9b, 109392-25-8; **10**, 109391-82-4; **11**, 109391-83-5; **12**, 109391-84-6; **13**, 109391-85-7; **14**, 109391-86-8; **15a**, 109391-87-9; **15b**, 109392-26-9; **16**, 109391-88-0; **17**, 109391-89-1; **18**, 109391-90-4; **19**, 109391-91-5; **20**, 109391-92-6; **21a**, 109391-93-7; **21b**, 109391-74-4; **21c**, 109391-75-5; **21d**, 109392-00-9; **22a**, 109391-94-8; **22b**, 109392-02-1; **22c**, 109392-03-2; **23**, 109391-95-9; **24**, 109432-28-2; **25**, 109391-96-0; **26**, 109391-97-1; **27**, 109391-98-2; **28**, 109391-99-3; **29**, 71404-67-6; **31**, 109392-01-0; **33**, 35468-33-8; **35**, 4541-85-9; **36**, 4541-86-0; (*Z*)-**38**, 109392-07-6; (*E*)-**38**, 109392-08-7; **39**, 692-72-8; (*Z*)-**40a**, 109392-09-8; (*E*)-**40a**, 109392-10-1; (*Z*)-**40b**, 109392-11-2; (*E*)-**40b**, 109392-12-3; (*Z*)-**40c**, 109392-13-4; (*E*)-**40c**, 109392-14-5; (*Z*)-**40d**, 109392-15-6; (*E*)-**40d**, 109392-16-7; (*Z*)-**41a**, 109392-17-8; (*E*)-**41a**, 109392-18-9; (*Z*)-**41b**, 109392-19-0; (*E*)-**41b**, 109392-20-3; (*Z*)-**41c**, 109392-21-4; (*E*)-**41c**, 109392-22-5; **42**, 10515-98-7; **43**, 109392-23-6; **46**, 51558-95-3; **47**, 93-52-7; *threo*-**50**, 21759-50-2; *erythro*-**50**, 21759-49-9; SO_2Cl_2, 7791-25-5; PhSeSePh, 1666-13-3; $PhSeBr_3$, 38927-01-4; $PhCH{=}CH_2$, 100-42-5; (*E*)-$PhCH{=}CHCH_3$, 624-64-6; (*Z*)-$PhCH{=}CHCH_3$, 766-90-5; (*E*)-$H_3CCH{=}CHCH_3$, 624-64-6; (*Z*)-$H_3CCH{=}CHCH_3$, 590-18-1; (*Z*)-PhCH=CHPh, 645-49-8; (*E*)-PhCH=CHPh, 103-30-0; $HOCH_2CH{=}CH_2$, 107-18-6; $AcOCH_2CH{=}CH_2$, 591-87-7; $PhCO_2CH_2CH{=}CH_2$, 583-04-0; 4-$ClC_6H_4CO_2CH_2CH{=}CH_2$, 15784-28-8; 4-$O_2NC_6H_4CO_2CH_2CH{=}CH_2$, 15727-80-7; 2,4-$(O_2N)_2C_6H_4CO_2CH_2CH{=}CH_2$, 109392-27-0; $PhOCH_2CH{=}CH_2$, 1746-13-0; 4-$H_3CC_6H_4OCH_2CH{=}CH_2$, 1758-10-7; 4-$ClC_6H_4OCH_2CH{=}CH_2$, 13997-70-1; $H_3CCH{=}CHCH_2OAc$, 628-08-0; $H_2C{=}CHCH_2CH_3$, 106-98-9; PhSeCl, 5707-04-0; $H_2C{=}C(CH{=}CH_2)_2$, 106-99-0; $H_2C{=}CHC(CH_3){=}CH_2$, 78-79-5; $PhC(Cl){=}CH_2$, 618-34-8; (*E*)-$PhCH{=}CHCH_2Cl$, 21087-29-6; (*Z*)-PhCH=C(Cl)Ph, 948-99-2; (*E*)-PhCH=C(Cl)Ph, 948-98-1; PhSeBr, 34837-55-3; cyclopentene, 142-29-0; cyclohexene, 110-83-8; cycloheptene, 628-92-2; cyclooctene, 931-88-4; acenaphthylene, 208-96-8; 2-cyclohexen-1-yl acetate, 14447-34-8; cyclopentadiene, 542-92-7; 3-cyclohexene-1-carboxylic acid, 4771-80-6; thiourea, 62-56-6; 3-chlorocyclopentene, 96-40-2; 2-cyclopenten-1-ol, 3212-60-0; di(2-cyclopenten-1-yl) ether, 15131-55-2; 3-chlorocycloheptene, 35021-99-9; 1-chlorocycloheptene, 13294-30-9; 3-chlorocyclooctene, 24618-80-2; 1-chlorocyclooctene, 1890-22-8; 1-chloroacenaphthylene, 65726-91-2.

Supplementary Material Available: ^1H NMR data for compounds **4b**, **5b**, **6–28**, **31**, (*Z*)-1-chloro-1,2-diphenylethylene, (*E*)-1-chloro-1,2-diphenylethylene, and **38–43** (6 pages). Ordering information is given on any current masthead page.

The Role of Neighboring Group Participation in the Acetolysis of α-(Phenylthio)-ω-[(*p*-tolylsulfonyl)oxy]alkanes

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In order to evaluate the relative importance of the neighboring group participation by the phenylthio group, the acetolysis of tosylates **1a–e** has been studied. The results obtained confirmed that the participation decreases with the increasing ring size of the intermediate cyclic sulfonium salts **2** in the order S-3 > S-5 > S-6. Among these salts only **2c** and **2d** were isolated, while the formation of **2b** and **2e** was indirectly demonstrated by the obtainment of mixtures of the isomeric acetates **4b,e** and **5b,e**, respectively. In the absence as well as in the presence of acetate, the acetolyses of **1a** and **1c** very probably proceed exclusively through the intermediacy of the corresponding cyclic sulfonium salt, while open-chain pathways predominate in the acetolyses of **1b** and **1e**. The acetolysis of **1d**, instead, follows a different pattern in the two media: in glacial AcOH only direct nucleophilic displacement of the leaving group occurs, along with cyclization to the stable salt **2d**, while in the presence of AcOK the latter undergoes solvolysis, presumably through counterion exchange, the reaction involving both open-chain and cyclic pathways.

Participation of thioether groups in solvolytic displacement reactions was studied by a number of authors to assess the effects of ring size on sulfur participation. In particular, in the hydrolysis and alcoholysis of a series of ω-(arylthio)alkyl halides, the anchimeric assistance was shown to decrease with the ring size in the order 3 > 5 > 6 > 4,[2-6] though Bordwell and Brannen[4] found no evidence of it in the methanolysis of 3-(phenylthio)propyl chloride. Indeed, sulfur participation involving four-membered ring intermediates is extremely rare[7,8] and seems to be restricted to substrates having the heteroatom rigidly placed so that formation of the strained thietanium cation might be facilitated.[9,10] However, it must be recognized that, in general, kinetic data cannot be taken by themselves as a proof that a reaction proceeds solely through a pathway involving neighboring group participation; indeed, there might be cases in which participation is involved after the transition state has been reached. In this case no rate acceleration can be observed, the neighboring group being able to capture the first formed intermediate following the rate-determining step.[11] On the other hand, the isolation

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Table I. Acetolysis of α-(Phenylthio)-ω-[(p-tolylsulfonyl)oxy]alkanes 1a–e

substr	reacn systm[a]	reacn time, min	recovd 1, %	products (% yield) 2	3	4	5
1a	A	1				4a (50)	5a (50)
1a	B	1				4a (50)	5a (50)
1a	A[b]	40	46		3a (15)	4a (24)	5a (15)
1a	B[b]	10	20		3a (20)	4a (30)	5a (30)
1b	A	120	68		3b (4)	4b (23)	5b (5)
1b	B	30	67		3b (5)	4b (24)	5b (4)
1c	A	5		2c (100)			
1c	A	90		2c (76)		4c (12)	5c (12)
1c	B	30				4c (50)	5c (50)
2c	A	60				4c (50)	5c (50)
1d	A	90	6	2d (79)		4d (15)	
1d	B	120				4d (80)	5d (20)
2d	B	90				4d (50)	5d (50)
1e	A	360	30		3e (10)	4e (56)	5e (4)
1e	B	360				4e (86)	5e (14)

[a] A = anhydrous AcOH; B = AcOH/AcOK (3 mol). Reaction temperature: 120 °C. [b] Reaction run at 40 °C.

of a cyclic intermediate does not necessarily imply that the resulting product originates exclusively through the assisted pathway, unless concurrent, unassisted pathways can be rigorously excluded. Therefore, in order to assess the role of neighboring group participation, additional chemical information is necessary and the latter can be obtained only from reactions on suitably labeled substrates. In the study of solvolytic reactions, in which an arylthio group might be involved in the cyclization of an unsubstituted polymethylene chain, substrates deuteriated at one of the terminal carbon atoms appear to be the most convenient.

Results and Discussion

During the preparation of α- or ω-deuteriated ω-(arylthio)alkyl chlorides or bromides, starting from the corresponding alcohols, a deuterium scrambling between the α- and ω-carbon atoms of the chain was always observed. The same result had been reported for the reaction of 1,1-dideuterio-2-(methylthio)ethanol with chlorinating agents, which gives a product equally labeled at the α- and β-position.[12] Instead, no scrambling occurred during the tosylation of the alcohols, since this reaction does not proceed through a cyclic intermediate. Tosylates **1a–e**, deuteriated at the carbon bearing the leaving group, were then selected to study the role of sulfur participation in solvolytic reactions. These substrates were easily obtained by $LiAlD_4$ reduction of the corresponding esters, followed by tosylation of the deuteriated primary alcohols.

We wish now to report on the acetolysis of tosylates **1a–e** in anhydrous AcOH and in the AcOH/AcOK system. The most significant results are reported in Table I.

From a mechanistic point of view, the acetolyses under investigation might in principle proceed through several pathways. As shown by the speculative scheme in Scheme I, only pathways a and d, involving "direct" nucleophilic displacement of the leaving group by the solvent or by the added nucleophile, lead to a single acetate. the other pathways, which require the intermediacy of a cyclic sulfonium salt, give rise to the isomeric acetates **4** and **5** in a 1:1 ratio. The scheme also indicates that both tosylates **1** and **3** may undergo reversible isomerization through the intermediacy of the cyclic sulfonium ion **2**. Furthermore, in the AcOH/AcOK system the first-formed sulfonium salts might undergo counterion exchange, affording **2′**. The data reported in Table I show that sulfonium salts **2** have been isolated only in the acetolysis of **1c** and **1d** (in the absence of acetate), i.e., only when participation

Scheme I

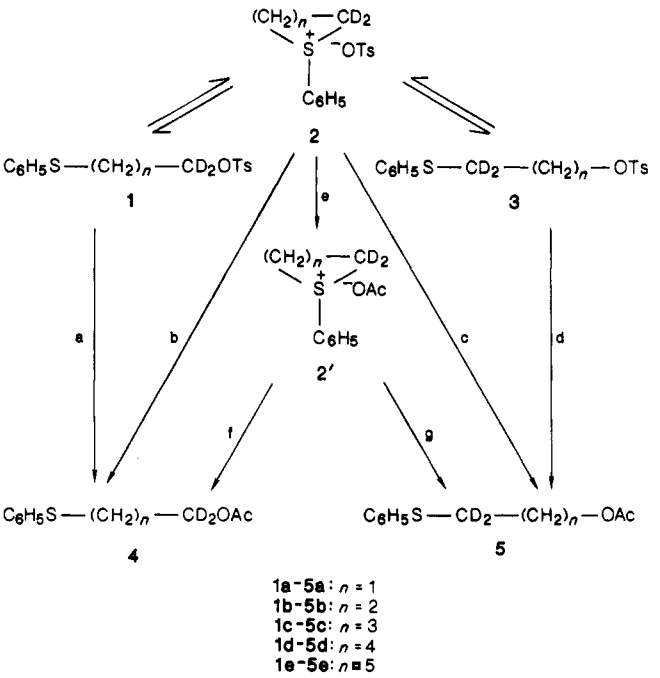

Table II. Acetolysis of 1a and the Isomeric 1,1-Dideuterio-1-(phenylthio)ethyl p-Toluenesulfonate (1′a) in AcOH at 40 °C[a]

substr	reacn time, min	% convrsn	% acetate 4a	5a
1a	10	19	11.4	7.6
1′a	10	24.2	12.1	12.1
1a	70	55.3	31.2	24.1
1′a	70	64.5	25.8	38.7
1a	100	61.9	34.3	27.6
1′a	100	74.9	28.1	46.8

[a] NMR determinations. The somewhat faster acetolysis of 1′a might be ascribed to a small isotopic effect. This is suggested by the kinetics of the acetolyses in AcOH at 40 °C of **1a** and **1′a** and of the undeuteriated substrate, which gave the following k_{obsd}: 0.9 × 10^{-2}, 1.5 × 10^{-2}, and 1.7 × 10^{-2} mol^{-1} s^{-1}, respectively.

by the distant sulfur atom allows the formation of stable five- or six-membered rings, respectively.

As expected, **1a** was by far the most reactive substrate in the series; in particular, the findings that **1a** undergoes acetolysis much faster than **1c** is consistent with the data reported by Bird and Stirling.[6] These authors, studying the solvolysis of a series of aryl ω-haloalkyl sulfides, found that three-membered sulfonium salts are formed more

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Table III. Acetolysis of 1,1-Dideuterio-1-(phenylthio)ethyl *p*-Toluenesulfonate (1'a) at 40 °C in the Presence of 0.6 M AcOK[a]

reacn time, min	% convrsn	% acetate 4a	% acetate 5a
10	60	30	30
20	84	42	42
35	97	50	50

[a] NMR determinations.

of activation for the three-membered ring formation being rapidly than their five-membered analogues, the enthalpy lower than for the five-membered ring.

Of particular interest are the data concerning the acetolysis of **1a** at different temperatures (see Tables I and II). Since both the acetolyses in anhydrous AcOH and in the AcOH/AcOK system at 120 °C gave the isomeric acetates **4a** and **5a** in a 1:1 ratio, it might be assumed that, under these conditions, the solvolysis proceeds entirely through the intermediacy of an episulfonium salt (**2a** or **2'a**), which may rapidly undergo symmetrical cleavage (pathway b and c or f and g, respectively). However, by quenching the reactions at 40 °C before completion, some of the rearranged tosylate **3a** was obtained, which proves that at low temperature the reverse reaction of **2a** is not suppressed.

Ion pair return in sulfonium ion **2a** must be a facile process in a poorly ionizing solvent such as AcOH. Evidence on the reversibility of episulfonium ion formation from β-thio-substituted ethyl halides, ethers, or esters have already been obtained.[7] As for solvolytic reactions on specifically deuteriated substrates, the hydrolysis 1,1-dideuterio-2-(methylthio)ethyl dinitrophenolate has been recently shown to result in complete rearrangement of the product alcohol.[12]

In the acetolysis of **1a** pathway a must also be operating, at least at low temperature and in the absence of AcOK. This emerges from the data reported in Table II, in which the acetolysis of **1a** is compared with that of the isomerically labeled 1,1-dideuterio-1-(phenylthio)ethyl *p*-toluenesulfonate (**1'a**). The results clearly show that with both substrates the unrearranged acetates prevail to a significant extent over the rearranged ones. Accordingly, the hypothesis can be made that in the above acetolyses sulfur participation is at work through two concurrent mechanisms: that characterized by a S_N1-like transition state, involving a simple coordination of the heteroatom to the electrophilic center, which allows "direct" displacement (without rearrangement) of the leaving group in spite of the poor nucleophile, and a S_Ni mechanism characterized by a S_N2-like transition state (of somewhat higher energy), which may collapse to the intermediate sulfonium salt **2a** before undergoing solvolysis.

However, the two-mechanisms hypothesis is difficult to square with the results of the acetolysis at 40 °C of **1'a** in the presence of 0.6 M AcOK (see Table III), unless one admits that under these experimental conditions the preequilibrium **1'a** ⇌ **2a** is very rapidly shifted toward the right, due to the irreversible formation of acetate **2'a** (see further discussion regarding the acetolysis of **1d**), and therefore the solvolysis may proceed entirely through pathway e.

From a mechanistic point of view, tosylate **1c** certainly represents a simple case, since after a few minutes heating in boiling AcOH the substrate was entirely converted into the cyclic sulfonium salt **2c**. Also, both the acetolyses of **1c** and **2c** gave equal amounts of the isomeric acetates **4c** and **5c**. This demonstrates beyond any doubt that in every case the acetolysis of **1c** proceeds exclusively through a thiolanium cation intermediate. As for its counterion, it can be hypothesized (by analogy with what has been assessed for the acetolysis of **2d**; see further) that, in the presence of acetate, **2c** may undergo counterion exchange leading to the sulfonium salt **2'c** before solvolysis occurs.

The above results also allow a clear answer about kinetic and thermodynamic control in the acetolysis of **1c**; at least in neat AcOH, the former control is represented by the formation of the cyclic sulfonium ion, the latter by the solvolysis of this intermediate. The same conclusion can be drawn also for the acetolysis of **1a**.

The data obtained from the reaction of **1d** indicate that its solvolysis follows a much more complex pattern. As expected, the substrate reacted both in anhydrous AcOH and, more rapidly, in the presence of acetate. However, in neat AcOH the acetate formation represented only a minor process, the main one being the cyclization to the thianium salt **2d**, which was shown to be completely stable in boiling AcOH. Therefore, in the absence of AcOK, the observed acetate **4d** has to be formed exclusively through pathway a. Instead, **2d** underwent easy acetolysis in the AcOH/AcOK system, affording acetates **4d** and **5d** in a 1:1 ratio, while the same acetolysis of tosylate **1d** led to a 4:1 mixture of the same acetates. These results prove that in the presence of acetate the acetolysis of **1d** follows two different pathways, no more than 40% of the reaction proceeding through the intermediate thianium cation.

The formation of acetate **4d** in AcOH through pathway a may well be explained in terms of the hypothesis put forward for the acetolysis of **1a**, which postulates that ipso substitution occurs through a S_N1-like transition state in competition with the cyclization reaction.

The inertness of the six-membered sulfonium salt **2d** in AcOH and its reactvity in the AcOK system could be explained by the much higher concentration of the anionic nucleophile or, more reasonably, by the formation of the more reactive sulfonium salt **2'd**. In order to verify the latter hypothesis, a concentrated solution of **2d** in water was treated with an anion-exchange resin to remove the tosylate anion: this experiment, although it did not allow us to isolate **2'd** in a pure state, was still quite conclusive because **2'd** was nevertheless formed. In fact, the solution obtained after the treatment with the resin showed in the NMR spectrum signals only for the thianium cation with its acetate counterion. Moreover, NMR experiments demonstrated that a very rapid reaction occurs in the tube and within 15 min all of **2'd** is converted into a 1:1 mixture of acetate **4d** and **5d**. The above results indicate that the acetolysis of **1d** in the AcOH/AcOK system, unlike that in plain AcOH, may involve all the pathways illustrated in Scheme I.

Kinetic experiments were performed on sulfonium salts **2c** and **2d** up to 50–60% conversion of the substrate. the acetolysis of **2c** in AcOH at 120 °C gave a k_{obsd} of 7.6×10^{-6} mol^{-1} s^{-1}, while in the AcOH/AcOK system at 120 °C the same constant was 1.7×10^{-3} mol^{-1} s^{-1}. The acetolysis of **2d** in the presence of acetate at 120 °C gave instead a k_{obsd} of 4.5×10^{-5} mol^{-1} s^{-1}, which shows that in these conditions the acetolysis of the thianium salt **2d** proceeds about 40 times slower than that of the thiolanium salt **2c**. These results appear to be in agreement with those obtained by Knipe and Stirling[5] who investigated the S-5 vs. S-6 participation in the alcoholysis of 1-bromo-4-(*p*-tolylthio)butane and the homologue 1-bromo-5-(p-tolylthio)pentane; these authors showed in fact that equilibria between the substrates and the respective cyclic sulfonium salt are involved in the solvolysis and that, although the equilibrium constant is more favorable for the six-membered ring formation, S-5 participation is faster than S-6

participation. Reasonably, the five-membered ring, which forms faster, also undergoes ring opening more rapidly than the six-membered one. However, it should be mentioned that the above kinetics were performed on unlabeled substrates, and therefore they do not allow discrimination between normal solvolytic pathways and internally assisted pathways involving participation by the thioether group.

Finally, the acetolyses of tosylates **1b** and **1e** revealed interesting novelties about neighboring group participation. Thus, while participation by an aryl thioether group involving a four- or seven-membered cyclic sulfonium salt was not expected on the basis of previous views based on kinetic experiments, the nature of the products obtained in the acetolysis of **1b** and **1e** proves that S-4 and S-7 participation by the sulfur is really at work, although, obviously, in a less efficient manner than with the other substrates of the series. Particularly unexpected were the results of the acetolysis of **1b**, if one considers that the methanolysis of the analogous (and certainly anchimerically more reactive) 1-(benzylthio)-3,3-dideuterio-4-p-tosylpropane had been reported to proceed, in the presence of $NaHCO_3$, without any scrambling of the deuterium labeling.[13] However, by use of a more ionizing and less nucleophilic solvent (CF_3CH_2OH), the latter substrate did solvolyze via a cyclic intermediate.[14]

The data reported in Table I show, anyhow, that in neat AcOH about 64% of **1b** and 86% of **1e** undergo acetolysis according to pathway a. As for the mechanism responsible for the formation of the unrearranged acetates **4b** and **4e**, participation by sulfur is assessed by the fact that the acetolyses of **1b** and **1c** proceeded faster than that of *n*-propyl and *n*-hexyl tosylates, chosen as models; thus, only 15% of the former and 28% of the latter tosylates underwent solvolysis after 6 h at 120° C in AcOH. Sulfur coordination to the electrophilic center of **1b** and **1e** is certainly much more difficult than with **1a**, due to unfavorable conformational factors; this may well account for their much slower solvolysis. Strain factors in the corresponding four- and seven-membered transition states or intermediates should also be considered. Indeed, it remains to be ascertained whether the rearranged acetates **5b** and **5e** are formed through the intermediacy of the corresponding cyclic sulfonium salt or through cyclic transition states resembling such intermediates.

Experimental Section

NMR spectra were recorded on a Varian XL 100 spectrometer using Me_4Si as the internal standard. The IR spectral data were obtained on a Perkin-Elmer 157 spectrometer.

Materials. Anhydrous AcOH was prepared by refluxing (4 h) 99.8% AcOH (Merck) with the calculated amount of Ac_2O (Merck). Anhydrous AcOK was obtained by drying at 130 °C in vacuo the Carlo Erba RPE reagent.

Substrates. Arenesulfonates **1a–e** were prepared by $LiAlD_4$ (98% atom D, Aldrich) reduction of ethyl esters of the corresponding ω-phenylthio carboxylic acids,[15-18] followed by the reaction of the deuteriated alcohols with a slight excess of p-toluenesulfonylchloride in anhydrous pyridine at −5 °C. Purification of the substrates was performed by crystallization. Melting points were in good agreement with those reported in the literature for the undeuteriated compounds.

1,1-Dideuterio-2-(phenylthio)ethyl p-toluenesulfonate (1a): mp 35 °C; NMR ($CDCl_3$) δ 7.65–7.00 (9 H, m), 3.03 (2 H, s), 2.40 (3 H, s).

2,2-Dideuterio-2-(phenylthio)ethyl p-toluenesulfonate (1'a): prepared by esterification with ethanol, followed by $LiAlH_4$ reduction and tosylation, from 2,2-dideuterio-2-(phenylthio)acetic acid; mp 77–78 °C; the latter was obtained from the undeuteriated acid by treatment with D_2O at 120 °C (20 h) in the presence of 0.12 M NaOD.

1,1-Dideuterio-3-(phenylthio)propyl p-toluenesulfonate (1b): mp 39 °C (lit. mp 35–36 °C);[19] NMR ($CDCl_3$) δ 7.66–7.00 (9 H, m), 2.87 (2 H, t), 2.40 (3 H, s), 1.90 (2 H, t).

1,1-Dideuterio-4-(phenylthio)butyl p-toluenesulfonate (1c): mp 51–52 °C (lit. mp 50–51 °C);[19] NMR ($CDCl_3$) δ 7.67–7.00 (9 H, m), 2.87 (2 H, t, virtual coupling, J = 5 Hz), 2.40 (3 H, s), 1.81–1.33 (4 H, m).

1,1-Dideuterio-5-(phenylthio)pentyl p-toluenesulfonate (1d): mp 112 °C (lit. mp 115–116 °C);[19] NMR ($CDCl_3$) δ 7.70–7.00 (9 H, m), 2.76 (2 H, t, virtual coupling, J = 5 Hz), 2.40 (3 H, s), 1.83–1.40 (6 H, m).

1,1-Dideuterio-6-(phenylthio)hexyl p-toluenesulfonate (1e): mp 120 °C; NMR ($CDCl_3$) δ 7.83–7.00 (9 H, m), 2.86 (2 H, t, virtual coupling, J = 5 Hz), 2.40 (3 H, s), 1.83–1.10 (8 H, m).

General Procedure for Acetolysis. The reactions were performed on an approximately 1–2-mmol scale, both in neat AcOH and in the presence of AcOK, under standard conditions (substrate concentration, 0.2 M; AcOK concentration, 0.6 M). The crude reaction mixtures were diluted with CH_2Cl_2 (25 mL) and washed with H_2O, aqueous $NaHCO_3$, and H_2O until neutrality. The organic layers were dried (Na_2SO_4) and the solvents removed at reduced pressure. Product distributions were determined by GLC and NMR analysis of the crude reaction mixtures. Column chromatography of the final mixtures was usually employed in order to separate mixtures of tosylates **1** and **2** from mixtures of acetates **4** and **5**; the latter were normally eluted by *n*-hexane with traces of ethyl acetate, while elution of the tosylates required mixtures of ethyl acetate and *n*-hexane at least in a 2:1 ratio. By comparison, acetates **4** were prepared through the reaction of the corresponding deuteriated alcohols with Ac_2O. GLC analysis was employed for identification purpose and to ascertain the purity of mixtures of the two isomeric acetates.

Acetolysis of 1a. A solution of **1a** in AcOH was heated for 40 min at 40 °C; after that time the reaction mixture had approximately the following composition: 46% **1a**, 15% **3a**, 24% **4a**, 15% **5a**. When the acetolysis was carried out until completion (70 min) a 1:1 mixture of **4a** and **5a** was obtained. In the presence of AcOK, when the reaction was quenched after 10 min at 40 °C, the product distribution was as follows: 20% **1a**, 20% **3a**, 30% **4a**, 30% **5a**. Column chromatography over silica gel allowed separation of the mixture of the acetates from that of the tosylates, the former being eluted by *n*-hexane–ethyl acetate (98:2) and the latter by *n*-hexane–ethyl acetate (30:70). **1-Acetoxy-1,1-dideuterio-2-(phenylthio)ethane (4a)** and **1-acetoxy-2,2-dideuterio-2-(phenylthio)ethane (5a)** were obtained in a 1:1 ratio, as a mixture boiling at 147 °C at 760 mmHg. The NMR spectrum (CCl_4) showed, in addition to the signals at 7.33–6.96 (5 H, m) and 1.93 (3 H, s) ppm, two singlets (1 H, each) at 3.03 and 4.06 ppm, due to the CH_2S and CH_2O groupings present in the two acetates, respectively. The mixture of the two tosylates (mp 35 °C) obtained in AcOH at 40 °C showed in the NMR spectrum ($CDCl_3$) a singlet at 4.03 ppm due to the CH_2O grouping of **2,2-dideuterio-2-(phenythio)ethyl p-toluenesulfonate (3a)** in addition to the signals reported for **1a**. The results obtained in the acetolyses at 120 °C, performed following the standard conditions, are reported in Table I.

Acetolysis of 1b. Both the acetolyses (in AcOH and in the AcOH/AcOK system), by column chromatography elution of the final residues with hexane–ethyl acetate (98:2), gave the same mixture of acetates **4b** and **5b** (5.6:1 respectively). Elution with *n*-hexane–ethyl acetate (30:70) gave **1b** impure of the isomeric tosylate **3b**. **1-Acetoxy-1,1-dideuterio-3-(phenylthio)propane**

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(4b) and **1-acetoxy-3,3-dideuterio-3-(phenylthio)propane (5b)** were obtained in mixture as an oil boiling at 152 °C at 760 mmHg. The NMR of the mixture, in addition to the signals at 7.33–7.00 (5 H, m), 2.00 (3 H, s), and 1.90 (2 H, t, J = 6 Hz) ppm, showed two triplets at 2.63 (J = 6 Hz) and 4.10 (J = 6 Hz) ppm, due to the SCH_2 and CH_2O groups, respectively. In the NMR spectrum of the tosylate mixture (mp 39 °C) the signal observed at 4.03 ppm was assigned to the CH_2O group of the rearranged tosylate **3b**.

Acetolysis of 1c. After 5 min of heating in AcOH at 120 °C, evaporation to dryness of the aqueous solution obtained according to the general procedure gave a quantitative yield of **2,2-dideuterio-1-phenylthiolanium *p*-toluenesulfonate (2c)** (mp 140 °C from hexane): NMR ($CDCl_3$) δ 7.66–7.00 (9 H, m), 4.30–3.48 (2 H, ABC system), 2.63 (3 H, s), 2.53–2.33 (4 H, m); IR (KBr) ν_{SO} 1210 cm^{-1}. When the heating of **1c** in AcOH was prolonged up to 1 h and 30 min, **2c** was obtained in 76% yield, while the CH_2Cl_2 extract afforded a 1:1 mixture (24%) of acetates **4c** and **5c**. The acetolysis in the presence of AcOK after 30 min of heating at 120 °C afforded a quantitative yield of a 1:1 mixture of acetates **4c** and **5c**, isolated as yellow oil, bp 160 °C at 760 mmHg. The NMR spectrum ($CDCl_3$) of the latter mixture showed the following signals: δ 7.33–7.00 (5 H, m), 4.03 (1 H, t, virtual coupling, J = 6 Hz, assigned to the OCH_2 group), 2.87 (1 H, t, virtual coupling, J = 6 Hz, due to the SCH_2 group), 2.00 (3 H, s), 1.83–1.50 (4 H, m).

Acetolysis of 2c. After 1 h of heating at 120 °C, a 1:1 mixture of the isomeric acetates **4c** and **5c** was obtained. Kinetic runs were performed on a 0.2 M AcOH solution of **2c** at 120 °C in a NMR tube up to 60% conversion, by following the increase of the signal due to the aromatic protons of **4c** and **5c**, which in this solvent appeared as a singlet. A k_{obsd} = (7.60 ± 0.14) × 10^{-6} s^{-1} was obtained. In the presence of AcOK (0.6 M), after 15 min at 120 °C, **2c** gave a 1:1 mixture of **4c** and **5c**. k_{obsd} = (1.70 ± 0.02) × 10^{-3} s^{-1}.

Acetolysis of 1d. After 1 h and 30 min of heating at 120 °C in AcOH, evaporation to dryness of the aqueous solution obtained according to the general procedure afforded 75% yield of **2,2-dideuterio-1-phenylthianium *p*-toluenesulfonate (2d)** crystals with mp 188 °C. The latter compound was recovered quantitatively after 96 h refluxing in AcOH: NMR ($CDCl_3$) δ 8.16–7.33 (9 H, m), 3.93–3.60 (3 H, m), 2.46 (3 H, s), 2.30–2.00 (6 H, m); IR (KBr) ν_{SO} 1190 cm^{-1}. The organic layer, after elimination of the solvent, gave a 1:1 mixture of the starting tosylate and **1-acetoxy-1,1-dideuterio-5-(phenylthio)pentane (4d).** The latter was separated by column chromatography over silica gel as an oily product [bp 167 °C (760 mmHg)], which was found to be identical with an authentic sample prepared by Ac_2O acetylation of **1,1-dideuterio-5-(phenylthio)pentanol**: NMR (CCl_4) δ 7.23–6.96 (5 H, m), 2.83 (2 H, t, virtual coupling, J = 6 Hz), 2.00 (3 H, s), 1.81–1.43 (6 H, m). The acetolysis in the AcOH/AcOK system after 2 h at 120 °C afforded a 4:1 mixture of **4d** and the isomeric **1-acetoxy-5,5-dideuterio-5-(phenylthio)pentane (5d).** The NMR (CCl_4) spectrum of the mixture, in addition to the signals due to **4d**, showed a triplet (J = 6 Hz) at 3.96 ppm (0.4 H) assigned to the CH_2O grouping, while the integration of the triplet at 2.83 ppm, due to the SCH_2 of **4d**, accounted for only 1.6 H.

Acetolysis of 2d. After 1 h and 30 min at 120 °C in AcOH/AcOK, a 1:1 mixture of acetates **4d** and **5d** was obtained. Kinetic experiments performed in AcOH in the presence of AcOK (conducted as for **2c**) afforded a k_{obsd} = (4.56 ± 0.05) × 10^{-5} s^{-1}.

Preparation of 2'd. A Dowex 1 FLUKA anion (Cl^-) exchange resin (**2g**) was converted into the acetate form by elution with a solution of 1 N NaOH (40 mL) followed by treatment with H_2O until pH 8.5 (8 mL), then with 1 N AcOH (4 mL), and finally with H_2O to pH 5 (8 mL). A solution of **2d** (0.2 g) in H_2O (10 mL) was then passed on the column prepared as above; after treatment with H_2O (10 mL), the eluate was rotary evaporated to dryness and the NMR spectrum of the residue was rapidly recorded: ($CDCl_3$) δ 8.30–8.06 (2 H, m), 7.73–7.53 (3 H, m), 4.10–3.90 (3 H, m), 2.16–2.00 (6 H, m), 1.93 (3 H, s). After 15 min a complete conversion of the thianium acetate **2'd** into a 1:1 mixture of acetates **4d** and **5d** was observed in the probe.

Acetolysis of 1e. After 2 h heating at 120 °C in AcOH, the residue obtained by evaporation to dryness was chromatographed over silica gel; the fraction eluted by *n*-hexane gave **1-acetoxy-1,1-dideuterio-6-(phenylthio)hexane (4e)** isolated in 22% yield as an oil; bp 175 °C (760 mmHg); NMR ($CDCl_3$) δ 7.36–7.00 (5 H, m), 2.90 (2 H, t, virtual coupling, J = 6 Hz), 2.00 (3 H, s), 1.90–1.16 (8 H, m). When the acetolysis was protracted up to 6 h, column chromatography allowed the separation of a mixture of acetates **4e** and **5e** from a mixture of tosylates **1e** and **3e**, the latter being eluted by ethyl acetate–*n*-hexane (70:30). In the NMR spectrum ($CDCl_3$) of the latter mixture, the signal at 4.01 ppm was assigned to CH_2O of **3e**. In the AcOH/AcOK system, after 6 h of heating at 120 °C, the acetolysis was complete, giving a 6:1 mixture of **4e** and **5e**, which in the GLC analysis showed a single peak, corresponding to that of a synthetic sample of **4e**. In the NMR spectrum ($CDCl_3$), in addition to signals due to **4e**, a triplet at 3.96 ppm (virtual coupling, J = 5 Hz) was attributed to the CH_2O grouping of the isomeric acetate **5e**.

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