

Synthesis of 1,1-Bis-[2-hydroxy-3-(3-Aryl-Prop-2-en-1-one)-5-Methyl Phenyl] Methane and Their Dibromo Derivatives

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New 1,1-bis-[2-hydroxy-3-(3-aryl-prop-2-en-1-one)-5-methyl phenyl] methane, (**4a-f**), have been synthesised by the reaction of 1,1-bis-[2-hydroxy-3-acetyl-5-methyl phenyl] methane (**3**) with aromatic aldehydes in alkali medium and their dibromo derivatives, 1,1-bis-[2-hydroxy-3-(2,3-dibromo-3-aryl-propan-1-one)-5-methyl phenyl] methane (**5a-f**) were synthesised by bromination of (**4a-f**) in acetic acid medium.

INTRODUCTION

A variety of methods are available for the synthesis of chalcones. The most convenient method is the one that involves the Claisen-Schmidt condensation of equimolar quantities of substituted acetophenones with aromatic aldehydes, in presence of aqueous alkali¹⁻⁵ and their dibromo derivatives have been prepared by the action of bromine in carbon disulfide or acetic acid medium⁶⁻⁸.

The chalcones and their bromo derivatives are found to be useful reactants in the synthesis of flavanones⁹, flavones¹⁰, pyrazoles¹¹, pyrazolines¹², isoxazoles¹³, and isoxazolines¹³ etc. From the survey of literature it is observed that 1,1-bis-[2-hydroxy-3-(3-aryl-prop-2-en-1-one)-5-methyl phenyl] methane and their dibromo derivatives have not yet been synthesised. It was, therefore, thought of interest to synthesise bis-chalcones and their dibromo derivatives.

The present work deals with the synthesis of 1,1-bis-[2-hydroxy-3-(3-aryl-prop-2-en-1-one)-5-methyl phenyl] methane (**4a-f**) by the condensation of 1,1-bis-[2-hydroxy-3-acetyl-5-methyl phenyl] methane (**3**) with aromatic aldehydes in alkali medium and their dibromo derivatives 1,1-bis-[2-hydroxy-3-[2,3-dibromo-3-aryl-propan-1-one]-5-methyl phenyl] methane (**5a-f**) by bromination of (**4a-f**) in acetic acid medium. The structures of these compounds have been established on the basis of analytical data and spectral analysis (IR, UV, NMR and mass).

EXPERIMENTAL

All melting points were taken in silicon oil bath instrument in open capillaries and are uncorrected. Purity of the compounds was checked by TLC on silica gel-G. IR spectra was recorded on Perkin-Elmer spectrophotometer, mass spectra on Jeol D-300 (EI/CI) spectrophotometer, PMR spectra on Brucker AC 300 F

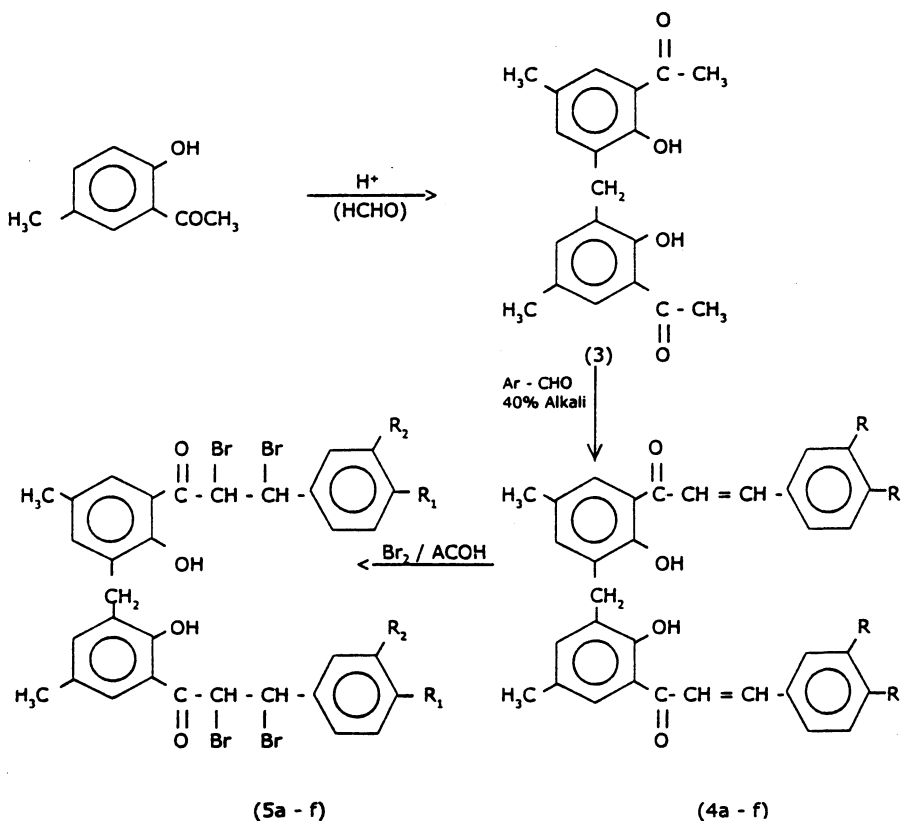
NMR spectrophotometer at 300 MHz and UV-spectra recorded on Shimadzu UV-spectrophotometer.

Preparation of 1,1-bis-[2-hydroxy-3-acetyl-5-methyl phenyl] methane (3)

2-Hydroxy-5-methyl acetophenone (0.01 M) was refluxed with 37–40% formaldehyde (15 mL) and dil. H_2SO_4 (17 : 33) in alcohol (40 mL) for about 30 h; the solid product obtained was filtered, washed, dried and crystallised from acetone or acetic acid. (m.p. 176°C , yield 70%).

(3): IR: ν_{max} (cm^{-1}): 2951 ν (methyl C—H str.), 1632 ν (C=O), 1456 ν (C=C), 1262 ν (Ph C—O abs); ^1H NMR (δ): 2.1 (s, 6H, two — CH_3), 2.6 (s, 6H, two — OCH_3), 2.9 (s, 2H, CH_2), 3.9 (s, 2H, —OH) 7.2–7.6 (m, 4H, Ar—H); MS (m/z): 312 (M^+); UV (λ_{max}): 351 nm, 261 nm.

SCHEME



System	a	b	c	d	e	f
R_1	-H	- OCH_3	-OH	- NO_2	-H	- NH_2
R_2	-H	-H	- OCH_3	-H	- OCH_3	-H

TABLE-1
PHYSICAL CHARACTERISATION DATA OF SYNTHESISED COMPOUNDS

Comp.	Name	m.f.	Yield (%)	m.p. (°C)
4a	1,1-Bis-[2-hydroxy-3-[3-phenyl-prop-2-en-1-one]-5-methyl phenyl]methane	C ₃₃ H ₂₈ O ₄	90	215–217
4b	1,1-Bis-[2-hydroxy-3-[3-(4-methoxy phenyl)-prop-2-en-1-one]-5-methyl phenyl] methane	C ₃₅ H ₃₂ O ₆	90	196–198
4c	1,1-Bis-[2-hydroxy-3-[3-(3-methoxy-4-hydroxy phenyl)-prop-2-en-1-one]-5-methyl phenyl] methane	C ₃₅ H ₃₂ O ₈	95	155–157
4d	1,1-Bis-[2-hydroxy-3-[3-(4-nitrophenyl)-prop-2-en-1-one]-5 methyl phenyl] methane	C ₃₃ H ₂₆ N ₂ O ₈	90	> 270
4e	1,1-Bis-[2-hydroxy-3-[3-phenyl-prop-2-en-1-one]-5-methyl phenyl] methane	C ₃₅ H ₃₂ O ₆	90	222–224
4f	1,1-Bis-[2-hydroxy-3-[3-(4-amino phenyl-prop-2-en-1-one)-5-methyl phenyl] methane	C ₃₃ H ₃₀ N ₂ O ₄	85	183–184
5a	1,1-Bis-[2-hydroxy-3-[2,3-dibromo-3-phenyl-propan-1-one]-5-methyl phenyl] methane	C ₃₃ H ₂₈ O ₄ Br ₄	90	197–199
5b	1,1-Bis-[2-hydroxy-3-[2,3-dibromo-3-(4'-methoxy phenyl)-propan-1-one]-5-methyl phenyl] methane	C ₃₅ H ₃₂ O ₆ Br ₄	90	232–234
5c	1,1-Bis-[2-hydroxy-3-[2,3-dibromo-3-(3'-methoxy-4'-hydroxy phenyl)-propan-1-one]-5-methyl phenyl] methane	C ₃₃ H ₂₆ N ₂ O ₈ Br ₄	95	> 270
5d	1,1-Bis-[2-hydroxy-3-[2,3-dibromo-3-(4'-nitrophenyl)-propan-1-one]-5-methyl phenyl] methane	C ₃₅ H ₃₂ O ₈ Br ₄	90	180–182
5e	1,1-Bis-[2-hydroxy-3[2,3-dibromo-3-(3'-methoxy phenyl)-propan-1-one]-5-methyl phenyl] methane	C ₃₅ H ₃₂ O ₆ Br ₄	90	236–238
5f	1,1-Bis-[2-hydroxy-3-[2,3-dibromo-3-(4'-amino phenyl)-propan-1-one]-5-methyl phenyl] methane	C ₃₃ H ₃₀ N ₂ O ₄ Br ₄	85	202–204

Preparation of 1,1-bis-[2-hydroxy-3-(3-aryl-prop-2-en-1-one)-5-methyl phenyl] methane (4a-f)

Bis-ketone (3) (0.01 mole) was condensed with aromatic aldehydes (0.02 mole) in presence of 40% alkali (8 mL) in alcoholic medium. The reaction mixture was kept overnight. Then it was decomposed by 1 : 1 HCl. The product obtained was filtered, washed with 2% sodium bicarbonate and water and crystallised from acetic acid.

(4a): IR: ν_{\max} (cm⁻¹): 2834 ν (methyl Ar—C—H str.), 1632 ν (C=O), 1454 ν (C=C), 1259 ν (C—O); ¹HNMR (δ): 2.1 (s, 6H, two—CH₃), 3.5 (s, 2H, —OH), 3.8 (s, 2H, CH₂), 4.5 (d, 1H, CH_A), 5.1 (d, 1H, —CH_B), 6.4–7.6 (m, 14H, Ar—H); mass (m/z): 488 (M⁺) UV (λ_{\max}): 340 nm, 261 nm.

Preparation of 1,1-bis-{2-hydroxy-3-(2,3-dibromo-3-aryl propan-1-one)-5-methyl phenyl} methane (5a-f)

To the solution of bis-chalcone (4a-f) (0.01 mole) and acetic acid (10 mL), bromine in acetic acid was slowly added with constant stirring. The reaction mixture was kept for 1 h at room temperature. The product obtained was filtered, washed, dried and crystallised from acetic acid.

(5a): IR: ν_{\max} (cm⁻¹): 2923 ν (C—H str.), 1634 ν (C=O), 1451 ν (C=C), 1262 ν (C—O); ¹HNMR (δ): 2.1 (s, 6H, two —CH₃), δ 3.4 (s, 2H, CH₂), 3.7 (s, 2H, —OH), 4.1 (d, 1H, CH_A), 5.2 (d, 1H, CH_B), 6.8–7.6 (m, 14H, Ar—H); UV (λ_{\max}): 347 nm, 261 nm.

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