ed with strongly acidic D_2O, and the extract had λ_{max} 270 nm. When excess KOH solution was added, the peak at 270 was replaced by one of equal intensity at 245 nm.[12,1] Reacidification returned the peak to 270 nm, but with somewhat diminished intensity, presumably owing to partial hydrolysis to **3**.[20]

An extinction coefficient for **4** was determined in the following manner. As previously demonstrated,[1] dehydration of **1** occurs predominantly by a third-order process at pH's near the pK_a (rate proportional to $[\mathbf{1}][RNH_2][RNH_3^+]$). Dilution about thirtyfold of a reaction mixture displaying a peak at 270 nm slows the production of **4** sufficiently so that the hydrolysis of **4** to **3** ($\epsilon_{247}{}^{H_2O}$ 15,500) could readily be followed. An isosbestic point was observed, and a value for **4** of $\epsilon_{max}{}^{H_2O}$ 16,000 was calculated.[21]

Other EH^+ species analogous to **4** have been observed under appropriate conditions with the following catalysts for **1** → **3**: pyrrolidine, proline, ethyl glycinate, methyl alanate, cyanomethylamine, histamine,[22] histidine,[22] and histidine methyl ester.[22] A value of $\epsilon_{max}{}^{H_2O}$ 17,000 was obtained by the method described for EH^+ incorporating histamine.

That EH^+ ($\rightleftarrows$E) is an intermediate in the formation of **3** from **1** is supported by the following facts: (1) when EH^+ appears it appears before **3** and (2) only **3** is present at the end of reaction, despite typical catalyst/substrate ratios of ~100.[23] In addition, the rate data for appearance and disappearance of EH^+ can be fitted successfully to a nonlinear least-squares consecutive first-order kinetics program.[24] For the reaction of 2.97×10^{-3} *M* **1** with 0.40 *M* ethoxyethylamine buffer at pH 9.16, this program yielded the following values for the pseudo-first-order rate constants in eq 1: $k_1 = 7.14 \times 10^{-5}$ sec^{-1} and $k_2 = 6.26 \times 10^{-4}$ sec^{-1}

$$\mathbf{1} \xrightarrow{k_1} EH^+ \xrightarrow{k_2} \mathbf{3} \qquad (1)$$

($k_2/k_1 = 9$). With 0.40 *M* cyanomethylamine buffer at pH 5.47, the values were $k_1 = 9.92 \times 10^{-5}$ sec^{-1} and $k_2 = 1.92 \times 10^{-3}$ sec^{-1} ($k_2/k_1 = 19$). The third-order rate constants for the conversion of **1** to EH^+ calculated from these values of k_1 are in good agreement with the rate constants (k_{AB}'s) previously determined[1b] for nucleophilic amine catalyzed dehydration of **1**.

The detection of these chromophoric eniminium ion intermediates in amine catalyzed β-ketol dehydration suggests that a search for analogous species in other model, as well as enzymic,[25] reactions would be worthwhile, and we are exploring some of these possibilities.

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(4) The methoxime formed from **3** shows analogous peaks at δ 5.80 and 6.40: C. W. Leong, unpublished work in these laboratories.

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(20) At pH <3, **4** appears to be stable indefinitely, but conversion to **3** is rapid at pH ≥ pK_a of **4**. See P. Bolla and M. Legrand, *Bull. Soc. Chim. Fr.*, 2143 (1973), for a study of dienamine hydrolysis in which eniminium ions figure prominently and for pertinent references.

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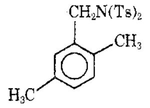
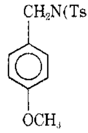
Reductive Deamination of Primary Amines. Sodium Borohydride Reduction of *N,N*-Disulfonimides in Hexamethylphosphoramide

Summary: Sodium borohydride in hexamethylphosphoramide provides a convenient and efficient reagent system for the reductive deamination of unhindered primary amines via initial conversion to *N,N*-disulfonimides and reduction at 150–175°.

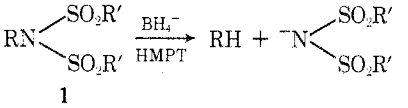
Sir: Although procedures for the activation of hydroxyl groups for displacement or elimination are numerous and

Table I
Reduction of Disulfonimides with Borohydride in HMPT

Entry	Compd [a, b]	Ratio of MBH_4^-/M compd	Temp, °C	Time, hr	% yield of hydrocarbon[c] (isold)
1	$CH_3(CH_2)_9N(Ts)_2$	2	25	48	30
2		2	110	46	43
3		2	150	4.0	80
4		2	175	4.0	84
5		2	175	8.0	88
6		2	175	8.0	91
7		4 ($NaBH_3CN$)	175	26.5	23
8		3 ($LiBHEt_3$)[d]	Reflux	8.0	0[e]
9	$CH_3(CH_2)_9N(Bs)_2$	2	150	4.0	73
10	$CH_3(CH_2)_{11}N(Ts)_2$	2	175	4.0	68
11		2	150	4.0	(78)
12		2	175	4.0	(78)
13	$CH_3(CH_2)_6CH(CH_3)N(Bs)_2$	4	175	8.0	66
				19.0	73
14	Cyclododecyl-$N(Ts)_2$	4	175	20	Trace[f]

[a] All new disulfonimides gave satisfactory elemental analysis, a copy of which was furnished to the Editor. [b] Solutions were 0.2 *M*. [c] Yields were determined by GLC using internal standards and corrected for detector response. [d] Solvent was a 1:1 mixture of THF and HMPT. [e] A 96% yield of *n*-decyl-*p*-toluenesulfonamide was isolated. [f] A 71% yield of cyclododecyl-*p*-toluenesulfonamide was isolated.

well documented, analogous functionalization of amines is considerably more difficult primarily because most nitrogen anions are relatively strong bases and, consequently, poor leaving groups. Recently, De Christopher and Baumgarten[1] and others[2] have successfully approached this problem using the anion of disulfonimides (i.e., 1) as the departing group, although competing substitution and elimination occurs with most nucleophiles.[1,2]



$$RN(SO_2R')_2 \xrightarrow[HMPT]{BH_4^-} RH + {}^-N(SO_2R')_2$$

1

Along this line, we wish to disclose our preliminary observations that borohydride anion in the SN2 enhancing solvent hexamethylphosphoramide (HMPT)[3] functions as an effective hydride source for the reductive deamination of unhindered primary amines[4] *via* initial conversion to disulfonimides.

The general synthetic procedure developed by Baumgarten and De Christopher[5] was employed to convert a variety of primary amines successively to the sulfonamides and disulfonimides. Initial experimentation with *N*-(*n*-decyl)-*N*,*N*-di(*p*-toluene)sulfonimide established that effective conversion to decane (80–91%) in reasonable reaction times (4–8 hr) was obtainable at 150–175° using a 2-fold excess of borohydride (entries 3–5, 9–12, Table I). The progress of the reductions were conveniently monitored by GLC (using internal standards) and the products were obtained simply by dilution with water and extraction with cyclohexane. In this fashion good to excellent yields of hydrocarbons were obtained with primary (entries 3–6, 9, 10), benzyl (entries 11, 12), and unhindered secondary alkyl groups (entry 13). The relatively congested cyclododecyl disulfonimide gave almost exclusive attack at nitrogen (entry 14), presumably because of the reluctance of this system to undergo SN2 displacements.[6] The following reduction is presented as a representative example of the procedure. A solution of *N*-(2,5-dimethylbenzyl)-*N*,*N*-di(*p*-toluene)sulfonimide (3.55 g, 8 mmol) and $NaBH_4$ (605 mg, 16 mmol) in 40 ml of HMPT was heated for 4 hr at 150°, then diluted with water and extracted three times with cyclohexane. The cyclohexane solution was washed three times with water, dried, and concentrated on a rotary evaporator to give 852 mg of colorless oil. Flash distillation at reduced pressure (Kugelrohr apparatus) afforded 747 mg (78%) of 1,2,5-trimethylbenzene product.

Predictably,[7] cyanoborohydride was much less potent as a hydride source (entry 7). Surprisingly, lithium triethylborohydride ("Super-Hydride"),[8] normally an exceptional nucleophile, afforded only *N*-decyl-*p*-toluenesulfonamide resulting from attack at nitrogen (entry 8). The reduction of *N*-(*n*-decyl)-*N*,*N*-d(*p*-toluene)sulfonimide with $LiBD(C_2H_5)_3$ gave the corresponding sulfonamide which showed no deuterium incorporation at the carbon adjacent to nitrogen. This excludes the possibility that the product was formed by initial hydride induced elimination of *p*-toluenesulfinic acid and subsequent reduction of the resulting *N*-tosylimine (2).

$$CH_3(CH_2)_8CH{=}N{-}Ts$$

2

Apparently, the steric requirement of the bulky triethylborohydride anion precludes attack at even a primary carbon next to a large *N*,*N*-disulfonimide group. Attack at nitrogen by borohydride seems to compete favorably only when carbon approach is slow as in *N*-cyclododecyl-*N*,*N*-di(*p*-toluene)sulfonimide (entry 14, Table I).[6]

We are currently exploring the possibility of enhancing the leaving capacity of the sulfonomide by incorporating more powerful electron-withdrawing sulfonyl derivatives such as trifluoromethyl[1,2a] and 2,4-dinitrophenyl groups.[9]

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