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CHEMISTRY OF TRIVALENT IODINE—III

THE ACTION OF IODOBENZENE DICHLORIDE ON PRIMARY ALCOHOLS AND ALDEHYDES[†]

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Abstract—Iodobenzene dichloride reacts with saturated primary alcohols at room temperature in the presence of pyridine to give esters and acid chlorides. With the corresponding aldehydes, only the latter type of product is obtained. While pivaldehyde reacts normally, benzaldehyde is unaffected by the reagent under the same conditions. Presence of moisture results in formation of acids. It is suggested that reactions of both types of substrates involve base catalysed fragmentation of iodonium intermediates.

Complexation of chlorine with various nucleophiles yields mild oxidising agents of considerable synthetic interest.[1-6] During the use of iodobenzene dichloride (IBD) for the oxidation of alcohols, it was found that while secondary alcohols could be converted into ketones in excellent yields, in presence of pyridine, the reaction with primary alcohols under the same conditions was much more complex, exceptions like benzyl alcohol being very limited.[6] Good selectivity for secondary alcohols has been obtained by suitable choice of reaction conditions.[7] However, the nature of the reactions that take place with primary alcohols and the reasons why some of them show exceptional behaviour have not so far been clarified. In this regard, the results are governed by the susceptibility of the primary products, the aldehydes, to further oxidation by the reagent concerned. We have investigated this question using a number of the lower homologues and the results are reported below.

The products obtained in the reactions of a number of alcohols and aldehydes with two molar equivalents of the reagent in pyridine are shown in Table 1. Since the reagent is thermally unstable and the reactions involved are exothermic, the addition of the reagent was done gradually and with cooling, whenever required, so that room temperature was maintained throughout. The mixtures were analyzed after 24 hr after more than 95% of the oxidising agent was consumed. The reaction with methanol was poor and the details were not examined closely. But, it was ascertained that even with excess of the material, IBD reacted only to the extent of about 68% in 24 hr. The results obtained with the other alcohols were roughly of the same pattern, the products being the corresponding acids and their esters. As reported earlier, benzyl alcohol gave a near quantitative yield of benzaldehyde. This aldehyde was unaffected by excess of the reagent. Aliphatic aldehydes were, however, converted into acids under similar conditions. Esters remained practically unaffected by the reagent.

The results clearly show that it is indeed the reactivity of the aldehydes towards IBD that complicates the behaviour of primary alcohols towards the reagent. The probable pathways for the products obtained are shown in Chart I. The alcohols are presumably converted into the aldehydes through the intermediacy of phenyl-alkoxy-iodonium chlorides (I), the heterolysis of the I-O bond being brought about by base attack on the α-H atom (path A). For further oxidation of the aldehydes, the most likely reaction appears to be one which involves an addition-elimination sequence (path B). The oxidising agent can co-ordinate to the aldehyde oxygen and any one of the available nucleophiles, pyridine, chloride ion

Table 1. Products of reactions of alcohols and aldehydes with IBD

Substrate	$R\text{-}C^{O}_{CH_2R}$(%)	$R\text{-}C^{O}_{OH}$(%)	Unreacted Material (%)
Ethanol[a]	56.76	31.17	7.09
Butanol[a]	14.30	35.70	39.30
2-Ethyl hexanol[a,b]	15.42	66.88	6.98
Octanol[a,b]	25.00	56.30	16.60
Neopentyl Alcohol[a]	32.88	40.20	12.50
n-Butyraldehyde[c]	—	56.82	
n-Heptaldehyde[c]	—	61.55	
Pivalaldehyde[a]	—	83.12	
Benzaldehyde[c]	No reaction.		

a,b,c: These subscripts indicate analysis by NMR, GLC and chemical work up respectively.

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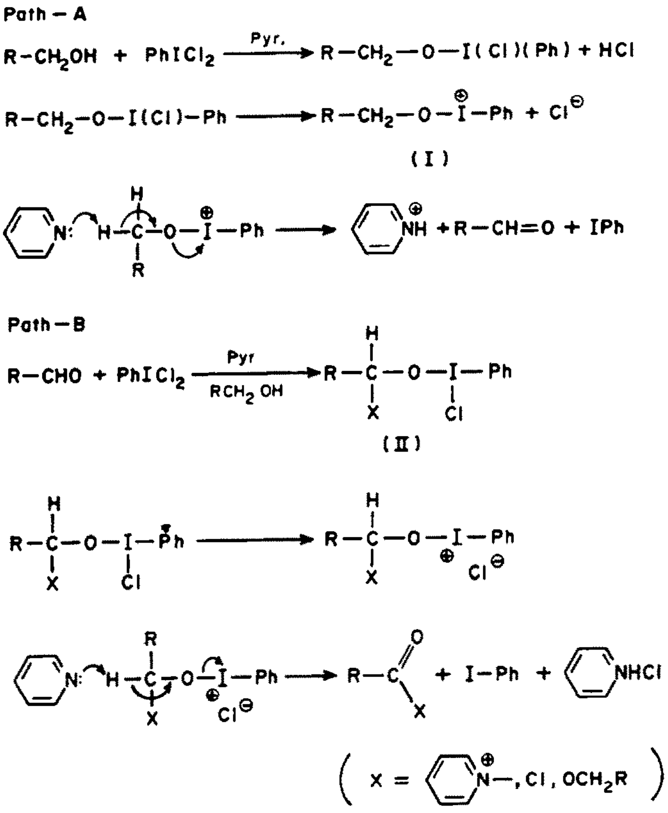

Chart I.

or alcohol, can add to the formyl carbon to give intermediates of type II. These intermediates can undergo base-catalyzed elimination in a concerted or step-wise manner to give the ester, acid chloride or its pyridinium complex. Perhaps, the latter mode is more likely.

In the reaction of the alcohols, formation of the carboxylic ester may take place *via* the acyl pyridinium chloride. The stability of benzaldehyde towards the reagent apparently has its origin in the ionic character of the C–X link of II. The carbenium ion formed by the coordination of IBD with the aldehyde oxygen is presumably stabilized by delocalization of the positive charge into the aromatic ring. This effectively cuts off the redox cleavage of the I-O bond.

Although no water was employed in the analytical procedures, the conditions were not quite anhydrous. It is presumably for this reason that carboxylic acids rather than their chlorides were obtained after removal of pyridine as hydrochloride. It was also ascertained that the introduction of small amounts of moisture into the mixture suppressed ester formation without affecting the oxidation reaction. This accounted for the lowering of the ester-acid ratio seen occasionally in experiments employing pyridine which was not carefully dried.

EXPERIMENTAL

A typical procedure for the analysis of the products of reaction. To a soln of the alcohol or aldehyde (0 01 mole) in pyridine (2 ml), a soln of iodobenzene dichloride (0.2 mole) in pyridine (8 ml) was added slowly and with cooling, so that room temp was maintained throughout the experiment. The mixture was allowed to stand for 24 hr. Some of the pyridine hydrochloride formed precipitated at this stage. For the analysis of the products formed, the mixture was diluted with 20 ml of dry benzene and the pyridine present in soln precipitated as hydrochloride by passing HCl gas generated from conc. HCL and washed once with conc. H_2SO_4. The HCl used was not quite dry, but was good enough for the precipitation of the hydrochloride which was removed by filtration. The filtrate was made up to 50 ml and the products of reaction as well as unreacted material in this solution were estimated mostly by NMR spectra. In the cases of *n*-octanol and 2-ethylhexanol, the results were confirmed by GLC. No aldehyde was indicated in the spectra. Since the methylenes α- to the carboxyl groups in the products gave resolved signals, the proportion of carboxyl derivatives (esters and acids) could be readily obtained. The proportions of the ester and unoxidised alcohols were obtained similarly from the intensities of their respective $-O-CH_2$ signals.

Reactions of aldehydes. In experiments on the oxidation of butylaldehyde and *n*-heptaldehyde, the corresponding acids were isolated by extraction methods, pyridine being removed as hydro-chloride in aqueous soln. With pivaldehyde, product analysis could be done conveniently using NMR spectra.

Reaction of methanol with IBD. IBD (0.005 mole) was reacted with excess methanol (10 ml) in presence of pyridine (3 ml) and allowed to stand for 24 hr. The liberated HCl was estimated by titration against standard NaOH. The unreacted trivalent iodine was estimated iodimetrically. It was found that the HCl formed corresponded to the trivalent iodine used up for oxidation. Only about 68% of reagent was found to be consumed.

REFERENCES

[1] E. J. Corey and C. U. Kim, *J. Am. Chem. Soc.* **94**, 7586 (1972).
[2] E. J. Corey and C. U. Kim, *J. Org. Chem.* **38**, 1233 (1973).
[3] E. J. Corey and C. U. Kim, *Tetrahedron Letters* 919 (1973).
[4] D. H. R. Barton, B. J. Garner and R. H. Wightman *J. Chem. Soc.* 1855 (1964).
[5] G. Carnduff, *Quart. Rev.* **20**, 171 (1966).
[6] J. Wicha, A. Zavecki and M. Kocor, *Tetrahedron Letters* 3635 (1973).
[7] J. Wicha and A. Zavecki, *Ibid.*, 3059 (1974).