was 2:3 in absolute alcohol and 3:2 in 85% alcohol.[15] We have noted little difference in the relative amounts of the two products in these two solvents (Table I). In both, **2a** was found to predominate, the product ratio being in each case about 3:2.

It is noteworthy that the diphenoxy compound **3a** was the major product in those reactions in which sodium phenoxide was insoluble in the solvent (ether and benzene).[16] However, when the phenol salt was soluble (alcoholic and tetrahydrofuran solvents), the principal product was the monophenoxy compound **2a**. It appears that the protic or aprotic nature of the solvent is relatively unimportant. The possibility that these solvent effects might be attributed to differences in the concentration of phenoxide ion available for reaction with bromo ester **1** was considered. The slow addition of phenoxide to **1** had no significant effect upon the ratio of **2a** to **3a**. At the present, the solvent effects noted remain unexplained.

Experimental Section

Melting points were determined on a Fisher–Johns hot state and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Infrared spectra were recorded on a Beckman IR-8 spectrophotometer, and nuclear magnetic resonance spectra in carbon tetrachloride (unless otherwise specified) on a Varian T-60 spectrometer. Chemical shifts are expressed in parts per million downfield relative to TMS (δ scale). Glpc analyses were made with an Aerograph A-90-P gas chromatograph using an 8 ft × 0.25 in. column of 20% SE-30 on Chromosorb W at a column temperature of 115°, programmed to 225°, using helium (100 cc/min) as carrier.

Materials.—Reagent grade diethyl bromomalonate (**1**) (Aldrich Chemical) was redistilled, bp 54–55° (0.08 mm), n^{20}D 1.4512. Glpc analysis showed less than 2% dibromo compound. Sodium phenoxide (>97% purity) was prepared as previously described.[17] Reagent grade solvents were employed. Tetrahydrofuran was distilled from lithium aluminum hydride and stored under nitrogen.

Diethyl monophenoxymalonate (2a) was isolated in 50% yield from the reaction of sodium phenoxide and diethyl chloromalonate in alcohol. The crude reaction product (glpc analysis) contained 88% of **2a**. The recrystallized product (alcohol) melted at 51–52° (lit.[7] mp 52–53°): ir (KBr) 1755, 1220, 1100, and 1030 cm^{-1}; nmr 7.05 (m, 5 H), 5.03 (s, 1 H), 4.19 (q, 4 H), and 1.25 (t, 6 H).

Diethyl diphenoxymalonate (3a) was prepared from dibromomalonate and sodium phenoxide in alcohol: bp 158–161° (0.3 mm) [lit.[18] bp 250–260° (60 mm)]; n^{24}D 1.5272; ir (neat) 1765, 1220, 1080, 755, and 695 cm^{-1}; nmr 7.22 (m, 10 H), 4.17 (q, 4 H), and 1.03 (t, 6 H).

Anal. Calcd for $C_{19}H_{20}O_6$: C, 66.27; H, 5.85. Found: C, 66.21; H, 5.92.

Tetraethyl 1,1,2,2-ethanetetracarboxylate (4) was obtained from **1** and sodium diethyl phosphite as previously described,[3] mp 76° (lit.[3] mp 76°).

Tetraethyl ethenetetracarboxylate (5) was synthesized according to the published procedure,[6] mp 52–53° (lit.[6] mp 52.5–53°).

Diethyl α-bromophenoxymalonate (7) was isolated in 10% yield from equimolar quantities of dibromomalonate and sodium phenoxide in alcohol: bp 135–137° (0.4 mm); n^{24}D 1.5125; ir (neat) 2985, 1750, 1230, 1135, 1050, 1020, 760, and 695 cm^{-1}; nmr 7.22 (m, 5 H), 4.30 (q, 4 H), and 1.27 (t, 6 H).

Anal. Calcd for $C_{13}H_{15}BrO_5$: C, 47.15; H, 4.57. Found: C, 47.40; H, 4.83.

Hexaethyl 1,1,2,2,3,3-propanehexacarboxylate (8) was prepared in 38% yield from dibromomalonate and diethyl sodiomalonate in alcohol: bp 178–179° (0.1 mm) [lit.[18] bp 246° (15 mm)]; n^{26}D 1.4532; ir (CCl_4) 1745, 1245, 1115, and 1040 cm^{-1}; nmr ($CDCl_3$) 4.30 (q, 12 H), 4.33 (s, 2 H), and 1.30 (t, 18 H). The quartet and singlet were superimposed; the quartet and triplet peaks appeared as unresolved doublets.

Anal. Calcd for $C_{21}H_{32}O_{12}$: C, 52.94; H, 6.77. Found: C, 53.08; H, 6.91.

Reaction of Diethyl Bromomalonate (1) with Sodium Phenoxide.—In a typical run, 7.2 g (0.030 mol) of **1** in 10 ml of solvent was added in one portion with stirring to 3.5 g (0.030 mol) of sodium phenoxide in 40 ml of solvent. The addition of **1** resulted in an exothermic reaction with rapid precipitation of sodium bromide. (In ether solvent, it was necessary to moderate the reaction by dropwise addition of **1**.) The mixture was heated (bath 90–95°) and stirred under nitrogen for 1 hr.

In the case of water-soluble solvents, the solvent was removed under reduced pressure (water aspirator) at 100°, and the residue was treated with water. With solvents insoluble in water, the reaction mixture was diluted directly with water. The organic materials were isolated in the usual manner by extraction with ether. The crude oily product (6–7.5 g) was dissolved in toluene for glpc analysis. Components were identified by retention times and by admixture with authentic materials. Weight ratios of the substances present were established from peak areas, with appropriate modifications based upon preliminary studies with known mixtures.

The dropwise addition (20-min period) of sodium phenoxide in 40 ml of alcohol to **1** dissolved in 15 ml of solvent afforded a crude product which contained **2a** and **3a** in the ratio of 3:1.8.

Registry No.—**1**, 685-87-0; **2a**, 4525-70-6; **3a**, 4525-71-7; **7**, 31593-62-1; **8**, 5435-96-1; sodium phenoxide, 139-02-6.

(15) The analytical methods employed were based upon differential solublilities of the substituted malonic acids and preferential amide formation. In our hands, using known mixtures of **2a** and **3a**, these methods gave unsatisfactory results (unpublished observations).

(16) Compound **3a** was reported to be the principal product of the reaction in xylene and in absence of solvent.[7] We assume that similar conditions existed in these reactions.

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An Improved Method of Resolution of Coniine[1]

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The hemlock alkaloids[2] constitute a large group of optically active 2-substituted piperidines of which coniine (2-*n*-propylpiperidine) is the major representative. Considerable current interest in these substances is due not only to the conflicting hypotheses for their biogenesis[3-5] but also to the recent extension of methods of optical rotatory dispersion and circular dichroism to the determination of their absolute configuration.[6-9]

The need for large quantities of optically pure enantiomers of coniine revealed that the published method[10]

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of optical resolution using tartaric acid was unsatisfactory for several reasons. These included the difficulty of inducing crystallization without seed crystals of the authentic diastereoisomeric salt, the need for many repeated crystallizations of the acid tartrate to achieve purity, and the low yield of the final resolved base.

The method of optical resolution was therefore reinvestigated using a number of optically active acids[11] as resolving agents. Mandelic acid was found to be the reagent of choice. Under the correct experimental conditions, crystallization commenced after a few minutes to give the less soluble diastereoisomeric salt in excellent yield. It had constant melting point and rotation after only one crystallization. The use of (−)- and (+)-mandelic acid,[12] respectively, afforded the enantiomeric salts, (+)-coniine (−)-mandelate and (−)-coniine (+)-mandelate, without difficulty. When basified, these yielded (+)- and (−)-coniine, shown to be both chemically and optically homogeneous by gas–liquid partition chromatographic techniques.[13]

The method is readily applicable to other alkyl-substituted piperidines; *e.g.*, 2-methyl- and 2-ethylpiperidine[9,14] were resolved into optically pure enantiomers in an equally facile manner.

Experimental Section

Resolution of (±)-Coniine.—Racemic coniine (6.35 g) and (−)-mandelic acid (7.6 g, 1 mol) were mixed with cooling, and methanol (20 ml) was added. The mixture was warmed to effect solution, cooled, and then treated with anhydrous ether (45 ml). After a few minutes crystals began to separate. After 22 hr at 0° the crystals were collected and dried *in vacuo*, yield 5.68 g. Recrystallization was effected by dissolving the salt (10 g) in dry methanol (30 ml) and adding dry ether (60 ml). After 22 hr at 0° the (+)-coniine (−)-mandelate was collected and dried *in vacuo* (9.1 g): feathery needles; mp 127.5°; $[\alpha]^{22}D$ −59.0° (*c* 0.5, 95% EtOH). Both the melting point and the rotation were unchanged by further recrystallization. The filtrate A was treated as described below.

Anal. Calcd for $C_{16}H_{25}NO_3$: C, 68.79; H, 9.02; N, 5.01. Found: C, 68.59; H, 8.95; N, 5.25.

The above salt (9.0 g) in water (75 ml) was cooled in ice and basified slowly with solid potassium hydroxide. The liberated (+)-coniine was extracted thrice with ether and the combined extracts were dried over powdered KOH. The ether was evaporated *in vacuo* at room temperature. The residual (+)-coniine distilled (yield 3.25 g, 86% based on salt) at 65–66° (20 mm): bp 164° (755 mm) [lit.[10,15] bp 64° (18 mm), 166–166.5° (1 atm)]; $[\alpha]^{25}D$ +8.4° (*c* 4.0, $CHCl_3$) [lit.[16] $[\alpha]^{25}D$ +8.0° (*c* 4.0, $CHCl_3$)]; $[\alpha]^{23}D$ +14.6° (neat) [lit.[10] $[\alpha]^{19}D$ +15.2° (neat)]. Glpc on a Carbowax column at 125° showed a single peak.

The ether–methanol filtrate A on evaporation of the solvents gave a syrupy residue which was dissolved in water and basified as above, yielding a base, bp 164–165° (755 mm), rich in (−)-coniine. This base (6.35 g) and (+)-mandelic acid (7.6 g, 1 mol) were dissolved in dry methanol (20 ml) and the warm solution was treated with dry ether (50 ml). After 22 hr at 0° the crystals of (−)-coniine (+)-mandelate were collected, dried (9.1 g), and recrystallized from methanol (27 ml) by careful addition of ether (54 ml), giving the pure salt, mp 127° (7.7 g), as feathery needles, $[\alpha]^{23}D$ +60.0° (*c* 0.5, 95% EtOH), unchanged by further crystallization. The same salt was obtained from racemic coniine and (+)-mandelic acid.

Anal. Calcd for $C_{16}H_{25}NO_3$: C, 68.79; H, 9.02; N, 5.01. Found: C, 68.71; H, 9.12; N, 5.34.

This salt (61.4 g) in water (300 ml) was cooled in ice and basified as described above, giving (−)-coniine distilling at 165° (756 mm) (24.4 g, 87% yield based on salt): $[\alpha]^{23}D$ −8.1° (*c* 4.0, $CHCl_3$), $[\alpha]^{23}D$ −14.2° (neat), $[\alpha]^{23}D$ −5.0° (*c* 2.0, 95% EtOH). Glpc on a Carbowax column at 125° showed a single peak.

2-Methyl- and 2-Ethylpiperidine.—Application of the same method gave (+)-2-methylpiperidine, $[\alpha]^{25}D$ +7.2° (*c* 6, 95% ethanol) [lit.[17] $[\alpha]^{15}D$ +31.2° (neat)], and (+)-2-ethylpiperidine, $[\alpha]^{25}D$ +6.6° (*c* 14, 95% ethanol) [lit.[18] $[\alpha]^{23}D$ +21.3° (neat)].

Registry No.—(±)-Coniine, 3238-60-6; (+)-coniine, 458-88-8; (−)-coniine, 5985-99-9; (+)-coniine (−)-mandelate, 31608-17-0; (−)-coniine (+)-mandelate, 31608-18-1.

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Catalyzed Hydrogenation of Tolane and Stilbene in Liquid Ammonia

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The reaction between the ammoniated electron and liquid ammonia has been shown to be reversible in the

$$e^-_{am} + NH_3 \rightleftharpoons NH_2^- + {}^1/_2H_2 \quad (1)$$

presence of certain solid catalysts and to have an equilibrium constant of 5×10^4 $atm^{1/2}$ at room temperature.[1] There are many compounds which are highly reactive toward ammoniated electrons[2] but which are essentially inert toward molecular hydrogen. We therefore felt that a liquid ammonia system containing potassium amide and a catalyst for reaction 1 might serve as a useful medium for "activating" molecular hydrogen. We have studied the reactions of stilbene (1,2-diphenylethylene) and tolane (diphenylacetylene) in this system at −45° and at room temperature. Both compounds are known to undergo reduction by the ammoniated electron[2-4] and we hoped that reaction sequences such as the following (illustrated by stilbene) would take place.

$$H_2 + 2NH_2^- \rightleftharpoons 2e^-_{am} + 2NH_3$$

$$2e^-_{am} + C_6H_5CHCHC_6H_5 + 2NH_3 \longrightarrow C_6H_5CH_2CH_2C_6H_5 + 2NH_2^-$$

Experimental Section

Reagents.—Hydrogen and argon (99.999%, Pacific Oxygen Supply) were used without further purification. Potassium metal (Baker and Adamson) was sealed in glass tubing and purified by heating it under high vacuum and allowing it to flow through constrictions in the glass. This procedure removed oil

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