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NUCLEOPHILIC SUBSTITUTIONS OF α-HALO-KETONES—XXII

ACETOLYSIS OF α′ - PHENOXY - α - CHLORO - KETONES. A COMPARISON OF THEIR REACTIVITY WITH THAT OF THE CORRESPONDING THIOETHERS

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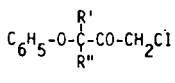
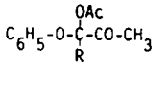
Abstract—The results obtained in the acetolysis of α - chloro - ketones **1a–e** are compared with those previously reported for the acetolysis of the corresponding α′ - phenylthio - α - chloro - ketones **15a–e** and discussed in terms of the enolization-solvolysis mechanisms (Schemes 1 and 2).

The study of solvolytic reactions of α - halo - ketones bearing an aryloxy substituent on the α′ - carbon has been restricted in the present series of papers to substrates such as 2 - haloacetyl - 1,4 - benzodioxanes,[1-5] only a preliminary communication on the acetolysis of open chain substrates having as yet been published.[6] The acetolysis of α′ - phenoxy - α - chloro - ketones **1a–e** are reported in the present paper in order to compare their reactivity with that of the corresponding α′ - phenylthio - α - chloro - ketones, which were the object of previous work.



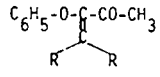
1a: R′=R″=H
1b: R′=H; R″=CH_3
1c: R′=H; R″=$CH(CH_3)_2$
1d: R′=H; R″=C_6H_5
1e: R′=R″=CH_3

The acetolyses were performed under standard conditions in AcOH and in the presence of 3 moles AcOK. The results are summarized in Table 1. Both the acetolyses of **1a** led exclusively to cine-substitution of the halogen, affording 1 - acetoxy - 1 - phenoxy - 2 - propanone **2a**, as the only product.



2a: R=H
2b: R=CH_3
2c: R=$CH(CH_3)_2$
2d: R=C_6H_5

Kinetic experiments were performed in parallel with α - chloro - ketone **1a** and the substrate **1′a** selectively deuteriated at the α′ - C (see Table 2). A strong isotope effect ($K_H/K_D = 13.4$) was observed only during acetolysis in plain AcOH. The rate of solvolysis in the AcOH/AcOK system was apparently unaffected by salt concentrations up to 10^{-3} moles/lit, and was accelerated only by a factor of ten with a 10^{-1} M AcOK concentration; however, the pattern of this reaction appeared to be significantly modified (as shown by the correlation factors), although **2a** was the only product in every case. In the acetolysis of **1′a** the resulting α - acetoxy-ketone was fully deuteriated at the methine group. The presence of an alkyl or aryl substituent on the α′-C of **1** caused a marked decrease in reactivity. Thus, only a very low conversion of **1b** could be achieved after prolonged heating in boiling AcOH, while in the presence of acetate the acetolysis was far from being completed even after 7 h at 120°. The two reactions gave different results, 3 - phenoxy - 3 - buten - 2 - one, **3a**, being the only product in plain AcOH, while a 3 : 2 ratio of **3a** and 3 - acetoxy - 3 - phenoxy - 2 - butanone **2b**, was obtained in the AcOH/AcOK system.



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

Chloro-ketone **1c** underwent solvolysis only in the AcOH/AcOK system giving a 1 : 2 ratio of the isomeric acetoxy-ketones 3 - acetoxy - 4 - methyl - 3 - phenoxy - 2 - pentanone **2c** and 1 - acetoxy - 4 - methyl - 3 - phenoxy - 2 - pentanone **4a**, with 4 - methyl - 3 - phenoxy - 3 - penten - 2 - one **3b**. The latter had previously been obtained by reacting phenol with 3 - bromo - 4 - methyl - 3 - penten - 2 - one.[7] An authentic sample of **4a** was prepared through the

Table 1. Acetolyses of chloro-ketones **1a–e** in neat AcOH (A) and in the presence of AcOK (B)*

Substrate	Experimental conditions	Conversion %	Products from: cine substitution	elimination	normal substitution	other reactions
1a	A 9 h	38	2a (100%)			
	B 1 h	100	2a (100%)			
1b	A 40 h	14		3a (100%)		
	B 7 h	70	2b (40%)	3a (60%)		
1c	A 24 h	0				
	B 12 h	66	2c (23%)	3b (30%)	4a (47%)	
1d	A 24 h	27	2d (50%)			6 (30%), 7 (10%), 8 (10%)
	B 2.5 h	100	2d (100%)			
1e	A 24 h	0				
	B 16 h	30			4b (100%)	

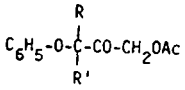
* Substrate conc: 0.2 M AcOK conc: 0.6 M. Reaction temperature 120°.

Table 2. Rate constants for the acetolyses of 1 - chloro - 3 - phenoxy - 2 - propanone **1a** and 1 - chloro-3,3 - dideuterio - 3 - phenoxy - 2 - propanone **1'a***

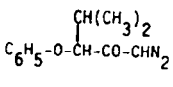
Substrate	System	Kobsd $sec^{-1} \times 10^{-5}$	Correlation factors
1a	AcOH	1.75	0.997
1a	AcOK 0.001 M	1.86	0.992
1a	AcOK 0.1 M	17.30	0.931
1'a	AcOH	0.13	0.993
1'a	AcOK 0.1 M	11.74	0.958

*Reaction temperature: 100° ± 0.1. The observed rates were obtained from the slope of the first-order plot of ln [substrate] vs time.

acetolysis of 1 - diazo - 4 - methyl - 3 - phenoxy - 2 - pentanone **5**.



4a: R=H; R'=$CH(CH_3)_2$
4b: R=R'=CH_3



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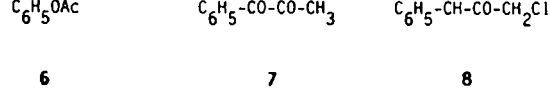
Chloro-ketone **1d** behaved differently in plain AcOH and in the presence of acetate. The latter acetolysis occurred easily affording 1 - acetoxy - 1 - phenoxy - 1 - phenyl - 2 - propanone **2d** as the only product. The substrate, instead appeared to be rather inert in boiling AcOH, the reaction resulting in various degradation products such as phenyl-acetate **6**, 1 - phenyl - 1,2 - propandione **7**, 1 - acetoxy - 3 - chloro - 1 - phenyl - 2 - propanone **8**, in addition to **2d**. A separate experiment confirmed that phenol forms **6** under the conditions employed in the acetolysis of **1d**.



6 **7** **8**

The acetolysis of **1d** was also performed in the presence of 0.5 M LiCl, $LiClO_4$, or LiOAc. The data reported in Table 3 show that, as expected, the reaction was considerably accelerated by these salts, due at least in part to the increased ionic strength of the medium. However, the product distribution was markedly different in the experiment with $LiClO_4$, in

Table 3. Acetolyses of **1d** in the presence of different lithium salts (15 h at 90°)

Salt conc.	Conversion	Products							
	0%								
0.5 M LiCl	32%	**2d**	(81%)	**6**	(15%)	**7**	(2%)	**8**	(2%)
0.5 M $LiClO_4$	38%			**6**	(14%)	**7**	(18%)	**8**	(68%)
0.5 M LiOAc	100%	**2d**	(100%)						

Table 4. Acetolyses of 1 - chloro - 3 - deuterio - 3 - phenoxy - 3 - phenyl - 2 - propanone, **1'd**

Substrates	Experimental conditions	conv.	Products			
1d	24 h at 120°	27%	**2d** (50%)	**6** (30%)	**7** (10%)	**8** (10%)
1'd	24 h at 120°	22%		**6** (32%)	**7** (9%)	**8** (59%)
1'd	2.5 h at 120°(*)	58%		**6** (24%)	**7** (traces)	**8** (76%)

(*) Run in the presence of 0.5 M $LiClO_4$.

which chlorine cine-substitution was completely absent, whereas it was predominant or the only process in the presence of LiCl and LiOAc, respectively.

The preparation of 1 - chloro - 3 - deuterio - 3 - phenoxy - 3 - phenyl - 2 - propanone **1'd**, was achieved through an independent synthesis starting from 2 - deuterio - 2 - phenyl - acetic acid. The results obtained in the acetolysis of **1'd** are reported in Table 4. Finally, chloro-ketone **1e** underwent acetolysis only in the presence of acetate, the very slow reaction leading exclusively to 1 - acetoxy - 3 - methyl - 3 - phenoxy - 2 - butanone **4b**.

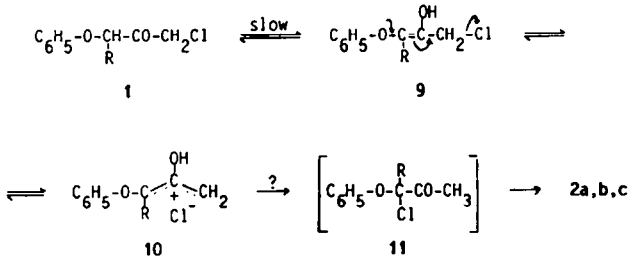
DISCUSSION

The possibility that α - halo - ketones might give substitution products via the enolization-solvolysis mechanism was already considered in our previous papers[1,2,3,8-12] and by Bordwell *et al.*[13-16]

The above results suggest that, in the absence of acetate, the acetolysis of **1a** proceeds according to the mechanism illustrated in Scheme 1, which postulates the formation of enol allylic chloride **9a** as the rate determining step. This hypothesis is supported by the strong isotope effect observed in the acetolysis of the deuteriated substrate **1'a**. In AcOH, an acidic solvent with low ionizing power,[17] ionization of **9a** would lead to bridged ion pairs **10a**,[18] which might undergo nucleophilic attack at the more electrophilic carbon, affording **2a**. As for the intermediate formation of **11a**, no evidence was obtained that isomerization of the substrate occurred during solvolysis, as it does in the acetolysis of the sulfur analogue **15a**;[19] however, failure to identify **11a** in the reaction medium might well be ascribed to the higher reactivity of α - chloro - ethers than of the corresponding α - chloro - thioethers.

As for the acetolysis in the presence of acetate the kinetics performed with **1a** and **1'a** seem to indicate that at high salt concentration a S_N2' displacement of the chlorine on enol allylic chloride **9a** might be concurrent with the mechanism operating in AcOH.

The lower reactivity of **1b** and **1c** can in turn be attributed to the enolization of these substrates being much slower, because of the weaker acidity of the methine carbon. According to the mechanism of Scheme 1, enol allylic chlorides **9b** and **9c**, or the

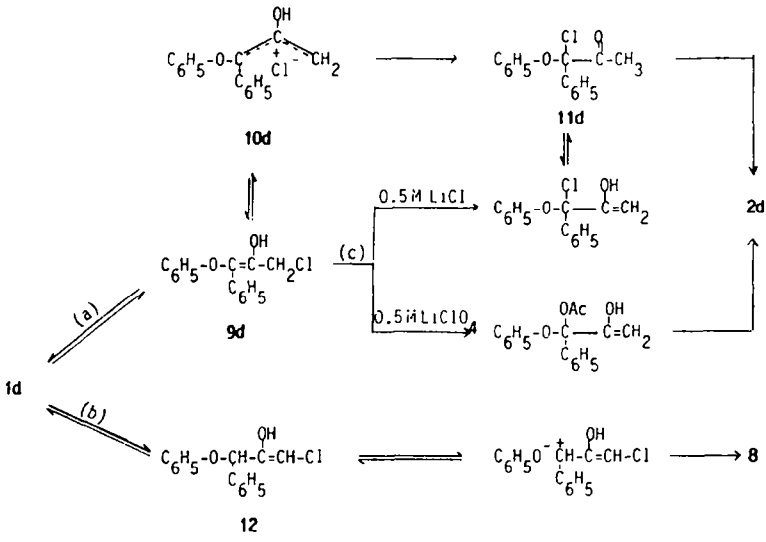


1a,9a,10a,11a: R=H

1b,9b,10b,11b: R=CH_3

1c,9c,10c,11c: R=$CH(CH_3)_2$

Scheme 1.



Scheme 2.

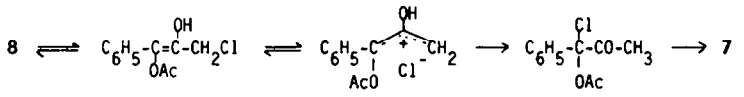
corresponding ion pairs **10b** and **10c**, may undergo acetolysis (leading to **2b** and **2c** respectively) or alternatively HCl elimination to **3a** and **3b**. Again, isomerization of the substrates prior to elimination is questionable, since the process leading from **9b, c** to **3a, b** might well be concerted. Moreover, no evidence of the intermediate formation of **11b, c** is available. In any case, AcOH elimination from **2b** and **2c**, which might be an alternative pathway, can only partly be responsible for the formation of α, β-unsaturated ketones **3a** and **3b**, which were shown to form rather slowly from **2b** and **2c** under the conditions employed in the solvolyses. Also, the presence of a bulky substituent may well account for normal substitution being a concurrent pathway in the acetolysis of **1c** with acetate.

The results obtained with α - chloro - ketone **1d** are better discussed in terms of the mechanisms reported in Scheme 2, which differentiates the solvolysis in plain AcOH from those run in the presence of the different salts. Unlike the acetolyses of **1a,b,c**, which apparently involve the corresponding enols **9a,b,c**, and not the alternative ones, the acetolysis of **1d** in plain AcOH clearly requires the intermediacy of both enols **9d** and **12**. Thus, while the former may undergo the solvolysis likewise enol allylic chlorides **9a,b,c** through the intermediate formation of ion pair **10d**, eventually collapsing to the isomeric chloro-ketone **11d** (pathway *a*), the latter enol may in turn originate chloro-ketone **8** through ionization of the allylic ether linkage, followed by nucleophilic displacement of phenol (pathway b). Indeed, the acetolysis of **1d** appeared to be strongly dependent on the ionic strength of the medium, the substrate being practically stable in rigorously anhydrous AcOH; the results under discussion were in fact obtained with a solvent containing traces (less than 0.1%) of water. The different reactivity of **1d** may possibly be due to enol allylic chloride **9d** being more stable, and therefore less reactive than the corresponding chlorides **9a,b,c** because of more extensive conjugation; the alternative enol **12** might then participate in the solvolytic process as an active intermediate.

The Scheme 2 also accounts for the results reported in Table 3. In the presence of LiCl, isomerization of **1d** to **11d** may occur in a process involving a S_N2' reaction, the nucleophilic attack by the external chloride on enol **9d** being followed by fast solvolysis of the resulting α - chloro - ether (pathway c). In the presence of acetate the same pathway involving nucleophilic displacement of the chlorine by a S_N2' mechanism may well lead directly to cine-substitution.

The acetolysis of **1d** in the presence of 0.5 M $LiClO_4$ cannot be explained solely in terms of the ionic strength of the medium, since the results differ substantially from those obtained with the same LiCl concentration. Winstein *et al.* have shown that low concentrations of $LiClO_4$ alter ion pair return in acetolysis of certain alkyl chlorides and tosylates.[18,20] Also they put forward evidence that salts like LiBr and $LiClO_4$ act as scavengers for the same solvolysis intermediates, both trapping the solvent-separated ion pair, but permitting internal return from the intimate ion pair.[21,22] In our case, however, the high $LiClO_4$ concentration, while increasing the ionic strength of the medium may exert their influence in preventing ionization of enol allylic chloride **9d** ultimately responsible for the allylic rearrangement; the solvolytic process may then occur exclusively through the alternative enol **12** (pathway b).

The different reactivity of **1d** and the deuteriated substrate **1'd** (see Table 4) can also be explained in terms of the enolization equilibria reported in Scheme 2. One may recall (see Experimental) that treatment of **1d** with tetradeuterio-acetic acid resulted in selective and complete deuteriation of its methylene, with concurrent solvolysis. This proves that enolization of **1d** is greatly favoured in the direction of **12**, rather than **9d**. However, mesomeric participation by the neighbouring ether oxygen may assist ionization of **9d** to ion pair **10d**, eventually leading to cine-substitution. The latter process was instead completely absent in the acetolysis of **1'd**, possibly because the formation of **9d** was depressed to such an extent to prevent pathway *a*. This point appears to be



13 14

in line with the strong isotope effect observed in kinetic experiments on the acetolysis of **1a** and **1'a**.

It is interesting to note that, as expected, cine-substitution did not occur also in the acetolysis of **1'd** in the presence of $LiClO_4$.

Enolization apparently plays an important role also in the case of α - chloro - ketone **8** the precursor of α-diketone **7**. The yield of the latter from **8** has already been reported in the literature, but no mechanistic hypothesis was put forward to explain the reaction.[23] In our opinion, the acetolysis very probably proceeds via isomerization of **8** to **14**, through the intermediate formation of enol allylic chloride **13**; hydrolytic cleavage of **14** would then produce **7** during the final work-up. It has been confirmed that the above diketone cannot be formed by hydrolysis of **2d**, which appeared to be stable under the conditions employed during the elaboration of the reaction mixture.

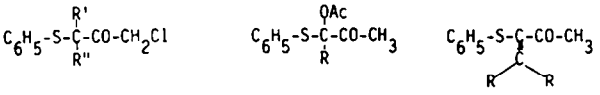
The inertness of α - chloro - ketone **1e**, which cannot yield an enol allylic chloride, fits well in the above mechanistic considerations. Steric hindrance did not, however, prevent the reaction from leading to acetoxy-ketone **4b** under forcing conditions.

The different reactivity of chloro-ketones **1** and **15**[19,24] can be discussed with reference to the data reported in Tables 1 and 5.

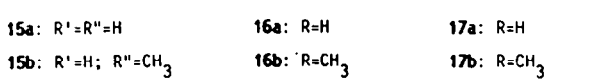
The easier solvolysis of **15a,b,c,d** can be ascribed to more efficient participation by sulfur in the ionization of enol allylic chlorides **20**.

Indeed, neighbouring thioether groups have been shown to be extremely active in reactions involving carbocations; also, measures of anchimeric assistance have proved thioethers to be far superior to ethers in solvolytic reactions.[25] Also, the different weight of cine vs normal substitution in the two series of substrates may be explained in terms of different charge distribution in the delocalized cationic species **10** and **21**, the more electronegative oxygen being responsible for predominant nucleophilic attack at the adjacent carbon. Reversible isomerization was evidenced only in the acetolysis of thioethers **15a,d**, while elimination reactions occurred in both series of α - chloro - ketones provided that one hydrogen was present on the β'-carbon atom.

Participation involving a σ bond between the heteroatom and the carbon bearing the leaving group has never been observed with α - chloro - ketones **1**, but only with thioethers **15c** and **15f**, having a bulky substituent on the α' - carbon; the acetolyses of these substrates afforded in fact acetoxy-ketones **22** and **23**, and thiolester **24**, respectively, the formation of which requires the intervention of the cyclic intermediate **25**.[24,26]

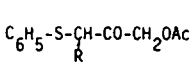


15a: R'=R"=H
15b: R'=H; R"=CH_3
15c: R'=H; R"=$CH(CH_3)_2$
15d: R'=H; R"=C_6H_5
15e: R'=R"=CH_3
15f: R'=H; R"=$C(CH_3)_3$

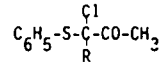


16a: R=H
16b: R=CH_3
16c: R=C_6H_5

17a: R=H
17b: R=CH_3

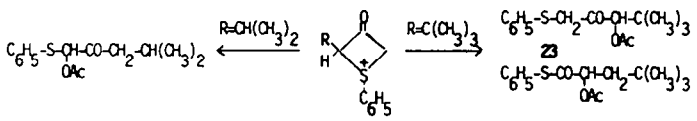


18a: R=H
18b: R=CH_3
18c: R=$CH(CH_3)_2$
18d: R=C_6H_5



19a: R=H
19b: R=C_6H_5

20 21



22 25 24

Table 5. Acetolysis of chloro-ketones **15a–e**[24] in neat AcOH(A) and in the presence of AcOK(B)*

Substrate	Experimental conditions	conversion %	Products from: cinesubstitution	elimination	normal substitution	other reactions
15a	A 2 h	54	**16a** (74%)		**18a** (9%)	**19a** (17%)
	B 1 h	100	**16a** (75%)		**18a** (25%)	
15b	A 2 h	0				
	B 5'	100	**16b** (63%)	**17a** (23%)	**18b** (14%)	
15c	A 9 h	40		**17b** (100%)		
	B 3 h	95		**17b** (76%)	**18c** (18%)	22 (6%)
15d	A 40'	15			**18d** (80%)	**19b** (20%)
	B 1'	100	**16c** (33%)		**18d** (67%)	
15e	A,B 24 h	0				

* Substrate conc: 0.2 M. AcOK conc: 0.6 M. Reaction temperature 120°.

The above results indicate that, unless steric factors inhibit the formation of enol allylic chloride **20** in the acetolysis of thioethers **15**, mesomeric participation of sulfur in the displacement of chlorine is a more favourable process than S-4 participation involving 3 - keto - thietanium cations.

EXPERIMENTAL

Melting points were determined on a Büchi apparatus and are uncorrected. NMR spectra were recorded on a Varian T-60 spectrometer using tetramethylsilane as the internal standard.

Materials

Anhydrous AcOH was prepared by refluxing (4 h) 99.8% AcOH (Merck) with the calculated amount of Ac_2O (Merck). The solvent was shown to be anhydrous by Karl Fischer titration. The solution of AcOK in glacial AcOH, was prepared from Carlo Erba RPE salt, dried at 120°C *in vacuo* to constant weight. Solutions of LiCl (Carlo Erba RPE reagent) in glacial AcOH were prepared in a similar manner.

The solns of $LiClO_4$ were prepared by dissolving the calculated amount of the trihydrate salt (Fluka) in anhydrous AcOH and treating it with the calculated amount of Ac_2O, to give a 0.01 M excess.

The soln of AcOLi was prepared by dissolving 1 mol $LiCO_3$ (Carlo Erba) in the appropriate amount of AcOH, containing 1 mol Ac_2O.

Substrates

Chloroketones **1a-e** were prepared starting from the corresponding α - diazo - ketones by reaction with 1.4 M ethereal HCl (mole ratio 1 : 1.5). After the usual work-up, the oily residues were chromatographed on silica gel (eluant 10 : 1 light petrol ether/ethyl acetate).

1 - *Chloro* - 3 - *phenoxy* - 2 - *propanone* **1a** was prepared from 1 - diazo - 3 - phenoxy - 2 - propanone.[27] M. p. 34–35°. NMR (CCl_4) δ: 7.33–6.60 (5H, m); 4.58 (2H, s); 4.20 (2H, s).

1 - *Chloro* - 3,3 - *dideuterio* - 3 - *phenoxy* - 2 - *propanone* **1'a** was prepared through the Clibbens–Nierenstein reaction starting from 2,2 - dideuterio - 2 - phenoxyacetyl chloride.

1 - *Chloro* - 3 - *phenoxy* - 2 - *butanone* **1b** was prepared from 1 - diazo - 3 - phenoxy - 2 - butanone.[27] Oil (b.p. 53–55° at 0.2 mm Hg). NMR (CCl_4) δ: 7.33–6.66 (5H, m); 4.78 (1H, q); 4.28 (2H, AB system); 1.50 (3H, d).

1 - *Chloro* - 4 - *methyl* - 3 - *phenoxy* - 2 - *pentanone* **1c**. A soln of 3 - methyl - 2 - phenoxy - butanoyl chloride (2 g) in 0.3 M ethereal diazomethane (100 ml) was stirred at − 10°C for 3 h. Evaporation of the solvent afforded 2 g of 1 - diazo - 4 - methyl - 3 - phenoxy - 2 - pentanone **5** (m.p. 42–43°). NMR (CCl_4) δ: 7.33–6.60 (5H, m); 5.40 (1H, s); 4.15 (1H, d, J = 5 Hz); 2.46–1.85 (1H, m); 1.08–0.95 (6H, m). A solution of the diazoketone (0.7 g) and $SOCl_2$ (0.8 ml) in CCl_4 (5 ml) was stirred for 3 h at room temp. After evaporation of the solvent and distillation *in vacuo* 1 - chloro - 4 - methyl - 3 - phenoxy - 2 - pentanone **1c** was obtained as an oil (b.p. 108–110° at 0.5 mm Hg). NMR (CCl_4) δ: 7.35–6.60 (5H, m); 4.35–3.98 (2H, ABq, J_{AB} = 17 Hz); 4.30 (1H, d, J = 5 Hz); 2.20 (1H, sept., J = 5 Hz); 1.20–0.95 (6H, m).

1 - *Chloro* - 3 - *phenoxy* - 3 - *phenyl* - 2 - *propanone* **1d** was prepared from 1 - diazo - 3 - phenyl - 3 - phenoxy - 2 - propanone.[27] Oil (b.p. 80–82° at 0.2 mm Hg). NMR (CCl_4) δ: 7.56–6.76 (10H, m); 5.73 (1H, s); 4.36 (2H, s).

1 - *Chloro* - 3 - *deuterio* - 3 - *phenoxy* - 3 - *phenyl* - 2 - *propanone* **1'd** was prepared through the Clibbens–Nierenstein reaction starting from 2 - deuterio - 2 - phenoxy - 2 - phenylacetyl chloride.

1 - *Chloro* - 3 - *methyl* - 3 - *phenoxy* - 2 - *butanone* **1e** was prepared from 1 - diazo - 3 - methyl - 3 - phenoxy - 2 - butanone.[28] NMR (CCl_4) δ: 7.43–6.56 (5H, m); 4.43 (2H, s); 1.48 (6H, m).

General procedure for the acetolysis

The acetolyses were performed on approximately 1–2 mmol substrate, both in neat AcOH and in the presence of AcOK under standard conditions (substrate 0.2 M; AcOK 0.6 M, temperature 120°). The crude mixture was quenched and treated twice with H_2O and CCl_4. After shaking, the CCl_4 solutions were dried over $MgSO_4$, filtered and evaporated. NMR and GLC analyses were performed on the residues; the results are summarized in Table 1.

Acetolysis of **1a**. The reaction gave 1 - acetoxy - 1 - phenoxy - 2 - propanone **2a** as the only product. Oil (b.p. 78–80°, 0.15 mm Hg). NMR (CCl_4) δ: 7.43–6.76 (5H, m); 6.20 (1H, s); 2.30 (3H, s); 2.10 (3H, s).

Acetolysis of **1b**. The crude reaction mixture by column

chromatography over silica gel (eluant 8 : 1 light petrol ether/ethyl acetate) afforded the pure compound **2b** and **3a**.

1 - *Acetoxy* - 1 - *phenoxy* - 2 - *butanone* **2b**. Oil (b.p. 140°, 0.3 mm Hg); NMR (CCl_4) δ: 7.36–6.83 (5H, m); 2.36 (3H, s); 2.03 (3H, s); 1.43 (3H, s).

3 - *Phenoxy* - 3 - *buten* - 2 - *one* **3a**. Oil (b.p. 86–88°, 0.1 mm Hg). NMR (CCl_4) δ: 7.05-6.65 (5H, m); 4.98 (2H, d); 2.28 (3H, s).[27]

Acetolysis of **1c**. Silica gel column chromatography (eluant 9 : 1 light petrol ether/ethyl acetate) of the crude reaction mixture afforded **2c**, **3b**[7] and **4a** in pure state.

3 - *Acetoxy* - 4 - *methyl* - 3 - *phenoxy* - 2 - *pentanone* **2c**, oil (b.p. 102–4° at 0.6 mm Hg). NMR (CCl_4) δ: 7.40–6.85 (5H, m); 2.42 (3H, s); 2.33–2.10 (1H, m); 2.05 (3H, s); 1.10–0.90 (6H, m).

1 - Acetoxy - 4 - methyl - 3 - phenoxy - 2 - pentanone **4a**, oil b.p. 120–2° at 0.5 mm/Hg). NMR (CCl_4) δ: 7.37–6.60 (5H, m); 4.73–4.50 (2H, ABq, J_{AB} = 17 Hz); 4.25 (1H, m); 2.56–2.33 (1H, m); 2.10 (3H, s); 1.15–0.96 (6H, m). Authentic **4a** was obtained by the acetolysis of 1 - diazo - 4 - methyl - 3 - phenoxy - 2 - pentanone **5**.

Acetolysis of **1d**. The crude mixture obtained from the reaction in plain AcOH was chromatographed over silica gel column (eluant 10 :1 light petrol ether/ethyl acetate) to give 1 - acetoxy - 1 - phenoxy - 1 - phenyl - 2 - propanone **2d** (m.p. 138–9°). NMR (CCl_4) δ: 7.66–6.73 (10H, m); 2.43 (3H, s); 2.10 (3H, s). Compounds **6**, **7** and **8** were identified by GLC and NMR comparison with authentic samples.

The acetolysis of **1d** was also performed in tetradeuterioacetic acid. The reaction was run at 70°, following the progress of deuteriation and solvolysis by NMR and GLC analyses. After 7 days complete deuteriation of the methylene of **1d** was achieved with practically no H/D exchange at the methine group, as proved by the recovered starting material. The amount of the concurrent solvolysis was not evaluated.

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REFERENCES

[1]V. Rosnati, D. Misiti and F. De Marchi, *Gazz. Chim. Ital.* **96**, 497 (1966).
[2]V. Rosnati, F. Sannicolò and G. Pagani, *Ibid.* **98**, 1085 (1968).
[3]V. Rosnati, F. Sannicolò and G. Zecchi, *Ibid.* **101**, 344 (1971).
[4]A. M. Bianchi, V. Rosnati, A. Saba, F. Soccolini and G. Zecchi, *Ibid.* **103**, 79 (1973).
[5]A. M. Bianchi, V. Rosnati and G. Zecchi, *Ibid.* **104**, 445 (1974).
[6]V. Rosnati, G. Pagani and F. Sannicolò, *Tetrahedron Letters* 1241 (1967).
[7]V. Rosnati, A. Saba, A. Salimbeni and U. Vettori, *Gazz. Chim. Ital.* **111**, 249 (1981).
[8]V. Rosnati, G. Pagani and F. Sannicolò, *Tetrahedron Letters* 4545 (1967).
[9]V. Rosnati, F. Sannicolò and G. Pagani, *Ibid.* 4649 (1968).
[10]V. Rosnati, F. Sannicolò and G. Pagani, *Gazz. Chim. Ital.* **99**, 152 (1969).
[11]V. Rosnati, F. Sannicolò and G. Zecchi, *Ibid.* **99**, 651 (1969).
[12]V. Rosnati, F. Sannicolò and G. Zecchi, *Tetrahedron Letters* 599 (1970).
[13]F. G. Bordwell and R. G. Scamehorn, *J. Am. Chem. Soc.* **90**, 6751 (1968).
[14]F. G. Bordwell, R. G. Scamehorn and W. R. Springer, *Ibid.* **91**, 2087 (1969).
[15]F. G. Bordwell, M. W. Carlson and A. C. Knipe, *Ibid.* **91**, 3949 (1969).
[16]F. G. Bordwell and M. W. Carlson, *Ibid.* **91**, 3951 (1969).
[17]E. Grunwald and S. Winstein, *Ibid.* **70**, 846 (1948).
[18]W. G. Young, S. Winstein and M. L. Goering, *Ibid.* **73**, 1958 (1951).
[19]A. Pusino, V. Rosnati, A. Saba, F. Soccolini and A. Selva, *Gazz. Chim. Ital.* **108**, 531 (1978).
[20]S. Winstein and K. C. Schreiber, *J. Am. Chem. Soc.* **74**, 2165 and 2171 (1952).
[21]S. Winstein, P. E. Klinedinst, G. C. Robinson, *Ibid.* **83**, 885 (1961).
[22]S. Winstein, P. E. Klinedinst, E. Clippinger, *Ibid.* **83**, 4986 (1961).
[23]W. Bradley and J. K. Eaton, *J. Chem. Soc.* 1913 (1937).
[24]A. Pusino, V. Rosnati, A. Saba and A. Franco, *Gazz. Chim. Ital.* **112**, 475 (1982).
[25]B. Capon and S. P. McManus, *Neighbouring Group Participation*, Vol. I, p. 195. Plenum Press, New York (1976).
[26]S. Gladiali, M. P. Porcu, V. Rosnati, A. Saba and A. Selva, *Gazz. Chim. Ital.* **107**, 293 (1977).
[27]A. Pusino, V. Rosnati, C. Solinas and U. Vettori, *Tetrahedron* **39**, 2259 (1983).
[28]V. Rosnati, F. De Marchi, D. Misiti, and C. Francescaglia, *Gazz. Chim. Ital.* **94**, 979 (1964).