Neighboring-Group Participation. A "Quasi-S_Ni" Mechanism in the Acetolysis and Thioacetolysis of 1-(Phenylthio)-2-[(*p*-tolylsulfonyl)oxy]ethane

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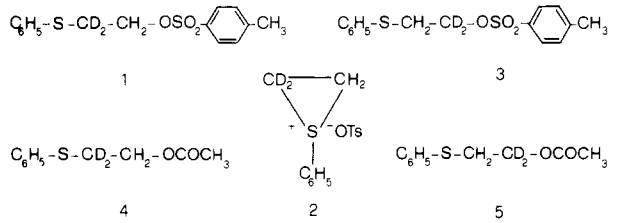
The acetolysis and the thioacetolysis of the title compound, selectively deuteriated at one of the two methylenes, was studied. The excess of the unrearranged acetate in the acetolysis at 40 °C has been explained in terms of coordination of the acid to the sulfur, followed by a "quasi-S_Ni" displacement of the leaving group. This pathway is concurrent with the equilibration of the two isomeric tosylates (through the agency of the episulfonium ion **2**) and with the acetolysis of **2**, resulting in a 1:1 mixture of **4** and **5**. The thioacetolysis of **1** and **3** at 40 °C gave in turn a 1:1 mixture of the thiolacetates **8** and **9**, along with the thionoacetate **6** in the reaction of **1** and the thionoacetate **7** in that of **3**. When the acetolysis and the thioacetolysis of **1** were run at the boiling temperature of the solvent, the reactions afforded only a 1:1 mixture of **4** and **5** and **8** and **9**, respectively, showing that at higher temperature coordination of the acid is not at work. In the dichloroacetolysis of **1**, a 1:1 mixture of the isomeric dichloroacetates **10** and **11** was always obtained. The results show that in the case of 2-(arylthio)ethyl tosylates there are several competing solvolytic pathways, whose relative importance depends upon the acidity and nucleophilicity of the solvent.

The acetolysis of the title compound, selectively deuteriated at one of the two methylenes, **1**, has been reported to afford at 40 °C a significant excess of the unrearranged acetate **4**; instead, when the same reaction was carried out in boiling AcOH or in the AcOH/AcOK system at 40 °C, a 1:1 mixture of the two isomerically labeled acetates was always formed.[1] Our previous analytical data, obtained by ^1H NMR determinations, have been confirmed by MS measurements on the basis of the relative abundance of diagnostic ions (see Table I). Thus, ratios of about 1.3 and 1.4 in favor of the unrearranged acetate were found in the acetolysis of **1** and **3**, respectively. Besides, control experiments confirmed that the acetates **4** and **5** do not undergo acid-catalyzed rearrangement after 18 h in boiling AcOH or in the AcOH/AcOK system.



These results suggested that not all of the acetolyses of **1** and **3** at 40 °C might proceed through the intermediate sulfonium ion **2**. However, this hypothesis was in striking contrast with the general views about S-3 participation in solvolytic reactions.[2] On the other side, the excess of the unrearranged acetate cannot be explained in terms of a concurrent S_N2 displacement of the tosylate. McManus and co-workers, studying the mechanism of solvolytic reactions of a number of thioethyl derivatives, pointed out the severe requisites necessary to overcome the powerful neighboring sulfur participation and to shift the reaction to a direct displacement S_N2 mechanism.[3] These requisites are by no means encountered in the acetolysis of substrates like **1** and **3**.

As previously reported,[1] tosylates **1** and **3** interconvert in AcOH, as well as in the absence of solvents. The relative kinetics is now graphically reported in Figure 1. Also, it has been proved that **1** and **3** do not undergo dimerization or polimerization unlike-β-ethylthio tosylates (and chlorides),[4] which can be ascribed to the greater nucleophilicity of the sulfur in alkyl thioethers.

The above results ruled out the possibility that the episulfonium **2** might in some way be responsible for the observed excess of the unrearranged acetate in the acetolysis at 40 °C. [If dimerization had occurred via the reaction of **2** with the starting tosylates, it can be seen that the two isomeric sulfonium ions thus originating may produce unequal amounts of the isomeric acetates, through different pathways (direct displacement by the solvent and neighboring-group participation by the remote sulfur).] To account for the latter results, never observed in other solvolytic reactions, it was anticipated that, along with the other pathways previously described, an additional one, characterized by simple coordination of the sulfur to the electrophilic center, might be concurrent and assist the direct displacement of the leaving group by the poor nucleophile *before* the episulfonium ion can be formed.[1] However, due to the several pathways involved, the kinetic study does not seem to guarantee any definite conclusion as to the presence of such mechanism involving a four-center transition state.

An alternative mechanism, involving competitive coordination of the acid to the ether sulfur, followed by a "quasi-S_Ni" process, was then considered, and the thioacetolysis of tosylates **1** and **3** was investigated, having in mind that the use of a potentially ambident acid, structurally related to AcOH, could allow us to discriminate between the above two mechanisms.

The thioacetolysis of **1** at 40 °C afforded the thiono ester **6** in approximately 20% yield, along with a 1:1 mixture of the two isomerically labeled thiol esters **8** and **9**. No traces of **3** and of the isomeric thiono ester **7** could be detected

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(1) Rosnati, V.; Saba, A.; Angius, A.; Casarini, D. *J. Org. Chem.* **1987**, *52*, 4094.
(2) Capon, B.; McManus, S. P. In *Neighboring Group Participation*; Plenum: New York, 1976; Vol. 1, Chapter 5.
(3) Sedaehat-Herati, M. R.; McManus, S. P.; Harris, J. M. *J. Org. Chem.* **1988**, *53*, 2539.
(4) McManus, S. P.; Sedaghat-Herati, M. R.; Harris, J. M. *Tetrahedron Lett.* **1987**, *28*, 5299.

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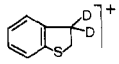
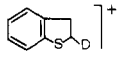
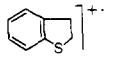
Table I. Diagnostic and Relevant Ions in the Mass Spectra of Compounds 4–6 and of 1:1 Mixtures of 8 + 9 and 10 + 11[a]

ionic species	4[b]	5[b]	6[c]	8 + 9[d]	10 + 11[e]
$M^{+\cdot}$	198 (12)	198 (13)	214 (26)	214 (29)	266 (15)
$C_6H_5-\overset{+}{S}<^{CD_2}_{CH_2}$					139 (40)
		138 (100)		138 (100)[f]	138 (71)[f]
	137 (100)		137 (100)[g]		137 (100)[g]
			136 (78)		
$C_6H_5-\overset{+}{S}=CD_2$	125 (27)		125 (34)	125 (20)	125 (21)
$C_6H_5-\overset{+}{S}=CH_2$		123 (22)		123 (21)	123 (20)

[a] A MS investigation on samples of **4** and **5** obtained by acetylation of the selectively deuteriated alcohols proved that the $C_6H_5\overset{+}{S}=CD_2$ or $C_6H_5\overset{+}{S}=CH_2$ ions are formed without any H scrambling, which demonstrates their diagnostic power. [b] From an authentic sample. [c] From the thioacetolysis of tosylate **1** at 40 °C. [d] From the thioacetolysis of tosylates **1** and **3** at 40 °C as well as at 90 °C. [e] From the dichloroacetolysis of tosylate **1** at 40 °C. [f] The isomeric ionic species (dideuteriated at C_α) were also formed. [g] The isomeric ionic species (monodeuteriated at C_β) were also formed.

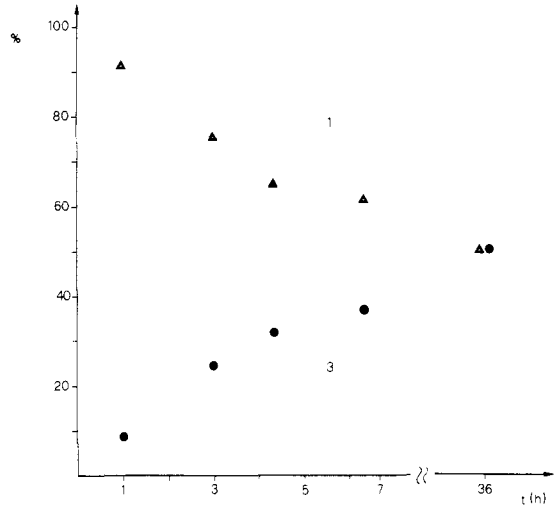
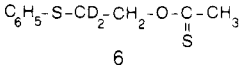


Figure 1. Equilibration of tosylate **1** to **3**. The determinations were obtained by MS measurements on the relative abundance of the diagnostic ions (m/z 125 for tosylate **1** and 123 for tosylate **3**).

in the final mixture by GC/MS. Analogously, the thioacetolysis of **3** gave **7**, in the absence of **1** and **6**, along with the same 1:1 mixture of **8** and **9**. Furthermore, at 90 °C the thioacetolysis of both **1** and **3** gave a 1:1 mixture of the thiolacetates **8** and **9** in the absence of the thionoacetates.



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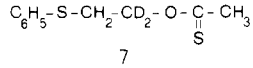

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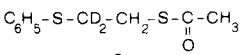

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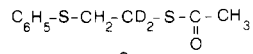
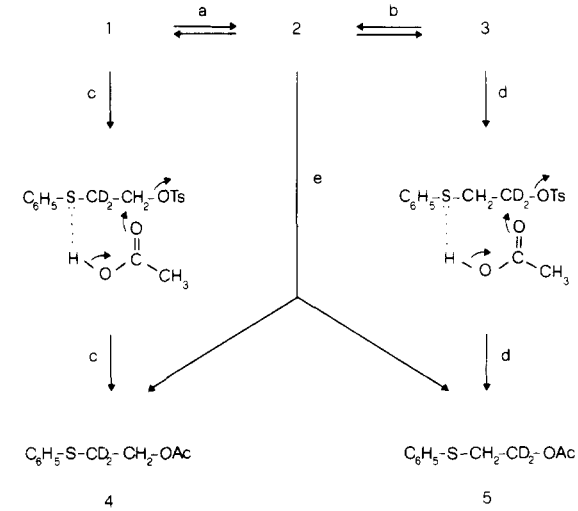


9

Simple thiono esters are stable in the thione form;[5] however, in our case ionization of **6** and **7** via S-3 participation by the ethereal sulfur might have occurred to some extent. In this case, due to the greater stability of thiol esters relative to thiono esters,[6] as well as to the greater nucleophilicity of sulfur compared to oxygen,[7] isomerization of **6** and **7** to **8** and **9**, respectively, could be expected.[8] However, this possibility has been excluded, since the above thionoacetates were shown to be stable in refluxing acetic acid.

Scheme I. Proposed Mechanism for the Acetolysis of Tosylates 1 and 3 at 40 °C in Neat AcOH



4 **5**

The results of the thioacetolyses of **1** and **3** indirectly support the mechanism proposed for the acetolyses at low temperature in neat AcOH. According to Scheme I, the acetolysis of the tosylates, which equilibrates through pathways a and b, proceeds only partly via pathway e, the episulfonium ion leading to a 1:1 mixture of the isomeric acetates. The excess of the unrearranged acetate is produced via pathway c or d, starting from **1** or **3**, respectively, both pathways involving the coordination of the acid to the thioether sulfur.

Analogously, the thioacetolysis proceeds partly via the episulfonium ion (pathway e), leading to a 1:1 mixture of the thiol esters **8** and **9**, whereas the thiono esters **6** and

(5) Kunz, D.; Scheithaner, S.; Bleish, S.; Mayer, R. *J. Prakt. Chem.* **1970**, *312*, 426.

(6) Smith, S. G. *J. Am. Chem. Soc.* **1961**, *83*, 4285.

(7) Streitwieser, A., Jr. *Chem. Rev.* **1956**, *56*, 571.

(8) Benzhydryl thionobenzoates have been found to undergo isomerization to the corresponding thiolbenzoates much more rapidly than they solvolyze. Smith, S. G. *Tetrahedron Lett.* **1962**, *21*, 979.

Table II. Acetolysis of Tosylate 1 in Neat AcOH at 40 °C

reacn time, min	tosylate 1, %	tosylate 3, %	acetate 4, %	acetate 5, %
30	41.4	27.9	20.3	10.4
60	25.6	26.7	20.3	18.5
120	17.3	16.6	36.3	29.8
180	10.6	8.9	46.6	33.9
240	7.7	3.6	49.5	39.2
300			56.0	44.0

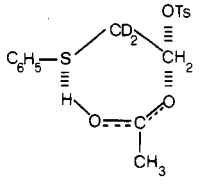
Table III. Acetolysis of Tosylate 3 in Neat AcOH at 40 °C

reacn time, min	tosylate 1, %	tosylate 3, %	acetate 4, %	acetate 5, %
30	23.3	38.1	12.7	25.9
60	22.7	30.4	16.9	30.0
120	7.6	12.2	32.7	47.5
180	6.1	8.8	37.0	48.1
240	2.4	4.7	38.3	54.6
300			42.0	58.0

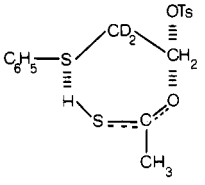
7 are formed *via* pathways c or d, from 1 and 3, respectively, through the intermediate coordination of the thioacid to the sulfur.

The previously described reaction of 1 and 3 in boiling AcOH and in the AcOH/AcOK system at 40 °C, both leading to equal amounts of acetates 4 and 5, can now be fully understood. The higher temperature, while favorably influencing the intramolecular process leading to the episulfonium ion, might well depress and eventually suppress coordination of the acid to the thioether group, thus avoiding the formation of the labile intermediate responsible for the "quasi-S_Ni" mechanism. On the other side, in a buffered solution (i.e. in the presence of 3 mol of AcOK), the reaction has to proceed entirely through the irreversible pathway e through counterion exchange as previously demonstrated.[1]

Transition states of type A and B might be involved in the acetolysis and the thioacetolysis, respectively.



A



B

As for the kinetic problems, it has been proven that in the thioacetolysis of 1 the formation of thionoacetate 6 and thiolacetates 8 and 9 occurs along with the fall in the concentration of the tosylate (see Table IV). Since pathway b has been excluded, and no traces of episulfonium 2 (and of the alcohols possibly deriving from the quenching) were detected, the hypothesis can be made that 2 must be present in a steady-state concentration; consequently k_e must be $\gg k_{-a}$. Pathway a must then be the rate-determining step in the process leading to 8 and 9. Accordingly, $k_a = 2.7 \times 10^{-4}$ s^{-1} and $k_c = 5.9 \times 10^{-5}$ s^{-1} were calculated from the k_{obsd} and from the ratio between the total concentration of 8 + 9 and that of 6.

A more complex situation is present in the acetolysis of 1 and 3, since interconversion of the starting tosylates does occur in this solvolysis, though without a fast preequilibrium (see data reported in Tables II and III). Therefore k_{-a} cannot be assumed to be negligible in comparison with k_e. Furthermore, the product distribution indicates that the "quasi-S_Ni" pathway and the one going through the episulfonium occur with comparable rates.

The study of the dichloroacetolysis of 1 gave a result that is in line with the "quasi-S_Ni" mechanism. The choice of this solvolytic reaction was made by assuming that, going from AcOH and AcSH to a stronger, structurally related acid, such as dichloroacetic acid (The pk_a values for AcOH, AcSH, and $Cl_2CHCOOH$ are 4.7, 3.3, and 1.3, respectively.[9]), protonation rather than coordination might be mechanistically more important. Indeed, the dichloroacetolyses of 1 and 3 at 40 °C afforded the two dichloroacetates 10 and 11 in a 1:1 ratio.

Table IV. Thioacetolysis of Tosylate 1 and 3

substrate	reacn time, min	% products 1	3	6	7	8	9
1	15	63		7		15	15
1	30	41		9		25	25
1	60	26		12		31	31
1	90	14		16		35	35
1	120	8		18		37	37
1	180			20		40	40
3	180				18	41	41

C_6H_5-S-CD_2-CH_2-OCOCHCl$_2$ (10)

C_6H_5-S-CH_2-CD_2-OCOCHCl$_2$ (11)

The structure of thionoacetates 6 and 7, thiolacetates 8 and 9, dichloroacetates 10 and 11, and in particular their deuterium label, have been established through MS on the diagnostic ions, which are reported in Table I.

Finally, coordination of the acid at the tosylate ether oxygen, if occurring, cannot be considered a relevant mechanistic event in the solvolytic reactions under investigation; indeed, the acetolysis, thioacetolysis, and dichloroacetolysis of ethyl tosylate taken as a model have been shown to proceed much more slowly than those of tosylate 1 (see Experimental Section).

Experimental Section

^{1}H NMR spectra were recorded on a Bruker WP 80 SY spectrometer. All MS measurements were performed on a Finnigan ITD 700 GC/MS system and/or on a VG ZAB-2F instrument. Both were operating in electron-impact conditions with a source temperature of 200 °C.

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. Dichloroacetic and thioacetic acids were purified Fluka reagents.

Substrates and Reference Products. As previously described,[1] arenesulfonates were prepared by $LiAlH_4$ and $LiAlD_4$ reduction of the corresponding ethyl esters, followed by tosylation. Standard procedure were employed for their purification.

2-(Phenylthio)ethyl *p*-toluenesulfonate: mp 35 °C; ^{1}H NMR δ 8–7 (9 H, m), 4.10 (2 H, t), 3.10 (2 H, t), 2.45 (3 H, s); MS, *m/z* (%) 308 (2), 154 (31), 136 (31), 123 (100), 110 (56), 109 (70).

2,2-Dideuterio-2-(phenylthio)ethyl *p*-toluenesulfonate (1):[1] mp 35 °C; ^{1}H NMR δ 8–7 (9 H, m), 4.10 (2 H, s), 2.45 (3 H, s); MS, *m/z* (%) 310 (2), 156 (61), 138 (15), 137 (25), 125 (100), 123 (3), 110 (65), 109 (42).

1,1-Dideuterio-2-(phenylthio)ethyl *p*-toluenesulfonate (3):[1] mp 35 °C; ^{1}H NMR δ 8–7 (9 H, m), 3.10 (2 H, s), 2.45 (3 H, s); MS, *m/z* (%) 310 (2), 156 (66), 138 (3), 137 (4), 125 (3), 123 (100), 111 (23), 110 (15), 109 (15).

1-Acetoxy-2-(phenylthio)ethane was obtained as an oil by treating the corresponding alcohol with Ac_2O: ^{1}H NMR δ 7.5–7.0 (5 H, m), 4.25 (2 H, t), 3.10 (2 H, t), 2.01 (3 H, s); MS, *m/z* (%) 196 (12), 136 (100), 123 (16), 110 (17), 109 (13).

2-(Phenylthio)-1-thioacetylethane was obtained as an oil from the thioacetolysis of the corresponding tosylate; isolation from the reaction mixture and purification were performed by

(9) *Dictionary of Organic Compounds*; Eyre & Spottiswoode Publishers, Ltd.: London, Vol. 2, p 957; Vol. 5, p 3048.

column chromatography over silica gel: ^{1}H NMR δ 7.5–7.0 (5 H, m), 3.10 (4 H, s broad), 2.35 (3 H, s); MS, m/z (%) 212 (13), 136 (100), 123 (26), 110 (74), 109 (27).

General Procedure for the Acetolysis of Tosylates 1 and 3. The reactions were performed on 1.5 g of the substrates dissolved in 50 mL of anhydrous AcOH, and the solutions were kept at 40 °C under a N_2 atmosphere. Samples were taken after 30, 60, 120, 180, 240, 300 min and treated as follows: dilution with 30 mL of cold CH_2Cl_2, repeatedly washings at 0 °C with H_2O, $NaHCO_3$ solution, and again with H_2O until neutral. The organic layers, dried over Na_2SO_4, were evaporated to dryness under reduced pressure at 20 °C. The progress of the reaction was followed by ^{1}H NMR analysis ($CDCl_3$). In particular, with tosylate 1 it was evaluated by the decay and/or the disappearance of the signals at δ 2.45 (arom CH_3) and 4.10 (CH_2OTs) and the appearance of the signals at δ 2.01 (CH_3COO), 3.10 (CH_2S), and 4.25 (CH_2OAc). With tosylate 3, the calculations were analogously made by measuring the decay and/or the disappearance of the signals at δ 2.45 (arom CH_3) and 3.10 (CH_2S) and the appearance of those at δ 2.01 (CH_3COO), 4.10 (CH_2OTs), and 4.25 (CH_2OAc). The final reaction mixtures were purified by chromatography over silica gel; elution by *n*-hexane gave mixture of acetates 4 and 5. When present, the tosylate 1 and 3 were obtained by elution with hexane–ethyl acetate, 1:2. MS/GC analyses were also performed on the final mixtures.

1-Acetoxy-2,2-dideuterio-2-(phenylthio)ethane (4): oil; ^{1}H NMR δ 7.5–7.0 (5 H, m), 4.25 (2 H, s), 2.01 (3 H, s); MS, m/z (%) 198 (12), 137 (100), 125 (27), 110 (11), 109 (22).

1-Acetoxy-1,1-dideuterio-2-(phenylthio)ethane (5): oil; ^{1}H NMR δ 7.5–7.0 (5 H, m), 3.10 (2 H, s), 2.01 (3 H, s); MS, m/z (%) 198 (13), 138 (100), 123 (22), 110 (5), 109 (15).

General Procedure for the Thioacetolysis of Tosylates 1 and 3. The reactions were run on 1.5 g of the substrates dissolved in 50 mL of CH_3COSH (Fluka) at 40 °C under stirring and in N_2 atmosphere, following the above described procedure for the acetolysis. In the thioacetolysis of 1 the ^{1}H NMR analysis of the samples (taken after 15, 30, 60, 90, 120, 180 min) was based on the decay of the signal at δ 4.10 (CH_2OTs) and the appearance of the signals at δ 3.10 (due to $CH_2SC_6H_5$ and/or CH_2SCOCH_3) and 4.25 (CH_2OCSCH_3), without considering the remaining signals at δ 2.00 (CH_3CSO), 2.35 (CH_3COS), and 2.45 (arom CH_3). Instead, ^{1}H NMR analysis did not result as a very effective tool in following the progress of the thioacetolysis of 3 except for the absence, through out the reaction, of the signals at δ 4.25 (due to the methylene on oxygen) and 4.10 (due to the rearranged tosylate 1). The crude mixtures were chromatographed over a silica gel column; elution with *n*-hexane gave first the thiol acetates 8 and 9 (in 1:1 ratio) and subsequently the pure thionoacetate 6 in the thioacetolysis of 1 and 7 in that of 3. The results are reported in Table IV. The thioacetolysis of 1, when performed at 90 °C, was completed after 15 min. In this case the final mixture, according to the above procedure, gave only a 1:1 mixture of the thiolacetates 8 and 9.

2,2-Dideuterio-2-(phenylthio)-1-thioacetylethane (6): oil; ^{1}H NMR δ 7.5–7.0 (5 H, m), 4.25 (2 H, s), 2.00 (3 H, s); MS, m/z (%) 214 (26), 137 (100), 136 (78), 125 (34), 110 (14), 109 (27).

1,1-Dideuterio-2-(phenylthio)-1-thioacetylethane (7): oil; ^{1}H NMR δ 7.5–7.0 (5 H, m), 3.10 (2 H, s), 2.00 (3 H, s).

2,2-Dideuterio-2-(phenylthio)-1-(acetylthio)ethane (8) and 1,1-dideuterio-2-(phenylthio)-1-(acetylthio)ethane (9) were obtained in a 1:1 ratio as an oily mixture: ^{1}H NMR δ 7.5–7.0 (5 H, m), 3.10 (2 H, s broad), 2.35 (3 H, s); MS, m/z 214 (19), 137 (100), 138 (76), 125 (16), 123 (15), 110 (45), 109 (30).

Dichloroacetolysis of Tosylate 1. The reaction was run on 0.5 g of substrate dissolved in 17 mL of $CHCl_2COOH$ (Fluka) at 40 °C with stirring and under a N_2 atmosphere. Samples were taken after 60 and 120 min and treated as for the above solvolyses. The progress of the reaction was followed by ^{1}H NMR analysis ($CDCl_3$), estimating the new signals at δ 3.20 ($C_6H_5SCH_2$), 4.40 (CH_2OCO), and 5.90 ($CHCl_2$) and the decay of those at δ 2.45 (CH_3 arom) and 4.10 (CH_2OTs). The conversion was 85% after 1 h and 100% after 2 h. Oily mixtures 1:1 of **2,2-dideuterio-2-(phenylthio)-1-(dichloroacetoxy)ethane (10)** and **1,1-dideuterio-2-(phenylthio)-1-(dichloroacetoxy)ethane (11)** were obtained: ^{1}H NMR δ 7.5–7.0 (5 H, m), 5.90 (1 H, s), 4.40 (1 H, s), 3.20 (1 H, s); MS, m/z (%) 266 (15), 139 (40), 138 (71), 137 (100), 125 (21), 123 (20), 110 (18), 109 (63).

Solvolytic Reactions of Ethyl *p*-Toluenesulfonate. Acetolysis, thioacetolysis, and dichloroacetolysis of the above tosylate were run at the refluxing temperature. After 18 h the relative conversion were 1%, 18%, and 25%, respectively.

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Registry No. 1, 109244-24-8; 3, 109244-17-9; 4, 109244-23-7; 5, 109244-22-6; 6, 118298-67-2; 7, 118298-68-3; 8, 118298-69-4; 9, 118298-70-7; 10, 118317-79-6; 11, 118317-80-9; 2-(phenylthio)ethyl *p*-toluenesulfonate, 116047-07-5; 1-acetoxy-2-(phenylthio)ethane, 20965-30-4; 1-hydroxy-2-(phenylthio)ethane, 699-12-7; 2-(phenylthio)-1-thioacetyl ethane, 14476-42-7; ethyl *p*-toluenesulfonate, 80-40-0.

Mechanism of *E*/*Z* Stereoisomerization of Imidate Anions

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Kinetics of *E*/*Z* stereoisomerization of *N*-arylformimidate anions, HC(O$^-$)=NAr, in *N*-methylpropionamide solvent were determined by an NMR saturation-transfer method. A Hammett plot of the rate constants gives a slope ρ of +2.3 ± 0.2 or +2.1 ± 0.3. This value is very close to the ρ of 2.2 observed in similar imine stereoisomerizations known to proceed by nitrogen inversion. It is inconsistent with the ρ of 3.8 expected for stereoisomerization by C–N rotation. It is therefore concluded that *E*/*Z* stereoisomerization of imidate anions proceeds by nitrogen inversion, despite a high-level MO calculation that favored C–N rotation.

Introduction

Despite continual investigation into the dynamic stereochemistry of amides,[1] their conjugate bases—imidate anions—have been largely neglected. These are important as catalysts,[2] as ligands for metal ions,[3] including those at enzyme active sites,[4] and as intermediates in organic

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