

INTERCONVERSION OF SUBSTITUTED 2-ARYL-2,3-DIHYDRO-4H-1-BENZOPYRAN-4-ONES AND CORRESPONDING 2'-HYDROXYCHALKONES OVER SILICA SURFACE

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INTERCONVERSION of substituted 2-aryl-2,3-dihydro-4H-1-benzopyran-4-ones and the corresponding 2'-hydroxychalkones has been studied in acidic and basic liquid medium¹⁻³. We report in this note a convenient interconversion of these compounds over silica surface.

Various substituted 2-aryl-2,3-dihydro-4H-1-benzopyran-4-ones (Ia-Xa, figure 1) and 2'-hydroxychalkones (Ib-Xb, figure 1) were prepared using methods reported earlier⁴⁻¹¹. A solution of substituted 4H-1-benzopyran-4-one (Ia-Xa) or 2'-hydroxychalkone (Ib-Xb) in chloroform was slurred with silica gel and evaporated to dryness. The amount of silica gel used was ten times the weight of reactant. The adsorbed compound on silica gel was heated at 110°C for 6 hr and subsequently extracted with ethyl acetate to give an oily product. The resolution of the oily product by column or preparative thin-layer chromatography furnished two compounds, the starting

4H-1-benzopyran-4-one or chalkone and the corresponding chalkone or 4H-1-benzopyran-4-one in each case. The compounds were identified by their m.p., m.m.p., co-TLC and superimposable IR spectra with those of authentic samples. The progress of the reaction was monitored spectrophotometrically using literature method³ and it was observed that heating the reaction mixture beyond 6 hr did not change its composition. Thus, an equilibrium between 2-aryl-2,3-dihydro-4H-1-benzopyran-4-one and the corresponding 2'-hydroxychalkone was achieved. The recovery of the reaction products at equilibrium attained from either direction is described in table 1. The total recovery was as much as 85 to 95%.

The interconversion was also carried out by the addition of silica gel in refluxing solution of Iab-Xab in methanol or ethanol. There was no change in recovery of the products as compared to that obtained by heating these compounds over silica gel in solid phase (table 1). However, when the relatively nonpolar solvent *viz* toluene was used, the reaction took 48 hr to attain equilibrium and only traces of conversion products were obtained in benzene on prolonged heating.

In a further extension of this interconversion over silica surface and to delineate the role of 2-aryl substituent, 2,3-dihydro-4H-1-benzopyran-4-one (XIa) or its 7-methoxy derivative (XIIa), prepared by known methods¹², were subjected to similar reaction conditions. However, in this reaction, no isomerization products, 2'-hydroxyacrylophenones (XIb, XIIb) were detected and the starting material was recovered unchanged. When the reaction was attempted in reverse direction using XIb, prepared by the method reported earlier¹³, as the substrate, XIb with other minor intractable products without expected isomerized product XIa, was obtained. This suggested that 2-aryl substituent has a specific role in this isomerization reaction.

It may thus be concluded that substituted 2-aryl-2,3-dihydro-4H-1-benzopyran-4-one \rightleftharpoons 2'-hydroxychalkone interconversion can be effectively carried out over silica gel at elevated temperature. However, the equilibrium lies towards 4H-1-benzopyran-4-one (table 1). Further, the use of silica gel is preferred to other acidic and basic catalysts, as the reaction can also be carried out directly by heating these compounds on silica gel-G coated thin-layer plates using only minute quantities of these compounds which may offer a method for direct comparison of 2-aryl-2,3-dihydro-4H-1-benzopyran-4-one with corresponding 2'-hydroxychalkone and vice-versa.

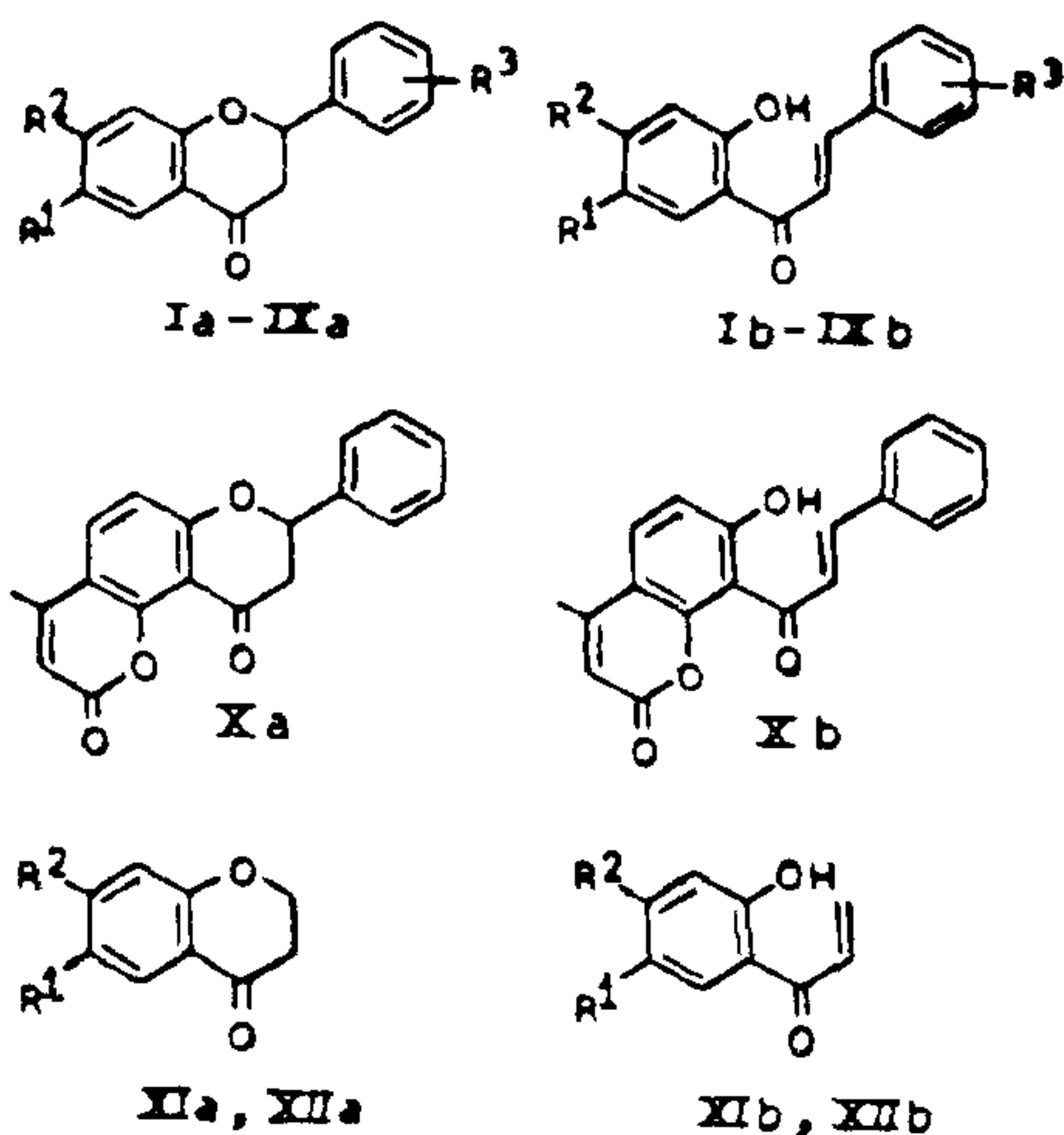


Table 1 Percent recovery of 2-aryl-2,3-dihydro-4H-1-benzopyran-4-one (1a-Xa) and 2'-hydroxychalkone (1b-Xb) at equilibrium attained from either direction over silica gel.

Comp. No ^a	R ¹	R ²	R ³	Percent recovery of		Total recovery (%)
				4H-1-benzopyran-4-one (a)	2'-hydroxychalkone (b)	
I	H	H	H	40	45	85
II	Br	H	H	75	18	93
III	Br	H	4-OMe	52	40	92
IV	COEt	H	4-OMe	55	38	93
V	COPh	H	H	60	29	89
VI	COPh	H	3-OMe	60	32	92
VII	COCH=CHPh	H	H	58	32	90
VIII	COCH=CHC ₆ H ₄ - OMe-p	H	4-OMe	55	40	95
IX	H	OMe	H	54	38	92
X	—	—	—	52	38	90

^a Compound numbers given in this column refer to those described in figure 1. For compounds XI and XII, R² is H and OMe respectively while R¹ is H for both.

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RUTHENIUM(III) CATALYZED OXIDATION OF SECONDARY ALCOHOLS BY N-METHYLMORPHOLINE-N-OXIDE

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OXIDATION of organic substrates by tertiary amine N-oxides like trimethylamine-N-oxide and N-methylmorpholine-N-oxide (N-oxide) in the presence of OsO₄ has been reported¹⁻³. Sharpless et al⁴ studied the Ru(III)-catalyzed oxidations by N-oxide of cholesterol, geraniol etc.

However, there are no reports of studies on the oxidation of secondary alcohols using N-oxide as oxidant. Pyridine-N-oxide and trimethylamine-N-oxide have been estimated using Ti(III) as a reductant⁵. We have carried out kinetic investigations on Ru(III)-catalyzed oxidation of cyclohexanol, 1-phenylethanol and 2-propanol by N-oxide in DMF as solvent, by determining titanometrically the concentration of N-oxide remaining at any instant. Aliquots of the reaction mixture were quenched by adding a known excess of Ti(III) solution. Conc. HCl and sodium citrate were added to prevent hydrolysis and to form a complex respectively. The excess of Ti(III) was back-titrated against standard Fe³⁺ using ammonium thiocyanate as indicator.

The oxidation reaction follows 1:1 stoichiometry