with *n*-hexane (2 × 6 mL). The resultant white solid was dissolved in 1.2 mL of THF distilled from sodium and the solution transferred to a serum-capped 8-mm NMR tube.

C. Preparation of 1-Ethoxy-1-lithioethene. To an 8-mm NMR tube capped with a rubber septum was introduced 1.0 mL of freshly distilled THF. Ethoxyethene (0.25 g, 0.0035 mol) was added via syringe and the sample then cooled to −78 °C. Slow addition of 3.0 mL (0.0054 mol) of 1.8 M *tert*-butyllithium in *n*-pentane to the mixture caused formation of a yellow precipitate. After the tube was shaken intermittantly, the solid dissolved at ca. −30 °C. The solution was recooled to −78 °C for 1 h and then warmed to −50 °C for 4 h. After the mixture was warmed to ambient temperature the carbon-13 spectrum showed quantitative conversion to the anion as well as a slight amount of the enolate of acetaldehyde and ethylene from the base-promoted decomposition of THF.

D. Preparation of 6-Methyl-2,3-dihydropyran. To a mixture of 3.0 g (0.036 mol) of 2,3-dihydropyran and 0.50 g (0.0043 mol) of TMEDA was added 18.0 mL (0.045 mol) of 2.5 M *n*-butyllithium in hexane. This solution was stirred overnight, the resulting suspension was centrifuged, and the hexane was removed. The solid was washed with ethyl ether and then suspended in that solvent. An excess of methyl iodide was added cautiously to the ether solution. This mixture was stirred for 3 h and the solution then filtered. The carbon-13 spectrum showed greater than 95% conversion of the anion to 6-methyl-2,3-dihydropyran. The shifts were 150.7, 95.0, 65.8, 22.3, 20.2, and 19.7 ppm.

E. Preparation of 6-Deuterio-2,3-dihydropyran. To 4.0 g (0.048 mol) of 2,3-dihydropyran in a serum-capped reaction vessel was added 23 mL (0.058 mol) of 2.5 M *n*-butyllithium in *n*-hexane. After several hours the lithiated vinyl ether precipitated. The solid was centrifuged and washed with hexane (3 × 10 mL) and then suspended in 10 mL of hexane. To this suspension was added excess D_2O and the layers were subsequently separated. The carbon-13 spectrum of the hexane layer showed a conversion of more than 95% of the anion to the 6-deuterio-2,3-dihydropyran. The shifts were 143.78 (t), 98.63, 64.69, 22.55, and 19.21 ppm. Proton NMR indicated the virtual absence of the α-vinyl ^{1}H resonance of the starting material.

F. Preparation of 5-Methyl-2,3-dihydrofuran and 5-(Trimethylsilyl)-2,3-dihydrofuran. Dihydrofuran (2.0 g, 0.029 mol) and TMEDA (0.6 g, 0.005 mol) were mixed and then 15.0 mL (0.032 mol) of 2.1 M *n*-butyllithium in hexane was added. The reaction mixture was cooled to room temperature after precipitation began. The solid was washed with hexane (2 × 4 mL) and then excess methyl iodide in ethyl ether or excess trimethylsilyl chloride was added cautiously. The solution containing the 5-methyl-2,3-dihydrofuran was centrifuged and the carbon-13 spectrum indicated ca 85% conversion to the methyl derivative based upon the washed anion. The 5-(trimethylsilyl)-2,3-dihydrofuran was distilled and the carbon-13 spectrum showed greater than 95% conversion based upon the washed anion. The shifts for the methyl derivative were 154.8, 93.55, 69.43, 29.94, and 12.73 ppm. The shifts for the trimethylsilyl derivative were 162.2, 109.9, 69.66, 30.39, and −2.76 ppm.

G. Preparation of 5-Deuterio-2,3-dihydrofuran. To a solution of 0.9 g (0.013 mol) of 2,3-dihydrofuran and 0.3 g (0.0025 mol) of TMEDA was added rapidly 6.0 mL (0.013 mol) of 2.1 M *n*-butyllithium until precipitation of solid began. The reaction mixture was cooled with a room-temperature water bath and then addition of *n*-butyllithium was completed. The resulting solid was washed with hexane (3 × 4 mL) and then suspended in 1.0 mL of hexane. To this solution was added 1.0 mL of D_2O. The carbon-13 and proton NMR spectra showed essentially quantitative conversion to the deuterio compound. The carbon-13 shifts were 145.40 (t), 97.11, 68.20, and 28.38 ppm.

H. Preparation of 1-Deuterio-1-ethoxyethene. To the sample of the 1-litho-1-ethoxyethene used in the NMR study described previously was added excess D_2O. The top layer was separated. The carbon-13 spectrum of this layer indicated a 70% yield of the deuterated product. The carbon-13 shifts were 150.65 (t), 83.79, 61.62, and 13.11 ppm.

Acknowledgment. We are grateful to the Faculty Research Committee of Miami University for partial support of this research.

Registry No. 2,3-Dihydrofuran, 1191-99-7; 2,3-dihydropyran, 110-87-2; ethoxyethene, 109-92-2; 5-lithio-2,3-dihydrofuran, 75213-94-4; 6-lithio-2,3-dihydro-4*H*-pyran, 72081-15-3; 1-ethoxy-1-lithioethene, 40207-59-8; 6-methyl-2,3-dihydropyran, 16015-11-5; 6-deuterio-2,3-dihydropyran, 75213-95-5; 5-methyl-2,3-dihydrofuran, 1487-15-6; 5-(trimethylsilyl)-2,3-dihydrofuran, 75213-96-6; 5-deuterio-2,3-dihydrofuran, 75213-97-7; 1-deuterio-1-ethoxyethene, 75213-98-8.

Neighboring-Group Participation by Hydroxyl Oxygen in Nucleophilic Aromatic Substitution. Smiles Rearrangements of (ω-Hydroxyalkyl)methyl(*p*-nitrophenyl)sulfonium Perchlorates in Aqueous Alkali

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Received April 9, 1980

(2-Hydroxyethyl)- (**1**), (3-hydroxy-*n*-propyl)- (**2**), and (4-hydroxy-*n*-butyl)methyl(*p*-nitrophenyl)sulfonium perchlorates (**3**) were prepared. Products by Smiles rearrangements (intramolecular S_NAr reactions) were obtained from **1** as β-(methylthio)ethyl *p*-nitrophenyl ether (**9**) in 37–42% yield and from **2** as γ-(methylthio)propyl *p*-nitrophenyl ether (**8**) in quantitative yields, and none were obtained from **3**. The rearrangement rates and yields were compared with an intermolecular S_N2 reaction of dimethyl(*p*-nitrophenyl)sulfonium perchlorate (**4**) (displacement of the sulfonium group by a *n*-propoxy group) to estimate participation by the ω-hydroxyl oxygen. The rate ratios between the rearrangements (first order) and the S_N2 *n*-propoxy attack (second order), effective molarities, were obtained as 6.02×10^3 M for **1** vs. **4** and 4.64×10^3 M for **2** vs. **4**.

The importance of neighboring-group participation has been well recognized in carbonium ion reactions (e.g., solvolysis) and substitution reactions of carbonyl (e.g., ester hydrolysis) but not in other kinds of reactions.[1] Recent papers including ours have provided evidence of participation by hydroxyl oxygen for the one-step substitution reactions at the saturated carbon (S_N2).[2-4] Intramolecular

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(1) Capon, B.; McManus, S. P. "Neighboring Group Participation"; Plenum Press: New York, 1976; Vol. 1.

(2) (a) Coward, J. K; Lok, R.; Takaki, O. *J. Am. Chem. Soc.* **1976**, *98*, 1057–1059. (b) Knipe, J. O.; Coward, J. K. *Ibid.* **1979**, *101*, 4339–4348. See also the subsequent two papers.

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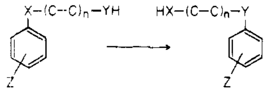
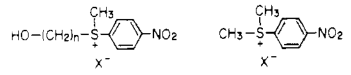
nucleophilic aromatic substitution reactions (S_NAr) involving skeletal rearrangements of the type $ArX(C-C)_nYH \rightarrow ArY(C-C)_nXH$ are generally termed Smiles rearrangements (eq 1). The carbon atoms joining X and Y may be

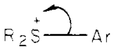


(1)



n = 2, 1
3, 2
4, 3
X = ClO4
4

part of an aliphatic or an aromatic system. One of the best known replaceable groups in the S_NAr reactions is a cationic sulfonium group:[5]



However, we have not found any quantitative study (including kinetics) of the Smiles rearrangement with the sulfonium compounds, which are fairly familiar to us in terms of their preparation and properties. Thus, we undertook rate and product studies of the rearrangements with (2-hydroxyethyl)- (**1**), (3-hydroxy-*n*-propyl)- (**2**), and (4-hydroxy-*n*-butyl)methyl(*p*-nitrophenyl)sulfonium perchlorates and compared the results with those from related intermolecular reaction, an S_N2 reaction of dimethyl(*p*-nitrophenyl)sulfonium perchlorate (**4**) with *n*-propyl alcohol. As a scale to estimate participation by hydroxyl oxygen in a reaction of this kind, we used the term effective molarity (EM).

Results

Preparations. *p*-Nitrothiophenol was condensed with ethyl bromoacetate in THF by using sodium hydride to afford **5** (*n* = 1), which was reduced to the alcohol **6** (*n* = 1) and then methylated with methyl iodide and silver perchlorate to give **1** (eq 2). When ethyl 2-bromopropionate or 3-bromobutyrate was used instead of ethyl bromoacetate, the same reaction sequence gave **2** or **3**, respectively. To test the effect of the *p*-nitro group in the rearrangement, we prepared the nitro-free alcohol **7** starting from condensation of thiophenol and methyl acrylate and proceeding through the reaction sequence, but no rearrangement was observed.

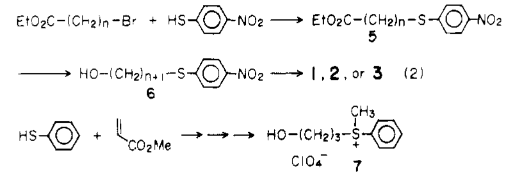


Table I. Rates of Reaction for (γ-Hydroxypropyl)methyl(*p*-nitrophenyl)sulfonium Perchlorate (**2**)

[NaOH], N	pH	10^3-[OH⁻], M	10^4k_{obsd}, s⁻¹ 31.0 °C	10^4k_{obsd}, s⁻¹ 18.2 °C	10^4k_{Ar}, s⁻¹ [a] (50 °C)
0.010	11.61	4.07	5.38	1.54	28.8
0.008	11.51	3.24	4.29	1.23	22.9
0.006	11.40	2.51	3.21	0.90	17.7
0.004	11.21	1.62	2.02	0.54	11.8

[a] Extrapolated by a FACOM computer from k_{obsd}.

Table II. Rates of Reaction for (β-Hydroxyethyl)methyl(*p*-nitrophenyl)sulfonium Perchlorate (**1**)

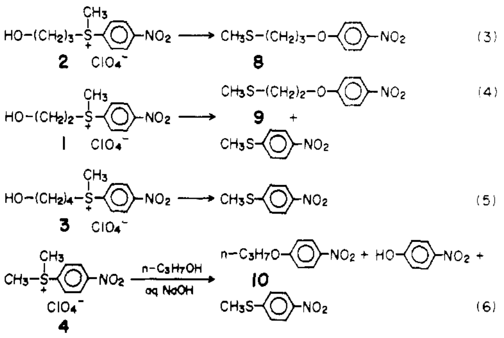
[NaOH], N	pH	10^4k_{obsd}, s⁻¹ 25 °C	10^4k_{obsd}, s⁻¹ 12 °C
0.010	11.61	6.48	1.244
0.008	11.51	5.06	0.981
0.006	11.40	3.74	0.729
0.004	11.21	2.46	0.473

Table III. Yields and Partial Rates of β-(Methylthio)ethyl *p*-Nitrophenyl Ether (**9**)

10^3-[OH⁻], M	yield, % 25 °C	yield, % 12 °C	partial rate × 10^4, s⁻¹ 25 °C	partial rate × 10^4, s⁻¹ 12 °C	k_{Ar},[a] (50 °C)
4.07	38.0	42.2	2.46	0.525	34.0
3.24	37.7	41.9	1.91	0.411	26.0
2.51	37.7	41.4	1.41	0.302	19.4
1.62	37.0	40.7	0.91	0.193	12.7

[a] Extrapolated by a FACOM computer from partial rates.

Rates and Products. The rearrangement of **2** was carried out in aqueous solution with excess amounts of sodium hydroxide at several pH values in the range of 11.61–11.21. For comparison with the intermolecular reaction of **4** with *n*-propyl alcohol, 1 M *n*-propyl alcohol and sodium perchlorate were added to the reaction mixture to maintain constant ionic strength (μ = 1.0). No detectable change in pH was observed during the reaction. The reaction of **2** gave a quantitative yield of γ-(methylthio)propyl *p*-nitrophenyl ether (**8**, eq 3), the structure of which



was assigned by NMR and confirmed by comparison with an authentic sample independently prepared. The rates were followed by the increasing intensities of the UV maximum at 310 nm due to the formation of **8** and/or the decreasing intensities of the UV maximum at 252 nm for **2**. The first-order plots gave satisfactorily straight lines in all runs. The observed rate constants, k_{obsd}, were extrapolated to k_{Ar} at 50 °C and are used for discussion. The data are summarized in Table I. The reactions with **1** were carried out under the same conditions, except for the temperature. Here the product was not a single one but rather a mixture of the predicted rearrangement product **9** accompanied by *p*-nitrothioanisole. The formation of the latter is thought to be due to an S_N2 attack of the hydroxyl oxygen at the methylene carbon α to the sulfonium sulfur. The yields of **9** were determined by high-pressure LC, and the partial rates of formation were calculated. Absence of detectable amounts of *p*-nitrophenol,

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(3) Irie, T.; Tanida, H. *J. Org. Chem.* **1979**, *44*, 325–330.
(4) Irie, T.; Tanida, H. *J. Org. Chem.* **1980**, *45*, 1795–1800.
(5) (a) Bolto, B. A.; Miller, J. *Aust. J. Chem.* **1956**, 74–82. (b) Miller, J. "Aromatic Nucleophilic Substitution"; Elsevier: New York, 1968; pp 164–165.

Table IV. **Rates of Reaction for Dimethyl(*p*-nitrophenyl)sulfonium Perchlorates (4)**

[NaOH], N	pH	10^4k_{obsd}, s^{-1} 100 °C	10^4k_{obsd}, s^{-1} 80 °C
0.010	11.61	3.29	0.441
0.009	11.56	2.78	0.398
0.008	11.51	2.51	0.334
0.007	11.47	2.13	0.297
0.006	11.40	1.84	0.267
0.005	11.33	1.57	0.211
0.004	11.21	1.27	0.176

Table V. **Yields and Partial Rates of Formation of *p*-Nitro-*n*-propoxybenzene (10)**

$10^5[n\text{-}C_3H_7O^-]$, M	yield, %		partial rate,[a] s^{-1}		
	100 °C	80 °C	100 °C	80 °C	50 °C[b]
5.50	18.5	22.8	6.09	10.04	4.40
4.90	18.3	22.6	5.09	8.99	4.49
4.37	18.1	22.0	4.55	7.35	3.15
3.98	18.1	21.2	3.86	6.27	2.71
3.39	17.5	20.8	3.22	5.55	2.66
2.69	16.9	18.9	2.66	3.98	1.49
2.19	15.0	16.8	1.90	2.96	1.19

[a] Values at 100 °C are $\times 10^5$, at 80 °C are $\times 10^6$, and at 50 °C are $\times 10^7$. [b] Extrapolated by a FACOM computer from the rates at 80 and 100 °C.

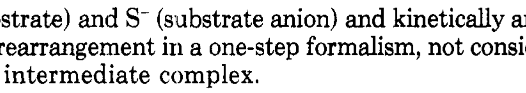
which might be expected to form by a reaction with hydroxide ion, was confirmed by high-pressure LC in both the reactions of 1 and 2. The results from 1 are summarized in Tables II and III.

The reaction with 3 did not afford the corresponding rearranged product but only *p*-nitrothioanisole in a quantitative yield.

The reaction with 4 under the same conditions as above proceeded to form *p*-nitro-*n*-propoxybenzene (10), *p*-nitrophenol, and *p*-nitrothioanisole (eq 6). The first two compounds were products of an S_NAr reaction, and the last was a product formed by nucleophilic attack by hydroxy or *n*-propyloxy oxygen on one of the methyl carbons. The yields and partial rates of formation of 9 were similarly determined and are presented in Tables IV and V.

Discussion

Because the Smiles rearrangements are well-known to be essentially base-catalyzed intramolecular S_NAr reactions,[5b-7] the present reactions may be represented as in eq 7. We can assume a fast equilibrium between S



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(substrate) and S⁻ (substrate anion) and kinetically analyze the rearrangement in a one-step formalism, not considering any intermediate complex.

$$S + OH^- \underset{}{\overset{K}{\rightleftharpoons}} S^- + H_2O \tag{8}$$

$$S^- \xrightarrow{k_r} P \text{ (product)} \tag{9}$$

$$d[P]/dt = k_r[S^-] \tag{10}$$

$$[S] + [S^-] + [P] = [S]_0 = \text{constant} \tag{11}$$

With equilibrium 8

$$K = \frac{[S^-][H_2O]}{[S][OH^-]} = \frac{[S^-][H^+]}{[S]}\frac{[H_2O]}{[H^+][OH^-]} = K_a'/K_{\text{HOH}}$$

where

$$S \overset{K_a'}{\rightleftharpoons} S^- + H^+,\ H_2O \overset{K_{\text{HOH}}}{\rightleftharpoons} H^+ + OH^-$$

Then

$$[S^-] = \frac{K[OH^-]}{[H_2O]}[S] = \frac{K_a'[OH^-]}{K_{\text{HOH}}[H_2O]}[S] = K'[S] \tag{12}$$

where

$$K' = \frac{K_a'[OH^-]}{K_{\text{HOH}}[H_2O]} = \text{constant}$$

From eq 11 and 12

$$(1 + K')[S] + [P] = [S]_0 \tag{13}$$

Since

$$[P] = 0 \text{ at } t = 0,\ [S]_0' = [S]_0/(1 + K') \tag{14}$$

$[S]_0'$ is defined as the concentration of S at the point that the equilibrium 8 is reached, but the reaction does not start. Differentiating eq 13 gives

$$(1 + K')\frac{d[S]}{dt} + \frac{d[P]}{dt} = \frac{d[S]_0}{dt} = 0$$

$$\frac{d[P]}{dt} = -(1 + K')\frac{d[S]}{dt} \tag{15}$$

From eq 10 and 12 is obtained eq 16. From eq 15 and 16

$$\frac{d[P]}{dt} = k_rK'[S] \tag{16}$$

is obtained eq 17. Integration under the condition of eq

$$\frac{d[S]}{dt} = -\frac{k_rK'}{1 + K'}[S] \tag{17}$$

14 gives eq 18. Substituting for [S] in eq 13 gives eq 19.

$$[S] = [S]_0' \exp[-k_rK't/(1 + K')] \tag{18}$$

$$\begin{aligned}[P] &= [S]_0 - (1 + K')[S]_0' \exp[-k_rK't/(1 + K')] \\ &= [S]_0[1 - \exp[-k_rK't/(1 + K')]]\end{aligned} \tag{19}$$

Therefore, k_{obsd} determined by formation of the product is given by eq 20. Under the present experimental con-

$$k_{\text{obsd}} = \frac{k_rK'}{1 + K'} = \frac{k_rK_a'[OH^-]}{K_{\text{HOH}}[H_2O]} \Bigg/ \left[1 + \frac{K_a'[OH^-]}{K_{\text{HOH}}[H_2O]}\right] \tag{20}$$

ditions, because $1 \gg K_a'[OH^-]/K_{\text{HOH}}[H_2O]$, eq 19 simplifies to eq 21.

$$k_{\text{obsd}} = \frac{k_rK_a'}{K_{\text{HOH}}[H_2O]}[OH^-] \tag{21}$$

Therefore, if this analysis is correct, k_{obsd} should be proportional to $[OH^-]$.

Indeed, plotting the k_{Ar} for 2 in Table I (rate constants at 50 °C extrapolated from the k_{obsd} at 31.0 °C and 18.2 °C) against $[OH^-]$ gives a straight line with a slope of 0.67 M^{-1} s^{-1} (Figure 1). The same treatments of the partial rates of formation at 50 °C for 1 (k_{Ar} in Table III) give another line in Figure 1 with a slope of 0.87 M^{-1} s^{-1}. The

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(6) Bunnett, J. F.; Zahler, R. E. *Chem. Rev.* **1951**, *49*, 273.

(7) Shine, H. J. "Aromatic Rearrangements"; Elsevier: New York, 1967; pp 307-316.

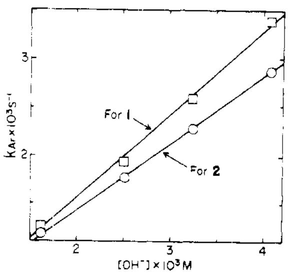


Figure 1. Dependence of the rate constants k_{Ar} for Smiles rearrangements of 1 and 2 on the hydroxide ion concentration at 50 °C.

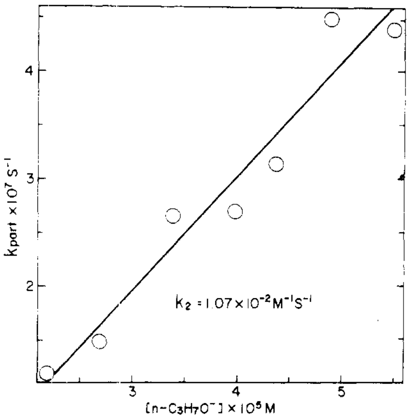
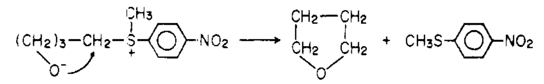


Figure 2. Dependence of the partial rate constants of formation of *p*-nitro-*n*-propoxybenzene from 4 on the *n*-propoxide ion concentration at 50 °C.

dissociation constants, K_a', of 1 and 2 are not known, but, when the pK_a of 15.87 for *n*-propyl alcohol[8] is applied as an approximation with a $K_{HOH}[H_2O]$ ($=k_w$) of $10^{-13.997}$, the k_r values are calculated as 64.4 s^{-1} for 1 and 49.6 s^{-1} for 2.[9]

The partial rates at 50 °C for the formation of *p*-nitro-*n*-propoxybenzene (10) in Table V are plotted against the concentration of $n\text{-}C_3H_7O^-$ to give a second-order rate constant ($k_2 = 1.07 \times 10^{-2}\ M^{-1}\ s^{-1}$) for the intermolecular reaction of 4 with $n\text{-}C_3H_7O^-$ as shown in Figure 2. Thus, comparison between the k_r values and this k_2 value gives effective molarities (EM) of 6.02×10^3 M for 1 and 4.64×10^3 M for 2. The rearrangement product for the reaction of 3 was absent. We believe that in this case an attack of



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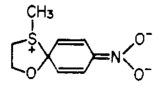
the nucleophilic hydroxyl oxygen takes place at the methylene carbon α to the sulfonium sulfur to form tetrahydrofuran much more easily than an attack at the aromatic carbon.

The sulfonium group is a very good leaving group in an S_NAr reaction (for example, 10^6 and 10^3 times more reactive than Cl and F, respectively, in a reaction of $p\text{-}NO_2ArX$ with OCH_3^-).[5] It is believed with the sulfonium group that the major energy requirement for nucleophilic aromatic substitution (addition–elimination mechanism) is the formation of the addition intermediate.[5,10] Then, the k_r and EM for 1 and 2 reflect the relative ease of forming the intermediates 11 and 12 where the oxasulfonium rings are five and six membered, respectively.



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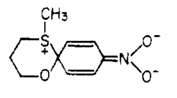

12

Experimental Section

Melting points were taken by using capillaries and are corrected. Infrared spectra were determined with a 215 Hitachi grating infrared spectrophotometer, ultraviolet spectra with an EPS-3T Hitachi recording spectrophotometer, ^1H NMR spectra with a Varian T-60A, ^{13}C NMR spectra with a Varian NV-14 at 15.087 MHz, and mass spectra with a Hitachi RMU-6 spectrometer.

Ethyl [(*p*-Nitrophenyl)thio]acetate (5, *n* = 1). To a solution of 3.34 g of ethyl bromoacetate in 200 mL of THF containing a suspension of 0.8 g of sodium hydride (60% in oil) was added 3.1 g of *p*-nitrothiophenol at room temperature with stirring under a nitrogen atmosphere. The reaction mixture immediately became dark red. The mixture was refluxed for 1 h, concentrated under reduced pressure, mixed with water, and extracted with ether. The ether solution was washed with water, dried, and evaporated. The residue was subjected to elution chromatography over silica gel (solvent, 3:7 hexane–benzene) and gave 3.64 g of 5 (n = 1): mp 47.5–48.5 °C (from ether–hexane); IR ($CHCl_3$) 1735 (CO), 1510 and 1340 (NO_2) cm^{-1}; NMR ($CDCl_3$) δ 1.3 (t, 3, CH_2CH_3), 3.85 (s, 2, O_2CCH_2S), 4.2 (q, 2, CH_2CH_3), 7.4 and 8.1 (two sets of doublets, 4, aromatic). Anal. Calcd for $C_{10}H_{11}NO_4S$: C, 49.78; H, 4.60; N, 5.81; S, 13.29. Found: C, 49.74; H, 4.55; N, 5.75; S, 13.51.

Ethyl β-[(*p*-nitrophenyl)thio]propionate (5, *n* = 2) was similarly prepared from ethyl β-bromopropionate and *p*-nitrothiophenol: mp 35–36 °C (from hexane–ether); IR ($CHCl_3$) 1725 (CO), 1510 and 1340 (NO_2) cm^{-1}; NMR ($CDCl_3$) δ 1.25 (t, 3, $CO_2CH_2CH_3$), 2.7 (t, 2, CH_2COOEt), 3.3 (t, 2, CH_2S), 4.15 (q, 2, $O_2CCH_2CH_3$), 7.35 and 8.1 (two sets of doublets, 4, aromatic). Anal. Calcd for $C_{11}H_{13}NO_4S$: C, 51.75; H, 5.13; N, 5.49; S, 12.56. Found: C, 51.77; H, 5.16; N, 5.51; S, 12.66.

Ethyl γ-[(*p*-nitrophenyl)thio]butyrate (5, *n* = 3) was prepared from ethyl γ-bromobutyrate and *p*-nitrothiophenol: oil; IR ($CHCl_3$) 1725 (CO), 1510 and 1340 (NO_2) cm^{-1}; NMR ($CDCl_3$) δ 1.25, (t, 3, $CO_2CH_2CH_3$), 2.05 (m, 2, $CH_2CH_2CH_2S$), 2.5 (t, 2, $O_2CCH_2CH_2$), 3.1 (t, 2, CH_2CH_2S), 4.2 (q, 2, $CO_2CH_2CH_3$), 7.4 and 8.15 (two sets of doublets, 4, aromatic).

β-[(*p*-Nitrophenyl)thio]ethanol (6, *n* = 1). Reduction of 3.19 g of the ester (5, n = 1) was carried out in 150 mL of anhydrous ether with lithium aluminum hydride. The usual workup gave 1.65 g of 6 (n = 1): mp 60–61 °C (from ether); IR ($CHCl_3$) 3600 (OH), 1510 and 1340 (NO_2) cm^{-1}; NMR ($CDCl_3$) δ 3.1 (s, 1, OH), 3.25 (t, 2, CH_2S), 3.9 (t, 2, $HOCH_2$), 7.35 and 8.1 (two sets of doublets, 4, aromatic). Anal. Calcd for $C_8H_9NO_3S$: C, 48.23; H, 4.52; N, 7.03; S, 16.09. Found: C, 48.50; H, 4.48; N, 6.90; S, 15.83.

γ-[(*p*-Nitrophenyl)thio]propanol (6, *n* = 2) was similarly prepared from 5 (n = 2): mp 34–35 °C (from ether–hexane); IR ($CHCl_3$) 3610 (OH), 1510 and 1340 (NO_2) cm^{-1}; NMR ($CDCl_3$) δ 2.05 (m, 2, CH_2CH_2S), 2.2 (s, 1, OH), 3.2 (t, 2, CH_2S), 3.8 (t, 2, $HOCH_2$), 7.35 and 8.1 (two sets of doublets, 4, aromatic). Anal. Calcd for $C_9H_{11}NO_3S$: C, 50.69; H, 5.20; N, 6.57; S, 15.03. Found: C, 50.82; H, 5.16; N, 6.48; S, 15.28.

δ-[(*p*-Nitrophenyl)thio]butanol (6, *n* = 3) was prepared from 5 (n = 3): mp 66–67 °C (from ether–hexane); IR ($CHCl_3$) 3610 (OH), 1510 and 1340 (NO_2) cm^{-1}; NMR ($CDCl_3$) δ 1.9 (m, 4, $CH_2CH_2CH_2CH_2S$), 2.45 (s, 1, OH), 3.1 (m, 2, CH_2S), 3.7 (m, 2, $HOCH_2$), 7.3 and 8.1 (two sets of doublets, 4, aromatic). Anal. Calcd for $C_{10}H_{13}NO_3S$: C, 52.84; H, 5.76; N, 6.16; S, 14.11. Found: C, 53.04; H, 5.76; N, 6.04; S, 14.38.

(β-Hydroxyethyl)methyl(*p*-nitrophenyl)sulfonium Perchlorate (1). To a solution of 1.08 g of β-[(*p*-nitrophenyl)-

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[8] Takahashi, S.; Cohen, L. A.; Miller, H. K.; Peake, E. G. *J. Org. Chem.* 1971, *36*, 1205–1209.

[9] All pH values in this paper were determined at about 25 °C. The dissociation constants cited from the literature were the values at 25 °C. However, rate data at 50 °C were used for the calculations because we tried to avoid large errors in the rate data for 4 due to extensive extrapolation from the experimental temperatures (100 and 80 °C) to 25 °C.

[10] Carey, F. A.; Sunderg, R. J. "Advanced Organic Chemistry"; Plenum Press: New York, 1977; Part B, pp 280–281.

thio]ethanol (**6**, *n* = 1) and 1.25 g of silver perchlorate (90% purity) in 15 mL of nitromethane was added a solution of 3.85 g of methyl iodide in 5 mL of nitromethane. A yellow precipitate immediately formed. The reaction mixture was left standing overnight at room temperature, filtered to remove the precipitate, and concentrated under reduced pressure. The residue was recrystallized from ether–methanol, giving yellow crystals: mp 78.5–79.5 °C; IR (Nujol) 3380 cm^{-1} (OH); NMR (CD_3OD) δ 3.4 (s, 3, CH_3S^+), 4.0 (m, 4, $\mathbf{CH_2CH_2}S^+$), 8.3 and 8.5 (two sets of doublets, 4, aromatic). Anal. Calcd for $C_9H_{12}NO_7SCl$: C, 34.45; H, 3.86; N, 4.47; S, 10.22; Cl, 11.30. Found: C, 34.39; H, 3.80; N, 4.46; S, 10.11; Cl, 11.03.

(γ-Hydroxypropyl)methyl(*p*-nitrophenyl)sulfonium Perchlorate (2). Methylation of 1.16 g of **6** (*n* = 2) was carried out with 3.85 g of methyl iodide and 1.25 g of silver perchlorate (90% purity) in 20 mL of nitromethane. The same workup as above gave 1.65 g of **2**: mp 88–90 °C (from ether–methanol); NMR (CD_3OD) δ 2.0 (m, 2, $CH_2\mathbf{CH_2}CH_2S^+$) 3.4 (s, 3, CH_3S^+), 3.6–4.1 (m, 4, $\mathbf{CH_2}CH_2\mathbf{CH_2}S^+$), 8.3 and 8.5 (two sets of doublets, 4, aromatic). Anal. Calcd for $C_{10}H_{14}NO_7SCl$: C, 36.64; H, 4.31; N, 4.27; S, 9.78; Cl, 10.82. Found: C, 36.28; H, 4.24; N, 4.23; S, 9.98; Cl, 10.87. **(δ-Hydroxy-*n*-butyl)methyl(*p*-nitrophenyl)sulfonium perchlorate (3)** was prepared from **6** (*n* = 3) as a heavy oil.

Methyl β-(Phenylthio)propionate. A solution of 4.45 g of thiophenol, 5.22 g of methyl acrylate, and a trace of sodium hydride in 100 mL of ether was stirred for 30 min at room temperature and then concentrated under reduced pressure. The residue was distilled at reduced pressure to give 8 g of an oil: bp 115 °C (1 mmHg); NMR ($CDCl_3$) δ 2.6 (t, 2, $\mathbf{CH_2}COOCH_3$), 3.2 (t, 2, CH_2S), 3.7 (s, 3, $COOCH_3$), 7.3 (m, 5, aromatic). Reduction with lithium aluminum hydride gave γ-(phenylthio)propanol: NMR ($CDCl_3$) δ 1.9 (m, 2, $CH_2\mathbf{CH_2}CH_2S$), 2.1 (s, 1, OH), 3.1 (t, 2, $CH_2CH_2\mathbf{CH_2}S$), 3.7 (t, 2, $HO\mathbf{CH_2}$), 7.3 (m, 5, aromatic). Methylation with methyl iodide and silver perchlorate in nitromethane gave **(γ-hydroxypropyl)methylphenylsulfonium perchlorate**: heavy oil; NMR (CD_3OD) δ 1.9 (m, 2, $CH_2\mathbf{CH_2}CH_2S$), 3.3 (s, 3, CH_3S^+), 3.6–3.9 (m, 4, $\mathbf{CH_2}CH_2\mathbf{CH_2}S^+$), 8.0 (m, 5, aromatic). A search for the rearrangement was carried out with this crude sulfonium salt.

Kinetic Measurements. The reactions of **2** were followed by monitoring the increase at the UV maximum at 310 nm for formation of **8**. The difference between absorption intensitive at infinite time and at specific times indicates the amount of remaining sulfonium compounds. Thus, the pseudo-first-order rate coefficients were calculated with a FACOM computer. The same rates were found by monitoring the decrease at the UV maximum at 252 nm for **2**. Similarly, the rate coefficients for **1** and **4** were determined by monitoring the decrease at the UV maximum at 252 nm. Also, an increase of the UV maximum at 340 nm due to the product mixture from **1** and an increase of the UV maximum at 400 nm due to *p*-nitrophenolate formation from **4** gave rate coefficients the same as those above. Determination of the increasing amounts of each of the products by high-pressure LC confirmed the above rates for the reactions of **1**, **2**, and **4**.

Products Studies. Portions at infinite time used for kinetic studies were subjected to high-pressure LC to determine the product yields in the tables. Stabilities of the products under the reaction conditions were confirmed by letting each of them stand for 10 half-lives in the reaction mixture. The high-pressure LC analyses were carried out by using a system comprised of the following components: Waters 6000-A pump, UVIDEC-100 UV detector, Reodyne 7120 injector. A Nucleosil 7, C_{18}, 4.0 mm i.d. × 25 cm, reverse-phase column was used for all experiments. For elution, 55% CH_3CN/45% H_2O was found to give the best separation of the required compounds. Samples for the products were obtained as follows.

***p*-Nitro-*n*-propoxybenzene (10)** was prepared by using a reported procedure[11] from *p*-nitrophenol and *n*-propyl bromide in acetone in which was suspended potassium carbonate: bp 120 °C (2 mmHg); NMR ($CDCl_3$) δ 1.1 (t, 3, $CH_3CH_2CH_2O$), 1.6–2.2 (m, 2, $CH_3\mathbf{CH_2}CH_2O$), 4.1 (t, 2, $CH_3CH_2\mathbf{CH_2}O$), 7.0 and 8.2 (two sets of doublets, 4, aromatic).

β-(Methylthio)ethyl *p*-Nitrophenyl Ether (9). A solution of 157 mg of the sulfonium salts **1** in 50 mL of 0.1 N aqueous sodium hydroxide was refluxed for 1 h and then extracted with ether. The ether solution was dried and evaporated. The residue was subjected to preparative layer chromatography (Merck precoated plate, 50% benzene–hexane). The ether **9** was isolated in 33% yield: mp 33.5–34.5 °C (from hexane); mass spectrum, *m/e* 213 (M^+); ^1H NMR ($CDCl_3$) δ 2.2 (s, 3, CH_3S), 2.9 (t, 2, $S\mathbf{CH_2}CH_2O$), 4.2 (t, 2, $SCH_2\mathbf{CH_2}O$), 6.9 and 8.1 (two sets of doublets, 4, aromatic); ^{13}C NMR ($CDCl_3$) δ 16.3 (CH_3S), 32.9 (SCH_2CH_2), 68.2 (CH_2CH_2O), 114.5 (aromatic C meta to NO_2), 126.0 (aromatic C ortho to NO_2), 163.5 (aromatic C para to NO_2). Anal. Calcd for $C_9H_{11}NO_3S$: C, 50.69; H, 5.20; N, 6.57; S, 15.30. Found: C, 50.81; H, 5.27; N, 6.39; S, 15.08.

γ-(Methylthio)propyl *p*-Nitrophenyl Ether (8). A solution of 134 mg of **2** and 69 mg of sodium bicarbonate in 50 mL of water was refluxed for 1 h and extracted with ether. The ether solution was dried and evaporated, leaving 73 mg of crystals: mp 32–33 °C (from hexane); mass spectrum, *m/e* 227 (M^+); ^1H NMR ($CDCl_3$) δ 2.2 (s, 3, CH_3S), 2.3 (m, 2, $SCH_2\mathbf{CH_2}CH_2$), 2.8 (t, 2, $S\mathbf{CH_2}CH_2$), 4.2 (t, 2, $CH_2\mathbf{CH_2}O$), 7.0 and 8.2 (two sets of doublets, 4, aromatic); ^{13}C NMR ($CDCl_3$) δ 15.6 (CH_3S), 30.5 (SCH_2CH_2), 28.4 ($CH_2CH_2CH_2$), 67.0 (CH_2CH_2O), 114.5 (aromatic C meta to NO_2), 125.9 (aromatic C ortho to NO_2), 141.6 (aromatic CNO_2), 164.0 (aromatic C para to NO_2). Anal. Calcd for $C_{10}H_{13}NO_3S$: C, 52.84; H, 5.76; N, 6.16; S, 14.11. Found: C, 52.88; H, 5.84; N, 6.07; S, 14.20.

Registry No. **1**, 75032-22-3; **2**, 75032-24-5; **3**, 75032-26-7; **4**, 29843-53-6; **5** (*n* = 1), 75032-27-8; **5** (*n* = 2), 75032-28-9; **5** (*n* = 3), 75032-29-0; **6** (*n* = 1), 13287-76-8; **6** (*n* = 2), 75032-30-3; **6** (*n* = 3), 75032-31-4; **8**, 75032-34-7; **9**, 75032-35-8; **10**, 7244-77-1; ethyl bromoacetate, 105-36-2; *p*-nilrothiophenol, 1849-36-1; ethyl β-bromopropionate, 539-74-2; ethyl γ-bromobutyrate, 2969-81-5; thiophenol, 108-98-5; methyl acrylate, 96-33-3; γ-(phenylthio)propanol, 24536-40-1; **7**, 75032-33-6; methyl β-(phenylthio)propionate, 22198-59-0.

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[11] "Organic Syntheses"; Wiley: New York, 1955; Collect. Vol. 3, p 140.