

### Note

## Effect of solvents on the rearrangement of aromatic acetals by iodobenzene dichloride

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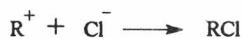
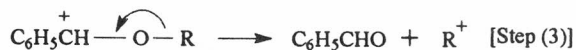
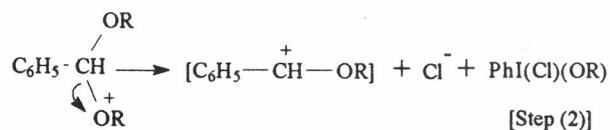
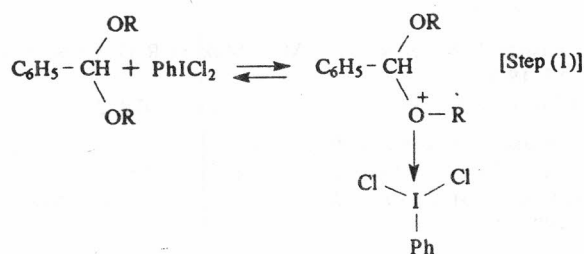
Iodobenzene dichloride reacts with aromatic acetals to give esters and aldehydes in different solvents. Ester is the predominant product in high polar solvents.

Hypervalent iodine compounds have been reported to be used in organic synthesis, conversion of organolithium compounds to hydrocarbons<sup>1</sup>, preparation of coordination compounds<sup>2</sup> and in chlorination reactions<sup>3</sup>. The present paper is a report on the reaction of iodobenzene dichloride on benzaldehyde di-*n*-butyl acetal and benzaldehyde di-*i*-isobutyl acetal in different solvents.

### Results and Discussion

The reaction between benzaldehyde di-*n*-butyl acetal and iodobenzene dichloride at 60°C in 1,2-dichloroethane medium gave *n*-butyl benzoate and benzaldehyde as products besides iodobenzene. The same reaction carried out at 50°C with benzaldehyde di-*i*-isobutyl acetal gave *i*-isobutyl benzoate and benzaldehyde. No reaction was observed at room temperature. The reaction was studied in solvents of varying dielectric constants and relative proportion of the products were determined by gas chromatography.

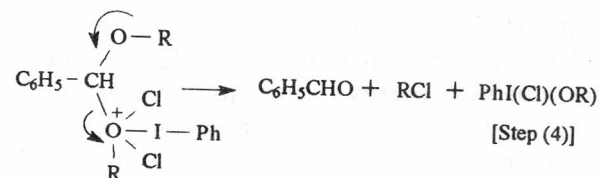
The reaction takes place with the formation of co-ordination complex linking iodine and oxygen of the acetal which undergoes cleavage to form a carbonium ion followed by the formation of aldehyde.



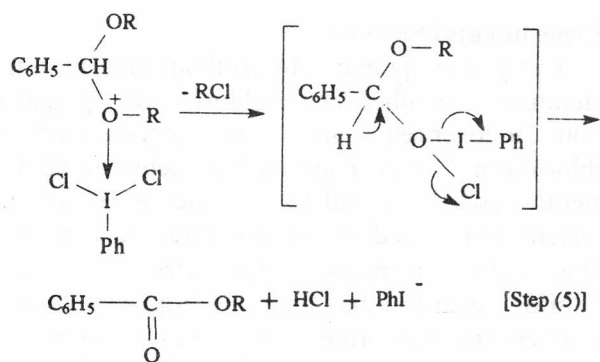
The carbonium ion may lose proton to give an alkene



Another probable mechanism for the formation of aldehyde may be through concerted mechanism.



The mechanism for ester formation was similar to that proposed for the oxidation of secondary and primary alcohols by iodobenzene dichloride<sup>4,5</sup>.



The trend in the formation of ester (Table I) indicates an increase of ester with solvent polarity and in the same solvent the *i*-isobutyl acetal yields more ester compared to *n*-butyl acetal. In a more polar medium step (5) is facilitated by stabilizing the polar complex and the enhancement of ester in *i*-isobutyl acetal is attributed to the steric factor due to bulkier *i*-isobutyl group causing the liberation of

Table I—Reaction of benzaldehyde di-*n*-butyl acetal with iodobenzene dichloride at 60° C (1:1 molar ratio) (A) and reaction of benzaldehyde di-isobutyl acetal with iodobenzene dichloride at 50° C (1:1 molar ratio) (B)

Entry	Solvents	Dielectric Constant	A		B	
			products %		products %	
			<i>n</i> -buty benzoate	benzaldehyde	isobutyl benzoate	benzaldehyde
1	1,2-Dichloro ethane	10.36	24	76	31	69
2	Chlorobenzene	5.621	22	78	46	53
3	Chloroform	4.806	21	79	22	78
4	Toluene	2.379	20	80		
5	Carbontetrachloride	2.238	10	90	19	81
6	xylene	2.200	11	85	15	85

<sup>1</sup>determined by GC

alkylchloride easier. The enhancement of ester formation in aromatic rather than aliphatic solvents is due to decrease in enthalpy of association between oxygen of the acetal and iodine in iodobenzene dichloride and increase in iodine solvent interaction<sup>6</sup>. Formation of polar complex in all the solvents depends on the dissociation of  $\text{PhICl}_2$  as  $\text{PhICl}$  and  $\text{Cl}^-$ . In carbontetrachloride and xylene medium which are low dielectric solvents, the activation energy needed for dissociation was very high<sup>7</sup>, and the formation of ester was minimum. Comparative analysis (Table I) shows that ester formation increases in aromatic solvents in the order  $\text{C}_6\text{H}_5\text{Cl} > \text{C}_6\text{H}_5\text{CH}_3 > \text{C}_6\text{H}_4(\text{CH}_3)_2$  and in aliphatic solvents the order is  $\text{ClCH}_2\text{CH}_2\text{Cl} > \text{CHCl}_3 > \text{CCl}_4$ .

### Experimental Section

Acetals were prepared by methods present in the literature<sup>8,9</sup>. Iodobenzene dichloride was prepared from iodobenzene and was recrystallised in chloroform and characterized in determining the melting point<sup>10</sup>. Acetal (0.02 mole) in 30 mL of solvent was placed in 250 mL three necked flask fitted with a mercury sealed stirrer, a calcium chloride guard tube and a dropping funnel. Iodobenzene dichloride (0.02 mole) in 30 mL of solvent was added slowly through the dropping funnel. The reaction mixture was allowed to stand for 1 hr. The mixture was then vigorously stirred at 60°C for benzaldehyde di-*n*-butyl acetal and at 50°C for benzaldehyde di-isobutyl acetal. The reaction was arrested by the addition of ice cold water and was finally washed with excess potassium iodide in aq sulfuric acid<sup>11</sup>. Formation of hydrochloric acid was detected with silver nitrate.

The products were separated by thin layer and column chromatography techniques and finally characterized by IR and NMR spectral data. Relative percentage of products in different solvents were determined by gas chromatography.

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