

## Dehydrogenation of Flavanones to Flavones using Thallium(III) Acetate(TTA)

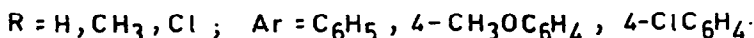
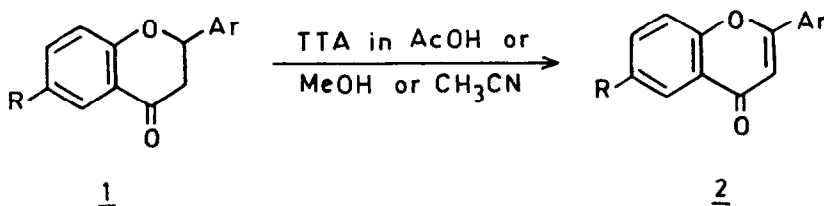
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**Summary:** A facile conversion of flavanones to flavones by dehydrogenation of the former using thallium(III) acetate is described.

Thallium(III) salts are versatile reagents for the oxidation of a wide variety of olefinic and enolic groups<sup>1,2</sup> either by oxidative rearrangements<sup>3</sup> or nucleophilic displacement of the thallium substituent in the intermediate oxythallation adduct leading to unrearranged products<sup>4,5</sup>. Further, thallium(III) acetate is known to oxidize reactive methylene groups to  $\alpha$ -acetoxy ketones in hot acetic acid<sup>6,7</sup>.

In the present communication we wish to report a successful dehydrogenation of flavanones(1) to flavones(2) using thallium(III) acetate(TTA) in acetic acid or methanol or acetonitrile in almost quantitative yields (Scheme I), the conversion occurring more readily in acetic acid.



### Scheme - I

In a typical procedure thallium(III) acetate (0.0011 mol) was added to a solution of flavanone (1a) (0.001 mol) in acetic acid (20 ml), the mixture refluxed for 3 hrs, cooled to room temperature and poured in ice cold water. The solid, so obtained, was crystallized from alcohol. All known compounds were identified by m.m.p. and comparison of IR and <sup>1</sup>H-NMR spectral data with those of the authentic samples (Table 1).

The most probable mechanistic course (Scheme II) may involve the initial electrophilic attack of thallium(III) acetate upon the enol form of 1 at the face of the molecule *cis* to C<sub>2</sub>-aryl ring to yield the intermediate 3. Reductive cleavage of carbon-thallium bond in 3 with concomitant loss of proton would

Table-1. Dehydrogenation of Flavanones with Thallium(III) Acetate.

Compounds	Products	Conditions		Yield <sup>b</sup> (%)	mp (lit. mp.) (°C)
		Solvent <sup>a</sup>	time(hr)		
<u>1a</u> =R=H, Ar=C <sub>6</sub> H <sub>5</sub>	<u>2a</u> =R=H, Ar=C <sub>6</sub> H <sub>5</sub>	AcOH	3	(96)	98(98) <sup>8</sup>
		MeOH	20	88(70)	
		CH <sub>3</sub> CN <sup>c</sup>	24	84(70)	
<u>1b</u> =R=H, Ar=4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	<u>2b</u> =R=H, Ar=4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	AcOH	3	(95)	156-7(157) <sup>9</sup>
		MeOH	20	86(72)	
		CH <sub>3</sub> CN <sup>c</sup>	24	84(70)	
<u>1c</u> =R=H, Ar=4-ClC <sub>6</sub> H <sub>4</sub>	<u>2c</u> =R=H, Ar=4-ClC <sub>6</sub> H <sub>4</sub>	AcOH	3	(98)	188(188-9) <sup>10</sup>
		MeOH	20	84(70)	
		CH <sub>3</sub> CN <sup>c</sup>	24	84(70)	
<u>1d</u> =R=CH <sub>3</sub> , Ar=C <sub>6</sub> H <sub>5</sub>	<u>2d</u> =R=CH <sub>3</sub> , Ar=C <sub>6</sub> H <sub>5</sub>	AcOH	3	(98)	121-2(122) <sup>11</sup>
		MeOH	20	88(72)	
		CH <sub>3</sub> CN <sup>c</sup>	24	94(70)	
<u>1e</u> =R=CH <sub>3</sub> , Ar=4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	<u>2e</u> =R=CH <sub>3</sub> , Ar=4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	AcOH	3	(96)	167-8(167) <sup>12</sup>
		MeOH	20	86(70)	
		CH <sub>3</sub> CN <sup>c</sup>	24	86(70)	
<u>1f</u> <sup>d</sup> =R=Cl, Ar=C <sub>6</sub> H <sub>5</sub>	<u>2f</u> =R=Cl, Ar=C <sub>6</sub> H <sub>5</sub>	AcOH	3	(96)	182(182-4) <sup>13</sup>
<u>1g</u> <sup>d</sup> =R=Cl, Ar=4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	<u>2g</u> =R=Cl, Ar=4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	AcOH	3	(98)	180-1(180-1) <sup>14</sup>
<u>1h</u> <sup>d</sup> =R=Cl, Ar=4-ClC <sub>6</sub> H <sub>4</sub>	<u>2h</u> =R=Cl, Ar=4-ClC <sub>6</sub> H <sub>4</sub>	AcOH	3	(96)	226-7(226) <sup>15</sup>

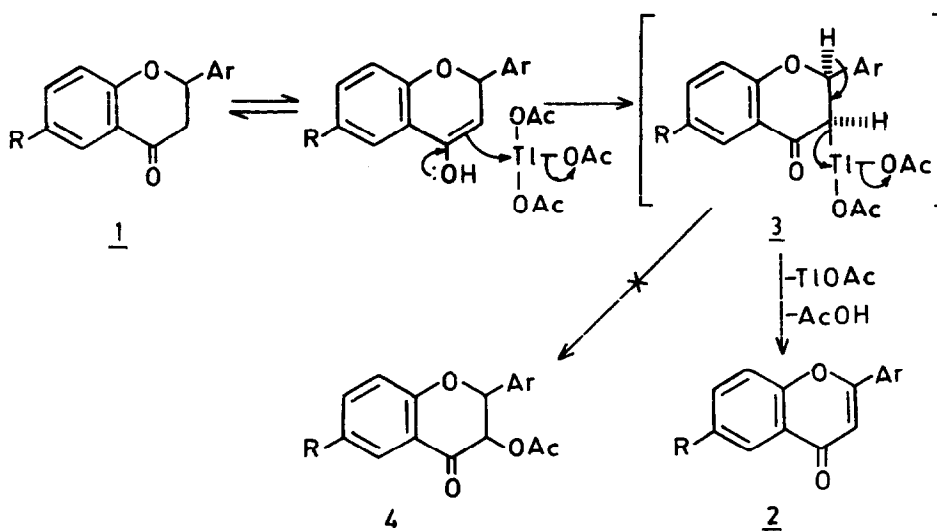
a) At reflux temperature.

b) The yields in parentheses are based upon the isolated crystalline product whereas others are based upon <sup>1</sup>H-NMR with respect to unreacted flavanones.

c) 2 equivalents of TTA were used with respect to flavanones, (A. McKillop, D.W. Young, M. Edwards, R.P. Hug and E.C. Taylor, *J. Org. Chem.*, **43**, 3773(1978).

d) Same results (as given for 1a-1f) were obtained using MeOH and CH<sub>3</sub>CN as solvents.

result in the formation of 2. Alternatively, C<sub>3</sub>-Tl(III) bond cleavage may be accompanied by the replacement of thallium(III) by acetoxy group leading to the formation of expected  $\alpha$ -acetoxy derivative (4). However, elimination is preferred over substitution because of the *cis*-relationship of C<sub>2</sub>-aryl ring and C<sub>3</sub>-Tl(III) as well as aromatic stabilization of 2.



R = H, CH<sub>3</sub>, Cl ; Ar = C<sub>6</sub>H<sub>5</sub> , 4-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub> , 4-ClC<sub>6</sub>H<sub>4</sub> .

Scheme-II

The present oxidative conversion of 1  $\rightarrow$  2 is significant because it offers a convenient route for the synthesis of 2 from 1 using TTA. This approach may be useful for the synthesis of naturally occurring flavonoids.

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