(C_2H_5OH) 206 (8,800), 260 (sh), 310 nm (1100); ^{1}H NMR ($CDCl_3$, 60 MHz) δ 6.44 (m, 2 H), 6.31 (m, 1 H), 6.14 (m, 1 H), 5.21 (d, J = 5.3 Hz, 1 H), 3.05 (s, 3 H), 2.97 (s, 3 H).

A crystalline Diels–Alder adduct of **7** was prepared by reaction with maleic anhydride in ether: mp 215.5–216 °C. Anal. Calcd for $C_{13}H_{13}NO_5$: C, 59.31; H, 4.97; N, 5.32. Found: C, 59.16: H, 5.03; N, 5.30.

Preparation of Deuterium-Labeled Arene Oxides 9 and 10. Hydrolysis of the ester of **8**, prepared as described previously,[5] gave acid **8** with the deuterium distribution as indicated in Scheme I. Arene oxides **9** and **10** were prepared from **8** by the same procedures described above for preparation of arene oxides **6** and **7** from **1**.

Aromatization of Arene Oxides 6 and 7. Aromatization of each arene oxide was studied under the conditions indicated in Table I. Buffer systems used were the same as described previously.[5] The time required for complete reaction at room temperature varied from a few hours under strongly acidic conditions to ~2 months at pH 7 or higher. Yields (Table I) were determined by integration of the aromatic region of the 250-MHz ^{1}H NMR spectrum of each product mixture.

Aromatization of 9 and 10. The aromatization procedure for the deuterium-labeled arene oxides was the same as described for the unlabeled materials. Deuterium-labeled amide **13** or **14** was isolated from each reaction, and the deuterium distribution was determined by analysis of the 250-MHz ^{1}H NMR spectrum as described previously.[5] Chemical shift data for the aromatic protons of unlabeled **13** and **14** were as follows: **13** ($CDCl_3$) δ 6.98 (H_5), 7.03 (H_3), 7.49 (H_4), 7.52 (H_6); **14** (CD_3OD) δ 6.97 (H_5), 6.99 (H_3), 7.22 (H_6), 7.34 (H_4).

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Registry No. **1** acid chloride, 95673-76-0; **2**, 95673-77-1; **3**, 95673-78-2; **4**, 95673-79-3; **5**, 95673-80-6; **6**, 95673-81-7; **6**–maleic anhydride Diels–Alder adduct, 95673-86-2; **7**, 95673-82-8; **7**–maleic anhydride Diels–Alder adduct, 95673-85-1; **13**, 65-45-2; **14**, 1778-08-1; 4,5-dibromocyclohex-1-ene-1-carboxamide, 95673-83-9; 4,5-dibromo-N,N-dimethylcyclohex-1-ene-1-carboxamide, 95673-84-0; maleic anhydride, 108-31-6.

Deconjugative Alkylation of α,β-Acetylenic Esters by Electrogenerated Base

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Electrolysis of ethyl propiolate (**1**) and an excess of methyl iodide at a platinum cathode in hexamethylphosphoric triamide (HMPA) or N,N-dimethylformamide (DMF) solution containing tetra-n-butylammonium salt gave the acetylenic esters **2**, **3**, and **4**. Similar electrochemical reactions of α,β-acetylenic esters **2**, **5**, and **9** with methyl iodide took place in good yields to give the corresponding α,α-dimethyl β,γ-acetylenic esters **3** and **4**, **4**, and **10**, respectively. Electrochemical reactions of **5** with ethyl, butyl, and allyl iodides also gave α,α-dialkyl β,γ-acetylenic esters **6**, **7**, and **8**, respectively. These facile deconjugative alkylations appeared to take place by the action of the electrogenerated base (EGB) which was formed by the electrochemical reduction of alkyl iodides. Alkyl iodides worked as both a probasic compound of the EGB and as an electrophile. Reaction pathways of the present deconjugative alkylations are also discussed.

α,β-Unsaturated esters[1,2] or amides[3] are known to give the corresponding β,γ-unsaturated isomers having an alkyl substituent at the α-position when they are treated with a strong base such as lithium diisopropylamide (LDA) and followed by an addition of alkyl halide. However, when such a deconjugative alkylation was applied to α,β-acetylenic acid, a mixture of conjugated allenic and acetylenic acids having an alkyl substituent at the α- and the γ-position, respectively, has been obtained.[4] It has also been reported that a treatment of methyl but-2-ynoate with lithium isopropylcyclohexylamide followed by a protonation gave methyl buta-2,3-dienoate in a 60% yield.[1] Under basic conditions in protic solvents, α,β-acetylenic acid usually gives an equilibrium mixture of α,β-acetylenic, β,γ-acetylenic, and allenic acids,[5] except several examples.[6] Therefore, it is not necessarily easy to prepare the β,γ-acetylenic ester via a deconjugative alkylation of α,β-acetylenic ester by a conventional method.

In our continuing study on the carbon–carbon bond formation by electrochemical reductions of organic halides,[7] we have studied the electrochemical reaction of acetylenic compounds with alkyl halides. We wish to report here that the β,γ-acetylenic ester having two alkyl substituents at the α-position is prepared by the electrochemical reduction of α,β-acetylenic ester in the presence of alkyl iodide.[8] This electrochemical reaction can be carried out under a mild condition without the use of any strong base and, therefore, provides a convenient method for a synthesis of β,γ-acetylenic esters. Synthetic methods for those compounds that have been reported involve an oxidation of alk-3-yn-1-ols with chromic acid,[6b,9] a reaction of propargylmagnesium halide with carbon dioxide,[10] reactions of alkyl diazoacetate with terminal acetylenes[11] or

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Table I. Electrochemical Alkylation of 1 with Methyl Iodide[a]

entry	CH_3I, mmol	supporting electrolyte (M)	current density, A/cm^2	conversion of 1, %	yield, %[b] 2	3	4
1	15	Bu_4NI (0.2)	0.1	76	17	17	50
2	15	Bu_4NBr (0.2)	0.1	73	21	29	25
3	15	Bu_4NClO_4 (0.2)	0.1	73	15	19	21
4	15[c]	Bu_4NI (0.2)	0.1		0	0	0
5	7.5	Bu_4NI (0.2)	0.1	79	22	19	16
6	30	Bu_4NI (0.2)	0.1	72	24	26	24
7	15	Bu_4NI (0.2)	0.05	74	22	26	38
8	15	Bu_4NI (0.2)	0.03	70	40	14	18
9	15[d]	Bu_4NI (0.2)	0.1	89	37	37	7

[a] Electrolysis of 1 (1.5 mmol) and methyl iodide in 15 mL of HMPA was carried out with a platinum cathode. Electricity passed was 5 Faradays per mol of 1. [b] Yields are based on reacted 1. [c] Mercury pool was used as a cathode. [d] Acetonitrile was used as a solvent. Electricity passed was 3 Faradays per mol of 1.

Table II. Electrochemical Alkylation of Ethyl Alk-2-ynoates with Alkyl Iodides[a]

entry	acetylenic ester	alkyl iodide R	solvent	conversion of 2, 5, or 9, %	prod	yield of prod, %[b]
1	2	CH_3	HMPA[c]	49	3	44
					4	28
2	2	CH_3	HMPA	69	3	19
					4	37
3	5	CH_3	HMPA	24	4	83
4	5	CH_3	DMF	47	4	71
5	5	C_2H_5	DMF	68	6	59
6	5	n-C_4H_9	HMPA	61	7	89
7	5	n-C_4H_9	DMF	70	7	82
8	5	$CH_2{=}CHCH_2$	DMF	49	8	74
9	9	CH_3	DMF	54	10	72

[a] Constant current electrolysis (0.1 A/cm^2) of acetylenic ester (1.5 mmol) and alkyl iodides (15 mmol) in 15 mL of HMPA or DMF solution containing 0.2 M Bu_4NI was carried out with a platinum cathode. Electricity passed was 5 Faradays per mol of acetylenic ester. [b] Yields are based on reacted acetylenic ester. [c] Electricity passed was 3.8 Faradays per mol.

with trialkynylboranes,[12] and miscellaneous methods.[13-15]

The present electrochemical reaction was found to be the base-induced reaction which took place by the action of the electrogenerated base (EGB). Although EGBs generated by a cathodic reduction of azobenzene,[16,19d] electron-deficient olefins,[16b,d,e,17] carbonyl compound,[18] oxygen,[19] carbon tetrachloride,[20] phosphonium salt,[16g,21a] ammonium salt,[21b] or 2-pyrrolidone[22] have been reported to promote several organic reactions, the present work is the first example which clearly shows that alkyl halide acts as the precursor to the EGB and that the EGB is effective to promote a deconjugation of the carbon–carbon triple bond of an α,β-acetylenic ester.

Results and Discussion

Electrochemical Reaction of Ethyl Propiolate (1) in the Presence of Methyl Iodide. Electrolysis of ethyl propiolate (1) and a tenfold excess of methyl iodide in hexamethylphosphoric triamide (HMPA) containing 0.2 M tetra-n-butylammonium salt as a supporting electrolyte gave ethyl but-2-ynoate (2), ethyl 2,2-dimethylbut-3-ynoate (3), and ethyl 2,2-dimethylpent-3-ynoate (4). Electrolysis

$$\underset{\mathbf{1}}{HC{\equiv}CCO_2Et} + CH_3I \xrightarrow[\text{HMPA}]{\text{Pt-Pt}} \underset{\mathbf{2}}{CH_3C{\equiv}CCO_2Et} + \underset{\mathbf{3}}{HC{\equiv}CC(CH_3)_2CO_2Et} + \underset{\mathbf{4}}{CH_3C{\equiv}CC(CH_3)_2CO_2Et}$$

was carried out at a constant current in a divided cell using two platinum electrodes. Conversion of 1 and yields of the products under various electrolytic conditions are summarized in Table I. Use of a mercury pool cathode failed to give 2, 3, and 4 (entry 4). Employment of a lower ratio of methyl iodide to 1 lead to a decreased yield of 4 (entry 5). Acetonitrile can be used as a solvent (entry 9). However, since an electrochemical alkylation of acetonitrile giving alkanenitrile took place under the same electrolytic conditions,[23] HMPA or N,N-dimethylformamide (DMF)

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was mainly used as a solvent in the present work.

The electrochemical reaction of **1** with ethyl iodide occurred in the same way to give the alkylated acetylenic esters. Thus, electrolysis of **1** and a tenfold excess of ethyl iodide under the same conditions as those of the entry 1 in Table I gave ethyl pent-2-ynoate (**5**; 31%) and ethyl 2,2-diethylpent-3-ynoate (**6**; 37%) in a 67% conversion of **1**.

$$\mathbf{1} + \mathrm{C_2H_5I} \xrightarrow[\text{HMPA}]{\text{Pt-Pt}} \underset{\mathbf{5}}{\mathrm{C_2H_5C{\equiv}CCO_2Et}} + \underset{\mathbf{6}}{\mathrm{CH_3C{\equiv}CC(C_2H_5)_2CO_2Et}}$$

Electrochemical Deconjugative Dialkylation of α,β-Acetylenic Ester. Electrochemical alkylation of α,β-acetylenic esters having no terminal acetylenic hydrogen also took place to give the β,γ-acetylenic esters containing two alkyl groups at the α-position. It is of synthetic interest that these electrochemical reactions can be carried out under a mild condition without the use of any strong base.

Electrolysis of **2** and a tenfold excess of methyl iodide gave ethyl 2,2-dimethylalk-3-ynoates **3** and **4** in the yields

$$\underset{\mathbf{2}}{\mathrm{CH_3C{\equiv}CCO_2Et}} + \mathrm{CH_3I} \xrightarrow{\text{Pt-Pt}} \mathbf{3} + \mathbf{4}$$

$$\underset{\mathbf{5}}{\mathrm{C_2H_5C{\equiv}CCO_2Et}} + \mathrm{RI} \xrightarrow{\text{Pt-Pt}} \mathrm{CH_3C{\equiv}CC(R)_2CO_2Et}$$

$$\begin{array}{l} \mathbf{4},\ \mathrm{R = CH_3} \\ \mathbf{6},\ \mathrm{R = C_2H_5} \\ \mathbf{7},\ \mathrm{R} = n\text{-}\mathrm{C_4H_9} \\ \mathbf{8},\ \mathrm{R = CH_2{=}CHCH_2} \end{array}$$

$$\underset{\mathbf{9}}{\mathrm{C_4H_9C{\equiv}CCO_2Et}} + \mathrm{CH_3I} \xrightarrow{\text{Pt-Pt}} \underset{\mathbf{10}}{\mathrm{C_3H_7C{\equiv}CC(CH_3)_2CO_2Et}}$$

$$\underset{\mathbf{11}}{\mathrm{(CH_3)_2CHC{\equiv}CCO_2Et}} + \mathrm{CH_3I} \overset{\text{Pt-Pt}}{\not\longrightarrow} \underset{\mathbf{12}}{\mathrm{(CH_3)_2C{=}C{=}C(CH_3)CO_2Et}}$$

shown in Table II. On the other hand, electrochemical reaction of **5** with methyl iodide gave **4**, alone, in a fairly good yield. Ethyl, butyl, and allyl iodides also reacted with **5** to give the corresponding 2,2-dialkylpent-3-ynoates **6**–**8**. Similar electrolysis of ethyl hept-2-ynoate (**9**) and methyl iodide gave ethyl 2,2-dimethylhept-3-ynoate (**10**). The results of these reactions are summarized in Table II. However, the electrochemical reaction of ethyl 4-methylpent-2-ynoate (**11**) with methyl iodide did not give the expected allenic ester **12** and most of **11** was recovered.

Reaction of Acetylenic Esters with Alkyl Halides in the Presence of Base. Since the electrochemical deconjugative alkylation of acetylenic esters seems to be a base-promoted reaction induced by the EGB, the reaction of acetylenic esters was also studied in the presence of conventional strong bases.

In the reaction of **1**, alkylmagnesium halide[24] or *n*-butyllithium[25] has been reported to act as a nucleophile to give 1,2- or 1,4-addition product rather than to act as a base. When LDA was used in the reaction, a preferential formation of the acetylide anion of **1** has been observed.[25] However, the expected product **2** was only produced in a very poor yield when an alkylation of **1** was carried out using LDA and methyl iodide. The reaction of **2** with LDA and methyl iodide, on the other hand, took place smoothly to give ethyl 2-methylbuta-2,3-dienoate (**13**) and **3** in the ratio of 2:1. The similar reaction of **13** using LDA and methyl iodide was found to give **3** in 70% yield. The product **3** was also obtained in 46% yield when *n*-butyllithium was used. In the base-promoted reaction of **2** or

$$\mathbf{2} \xrightarrow[\text{2. CH}_3\text{I}]{\text{1. LDA, }-78\ ^\circ\text{C}} \underset{\mathbf{13}}{\mathrm{CH_2{=}C{=}C(CH_3)CO_2Et}} + \mathbf{3}$$

$$\mathbf{13} \xrightarrow[\text{2. CH}_3\text{I}]{\text{1. LDA, }-78\ ^\circ\text{C}} \mathbf{3}$$

13, the γ-hydrogen was deprotonated by LDA as has been reported in the reactions of crotonate ester,[1,2a] methyl but-2-ynoate,[1] or but-2-ynoic acid.[4] It has also been reported that a deprotonation of a vinylic hydrogen of allenes having no electron-withdrawing group readily occurred by the action of lithium dialkylamide.[26]

Electrogenerated Base. All of the results obtained in the present electrochemical reactions suggest that a strong base comparable in strength with lithium dialkylamide is generated by electrolysis. In our system, the probasic compound must be the alkyl iodide. A voltammetric study showed that the half-wave potentials of **1**, **2**, **13**, and methyl iodide using a dropping mercury electrode were −2.22, −2.35, −2.30, and −1.85 V vs. SCE, respectively. On the other hand, the reduction peaks of **1** and methyl iodide using a platinum disc electrode appeared at the potentials of −2.10 and −1.62 V vs. Ag/AgI. Both results show that methyl iodide is more readily reduced than acetylenic esters. Actually, the potential measured in the constant-current electrolysis of **1** in the presence of methyl iodide was −1.6 V vs. Ag/AgI, which corresponded to the reduction potential of methyl iodide. Accordingly, the EGB in this system is the methyl carbanion which is formed by a two-electron reduction of methyl iodide in aprotic solvent containing $\mathrm{R'_4NX}$ electrolyte. The methyl carbanion with $\mathrm{R'_4N^+}$ counterion readily deprotonates an acidic hydrogen of acetylenic esters to give methane and the carbanions derived from the esters. An evolution of methane gas at a cathode was confirmed to occur in the electrochemical reaction of **1** with methyl iodide. It is of interest that the EGB obtained in the present reaction undergoes the facile deprotonation rather than a Michael addition to a α,β-acetylenic ester. These features and the ease with which an alkylation of the acetylenic ester-derived carbanions occurred may be ascribed to the important role of the countercation $\mathrm{R'_4N^+}$.

Reaction Pathway of the Electrochemical Deconjugative Alkylation. The isolated product **2**, **3**, or **4** corresponds to that in which a one-, three-, four-carbon unit was, respectively, introduced to the starting acetylenic ester **1**. One of the possible products that may be formed by the introduction of the two-carbon unit into **1** is **13**. It could be actually isolated in 14% yield along with **2** (15%), **3** (14%), and **4** (37%) when the electrochemical reaction of **1** with methyl iodide was carried out in DMF solvent instead of HMPA. Furthermore, it was found that the electrolysis of **13** in the presence of methyl iodide gave **3** and **4** in the yield shown in Table III. Since the electrochemical reaction of **2** leading to the products **3** and **4** has already been shown to occur (Table II), we now propose that the present electrochemical reaction of **1** proceeds via the pathway of **1** → **2** → **13** → **3** → **4** as shown in Scheme I. Thus, a deprotonation of an acetylenic hydrogen of **1** by the EGB would give the acetylide anion,

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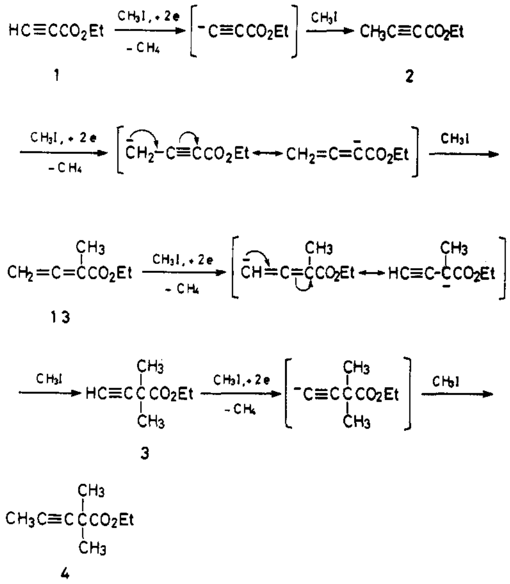
Table III. Electrochemical Alkylation of 13 with Methyl Iodide[a]

entry	electricity, Faraday/mol	conversion of 13, %	yield, %[b] 3	yield, %[b] 4
1	2.5	34	76	23
2	3.8	57	60	40

[a] Constant current electrolysis (0.1 A/cm^2) of 13 (1 mmol) and methyl iodide (15 mmol) in 15 mL of HMPA solution containing 0.2 M Bu_4NI was carried out with a platinum cathode. [b] Yields are based on reacted 13.

Scheme I



which undergoes a nucleophilic attack on methyl iodide to give 2. A γ-hydrogen of 2, a vinylic hydrogen at the γ-position of 13, and an acetylenic hydrogen of 3 are readily deprotonated by the EGB and the resulting carbanions react with methyl iodide to give 13, 3, and 4, respectively.

The total yield of 2, 3, and 4 from 1 and that of 3 and 4 from 2 are nearly the same (Table I and entry 1 in Table II), while the electrochemical reaction of 13 giving 3 and 4 took place in a quantitative yield (Table III). These results suggest that the reaction steps of 1 to 2, 13 to 3, and 3 to 4 were nearly the quantitative reactions but the reaction of 2 to give 13 occurred in a little lower efficiency.

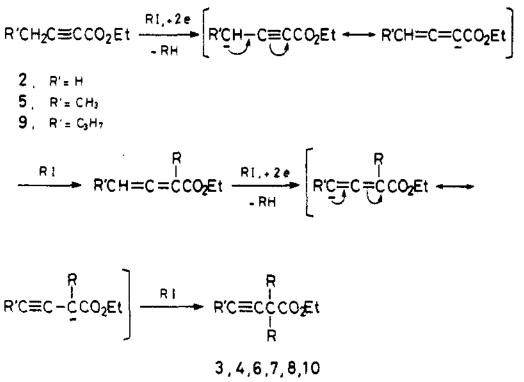
Base-promoted alkylation of α,β-unsaturated esters or amides always occurred exclusively or predominantly at the α-position of the esters or amides.[14] Protonation of the anion derived from methyl but-2-ynoate also took place at the α-position[1] although there is one exception in which γ- and α-alkylations of but-2-ynoic acid occurred in the ratio of 2.2:1.[4] In the present electrochemical reactions of 2 and 13, the alkylation was found to take place exclusively at the α-position.

The electrochemical deconjugative dialkylation of 5 to give 4, 6, 7, or 8 and that of 9 to give 10 proceed in the same ways as that of 1. It is shown in Scheme II. In these cases, ethyl, butyl, or allyl carbanion worked as the EGB. A tertiary hydrogen at the γ-position of α,β-acetylenic ester would be difficult to be deprotonated by the EGB since no alkylation of 11 was observed.

Experimental Section

General Method. Hexamethylphosphoric triamide (HMPA) was dried over calcium hydride and distilled before use under nitrogen at a reduced pressure. DMF was dried over 5-Å molecular sieves and distilled before use. THF was dried over sodium benzophenone ketyl and distilled before use. Alkyl iodides were also distilled before use.

Scheme II



For most of the preparative electrolysis, a normal divided cell equipped with a magnetic stirrer, a reflux condenser, and a serum cap for introduction of a nitrogen gas was used. Electrolysis was carried out at a constant current using a platinum plate (2 × 2 cm^2) as a cathode. Electrolytic conditions in each electrolysis are shown in Tables I–III. After electrolysis, the reaction mixture was dissolved in diethyl ether and the solution was washed with sodium thiosulfate solution and water and dried over magnesium sulfate. The usual workup of the solution gave a product mixture which was subjected to distillation and preparative GLC.

All the products were isolated and purified by distillation and by preparative GLC with a JEOL GC-20K or a Varian Autoprep 700 instrument. IR spectra were obtained with a Hitachi EPI-22 spectrometer, and NMR spectra in CCl_4 were measured with a Hitachi R-22 spectrometer (90 MHz) using Me_4Si as an internal reference. Mass spectra were obtained with a Hitachi RM 50 GC mass spectrometer. Quantitative GLC analyses were carried out with a Hitachi 063 instrument by an internal standard method.

Preparations of α,β-Acetylenic Esters. Ethyl propiolate (1) was prepared by an esterification of propiolic acid which was obtained by an oxidation of propargyl alcohol.[27]

Ethyl but-2-ynoate (2) was prepared by an esterification of but-2-ynoic acid which was prepared from ethyl acetoacetate and hydrazine hydrate by the described procedure.[28]

Ethyl pent-2-ynoate (5) was also prepared from ethyl 3-oxopentanoate and hydrazine hydrate by the described procedure:[28] n_D^{25} 1.4367; IR (neat) 2240, 1715 cm^{-1}; ^1H NMR (CCl_4) δ 1.22 (t, 3 H), 1.29 (t, 3 H), 2.34 (q, 2 H), 4.14 (q, 2 H); mass spectrum, m/e 126 (M^+, 2), 111 (11), 81 (100), 53 (36). Anal. Calcd for $C_7H_{10}O_2$: C, 66.64; H, 7.99. Found: C, 66.36; H, 7.89.

Ethyl hept-2-ynoate (9) was prepared from hexynyllithium and ethyl chloroformate by the described procedure:[29] n_D^{25} 1.4435; IR (neat) 2230, 1710 cm^{-1}; ^1H NMR (CCl_4) δ 0.96 (t, 3 H), 1.29 (t, 3 H), 1.48 (m, 4 H), 2.32 (t, 2 H), 4.14 (q, 2 H); mass spectrum, m/e 154 (M^+, 6), 135 (24), 112 (24), 109 (100), 84 (26), 81 (33), 79 (26), 67 (24), 66 (24). Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.34; H, 9.34.

Ethyl 4-methylpent-2-ynoate (11) was prepared according to the published procedure.[30,31] (Carbethoxymethylene)triphenylphosphorane (13.8 g, 40 mmol)[32] in 100 mL of benzene was added dropwise to isobutyryl chloride (2.1 g, 20 mmol) in benzene (20 mL) during a period of 3 h. After a precipitated solid was removed by filtration, the filtrate was evaporated to give an oily residue. A recrystallization from ethyl acetate–petroleum ether gave (carbethoxyisobutyrylmethylene)triphenylphosphorane (mp 175 °C), which was thoroughly dried and heated at 240–260 °C

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under reduced pressure (16 mmHg). Distillation gave 1.60 g (57%) of **11**: bp 73 °C (16 mmHg); n_D^{25} 1.4370; IR (neat) 2215, 1710 cm^{-1}; ^1H NMR (CCl_4) δ 1.25 (d, 6 H), 1.30 (t, 3 H), 2.69 (m, 1 H), 4.16 (q, 2 H); mass spectrum, *m/e* 140 (M^+, 7), 125 (56), 96 (33), 95 (100), 81 (64), 79 (44), 67 (82), 65 (34), 64 (67), 51 (38). Anal. Calcd for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.23; H, 8.71.

Ethyl 2,2-dimethylbut-3-ynoate (3): n_D^{25} 1.4812; IR (neat) 3290, 2120, 1735, 1265, 1150 cm^{-1}; ^1H NMR (CCl_4) δ 1.31 (t, 3 H), 1.45 (s, 6 H), 2.09 (s, 1 H), 4.19 (q, 2 H); mass spectrum, *m/e* 140 (M^+, 4), 95 (8), 81 (18), 67 (100), 51 (15), 41 (44). Anal. Calcd for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.27; H, 8.67.

Hydrogenation of **3** in an ethanol solution containing Urushibara Ni[33] gave ethyl 2,2-dimethylbutanoate, which was identical with the authentic sample prepared by the described procedure.[34] Ethyl isobutyrate was added dropwise to a THF solution containing 1 equiv of LDA at −78 °C and followed by an addition of 1.2 equiv of ethyl iodide at −78 °C. Usual workup and distillation gave ethyl 2,2-dimethylbutanoate: n_D^{25} 1.3977; IR (neat) 1720, 1150, 1025 cm^{-1}; ^1H NMR (CCl_4) δ 0.82 (t, 3 H), 1.11 (s, 6 H), 1.22 (t, 3 H), 1.54 (q, 2 H), 4.09 (q, 2 H).

Ethyl 2,2-dimethylpent-3-ynoate (4): n_D^{25} 1.4355; IR (neat) 2230, 1735, 1275, 1160 cm^{-1}; ^1H NMR (CCl_4) δ 1.28 (t, 3 H), 1.39 (s, 6 H), 1.80 (s, 3 H), 4.17 (q, 2 H); mass spectrum, *m/e* 154 (M^+, 13), 109 (8), 81 (100), 79 (14), 53 (22), 41 (22). Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.10; H, 9.20.

Hydrogenation of **4** in an ethanol solution containing Raney Ni (W-1) at 20 atm of hydrogen gave ethyl 2,2-dimethylpentanoate which was identical with an authentic sample prepared from the lithium ester enolate of ethyl isobutyrate and propyl bromide.[34] The workup and distillation gave ethyl 2,2-dimethylpentanoate: n_D^{25} 1.4038; IR (neat) 1720, 1150, 1020 cm^{-1}; ^1H NMR (CCl_4) δ 0.90 (t, 3 H), 1.11 (s, 6 H), 1.23 (t, 3 H), 1.30 (m, 4 H), 4.10 (q, 2 H).

Ethyl 2,2-diethylpent-3-ynoate (6): n_D^{25} 1.4407; IR (neat) 2230, 1730, 1230, 1140 cm^{-1}; ^1H NMR (CCl_4) δ 0.90 (t, 6 H), 1.27 (t, 3 H), 1.62 (q, 4 H), 1.85 (s, 3 H), 4.15 (q, 2 H). Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.96. Found: C, 72.56; H, 9.94.

Ethyl 2,2-dibutylpent-3-ynoate (7): n_D^{25} 1.4459; IR (neat) 2230, 1730, 1210, 1035 cm^{-1}; ^1H NMR (CCl_4) δ 0.92 (t, 6 H), 1.28 (t, 3 H), 1.0–1.6 (m, 12 H), 1.85 (s, 3 H), 4.14 (q, 2 H); mass spectrum, *m/e* 193 (M^+ − OEt, 41), 181 (41), 165 (77), 123 (50), 109 (100), 95 (72), 81 (77), 67 (72), 55 (77). Anal. Calcd for $C_{15}H_{26}O_2$: C, 75.58; H, 11.00. Found: C, 75.45; H, 11.02.

Ethyl 2,2-bis(2-propenyl)pent-3-ynoate (8): n_D^{25} 1.4641; IR (neat) 2250, 1740, 1645, 1215 cm^{-1}; ^1H NMR (CCl_4) δ 1.28 (t, 3 H), 1.86 (s, 3 H), 2.41 (m, 4 H), 4.15 (q, 2 H), 5.05 (m, 4 H), 5.6–6.1 (m, 2 H); mass spectrum, *m/e* 206 (M^+, 31), 133 (66) 117 (41), 105 (62), 91 (100), 79 (62), 77 (69), 65 (52), 41 (52), 39 (72). Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 75.90; H, 8.72.

Ethyl 2,2-dimethylhept-3-ynoate (10): n_D^{25} 1.4328; IR (neat) 2230, 1735, 1260, 1150 cm^{-1}; ^1H NMR (CCl_4) δ 1.00 (t, 3 H), 1.26 (t, 3 H), 1.38 (s, 6 H), 1.1–1.8 (m, 2 H), 2.13 (t, 2 H), 4.14 (q, 2 H); mass spectrum, *m/e* 182 (M^+, 2), 154 (32), 109 (100), 67 (87), 55 (34). Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.96. Found: C, 72.45; H, 10.04.

Ethyl 2-methylbuta-2,3-dienoate (13): n_D^{25} 1.4602; IR (neat) 1945, 1715, 1280, 855 cm^{-1}; ^1H NMR (CCl_4) δ 1.27 (t, 3 H), 1.84 (t, 3 H), 4.18 (q, 2 H), 5.03 (q, 2 H); mass spectrum, *m/e* 126 (M^+, 23), 98 (50), 82 (21), 81 (40), 70 (26), 67 (39), 54 (44), 53 (100). Anal. Calcd for $C_7H_{10}O_2$: C, 66.64; H, 7.99. Found: C, 66.82; H, 8.15.

Spectral data of **13** were identical with those of the authentic sample which was prepared from **2** and methyl iodide using LDA.

Reaction of 2 with Methyl Iodide by Use of LDA. To a 0.29 M solution of LDA (80 mmol) in THF (200 mL) and HMPA (80 mL) was added 70 mmol of **2** at −78 °C. After an anion formation was complete (30 min at −78 °C), 90 mmol of methyl iodide was added to the solution at −78 °C. The reaction mixture was allowed to raise gradually to room temperature and treated with water. Ether extraction, drying over magnesium sulfate, and then distillation gave a mixture of **13** and **3** in the ratio of 2:1 (43–46 °C (13 mmHg)). The products **13** and **3** were separated by a preparative GLC (Carbowax 20M, 120 °C). Their structures were determined by spectral data.

Reaction of 13 with Methyl Iodide by Use of LDA or *n*-BuLi. To 1 mmol of LDA in THF (4 mL) containing 1.1 mmol of HMPA was added 1 mmol of **13** at −78 °C. After the solution was stirred for 30 min, 1.3 mmol of methyl iodide was added at −78 °C. The reaction mixture was treated as usual. GLC analysis showed that **3** and unreacted **13** were obtained in the yields of 70% and 9%, respectively. The same reaction of **13** using *n*-butyllithium as a base gave **3** and recovered **13** in the yields of 46% and 22%, respectively.

Voltammetry. Half-wave potentials were measured in 0.1 M Bu_4NI–DMF by using a dropping mercury electrode with a Yanagimoto V-8 instrument. Half-wave potentials ($E_{1/2}$) of acetylenic ester and alkyl iodides are as follows: **1**, −2.22 V; **2**, −2.35 V; **5**, −2.30 V; **13**, −2.30 V; CH_3I, −1.85 V; C_2H_5I, −2.00 V; C_4H_9I, −2.05 V vs. SCE. Since the present preparative electrolysis was carried by using a platinum cathode, the reduction potential was also measured at a platinum disc electrode (1-mm diameter). Cyclic voltammetry in 0.1 M Bu_4NClO_4–DMF at 0.1 V s^{-1} showed that the reduction potential (E_p) of **1** was −1.77 and −2.10 V, whereas that of methyl iodide was −1.62 V vs. Ag/AgI.

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Registry No. **1**, 623-47-2; **2**, 4341-76-8; **3**, 74460-84-7; **4**, 74460-85-8; **5**, 55314-57-3; **6**, 74460-86-9; **7**, 74460-87-0; **8**, 74460-88-1; **9**, 16930-95-3; **10**, 74460-89-2; **11**, 38491-47-3; **12**, 5717-30-6; **13**, 5717-41-9; methyl iodide, 74-88-4; ethyl iodide, 75-03-6; butyl iodide, 542-69-8; allyl iodide, 556-56-9; ethyl 3-oxopentanoate, 4949-44-4; hydrazine, 302-01-2; 1-hexynyllithium, 17689-03-1; ethyl chloroformate, 541-41-3; (carbethoxymethylene)triphenylphosphorane, 1099-45-2; isobutyryl chloride, 79-30-1; (carbethoxyisobutyrylmethylene)triphenylphosphorane, 95648-08-1.

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