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SYNTHESIS OF 1,4-DIKETONES BY THE COUPLING REACTION OF TRIMETHYLSILYL ENOL ETHERS WITH LEAD TETRAACETATE

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Summary. Synthesis of 1,4-diketones in good yields was achieved by the coupling reaction of the trimethylsilyl enol ethers of acetophenone, thiophene or furan with lead tetraacetate in dry dichloromethane and tetrahydrofuran at -78°C.

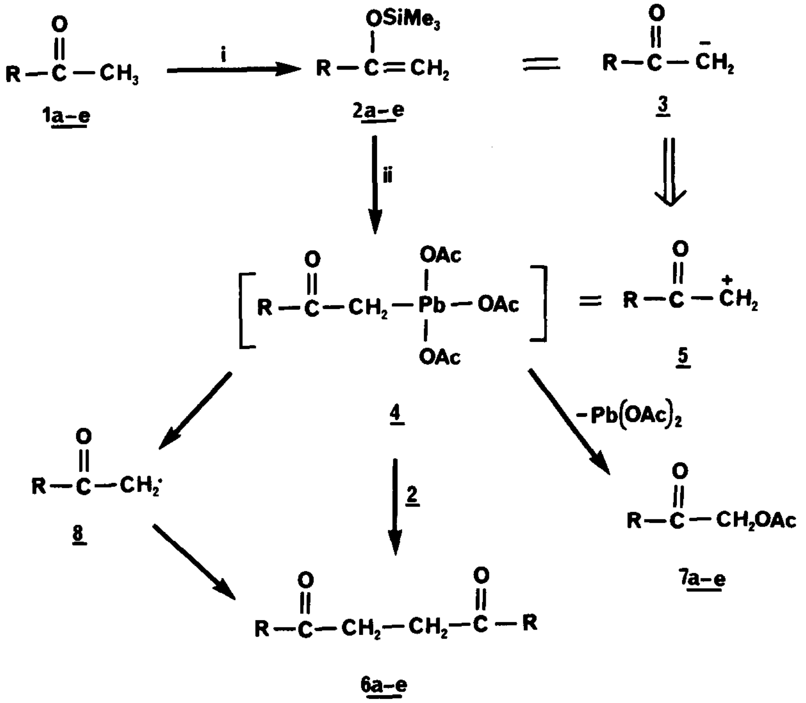
1,4-Diketones are important precursors for the synthesis of cyclopentanone, furan, thiophene and pyrrole ring systems[1]. A variety of synthetic methods have been achieved which are based upon coupling reactions using Ag_2O[2], $CuCl_2$[3], CuOTf[4], $Mn(III)(OAc)_3$[5]. Recently we have reported the synthesis of 1,4-diketones by the reaction of trimethylsilyl enol ethers of acetophenone with iodosobenzene in the presence of $BF_3 \cdot Et_2O$.[6] As a part of our study of the reaction of trimethylsilyl enol ethers of acetophenone with aryl thallium(III) trifluoroacetate, aryl lead(IV) acetate and aryl mercury acetate,[7] it became of interest to study the reaction of trimethylsilyl enol ethers of acetophenone, thiophene, furan with lead tetraacetate. Now we wish to report the synthesis of 1,4-diketones by the reaction of trimethylsilyl enol ethers with lead tetraacetate in dichloromethane and tetrahydrofuran.

Trimethylsilyl enol ethers (2a-e) react readily with lead tetraacetate in dichloromethane and tetrahydrofuran at -78°C to give 1,4-diketones (6a-e) (Scheme 1). In a typical experiment $Pb(OAc)_4$ (0.1 mole) was added in one portion with stirring to a solution of trimethylsilyl enol ether (0.2 mole) in dry CH_2Cl_2 (10ml) at -78°C, followed by immediate addition of tetrahydrofuran (5ml) to the reaction mixture to dissolve the $Pb(OAc)_4$. The reaction mixture was allowed to stir at -78°C for 1.5 hr and then at room temperature for 1 hr. The reaction mixture was poured into water (50ml) and the product was isolated by extraction with ether. Addition of ethanol (10ml) to the residue from concentration of the ether extracts yielded the crystalline 1,4-diketone.

1,4-Diketones of acetophenones, thiophene and furan (6a-e) were obtained in fairly good yields (40-60%).[8] These results may be compared with the synthesis of 1,4-diketones by the reaction of trimethylsilyl enol ethers with Ag_2O[2] and $(C_6H_5I{=}O)_n$ - $BF_3 \cdot Et_2O$.[6] In all cases variable amount of α-acetoxy ketones (7a-e) were also formed. Rubottom et al[9] have also reported the reaction of trimethylsilyl enol ethers of acetophene (2) with lead tetraacetate in benzene at room temperature. They have reported the formation of only α-acetoxy acetophenones (7) in high yields (90-95%). They did not report any coupling product. The difference in Rubottom et al. method and our procedure is that he uses a 1:1 molar ratio of trimethylsilyl enol ether and lead tetraacetate in benzene at room temperature whereas we use 2:1 molar ratio of trimethylsilyl enol ether and lead tetraacetate in CH_2Cl_2 and THF at -78°C for 1.5 hr and then the reaction is maintained at room temperature for 1 hr.

Formation of 1,4-diketones (6a-e) may be explained by initial reaction of the trimethylsilyl enol ether with lead tetraacetate to give an intermediate 4. This intermediate 4 may be viewed as an equivalent of cation 5. It can react with another molecule of trimethylsilyl enol ether to give the 1,4-diketone. Alternatively, intermediate 4 may also form radical (8) by homolytic cleavage of the carbon-lead bond. The radical may dimerize or may be oxidized by the excess of lead tetraacetate to give 1,4-diketones. Formation of α-acetoxy ketones may also be understood on the basis of the intermediate 4 formed via oxidative demetallation.[10]

There is one report in the literature[11] of the reaction of trimethyl silyl enol ether of cyclohexanone with lead tetraacetate in CH_2Cl_2 at room temperature. These workers do not report any coupling product but rather they obtain (1,2-diacetoxycyclohexyloxy)trimethylsilane and (2-acetoxy-1-cyclohexenyloxy)trimethylsilane. When they used the triethyltin enol ether of cyclohexanone instead of the trimethylsilyl enol ether of cyclohexanone, a coupling product in minor quantity was obtained; the major compound was α-acetoxycyclohexanone.

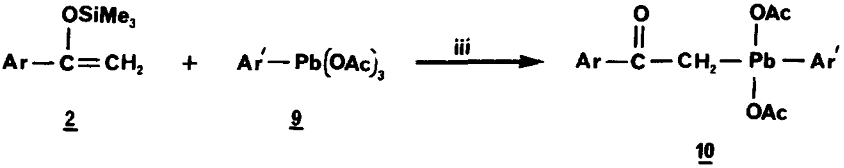


6a; R = C_6H_5
6b; R = p- ClC_6H_4
6c; R = p- $CH_3OC_6H_4$
6d; R = 2-thienyl
6e; R = 2-furyl

i) $ClSiMe_3$, Et_3N/DMF
ii) $PbOAc_4$

Scheme 1

It is interesting to note that when trimethylsilyl enol ethers of acetophenone (2) reacts with aryllead triacetate (9) (Scheme 2) in dry benzene, stable α-plumbated ketones(10)[7,12] are obtained whereas lead tetracetate yields 1,4-diketones or α-acetoxyacetophenones.[9]



Scheme 2

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