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ENOL INTERMEDIATES IN THE ACETOLYSIS OF 1,1-DIPHENYLCHLOROPROPANONES

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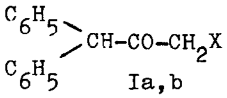
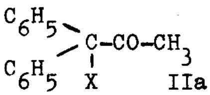
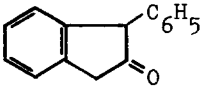
Acetolysis of 1-chloro-3,3-diphenylpropanone (Ia) in the presence of potassium acetate is known to give both 1-acetoxy-3,3-diphenylpropanone (Ib) and 1-acetoxy-1,1-diphenylpropanone (IIb); enolization of the substrate to give an allylic chloride was proposed as the initial stage of the process.(1) The intermediacy of enol allylic halides in the methanolysis of α-haloketones, previously proposed,(2) has been strongly supported by recent work.(3)


$(C_6H_5)_2CH\text{-}CO\text{-}CH_2X$

Ia,b


$(C_6H_5)_2C(X)\text{-}CO\text{-}CH_3$

IIa,b



III

a : X=Cl
b : X=OAc

We now wish to report kinetic results on the acetolysis of Ia at 90° and of 1-chloro-1,1-diphenylpropanone (IIa) at 50° in anhydrous AcOH. First-order rate coefficients of acetolysis (k) were derived from determinations of chloride ion by electrometric titration with 0.02 M $AgNO_3$. Products were determined by nmr.

The reaction of Ia in 0.01 M solution gave the following products at 40-50% conversion: in pure AcOH, Ib (28%), IIb (35%), IIa (11%), and 1-phenylindan-2-one (III,26%); in the presence of 0.02 M LiCl, Ib (23%), IIb (44%), IIa (10%), and III (23%); in the presence of 0.20 M $LiClO_4$, Ib (24%), IIb (28%), and III (48%); in the presence of 0.21 M LiOAc, Ib (14%), IIb (81%), and IIa (5%). Acetolysis of IIa in all the above conditions produced IIb, with the exclusion of Ib and III; occasionally, traces of Ia were also detected.

Kinetics were run with 0.008-0.019 M solutions of Ia at 90.0°. In pure AcOH a rate coefficient $10^5k = 0.174$ sec^{-1} was measured; with 0.0096 and 0.029 M LiCl, values 0.107 and 0.191 sec^{-1}, respectively, were found; with 0.014 and 0.023 M HCl, values of 10^5k were 0.120 and 0.167 sec^{-1}, respectively.

Chloride exchange in the presence of 0.028 M LiCl labelled with ^{36}Cl was found to proceed with a rate coefficient $10^5k_e = 1.38\ sec^{-1}$.

The accelerating effect of $LiClO_4$ on the kinetics of Ia is shown in Fig.1; for concentrations $C_{LiClO_4} \geqslant 0.1$ M, equation (1) was obeyed:

$$10^5k(sec^{-1}) = 1.64 + 3.34\ C_{LiClO_4} \qquad (1)$$

The reaction was also accelerated by LiOAc. In solutions containing $LiClO_4$ and LiOAc at variable concentration of the latter (C_{LiOAc} up to 0.05 M) and constant total salt concentration (0.20 M), rate coefficients were found to fit eqn. (2):

$$10^5k(sec^{-1}) = 2.22 + 44.8\ C_{LiOAc} \qquad (2)$$

Rate of H/D exchange of Ia was measured by nmr in CD_3COOD alone and in the presence of 0.10 M $LiClO_4$; at the methinic carbon, rate coefficients $10^5k_D=12.1$ and $31.3\ sec^{-1}$, respectively, were found. The exchange was only slightly faster at the methylenic group.

Kinetic experiments with IIa (initial concentration 0.02 M) were performed at 50.0°. In AcOH, without salts addition, a first-order rate coefficient $10^5k = 0.051\ sec^{-1}$ was found. The effect of $LiClO_4$ was tested at concentrations up to 0.2 M, and found consistent with equation (3):

$$10^5k(sec^{-1}) = 0.051 + 23.7\ C_{LiClO_4} \qquad (3)$$

In the presence of $LiClO_4$ and LiOAc (total concn. 0.20 M; maximum C_{LiOAc}=0.03 M),

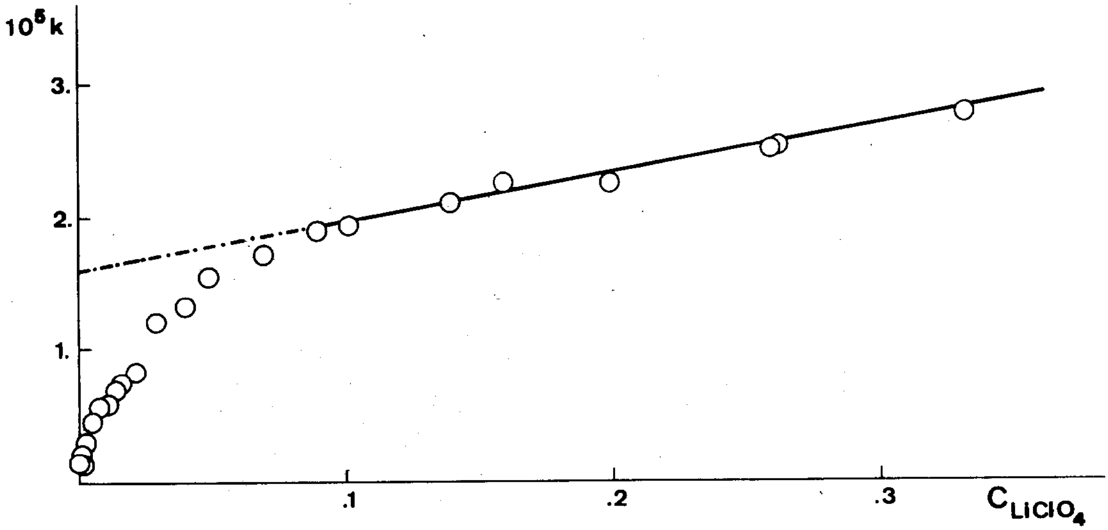
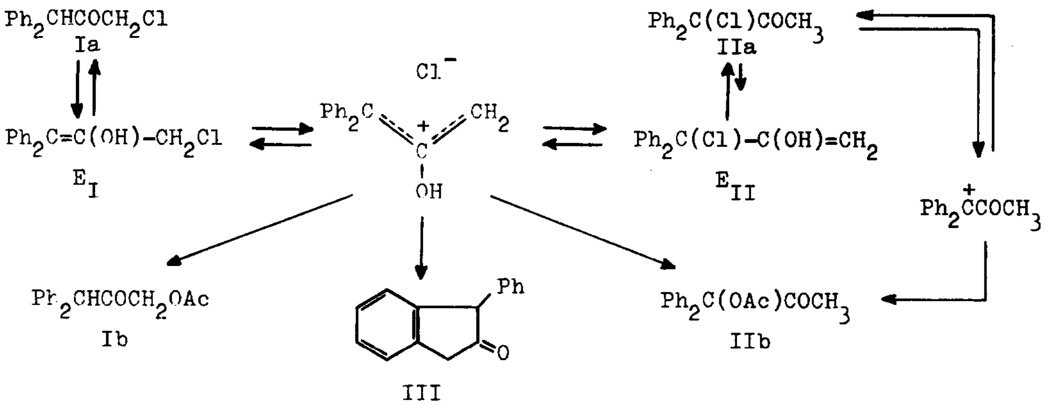


Fig.1 - Salt effect of $LiClO_4$ on the acetolysis of Ia at 90.0°.

the rate coefficient was not observed to be dependent on acetate concentration. Acetolysis with $LiClO_4$ and LiCl (total concn. 0.20 M) showed common-ion rate depression: a coefficient $10^5k = 0.60\ sec^{-1}$ was obtained with 0.0084 M LiCl. A similar effect was given by HCl.

Experiments with $Li^{36}Cl$ (0.025 M lithium chloride) gave for IIa an exchange rate coefficient $10^5k_e = 0.322\ sec^{-1}$.

The above results can be interpreted on the basis of the following scheme:



In the acetolysis of Ia, the scheme suggests the intervention of an allylic carbonium ion, capable of capturing nucleophilic species at both C_1 and C_3 carbon atoms; this is supported by: a) the presence of both Ib and IIb among the products; b) the fast chloride exchange, compared with the rate of acetolysis; c) the formation of indanone III, which clearly involves an intramolecular electrophilic attack; d) the partial common-ion rate depression given by LiCl and HCl; e) the "special" salt effect(4) (Fig.1) and the subsequent "normal" salt effect (eqn.1) produced by $LiClO_4$. The formation of enol E_I as the immediate precursor of the allylic carbonium ion is required. The high deuteration rate of Ia at the methinic position is consistent with a fast equilibration of Ia and E_I, compared with the acetolysis of the latter.

Kinetic results (see (b),(d), and (e) above) prove that the rate-determining step is an ionization and that products derive partly from ion pairs and partly from free ions. The specific effect of LiOAc on the acetolysis rate (eqn.2) has not yet found a satisfactory explanation. Lithium acetate determines also a larger fraction of IIb in the products, at the expense of the other products, particularly of III. An S_N2' process seems unlikely, since the normal S_N2 reaction would not be sterically hindered. A more reasonable hypothesis is that the allylic carbonium ion, when capturing acetate ions, behaves differently from the case of the reaction with the solvent.

The acetolysis of IIa is characterized by: a) a strong common-ion rate depression (during kinetic runs, a downward drift was observed, and initial rates had to be determined); b) a fast chloride exchange; c) normal salt effects of similar magnitude produced by $LiClO_4$ (eqn.3) and LiOAc; d) the lack of formation of Ib and III. All these facts point to an S_N1 mechanism, through the intervention of the non-allylic carbonium ion indicated in the scheme.

Enol E_{II} has been postulated in order to explain the formation of some IIa during the acetolysis of Ia, although in all the above conditions acetolysis of IIa seems to proceed without the intervention of E_{II}, the S_N1 process being prevalent. However, extensive isomerization of IIa to Ia has been observed during deuteration experiments with high concentration of IIa in CD_3COOD; such a process should involve E_{II} and its allylic rearrangement. Since isomerization of IIa to Ia occurs without formation of Ib and III, the rearrangement of the enols probably proceeds through an intimate ion pair, different from the one that is capable of producing Ib and III. Such a species, as well as the dissociated allylic carbonium ion, have not been drawn in the scheme, for sake of brevity.

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