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FAVORSKI TYPE REARRANGEMENT IN THE LEAD TETRAACETATE OXIDATION OF ENAMINES PROMOTED BY BORON TRIFLUORIDE

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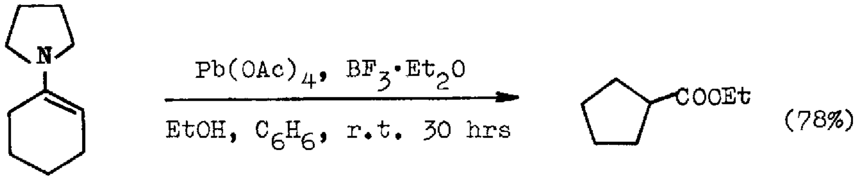
Abstract: Favorski type rearrangement has been achieved in the lead tetraacetate oxidation of enamines in the presence of boron trifluoride etherate and alcohol.

Lead tetraacetate as a versatile oxidizing agent has been used in the oxidative transformations of diffrent types of many oxygen and nitrogen functional groups[1-4]. Among nitrogen compounds enamines also were oxidized with lead tetraacetate and complex mixture of acetoxylated products was obtained[5].

In this paper we present a new approach to Favorski type rearrangement which consists in the oxidative conversion of enamines of cyclic ketones into esters of contracted cycloalkanoic acids, and enamines of aryl methyl ketones into esters of arylacetic acids, achieved by using lead tetraacetate-boron trifluoride etherate reagent and alcohol. Thus, to the mixture of 0.03 mole of 1-pyrolidino-1-cyclohexene (1), 0.03 mole of boron trifluoride etherate and 0.03 mole of ethanol in 50 ml of benzene, 0.03 mole of lead tetraacetate was added and reaction mixture stirred at room temperature for 30 hours. Precipita-



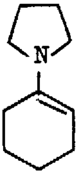
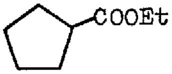
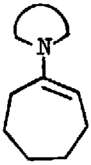
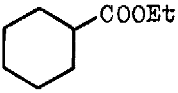
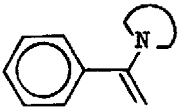
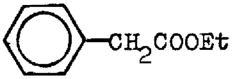
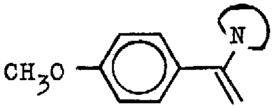
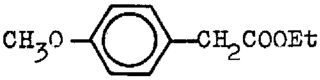
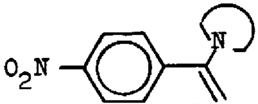
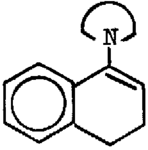
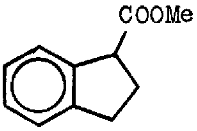
1

2

ted lead salts were removed by filtration and filtrate treated with diluted hydrochloric acid. Organic solvent washed with water and aqueous sodium bicarbonate, dried and after removing of the solvent ethyl cyclopentancarboxylate (2) distilled, analyzed by GLC and characterized by IR, NMR and mass spectra. Ester (2) was obtained in 78% while cyclohexanone was recovered in 15% yield. It is important to notify that no α-acetoxylated products were observed.

Oxidative transformation of enamines of symetrical six- and seven-membered cyclic ketones by lead tetraacetate-boron trifluoride etherate reagent proceeds with contraction of ring skeleton, as well as in the classical Favorski rearrangement of α-halogen ketones under basic conditions, affording the corresponding esters of cycloalkanoic acids in good yields. In the same way, high yields of

Table 1. Oxidation of enamines by LTA-$BF_3 \cdot Et_2O$ reagent; products and yields

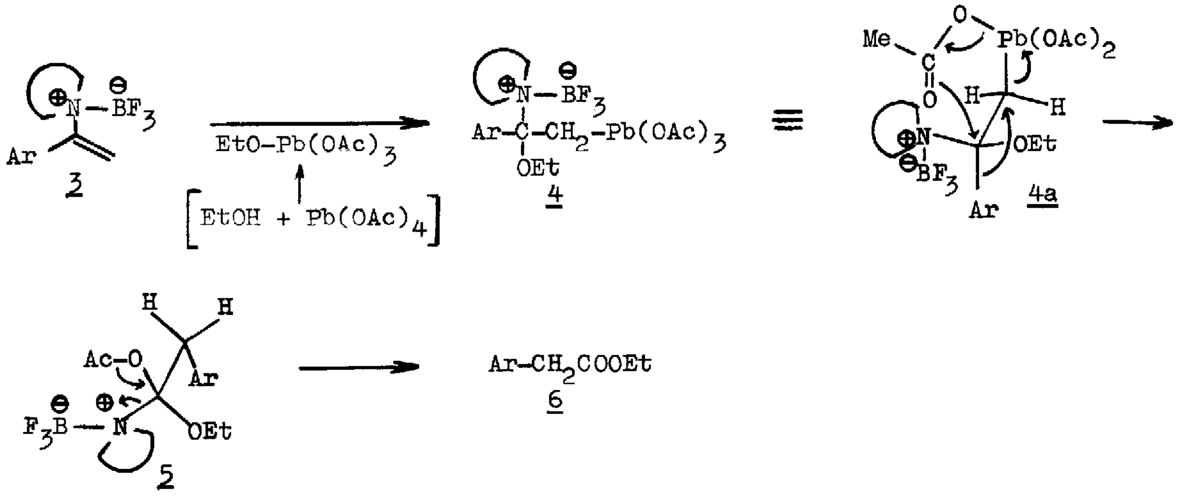
Enamines	Rearranged Products*	Yields (%)
		78
		72
		84
		86
	No rearrangement	
		56

*Ketones and α-acetoxylated ketones were idetified as a side products rearranged arylacetic acid esters were obtained in the oxidation of enamines obtained from unsubstituted and by electron-donating group substituted aryl methyl ketones with this reagent. However, when aromatic ring is deactivated by electron-withdrawing substituents, such as nitro group, aryl migration is suppressed and poor yield of rearranged ester was obtained (Table 1.).

Enamines of unsymmetrical dialkyl ketones, under these oxidative conditions, also falled to give preparative yields of rearranged esters and complex mixtures of rearranged esters and α-acetoxylated ketones were obtained. The ratio of rearranged esters corresponds to the ratio of isomeric enamines used as a substrates[6].

Favorski type rearrangement in the oxidative transformations of ketones were also observed in the lead tetraacetate oxidation of ketone and their derivatives[7,8] and tallium nitrate oxidation of ketones[9].

Oxidative rearrangement of enamines by lead tetraacetate-boron trifluoride reagent mechanistically is complex reaction involving several intermediates and transition states. We belive that mechanism should be rationalized in the sense that first step involves alkoxyplumbation of double bond of the enamine-boron trifluoride aduct 3, thus generating an intermediate 4 which undergoes to concerted 1,2-migration of aryl (or alkyl) group, intramolecular acetoxylation of pro-carbonyl carbon atom and extrusion of lead(II) acetate (4a), followed by hydrolytic decomposition of intermediate 5 to give rearranged ester 6.



Similar ring contraction, i.e. 1,2-migration of alkyl group, has been suggested for lead tetraacetate oxidation of cyclohexene to the cyclopentancarboxaldehyde[10,11].

In the oxidative rearrangement of enamines by lead tetraacetate the other than pyrolidinino-enamines, such as morpholino- and pyperidino-enamines, also can be used. When ethanol was used as alcohol the corresponding rearranged ethyl esters were obtained, while the other alcohols used in the oxidative rearrangement of enamines afforded the corresponding ester.

From the present stage of investigations within mentioned limitations described procedure should be method of choice for the Favorski type rearrangement by using enamines as substrates.

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