Regioselectivity in Electrochemical Allylation of Carbonyl Compounds. A Synthesis of Egomaketone by Regioselective Allylation

Masao Tokuda,* Shohei Satoh, and Hiroshi Suginome*

Organic Synthesis Division, Department of Chemical Process Engineering, Faculty of Engineering, Hokkaido University, Sapporo 060, Japan

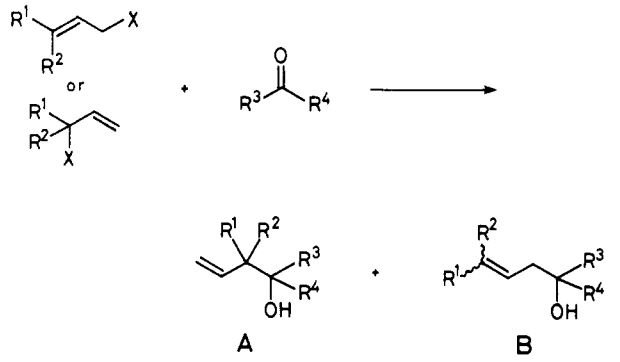
Received April 25, 1989

The regioselectivity in the electrochemical allylations of acetone, propanal, and benzaldehyde with several allylic halides (**1a**, **4a**, **4b**, **5**, **11**) has been studied. We found that the electrochemical allylation with the allylic halides, which are more readily reduced than carbonyl compounds (the allylation of acetone or propanal), took place preferentially at the more highly substituted carbon terminus of the allylic group to give homoallyl alcohol **6**, **9**, or **17** as the major product. When carbonyl compounds are more readily reduced than allylic halides (the allylation of benzaldehyde), on the other hand, the electrochemical allylation took place preferentially at the less highly substituted carbon terminus to give **13**, **14**, or **16**, which are not readily obtainable by the conventional methods. We also investigated other factors that might affect the regioselectivity in the electrochemical allylation. Cathode material was found to affect the regioselectivity significantly. When Pt, Zn, Ni, or Al cathodes were used in the allylation of acetone with allylic halide **4a** or **5**, the allylic halides preferentially reacted to the more highly substituted carbon to give **6**. When Hg or carbon cathode was used, on the other hand, allylation took place at both carbon termini of the allylic groups and, in some cases, preferentially at the less highly substituted carbon terminus to give **7** or **8**. The electrochemical introduction of the allylic groups by their less highly substituted carbon termini to aldehydes was applied to a new synthesis of egomaketone (**23**) by the reaction of 1-chloro-3-methyl-2-butene (**1a**) with 3-furancarbaldehyde (**20**).

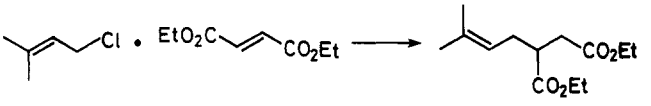
The introduction of allylic groups to organic substrates is of importance in organic synthesis. The introduction of allylic groups into carbonyl compounds has been achieved by using allylic organometallics where their allylic groups act as the nucleophiles.[1] Allylation can also be achieved when allylic groups in the allylic compounds serve as the electrophile.[2] An electrochemical method for the introduction of allylic groups, on the other hand, has been developed by Baizer[3] and by ourselves[4,5] for the allylation of α,β-unsaturated esters[3,4] or aliphatic ketones[5] with allylic halides. Since we published our study, several electrochemical allylations of carbonyl compounds with allylic halides by using metallic tin,[6] sacrificial anode,[7a] or nickel complex coupled with sacrificial anode,[7b] have been reported.

If substituted allyl halides are used in the allylations, the carbon–carbon bond formation can take place at two different sites of the allylic component to give rise to two types of regioisomers. The allylation of an aldehyde or a ketone, for instance, results in two types of homoallyl alcohol, A and/or B (Scheme I). When organometallic compounds derived from allylic halides are used for the allylation, the allylation always takes place at the more highly substituted carbon termini of the allylic groups to give the product of type A, exclusively.[1] As we describe below, our electrochemical allylation was found to take place at both carbon termini of the allylic groups of allylic halides to give the products of types A and B[5] or, in some cases, at the less highly substituted carbon terminus to give exclusively the homoallyl alcohol of type B.[8]

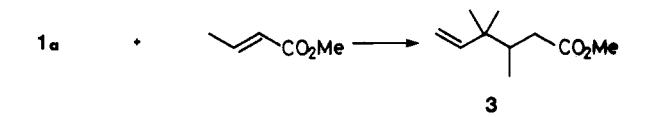
Scheme I



The regioselectivity found in the present experiments is similar to those in the electrochemical allylation of α,β-unsaturated esters reported by us previously; an electrochemical conjugate addition of 1-chloro-3-methyl-2-butene (**1a**) to diethyl fumarate took place exclusively at the less highly substituted carbon terminus of the allyl group to give the adduct **2**, while the addition of **1a** to methyl crotonate took place exclusively at the more highly substituted carbon terminus to give **3**.[4,8]



1a **2**



3

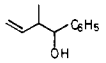
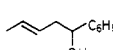
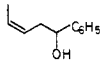
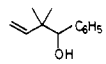
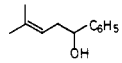
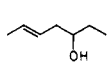
Several terpenoids possess allylic groups attached at their less highly substituted carbon termini. Conventional allylation, however, has not been able to achieve direct introduction of allylic groups attached at their less highly substituted carbon termini.

We here describe some details of our study of the regioselectivity of electrochemical allylation of carbonyl compounds. We found that it is possible to exercise some

(1) (a) Courtois, G.; Miginiac, L. *J. Organomet. Chem.* **1974**, *69*, 1. (b) Rautenstrauch, V. *Helv. Chim. Acta* **1974**, *57*, 496. (c) Yamamoto, Y. *Acc. Chem. Res.* **1987**, *20*, 243.
(2) Magid, R. M. *Tetrahedron* **1980**, *36*, 1901.
(3) Baizer, M. M.; Chruma, J. L. *J. Org. Chem.* **1972**, *37*, 195.
(4) Satoh, S.; Suginome, H.; Tokuda, M. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 3456.
(5) Satoh, S.; Suginome, H.; Tokuda, M. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 1791.
(6) Uneyama, K.; Matsuda, H.; Torii, S. *Tetrahedron Lett.* **1984**, *25*, 6017.
(7) (a) Sibille, S.; d'Incan, E.; Laport, L.; Perichon, J. *Tetrahedron Lett.* **1986**, *27*, 3129. (b) Sibille, S.; d'Incan, E.; Laport, L.; Massebiau, M.-C.; Perichon, J. *Ibid.* **1987**, *28*, 55.
(8) Satoh, S.; Suginome, H.; Tokuda, M. *Tetrahedron Lett.* **1981**, *22*, 1895.

0022-3263/89/1954-5608$01.50/0 © 1989 American Chemical Society

Table I. Electrochemical Allylations of Acetone, Benzaldehyde, and Propanol

allylic halide	carbonyl compd	products (yield[a])		
4a	$(CH_3)_2CO$[b]	 6 (40%)	 7 (16%)	 8 (0.6%)
 5	$(CH_3)_2CO$[b]	6 (50%)	7 (14%)	8 (17%)
 1a	$(CH_3)_2CO$[b]	 9 (55%)	 10 (16%)	
 11	$(CH_3)_2CO$[b]	9 (54%)	10 (18%)	
4a	C_6H_5CHO[c]	 12 (12%)	 13 (30%)	 14 (5%)
 4b	C_6H_5CHO[c]	12 (21%)	13 (27%)	14 (11%)
5	C_6H_5CHO[c]	12 (19%)	13 (18%)	14 (17%)
1a	C_6H_5CHO[c]	 15 (20%)	 16 (49%)	
4b	C_2H_5CHO[c]	 17 (19%)	 18 (11%)	 19 (4%)

[a] Yields are based on allylic halides used. [b] A mixture of allylic halides (10 mmol) and acetone (50 mmol) in 5.5 mL of HMPA containing 0.1 M TBAP was electrolyzed at 0 °C by using two platinum plate electrodes. Current density was 25 mA cm^{-2}, and electricity passed was 2.0 F/mol of halide. [c] A mixture of allylic halides (5 mmol) and aldehyde (20 mmol) in 20 mL of HMPA containing 0.1 M TBAP was electrolyzed in the same conditions as those described in footnote *b*.

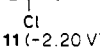
control over the regioselectivity and that an application of the regiocontrolled electrochemical allylation can lead to a new synthesis of a natural product, egomaketone.

Results and Discussion

Electrochemical Allylation of Acetone, Propanal, and Benzaldehyde. We have already reported on the electrochemical addition of the allylic groups of allyl halides to ketones in hexamethylphosphoric triamide (HMPA) as the solvent.[5,8] The present electrolysis was again carried out in an HMPA solution containing 0.1 M tetrabutylammonium perchlorate (TBAP), and an undivided cell equipped with two platinum plate electrodes was used. Constant-current electrolysis of allylic halides in the presence of 4–5 molar excess of carbonyl compounds gave a mixture of homoallyl alcohols A and B (Scheme I). We chose (*E*)-1-chloro-2-butene (**4a**), (*E*)-1-bromo-2-butene (**4b**), 3-chloro-1-butene (**5**), 1-chloro-3-methyl-2-butene (**1a**), 1-bromo-3-methyl-2-butene (**1b**), and 3-chloro-3-methyl-1-butene (**11**) as allylic halides, while we used acetone, propanal, and benzaldehyde as the carbonyl compounds. Structures of the homoallyl alcohols obtained and their yields under our electrolytic conditions[9] are summarized in Table I.

We found that in most of the electrolysis the geometry of the carbon–carbon double bond in the products retained

Table II. Regioselectivity in the Electrochemical Allylations of Acetone, Benzaldehyde, and Propanal

carbonyl compd	regioselectivity	
$(CH_3)_2CO$ (<−2.5 V)[a]	 71% 29%  **4a** (−2.23 V)[a]	 62% 38%  **5** (−2.28 V)[a]
	 78% 22%  **1a** (−2.20 V)[a]	 73% 27%  **11** (−2.20 V)[a]
C_6H_5CHO (−1.52 V)[a]	 26% 74%  **4a**	 35% 65%  **5**
	 36% 64%  **4b** (−1.70 V)[a]	
	 29% 71%  **1a**	
C_2H_5CHO (−2.20 V)[a]	 56% 44%  **4b**	

[a] Reduction potentials (E_p; volts vs Ag/AgI) were obtained by cyclic voltammetry in 0.1 M TBAP–HMPA by using a Pt disk electrode.

that of the starting allylic halides **4a** and **4b**. Electrochemical allylation of acetone, benzaldehyde, or propanal with **4a** or **4b** gave (*E*)-homoallyl alcohol (**7**, **13**, or **18**) as the major product, while a nearly 1:1 mixture of (*E*)- (**7** or **13**) and (*Z*)-homoallyl alcohols (**8** or **14**) was obtained when **5** was used as the allylic halide.

Extensive study has been made of diastereoselectivity in the formation of homoallyl alcohols from the reaction of crotyl-type organometallics with aldehydes.[1c,10] In the present electrochemical allylations, we observed that ratios of syn to anti in homoallyl alcohols **12** and **17** were 54:46 and 53:47 and that there was no appreciable difference of the ratio when the electrolytic conditions were changed.

Regioselectivity in the Electrochemical Allylations. Table II summarizes the results of the regioselectivities in the electrochemical additions of the allylic groups of substituted allyl halides to acetone, benzaldehyde, or propanal; these were calculated from the yield of each homoallyl alcohol resulting from the electrolysis recorded in Table I.

Table II also shows the reduction potentials of the allylic halides and the carbonyl compounds used in the electrolysis; these were obtained by a cyclic voltammetry. Comparison of the regioselectivity in the electrochemical allylation of acetone with two pairs of isomeric allylic halides (**4a** and **5**; **1a** and **11**) indicates that there was no significant difference between either given pair. The regioselectivity in the electrochemical allylation of propanal with (*E*)-1-bromo-2-butene (**4b**) is also similar to the case of the reaction of acetone with (*E*)-1-chloro-2-butene (**4a**). The regioselectivity in the electrochemical allylation of benzaldehyde with allylic halides **4a**, **5**, **4b**, and **1a**, however, were the reverse of those found for acetone or propanal.

The observed reversion in the regioselectivity in the electrochemical allylations of benzaldehyde with acetone can be rationalized in terms of the different mechanisms involved in the allylation of the two carbonyl compounds. Comparison of the reduction potentials of the carbonyl

(9) Since the main purpose of the present investigation was to study the regioselectivity of the electrochemical allylations, the yields of homoallyl alcohols described in this paper are not necessarily optimized.

(10) For reviews, see: (a) Bartlett, P. A. *Tetrahedron* **1980**, *36*, 2. (b) Seebach, D.; Prelog, V. *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 654.

Scheme II

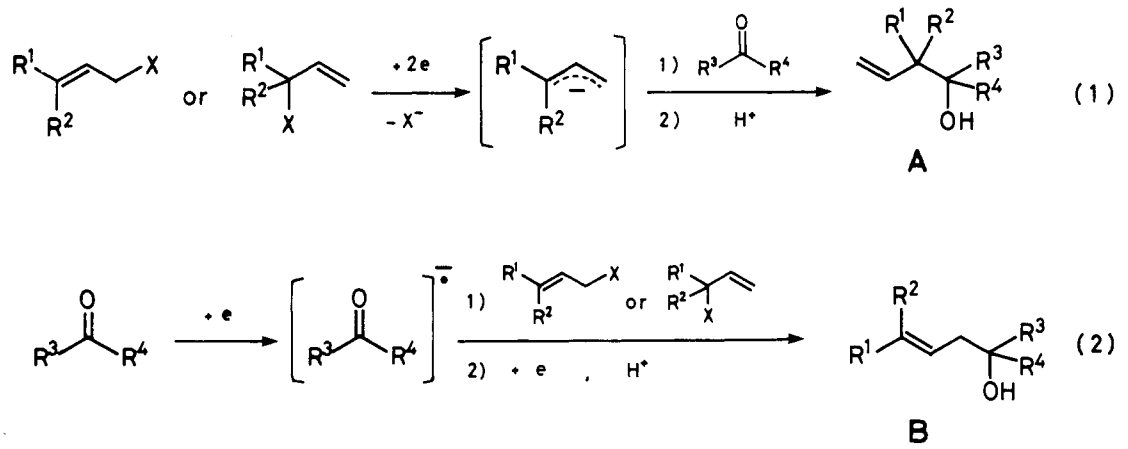


Table III. Regioselectivity in the Electrochemical Allylations of Acetone with 1a and 11 under Various Electrolytic Conditions[a]

entry	cathode	supporting electrolyte[b] (M)	current density, mA cm^{-2}	electricity, F mol^{-1}	1a yield,[c] %	1a 9:10	11 yield,[c] %	11 9:10
1	Pt	TBAP (0.5)	25	2	58	73:27	72	75:25
2	Pt	TBAP (0.1)	25	2	70	78:22	60	73:27
3	Pt	TBAP (0.5)	10	1	17	82:18	26	76:24
4	Pt	TBAP (0.1)	10	1	21	84:16	20	77:23
5	C	TBAP (0.5)	25	2	49	59:41	84	64:36
6	C	TBAP (0.1)	25	2	42	60:40	83	51:49
7	C	TBAP (0.05)	25	2	46	54:46	62	44:56
8	C	TBAP (0.1)	25	1	26	71:29	38	53:47
9	C	TBAP (0.1)	10	1	16	57:43	36	26:74
10	C	TBAP (0.1)	2.5	0.26			5	9:91
11	C	$LiClO_4$ (0.5)	25	2	43	64:36	52	57:43
12	C	$LiClO_4$ (0.1)	25	2	41	61:39	63	59:41

[a] Electrolytic conditions were almost the same as those in footnote *b*, Table I. [b] TBAP: Bu_4NClO_4. [c] A combined yield of **9** and **10**.

compounds and the allylic halides used in the present electrolysis (Table II) indicates that when the allylic halide is more readily reduced than the carbonyl compound as in the case of the electrochemical allylation of acetone or propanal, the allylation takes place preferentially at the more highly substituted carbon terminus of the allylic species. On the other hand, the allylation takes place preferentially at the less highly substituted carbon terminus when the carbonyl compound is more readily reduced than the allylic halide, as in the case of the allylation of benzaldehyde. We therefore assume that a two-electron reduction of the allylic halide generates the allylic carbanion, which adds to a carbonyl compound to afford the product of type A [Scheme II(1)] in the electrochemical allylation of acetone or propanal, while a reduction of benzaldehyde to an anion radical precedes the reduction of the allylic halides in the electrochemical allylation of benzaldehyde, and the anion radical generated reacts in an S_N2 fashion to afford the product of type B [Scheme II(2)].[2] The reported regioselectivity in the allylation of carbonyl compounds with allylic organometallics is similar to the electrochemical allylation of acetone or propanal.

Control of the Regioselectivity in the Electrochemical Allylation. Although the foregoing investigation indicated that the regioselectivity in the present electrochemical allylation depends mainly on a kind of anionic species generated during the electrolysis, we found that other factors also affect the regioselectivity.

Table III summarizes the results of the electrochemical allylation of acetone with allylic halides **1a** or **11** under a variety of electrolytic conditions. No appreciable effect on the regioselectivity was found when we changed the cationic counterion in supporting electrolytes, tetrabutylammonium or lithium cation (entries 5 and 11, 6 and 12). Nor did the alteration of the concentration of the supporting electrolyte affect the regioselectivity significantly when we used a platinum cathode (entries 1 and 2, 3 and 4). When we used a carbon cathode, however, the formation of **10** from **11** slightly increased over the formation of **9** by lowering the concentration of the supporting electrolyte (entries 5–7).

Table IV. Regioselectivity in the Electrochemical Allylation of Acetone with 4a and 5 Using Carbon Cathode[a]

potential, V vs Ag/AgI	4a yield,[b] %	4a 6:(7 + 8)	5 yield,[b] %	5 6:(7 + 8)
−2.0	63	59:41	58	56:44
−1.8	41	69:31	46	50:50
−1.7	40	66:34	35	43:57
−1.6	36	69:31	18	39:61

[a] Electrolytic conditions are almost the same as those indicated in footnote *b*, Table I. [b] A combined yield of **6**, **7**, and **8**.

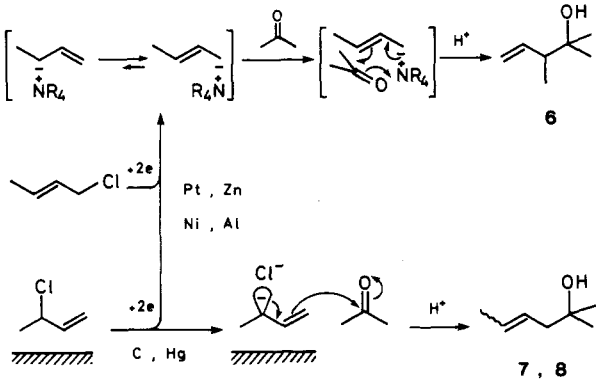
We found that the control of the regioselectivity of the electrochemical allylation can be made more effectively by varying the current density or cathode material. Table III summarizes the results, which indicate that a decreasing current density in the allylation of acetone lead to the enhancement in the product ratio of **10** (type B product in Scheme I) when a carbon cathode is used (entries 8–10). Table IV summarizes similar results obtained in the electrochemical allylation of acetone with **5** under a controlled-potential electrolysis when a carbon cathode is used. Table IV indicates that electrolysis at a less cathodic po-

Table V. Regioselectivity in the Electrochemical Allylation of Acetone with 4a and 5 Using Various Cathode Materials[a]

	4a		5	
cathode	yield,[b] %	6:(7 + 8)	yield,[b] %	6:(7 + 8)
Pt	57	71:29	81	62:38
C	89	60:40	82	29:71
Zn	77	92:8	72	90:10
Ni	61	80:20	76	74:26
Al	54	76:24	31	74:26
Hg	15	87:13	22	45:55

[a] Electrolytic conditions are almost the same as those indicated in footnote *b*, Table I. [b] A combined yield of **6**, **7**, and **8**.

Scheme III

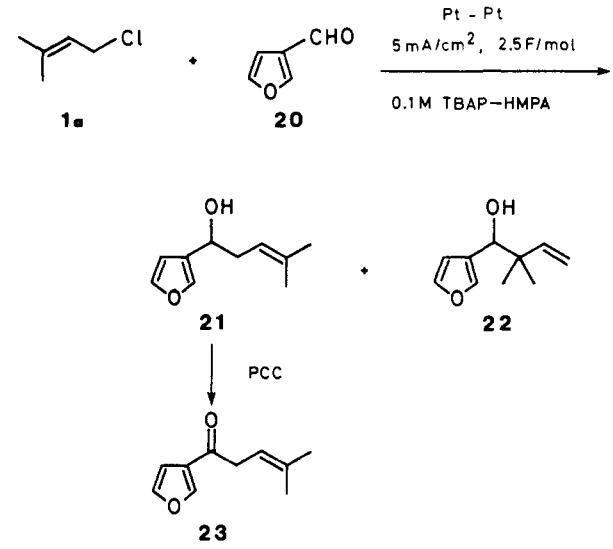


tential[11] leads to an enhanced formation of **7** and **8** (type B products).

Table V summarizes the results on the regioselectivity in the electrochemical allylation of acetone with **4a** or **5** when various cathode materials are used. Nearly the same regioselectivities were obtained from both **4a** and **5** in the electrochemical allylation when zinc is used as the cathode. The allylation thus took place almost exclusively at the more highly substituted carbon terminus to give **6** (type A product). This regioselectivity is nearly the same as that found in the allylations with allylic organometallic reagents. This suggests that an allylic zinc compound such as RZnCl may well be involved as the intermediate in the electrochemical allylation. When we used a platinum, nickel, or aluminum cathode, the allylation at the less highly substituted carbon terminus to give **7** or **8** (type B products) increased to the extent of 20–30%. When we used a carbon cathode instead of a platinum cathode in the electrochemical allylation of acetone with **4a** or **5**, this not only led to an appreciable enhancement of the yield of **7** and **8** at the expense of their regioisomer **6** but also resulted in the reversion of the regioselectivity in the allylation with allylic halide **5** and in the preferential allylation at the less highly substituted carbon terminus to give **7** and **8**. Analogous effects were also observed in the allylation of acetone with **1a** or **11** (entries 1 and 5, 2 and 6, 4 and 9, Table III). When a mercury cathode was used, we obtained results, with regard to the regioselectivity, similar to those when we used carbon cathode.

The effects of the cathode material described above on regioselectivity are not simple and are not easily rationalized. One possible explanation of the results, however, is outlined in Scheme III; allylic halides are reduced on the surface of the electrode in the electrochemical allylation when a carbon or a mercury cathode is used, and the attack of the resulting anion upon a carbonyl carbon may take place with an allylic rearrangement to give **7** and **8** (type B product) before the anion is desorbed from the surface of the electrode. The anion formed on the surface of the electrode may readily be desorbed in a zinc, platinum, nickel, or aluminum cathode. A free anion or an allylic organometallic then attacks the carbonyl carbon to give **6** (type A product) as a major product.

Scheme IV



Synthesis of Egomaketone (23). Our study indicates that allylation takes place preferentially at less highly substituted carbon terminus of the allylic halide when a carbonyl compound is more readily reduced than the allylic halide. We therefore applied this regioselective electrochemical allylation to the synthesis of egomaketone (**23**) carrying the allylic group attached to the furan ring with less highly substituted carbon terminus. The synthesis of **23**, isolated from the essential oil of *Perilla frutescens* Brit,[12] was first achieved by Hoppmann and Weyerstahl[13] and later by four other groups.[14,15] The present electrochemical synthesis of **23** circumvents the tediously lengthy steps previously reported.[13,14]

Cyclic voltammetry indicated that the reduction potentials of **1a** and 3-furancarbaldehyde (**20**) are −2.20 and −1.94 V vs Ag/AgI. A preferential reduction of **20** over allylic halide **1a** is therefore expected to result in the homoallyl alcohol (**21**) as the major product. An electrolysis of a mixture of **1a** and **20** (1:4) at a constant current of 5 mA cm^{-2} (−1.9 V) in fact gave a 62:38 mixture of **21** and **22** in a combined yield of 45% (Scheme IV). When the electrolysis was carried out in the presence of 2 equiv of chlorotrimethylsilane/mol of **1a**, both the yield and the regioselectivity were appreciably improved, to 67% and 74:26. Oxidation of the major isomer (**21**) with pyridinium chlorochromate gave egomaketone **23** in a 80% yield.

Grignard reactions of **1a** or 1-bromo-3-methyl-2-butene (**1b**) with **20** gave a mixture of **21** and **22** in combined yields of 12% (15:85) and <1%.

(11) Cyclic voltammetry of **4a** or **5** did not produce a clear result since the rough surface of the carbon electrode was used as a working electrode. A reduction current gradually flowed from −1.2 V, and a reduction peak was observed at −2.1 V even in HMPA/0.1 M TBAP that contained no substrate. When **4a** was added to the solution, the reduction peak was moved to −2.2 to −2.3 V with an enhanced current. The potentials indicated in Table IV, therefore, may show only relative values rather than correct electrode potentials.

(12) Ueda, T.; Fujita, Y. *Chem. Ind.* **1962**, 1618.
(13) Hoppmann, A.; Weyerstahl, P. *Tetrahedron* **1978**, *34*, 1723.
(14) (a) Gosselin, P.; Masson, S.; Thuillier, A. *J. Org. Chem.* **1979**, *44*, 2807. (b) Ohtsuka, Y.; Sasahara, T.; Oishi, T. *Chem. Pharm. Bull.* **1982**, *30*, 1106. (c) Gast, J. E.; Wilson, B. J. *J. Agric. Food Chem.* **1984**, *32*, 1083.
(15) Sheffy, F. K.; Godschalx, J. P.; Stille, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 4833.

Experimental Section

^{1}H NMR spectra were measured in $CDCl_3$ with a Hitachi R-90H (90 MHz) or a JEOL FX200 spectrometer (200 MHz, tetramethylsilane as an internal reference), and the IR spectra were measured with a Hitachi EPI-22 spectrometer. Mass spectra were measured with a Hitachi RM-50GC or a JEOL JMS-D300 mass spectrometer. Quantitative GC analyses were carried out with a Hitachi 063 instrument and by an internal standard method.

1-Chloro-3-methyl-2-butene (**1a**) was prepared from isoprene and hydrogen chloride[4,16] or from 3-methyl-2-buten-1-ol, methanesulfonyl chloride, and lithium chloride according to reported methods.[17] 3-Chloro-3-methyl-1-butene (**11**) was prepared from isoprene.[5,16] 1-Bromo-3-methyl-2-butene (**1b**) and (*E*)-1-bromo-2-butene (**4b**) were prepared from the corresponding alcohols and phosphorus tribromide by conventional methods. Other allylic halides are commercially available, and most of the halides were purified by repeated distillation. The contents of the corresponding regioisomers in each of the allylic halides **1a**, **1b**, **4a**, **4b**, **5**, and **11** were found to be less than 3% by GC analysis. 3-Furancarbaldehyde (**20**) was prepared according to either a Rosenmund reduction of 3-furancarboxylic acid chloride[18] or an oxidation of 3-furanmethanol with pyridinium chlorochromate.[19] 3-Furanmethanol was prepared by a reduction of 3-furancarboxylic acid[20] with lithium aluminum hydride.[21] Purification of solvents was carried out according to cited methods.[5]

General Procedure for Electrolysis. For the most of the preparative electrolyses, we used a normal undivided cell equipped with a magnetic stirrer and a serum cap for the introduction of nitrogen gas. Most of the electrolyses were carried out at a constant current, using two platinum electrodes (2 × 2 cm^2). A carbon, zinc, nickel, or aluminum plate electrode and a mercury pool electrode were also used as cathodes. Typical procedures for electrolysis are described in footnotes *b* and *c* of Table I. After electrolysis, the reaction mixture was dissolved in diethyl ether, and the solution was washed with thiosulfate solution and then with water, after which it was dried over anhydrous magnesium sulfate. The usual workup of the solution gave a product mixture which was subjected to distillation followed by a preparative GC or TLC to give a pure product. The yields of the products were obtained by GC analysis and by an internal standard method. Regioselectivities of the allylations were calculated from the GC yields of each isomeric product. Spectral data of **6–10** have previously been reported,[5] and those of the other products are recorded below.

2-Methyl-1-phenyl-3-buten-1-ol (12): n^{20}_D 1.5259; IR (neat) 3400, 3040, 1645, 1600, 1500, 1000, 920, 765, 705 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.87 (d, 3 H, J = 7.0 Hz, anti), 1.01 (d, 3 H, J = 6.8 Hz, syn), 2.60 (s, 1 H), 2.25–2.7 (m, 1 H), 4.43 (d, 1 H, J = 8.5 Hz, anti), 4.66 (d, 1 H, J = 5.0 Hz, syn), 5.0–5.7 (m, 2 H), 5.6–6.1 (m, 1 H), 7.35 (s, 5 H); MS, m/z (rel intensity) 160 (M$^+$ − 2, 5), 107 (100), 79 (64), 77 (33), 51 (41). Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.30; H, 8.85. The ratio of syn to anti was calculated to be 54:46 from an area ratio of two doublets at δ 1.01 and 0.87 in the ^{1}H NMR spectrum.

(*E*)-1-Phenyl-3-penten-1-ol (13): n^{20}_D 1.5390; IR (neat) 3400, 3035, 1600, 1495, 1045, 970, 910, 760, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.61 (d, 3 H), 2.03 (br s, 1 H), 2.34 (t, 2 H), 4.57 (t, 1 H), 5.1–5.8 (m, 1 H, 1 H), 7.22 (s, 5 H); MS, m/z (rel intensity) 162 (M$^+$, 1), 160 (5), 107 (100), 79 (67), 77 (40), 51 (21). Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.25; H, 8.65. Irradiation of the doublet at δ 1.61 caused the multiplet at δ 5.1–5.8 to collapse into one doublet (J = 15.0 Hz) and one double–triplet (J = 15.0 Hz, J = 5.6 Hz).

(*Z*)-1-Phenyl-3-penten-1-ol (14): n^{20}_D 1.5358; IR (neat) 3400, 3025, 1600, 1500, 1055, 915, 760, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.53 (d, 3 H), 1.90 (br s, 1 H), 2.47 (t, 2 H), 4.64 (t, 1 H), 5.1–5.9 (m, 1 H, 1 H), 7.24 (s, 5 H); MS, m/z (rel intensity) 162 (M$^+$, 1), 107 (100), 79 (68), 77 (32), 51 (13). Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.69; H, 8.87. Irradiation of the doublet at δ 1.53 caused a collapse of the multiplet at δ 5.1–5.9 into one doublet (J = 11.0 Hz) and one doublet–triplet (J = 11.0 Hz, J = 5.6 Hz).

2,2-Dimethyl-1-phenyl-3-buten-1-ol (15): n^{20}_D 1.5291; IR (neat) 3450, 3030, 1635, 1600, 1495, 1025, 1000, 915 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.96 (s, 3 H), 1.01 (s, 3 H), 2.00 (s, 1 H), 4.43 (s, 1 H), 4.9–5.3 (m, 2 H), 5.7–6.2 (m, 1 H), 7.29 (s, 5 H); MS, m/z (rel intensity) 176 (M$^+$, 0.3), 107 (100), 78 (49), 70 (100). Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.50; H, 9.08.

4-Methyl-1-phenyl-3-penten-1-ol (16): n^{20}_D 1.5392; IR (neat) 3400, 3070, 3040, 1605, 1495, 1055, 760, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.61 (s, 3 H), 1.72 (s, 3 H), 2.02 (s, 1 H), 2.45 (t, 2 H), 4.68 (t, 1 H), 5.17 (t, 1 H), 7.34 (s, 5 H); MS, m/z (rel intensity) 176 (M$^+$, 1), 107 (88), 78 (55), 70 (100). Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.65; H, 9.22.

4-Methyl-5-hexen-3-ol (17): n^{20}_D 1.4356; IR (neat) 3370, 3080, 1640, 1000, 975, 915 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.97 (t, 3 H), 1.03 (d, 3 H), 1.1–1.8 (m, 2 H), 1.99 (br s, 1 H), 2.23 (m, 1 H, anti), 2.30 (m, 1 H, syn), 3.33 (m, 1 H, J = 5.6 Hz, anti), 3.43 (m, 1 H, J = 4.9 Hz, J = 8.1 Hz, syn), 4.9–5.2 (m, 1 H, 1 H), 5.5–6.0 (m, 1 H); MS, m/z (rel intensity) 114 (M$^+$, 3), 59 (86), 56 (100), 41 (30). Anal. Calcd for $C_7H_{14}O$: C, 73.63; H, 12.36. Found: C, 73.95; H, 12.50. The ratio of syn to anti was calculated to be 53:47 by a GC analysis (CW 20M 15%, Uniport B).

(*E*)-5-Hepten-3-ol (18): n^{20}_D 1.4352; IR (neat) 3400, 3020, 1680, 970 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.95 (t, 3 H), 1.69 (d, 3 H), 1.1–1.6 (m, 2 H), 2.0–2.6 (m, 2 H), 3.0 (br s, 1 H), 3.52 (m, 1 H), 5.1–5.9 (m, 1 H, 1 H); MS, m/z (rel intensity) 114 (M$^+$, 4), 59 (79), 56 (100), 41 (41). Anal. Calcd for $C_7H_{14}O$: C, 73.63; H, 12.36. Found: C, 73.44; H, 12.30. The pattern of the absorption of vinylic protons at δ 5.1–5.9 was very similar to that of **13**.

(*Z*)-5-Hepten-3-ol (19): n^{20}_D 1.4335; IR (neat) 3400, 3020, 1660, 740 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.96 (t, 3 H), 1.65 (d, 3 H), 1.1–1.6 (m, 2 H), 2.23 (t, 2 H), 2.9 (br s, 1 H), 3.58 (qi, 1 H), 5.1–5.9 (m, 1 H, 1 H); MS, m/z (rel intensity) 114 (M$^+$, 5), 59 (83), 56 (100). Anal. Calcd for $C_7H_{14}O$: C, 73.63; H, 12.36. Found: C, 73.95; H, 12.20. The pattern of the absorption of vinylic protons at δ 5.1–5.9 was very similar to that of **14**.

Synthesis of Egomaketone (23). A mixture of **1a** (5 mmol) and **20** (20 mmol) in 25 mL of HMPA containing 0.1 M TBAP was electrolyzed at 0 °C with a current density of 5 mA cm^{-2} until 2.5 F of electricity/mol of **1a** has been passed. Electrolysis was carried out under a nitrogen atmosphere with an undivided cell equipped with two platinum electrodes. The usual workup of the solution and a separation of the product mixture by TLC (silica gel, benzene) gave homoallyl alcohols **21** (207 mg) and **22** (118 mg). GC analysis of the crude reaction mixture by an internal standard method showed the ratio of **21** to **22** to be 62:38 while the combined yield was 45%. Similar electrolysis of a mixture of **1a** (5 mmol) and **20** (20 mmol) in the presence of chlorotrimethylsilane (10 mmol) gave a 74:26 mixture of **21** and **22** in a combined yield of 67%. Oxidation of the major isomer **21** (83 mg, 0.5 mmol) with PCC (0.2 g) in 15 mL of dichloromethane gave **23** (66 mg; 0.4 mmol) in a 80% yield.

The reaction of the Grignard reagent derived from **1a** (2 mmol) with **20** (2 mmol) in diethyl ether was found to give a 15:85 mixture of **21** and **22** in a combined yield of 12%. Spectral data of **21–23** are recorded below.

1-(3-Furyl)-4-methyl-3-penten-1-ol (21): n^{20}_D 1.5134; IR (neat) 3350, 1665, 1595, 1500, 1025, 877, 795 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.64 (s, 3 H), 1.73 (s, 3 H), 1.83 (s, 1 H), 2.46 (t, 2 H), 4.66 (t, 1 H), 5.16 (t, 1 H), 6.40 (s, 1 H), 7.38 (s, 1 H, 1 H); MS, m/z (rel intensity) 166 (M$^+$, 6), 148 (2), 97 (100), 70 (73), 69 (38), 55 (19). HRMS calcd for $C_{10}H_{14}O_2$, m/z 166.0993; found, m/z 166.0975.

1-(3-Furyl)-2,2-dimethyl-3-buten-1-ol (22): n^{20}_D 1.4990; IR (neat) 3440, 3080, 1670, 1580, 1500, 1020, 915, 875, 795 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.00 (s, 3 H), 1.03 (s, 3 H), 1.81 (s, 1 H), 4.40 (s, 1 H), 4.9–5.25 (m, 1 H, 1 H), 5.7–6.1 (m, 1 H), 6.37 (s, 1 H), 7.35 (s, 1 H, 1 H); MS, m/z (rel intensity) 166 (M$^+$, 2), 97 (100), 70 (60), 69 (30), 55 (18). HRMS calcd for $C_{10}H_{14}O_2$, m/z 166.0993; found, m/z 166.0997.

(16) Jones, W. J.; Chorley, H. W. T. *J. Chem. Soc.* **1946**, 832.
(17) (a) Collington, E. W.; Meyers, A. I. *J. Org. Chem.* **1971**, *36*, 3044. (b) Meyers, A. I.; Collington, E. W. *Tetrahedron* **1971**, *27*, 5979.
(18) (a) Hayes, K. *J. Am. Chem. Soc.* **1949**, *71*, 2581. (b) Egawa, Y.; Suzuki, M.; Okuda, T. *Chem. Pharm. Bull.* **1963**, *11*, 589.
(19) Corey, E. J.; Suggs, J. W. *Tetrahedron Lett.* **1975**, 2647.
(20) (a) Reichstein, T.; Grussner, A.; Schindler, K.; Hardmeier, E. *Helv. Chim. Acta* **1933**, *16*, 276. (b) Sutter, H. *Justus Liebigs Ann. Chem.* **1932**, *499*, 47.
(21) Sherman, E.; Amstutz, E. D. *J. Am. Chem. Soc.* **1950**, *72*, 2195.

Egomaketone (23): IR (neat) 3140, 1675, 1560, 1508, 1155, 875, 788 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.68 (s, 3 H), 1.76 (s, 3 H), 3.45 (d, 2 H), 5.39 (t, 1 H), 6.77 (s, 1 H), 7.42 (s, 1 H), 8.02 (s, 1 H); MS, m/z (rel intensity) 164 (M^+, 20), 95 (100). HRMS calcd for $C_{10}H_{12}O_2$, m/z 164.0838; found, m/z 164.0857. The spectral data are consistent with those reported.[13-15]

Cyclic Voltammetry. Cyclic voltammetry was carried out with a Nichia HP-E_{500H} potentiostat at a sweep rate of 0.2 V s^{-1} with a platinum disk electrode (1-mm diameter) in HMPA containing 0.1 M Bu_4NClO_4. The potential was measured in volts vs Ag/AgI.

Acknowledgment. This work was supported by a Grand-in-Aid for Scientific Research on Priority Areas (No. 01607001) and a Grand-in-Aid for General Scientific Research (No. 58550553) from the Ministry of Education, Science and Culture, Japan.

Registry No. **1a**, 503-60-6; **1b**, 870-63-3; **4a**, 4894-61-5; **4b**, 29576-14-5; **5**, 563-52-0; **6**, 19781-52-3; **7**, 19639-97-5; **8**, 19639-96-4; **9**, 36934-19-7; **10**, 14908-27-1; **11**, 2190-48-9; **12**, 25201-44-9; **13**, 75851-77-3; **14**, 75851-76-2; **15**, 27644-02-6; **16**, 27644-03-7; **17**, 1838-77-3; **18**, 64884-87-3; **19**, 64884-86-2; **20**, 498-60-2; **21**, 123030-45-5; **22**, 123030-46-6; **23**, 59204-74-9; TBAP, 1923-70-2; HMPA, 680-31-9; Pt, 7440-06-4; C, 7440-44-0; Zn, 7440-66-6; Ni, 7440-02-0; Al, 7429-90-5; Hg, 7439-97-6; $LiClO_4$, 7791-03-9; chlorotrimethylsilane, 75-77-4; pyridinium chlorochromate, 26299-14-9; acetone, 67-64-1; propanal, 123-38-6; benzaldehyde, 100-52-7.

Concerning the Mechanism of the Peterson Olefination Reaction

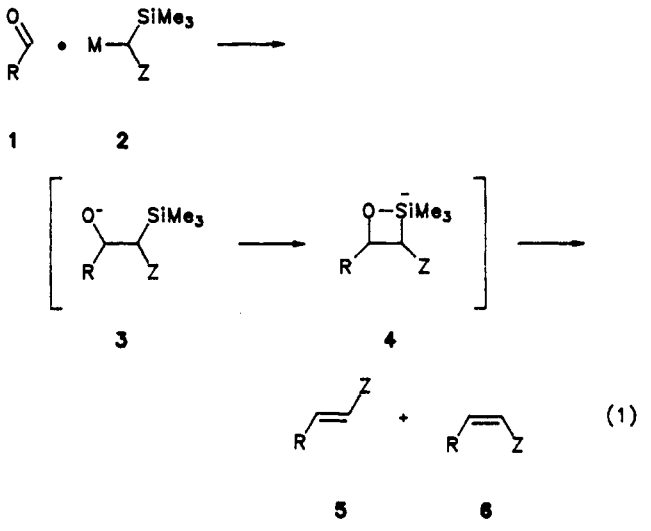
Paul F. Hudrlik,* Edwin L. O. Agwaramgbo,[1] and Anne M. Hudrlik

Department of Chemistry, Howard University, Washington, DC 20059

Received February 3, 1989

The Peterson olefination reaction of benzaldehyde with [bis(trimethylsilyl)methyl]lithium (**2a**) in THF/HMPA gives a 1.4:1 mixture of *trans*- and *cis*-vinylsilanes **5a** and **6a** [PhCH=CHSiMe$_3$] as reported by Gröbel and Seebach. In contrast, treatment of the corresponding β-hydroxysilane **13** [PhCHOHCH(SiMe$_3$)$_2$] with *t*-BuLi in THF/HMPA (or other bases) gives vinylsilane **5a**, which is >90% trans. Since the latter reaction must involve the β-oxidosilane **3a** [PhCHOLiCH(SiMe$_3$)$_2$], these results suggest that the Peterson olefination reaction may proceed, at least in part, by a pathway which does not involve this β-oxidosilane.

The Peterson olefination,[2,3] the reaction of an α-silyl organometallic (usually organolithium) reagent with an aldehyde or ketone to yield an olefin (eq 1), is a useful alternative to the Wittig reaction. When carbanion-stabilizing groups (Z) are not present on the carbon-bearing silicon, β-hydroxysilanes are generally isolated; these can be converted to the olefin by treatment with either acid or base. However, when a carbanion-stabilizing group (Z) is present, the olefin (usually a trans–cis mixture) is generally isolated directly from the reaction; although it has usually not been possible to isolate the β-hydroxysilane,[4] the reaction has generally been assumed to take place via a β-oxidosilane intermediate (e.g. **3**). [By analogy to the Wittig reaction, the reaction pathway has been assumed to involve a 4-centered species (e.g. **4**).] We report here an example of a Peterson olefination which may *not* involve a β-oxidosilane intermediate, since it gives a stereochemical result that is different from that obtained from the corresponding β-oxidosilane generated by other methods.[5]



a: R = Ph, Z = $SiMe_3$, M = Li

b: R = p-tolyl, Z = $SiMe_3$, M = Li

In 1974 Gröbel and Seebach[6] reported the following example of the Peterson olefination reaction: the reaction

(1) Current address: Department of Chemistry, Fitchburg State College, Fitchburg, MA 01420.

(2) (a) Peterson, D. J. *J. Org. Chem.* **1968**, *33*, 780–784. For a review, see: (b) Ager, D. J. *Synthesis* **1984**, 384–398.

(3) The terms "Peterson olefination" and "Peterson reaction" have also been used to describe other olefin-forming elimination reactions of β-functional organosilicon compounds (for example, see ref 2b). We use these terms only for the reaction of an α-silyl organometallic reagent with an aldehyde or ketone to yield an olefin. For studies relating to the mechanism of the Peterson olefination, see the following: (a) Trindle, C.; Hwang, J.-T.; Carey, F. A. *J. Org. Chem.* **1973**, *38*, 2664–2669. (b) Larchevêque, M.; Debal, A. *Chem. Commun.* **1981**, 877–878. (c) Bassindale, A. R.; Ellis, R. J.; Taylor, P. G. *Tetrahedron Lett.* **1984**, *25*, 2705–2708. (d) Boeckman, R. K., Jr.; Chinn, R. L. *Tetrahedron Lett.* **1985**, *26*, 5005–5008. (e) Bassindale, A. R.; Ellis, R. J.; Lau, J. C.-Y.; Taylor, P. G. *J. Chem. Soc., Perkin Trans. 2* **1986**, 593–597. See also: (f) Bassindale, A. R.; Ellis, R. J.; Lau, J. C.-Y.; Taylor, P. G. *Chem. Commun.* **1986**, 98–100.

(4) For an exception, see ref 3b.

(5) Presented in part at the 8th International Symposium on Organosilicon Chemistry, St. Louis, MO, June 11, 1987. See also: Hudrlik, P. F.; Agwaramgbo, E. L. O. In *Silicon Chemistry*; Corey, E. R., Corey, J. Y., Gaspar, P., Eds.; Ellis Horwood, Ltd.: Chichester, 1988; pp 95–104.

(6) (a) Gröbel, B.-T.; Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 83–84. (b) Gröbel, B.-T.; Seebach, D. *Chem. Ber.* **1977**, *110*, 852–866.

0022-3263/89/1954-5613$01.50/0 © 1989 American Chemical Society