polar and π-electron effects. Secondly, although the angular and distance factors can be established with some confidence for their system 11, system 111 is a stereochemically ill-defined structure. Their crucial assumption that angular and distance factors are the same for 11 and 111 is an extremely gross one.

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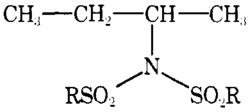
Orientation in Base-Promoted β Eliminations from 2-Butyl-*N*,*N*-disulfonimides

Sir:

Orientation in alkene formation by base-promoted β elimination has been a topic of research interest since the 1850's.[1] Early results[1,2] led to the formulation of the Hofmann and Saytzeff rules[3,4] for positional orientation.[5] Although these rules currently are recognized as only broad generalizations with numerous exceptions,[3] their existence underscores the pronounced effect of leaving group identity upon positional orientation.

Continuing investigations[6] of factors which control orientation in base-promoted β eliminations led us to examine the reaction of *N*-2-butyl-*N*,*N*-di(*p*-toluene)sulfonimide, **1a**, with *t*-BuOK-DMSO at 50°. To our surprise, the olefinic reaction product consisted *entirely* of 1-butene! It is estimated that 0.1% of *trans*-2-butene and/or *cis*-2-butene could have been detected. Subsequent experiments revealed that the observed regiospecificity was not due to some peculiarity of the base-solvent system, since eliminations from **1a** promoted by MeONa-DMSO and MeONa-MeOH at 50° also yielded only 1-butene.



1a, R = $-C_6H_4$-*p*-CH_3
b, R = $-CH_3$
c, R = $-C_6H_4$-*m*-NO_2

The significance of these observations is revealed by comparison with literature data for orientation in reactions of *t*-BuOK-DMSO with a variety of 2-substituted butanes (Table I). Regiospecificity of base-induced eliminations from **1a** is greater than that found with any previously reported leaving group!

In order to probe the factors responsible for this remarkable orientation control, eliminations from other 2-butyldisulfonimides, **1b** and **1c**, were conducted. The elimination product which resulted from reaction of *N*-2-butyl-*N*,*N*-dimethylsulfonimide, **1b**, with *t*-BuOK-DMSO at 50° was solely 1-butene. The inessential nature of the aryl portion of disulfonimide leaving groups for the observed regiospecificity is therefore demonstrated. An alkene mixture comprised of 98.8% 1-butene and 1.2% 2-butenes resulted from reaction of *N*-2-butyl-*N*,*N*-di(*m*-nitrobenzene)sulfonimide, **1c**, with *t*-BuOK-DMSO at 50°. Formation of less terminal alkene with change to a more reactive[11] leaving group is consistent with previous observations for alkyl halides and tosylates.[3]

Table I. Positional Orientation in Eliminations from 2-Substituted Butanes Induced by *t*-BuOK–DMSO at 50°

Leaving group	% of 1-butene in total butenes	Ref
–I	21	7
–Br	30	8
–Cl	41	9
$-OSO_2C_6H_4$-*p*-CH_3	57	8
$-\overset{+}{N}(CH_3)_3{}^{+}$	97[a]	10

[a] The base was EtOK. However, only a small increase in % of 1-butene would be anticipated for a change from EtOK to *t*-BuOK in DMSO.[7]

According to Brown's steric theory of orientation,[12] very large leaving groups favor the formation of 1-alkene from a 2-substituted alkane. Destabilizing steric repulsions between the leaving group and α- and β-alkyl groups are smaller in the transition state for formation of terminal alkene than in those for production of internal olefins. It seems most reasonable to attribute the orientation control observed for eliminations from **1a–c** to a steric effect of the $-N(SO_2-)_2$ portion of the leaving group.

Qualitatively, the facility of the alkyl *N*,*N*-disulfonimide eliminations which were examined resembles that of corresponding alkyl chlorides. Reactivity of the disulfonimide leaving group is therefore anticipated to be considerably greater than that of the trimethylammonio leaving group.

Additional studies of mechanistic and synthetic aspects (e.g., conversion of 2-alkyl alcohols to pure 1-alkenes via the route 2-alkyl alcohol, tosylate, amine, disulfonimide, 1-alkene) of elimination reactions involving disulfonimide leaving groups are in progress.

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(4) According to the Hofmann rule, a predominance of the less substituted alkene will be produced in eliminations involving an "onium" leaving group ($-NR_3{}^+$, $-SR_2{}^+$). Whereas, the Saytzeff rule predicts a preference for formation of the more substituted olefin in eliminations from alkyl halides and sulfonate esters.[3]
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Monomeric Methyl Metaphosphate. II. Electrophilic Aromatic Substitution

Sir:

In an earlier publication,[1] we described the evidence that monomeric methyl metaphosphate can be produced in the gas phase by the flash pyrolysis of methyl 2-butenylphostonate (A) and that the metaphosphate reacts at dry ice temperatures with *N*-methylaniline to produce a salt of methyl *N*-methyl-*N*-phenylphosphoramidate. We have now found that monomeric methyl metaphosphate will even attack the aromatic ring of *N*,*N*-diethylaniline at low temperature to