dichloroethane was conducted. As may be seen in Table I (compare the penultimate and last entries), the presence of 1 equiv of crown ether reduces the coupling reaction rate to approximately 10% of its value under comparable conditions in the absence of crown ether. Therefore, azo coupling reactions are subject to the same aryldiazonium ion deactivation recently reported for thermolysis,[13] photolysis,[14] and nucleophilic replacement of para substituents[15] in crown ether complexed arenediazonium ions. Despite the rate retardation, reaction of **1** with excess **2** in the presence of 1 equiv of 18-crown-6 produced a quantitative yield of azo coupling product **4**.

An attempt to study the azo coupling of *p-tert*-butylbenzenediazonium chloride (produced from the corresponding diazonium tetrafluoroborate and tetraethylammonium chloride) with excess **2** in 1,2-dichloroethane at 25.0 °C was unsuccessful. Curved kinetic plots and lower (60%) yields of azo coupling product **4** were observed.

Experimental Section

Materials. *p-tert*-Butylbenzenediazonium tetrafluoroborate was prepared according to Swain.[8] *N*,*N*-Dimethylaniline was Mallinckrodt reagent grade and was used directly. Gold label 1,2-dichloroethane from Aldrich was used directly. 4-Deuterio-*N*,*N*-dimethylaniline (98% D) was obtained from Merck.

An authentic sample of 4-*tert*-butyl-4′-*N*,*N*-dimethylaminoazobenzene (**4**) was prepared by dropwise addition of a solution of **1** (1 equiv) in 1,2-dichloroethane to a solution of **2** (1 equiv) and pyridine (10 equiv) in the same solvent. The reaction mixture was stirred at room temperature for 45 min. The solvent was removed in vacuo and diethyl ether was added to the residue. Filtration afforded a yellow ether layer which was reduced in volume and absorbed onto a small amount of basic alumina which was then placed on top of a basic alumina column (Fisher-Brockman activity I). The column was eluted with diethyl ether and the product was isolated by removal of diethyl ether in vacuo from the eluent. A yellow-orange solid was obtained: mp 137–137.5 °C; λ_{max} (1,2-dichloroethane) 410 (log ϵ 5.44). Anal. Calcd for $C_{18}H_{23}N_3$: C, 76.87; H, 8.18; N, 14.95. Found (Chemalytics, Tempe, Arizona): C, 76.62; H, 8.18; N, 14.85.

Kinetic Measurements. The rates of reaction of **1** and **2** or **3** were determined under pseudo-first-order conditions (**2** or **3** in at least a tenfold excess) by measuring the rate of appearance of absorption at 410 nm due to **4**. Plots of log ($A_\infty - A_t$) vs. time were linear over at least 2 half-lives.

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Registry No.—**1**, 52436-75-6; **2**, 121-69-7; **3**, 19125-73-6; **4**, 24596-41-6.

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Orientation in Base-Promoted Dehydrohalogenation of *N*-(Chlorobenzyl)-*n*-butylamine[1]

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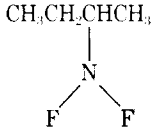
Although the mechanisms of olefin formation by base-promoted dehydrohalogenation have been extensively investigated,[3,4] the removal of hydrogen halide across C-N bonds has received little attention. The only kinetic studies of imine-forming dehydrohalogenation involve the reactions of alkyldifluoroamines, RCH_2NF_2, in water–diglyme at 25–75 °C reported by Braumann and Hill.[5,6] In contrast to the strongly basic conditions required for alkene formation by dehydrofluorination of closely related 1,1-difluoro-2-arylethanes,[7] water was a sufficiently strong base to induce eliminations from the alkyldifluoroamines. These observations underscore the marked facility of carbon–heteroatom multiple bond forming eliminations when compared with analogous processes leading to alkenes or alkynes.

In order to rationalize the differences between imine- and alkene-forming dehydrohalogenations, it is important to assess the extent of double-bond formation in concerted, imine-producing eliminations. The kinetic data for alkyldifluoroamine dehydrofluorination[5,6] were interpreted by Braumann and Hill in terms of a concerted E2 elimination having extensive C_β–H bond scission, N_α–F bond rupture, and carbon–nitrogen double bond formation in the transition state. However, elimination rates of **1** and **2** were found to be nearly the same. Significant transition state double bond character is seemingly inconsistent with the negligible conjugative effect of an unsaturated linkage attached to the β carbon.



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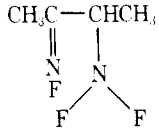

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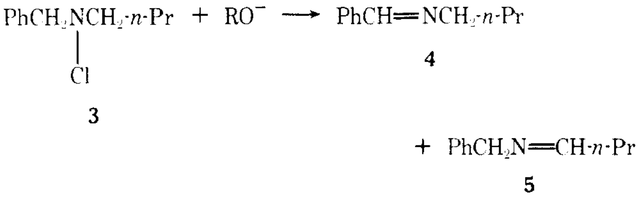
To gain insight into the degree of double bond character in transition states for imine-forming dehydrohalogenation, we have measured positional orientation for reactions of *N*-chlorobenzyl-*n*-butylamine (**3**) with several base–solvent systems.[8] The *N*-chloroamine **3** was prepared by chlorination of benzyl-*n*-butylamine with *N*-chlorosuccinimide in pentane, followed by solvent exchange. Conceivable dehydrohalogenation products are *N*-benzylidene-*n*-butylamine (**4**) and *N*-*n*-butylidenebenzylamine (**5**). Results are recorded in Table I. The percentage yields are calculated based upon the starting amine.



$$\underset{\mathbf{3}}{\mathrm{PhCH_2N(Cl)CH_2\text{-}}n\text{-}\mathrm{Pr}} + \mathrm{RO^-} \longrightarrow \underset{\mathbf{4}}{\mathrm{PhCH{=}NCH_2\text{-}}n\text{-}\mathrm{Pr}} + \underset{\mathbf{5}}{\mathrm{PhCH_2N{=}CH\text{-}}n\text{-}\mathrm{Pr}}$$

Reactions of MeONa–MeOH, EtONa–EtOH, *t*-BuOK–*t*-BuOH, and *t*-BuOK–hexane with **3** at room temperature are regiospecific, producing 91–95% yields of the conjugated imine **4**.[9] The positional isomer **5** could not be detected as a reaction product by either gas chromatography or proton magnetic resonance spectroscopy. The small deviations of measured product yields from 100% are attributed to minor losses attending the in

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Table I. Reactions[a,b] of 3 with Several Base–Solvent Combinations

base–solvent	time for complete reaction, h	% yield of 4[c]
0.24 M MeONa–MeOH	32	91
0.27 M EtONa–EtOH	24	95
0.09 M *t*-BuOK–*t*-BuOH	32	94
0.13 M *t*-BuOK–hexane[d]	2	95

[a] All reactions were conducted at room temperature. [b] [Chloramine] = 0.07–0.08 M. [c] Yields determined by gas chromatography using an internal standard. Estimated error is ±2%. [d] Heterogeneous reaction mixture.

situ preparation of **3**.

The rates at which the four base–solvent combinations induced elimination from **3** were estimated by periodic sampling of the reaction mixture and analysis by gas chromatography. The time required for complete reaction is listed in Table I. As may be seen, *t*-BuOK–hexane gave considerably more rapid dehydrochlorination than did any alkoxide–alcohol combination.

Control experiments demonstrated the stability of **4** and **5** and the absence of solvolysis of **3** under the reaction conditions. Since imine-forming reactions of *N*-chlorobenzylmethylamine with alkoxide bases have been found to exhibit substantial primary deuterium isotope effects,[11] an E2 mechanism seems most reasonable for the dehydrohalogenation of **3**.

In base-promoted eliminations from 1-aryl-2-halopropanes, exclusive or highly predominate formation of 1-arylpropenes is observed.[12–14] Preferential elimination toward the aryl group is considered to result from a combination of two factors: (1) conjugation of the aryl group with the developing double bond in the transition state and (2) acidification of the β hydrogens by the aryl group.[15]

In comparing eliminations from 1-aryl-2-halopropanes and **3**, acidification of the β hydrogen by the β-aryl group should be a relatively constant factor.[16] On the other hand, if the imine-forming eliminations pass through transition states with little double-bond character, there would be less stabilization by phenyl group conjugation. This would result in a reduced propensity for production of the conjugated elimination product. In contrast to this prediction, eliminations from **3** exhibit the same positional orientation as that observed in dehydrohalogenations of 1-aryl-2-halopropanes. These findings are consistent with considerable carbon–nitrogen double-bond development in transition states for base-promoted imine formation.

A carbon–carbon double bond is about 60 kcal mol^{-1} stronger than the corresponding single bond, whereas a carbon–nitrogen double bond is approximately 80 kcal mol^{-1} stronger than the single bond.[18] With significant double bond character in transition states for dehydrohalogenations forming both carbon–carbon and carbon–nitrogen double bonds, an important factor in the greater facility of the latter must be the greater strength of the resultant double bond relative to the corresponding single bond.

Experimental Section

Materials. *N*-Benzylidene-*n*-butylamine (**4**) and *N*-*n*-butylidenebenzylamine (**5**) were prepared by the method of Campbell, Sommers, and Campbell.[19] Catalytic hydrogenation[19] of **4** gave benzyl-*n*-butylamine.

Base–solvent combinations of MeONa–MeOH and EtONa–EtOH were prepared by reacting freshly cut sodium metal with the dry alcohols under nitrogen. Combinations of *t*-BuOK–*t*-BuOH and *t*-BuOK–hexane were prepared by adding *t*-BuOK (Aldrich) to dried *t*-BuOH and hexane, respectively.

Chlorination of Benzyl-*n*-butylamine. Benzyl-*n*-butylamine (1.0 mmol) and *N*-chlorosuccinimide (1.3–1.5 mmol) (Parish Chemical) were magnetically stirred in 10 mL of pentane for 30 min at room temperature. The mixture was filtered and 10 mL of MeOH, EtOH, *t*-BuOH, or hexane was added to the pentane solution. Evaporation of the pentane in vacuo at room temperature gave solutions of **3** in the desired solvent.

In a proton magnetic resonance spectrum of **3** in pentane taken prior to solvent exchange, no absorptions due to N–H of the starting amine could be detected.

Elimination from 3. A reaction solution or mixture (15 mL total volume) containing 1.0 mmol of **3**, 1.0 mmol of cyclohexylbenzene (internal standard for gas chromatography), and 1.3–3.6 mmol of the base was magnetically stirred in a closed vessel at room temperature. Periodically samples were removed and analyzed by gas chromatography on a 4 ft × ⅛ in. column of 20% Carbowax 400 on Chromosorb P at 130 °C (retention times: cyclohexylbenzene, 24 min; **4**, 38 min; **5**, 47 min).

Reactions of **3** with MeONa–MeOH and *t*-BuOK–hexane were also conducted in the absence of cyclohexylbenzene. Proton magnetic resonance spectra of the isolated reaction products were identical with that of **4**.

Control Experiments. The chloramine **3** was recovered unchanged after treatment with methanol and with hexane under conditions more forcing than those of the reactions with base. Mixtures of **4** and **5** were unaffected by treatment with the base–solvent combinations under conditions used for eliminations from **3**.

Registry No.—**3**, 68185-83-1; **4**, 1077-18-5; **5**, 56249-61-7; benzyl-*n*-butylamine, 2403-22-7; *N*-chlorosuccinimide, 128-09-6.

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The C(15) Configuration of Naturally Occurring Pimaren-15,16-diols[1]

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Among natural substances of the pimarane skeletal type there exist a limited number containing a vicinal glycol unit in the form of a 13-dihydroxyethyl group, i.e., the 15,16-diol moiety, in place of the more common 13-vinyl function.[2]

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