gave a high yield of the desired 1-bromo-2-ethyl-1-(trimethylsilyl)-1-hexene, which was determined via the trisubstituted olefin to be a 97:3 mix-

(1) For the utility of 1-halo-1-(trimethylsilyl)-2-alkyl olefins in the synthesis of trisubstituted olefins, see: Miller, R. B.; McGarvey, G. *J. Org. Chem.* **1979**, *44*, 4623.
(2) Seyferth, D.; Lefferts, J. L.; Lambert, R. L., Jr. *J. Organomet. Chem.* **1977**, *142*, 39.
(3) Snider, B. B.; Karras, M.; Conn, R. S. E. *J. Am. Chem. Soc.* **1978**, *100*, 4624. Snider, B. B.; Conn, R. S. E.; Karras, M. *Tetrahedron Lett.* **1979**, 1679.
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(5) Snider, B. B.; Karras, M. *J. Organomet. Chem.* **1979**, *179*, C37.
(6) Zweifel, G.; Lewis, W. *J. Org. Chem.* **1978**, *43*, 2739.
(7) Miller, R. B.; McGarvey, G. *J. Org. Chem.* **1978**, *43*, 2739.
(8) It is important to protonate the vinyllithium intermediate at −78 °C to insure that isomerization does not take place, see: Zweifel, G.; Murray, R. E.; On, H. P. *J. Org. Chem.* **1981**, *46*, 1292.

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