The Reaction of Lead(IV) Acetate with Enolates

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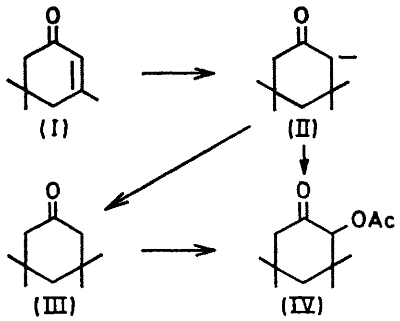
Summary Enolates formed by the conjugate addition of a Grignard reagent to an $\alpha\beta$-unsaturated ketone were trapped with lead(IV) acetate to form the α-acetoxy-ketone.

EVIDENCE concerning the mechanism of the reaction of lead(IV) acetate with ketones suggests that the rate-determining step is the enolization of the ketone. This is presumably followed by the formation and decomposition of the lead ester, as suggested by Corey.[1] Since the enol acts as a nucleophile the corresponding enolate ion should react more rapidly. The enolate would not only be more nucleophilic than the enol but could be obtained in a much higher concentration.

To test the hypothesis and to demonstrate the synthetic usefulness of such a reaction, isophorone (I) was chosen, since all the products were known compounds. The ketone (I) was added to methylmagnesium bromide at room temperature in the presence of copper(I) acetate to generate the enolate (II).



Hydrolysis of the enolate gave the ketone (III)[2] which on treatment with lead acetate in refluxing benzene gave the known acetoxy-ketone (IV).[3] This reaction was monitored by the KI–starch test and required approximately 18 hr. for complete loss of oxidant. Analysis by g.l.c. showed the reaction mixture to be mainly the acetoxy-ketone (IV) with a small amount of the starting ketone. Addition of the enolate to a slightly more than equimolar suspension of lead(IV) acetate in benzene at room temperature resulted in an exothermic reaction and the immediate consumption of the lead(IV) acetate. Any excess of lead(IV) resulted in oxidation of bromide to free bromine. After stirring the reaction mixture for several minutes at room temperature, the usual work-up[4] gave the crude reaction mixture which when analysed by g.c. was found to contain one main component identified as the acetate (IV) by g.l.c. comparison with the authentic sample. The acetate was formed from isophorone *via* trapping of the enolate in approximately 60% yield as determined by g.c. using an internal standard. The structure of the acetate was confirmed by its i.r. and n.m.r. spectra.

The other materials in the crude reaction mixture were mainly isophorone and the ketone (III) but traces of several other products, possibly from 1,2-addition and the resulting dehydration products, were detected. Although several runs were made, no attempts were made to optimize yields.

Thus the enolate reacted much faster than the ketone to produce the α-acetoxy-ketone in good yield, demonstrating the synthetic utility of the reaction.

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