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OXIDATIVE CYCLISATION WITH THALLIUM (III) ACETATE: SYNTHESIS OF 3(2H)-BENZOFURANONES

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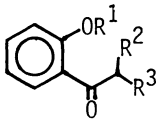
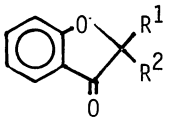
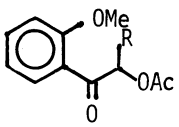
The reaction of thallium (III) acetate with enolisable o-hydroxy and o-methoxyphenyl ketones in acetic acid gave predominantly 2-acetoxy-3(2H)-benzofuranones.

Oxidation of acetophenone and o-methoxyacetophenone with thallium (III) nitrate in methanol is known to give methyl arylacetates via an aryl rearrangement.[1] However we have found that treatment of o-methoxyacetophenone with thallium (III) acetate in glacial acetic acid gives, instead of the rearrangement product, 2-acetoxy-3(2H)-benzofuranone (6). Similar cyclisations of o-hydroxyaryl ketones with thallium (III) acetate have been previously noted,[2] but the reaction has received little attention. We wish to report that this mode of ring formation seems general to enolisable o-hydroxy-and o-methoxyphenyl ketones and privides a one step synthesis of 2-acetoxy-3(2H)-benzofuranones from the readily available ketones.

Ketones (1a) - (3a) were cyclised to benzofuranones (6) - (8) respectively on heating (75 - 85°C) with three equivalents of thallium (III) acetate in glacial acetic acid (Table I). The products were separated by addition of water followed by extraction with chloroform and chromatography on silica gel plates. o-Methoxy derivatives (1b) - (3b) were demethylated and cyclised to give the same benzofuranones (6) - (8) as their hydroxyl counterparts in comparable yields, accompanied by products (10) - (12) apparently from α-acetoxylation of the ketones.[3] Under these reaction conditions 3(2H)-benzofuranone itself was smoothly converted to the 2-acetoxy derivative (6). Ketone (4a) gave, rather unexpectedly, benzofuranone (7), while ketone (4b) gave the more usual product benzofuranone (9) accompanied by a small quantity of (7). The best yields of cyclised products (65-84%) were observed with ketones monosubstituted at the α carbon, while unsubstituted and disubstituted ketones gave lower yields (~30%).

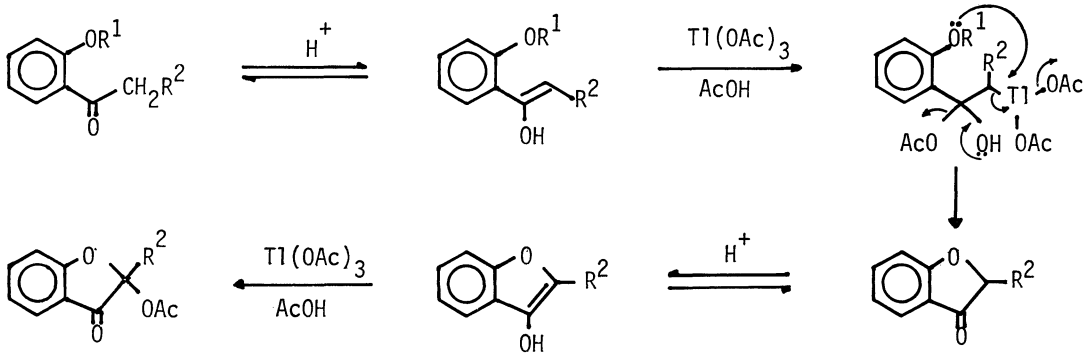
TABLE I Reactions of o-hydroxy and o-methoxyphenyl ketones with $Tl(OAc)_3$

	KETONES	PRODUCTS* (% yield)		
				
1a	R^1,R^2,R^3 = H	6 (31) R^1 = H; R^2 = OAc		
1b	R^1 = Me; R^2,R^3 = H	6 (31)	+	10 (35) R = H
2a	R^1,R^2 = H; R^3 = Me	7 (71) R^1 = Me; R^2 = OAc		
2b	R^1,R^2 = Me; R^3 = H	7 (84)	+	11 (13) R = Me
3a	R^1,R^2 = H; R^3 = Bz	8 (65) R^1 = Bz; R^2 = OAc		
3b	R^1 = Me; R^2 = H; R^3 = Bz	8 (32)	+	12 (14) R = Bz
4a	R^1 = H; R^2,R^3 = Me	7 (25)		
4b	R^1,R^2,R^3 = Me	9 (33) R^1,R^2 = Me + 7 (9)		

* All compounds gave satisfactory IR, NMR, and mass spectral data.

A plausible mechanism could involve oxythallation of the enol, followed by, in the case of cyclisation, an intramolecular nucleophilic substitution at the α-carbon to give the benzofuranone (Scheme I). Repetition of the sequence with the solvent as nucleophile would lead to α-acetoxylation of the ketone.

Scheme I



We anticipate the use of this oxidative cyclisation in the synthesis of heterocycles, work on which is being carried out in our laboratory.

References:

1. A. Mckillop, B.P. Swann, and E.C. Taylor, J. Am. Chem. Soc., 93, 4919 (1971).
2. W.D. Ollis, K.L. Ormand, and I.O. Sutherland, J. Chem. Soc. (C), 119 (1970).
3. S. Uemura, T. Nakano, and K. Ichikawa, J. Chem. Soc. Jap., 88, 1111 (1967).

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