190 mμ. The slope of line B in Figure 2 in similar manner gives the value $+34 \times 10^{-40}$.

Moffitt[11] plots derived from the (smoothed) observed ORD data in Figure 1, and from the ORD curve calculated from the CD data observed below 260 mμ, lead to $b_0 = -100°$, corresponding to 16% α helix, in agreement with the α-helical content inferred from the original ORD and CD spectra.

The results reported here show that the observed ORD spectrum of cytochrome b_2 can be quantitatively accounted for on the basis of the observed CD spectrum plus an additional positive CD band centered at 150 mμ. A possible interpretation of the data attributes this band to a transition involving peptide units in α-helical array and assigns to the band a mean residue rotational strength of $+33 \times 10^{-40}$ erg cm^3.

Acknowledgment. Mr. S. Rudolph wrote the computer program for the integration of eq 1. The work was supported in part by Research Grant GM 04725 and Equipment Grant GM 12246 from the National Institutes of Health, U. S. Public Health Service. The authors are indebted to Professor John A. Schellman for very helpful suggestions.

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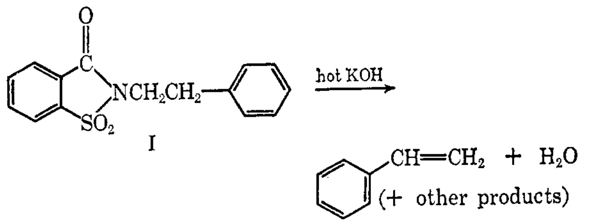
A New Approach to Deamination. III. A Simple Procedure for the High-Yield Conversion of Primary Aliphatic Amines into Alkyl Halides and Alkenes *via* the Use of Sulfonimide Leaving Groups

Sir:

One of the most frequently used activating groups for the E2 and SN2 cleavage of carbon–oxygen bonds in aliphatic alcohols is the *p*-toluenesulfonyl (*i.e.*, tosyl) group. Tosylate and related anions are presumably much better leaving groups than the hydroxide anion, mainly because of the relatively weakly basic nature of the tosylate anion.

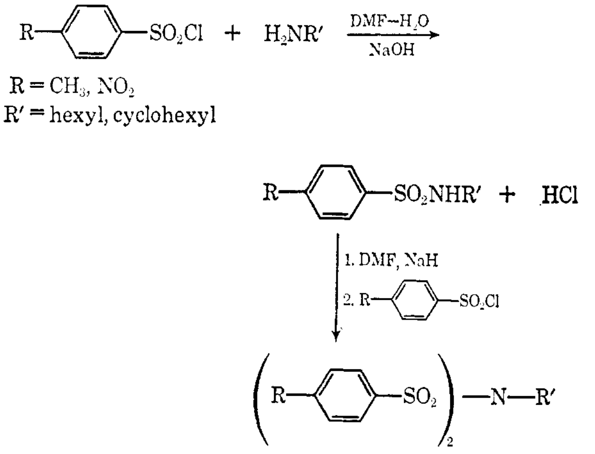
Analogous reasoning in respect to primary aliphatic amines leads to the prediction that sulfonimides should behave in a similar manner. In this event, a simple two- or three-step procedure for the conversion of primary aliphatic amines into alkyl halides and other alkyl derivatives would be available to the synthetic chemist for the first time.[1] Our previous work was concerned primarily with the use of the saccharin functionality as an activating group. We found that deamination only occurred with the saccharin derivatives of certain special amines such as 2-phenylethylamine (I) (eq 1). When simple alkylsaccharins were treated with nucleophiles such as iodide ion, aniline, or hot KOH, either no reaction was observed or the products of saponification were isolated.[2,3]

The search for a generally potent activating group for primary aliphatic amines, nonetheless, continued,

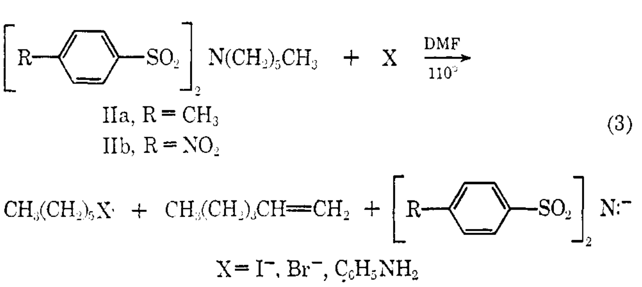


(1)

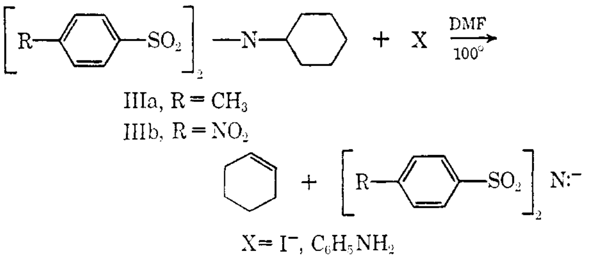
and we wish to report that activating groups such as the N,N-di-*p*-toluenesulfonyl and the N,N-di-*p*-nitrobenzenesulfonyl functionalities (both are obtained in up to 95% over-all yield by twice treating the parent amine with the appropriate sulfonyl chloride; eq 2) are effective for promoting carbon–nitrogen bond cleavages of primary aliphatic amines. For example, we have found that activated amines such as N-*n*-hexyl-*p*-toluenesulfonimide (IIa) (mp 114–115°) and N-*n*-hexyl-*p*-nitrobenzenesulfonimide (IIb) (mp 132–133°) give, when treated with iodide ion in DMF at 90–120° for 2–40 hr, *n*-hexyl iodide (up to 79% isolated yield), imide leaving group (up to 75%), and 1-hexene (0 to 31% yield) (eq 3). Similarly, N-cyclohexyl-*p*-toluenesulfonimide (IIIa) (mp 159–161°) and N-cyclohexyl-*p*-nitrobenzenesulfonimide (IIIb) (mp 192–193°) give, when treated with iodide ion in DMF at 90–150° for 40–69 hr, cyclohexene (up to 90% yield) and imide leaving group (up to 94% yield) (eq 4). Nucleophiles such as bromide anion and aniline likewise have been observed to displace the imide anion. Quantitative



(2)



(3)



(4)

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Table I

Starting imide	Nucleophiles (all in DMF)	% yield of products (isolated)		
		Olefin	Substitution	Leaving group
IIa	I^-	1-Hexene, 31	*n*-Hexyl iodide, 19	75
	$C_6H_5NH_2$		N-Hexylaniline, 76	84
IIb	I^-	1-Hexene, 0–1.5	*n*-Hexyl iodide, 79	
	Br^-		*n*-Hexyl bromide, 60	
IIIa	I^-	Cyclohexene, 90		93
	$C_6H_5NH_2$	Cyclohexene, 40	N-Cyclohexylaniline, 31	83
IIIb	I^-	Cyclohexene, 90		

results in respect to isolated yields are included in Table I.

Preparative samples of the alkenes and the hexyl halides were obtained *via* glpc and/or fractional distillation. The hexyl iodide was sensitive to decomposition under many attempted glpc runs, but pure samples were obtained on a $^3/_8$ in. × 20 ft 30% SF-96 column at 190°. The analytical glpc retention times of all reported liquids were identical with the glpc retention behavior of the authentic reagent grade samples Similarly the ir, nmr, and mass spectra of the product liquids were essentially identical with the corresponding spectra of the authentic samples. The melting point and ir spectrum of the *p*-toluenesulfonimide leaving group were identical with the corresponding data for the imide prepared by another method. The N-hexylaniline was characterized *via* its *p*-tosyl derivative, mp and mmp 67–68° (lit.[4] mp 67–68°) and *via* its ir and nmr spectra. Satisfactory elemental analyses were obtained on starting imides IIa,b and IIIa,b.

Typical runs were conducted as follows. Sulfonimide IIb (0.050 mol) and KI (0.10 mol) were dissolved in 75 ml of DMF and stirred at 110–120° for 2.5 hr. Immediate bulb-to-bulb, high-vacuum distillation of the product, followed by the addition of 50 ml of water to the distilled material, extraction with hexane, washing with water, drying over molecular sieves, and vacuum distillation, gave 0.0395 mol (79%) of pure hexyl iodide as indicated by homogeneous glpc behavior and the spectral analyses. The leaving group derived from sulfonimide IIb is apparently unstable under the reaction conditions, but acidification and recrystallization of the nonvolatile N,N-di-*p*-toluenesulfonimide from a similar run with sulfonimide IIa gave 75% of material which melts at 168–170° (lit.[5] mp 169°). Sulfonimide IIIb was treated similarly at 90° for 41 hr to give 90% of cyclohexene. The cyclohexene was isolated by fractional distillation. The runs with bromide anion and aniline were conducted in a similar manner.

The reaction of IIa and IIIa with aniline constitutes a new technique for obtaining N-alkylanilines. This reaction may eventually prove to be generally useful for the synthesis of secondary amines. Preliminary results also indicate that cyanide and hydroxide anions react with these sulfonimides. The yields with the cyanide and hydroxide nucleophiles have thus far been poor. Further investigations relating to the synthetic possibilities as well as to the mechanistic details of all these reactions are currently in progress.

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Anisotropic Nuclear Spin–Spin Coupling in Methyl Fluoride

Sir:

We wish to report evidence for anisotropic indirect nuclear spin–spin coupling in methyl fluoride. Previous nmr spectral studies of the fluoromethanes[1–3] partially oriented in a liquid crystal[4] showed no evidence for anisotropic contributions to the *geminal* indirect spin–spin interactions. When a sample of CH_3F enriched with 55% ^{13}C is examined, an unexpectedly large apparent anisotropy in the ^{13}C–H and ^{13}C–F indirect coupling is found as described below. Possible reasons for the large values of the measurements are discussed.

The spin-Hamiltonian for molecules partially oriented in a magnetic field is[5]

$$\mathcal{H} = -(H_Z/2\pi)\sum_i \gamma_i(1 - \overline{\sigma_{ZZi}})I_{Zi} + \sum_{i<j} J_{ij}\mathbf{I}_i\cdot\mathbf{I}_j + \frac{1}{2}\sum_{i<j}(\overline{T_{ZZij}} + \overline{J_{ZZij}} - J_{ij})(3I_{Zi}I_{Zj} - \mathbf{I}_i\cdot\mathbf{I}_j)$$

where the bars denote averages over the molecular motion with respect to the space-fixed axis Z. The total anisotropic coupling is composed of two parts. One contribution, $\overline{J_{ZZij}} - J_{ij}$, is the averaged anisotropy in the electron-coupled spin–spin interaction

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