Direct Conversion of 2′-Hydroxychalcones into Isoflavones using Thallium(III) Nitrate: Synthesis of (±)-Sophorol and (±)-Mucronulatol

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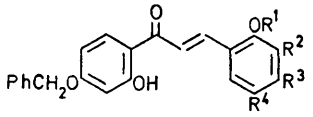
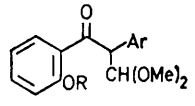
Summary Rearrangement of 2′-hydroxychalcones with methanolic $Tl(NO_3)_3$ followed by treatment with acid gives isoflavones.

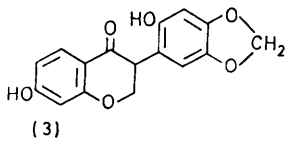
THE oxidative rearrangement of 2′-benzyloxychalcones by $Tl(OAc)_3$ in hot methanol to acetals of the type (**2**; R = CH_2Ph) was first reported by Ollis and his co-workers[1] and provided a synthetical route to isoflavones though it could not be applied directly to 2′-hydroxychalcones. Later it was shown that using $Tl(NO_3)_3$ the rearrangement of simple chalcones was quantitative at room temperature[2] and we now report that 2′-hydroxychalcones, *e.g.* (**1a** and **b**) can themselves be directly and smoothly rearranged by $Tl(NO_3)_3$ in methanol to hydroxyacetals of the type (**2**; R = H) which gives the corresponding isoflavones on treatment with acid.



(1a) R^1 = CH_2Ph, R^2 = H, R^3, R^4 = OCH_2O
(1b) R^1 = Me, R^2 = OCH_2Ph, R^3 = OMe, R^4 = H



(2)



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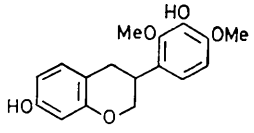

(4)

Chalcone (**1a**) (m.p. 201—203°) was converted into 2′,7-dibenzyloxy-4′,5′-methylendioxyisoflavone (m.p. 155—156°) (yield 25%). Transformation to 2′,7-diacetoxy-4′,5′-methylenedioxyisoflavone (m.p. 191—192°), hydrogenation to (±)-2′,7-diacetoxy-4′,5′-methylenedioxyisoflavanone (m.p. 156—158°), and deacetylation completed the first synthesis of (±)-sophorol (**3**) (m.p. 178—180°). (3*R*)-

Sophorol (m.p. 180—181°) was isolated from *Sophora japonica*.[3]

Similarly, chalcone (**1b**) (m.p. 119—121°) yielded 3′,7-dibenzyloxy-2′,4′-dimethoxyisoflavone (m.p. 144—146°) (yield 70%), which gave on hydrogenation (±)-mucronulatol (**4**) (m.p. 227—229°),[4] one of the isoflavan components of *Macherium mucronulatum*.[4]

All new compounds gave the expected i.r. and n.m.r. spectra and correct elemental analyses.

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[2] A. McKillop, B. P. Swann, and E. C. Taylor, *Tetrahedron Letters*, 1970, 5281.
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[4] K. Kurosawa, W. D. Ollis, I. O. Sutherland, A. Braga de Oliviera, O. R. Gottlieb, and Magelhaes Alves, *Chem. Comm.*, 1968, 1263.