moved in vacuo, and water (30 mL) was added to the residue obtained. This mixture was extracted with *n*-hexane (3 × 50 mL) to remove the *l*-menthol. The water layer was subsequently concentrated in vacuo, and the residue was dissolved in CH_2Cl_2 (50 mL). Finally the solution was dried over Na_2SO_4, and the solvent was evaporated under reduced pressure to afford 0.29 g (100%) of pure (*R*)-(+)-**16** as a colorless oil: Kugelrohr distillation yielded 0.25 g (87%) (*R*)-(+)-**16** (bp 130 °C/15 mmHg; lit.[26] bp 132 °C/18 mmHg); $[\alpha]^{20}{}_D$ +13.2° (*c* 1.0, MeOH); $[\alpha]^{20}{}_D$ +13.6° (*c* 3.3, MeOH); (*S*)-(−)-**16** (lit.[26] $[\alpha]^{20}{}_D$ −14.4° (*c* 0.6, MeOH)); ^1H NMR ($CDCl_3$, ppm) 0.92 (d, 3 H, *J* = 6 Hz), 1.50–1.62 (m, 2 H), 1.70 (m, 1 H), 3.42–3.84 (m, 4 H), 4.20 (br s, 2 H); ^{13}C NMR ($CDCl_3$, ppm) 17.06 (q), 33.77 (d), 37.20 (t), 60.53 (t), 67.77 (t).

(*R*)-(+)-**16** obtained from (+)-**14** via this procedure: $[\alpha]^{20}{}_D$ +13.4° (*c* 0.6, MeOH). (*S*)-(−)-**16** obtained from (−)-**14** via this procedure: $[\alpha]^{20}{}_D$ −13.1° (*c* 3.3, MeOH). Further spectral data of (*R*)- and (*S*)-**16** were identical with those reported.[26]

(*R*)-2-Methylbutane-1,4-diol Dibenzoate ((*R*)-18). To a solution of 0.50 g (4.8 mmol) of (*R*)-**16** in 10 mL of dry pyridine was added 1.35 g (9.6 mmol) of benzoyl chloride. This mixture was heated at reflux for 6 h. After the mixture was cooled to room temperature, ether (50 mL) was added, and the solution was washed with saturated aqueous ammonium chloride (2 × 50 mL) and water (50 mL) and subsequently concentrated in vacuo. The yellow residue was purified by Kugelrohr distillation to afford 1.3 g (88%) of (*R*)-2-methylbutane-1,4-diol dibenzoate as a colorless oil: bp 190 °C (0.1 mmHg); $[\alpha]^{20}{}_{589}$ −9.5° (*c* 2.0, $CHCl_3$).

(*S*)-2-Methylbutane-1,4-diol Dibenzoate ((*S*)-18): $[\alpha]^{20}{}_{589}$ +9.4° (*c* 2.0, $CHCl_3$). (*R*,*S*)-2-Methylbutane-1,4-diol dibenzoate was prepared similarly from (*R*,*S*)-2-methylbutane-1,4-diol (bp 132 °C/15 mmHg):[27] IR (neat) 3100, 2900, 1710 cm^{-1}; ^1H NMR ($CDCl_3$, ppm) 0.95 (d, 3 H, *J* = 8 Hz), 1.44–1.62 (m, 1 H), 1.79–1.91 (m, 1 H), 1.97–2.10 (m, 1 H), 4.08 (d, 2 H, *J* = 6 Hz), 4.21–4.36 (m, 2 H), 7.19–7.91 (m, 10 H); ^{13}C NMR $CDCl_3$, ppm) 16.60 (q), 29.91 (d), 32.20 (t), 62.66 (t), 69.07 (t), 128.08 (d), 129.22 (d), 129.93 (d), 132.61 (d), 166.15 (s).

Enantiomeric Excess Determination. (*R*,*S*)-2-Methylbutane-1,4-diol dibenzoate was separated into its enantiomers by HPLC on a Chiracel OB (Daicel) column using 2-propanol/*n*-hexane (5:95) as the eluents. The dibenzoates from (*R*)- and (*S*)-**16**, prepared via the routes outlined above, were single enantiomers with different retention times indicating an enantiomeric excess ≥98%. The minor enantiomer of artificial mixtures of either (*R*)- or (*S*)-**18** with <5% of its antipode was readily detected.

Supplementary Material Available: Tables of final atomic positional parameters, atomic thermal parameters, and bond distances and angles from the X-ray determination of **17** (7 pages). Ordering information is given on any current masthead page.

Electroorganic Synthesis Using Organometals. 1. Cathodic Ester Formation from Alcohols and Alkyl Halides in the Presence of Catalytic Amounts of Iron(0) Pentacarbonyl at Atmospheric Pressure of Carbon Monoxide

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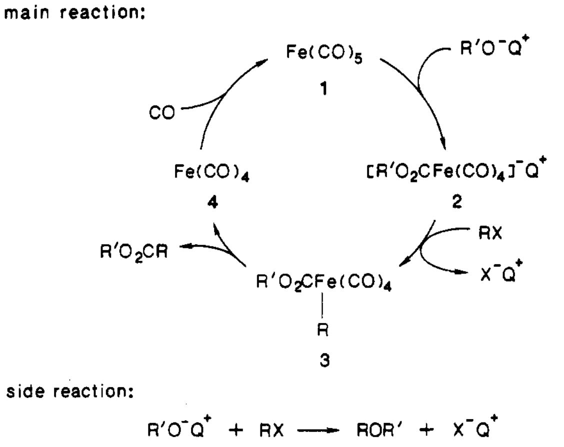
Electrochemical reactions of carbon monoxide are interesting from the aspect of C_1 electrochemistry and provide new synthetic routes to useful organic compounds.[1] However, carbon monoxide must be used at high pressures of 10 to >100 atmospheres in most cases, since its solubility in solvents used for the electrolytic solutions is generally low. This is a very serious problem not only in designing practical cells but also in performing electrolysis. Yet, Cipris[2] reported that satisfactory results in the formation of methyl formate and *N*-alkylformamides could be obtained by cathodically reducing methanol to methoxide ion in the absence and presence of amines, respectively, at ca. 100 atm of carbon monoxide pressure. Equivalent reactions would be also performed by using bases other than the electrogenerated methoxide ion.

Scheme I



Q^+: K^+, Na^+ (in chemical method); quaternary ammonium cations (in cathodic method)

Table I. Reaction of Electrogenerated Methoxide Ion Having Tetramethylammonium Counterion with Benzyl Bromide and Various Amounts of Iron(0) Pentacarbonyl under a Nitrogen Atmosphere

$Fe(CO)_5$, equiv[a]	methyl phenylacetate yield, %
0.05	16
0.1	32
0.2	56
0.5	92
1.0	93

[a] To benzyl bromide used.

It is well-known that the troublesome use of high pressures can be avoided by using transition metal carbonyls and carbon monoxide at atmospheric pressure.[3]

For example, Tustin and Hembre[4] reported the formation of methyl benzoate (22–68% yield) and methyl benzyl ether (5–38%) from the reaction of benzyl halides with potassium carbonate, iron(0) pentacarbonyl, and carbon monoxide at atmospheric pressure and room temperature in methanol [Scheme I ($Q^+ = K^+$)].

There has been an increasing interest in the utilization of anionic species with onium counterions in organic synthesis, since their reactivities are sometimes quite different from those of the same kind of anions with alkali metal counterions.[5] However, the preparation of the anionic species with onium counterions from the corresponding

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Table II. Reaction of Alkoxide Ions Generated Cathodically and Chemically with Alkyl Halides in the Presence of a Catalytic Amount of Iron(0) Pentacarbonyl under Carbon Monoxide Atmosphere

		product yields, %				
		cathodic method			chemical method[a]	
RX	R'OH	Q^+Y^-	RCOOR'	ROR'	RCOOR'	ROR'
$C_6H_5CH_2Br$	MeOH	$Me_4N^+Cl^-$	96	tr	66	4
$C_6H_5CH_2Br$	MeOH	$Bu_4N^+ClO_4^-$	80	–[b]		
$C_6H_5CH_2Br$	EtOH	$Me_4N^+Cl^-$	67	–[b]	45	–[b]
$C_6H_5CH_2Br$	^iPrOH	$Et_4N^+Cl^-$	28	–[b]	tr	–[b]
p-CH_3-$C_6H_4CH_2Br$	MeOH	$Me_4N^+Cl^-$	62	7	47	20
p-Br-$C_6H_4CH_2Br$	MeOH	$Me_4N^+Cl^-$	49	15	46	16
$C_6H_5CH{=}CHCH_2Br$	MeOH	$Me_4N^+Cl^-$	49	–[b]		
$C_6H_5CH{=}CHCH_2Br$	MeOH	$Bu_4N^+ClO_4^-$	50	–[b]		
MeI	MeOH	$Me_4N^+Cl^-$	100	0	82	–[b]

[a] Using NaH. [b] Not analyzed quantitatively.

alkali metal salts is often troublesome and not practical, since the use of expensive crown ethers or onium fluorides is required. While phase-transfer catalysts enhance the nucleophilicity of the anionic moiety, they are not always applicable, owing to their instability under heating[6] and the impossibility of realizing anhydrous conditions. On the other hand, cathodic reduction of organic compounds easily generates anionic species with onium counterions when onium salts are used as supporting electrolytes. Previously,[7] it was confirmed that cathodically generated anionic species from alcohols, carboxylic acids, amides, and carbon acids in nonaqueous cathodic solutions containing quaternary ammonium salts as the supporting electrolytes are much more reactive bases than those generated with alkali metal salt electrolytes.

In this work, the reaction of electrogenerated methoxide ion with benzyl bromide was first examined in the presence of various amounts of iron(0) pentacarbonyl under a nitrogen atmosphere. After the electrolysis of a methanol solution of tetramethylammonium chloride, benzyl bromide and iron(0) pentacarbonyl were added to the catholyte, and the resulting reaction mixture was stirred at room temperature overnight. Two faradays per mole of benzyl bromide were consumed. The relationship between the yield of methyl phenylacetate formed and the amount of iron(0) pentacarbonyl used is shown in Table I and indicates that three of the five carbon monoxide ligands may be stoichiometrically incorporated into the reaction.

A satisfactory yield of methyl phenylacetate could be obtained by using 0.1 equiv of iron(0) pentacarbonyl per equiv of benzyl bromide. As shown in Table II, the reaction could be performed with a variety of alcohols (R'OH), alkyl halides (RX), and quaternary ammonium salt supporting electrolytes (Q^+Y^-). The desired and byproducts were the corresponding esters (RCOOR') and ethers (ROR'), respectively. The latter seems to be formed by the reaction of the alkoxides with the alkyl halides. For comparison, sodium hydride was used to generate alkoxide ions under otherwise similar conditions. As expected, yields of the esters in the cathodic method were higher than those in the chemical one.[8] Furthermore it is notable that the formation of the byproducts (ethers) was somewhat suppressed in the cathodic method. Methyl iodide gave methyl acetate in high yield, while less reactive alkyl iodides such as butyl and octyl iodides did not give the corresponding methyl esters at all.

Experimental Section

A typical procedure is as follows: The catholyte and anolyte were 10-mL methanol solutions containing tetramethylammonium chloride (0.4 M). Platinum plates (6 cm^2) were used as the cathode and anode. The electrolysis was carried out galvanostatically (1 A dm^{-2}) by passing 2 mF of electricity at room temperature under a nitrogen atmosphere. After the electrolysis, 0.015 mL (0.1 mmol) of iron(0) pentacarbonyl was added to the catholyte. The resulting mixture was stirred for 15 min, and then 0.12 mL (1 mmol) of benzyl bromide was added, and the reaction mixture was stirred vigorously overnight under atmospheric carbon monoxide. The reaction mixture was poured into a solution of 1% hydrochloric acid and extracted three times with ether. The combined extract was washed with a solution (20 mL) of 1% sodium hydrogen carbonate and water, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. Yields were determined by GLC (polyethylene glycol 20 M, 140 °C). Methyl phenylacetate and methyl benzyl ether were isolated by TLC (silica gel, hexane–ethyl acetate, 8:1) and analyzed qualitatively by ^1H NMR spectroscopy.

In the chemical method, a sodium methoxide solution was prepared by stirring a mixture of 0.08 g (1 mmol) of sodium hydride and 10 mL of methanol under a nitrogen atmosphere until hydrogen evolution ceased. Successive procedures for the reaction of benzyl bromide with carbon monoxide in the presence of iron(0) pentacarbonyl were similar to those in the cathodic method described above.

Registry No. $C_6H_5CH_2COOMe$, 101-41-7; $C_6H_5CH_2COOEt$, 101-97-3; $C_6H_5CH_2COO^iPr$, 4861-85-2; p-CH_3-$C_6H_4CH_2COOMe$, 23786-13-2; p-Br-$C_6H_4CH_2COOMe$, 41841-16-1; $C_6H_5CH{=}CHCH_2COOMe$, 24891-74-5; MeCOOMe, 79-20-9; $C_6H_5CH_2Br$, 100-39-0; p-CH_3-$C_6H_4CH_2Br$, 104-81-4; p-Br-$C_6H_4CH_2Br$, 589-15-1; $C_6H_5CH{=}CHCH_2Br$, 4392-24-9; MeI, 74-88-4; MeOH, 67-56-1; EtOH, 64-17-5; ^iPrOH, 67-63-0; $Me_4N^+Cl^-$, 75-57-0; $Bu_4N^+ClO_4^-$, 1923-70-2; $Et_4N^+Cl^-$, 56-34-8; p-Br-$C_6H_4CH_2OMe$, 1515-88-4; p-CH_3-$C_6H_4CH_2OMe$, 3395-88-8; $Fe(CO)_5$, 13463-40-6; $C_6H_5CH_2OMe$, 538-86-3.

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[8] A similar result was reported in another chemical method[4] using potassium carbonate instead of sodium hydride.

Synthesis of α- and β-Nicotyrines. Use of Phenyl Vinyl Sulfoxide as a Masked Equivalent of Acetylene Dipolarophile

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Over the years, α-nicotyrine (**1**) and its positional isomer β-nicotyrine (**2**) have been studied extensively for their insecticidal properties.[1-3] β-Nicotyrine, an alkaloid com-

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