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NEIGHBOURING GROUP PARTICIPATION
IN SOLVOLYTIC REACTIONS OF α-CHLOROKETONES.

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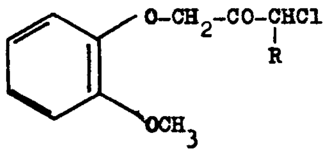
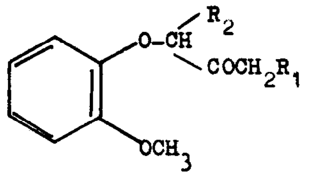
The acetolysis and the alcoholysis of 2-chloroacetyl-1,4-benzodioxane (I) to the corresponding 2-acetoxy- or respectively 2-alcoxy-2-acetyl-1,4-benzodioxanes have been interpreted as a new type of allylic rearrangement, essentially involving: a) the enolization of the α-chloroketone, through the agency of the hydrogen in α'; b) the ionization of such enol form, through the anchimeric assistance of the neighbouring group; c) the nucleophylic attack on the intermediate carbonium ion.$^{(1)}$

We now wish to report the solvolytic reactions of a number of α-chloroketones, somehow structurally related to (I).

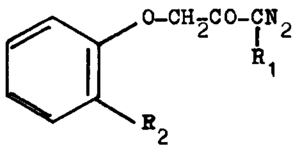
1-Chloro-3-(o.methoxyphenoxy)-propanone (IIa), prepared from o.methoxyphenoxyacetyl chloride and CH_2N_2 following the usual procedure, gave about 70% of 1-acetoxy-1-(o.methoxyphenoxy)-propanone (IIIa) upon treatment with potassium acetate in glacial acetic acid. The NMR spectra unequivocally confirmed the structures of both the chloroketone (IIa) and the reaction product (IIIa).(See Table). However, by treating with dry HCl the diazoketone (IVa) (prepared from



IIa : R = H
IIb : R = CH_3



IIIa : R_1=H, R_2= $OCO-CH_3$
IIIb : R_1=CH_3, R_2= $OCO-CH_3$
V : R_1=CH_3, R_2= Cl

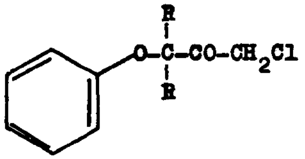


IVa : R_1= CH_3, R_2=OCH_3
IVb : R_1= R_2= H

o.methoxyphenoxyacetyl chloride and diazoethane), a mixture of the two isomeric chloroketones (IIb) and (V) was obtained. The former isomer could not be isolated in a pure state, while repeated vacuum distillations of the mixture allowed the isolation of pure 1-chloro-1-(o.methoxyphenoxy)-butan-2-one (V). The mixture of the two isomeric chloroketones, when heated with potassium acetate in glacial acetic acid, gave 1-acetoxy-1-(o.methoxyphenoxy)-butan-2-one (IIIb), as the only reaction product.

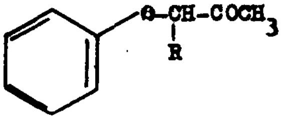
The structural assignments concerning compounds (IIIb) and (V) were based on the full interpretation of their NMR spectra (see Table). The presence of the isomeric chloroketone (IIb) in the mixture was inferred from its NMR spectrum, which showed a singlet at 5.27 τ ($O{-}CH_2{-}CO$), a quartet at 5.35 τ ($CO{-}\underset{\substack{|\\ CH_3}}{CH}{-}Cl$), a doublet at 8.5 τ ($CO{-}\underset{\substack{|\\ CH_3}}{CH}{-}Cl$); since these signals were present in the ratio of 2:1:3 , they could confidently be assigned as above indicated.

Similarly, the reaction of dry HCl on an ethereal solution of diazoketone (IVb) (obtained from phenoxyacetyl chloride and CH_2N_2) gave a mixture of the two isomeric chloroketones (VIa) and (VIIa), from which only the latter compound could be isolated in a pure state.



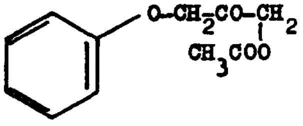
VIa : R = H

VIb : R = CH_3



VIIa : R = Cl

VIIb : R = $OCOCH_3$



VIII

The acetolysis of the above mixture with potassium acetate in acetic acid gave phenol (35%) and 1-acetoxy-1-phenoxy-propanone (VIIb)(30%).

The NMR spectra of compounds (VIIa) and (VIIb) were in perfect agreement with the assigned structures (see Table). The presence of the chloroketone (VIa) in the reaction mixture could easily be inferred from its NMR spectrum. Treatment of the diazopropanone (IVb) with boiling acetic acid afforded a mixture (1:7) of (VIIb) and 1-acetoxy-3-phenoxy-propanone (VIII). The structure of the latter compound has been proved by the occurence in its NMR spectrum of three singlets, respectively at 5.13 τ (2H), 5.44 τ (2H) and 7.85 τ (3H).

3-Phenoxy-3-methyl-1-chloro-butan-2-one (VIb) practically did not react with potassium acetate in acetic acid, since, even after prolonged heating, at least 90% of the starting material was recovered unaffected, together with a small quantity of phenol.

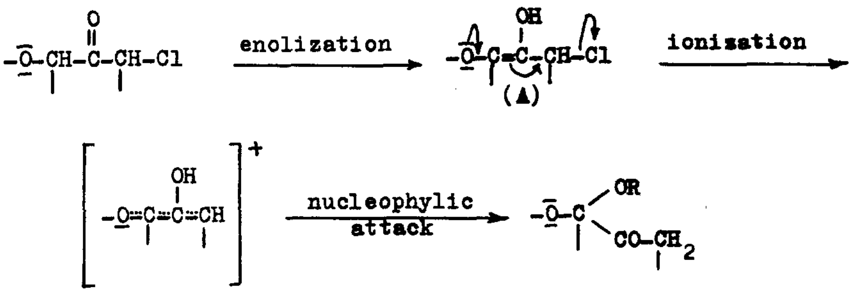
TABLE (°)

Comp.N.	Multiplicity	Chem. Shift τ p.p.m.	Area	Assignment
IIa	Complex	3.11	4H	aromatic
	Singlet	5.40	2H	$O-C\underline{H}_2-CO$
	Singlet	5.56	2H	$CO-C\underline{H}_2-Cl$
	Singlet	6.17	3H	$O-C\underline{H}_3$
IIIa	Complex	3.05	4H	aromatic
	Singlet	3.93	1H	$O-C\underline{H}-O$
	Singlet	6.16	3H	$O-C\underline{H}_3$
	Singlet	7.63	3H	$CO-C\underline{H}_3$
	Singlet	7.98	3H	$OCO-C\underline{H}_3$
IIIb	Complex	3.12	4H	aromatic
	Singlet	3.98	1H	$-C\underline{H}$
	Singlet	6.17	3H	$O-C\underline{H}_3$
	Quadruplet	7.19	2H	$C\underline{H}_2-CH_3$
	Singlet	7.95	3H	$OCO-C\underline{H}_3$
	Triplet	8.90	3H	$CH_2-C\underline{H}_3$
V	Complex	3.02	4H	aromatic
	Singlet	3.99	1H	$-C\underline{H}$
	Singlet	6.14	3H	$O-C\underline{H}_3$
	Quadruplet	7.08	2H	$C\underline{H}_2-CH_3$
	Triplet	8.82	3H	$CH_2-C\underline{H}_3$
VIIa	Complex	2.82	5H	aromatic
	Singlet	3.85	1H	$-C\underline{H}$
	Singlet	7.51	3H	$CO-C\underline{H}_3$
VIIb	Complex	2.76	5H	aromatic
	Singlet	3.72	1H	$-C\underline{H}$
	Singlet	7.70	3H	$CO-C\underline{H}_3$
	Singlet	7.91	3H	$OCO-C\underline{H}_3$

(°)- **All NMR spectra were recorded on a Perkin Elmer spectrometer** mod. R 10 **employing** T.M.S. **as internal standard**

The results obtained with (IIa) and the mixtures of the isomeric chloroketones (IIb-V) and (VIa-VIIa) can be interpreted in terms of the reaction mechanism previously proposed for the solvolytic reactions of 2-chloroacetyl-1,4-benzodioxane (I). Such a mechanism is summarized in the Scheme 1, where partial molecular structures have been used:

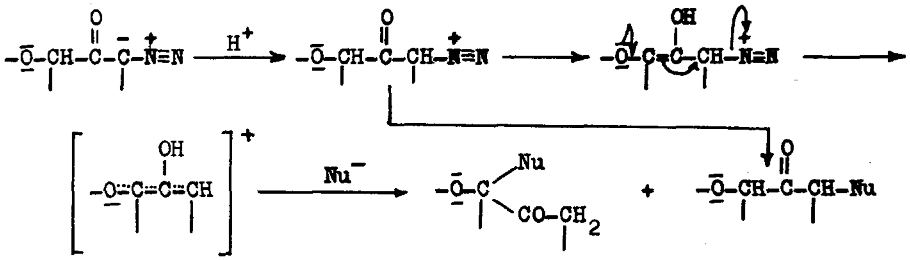
SCHEME 1



Since obviously (VIb) cannot enolize according to the above scheme, this clearly accounts for its lack of reactivity.

The reaction mechanism summarized in the Scheme 2 affords a rational interpretation of both the formation of the pairs of isomeric chloroketones (IIb-V) and (VIa-VIIa) from the corresponding diazoketones (IVa or IVb), as well as that of the isomeric acetoxyketones (VIIb-VIII) from diazoketone (IVb).

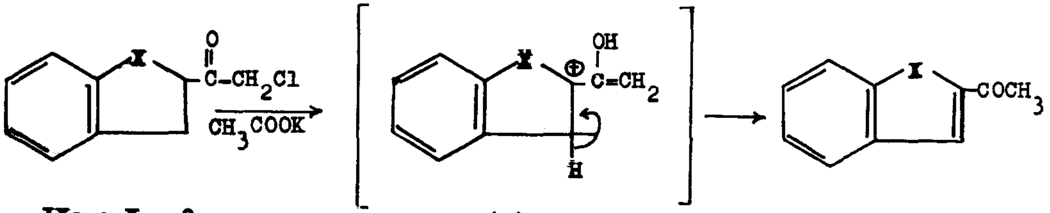
SCHEME 2



(Nu = Cl or CH_3COO)

The occurence of an allylic carbonium ion of type (B) in the course of the above solvolytic reactions received a clear confirmation by the analogous reactions on 2-chloroacetyl-2,3-dihydro-benzofuran (IXa) and 2-chloroacetyl-2,3-dihydro-benzothiophene (IXb): these substrates, in which a benzylic hydrogen is present in the β' position to the carbonyl group, readily aromatised giving 2-acetyl-benzofuran (Xa) and 2-acetyl-benzothiophene (Xb) respectively, accord ing with the mechanism outlined in the following Scheme 3:

SCHEME 3



IIa : X = O
IIb : X = S

(B)

Xa : X = O
Xb : X = S

Satisfactory analyses were obtained for all new compounds.

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1) V.Rosnati, D.Misiti and F.De Marchi, *Gazz.Chim.Ital.* **96** , 497 (1966).