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]
$C_6H_5CH_2Br$	^{i}PrOH	$Et_4N^+Cl^-$	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.

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

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; ^{i}PrOH, 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.

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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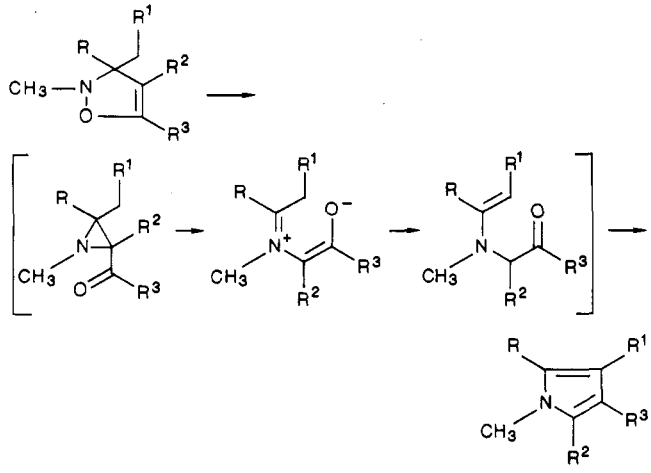
0022-3263/89/1954-2476$01.50/0

Scheme I

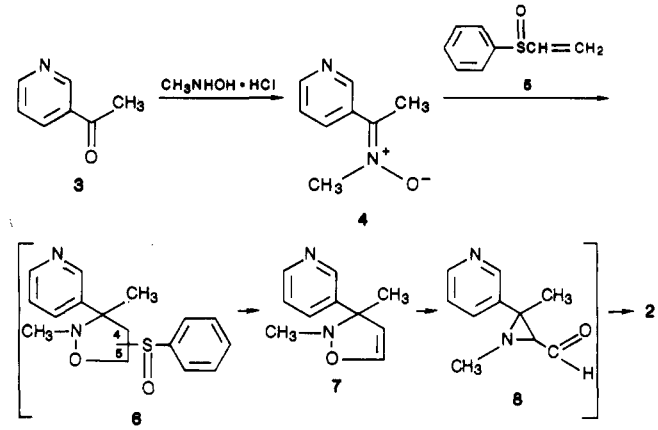


monly found in *Nicotiana* sp.,[4] when applied to human skin or fabric, exerted potent activity against *Aedes aegypti* and *Anopheles quadrimaculatus*.[3]

1 2

Presently available procedures[5-13] for the preparation of β-nicotyrine utilize only nicotine as starting material and are handicapped by either low yields or the necessity of using harsh experimental conditions (temperatures of over 300 °C in sealed or electrically heated reaction vessels). Such conditions would undoubtedly limit the scale of the synthesis. Therefore, new methods for the preparation of β-nicotyrine continue to be of interest, especially in connection with the synthesis of other biologically active ring-substituted analogues of **2**.[14] One attractive option in this direction is to pursue the Δ^4-isoxazoline → pyrrole rearrangement. This rearrangement (Scheme I) is reported to proceed readily and under comparatively mild reaction conditions.[15]

Scheme II



In previous studies,[16] we have described the synthesis of a number of biologically active isoxazolidine derivatives via a 1,3-dipolar cycloaddition reaction of α-substituted ketonitrones with various dienophiles. When acetylene precursors are used as dipolarophiles in place of alkenes, the corresponding Δ^4-isoxazolines are obtained.[17] Our continuing interest in 1,3-dipolar cycloaddition reactions prompted us to explore the possibility to synthesize α- and β-nicotyrines via Δ^4-isoxazoline → pyrrole rearrangement. The results of our efforts are presented in this paper.

The synthesis of β-nicotyrine (**2**) is depicted in Scheme II. Commercially available 3-acetylpyridine (**3**) is treated with *N*-methylhydroxylamine hydrochloride to give nitrone **4**. In order to obtain the corresponding Δ^4-isoxazoline intermediate **7** we decided to use phenyl vinyl sulfoxide (**5**) as a masked equivalent for an acetylene dipolarophile in the 1,3-dipolar cycloaddition reaction with **4**. It was anticipated that by being an efficient leaving group, the phenylsulfinyl function of **6** would undergo cis elimination[18] to form the Δ^4-isoxazoline compound **7**, which in turn will rearrange to generate β-nicotyrine (**2**) through the intermediacy of the aziridine species **8**. Indeed, when phenyl vinyl sulfoxide was heated with nitrone **4** in toluene solution, β-nicotyrine was obtained in one step in what amounts to an overall two-step synthesis of **2**.

α-Nicotyrine (**1**) was synthesized in a similar manner with 2-acetylpyridine as starting material. The preparation of the corresponding nitrone, the *N*-methyl-1-(2-

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pyridyl)ethanimine *N*-oxide (first step) and its reaction with phenyl vinyl sulfoxide followed by rearrangement to 1 (second step) were carried out in 80 and 29% yields, respectively.

In summary, we have demonstrated that phenyl vinyl sulfoxide may be used successfully as a masked equivalent of acetylene dipolarophile in 1,3-dipolar cycloaddition reactions. As an example, the synthesis of α- and β-nicotyrines was accomplished in only two steps by using a Δ^4-isoxazoline → pyrrole rearrangement. This new synthetic approach should allow for the convenient preparation of other biologically active ring-substituted congeners of the insecticidal β-nicotyrine. Previous synthetic approaches toward β-nicotyrine were limited to the use of nicotine only as starting material.

Experimental Section

Melting points were determined on a Thomas-Hoover melting point apparatus and are uncorrected. The infrared (IR) spectra were obtained on a Nicolet MX-1 FT spectrometer as KBr disks. The proton nuclear magnetic resonance (^{1}H NMR) spectra were taken on a Varian EM-360A (60 MHz) spectrometer with tetramethylsilane as an internal standard; the 200-MHz ^{1}H NMR spectra were recorded on a Bruker-IBM 200 SY Fourier transform spectrometer with the same internal standard. All spectra were consistent with the assigned structures. Elemental analyses were within the acceptable limits of 0.4% of theory.

***N*-Methyl-1-(3-pyridyl)ethanimine *N*-Oxide (4).** A suspension of 16.20 g (0.134 mol) of 3-acetylpyridine (3), 13.0 g (0.156 mol) of *N*-methylhydroxylamine hydrochloride, and 25.61 g (0.312 mol) of sodium acetate in 80 mL of ethanol was stirred at ambient temperature for 24 h under a nitrogen atmosphere. The suspension was diluted with 500 mL of water, basified with potassium carbonate, and extracted with chloroform (4 × 150 mL). The combined organic extract was dried ($MgSO_4$) and concentrated. The residual oil crystallized from ethyl acetate–hexane (1:1), yielding 16.83 g (84%) of nitrone 4, mp 77–80 °C. IR (KBr, cm^{-1}): 3032 (m), 1578 (m), 1417 (m), 1254 (s), 1128 (m), 1084 (m), 1059 (m), 1025 (m), 894 (m), 826 (m), 719 (m). ^{1}H NMR (200 MHz, $CDCl_3$): 2.45 (d, 3 H, J = 1.3 Hz, CCH_3), 3.69 (d, 3 H, J = 1.3 Hz, NCH_3), 7.37–7.43 (m, 1 H), 7.58–7.64 (m, 1 H), 8.56–8.58 (m, 1 H), 8.64–8.67 (1, 1 H) ppm. Anal. Calcd for $C_8H_{10}N_2O$: C, 63.98; H, 6.71; N, 18.65. Found: C, 63.85; H, 6.67; N, 18.57.

***N*-Methyl-1-(2-pyridyl)ethanimine *N*-oxide** was prepared from 2-acetylpyridine by a procedure similar to that described for 4. Yield 80%, mp 61-64 °C (ether). IR (KBr, cm^{-1}): 1584 (s), 1565 (m), 1473 (m), 1436 (m), 1290 (m), 1255 (s), 1237 (s), 1100 (m), 1084 (m), 989 (m), 788 (m). ^{1}H NMR (200 MHz, $CDCl_3$): 2.47 (d, 3 H, J = 1.3 Hz, CCH_3), 3.83 (d, 3 H, J = 1.3 Hz, NCH_3), 6.71–6.82 (m, 2 H), 7.73–7.82 (m, 1 H), 8.66–8.69 (m, 1 H) ppm. Anal. Calcd for $C_8H_{10}N_2O$: C, 63.98; H, 6.71; N, 18.65. Found: C, 63.48; H, 6.73; N, 18.49.

3-(1-Methylpyrrol-2-yl)pyridine (β-Nicotyrine) (2). Under a nitrogen atmosphere, a solution of 4.59 g (30.6 mmol) of *N*-methyl-1-(3-pyridyl)ethanimine *N*-oxide (4) and 5.25 g (34.6 mmol) of phenyl vinyl sulfoxide in 50 mL of toluene was heated to reflux and stirred for 6 h. Upon cooling to ambient temperature, the reaction mixture was filtered through a short column of neutral silica gel with ethyl acetate as eluent. The filtrate was concentrated, and the residual oil was flash chromatographed on neutral silica gel with a 2:3 mixture of ethyl acetate–hexane as eluent; 0.66 g (14%) of 2 was obtained after bulb-to-bulb distillation, bp 78–80 °C (0.15 mm).

The tartrate dihydrate salt of 2 was also prepared, mp 101–104 °C (water) (lit[21] mp 105–106 °C). IR (KBr, cm^{-1}): 3320 (s), 3270 (s), 2800–2560 (br, m), 1736 (m), 1563 (s), 1415 (m), 1306 (s), 1263 (s), 1215 (m), 1136 (m), 1076 (m), 1068 (m), 738 (m), 682 (s). ^{1}H NMR (200 MHz, DMSO-d_6): 3.22–3.59 (m, 4 H, 2 H_2O), 3.68 (s, 3 H, NCH_3), 4.32 (s, 2 H, 2 CH), 4.84–5.47 (m, 2 H, 2 OH), 6.12–6.30 (m, 2 H), 6.91–6.95 (m, 1 H), 7.44–7.51 (m, 1 H), 7.85–7.93 (m, 1 H), 8.49–8.68 (m, 2 H), 12.31–13.33 (m, 2 H, 2 CO_2H) ppm. Anal. Calcd for $C_{14}H_{20}N_2O_8$: C, 48.84; H, 5.85; N, 8.14. Found: C, 48.81; H, 5.79; N, 8.12.

2-(1-Methylpyrrol-2-yl)pyridine (α-nicotyrine) (1) was obtained from *N*-methyl-1-(2-pyridyl)ethanimine *N*-oxide and phenyl vinyl sulfoxide. Yield 29%, bp 106–110 °C (1.1 mm) [lit.[21] bp 150 °C (22 mm)]. IR (NaCl plate, cm^{-1}): 1589 (s), 1560 (m), 1542 (m), 1490 (s), 1455 (s,) 1437 (m), 1318 (m), 773 (m), 720 (m). ^{1}H NMR (200 MHz, $CDCl_3$): 3.98 (s, 3 H, NCH_3), 6.15–6.18 (m, 1 H), 6.54–6.57 (m, 1 H), 6.70–6.72 (m, 1 H), 7.00–7.07 (m, 1 H), 7.48–7.65 (m, 2 H), 8.53 (d, 1 H, J = 4.4 Hz) ppm. Anal. Calcd for $C_{10}H_{10}N_2$: C, 75.92; H, 6.37; N, 17.71. Found: C, 75.98; H, 6.43; N, 17.71.

Registry No. 1, 525-75-7; 2, 487-19-4; 2·tartrate, 4315-37-1; 3, 350-03-8; 4, 119908-57-5; 5, 20451-53-0; 2-acetylpyridine, 1122-62-9; *N*-methyl-1-(2-pyridyl)ethanimine *N*-oxide, 119908-58-6.

(21) *Merck Index*, 10th ed.; Merck & Co., Inc.: Rahway, NJ, 1983, p 936.

Microbial Transformations. 10. Evidence for a Carbon-Radical Intermediate in the Biohydroxylations Achieved by the Fungus *Beauveria sulfurescens*

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The ability of cytochrome P-450 type enzymes to achieve selective hydroxylation of nonactivated carbon atoms is one of the most fascinating aspects of enzymatic reactions that the organic chemist can use to perform chemical synthesis. These reactions are, up to now, almost impossible to achieve with acceptable selectivities and yields by using chemical methods.[1] However, the mechanism involved in these reactions is still not unambiguously established. In particular, a widespread belief exists that the cytochrome P-450 enzymes perform their hydroxylation reactions with retention of configuration at the hydroxylated carbon, perhaps by way of a direct insertion into a C–H bond achieved by a so-called "oxenoid" species. However, some apparently puzzling results have been obtained recently as far as the stereochemical outcome of these processes is concerned. Starting from prochiral or enantiomerically pure compounds, four possibilities can be selected out of these results: (a) The observed reactions are highly stereoselective, as far as the abstracted hydrogen is concerned, and lead to one single stereoisomeric alcohol with retention of configuration. (b) The hydrogen abstraction is stereoselective, but the reaction leads to a mixture of stereoisomeric alcohols. (c) The reaction involves nonstereoselective hydrogen abstraction but leads to one single stereoisomeric alcohol. (d) No stereoselectivity is observed in either the hydrogen abstraction or the formation of the resulting alcohols. Case a has been observed in numerous studies[2] as, for instance, by Corey et

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