

Reaction of 2-Alkyl-2-phenyl-1,3-dioxolans with Iodine Monochloride: Formation of α -Phenylalkanoate Esters

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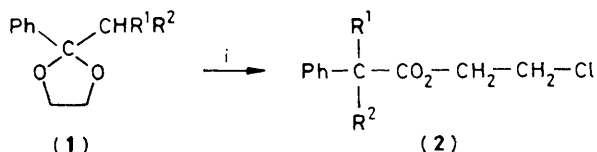
2-Alkyl-2-phenyl-1,3-dioxolans undergo a high-yield transformation into 2-chloroethyl α -phenylalkanoates upon treatment with iodine monochloride in dichloromethane.

Recent interest in reactions in which arylalkanones can be oxidatively rearranged to α -arylalkanoic acids¹⁻⁴ has prompted us to report our preliminary findings in this regard.

Thallium(III) nitrate and a mixture of silver(I) nitrate and iodine, in acidic methanol^{1,3} or trimethylorthoformate,^{2,3} have been found to effect this transformation successfully. The mechanisms of these reactions have been elucidated recently³ and they have been shown to involve conversion of the arylalkanone into an intermediate phenacylthallium or phenacyliodide species, respectively, which is then transformed into its dimethyl acetal. Subsequent rearrangement of the acetal leads to the α -arylalkanoate ester. Although these reagents function effectively, they suffer from the disadvantages of toxicity or high cost.

Continuing our study of the reactions of dioxolans and related compounds with halogens,⁵ we have observed that 2-alkyl-2-phenyl-1,3-dioxolans (1) are converted, in high yields, into the appropriate 2-chloroethyl phenylalkanoates (2) upon treatment with iodine monochloride in dichloromethane (Scheme 1, Table 1). The most plausible mechanism for this reaction has been outlined in Scheme 2.

The proposed intermediacy of the iodide (3) is supported by the observation that dioxolan (1d) is smoothly converted

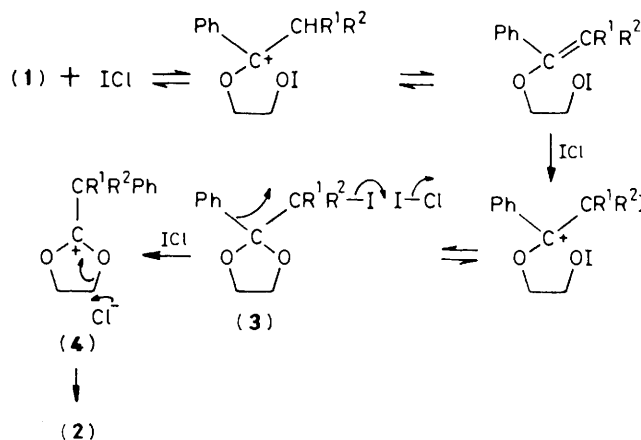


Scheme 1. Reagents and conditions: i, ICl, CH₂Cl₂, heat, 30 min.

Table 1. Results of the conversion of 2-alkyl-2-phenyl-1,3-dioxolans (2.5 mmol) into 2-chloroethyl phenylalkanoates with iodine monochloride (10 mmol) in refluxing dichloromethane (10 ml).

Dioxolan (1)		Yield of ester (2), % ^a		
	R ¹	R ²		
a	H	H	a	92
b	H	Me	b	93
c	Me	Me	c	82
d	H	I	a	93

^a Yield determined by ¹H n.m.r. spectroscopy using an added internal standard.



Scheme 2

into the ester (**2a**) in the presence of iodine monochloride. Iodine monochloride has previously been reported to facilitate the deiodination of alkyl iodides through complexation.⁶ The driving force for phenyl migration is undoubtedly the high relative stability of the resultant dioxolanylium ion (**4**).

This procedure for the synthesis of α -phenylalkanoate esters constitutes a viable alternative to the thallium(III) nitrate and silver(I) nitrate-iodine processes for the conversion of aryl ketones into α -arylalkanoate esters. Although prior synthesis of the dioxolan from the ketone is required, this is generally a straightforward operation, and its subsequent conversion into the ester may be accomplished in very high yield under relatively nonpolar conditions. In addition, the use of iodine monochloride avoids the disadvantages of toxicity and high cost associated with the thallium and silver salts.

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