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The Acetoxylation of *p*-Substituted Acetophenones and *β*-Diketones with (Diacetoxyiodo)benzene

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Synopsis. The methyl groups of *p*-substituted acetophenones and the methylene groups of *β*-diketones were acetoxylated with (diacetoxyiodo)benzene. When the substrates were *p*-chloroacetophenone, *p*-nitroacetophenone and 4,4,4-trifluoro-1-phenyl-1,3-butanedione, the corresponding acetoxylated compounds were obtained in high yields.

The oxidations of glycols and alkenes with (diacetoxyiodo)benzene ($PhI(OAc)_2$) are well known to proceed by means of a mechanism[1–3] similar to those with lead tetraacetate, and the acetoxylation of the methylene group adjacent to the carbonyl group with lead tetraacetate has been reported.[4] However, there have been no reports on the acetoxylation of the methyl and methylene groups adjacent to the carbonyl group with $PhI(OAc)_2$. In the present work, we will report that *p*-substituted acetophenones (*p*-$XC_6H_4COCH_3$) and *β*-diketones are acetoxylated with $PhI(OAc)_2$.

Results and Discussions

The reactions of *p*-$XC_6H_4COCH_3$ (X=CH_3O, CH_3, H, Cl, NO_2, CN) and *β*-diketones with $PhI(OAc)_2$ were carried out at 30 °C in a mixed solvent of acetic acid and acetic anhydride, using sulfulic acid as the catalyst. When X in *p*-$XC_6H_4COCH_3$ was CH_3, H, Cl, or NO_2, the acetoxylated compounds were obtained; their structures were determined from the spectra (IR and NMR) and elemental analyses, as is shown in Tables 1 and 2. When X in *p*-$XC_6H_4COCH_3$ was OCH_3, the diaryliodonium salt ($[CH_3O(CH_3CO)\text{-}C_6H_3\text{-}I^+\text{-}Ph]Br^-$) was obtained in a 59.1% yield and the acetoxylated compound occurred in a trace amount. In the reaction of *p*-cyanoacetophenone with $PhI(OAc)_2$, neither the acetoxylated compound nor the diaryliodonium salt could be isolated, although both $PhI(OAc)_2$ and *p*-cyanoacetophenone were easily consumed at 30 °C and a tarry matter was obtained. The yields of the acetoxylated compounds increased in this order: X= $Cl > NO_2 \gg H > CH_3 \ggg CH_3O$. High yields were obtained in the case of the substrates in which the *p*-substituents are electron-attracting, execpt for X=CN.

4,4,4-Trifluoro-1-phenyl-1,3-butanedione ($C_6H_5COCH_2COCF_3$) was easily acetoxylated with $PhI(OAc)_2$. Acetylacetone and dibenzoylmethane were also confirmed from the NMR spectra to be acetoxylated with $PhI(OAc)_2$, although their acetoxylated compounds gave only an approximate coincidence between found and calculated analytical results. As is shown in Table 1, the acetoxylated compound of $C_6H_5COCH_2COCF_3$ was obtained in a higher yield than those of *p*-substituted acetophenones.

It has been stated that the acetoxylation of the methylene group adjacent to the carbonyl group with lead tetraacetate seems to proceed by means of the following mechanism:[3]

Table 1. The acetoxylation of *p*-substituted acetophenones and *β*-diketone with (diacetoxyiodo)benzene

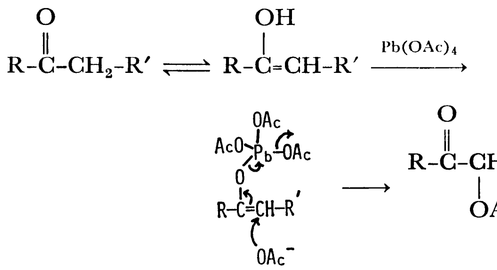
Substrate	Product						
	Structure	Yield[a] (%)	Mp (°C)	Found (%) C	Found (%) H	Calcd (%) C	Calcd (%) H
p-$CH_3C_6H_4COCH_3$	*p*-$CH_3C_6H_4COCH_2OAc$	21.9	84.5	68.56	6.09	68.74	5.42
$C_6H_5COCH_3$	$C_6H_5COCH_2OAc$	25.0	125/5[b]	67.10	5.44	67.41	5.66
p-$ClC_6H_4COCH_3$	*p*-$ClC_6H_4COCH_2OAc$	56.5	70.3	56.20	4.34	56.49	4.27
p-$NO_2C_6H_4COCH_3$	*p*-$NO_2C_6H_4COCH_2OAc$[c]	50.4	123.8	53.82	4.06	53.72	4.15
$C_6H_5COCH_2COCF_3$	$C_6H_5COCH(OAc)COCF_3$	62.8	92.0	52.09	3.80	52.56	3.30

a) Based on (diacetoxyiodo)benzene. b) Bp (°C)/mmHg. c) Nitrogen analysis: found, 6.28; calcd, 6.12.

Table 2. IR and ^1H NMR data for the acetoxylated compounds

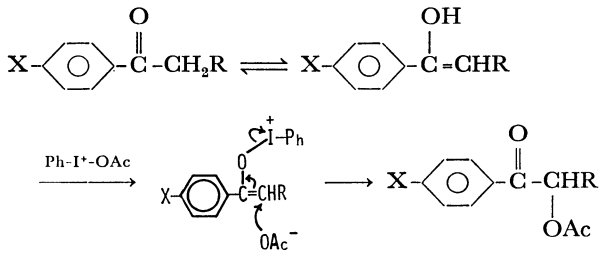
Compound	IR[a] (ν_{CO}, cm^{-1})	NMR[b] δ, (ppm)
p-$CH_3C_6H_4COCH_2OAc$	1695, 1740	2.25(OAc), 2.45(-CH_3), 5.34(OCH_2O), 7.2—8.0(C_6H_4)
$C_6H_5COCH_2OAc$	1705, 1750	2.20(OAc), 5.34(OCH_2O), 7.3—8.1(C_6H_5)
p-$ClC_6H_4COCH_2OAc$	1690, 1740	2.21(OAc), 5.26(OCH_2O), 7.3—8.0(C_6H_4)
p-$NO_2C_6H_4COCH_2OAc$	1698, 1742	2.25(OAc), 5.37(OCH_2O), 8.0—8.6(C_6H_4)
$C_6H_5COCH(OAc)COCF_3$	1690[c], 1750	2.10(OAc), 6.20, 6.40(keto and enol COCH), 7.4—8.2(C_6H_5)

a) KBr disk. b) In $CDCl_3$. c) Broad band.



Briody[5] has also reported that, in the presence of sulfuric acid, (diacetoxyiodo)benzene in acetic acid seems to dissociate into ions according to the following equilibria: $\mathrm{PhI^{+}(OAc)+OAc^{-}} \rightleftharpoons \mathrm{PhI(OAc)_2} \overset{\mathrm{H_2SO_4}}{\rightleftharpoons} \mathrm{PhI^{+}(OAc)+HSO_4^{-}}$.

Accordingly, if the oxidation with $\mathrm{PhI(OAc)_2}$ in the present work proceeds by means of a mechanism similar to that with lead tetraacetate, the acetoxylation mechanism may be thought to be as follows:



The fact that such substrates p-$\mathrm{ClC_6H_4COCH_3}$, p-$\mathrm{NO_2}$-$\mathrm{C_6H_4COCH_3}$, and $\mathrm{C_6H_5COCH_2COCF_3}$ produce the acetoxylated compounds in high yields seems to be explained by the above Scheme, because these substrates tend to be converted into enol forms.

Experimental

All the melting points and boiling points are uncorrected. The IR spectra were obtained on Shimadzu 27G and 400 spectrometers. The NMR spectra were obtained on a JEOL C-60-HL spectrometer, using tetramethylsilane as the internal standard. The amount of acetoxylated compound in the reaction mixture was determined by means of a JEOL JGC-1100 chromatograph with a 2 m × 3 mm column packed with Silicone DC550 (20%) coated on Chromosorb AW-DMCS.

Materials. Reagent-grade p-substituted acetophenones and β-diketones were used without further purification. The (diacetoxyiodo)benzene was synthesized according to the procedure submitted by Sharefkin and Saltzman[6] and was used after recrystallization from 5M acetic acid.

Preparation of Acetoxylated Compounds. The p-substituted acetophenone or β-diketone (0.06 mol) was dissolved in 55 cm^3 of a mixed solution (AcOH 50 cm^3, $\mathrm{Ac_2O}$ 5 cm^3) with stirring at 30 °C. To the vigorously stirred solution, we then added 5 cm^3 of sulfuric acid and then eight 2-g portions of $\mathrm{PhI(OAc)_2}$ (total 0.05 mol) at 30-min intervals. The temperature was kept at about 30 °C throughout the additions. The reaction mixture was then stirred at 30 °C for another 6 h.

In the first stage, the reaction mixture was extracted with three 100-cm^3 portions of water and the extract was concentrated. Potassium bromide was then added to the concentrated solution. When diaryliodonium salt was present in the solution, white crystals were deposited.

In the second stage, the above reaction mixture was extracted with three 100-cm^3 portions of chloroform or ether and the extract was concentrated under reduced pressure. When the acetoxylated compound was crystalline, the concentrated solution was cooled to 0 °C. The crystals were filtered off and recrystallized from hexane. When the acetoxylated compound was liquid, the concentrated solution was distilled under reduced pressure.

References

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