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°; $[\alpha]^{22}\text{D}$ −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)]; $[\alpha]^{25}\text{D}$ +8.4° (*c* 4.0, $CHCl_3$) [lit.[16] $[\alpha]^{25}\text{D}$ +8.0° (*c* 4.0, $CHCl_3$)]; $[\alpha]^{23}\text{D}$ +14.6° (neat) [lit.[10] $[\alpha]^{19}\text{D}$ +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, $[\alpha]^{23}\text{D}$ +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): $[\alpha]^{23}\text{D}$ −8.1° (*c* 4.0, $CHCl_3$), $[\alpha]^{23}\text{D}$ −14.2° (neat), $[\alpha]^{23}\text{D}$ −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, $[\alpha]^{25}\text{D}$ +7.2° (*c* 6, 95% ethanol) [lit.[17] $[\alpha]^{15}\text{D}$ +31.2° (neat)], and (+)-2-ethylpiperidine, $[\alpha]^{25}\text{D}$ +6.6° (*c* 14, 95% ethanol) [lit.[18] $[\alpha]^{23}\text{D}$ +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

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

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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TABLE I

REACTION OF HYDROGEN WITH TOLANE AND STILBENE. DATA FOR FLOW EXPERIMENTS AT −45°

Substrate (mmol)	Fe_2O_3 catalyst, mg	KNH_2, mmol	Gas	Reaction time, hr	Conversion, %		Substrate recovered, %
					$(C_6H_5CH)_2$	$(C_6H_5CH_2)_2$	
$(C_6H_5C)_2$ (5.3)	120	30	Ar	20	0	0	96
$(C_6H_5C)_2$ (3.1)	114	0	H_2	25	0	0	98
$(C_6H_5C)_2$ (2.25)	0	20	H_2	160	0	0	98
$(C_6H_5C)_2$ (2.2)	123	50	H_2	8	3	26	68
$(C_6H_5C)_2$ (1.34)	190[a]	100	H_2	27	4	30	63
$(C_6H_5CH)_2$ (1.8)	232	48	Ar	6		0	97
$(C_6H_5CH)_2$ (1.0)	219	0	H_2	8		0	97
$(C_6H_5CH)_2$ (3.7)	0	45	H_2	8		0	98
$(C_6H_5CH)_2$ (3.1)	240	60	H_2	12		80	16
$(C_6H_5CH)_2$ (2.1)	198[a]	100	H_2	20		90	6

[a] $Fe(NO_3)_3 \cdot 9H_2O$ used instead of Fe_2O_3.

and oxides from the metal, and allowed easy weighing and transferring of the metal.

Either Fe_2O_3 (Baker Analyzed Reagent) or $Fe(NO_3)_3 \cdot 9H_2O$ (Baker and Adamson) was reduced to a black solid by potassium in liquid ammonia, and used as the catalyst for reaction 1. Tolane (mp 61–62°, Aldrich Chemicals) and *trans*-stilbene (mp 123–124°, Eastman Organic Chemicals) were checked for purity by gas chromatography (Aerograph Model A-90-P) and found to be at least 99% pure. Deoxybenzoin (mp 54–56°, Matheson Coleman and Bell) was used without further purification. For simplicity, *trans*-stilbene is referred to as stilbene throughout this paper.

Products were separated by gas chromatography (G.E.-S.F.-96 silicone on firebrick at 190°), isolated in small traps, and identified by mass spectrometry and (in the case of solids) by melting point determination.

Flow Experiments.—The apparatus used for bubbling hydrogen through liquid ammonia systems was essentially a gas-washing bottle (with a sintered-glass bubbler) fitted with inlet and outlet stopcocks, a side arm, and an O-ring joint for closure. Traces of oil and water were removed from the hydrogen by passing it through a −78° trap attached to the inlet to the reaction vessel. The flow rate of hydrogen was estimated by use of a mineral oil bubbler attached to the outlet. The substance to be hydrogenated was placed in the side arm. The solid catalyst [Fe_2O_3 or $Fe(NO_3)_3 \cdot 9H_2O$] and a glass-enclosed magnetic stirring bar were placed in the vessel. About 100 ml of ammonia was distilled into the apparatus from a reservoir containing sodium and sodium amide. The apparatus was placed in a dewar of liquid ammonia, which maintained a temperature of approximately −45°. The bubbling of hydrogen through the ammonia was started; the O-ring joint was disconnected, and the glass tubing containing the purified potassium was dropped into the vessel. The joint was then quickly reconnected, and shortly thereafter the hydrogen flow was stopped. When the blue color of the solvated electron disappeared, the compound to be reduced was introduced from the side arm. Magnetic stirring was begun, and the hydrogen bubbling was resumed.

To stop the reaction, the vessel was opened and ammonium chloride or water was added to destroy the potassium amide. The ammonia was allowed to evaporate and the products and the iron catalyst were washed with 25 ml of water into a sintered glass crucible and dried by suction filtration. The solids were extracted with 25 ml of benzene. A portion of the benzene solution was passed through a gas chromatograph, and each fraction was collected in a small trap for identification by mass spectrometry and melting point determination.

The reactivity of tolane and stilbene toward hydrogen in the absence of potassium amide was determined. The catalyst was prepared as above (*i.e.*, reduced by potassium) and was then washed free of potassium amide by repeatedly decanting the supernatant solution into a side arm and distilling the ammonia back onto the catalyst. The rest of the procedure was unchanged. Similarly, the reduction was attempted without the iron catalyst. The formation of potassium amide was catalyzed by an iron wire which was subsequently removed with a magnet.

Static Experiments.—Experiments employing static pressures of hydrogen or argon were performed at −45° in a 500-ml round-bottomed flask. After introduction of a stirring bar, the catalyst, and a piece of pure potassium, ammonia was distilled into the vessel. The metal–ammonia solution was allowed to decompose, and the solution was degassed by freezing, pumping, and thawing. An accurately known quantity (8–10 mmol) of hydrogen or argon was admitted, and the compound to be reduced was introduced from a side arm. The products were separated and identified as described above.

Room-Temperature Experiments.—To determine the reactivity of stilbene (or tolane) toward potassium amide at room temperature in the absence of solid catalyst and hydrogen, a solution of 3–5 mmol of stilbene (or tolane) in 50 ml of ammonia containing a 10- to 30-fold excess of potassium amide was prepared in a sealed tube fitted with a breakable tip.[5] To stop the reaction, water was distilled into the tube through a stopcock attached to the breakable tip. The ammonia was allowed to evaporate; the tube was broken in a nitrogen glove bag, and the product was transferred to a funnel and washed with 10 ml of degassed distilled water. The white, air-sensitive solid product was then dried at room temperature under high vacuum. The melting point, mass spectrum, and Nujol mull infrared spectrum were obtained.

Results and Discussion

The results of experiments at −45° are shown in Table I. Reduction of stilbene produced 1,2-diphenylethane in high yield. Reduction of tolane produced stilbene and 1,2-diphenylethane (the major product). In the absence of either hydrogen, potassium amide, or catalyst, no products were formed.

We verified that hydrogen is consumed when tolane is reduced. When 8–10 mmol of hydrogen was added at −45° to an apparatus containing a degassed ammonia solution of substrate, iron catalyst, and potassium amide, a significant amount (up to 0.81 mmol/mmol of substrate) of hydrogen was consumed. In the absence of potassium amide, however, only a small amount (0.03 mmol/mmol of substrate) of hydrogen was apparently consumed. Because of the difficulty in measuring the difference between relatively large amounts of hydrogen, this latter quantity is probably not significant.

Walling and Bollyky have shown that the homogeneous *tert*-butoxide-catalyzed hydrogenation of benzophenone probably involves an H^- intermediate.[6] In view of the fact that hydrogen shows some acidity in potassium amide–ammonia solutions,[7] a similar homogeneous mechanism is conceivable for our reductions. However, because we found that a heterogeneous catalyst was required for our reductions, such a mechanism is ruled out.

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Olefins are the principal products when iron is used as a heterogeneous catalyst for the gas-phase hydrogenation of acetylenes.[8] In our study of the reduction of tolane, the alkane was the principal product even before half of the tolane had reacted. This result indicates that stilbene is reduced to the alkane more rapidly than tolane is reduced to stilbene (see Table I). Strel'tsova and Shilov found the same order of reactivity when acidic protons were available (in the form of ethanol, for example) in the homogeneous reduction of tolane by potassium metal in liquid ammonia.[3] In fact, they obtained no stilbene as product. However, in the absence of a protonic acid, Strel'tsova and Shilov found the reverse order of reactivity. When half the stoichiometric amount of sodium for reduction of tolane to 1,2-diphenylethane was used, essentially pure stilbene was isolated as the reduction product. The highly basic, heterogeneous system of this study surprisingly yields the same kinetic results as the relatively acidic homogeneous system of Strel'tsova and Shilov.

Our experimental results can be explained in terms of a mechanism involving the following initial steps. (Here M denotes an active site on the catalyst surface.)

$$2M + H_2 \rightleftharpoons 2MH$$

$$MH + NH_2^- \rightleftharpoons M^- + NH_3$$

$$M^- \rightleftharpoons M + e^-_{am}$$

Subsequent steps are uncertain; they involve the substrate accepting either electrons (from M^- or e^-_{am}) or hydride ions (from MH^-). Although the details of the overall hydrogenation mechanism are uncertain, it seems very likely that the first two steps (the bonding of hydrogen atoms to the catalyst and the formation of a low oxidation state form of the catalyst) are involved.[9,10] The facts that these steps fit the data for *both* reaction 1 and the hydrogenations and that they are common features of hydrogenations[9] are strong support for their involvement.

When stilbene was treated at room temperature for several days with a potassium amide–ammonia solution, a product was obtained that had a melting point of 57–60° and a mass spectrum with a parent peak at *m/e* 195 (corresponding to the elemental composition $C_{14}H_{13}N$) and a fragmentation pattern suggesting either phenylbenzyl ketimine (1,2-diphenylethylidenimine) or 2,3-diphenylaziridine.[11] Because of the air sensitivity of the compound, only poor infrared spectra could be obtained. There definitely was no strong absorption in the 1100–1250-cm^{-1} region; therefore the compound cannot be 2,3-diphenylaziridine, which does have a very strong absorption at about 1200 cm^{-1}.[12] Phenylbenzyl ketimine (mp 57°) is known to decompose in air to produce deoxybenzoin.[13] When our product was allowed to come in contact with the atmosphere, a material was obtained which gave a mass spectrum identical with that obtained for a known sample of deoxybenzoin.

A similar analysis of the product obtained from the room temperature reaction of tolane with excess potassium amide in liquid ammonia again showed the product to be phenylbenzyl ketimine. When liquid ammonia solutions containing stilbene or tolane and potassium amide were allowed to stand for several weeks, high molecular weight species were produced in yields of a few per cent. These compounds were observed in the gas chromatogram of the product mixture, but were not identified.

The reaction of tolane with ammonia to form phenylbenzyl ketimine is a straightforward example of a well-known class of reactions: the reaction of acetylenes with amines and ammonia to form ketimines.[14] The reaction of stilbene with a potassium amide–ammonia solution to form phenylbenzyl ketimine probably involves the addition of ammonia to form 1,2-diphenyl-1-aminoethane followed by the amide-catalyzed conversion of the amine to the ketimine.[15] The high molecular weight products found when tolane and stilbene were in potassium amide-ammonia solutions for several weeks may be due to polymerization of the unstable phenylbenzyl ketimine or to the base-catalyzed polymerization of unreacted stilbene or tolane in a reaction similar to the polymerization of styrene in ammonia.[16]

Registry No.—Tolane, 501-65-5; stilbene, 103-30-0.

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Halogen Metathesis in Fluorocarbons

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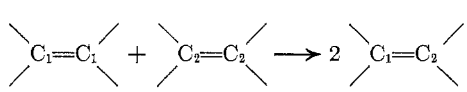
The term metathesis is used in chemistry to describe reactions in which groups are transferred or exchanged. In organic chemistry the term has been used for the "scrambling" of olefins[1,2] and acetylenes[3] or the radical abstraction of an atom to produce another radical. The term can be extended to other reactions where there is a transfer of groups. For example, the transfer of chlorine in fluorocarbons fits within this defi-



$$R'\cdot + RX \longrightarrow R'X + R\cdot$$

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