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NUCLEOPHILIC SUBSTITUTION OF α-HALO-KETONES. XXIII. ACETOLYSIS OF 1-CHLORO-3-PHENOXY-1-PHENYLTHIO-2-PROPANONES. AN INTRAMOLECULAR TRANS-ACETYLATION INVOLVING PHENOXIDE ANION AS THE LEAVING GROUP

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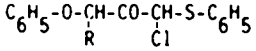
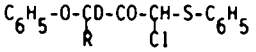
Abstract - The acetolyses of α-chloro-ketones **1a-c**, **2a-c**, **9a** and **11a** have been investigated parallely. Several aspects of the mechanisms involved in chlorine normal and cine substitution have been elucidated. Intramolecular trans-acetylation, ultimately leading to fragmentation of acetoxy-ketones **3b**, **4a** and **4c**, have been postulated to account for the formation of thiol ester **6**, aldehyde **5a** and ketone **5c**, respectively.

The acetolysis of α'-arylthio- and α'-aryloxy-α-chloro-ketones has been shown to proceed through the enolization-solvolysis mechanism; the different reactivity observed in the two series has been essentially ascribed to the different aptitude of the neighbouring heteroatom to assist ionization of the intermediate enol allyl chlorides and delocalization of the charge in the cationic species involved in the solvolysis.[1] Aiming to throw further light on the role played by the neighbouring heteroatom, the research has been extended to the acetolysis of substrates **1a,b,c** and **2a,b,c** taken as models for investigating the contrasting influence of the two ether functions.



1a: R=H
1b: R=CH_3
1c: R=C_6H_5



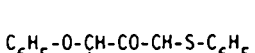
2a: R=D
2b: R=CH_3
2c: R=C_6H_5

RESULTS

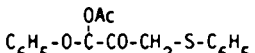
α-Chloro-ketones **1a,b,c** were prepared by reacting phenyl sulphenyl chloride with 1-diazo-3-phenoxy-2-butanone and 1-diazo-3-phenoxy-3-phenyl-2-propanone,[2] respectively. The reaction of the corresponding 2-deuterio-2-phenoxyacetyl chlorides with CH_2N_2 afforded the above α-diazo ketones deuteriated at the α'-C, which were converted into the corresponding α-chloro-ketones **2a,b,c** by reaction with sulphenyl chloride. The acetolyses were performed under standard conditions in plain AcOH and in the presence of AcOK. The reactivity of **1a** was also tested in the AcOH/Ac_2O system, as well as in the presence of LiCl and $LiClO_4$. The main results are summarized in the Tables.

The acetolysis of **1a** in plain AcOH gave an approximately 5:1 mixture of the isomeric acetoxy ketones **3a** and **4a**, traces of α,β-unsaturated aldehyde **5a** being detected in the crude product by GC/MS analysis. As shown in Table 1, the solvolysis was moderately depressed in 1:1 AcOH/Ac_2O, but practically inhi-

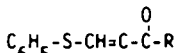
bited in 1:9 AcOH/Ac_2O; on the other side, 0.02 M concentrations of p-toluenesulfonic acid or potassium acetate apparently did not speed up the solvolysis. However interesting differences in product distribution were observed in the different media. Thus, while both the products of normal and cine substitution were obtained in neat AcOH as well as in the presence of 0.02 M AcOK, the former was the only reaction in the AcOH/Ac_2O system and the main one in the acid catalyzed solvolysis, along with the formation of considerable amounts of aldehyde **5a**.



3a: R=H
3b: R=CH_3
3c: R=C_6H_5



4a: R=H
4b: R=CH_3
4c: R=C_6H_5



5a: R=H
5b: R=CH_3
5c: R=C_6H_5

The aldehyde was also obtained in the acetolysis of **1a** in the presence of high AcOK concentrations (see Table 3), eventually being the only product when the solvolysis was prolonged up to 3 h. In a separate experiment it was shown that acetoxy ketone **4a** is the precursor of **5a** when heated in the AcOH/AcOK system.

The acetolysis of **1a** showed the normal salt effect pattern in the presence of LiCl, while the special salt effect could be evidenced on addition of $LiClO_4$ (see Fig. 1). As for product distribution, normal substitution was the only reaction observed with $LiClO_4$, while considerable amounts of cine substitution were obtained with high LiCl concentrations (see Table 2).

Table 1. Acetolysis of **1a** in different media.[a]

Media	Conversion (%)	Products (%)		
		3a	4a	5a
AcOH	81	84	16	traces
AcOH/Ac_2O (1:1)	75	100		
AcOH/Ac_2O (1:9)	8	100		
AcOH/TsOH (0.02 M)	81	80		20
AcOH/AcOK (0.02 M)	83	80	20	traces

[a] Substrate concentration: 0.2 M. Reaction temperature: 120°. Reaction time: 2 h.

Table 2. Acetolysis of **1a** in the presence of LiCl and $LiClO_4$.[a]

Salt	Molarity	Conversion (%)	Products (%)	
			3a	4a
—		64	92	8
LiCl	0.001	64	92	8
LiCl	0.01	69	91	9
LiCl	0.02	71	83	17
LiCl	0.04	78	78	22
$LiClO_4$	0.001	74	96	4
$LiClO_4$	0.01	75	100	traces
$LiClO_4$	0.02	80	100	—
$LiClO_4$	0.04	88	100	—

[a] Substrate concentration: 0.2 M. Reaction temperature: 120°. Reaction time: 1 h.

Table 3. A comparison of the acetolyses of **1a-c** substrates in plain AcOH (A) and in the presence of AcOK (B).[a]

Substrate	Reaction system	Reaction time	Conversion	Products
1a	A	2 h	81	3a (84%) 4a (16%)
	B	30 min	100	4a (33%) 5a (67%)
1b	A	2.5 h	60	3b (100%)
	B	30 min	100	6 (75%) 7 (25%)
1c	A	3 h	73	3c (100%)
	B	1 h	100	5c (100%)

[a] Substrate concentration: 0.2 M. AcOK concentration: 0.6 M. Reaction temperature: 120°.

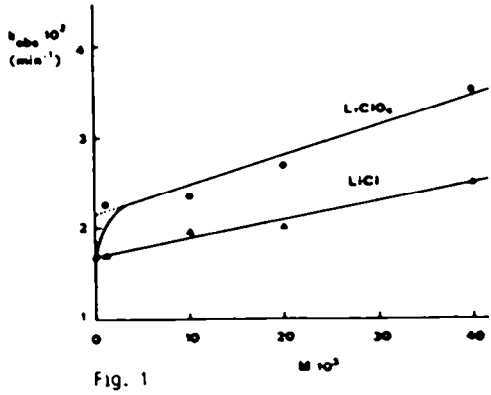
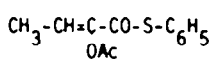


Fig. 1

The data reported in Table 3 illustrate a comparison of the reactivity of chloro-ketones **1a–c** in the acetolysis in AcOH and in the presence of 3 moles AcOK. The solvolysis of **1b** and **1c** in the absence of acetate occurred less easily than that of **1a**, both substrates affording exclusively normal substitution. In the presence of AcOK the reaction followed a different course: a 3:1 mixture of thiol ester **6** and α,β-unsaturated ketone **7** was obtained in the acetolysis of **1b** with no traces of ketone **5b**, while α,β-unsaturated ketone **5c** was the only product in that of **1c**.

As for the deuteriated substrates **2a,b,c**, the acetolyses in refluxing AcOH afforded exclusively the corresponding α-acetoxy-ketones **8a,b,c**, with 60-80% conversion after 2-3 h; also, the recovered starting materials were shown to be 100% deuteriated at the α'-C. In the presence of 0.6 M AcOK, the acetolysis of **2a** gave instead a roughly 1:1 mixture of acetoxy-ketone **4a** (about 95% deuteriated at the methinic carbon) and aldehyde **5a** (completely deuteriated at the formyl group).



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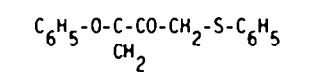

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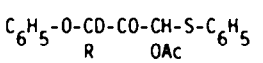
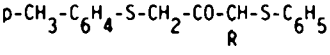
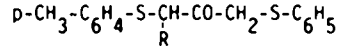


8a: R=D
8b: R=CH
8c: R=C_6H_5

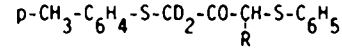
Finally, chloro-ketone **9a**, having different but electronically equivalent arylthio groups, after 2.5 h refluxing in AcOH afforded 32% of each of the isomeric acetoxy-ketones **9b** and **10b**, along with the isomeric chloro-ketones **9a** and **10a**, also in 1:1 ratio. Even the deuteriated chloro-ketone **11a** was shown to undergo exclusively normal substitution, affording acetoxy-ketone **11b**, with full retention of the isotopic labelling.



9a: R=Cl
9b: R=OAc



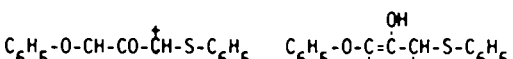
10a: R=Cl
10b: R=OAc



11a: R=Cl
11b: R=OAc

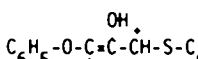
DISCUSSION

Different mechanisms are clearly at work in the various acetolyses of α-chloro-ketone **1a**. In AcOH, a solvent of low ionizing power,[3] α-acetoxy-ketone **3a** very probably forms via intimate ion pair **12a**. Instead, preliminary enolization of the substrate to enol allylic chloride **13a** is required for the formation of the isomeric α-acetoxy-ketone **4a**, which may originate via ion pair **14a** and/or bridged ion pair **15a**. These views are strongly supported by the acetolysis of the deuteriated substrate **2a**, which gave no cine substitution at all and afforded **8a** in the absence of any D/H exchange.

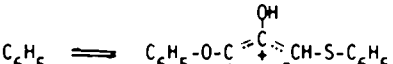


12a: R=H
12b: R=CH_3
12c: R=C_6H_5

13a: R=H
13b: R=CH_3
13c: R=C_6H_5



14a: R=H
14b: R=CH_3
14c: R=C_6H_5



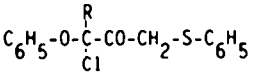
15a: R=H
15b: R=CH_3

α-Chloro esters were already shown to undergo solvolysis through a S_N1 mechanism.[4] The possibility that dissociated carbonium ions might be involved in the formation of **3a** is ruled out by the experiments with added Ac_2O, which showed a slow down of the acetolysis with mixtures of AcOH/Ac_2O of decreasing ionizing power and increasing dissociating ability.[5] The same conclusion can be argued from the salt effects observed in the acetolysis of **1a** in the presence of LiCl and $LiClO_4$. While in the former the external chloride may be involved in a S_N2' reaction leading to the isomeric chloro-ketone **16a**, ultimately responsible for the formation of **4a**, the total absence of chlorine cine-sub-

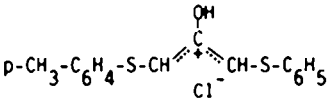
stitution in the presence of $LiClO_4$ may be explained in terms of the occurrence of a new type of ion pairs, no more fitted for isomerization of the substrate.

Indeed, chlorine cine substitution may occur through different pathways. Thus, in AcOH ion pair **14a** may be in equilibrium with non-classical bridged ion pair **15a**,[6] which may collapse to the isomeric α-chloro-ketone **16a**, or directly undergo solvolysis to acetoxy-ketone **4a**. In the presence of acetate, and particularly with high salt concentrations, **13a** and/or **14a** may undergo nucleophilic attack at the more electrophilic carbon, possibly through a S_N2' mechanism.

As for the possibility that **15a** may really be involved in the acetolysis of **1a**, one may recall that reversible isomerization has been proved in several acetolyses of α'-arylthio-α-chloro-ketones,[7] but in no case with α'-aryloxy-α chloro-ketones.[1] Clearly, the presence of an additional ether group may well determine a different reactivity. However, the acetolysis of α-chloro-ketone **9a** did not lead exclusively to normal substitution, as it might be expected due to the high reactivity of the α-chloro thioether function: indeed, the yield of practically equal amounts of acetoxy-ketone **9b** and **10b** on one side and of the isomeric chloro-ketone **9a** and **10a** on the other side strongly supports the view that the acetolysis of **9a** proceeds, at least partly, through preliminary enolization of the substrate, bridged ion pair **17** being responsible for reversible isomerization, as well as for normal and cine substitution.



16a: R=H
16b: R=CH_3
16c: R=C_6H_5



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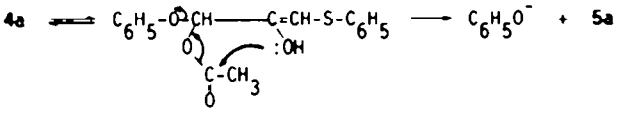
Accordingly, the acetolysis of the deuteriated chloro-ketone **11a** gave exclusively normal substitution. The above results, however, leave open the question whether **1a,b,c** isomerize during solvolysis, or whether **16a,b,c** do form in the AcOH/AcOK system, but are so reactive as to make their identification impossible.

As for aldehyde **5a**, obtained in the acetolysis of **1a** in the presence of p-toluenesulfonic acid or high acetate concentrations, the following mechanism accounts for its formation from acetoxy-ketone **4a**.

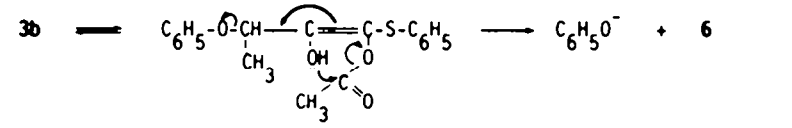


The mechanism is consistent with the finding that the aldehyde obtained from the acetolysis of **2a** was selectively deuteriated at the formyl group.

The acetolyses of **1b** and **1c** must also involve different mechanisms in the different media. In the pure solvent, as in the case of **1a**, normal substitution is likely to occur *via* the corresponding ion pair **12b,c** rather than enol allylic ion pair **14b,c**; this is in line with the acetolyses of **2b,c** which were shown to occur as easily as those of the undeuteriated substrates, affording the corresponding acetoxy-ketones **8b,c** with full retention of the isotopic labelling. The enol allylic chloride **13b** and/or the corresponding ion pairs **14b**, **15b** may instead be involved in the acetolysis of **1b** in the presence of acetate, undergoing HCl elimination to give **7**, possibly through a concertated mechanism assisted by the acetate. The possibility that **7** might originate from acetoxy-ketone **4b**, through AcOH elimination, seems a rather remote one, on the basis of previous work dealing with the formation of 3-phenoxy-3-buten-2-one in the acetolysis of 1-chloro-3-phenoxy-2-butanone.[1]

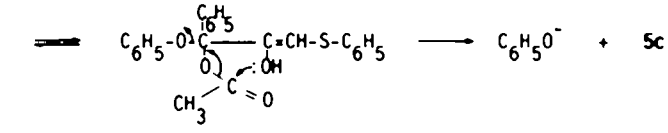
As for thiol ester **6**, the main product obtained in the acetolysis of **1b** in the AcOH/AcOK system,

the following mechanism accounts for its formation from acetoxy-ketone **3b**.



Both this mechanism and the one proposed for the formation of aldehyde **5a**, involve an intramolecular transacetylation, ultimately resulting in phenoxy anion elimination. Simple transacetylations leading to thiol esters have already been encountered in the acetolysis of 1-acetoxy-1-phenylthio-2-propanone[8] and 1-acetoxy-4,4-dimethyl-1-phenylthio-2-pentanone.[9]

Finally, the formation of α,β-unsaturated ketone **5c**, the only product obtained in the acetolysis of **1c** in the presence of acetate, may also be interpreted with the mechanism proposed for the formation of aldehyde **5a**; however, the potential precursor **4c** was not identified in the reaction mixture.



Notice that all the mechanisms proposed for the formation of aldehyde **5a**, ketone **5c** and thiol ester **6** require enolization of the corresponding precursor through a prototropic shift involving the C_6H_5-S-$\underline{C}$H-CO- rather than the C_6H_5-O-$\underline{C}$H-CO- grouping; this is in line with the stronger acidity of the former proton.[10]

EXPERIMENTAL

NMR spectra were recorded on a Varian T60 spectrometer using tetramethylsilane as the internal standard. The mass spectral data were obtained on a Perkin Elmer 270 spectrometer.

Materials. Anhydrous AcOH was prepared by refluxing (4 h) 99.8% AcOH (Merck) with the calculated amount of Ac_2O (Merck).

The solutions of AcOK and LiCl in glacial AcOH, prepared from Carlo Erba RPE salts dried at 120°C in vacuo until constant weight. Anhydrous solution of 0.02 M p-toluenesulphonic acid in AcOH was prepared by adding the calculated amount of Ac_2O to the solution of the p-toluenesulphonic acid monohydrate (Carlo Erba) in glacial AcOH. $LiClO_4$ solutions were prepared by treating the calculated amount of the trihydrate salt (Fluka) in anhydrous AcOH with a small Ac_2O excess.

Substrates. Chloro-ketones **1a-c** and **2a-c** were prepared by reacting at room temperature, under nitrogen, the corresponding diazo-ketone with a slight excess of phenyl sulphenyl chloride[11] in ether, in the presence of K_2CO_3. After stirring for 15 min the usual work-up afforded the chloro-ketones in 90-95% yield. The products were purified by column chromatography. The deuteriated diazo-ketones employed in the synthesis of **2a-c** were prepared through the Clibbens-Nierenstein reaction starting from the corresponding α-deuteriophenoxy acetylchlorides.

1-Chloro-3-phenoxy-1-phenylthio-2-propanone **1a**, prepared from 1-diazo-3-phenoxy-2-propanone.[2] Yellow oil. NMR (CCl_4) δ : 7.66-6.66 (10H,m); 5.80 (1H,s); 4.76 (2H,s).

1-Chloro-3-phenoxy-1-phenylthio-2-butanone **1b**, prepared from 1-diazo-3-phenoxy-2-butanone.[2] Yellow oil. NMR (mixture of diastereomers) (CCl_4)δ : 7.66-6.66 (10H,m); 6.03,5.96 (1H,s,CHCl); 5.03,4.92 (1H,q,J=6Hz,CH-CH_3); 1.60 (3H,t,J=6Hz,CH_3).

1-Chloro-3-phenoxy-3-phenyl-1-phenylthio-2-propanone, **1c**, prepared from 1-diazo-3-phenoxy-3-phenyl-2-propanone.[2] Yellow oil. NMR (mixture of diastereomers) (CCl_4)δ: 7.66-6.66 (15H,m); 5.97 (1H,s, CHCl); 5.80,5.73 (1H,m,CHPh).

General procedure for the acetolyses. Acetolyses were performed on 1-2 mmol, both in neat AcOH and in the presence of AcOK, under standard conditions. The crude mixture was quenched and treated twice with H_2O (10 ml) and CCl_4) (20 ml). After shaking, the CCl_4 solns. were dried over $MgSO_4$ and evaporated. The residues were submitted to NMR and GC/MS analyses. Purification of the products was obtained by chromatography over silica gel. Kinetic experiments were run up to 65-85% conversion. The results are reported in Tables 1 and 2.

1-Acetoxy-3-phenoxy-1-phenylthio-2-propanone, **3a**. (Oil b.p. 97-8° 0.5 mmHg). NMR (CCl_4)δ: 7.67-6.67 (10H,m); 6.37 (1H,s); 4.78 (2H,s); 2.22 (3H,s). MS, m/z: 316(M^+); 207 (M - PhS); 180 (M - PhO - CH_3CO); 165 (M - PhS - CH_2=CO); 164 (M - PhS - CH_3CO).

1-Acetoxy-1-phenoxy-3-phenylthio-2-propanone, **4a**. (Oil 95-6° 0.5 mmHg). NMR (CCl_4)δ: 7.50-6.66 (10 H,m); 6.53 (1H,s); 3.88 (2H,AB); 2.10 (3H,s).

2-Acetoxy-3-phenylthio-2-propenale, **5a**. (Oil 58-60° at 1 mmHg). NMR (CCl_4)δ: 9.03 (1H,s); 7.66-7.26 (5H,m); 7.13 (1H,s); 2.23 (3H,s). MS, m/z: 222 (M^+); 180 (M - CH_2=CO); 151 (M - CH_2=CO - CHO).

1-Acetoxy-3-phenoxy-1-phenylthio-2-butanone, **3b**. Oil. NMR (mixture of diastereomers) (CCl_4)δ: 7.50-6.66 (10H,m); 6.66,6.38 (1H,s,CHOAc); 4.92,4.85 (1H,q,J=6Hz, $CHCH_3$); 2.13,2.03 (3H,s,OAc); 1.50 (3H,t,J=6Hz, CH_3). MS, m/z: 330 (M^+); 209 (M - $PhOCHCH_3$); 181 ($PhSCHOAc$); 121 ($PhOCHCH_3$).

Benzenethiol-2-acetoxy-2-butenoate, **6**. (Oil 80-2° at 0.5 mmHg). NMR (CCl_4)δ: 7.50-6.83 (5H,m); 6.57 (1H,q,,J=6Hz); 2.25 (3H,s); 1.73 (3H,d,J=6Hz). MS, m/z: 236 (M^+); 137 (PhSCO); 127 (M - PhS); 99 (M - PhSCO).

3-Phenoxy-1-phenylthio-3-buten-2-one, **7**. (Oil b.p. 90-2° at 0.5 mmHg). NMR (CCl_4)δ: 7.53-6.83 (10H, m); 5.03 (2H,d,J=2Hz); 4.00 (2H,s).

1-Acetoxy-3-phenoxy-3-phenyl-1-phenylthio-2-propanone, **3c**. Oil. NMR (mixture of diastereomers) (CCl_4)δ: 7.50-6.66 (15H,m); 6.76,6.50 (1H,s,CHOAc); 5.72,5.63 (1H,m,CHPh); 2.06 (3H,s,OAc). MS, m/z: 299 (M - PhO); 283 (M - PhS); 256 (M - PhO - CH_3CO); 241 (M - PhS - CH_2=CO); 240 (M - PhS - CH_3CO); 189 (M - PhS - PhOH); 183 ($PhOCHPh$); 118 ($PhCHCO$).

2-Acetoxy-1-phenyl-3-phenylthio-2-propen-1-one, **5c**. (Oil b.p. 92-3° at 0.5 mmHg). NMR (CCl_4)δ: 7.87-7.13 (10H,m); 6.97 (1H,s); 2.22 (3H,s). MS, m/z: 298 (M^+); 256 (M - CH_2=CO); 146 (M - CH_3CO - PhS); 105 (PhCO).

Acetolysis of **2a**. The reaction in plain AcOH after 2 h at 120° afforded: 80% acetoxy-ketone **8a** and 20% starting chloro-ketone. The acetolysis in the presence of AcOK (0.6 M) after 30' at 120° gave the following product composition: 46% **4a** (about 95% deuteriated at the methinic carbon) and 54% **5a** (fully deuteriated at the formyl group).

Acetolysis of **2b**. The reaction was run only in plain AcOH for 2.5 h at 120°. NMR analysis show the formation of 59% **8b** and 41% **2b**.

Acetolysis of **2c**. After 3 h reacting in AcOH at 120°. NMR analysis afforded the following composition of the crude reaction mixture: 74% **8c** and 26% **2c**.

1-Chloro-1-phenylthio-3-p-tolylthio-2-propanone, **9a**. The reaction of p-tolylthio acetylchloride with an ethereal solution of CH_2N_2 afforded 1-diazo-3-p-tolylthio-2-propanone. Yellow crystals, m. p. 36-7°. NMR ($CDCl_3$)δ: 7.30-6.83 (4H,m); 5.63 (1H,s); 3.50 (2H,s); 2.30 (3H,s).
The latter was submitted to action of phenyl sulphenyl chloride. Chloro-ketone **9a** was obtained as an oil. NMR (CCl_4)δ: 7.50-6.83 (9H,m); 5.75 (1H,s); 3.72 (2H,s); 2.27 (3H,s).

1-Chloro-3,3-dideuterio-1-phenylthio-3-p-tolylthio-2-propanone, **11a** was prepared through the Clibbens-Nierenstein reaction starting from 2,2-dideuterio-p-tolylthio acetyl chloride.

1-Chloro-1-p-tolylthio-3-phenylthio-2-propanone, **10a** prepared from 1-diazo-3-phenylthio-2-propanone[12] by reaction with p-tolyl sulphenyl chloride.[13] Yellow oil. NMR (CCl_4)δ: 7.33-6.75 (9H,m); 5.66 (1H,s); 3.78 (2H,s); 2.32 (3H,s).

Acetolysis of **9a**. After 2.5 refluxing in plain AcOH, NMR analysis afforded the following composition of the crude reaction mixture: 17% (**9a**); 16% (**10a**); 32% (**9b**); 35% (**10b**).

1-Acetoxy-1-phenylthio-3-p-tolylthio-2-propanone, **9b**. Oil. NMR (CCl_4)δ: 7.50-6.83 (9H,m); 6.50 (1H, s); 3.77 (2H, AB system); 2.33 (3H,s); 2.13 (3H,s).

3-Acetoxy-1-phenylthio-3-p-tolylthio-2-propanone, **10b**. Oil. NMR (CCl_4)δ: 7.50-6.83 (9H,m); 6.40 (1H,s); 3.70 (2H, AB system); 2.33 (3H,s); 2.13 (3H,s).

Acetolysis of **11a**. After 2.5 h at 120° in plain AcOH, the reaction mixture had the following composition: 34% **11a** and 66% **11b**. The latter was purified by column chromatography. NMR (CCl_4)δ: 7.50-6.83 (9H,m); 6.50 (1H,s); 2.33 (3H,s); 2.13 (3H,s).

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