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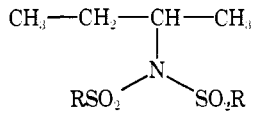
Orientation in Base-Promoted β Eliminations from 2-Butyl-*N,N*-disulfonimides

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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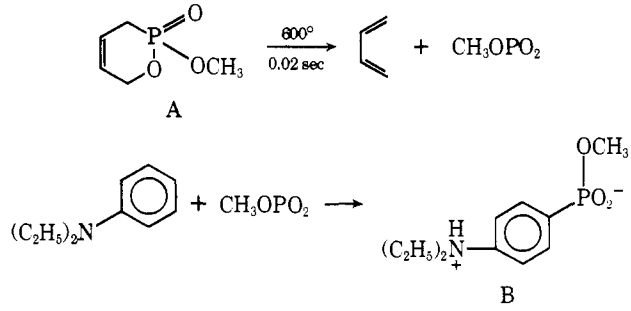
Monomeric Methyl Metaphosphate. II. Electrophilic Aromatic Substitution

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

yield (among other products) the monomethyl ester of *p*-diethylaminobenzenephosphonic acid (B). This aromatic electrophilic substitution reaction fully substantiates the claim[1] for monomeric methyl metaphosphate.



The pyrolyses of 0.5–1.0 mmol of phostonate, A, were conducted as previously described;[1] mixtures of 1.2 g of purified diethylaniline and 3.5 g of purified *n*-butylbenzene were cooled in a dry ice–isopropyl alcohol bath and stirred magnetically in the pyrolysis trap. After the furnace had cooled to 30°, the volatile materials were vacuum distilled from the trap at room temperature. The trap was washed with 8 ml of methylene chloride and 10 ml of 0.1 *N* barium hydroxide. The aqueous layer was extracted with 7 ml of methylene chloride, neutralized with CO_2, centrifuged, and evaporated; the resulting white residue was extracted with four portions of methanol totaling 7 ml. The extract was then evaporated to 0.1 ml, diluted with 0.1 ml of water, and chromatographed on a 20 × 20 × 0.25 cm precoated silica gel plate with acetonitrile–methanol–water (6:3:1) as developing solvent; the material from the major zone (R_f = 0.35–0.42) was freed of several impurities by high-pressure liquid chromatography, using a ⅛ in. × 2 ft Bondapak C-18/Porasil B column and a Waters Associates ALC 202 high-pressure liquid chromatography apparatus. The product was monitored at 254 nm and appeared after approximately 27 min elution with deionized water at 500 psi.

An authentic sample of phosphonate was prepared by the photochemical analogue[2] of the Arbuzov reaction followed by saponification. *p*-Iododiethylaniline[3] (6.35 g) and trimethyl phosphite (20 g) were photolyzed under nitrogen for 78 hr at 253.7 nm in a Srinivasan-Griffin Rayonet photochemical reactor at 10–15°. Excess trimethyl phosphite and dimethyl methylphosphonate were removed by low pressure distillation at 35°. The viscous yellow residue was extracted with 150 ml of boiling hexanes in four portions, to produce 2.2 g of crystalline product; subsequent sublimation at 100–110° (0.8 mm) and recrystallization from hexanes gave 1.3 g of colorless needles of dimethyl *p*-diethylaminobenzenephosphonate, mp 84–85°. Anal. Calcd for $C_{12}H_{20}NO_3P$: C, 56.03; H, 7.84; N, 5.44; P, 12.04. Found: C, 56.22; H, 7.88; N, 5.41; P, 12.10. NMR (CCl_4) δ 1.18 (t, J = 7 Hz; CH_3), 3.62 (d, J = 11 Hz; OCH_3), 3.40 (q, J = 7 Hz), 6.6, 7.5 (aromatic multiplet).

Dimethyl *p*-diethylaminobenzenephosphonate (223 mg) was hydrolyzed with saturated barium hydroxide solution at 95° for 2.5 hr. The barium salt of methyl *p*-diethylaminobenzenephosphonic acid (227 mg) was isolated from the reaction mixture and purified by high-pressure chromatography as with the salt obtained from the trapping experiment. Anal. Calcd for $(C_{11}H_{17}NO_3P)_2Ba{\cdot}H_2O$: C, 41.30; H, 5.67; N, 4.38; P, 9.68; Ba, 21.47. Found: C, 41.43; H, 5.55; N, 4.30; P, 9.65; Ba, 21.62.

The ^1H NMR spectra of the barium salts from the synthesis and from the trapping experiments, shown in Figure 1, were obtained in D_2O as solvent, with added K_2CO_3, with a Varian Associates XL-100 spectrometer, equipped for Fourier Transform spectra. The spectra demonstrate

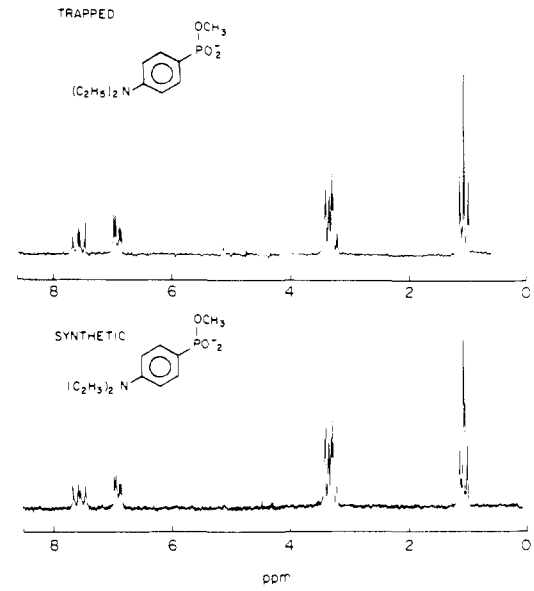


Figure 1. The 100-MHz ^1H NMR spectra of the barium salts of methyl *p*-diethylaminobenzenephosphonate from trapping and synthesis.

that the salts prepared from monomeric methyl metaphosphate and by conventional synthesis are identical; additionally, they confirm the structure. The ^{31}P spectrum of the crude reaction mixture from the trapping experiment, taken in $CDCl_3$ with added triethylamine, shows that methyl diethylaminobenzenephosphonate is present; the relevant peak appears at −16.8 ppm, relative to that of 85% phosphoric acid. The best yields of the phosphonate were estimated as only about 3–5%, and were obtained when the 600° zone was less than 0.5 cm from the end of the furnace, and when the butylbenzene–diethylaniline solution was stirred vigorously. In addition to NMR signals from methyl diethylaminobenzenephosphonate and from some unreacted starting material, ^{31}P spectra associated with pyro, trimeric, and polymeric methyl metaphosphate were observed; these materials constitute the bulk of the pyrolysate.

Despite the low yield, the identification of the aromatic substitution product is definitive; the attack on the ring of diethylaniline at low temperature provides some measure of the electrophilicity of monomeric methyl metaphosphate.

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Evidence for Hydrogen-Bonded Intermediates in Amine Substitution Reactions Involving Group 6B Metal Pentacarbonyl Amine Derivatives with Phosphines

Sir:

The kinetics of reactions of amine substitution in group 6B metal pentacarbonyl amine derivatives with phosphines