OXIDATIVE CYCLIZATION OF 3-CINNAMOYLTROPOLONES WITH MANGANESE(III) ACETATE AND LEAD(IV) ACETATE

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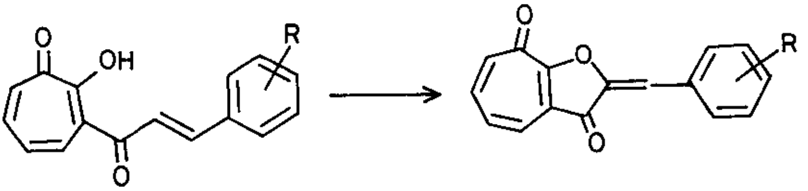
Abstract —— 3-Cinnamoyltropolones (1a-i) were oxidized with manganese(III) acetate and lead(IV) acetate to give 2-arylidene-3,8-dihydro-2H-cyclohepta[b]furan-3,8-diones (4a-i), which have an aurone-like structure.

Recently, we obtained 3-cinnamoyltropolones (1a-i) by the condensation of 3-acetyltropolone with benzaldehydes.[1] These 3-cinnamoyltropolones (1) have a 2'-hydroxychalcone-like structure and were cyclized with 95% orthophosphoric acid to afford 2-aryl-2,3,4,9-tetrahydrocyclohepta[b]pyran-4,9-diones (2),[1] while oxidized with selenium dioxide[1] and alkaline hydrogen peroxide[2] to give 2-aryl-4,9-dihydrocyclohepta[b]pyran-4,9-diones (3) and 2-arylidene-3,8-dihydro-2H-cyclohepta[b]furan-3,8-diones (4), respectively. On the other hand, 2'-hydroxychalcones undergo oxidative cyclization by various metal salts such as mercury(II),[3] palladium(II),[4] manganese(III),[5] thallium(III),[6,7] and lead(IV) acetate.[5]

In an extension of our work on reactions of the 3-cinnamoyltropolones (1), we found that the oxidation of 1 with manganese(III) acetate and lead(IV) acetate gave 2-arylidene-3,8-dihydro-2H-cyclohepta[b]furan-3,8-diones (4).



1

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Scheme 1

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A benzene solution of 3-cinnamoyltropolones (1) was refluxed with manganese(III) acetate (3 molar equivalents) in the presence of acetic anhydride to give aurone-like compounds, 2-arylidene-3,8-dihydro-2H-cyclohepta[b]furan-3,8-diones (4). The oxidation of 1 with lead(IV) acetate also gave the same compounds. Each of the products is the same as the product from Algar-Flynn-Oyamada-type oxidation of 3-cinnamoyltropolones (1)[2] and were identified by measuring their melting points and Ir and Nmr spectra. The results are summarized in Table 1.

Table 1. Oxidation of 3-Cinnamoyltropolones

	R	Mn(III) Oxidation		Pb(IV) Oxidation		Mp
		Reaction time (min)	Yield (%)	Reaction time (min)	Yield (%)	(°C)
a	H	60	trace	30	trace	201-203
b	2-OCH_3	30	4.0	30	1.1	261-262
c	3-OCH_3	20	trace	30	trace	209-211
d	4-OCH_3	30	3.2	30	2.9	227-228
e	2,3-$(OCH_3)_2$	30	6.5	20	trace	225-226
f	2,4-$(OCH_3)_2$	30	15.5	5	27.4	231-233
g	3,4-$(OCH_3)_2$	50	7.6	5	11.3	285-286
h	2,3,4-$(OCH_3)_3$	60	16.4	20	8.3	183-184
i	3,4-(OCH_2O)	25	12.1	30	8.1	279-280

As shown in Table 1, the yields were considerably low. It is thought that this is attributed to the formation of tropolone-metal complex. A occurrence of a methoxyl group at both of 2'- and 4'-position of 1 enhanced the oxidation reaction. We could not find any difference between the oxidations with manganese(III) acetate and lead(IV) acetate.

Experimental

Oxidation with Manganese(III) Acetate. A solution of 3-cinnamoyltropolones (**1**a-i) (1mM, 252-342 mg) and manganese(III) acetate dihydrate (3mM, 804 mg) in benzene (60 ml) containing acetic anhydride (2 ml) was refluxed for 20 to 60 min. After removal of benzene, the residue was treated with chloroform and an insoluble material was filtered off. The chloroform solution was washed with sodium hydrogen carbonate solution and water and dried over sodium sulfate. The evaporation residue was chromatographed on a Wakogel B-10 plate (30 x 30 cm^2) by using ethyl acetate to afford 2-arylidene-3,8-dihydro-2H-cyclohepta[b]furan-3,8-diones (**4**a-i). The crude products were recrystallized from benzene or ethanol.

Oxidation with Lead(IV) Acetate. A mixture of 3-cinnamoyltropolones (**1**a-i) (1 mM, 252-342 mg) and lead(IV) acetate (1 mM, 380 mg) was refluxed in benzene (60 ml). The reaction mixture was worked up, as mentioned above, to give the products (**4**a-i).

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