

Based on this kinetic scheme, the following relationships for IP are apparent.

$$k_{rp} = k_{1p}(F) \quad (28)$$

$$k_{tp} = k_{1p}(1 - F) \quad (29)$$

$$k_{rp} + k_{tp} = k_{mp} + k_{tp} = k_{1p} \quad (30)$$

$$k_{rs} + k_{ts} = k_{ms} + k_{ts} = k_{1s} \quad (31)$$

Similarly, eq 31 can be written for the IS ester.

**Steady-State Concentrations for Solvolysis Scheme I.** Application of the usual steady-state approximation to solvolysis Scheme I gives relations 32, 33, and 34 for the steady-state concentrations of  $R^+$ ,  $R^+||X^-$ , and  $R^+X^-$ , respectively.

$$(R^+) = k_3(R^+||X^-)/[k_{-3}(X^-) + k_s^{IV}] \quad (32)$$

$$(R^+||X^-) = \frac{k_2(R^+X^-)}{k_{-2} + k_s^{III} + k_3 \frac{k_s^{IV}}{k_{-3}(X^-) + k_s^{IV}}} \quad (33)$$

$$(R^+X^-) = \frac{k_1(RX)}{k_{-1} + k_s^{II} + k_2 \left[ 1 - \frac{k_{-2}}{k_{-2} + k_s^{III} + k_3 \frac{k_s^{IV}}{k_{-3}(X^-) + k_s^{IV}}} \right]} \quad (34)$$

## The Role of Neighboring Groups in Replacement Reactions. XXIX. 5-Methoxyl Participation and Lithium Aluminum Hydride Reduction<sup>1</sup>

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**Abstract:** Reduction of 4-methoxy-1-pentyl (IP) and 5-methoxy-2-pentyl (IS) *p*-bromobenzenesulfonates with lithium aluminum hydride in ether solvent results in formation of rearranged methyl pentyl ether, 2-methyltetrahydrofuran, and unrearranged methyl pentyl ether. The mechanistic implications are discussed; the results are considered to be consistent with salt-promoted anchimerically assisted ionization and fit in the *N* category of the *N-Lim* mechanism spectrum.

Since complex metal hydrides were first introduced as reducing agents,<sup>2,3</sup> several aralkyl and alkyl arenesulfonate and halide systems have been observed to yield appreciable amounts of rearranged hydrocarbons as a consequence of reduction.<sup>4-9</sup> These reductions are clearly the result of neighboring group participation, and in most cases appear to follow anchimerically assisted ionization. However, to date, little attention has been given to the mechanistic details for such product formation. In this regard, the reductions of 4-methoxy-1-pentyl (IP) and 5-methoxy-2-pentyl (IS) *p*-bromobenzenesulfonates are informative. It has been observed that both IP and IS give rearranged methyl pentyl ether and 2-methyltetrahydrofuran as well as unrearranged methyl pentyl ether when reduced with lithium aluminum hydride in ether.<sup>10</sup> Thus with the same molecular species reduction involves reaction

at methyl, primary, and secondary carbon atoms. Reduction also can be compared directly with the related extensively studied solvolytic displacement reactions of IP and IS.<sup>10,11</sup>

The present paper further describes the experimental results of the lithium aluminum hydride reduction of the IP and IS system in ether,<sup>10</sup> and discusses the mechanistic implications.

### Results

The samples of 4-methoxy-1-pentyl (IP) and 5-methoxy-2-pentyl (IS) *p*-bromobenzenesulfonates<sup>11</sup> used for the investigation were recrystallized three times at low temperature from 40:60 ether-pentane solvent. Three separate standardized reduction experiments were performed for each bromobenzenesulfonate using the same clear, homogeneous lithium aluminum hydride stock solution for all reductions. The standard conditions consisted of adding the bromobenzenesulfonate dissolved in anhydrous ether to an excess of 0.5 *M* lithium aluminum hydride in ether. After reflux overnight, the reduced mixture was worked up by addition of water and 10% aqueous sodium hydroxide. Following filtration to remove the aluminum salts, most of the ether was removed by careful distillation, and the concentrate was analyzed by gas chromatography.

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- (9) S. Winstein, A. H. Lewin, and K. C. Pande, *ibid.*, **85**, 2324 (1963).
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**Table I.** Products of Lithium Aluminum Hydride Reduction of 4-Methoxy-1-pentyl (IP) and 5-Methoxy-2-pentyl (IS) *p*-Bromobenzenesulfonates in Ether

<i>p</i> -Bromobenzene sulfonate	Expt no. <sup>a</sup>	Ratio of products, mole % <sup>b,c</sup>		
		Methyl 2-pentyl ether	Methyl 1-pentyl ether	2-Methyl tetrahydrofuran
IP	1	96.53	0.31	3.16
	2	96.10	0.51	3.39
	3	96.54	0.47	2.99
	Av	96.39 ± 0.14	0.43 ± 0.08	3.18 ± 0.12
IS	4	17.35	72.73	9.92
	5	16.99	72.88	10.13
	6	17.27	72.38	10.35
	Av	17.20 ± 0.15	72.66 ± 0.17	10.14 ± 0.13

<sup>a</sup> The numerical values reported for each experiment are an average of three gas chromatography determinations. <sup>b</sup> The identification of these ethers was confirmed by comparison of retention times with pure authentic samples. <sup>c</sup> These ratios as determined by gas chromatography are reported as wt %. These reported values have been corrected.

The products methyl 2-pentyl ether, methyl 1-pentyl ether, and 2-methyltetrahydrofuran were identified by comparison with authentic samples. The analytical results for each reduction experiment are listed in Table I. To determine the total over-all yield of the three ether products two more samples of each bromobenzenesulfonate were reduced and this time the fraction boiling between 77 and 100° was recovered. The average total recovered yield was 80%.

## Discussion

**Mechanism.** The product summary in Table I shows that lithium aluminum hydride reduction of both IP and IS bromobenzenesulfonates results in formation of appreciably more of the unrearranged normal product. This, coupled with the fact that IP gives considerably less abnormal products than the IS isomer, indicates that the major reaction for both is a simple nucleophilic displacement of the bromobenzenesulfonate group by the alumino hydride anion. Since both bromobenzenesulfonates do give abnormal products, it is also clear that some reduction involves participation by the  $\delta$ -methoxyl group.

The participation mechanism demanded by the product data is open to more than one kind of description. As in the case of solvolysis it could be a methoxyl group assisted ionization<sup>11</sup> followed by reduction, or it conceivably could involve completely concerted reductive rearrangements favored by an especially nucleophilic reagent. While it is not possible to choose between these alternatives solely on the basis of the product results, there are a number of reasons to favor prior ionization. First of all, if the rearrangements are concerted, the formation of 2-methyltetrahydrofuran and rearranged methyl pentyl ether requires two separate concerted participation paths for each bromobenzenesulfonate. This certainly is not as economical an explanation as a one-transition-state methoxyl-assisted ionization.

There is some experimental evidence that complex metal hydride reduction of certain *p*-toluenesulfonate and chloride systems do proceed by prior ionization processes. Karrer and Schmid<sup>5</sup> found that reduction of cholesteryl *p*-toluenesulfonate with lithium aluminum

hydride gives  $\Delta^5$ -cholestene and 3,5-cyclocholestane. Corey and co-workers<sup>6</sup> appear to have ruled out direct nucleophilic displacement (SN2) in this particular case with the observation that 3 $\beta$ -deuterio- $\Delta^5$ -cholestene is formed when lithium aluminum deuteride is employed. An SN2 attack at C<sub>3</sub> would give rise to  $\Delta^5$ -cholestene by a Walden inversion and produce the 3 $\alpha$ -deuterio epimer. Since the 3 $\beta$ -deuterio isomer was obtained, the results are best explained by an ionization to the bridged cholesteryl ion<sup>12</sup> which then is reduced to the observed products.

Other pertinent reductive rearrangements involve highly reactive 7-norbornadienyl and *anti*-7-norbornenyl derivatives.<sup>7-9</sup> Story made the striking observation that lithium aluminum hydride reduction of 7-norbornadienyl chloride in ether affords an 88:12 ratio of tricyclo[4.1.0.0<sup>3,7</sup>]hept-4-ene:norbornadiene.<sup>7</sup> From Story's results it was not clear whether reduction involved prior ionization, or was more or less concerted. However, on the basis of a comparison of the rates of reaction of *anti*-7-norbornenyl chloride in aqueous diglyme and in aqueous diglyme containing sodium borohydride<sup>9,13</sup> it appears that 7-norbornadienyl chloride is reacting by prior ionization *via* a nonclassical intermediate.

The question of ionization occurring in solutions of lithium aluminum hydride in ether needs further comment.<sup>4,6</sup> Recent investigation has shown that salt effects on the rate of ionization of organic substrates can be enormous in poorly ionizing solvents like ether.<sup>14</sup> For example, addition of 0.1 *M* lithium perchlorate has been found to accelerate ionization rates of arenesulfonates by factors of 10<sup>5</sup> to 10<sup>6</sup>.<sup>14</sup> At concentrations of lithium perchlorate above 0.036 *M*, ether becomes a better ionizing medium than acetic acid for *p*-methoxyneophyl *p*-toluenesulfonate.<sup>14</sup> Thus, ether solutions of lithium aluminum hydride undoubtedly can promote ionization and with appropriate substrate structures have ionization predominate over direct SN2 displacement.

In view of these observations, it is probable that lithium aluminum hydride reduction of IP and IS gives abnormal products through salt-promoted anchimerically assisted ionization, rearranged methyl pentyl ether and 2-methyltetrahydrofuran arising from the O-methyl-2-methyltetrahydrofuranium ion.<sup>10,11</sup> The intimate mechanistic details for the formation of final products by this route are unknown. We still have no definitive information as to the number of intermediate ion and ion-pair species which may be involved.<sup>15</sup> In line with this, the reduction of IP and IS is treated on the basis of the following simplified reaction scheme.

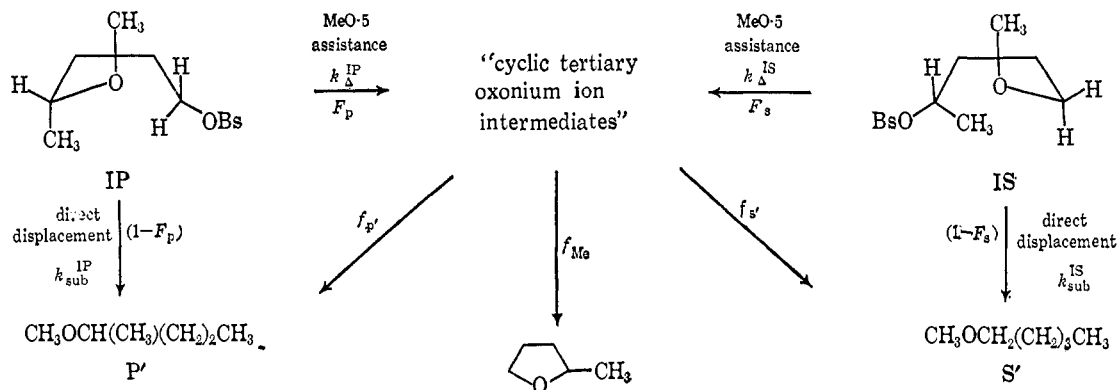
In this formulation  $F_p$  and  $F_s$  are the fractions of IP and IS, respectively, which react by MeO-5 assisted ionization, and correspondingly  $(1 - F_p)$  and  $(1 - F_s)$  are the fractions proceeding by simple nucleophilic displacement. For present purposes, the reaction of

(12) S. Winstein and R. Adams, *J. Am. Chem. Soc.*, **70**, 838 (1948).

(13) In the presence of sodium borohydride, hydrolysis of *anti*-7-norbornenyl chloride is diverted largely to hydrocarbon which is ca. 1:4 tricyclic isomer:norbornene.<sup>9</sup>

(14) S. Winstein, E. C. Freidrich, and S. Smith, *J. Am. Chem. Soc.*, **86**, 305 (1964); S. Winstein, S. Smith, and D. Darwish, *ibid.*, **81**, 5511 (1959).

(15) Besides the ion and ion pair species discussed in connection with acetolysis,<sup>10</sup> more aggregated ionic species must here be considered. For example, Li<sup>+</sup>AlH<sub>4</sub><sup>-</sup>-promoted ionization<sup>14</sup> of a substrate molecule may be expected to give rise initially to an ion quadruplet.



the cyclic oxonium ion is dissected into three fractions:  $f_{p'}$ , the fraction giving methyl 2-pentyl ether (P');  $f_{s'}$ , the fraction leading to methyl 1-pentyl ether (S'); and  $f_{Me}$ , the fraction resulting in 2-methyltetrahydrofuran.

**Rate Ratios and Partition Factors.** On this basis, the division of the reduction into direct displacement and MeO-5 paths and the subdivision of the MeO-5 path into  $f_{p'}$ ,  $f_{s'}$ , and  $f_{Me}$  routes may be readily accomplished for each bromobenzenesulfonate by reference to the average product ratios listed in Table I. In these calculations it is assumed that once the cyclic oxonium ion is formed, the same ratio of methyl 2-pentyl ether:methyl 1-pentyl ether:2-methyltetrahydrofuran always results. The resulting fractions are tabulated in Table II. As anticipated above, IP reacts more by direct nucleophilic substitution than IS, the amounts being 91 and 71%, respectively.

**Table II.** Assignment of Reaction Paths in the Lithium Aluminum Hydride Reduction of 4-Methoxy-1-pentyl (IP) and 5-Methoxy-2-pentyl (IS) *p*-Bromobenzenesulfonates

Path	IP	IS
$1 - F$	0.910	0.713
$F$	0.090	0.287
$f_{p'}$	0.599 <sup>a</sup>	0.599
$f_{s'}$	0.048	0.048 <sup>a</sup>
$f_{Me}$	0.353	0.353

<sup>a</sup> It is assumed that once the cyclic tertiary oxonium ion is formed, the same ratio of methyl 2-pentyl ether:methyl 1-pentyl ether:2-methyltetrahydrofuran always results.

In connection with the competition between MeO-5 participation and direct substitution, it is instructive to examine the variation of  $k_{\Delta}/k_{sub}$  values for IP and IS with change in nucleophile.<sup>17</sup> For the lithium aluminum hydride reduction these ratios are evaluated with the aid of eq 1 and 2 for IP and IS, respectively. The corresponding values for ethanol and acetic acid may be calculated directly from the kinetic data presented earlier.<sup>10,11</sup> These estimated  $k_{\Delta}/k_{sub}$  ratios are

$$k_{\Delta}^{IP}/k_{sub}^{IP} = F_p/(1 - F_p) \quad (1)$$

$$k_{\Delta}^{IS}/k_{sub}^{IS} = F_s/(1 - F_s) \quad (2)$$

(16) We might imagine some reaction of the tertiary oxonium ion with the very nucleophilic  $AlH_4^-$  ion at a stage before the intermediates from IP and IS have become identical. However, it seems best to formulate the reaction as given in the scheme in accord with what is known about ion pair formation in solvents like ethyl alcohol.<sup>10,11</sup> Even if this turns out to be wrong, the analysis to be made is changed only a little in terms of numerical values.

(17)  $k_{\Delta}$  and  $k_{sub}$  are the rate constants for anchimerically assisted ionization and unassisted direct displacement, respectively, as indicated in the reduction scheme.

summarized in Table III along with some other  $k_{\Delta}$  and  $k_{sub}$  comparisons.

From the  $k_{\Delta}/k_{sub}$  values in Table III it is clear that

**Table III.** Summary of Some  $k_{\Delta}$  and  $k_{sub}$  Comparisons for Nucleophilic Substitution of 4-Methoxy-1-pentyl (IP) and 5-Methoxy-2-pentyl (IS) *p*-Bromobenzenesulfonates

Nucleophilic reagent	Temp, °C	IP, $k_{\Delta}^{IP}/k_{sub}^{IP}$	IS, $k_{\Delta}^{IS}/k_{sub}^{IS}$	$k_{sub}^{IP}/k_{sub}^{IS}$	$k_{\Delta}^{IP}/k_{\Delta}^{IS}$
AcOH	25.20	13581 <sup>a</sup>	95.9 <sup>b</sup>	0.00715	1.0
EtOH	25.20	106.5 <sup>c</sup>	17.8 <sup>d</sup>	0.185	1.1
LiAlH <sub>4</sub> (ether)	Ca. 35	0.099	0.40	Ca. 5 <sup>e</sup>	Ca. 1.3

<sup>a</sup> Based on  $k_1^0$ , with  $k_{sub}^{IP}$  estimated as equal to the rate constant for *n*-butyl *p*-bromobenzenesulfonate in acetic acid.<sup>10,11</sup>

<sup>b</sup> Based on  $k_1^0$ , with  $k_{sub}^{IS}$  estimated as equal to the rate constant for *sec*-butyl *p*-bromobenzenesulfonate in acetic acid.<sup>10,11</sup> <sup>c</sup> Based on  $k_1^0$ , with  $k_{sub}^{IP}$  estimated as equal to the rate constant for *n*-butyl *p*-bromobenzenesulfonate in ethanol.<sup>11</sup> <sup>d</sup> Based on  $k_1^0$ ,<sup>11</sup> with  $k_{sub}^{IS}$  estimated as equal to the rate constant for isopropyl *p*-bromobenzenesulfonate in ethanol [data of R. E. Robertson, *Can. J. Chem.*, **31**, 589 (1953)]. <sup>e</sup> Estimated from the data of Eliel and Ro<sup>20</sup> for the displacement rates of *n*-butyl and *sec*-butyl *p*-toluenesulfonates with thiophenolate ion in 87% ethanol at 25°.

the nucleophile sequence AcOH:EtOH:LiAlH<sub>4</sub> involves a shift in the reaction process from the limiting (*Lim*) toward the nucleophilic (*N*) category,<sup>18</sup> according to the nucleophilicity order AcOH < EtOH << LiAlH<sub>4</sub>. For the primary IP bromobenzenesulfonate the value of the ratio drops by five powers of ten in the change AcOH → LiAlH<sub>4</sub> indicating the extreme sensitivity of  $k_{sub}^{IP}$  to variation of nucleophilicity. In the case of the secondary IS isomer the trend is in the same direction, but the ratio decrease is compressed to two powers of ten. This difference in magnitude is due mainly to the fact that the secondary compound has a more *Lim* type structure with an  $\alpha$ -methyl group increasing  $k_{sub}^{IS}$  more than  $k_{\Delta}^{IS}$ . In agreement with this  $k_{\Delta}^{IS}/k_{sub}^{IS}$  trend, it has been observed previously<sup>18,19</sup> that  $\alpha$ -methyl substitution becomes more rate enhancing as the reaction medium changes in the direction of the *Lim* category. This same effect also is demonstrated strikingly by the  $k_{sub}^{IP}/k_{sub}^{IS}$  column in Table III.<sup>20</sup>

(18) S. Winstein, E. Grunwald, and H. W. Jones, *J. Am. Chem. Soc.*, **73**, 2700 (1951).

(19) S. Winstein and H. Marshall, *ibid.*, **74**, 1120 (1952).

(20) In this latter comparison the value 5 for lithium aluminum hydride in ether is estimated from the rates of displacement of *n*-butyl and *sec*-butyl *p*-toluenesulfonates with thiophenoxide ion in 87% ethanol [E. L. Eliel and R. S. Ro, *ibid.*, **79**, 5995 (1957)]. This estimate seems reasonable since the relative rates of displacement for simple primary and secondary systems appear to be fairly independent of the structure

**Table IV.** Comparison of Me-O and Primary and Secondary C-O Cleavage of the O-Methyl-2-methyltetrahydrofuranium Ion in Nucleophilic Displacement Reactions

Nucleophilic reagent	% Me-O cleavage	Primary C-O cleavage	Secondary C-O cleavage
LiAlH <sub>4</sub> (ca. 0.5 M in ethyl ether) <sup>a</sup>	35.3	59.9	4.8
EtOH (anhy)	1.5	59.1	39.4
AcOH (anhy)	Ca. 0	40	60

<sup>a</sup> If the cyclic oxonium ion is reduced directly to methyl 2-pentyl and methyl 1-pentyl ethers,  $f_p'$  and  $f_s' \times 100$  are the percentages giving primary and secondary C-O cleavage, respectively;  $100f_{Me}$  is the percentage giving Me-O cleavage.

From the above analysis, it is possible to compare the effects of  $\alpha$ - and  $\delta$ -methyl groups on MeO-5 participation in all three reaction media. This is accomplished explicitly with eq 3, the results being summarized in

$$\frac{k_{\Delta}^{IP}}{k_{\Delta}^{IS}} = \left( \frac{k_{\Delta}^{IP}/k_{sub}^{IP}}{k_{\Delta}^{IS}/k_{sub}^{IS}} \right) \left( \frac{k_{sub}^{IP}}{k_{sub}^{IS}} \right) \quad (3)$$

Table III. It is interesting that  $k_{\Delta}^{IP}/k_{\Delta}^{IS}$  remains so insensitive (ca. 1.0–1.3) to such an obviously enormous variation of reaction conditions. As pointed out previously,<sup>11</sup> it is coincidence that this pair of isomers has almost identical reactivities as far as anchimerically assisted ionization is concerned.

**Me-O and Primary and Secondary C-O Cleavage.** It is of interest to compare the relative amounts of Me-O and primary and secondary C-O cleavage which result from the reaction of the O-methyl-2-methyltetrahydrofuranium ion with the various nucleophiles. In making this comparison for the reduction reaction, the question of the actual source of methyl 2-pentyl ether and methyl 1-pentyl ether arising from the MeO-5 participation route becomes pertinent. Although some MeO-5 products may have arisen from reduction of rearranged bromobenzenesulfonate, the occurrence of 2-methyltetrahydrofuran strongly suggests that a greater amount was the result of the reduction of the cyclic oxonium ion. On this basis,  $100f_p'$ ,  $100f_s'$ , and  $100f_{Me}$  estimate the percentages of primary C-O, secondary C-O, and Me-O cleavage, respectively. These values are listed in Table IV along with similar estimates for ethanol and acetic acid based on the product results reported earlier.<sup>11</sup>

The salient points of the comparison are that Me-O cleavage increases from ca. 0 to 35% in the change AcOH  $\rightarrow$  LiAlH<sub>4</sub>, primary C-O cleavage increases to a somewhat lesser extent from 40 to 60%, and secondary

and nucleophilic ability of the attacking base. See A. Streitwieser, "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, Table 4, p 12.

C-O cleavage decreases quite markedly from 60 to 5%. These trends can be demonstrated even more strikingly by expressing the data of Table III as the ratios of (secondary C-O):(primary C-O) cleavage and (primary C-O):(Me-O) cleavage. Thus the (secondary C-O):(primary C-O) cleavage ratio for the nucleophile sequence AcOH:EtOH:LiAlH<sub>4</sub> is 1.5:0.67:0.08. For the (primary C-O):(Me-O) cleavage ratio the comparison is ca.  $\infty$ :39.4:1.7 for the same nucleophile order. Again, these trends are the proper direction for a shift toward *N* in the *N-Lim* mechanism spectrum according to the sequence AcOH:EtOH:LiAlH<sub>4</sub>. As the reaction becomes more *N* in character the charge separation in the transition state leading from the cyclic intermediate to final product becomes less important, and consequently reaction at the more unsubstituted centers increases.

## Experimental Section

**Bromobenzenesulfonates.** 4-Methoxy-1-pentyl (IP) and 5-methoxy-2-pentyl (IS) *p*-bromobenzenesulfonates were samples prepared previously.<sup>11</sup> Each bromobenzenesulfonate was purified by three low-temperature (ca.  $-20^{\circ}$ ) recrystallizations from 40:60 ether-pentane.

**Standard Lithium Aluminum Hydride Solution.** A 100-g sample of lithium aluminum hydride (Metal Hydrides, Inc.) was stirred and refluxed for 7 hr in about 1200 ml of anhydrous ether, and then allowed to stand overnight. The opaque ether solution was filtered through a medium fritted disk filter stick under a slight nitrogen pressure to give a clear homogeneous solution. This was standardized by measuring hydrogen evolution when a 2-ml aliquot was added slowly to ice-cold 10% sulfuric acid solution. The lithium aluminum hydride concentration was 2.3 M.

**Reduction Experiments.** A standard set of reaction conditions was used for each experiment. A 2.11-g (0.006 mole) sample of bromobenzenesulfonate dissolved in 30 ml of anhydrous ether was added dropwise to a stirred 25-ml solution of 0.5 M lithium aluminum hydride in ether (prepared from the above stock solution). The reduction was completed under reflux conditions. After stirring overnight, the excess hydride was decomposed by careful addition of 1.0 ml of water followed by 0.7 ml of 10% aqueous sodium hydroxide. Following removal of the white precipitate by filtration, and after drying with anhydrous magnesium sulfate, the filtrate was concentrated by carefully controlled distillation on a 15-cm Vigreux column. The concentrate was analyzed quantitatively by gas chromatography using a 2 m  $\times$  0.6 cm column packed with 30% by weight Carbowax 1500 on 40–60 mesh C-22 Firebrick. Three products, methyl 2-pentyl ether, methyl 1-pentyl ether, and 2-methyltetrahydrofuran, were identified by comparison of retention times with authentic samples of each. The results for each experiment are summarized in Table I.

Two additional samples each of IP and IS were reduced under the standard conditions. This time the product was distilled through an 8.0 mm  $\times$  80 cm concentric tube column and the material boiling from 77 to 100 $^{\circ}$  was recovered. The total recovered yield of product ethers averaged ca. 80%.

**Authentic Product Ethers.** The authentic samples of methyl 2-pentyl ether, methyl 1-pentyl ether, and 2-methyltetrahydrofuran used for comparison and identification purposes have been described previously.<sup>10</sup>