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Reaction Between Unsaturated Alcohols and Potassium lodide in the Presence of Polyphosphoric Acid

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Treatment of a series of unsaturated alcohols with potassium iodide in polyphosphoric acid gave none of the expected corresponding unsaturated iodides. Instead, in most cases, alkyl iodides, in which the position of iodine was different from that of the original hydroxy-group, were obtained.

CONVERSION of alcohols into alkyl iodides with potassium iodide in phosphoric acid-phosphorus pentoxide mixtures is a well established reaction.¹ Since the reaction appeared to be a convenient one for making primary, secondary, and tertiary iodides,^{1,2} it seemed of interest to see whether it could be generally applied to alcohols which contained other functional groups.

We subjected but-3-enol (I) to the reaction in an attempt to make 4-iodobut-1-ene (II) for subsequent conversion to dibut-3-envlamine (III). Surprisingly, 2-iodobutane was the major volatile product and the crude product contained no unsaturated component.

Results are given in the Table where the alcoholic substrates are listed together with reaction products, yields, and the method(s) used for identification.

Four of the six alcohols (I) and (V)-(VII) examined gave some saturated iodoalkanes. The yield of isopropyl iodide from allyl alcohol (V) was considerable (32%), and in each case the products listed were the only volatile ones. The absence of any unsaturated product was clearly shown by the absence of resonance peaks in the olefinic region of the n.m.r. spectra of the products prior to purification. In cases where the yield of volatile products was small, extensive polymerisation had

Reaction between unsaturated alcohols and KI in $H_3PO_4-P_2O_5$			
Alcohol	Products	Yield (%) "	Method of product identification
CH2:CH·CH2·OH (V)	MeCH·I·Me	32	n.m.r., i.r., n _D ²² , g.l.c.
$CH_2:CH \cdot [CH_2]_2 \cdot OH$ (I)	MeCHIEt	16	n.m.r., i.r., g.l.c.
	$Me[CH_2]_3 \cdot I$	2	mass spectrometry, i.r., g.l.c.
MeCH:CH·CH ₂ ·OH (VI)	MeCHIEt	9	mass spectrometry, i.r., g.l.c.
CH, CMe CH, OH (VII)	MeCHIMe	2	g.l.c. ^b
,	MeCIMe ₂	7	g.l.c. ^b
	MeCHIEt	4	g.l.c. ^b
PhCH:CH·CH ₂ ·OH (VIII)	Mainly dimeric and oligomeric hydrocarbons	ca. 90 °	mass spectrometry, i.r.
MeCH ₂ ·CH:CH·[CH ₂] ₂ ·OH (IX)	MeCH:CH \cdot [CH ₂] ₃ \cdot I (<i>cis</i> and <i>trans</i>)	12	mass spectrometry, n.m.r., i.r., n_D^{22}

TABLE

^a Determined by g.l.c. ^b The retention time for each substance was identical to authentic samples on two different stationary phases. • This figure represents a conversion of (VIII) to the products described.

The required secondary amine was subsequently synthesised in good yield by way of the bromide (IV).³

In view of the unexpected 'hydrogenation' of (I), a series of unsaturated alcohols was treated similarly.

$$\begin{array}{c} CH_2:CH \cdot CH_2 \cdot CH_2 X \quad CH_2:CH \cdot [CH_2]_2 \cdot NH \cdot [CH_2]_2 \cdot CH:CH_2 \\ (I) \quad X = OH \qquad (III) \end{array}$$

$$\begin{array}{ll} (II) & X = I \\ (IV) & X = Br \end{array}$$

¹ H. Stone and H. Shechter, J. Org. Chem., 1950, 15, 491; Org. Synth., Coll. Vol. IV, 1963, p. 323.

occurred. This is not surprising in view of the somewhat drastic reaction conditions. No significant quantity of any iodine-containing product could be detected from the reaction with cinnamic alcohol (VIII). Thus none of the products gave peaks at m/e 127 or 128 in

² H. Chihara, M. Otsuru, and S. Seki, Bull. Chem. Soc. Japan, 11. Contata, M. Ocsatti, and S. Sch, Dam. Comm. Soc. Jupan, Coll.
1966, 30, 2145; K. Stransky, M. Streibl, and F. Storm, Coll.
Czech. Chem. Comm., 1966, 31, 4694; L. L. Miller and A. K.
Hoffmann, J. Amer. Chem. Soc., 1967, 89, 593.
³ M. J. S. Dewar and R. Jones, J. Amer. Chem. Soc., 1968, 90,

^{2137.}

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their mass spectra, and the n.m.r. spectra lacked signals which could be attributed to protons vicinal to iodine. From spectral data (see Table) it was clear that a mixture of di- and poly-meric hydrocarbons had been formed. Hex-3-enol (IX) alone reacted to produce an unsaturated iodo-derivative, yet even this was accompanied by double-bond isomerisation.

DISCUSSION

The results reported above are of interest for two reasons. Firstly, the reaction clearly cannot be extrapolated to unsaturated alcohols since none of the substrates was converted into the corresponding iodide. Indeed, one of the products from (VII) contains one carbon atom less than the substrate. Only the alcohol (IX) gave an alkenyl iodide and in this case the complication of isomerisation arises. Furthermore there was no evidence of products formed by the straightforward addition of hydrogen iodide (i.e. iodoalcohols) which were shown to result from the reaction between simple olefins and potassium iodide,¹ yet these compounds cannot be ruled out as intermediates. Therefore the presence of both a double-bond and a hydroxy-group, even when they are separated by more than two carbon atoms, has a profound effect on the course of the reaction.

Secondly, the mechanisms of the reactions are of interest, particularly with respect to the origin of the hydrogen. The two hydrogen atoms required for the formation of a molecule of alkyl iodide must originate either from a molecule of the alcohol substrate or the phosphoric acid.

From the experimental evidence so far collected, it is not possible to propose a definite mechanism for the formation of the alkyl iodides. However, it is likely that free iodine, which is formed in considerable quantities during each experiment, is the causal factor, since 'normal' products resulted from the reaction between two of the alcohols with potassium bromide. Thus allyl alcohol was converted smoothly into allyl bromide, and but-3-enol yielded 4-bromobut-1-ene together with some dibromo-derivatives.

EXPERIMENTAL

Reaction between Various Unsaturated Alcohols and Potassium Iodide in Polyphosphoric Acid.—A mixture of orthophosphoric acid (2 mole) and phosphorous pentoxide (0.46 mole) was cooled to $15-20^{\circ}$. Potassium iodide (0.35 mole) was added to the mixture followed by the dropwise addition of the appropriate alcohol (0.5 mole). The mixture was then heated on a boiling water-bath for $2\frac{1}{2}$ hr., and then cooled and poured into water (135 g.). The organic material, which had assumed a dark brown colour and contained iodine was separated by extraction with ether $(3 \times 250 \text{ ml.})$. The combined ether layers were washed first with 20% (w/v) sodium thiosulphate solution to remove the iodine and then with water; they were finally dried and made up to a convenient volume with dry ether. Aliquots were set aside for g.l.c. analysis and the ether was removed from the remainder by distillation. The residues were purified by distillation or preparative g.l.c.

Identification of Reaction Products.—Purified products were characterised as indicated in the Table. N.m.r. spectra were measured with a Varian 220 MHz spectrometer. Samples were examined in deuteriochloroform solutions with tetramethylsilane as internal reference. The i.r. spectra were taken as neat liquids or potassium bromide discs on a Perkin-Elmer 237 spectrometer. Mass spectra were determined with an A.E.I. MS-9 mass spectrometer operating at an ionising voltage of 70 ev. G.l.c. separations were made on Apiezon L and Carbowax 20M 5-ft. analytical and preparative columns.

Determination of Reaction Yields by G.l.c.—The ether solutions containing the products were examined by g.l.c. with a flame-ionisation detector. Convenient volumes of the solutions to be estimated, containing a known weight of an appropriate internal standard, were compared with standard solutions of authentic material containing the same internal standard.

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