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## **Reaction of Iodonium Nitrate with Some Olefinic Alcohols**

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Iodonium nitrate in pyridine-chloroform at room temperature undergoes preferential electrophilic addition to certain olefinic alcohols to form (i) hydroxyiodoalkyl nitrates and (ii) hydroxyiodoalkylpyridinium nitrates. Parallel reactions in sym-collidine-chloroform gave three-, four-, and five-membered cyclic ethers as well as products of type (i). Introduction of a hydroxy-function stabilises the intermediate iodonium ion leading to an increase in the product ratio (ii): (i) relative to the additions to alkenes of comparable structure. The trans stereospecific addition of iodonium nitrate to cyclohex-2-en-1-ol indicates that the iodonium ion is formed cis to the hydroxy-group during the reaction.

RECENTLY it has been shown <sup>1,2</sup> that iodonium nitrate (generated in situ by the reaction of iodine chloride with silver nitrate in chloroform-pyridine) readily undergoes a trans stereospecific electrophilic addition to alkenes to form (i) iodoalkyl nitrates, (ii) iodoalkylpyridinium nitrates, or (iii) alkenyl pyridinium iodides, depending on the substrate. The iodonium nitrate reagent also readily dehydrogenates primary and secondary aliphatic alcohols and benzylic alcohols to the corresponding carbonyl compounds; in this reaction<sup>3</sup> the order of reactivities of the alcohols is benzylic >

- U. E. Diner and J. W. Lown, Chem. Comm., 1970, 333.
   U. E. Diner and J. W. Lown, Canad. J. Chem., 1971, 49, 403.
   U. E. Diner, J. Chem. Soc. (C), 1970, 676.

secondary > primary. We report here the reaction of this reagent with some olefinic mainly allylic alcohols to examine the competition between these reactions.

Since allylic alcohols have the same redox potentials as benzyl alcohol,<sup>4</sup> and these potentials are lower than those for saturated primary alcohols, it was anticipated that allylic alcohols should be more readily dehydrogenated by iodonium nitrate. This is in agreement with the suggestion that these reactions proceed by initial hydride transfer.<sup>3</sup> However electrophilic additions proved to be the dominant type of reaction. Even in the case when a 1 mol. excess of reagent was used, no oxidation to a carbonyl compound was observed. Also, in the case of certain alcohols, hydroxygroup participation resulted in the formation of three-, four-, and five-membered cyclic ethers. In no reaction was oxidation of the hydroxy-function observed. The reactions were carried out both in chloroform-pyridine and in chloroform-sym-collidine. In the former solvent iodopyridinium nitrates were formed, together with products of direct electrophilic addition whereas use of the latter solvent prevented formation of the iodoquaternary salts and allowed isolation and examination of the other reactions.

The reaction with allyl alcohol in pyridine-chloroform formed an isomeric mixture (30% yield; ratio 80:20) of the iodo-nitrates (I) and (II). The composition of

$$\begin{array}{c} \mathsf{HO}\mathsf{\cdot}\mathsf{CH}_2\mathsf{\cdot}\mathsf{CH}(\mathsf{O}\mathsf{\cdot}\mathsf{NO}_2)\mathsf{\cdot}\mathsf{CH}_2\mathsf{I} & \mathsf{HO}\mathsf{\cdot}\mathsf{CH}_2\mathsf{\cdot}\mathsf{CH}\mathsf{I}\mathsf{\cdot}\mathsf{CH}_2\mathsf{\cdot}\mathsf{O}\mathsf{\cdot}\mathsf{NO}_2\\ (\mathsf{I}) & (\mathsf{II}) \end{array}$$

the mixture was determined in this and similar cases by measuring the ratio of the intensity of the CH<sub>2</sub>I n.m.r. absorption<sup>2</sup> to that of the rest of the spectrum. The accompanying iodopyridinium salt consisted of only one isomer, N-(2-hydroxy-1-iodomethylethyl)pyridinium nitrate (III) in 23% yield. In this case, as will be shown later and as was previously found to be generally true for electrophilic addition of iodonium nitrate to alkenes, the pyridine becomes attached to the more stable cationic centre. In view of the reported relative nucleophilicities of pyridine and nitrate (20:1



for aqueous solutions),<sup>5</sup> the isolation of substantial quantities of hydroxyiodoalkyl nitrates in these additions is surprising. However, since the reported heat of hydration of the nitrate ion is  $-61 \pm 2$  kcal (g ion)<sup>-1</sup>,<sup>6a</sup> and therefore comparable with that of iodide <sup>6b</sup>  $[-68 \text{ kcal } (g \text{ ion})^{-1}]$ , then the nucleophilicity of this ion may be expected to be increased relative to that of the unchanged pyridine upon going to an aprotic solvent. No data are available for a more direct comparison.

When the reaction of allyl alcohol with iodonium nitrate was performed in chloroform-sym-collidine the yield of the iodo-nitrates was increased to 60% and no quaternary salt was formed.

When the central carbon atom of the allylic system bears a methyl group the resulting increased stabilisation of the corresponding carbonium ion results in the formation of the iodopyridinium salt (IV) to the complete exclusion of other (isolable) products.

The reaction of 1,1-dimethylallyl alcohol in pyridinechloroform produced one isomeric form of the iodonitrate (V) (20% yield) and only one iodopyridinium salt (VI) (40% yield), corresponding to the same mode of addition. This is the first case noted in which the

$$\begin{array}{c} \mathsf{Me}_{2}\mathsf{C}(\mathsf{OH})\cdot\mathsf{CHI}\cdot\mathsf{CH}_{2}\cdot\mathsf{O}\cdot\mathsf{NO}_{2}\\ (V)\\ \mathsf{Me}_{2}\mathsf{C}(\mathsf{OH})\cdot\mathsf{CHI}\cdot\mathsf{CH}_{2}-\overset{\dagger}{\mathsf{N}}\underbrace{\overset{\bullet}{\underset{\mathsf{NO}_{3}}}}\\ (VI) & \mathsf{NO}_{3} \end{array}$$

pyridine becomes attached to a primary position. That this effect may be attributed to steric hindrance by the three groups at the 1-position of the allyl alcohol is demonstrated by the exclusive formation of compounds (VII) and (VIII) from the addition of iodonium nitrate to 3,3-dimethylbut-1-ene. Precisely the same mode of addition has been observed in the reaction of 3,3-dimethylbut-1-ene with bromine in methanol to give 2-bromo-1-methoxy-3,3-dimethylbutane exclusively.5b

$$\begin{array}{ccc} Me_{3}C \cdot CHI \cdot CH_{2} \cdot O \cdot NO_{2} & Me_{3}C \cdot CHI \cdot CH_{2} - N \\ (VII) & (VIII) & NO_{3} \end{array}$$

The reaction of 1,1-dimethylallyl alcohol in symcollidine-chloroform takes a different course, the products being the iodonitrate (V) and the epoxide (IX). The epoxide structure (IX) was proved and the altern-

ative oxetan structure (X) discounted by the ready reductive cleavage with lithium aluminium hydride in ether at 5° to t-pentyl alcohol, identified by comparison with an authentic sample. Oxentans require much more vigorous conditions for reductive cleavage<sup>7</sup> (see later). The isolation of the epoxide in this and other cases involving allylic alcohols in which the

<sup>&</sup>lt;sup>4</sup> H. Adkins, R. M. Elofson, A. G. Rossow, and C. C. Robinson, J. Amer. Chem. Soc., 1949, 71, 3622.
<sup>5</sup> R. Breslow, 'Organic Reaction Mechanisms,' 2nd edn., Benjamin, New York, 1969, (a) p. 85; (b) p. 125.

<sup>&</sup>lt;sup>6</sup> (a) M. F. C. Ladd and W. H. Lee, J. Inorg. and Nuclear Chem., 1960, 13, 218; (b) J. D. Roberts and M. C. Caserio, 'Basic Principles of Organic Chemistry,' Benjamin, New York, 1965, p. 303.

<sup>7</sup> L. A. Paquette, ' Principles of Modern Heterocyclic Chemistry,' Benjamin, New York, 1968, p. 92.

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hydroxy-bearing carbon atom is secondary or tertiary, in contrast with the behaviour of allyl alcohol, is in agreement with the observations of Winstein and Goodman on the addition of hypobromous acid to allylic alcohols.8,9

$$Me_{2}C(OH)\cdot CH:CH_{2} \xrightarrow{BrOH} Me_{2}C \xrightarrow{---} CH\cdot CH_{2}Br$$
$$HO\cdot CH_{2}\cdot CH:CH_{2} \xrightarrow{BrOH} HO\cdot CH_{2}\cdot CH(OH)\cdot CH_{2}Br$$

The facilitating effect of alkyl substitution upon epoxide formation is also illustrated by the following comparison of rate constants <sup>10</sup> (water at 18°):

The effect has been attributed to relief of steric crowding in the parent chlorohydrin as the epoxide is formed.<sup>11,12</sup> The lesser steric hindrance offered to approaching nitrate ion by the iodonium ion formed from a secondary allylic alcohol compared with that from a tertiary alcohol is illustrated by hex-1-en-3-ol. In pyridinechloroform the isomeric mixture of iodo-nitrates (XI)

$$\begin{array}{cc} \Pr^{n}CH(OH) \cdot CH(O \cdot NO_{2}) \cdot CH_{2}I & \qquad \Pr^{n}CH(OH) \cdot CHI \cdot CH_{2} \cdot O \cdot NO_{2} \\ (XI) & (XII) \end{array}$$

and (XII) (50:50) was produced in 34% yield, indicating the less stringent steric demands of the intermediate

iodonium ion. However the larger size of the pyridine results in the exclusive formation of the 2-iodo-1pyridinio-nitrate (XIII).

The reaction of hex-1-en-3-ol in sym-collidine-chloroform gave the oxetan (XIV), which was completely resistant to reductive cleavage by lithium aluminium hydride in ether at 5° for 1.5 h under conditions in which compound (IX) was cleaved in 10 min. Treatment of the oxetan (XIV) with lithium aluminium



hydride in tetrahydrofuran for 24 h at 60° removed it completely (g.l.c. analysis). The main product was 8 S. Winstein and L. Goodman, J. Amer. Chem. Soc., 1954, 76,

4368. <sup>9</sup> L. Goodman and S. Winstein, J. Amer. Chem. Soc., 1957, 79, 4788.

<sup>10</sup> H. Nilsson and L. Smith, Z. phys. Chem., 1933, 166A, 136.
 <sup>11</sup> E. S. Gould, 'Mechanism and Structure in Organic Chemis-

try,' Holt, Rinehart, and Winston, 1959, p. 567. <sup>12</sup> R. M. Beesley, C. K. Ingold, and J. F. Thorpe, J. Chem. Soc.,

1915, 105, 1080.

<sup>13</sup> M. Bartok and A. S. Gilde, Acta Univ. Szeged. Acta Phys.

Chem., 1963, 9, 25 (Chem. Abs., 1964, 60, 4094a).
 <sup>14</sup> I. M. Gverdtsiteli, R. Yu. Papava, and E. S. Gelashvili, Zhur. obshchei Khim., 1966, 36, 112 (Chem. Abs., 1966, 64, 14, 207g).

2-propyloxetan (XV)<sup>13,14</sup> and only traces of hexan-3-ol were produced, consistent with the known resistance of oxetans to reductive cleavage.7 The mass spectrum of compound (XV) (combined g.l.c.-mass spectrometer system) exhibited a major  $\alpha$ -fission (m/e 57, base peak) and minor  $\gamma$ -fission, consistent with an oxetan structure.<sup>15</sup> The alternative 2,3-epoxyhexane structure (XVI), which would not have survived the reduction process, would be expected to show prevalent loss of Me.

The behaviour of a homoallylic alcohol was examined. In pyridine-chloroform with iodonium nitrate hex-5-en-3-ol gave the isomeric iodo-nitrates (XVII) and (XVIII) (25:75), indicating a normal preference by the nitrate ion attacking the more stable centre of the iodonium ion.<sup>2</sup> The isolated pyridinium salt was not the expected N-(3-hydroxy-1-iodomethylpentyl)pyridinium nitrate (XIX). Instead, N-(5-ethyltetrahydrofuran-3-yl)pyridinium nitrate (XX) was obtained in 20% yield, as shown by its n.m.r. and i.r. spectra and elemental analysis. In sym-collidine-chloroform, 5ethyltetrahydrofuran-3-yl nitrate (XXI) was isolated in 30% yield, together with the isomeric iodo-nitrates (XVII) and (XVIII). Treatment of the mixture of (XVII) and (XVIII) with sym-collidine under conditions comparable with the formation of (XXI) and for up to 72 h produced no reaction, thus discounting their intermediacy in the formation of (XXI). This suggests that the latter is formed by hydroxy-group attack on the intermediate iodonium ion, followed by displacement of iodide (Scheme). This reaction parallels the displacement of the secondary iodide in compound (XXIV) by pyridine in the formation of compound (XX). Despite the relatively low nucleophilicity of the nitrate ion,<sup>5,16</sup> the displacement of secondary iodide from



compound (XXII) would be favoured by the much greater leaving ability of iodide (300 times that of nitrate 17), reflecting the low C-I bond dissociation energy,18 and by the fact that the concentration of nitrate ion during formation of (XXI) will be far in excess of that in the formation of (XXII). In addition the known propensity of iodide ion towards charge-transfer complexation 19,20 with pyridinium salts may assist in its departure.

<sup>15</sup> H. Budzikiewicz, C. Djerassi, and D. H. Williams, 'Mass Spectrometry of Organic Compounds,' Holden-Day, San Francisco, 1967, p. 449. <sup>16</sup> P. R. Wells, Chem. Rev., 1963, **63**, 171.

<sup>17</sup> Ref. 11, p. 262.
 <sup>18</sup> J. March, 'Advanced Organic Chemistry; Reactions, Mechanisms and Structure,' McGraw-Hill, New York, 1968, p. 26.
 <sup>19</sup> E. M. Kosower, 'Molecular Biochemistry,' McGraw-Hill,

New York, 1962, p. 180. <sup>20</sup> E. M. Kosower, 'An Introduction to Physical Organic Chemistry,' Wiley, New York, 1968, p. 1979.

An earlier study of the electrophilic addition of iodonium nitrate to a series of alkenes revealed that those alkenes leading to more stable cationic iodonium ion intermediates favour attack by pyridine over nitrate



with a resulting increase in the relative proportion of iodopyridinium nitrate salts.<sup>2</sup> In the present study a comparison of the relative yields of iodonitrate esters and pyridinium salts for the olefinic alcohols and the alkenes of comparable structure (Table 1) reveals that in all cases introduction of a hydroxy-function results in a marked increase in the proportion of the pyridinium salt relative to that of the iodo-nitrate. This suggests that the hydroxy-function contributes to the increased

TABLE 1

	Relative yields								
Substrate	Iodonitrates		Pyridinium salts						
∫Me <sub>2</sub> C(OH)·CH:CH <sub>2</sub>	1	:	2						
lMe <sub>3</sub> C·CH:CH₂	1	:	0.267						
(EtCH(OH)·CH <sub>2</sub> ·CH:CH <sub>2</sub>	1	:	<b>2</b>						
PrCH(OH)·CH:CH <sub>2</sub>	1	:	0.47						
BuCH:CH <sub>2</sub>	83%	:	0						
EtCHMe·CHMe·CH:CH <sub>2</sub>	75%	:	0						
∫Cyclohex-2-enol	1	:	0.802						
lCyclohexene	1	:	0.66						

stabilisation of the intermediate iodonium ion rather than to its inductive destabilisation. Recently Olah and his co-workers have provided spectral evidence for the presence of bridged halogenonium ions in solution.<sup>21</sup> The enhanced stabilisation afforded the iodonium ion by the hydroxy-group can be envisaged in a number of ways, e.g. participation to carbon (XXIII).

Examination of the appropriate coupling constants



in the n.m.r. spectrum of the iodonitrate obtained from cyclohex-1-enol showed it to be 3-hydroxy-2-iodocyclo-

<sup>21</sup> G. A. Olah, J. M. Bollinger, and J. Brinich, J. Amer. Chem. Soc., 1968, 90, 2587.
 <sup>22</sup> H. B. Henbest and R. L. Wilson, J. Chem. Soc., 1957, 1958.

hexyl nitrate, with the stereochemistry shown (XXIV) in which the hydroxy-group is axial. Consideration of the stereochemistry of the two possible intermediates



(XXV) and (XXVI) favours an intermediate of type (XXV) and proves that the iodonium ion is formed *cis* to the hydroxy-group. This is in agreement with the observed stereochemistry of epoxidation of cyclohex-2enols in which the oxiran ring is formed cis- to the hydroxy-group.<sup>22,23</sup> Apparently the epoxidation reagent becomes associated in some way with the hydroxygroup in the molecule prior to attacking the double bond, and is therefore constrained to approach the latter



from that side of the ring which bears the hydroxygroup.24



## EXPERIMENTAL

M.p.s were determined with a Fisher-Jones apparatus. I.r. spectra were recorded with a Perkin-Elmer model 221 spectrophotometer, and n.m.r. spectra with Varian A-60 and A-100 analytical spectrometers for ca. 10-15%(w/v) solutions in [<sup>2</sup>H]chloroform or [<sup>2</sup>H<sub>6</sub>]dimethyl sulphoxide with tetramethylsilane as a standard. Mass spectra were obtained with a Perkin-Elmer model 270 gas chromatograph-mass spectrometer (ionization energy 70 eV). G.l.c. analyses were performed with an F and M model 700 gas chromatograph. Several columns packed with polar and nonpolar liquid phases were used to confirm the chromatographic identifications.

General Procedure for the Reaction of Iodonium Nitrate with Unsaturated Alcohols .- The procedure in pyridinechloroform was similar to that described previously.<sup>2</sup> When the reactions were carried out in sym-collidinechloroform the following procedure was adopted. Sufficient

<sup>23</sup> H. B. Henbest, Proc. Chem. Soc., 1963, 159.
<sup>24</sup> E. L. Eliel, 'Stereochemistry of Carbon Compounds,' McGraw-Hill, New York, 1962, p. 293.

ether was added to the mixture to precipitate the collidinium salt. The precipitate was collected and the ethereal

	Ταβι	.е 2					
	In p	yridine Iodo-	In sym-collidine				
	Iodo- nitrate ª	pyridinium salt <sup>b</sup>	Iodo- nitrate ª	Cyclic ether			
Olefinic alcohol	Yie	eld (%)	Yield (%)				
Allyl alcohol	30	23	60				
2-Methyl-2-prop-2-en- 1-ol		75					
l,l-Dimethylallyl alcohol ¢	20	40	20	20			
3,3-Dimethylbut-1-ene	75	20					
Hex-1-en-3-ol	34	16	53	11			
Hex-5-en-3-ol •	10	20 d	17	30			
Cyclohex-2-enol	36	<b>29</b>					

<sup>a,b</sup> Mixture of isomers. <sup>e</sup> The yield of cyclic ether in pyridine was close to 5%. <sup>d</sup> N-(5-Ethyltetrahydrofuran-3-yl) pyridinium nitrate. <sup>e</sup> The yield of (XX) in pyridine was 25%.

layer was washed several times successively with (a) cold 5% hydrochloric acid saturated with sodium chloride,

(b) saturated aqueous sodium chloride, (c) 5% sodium hydrogen carbonate saturated with sodium chloride until neutral, and finally (d) saturated sodium chloride solution containing sodium thiosulphate. The ether layer was dried (MgSO<sub>4</sub>) and evaporated *in vacuo*. The residual oil was distilled under reduced pressure.

Procedure B described in a previous publication <sup>2</sup> was found satisfactory for crystallisation of the iodopyridinium salts. In one instance [that of the mixture of (XIX) and (XX)] purification was achieved by chromatography on silica gel as previously described.<sup>2</sup>

The analytical and spectral data on the products thus obtained are summarised in the Tables.

Lithium Aluminium Hydride Hydrogenolysis of 3-Iodo-2-propyloxetan (XIV).—A solution of the oxetan (XIV), (0.8 g, 0.0035 mol) in tetrahydrofuran (10 ml) was added to a stirred solution of lithium aluminium hydride (0.2 g, 0.0052 mol) in tetrahydrofuran (20 ml) at room temperature. The mixture was heated under reflux for 1.5 h, then aqueous potassium hydroxide (15%; 3 ml) was added at 0 °C with stirring. The filtered solution was dried (MgSO<sub>4</sub>) and evaporated *in vacuo*. The residual oil was distilled

Isomer ratio 80 20	Alkyl nitrate 2-Hydroxy-1-iodo- methylethyl (I) 3-Hydroxy-2-iodo- propyl (II)	M+ 247	B.p. (°C/ mmHg) 78/0·15	Pyridinium nitrate N-(2-Hydroxy-1- iodomethylethyl) (III)	M.p. (°C) 48—52	Cyclic ether	$M^+$	B.p. (°C/ mmHg)
	FF)- (/			N-(2-Hydroxy-1- iodomethyl-1- methylethyl) (IV)	108-110			
	3-Hydroxy-2-iodo- 3-methylbutyl (V)	275	<b>70/0·1</b>	N-(3-Hydroxy-2- iodo-3-methyl- butyl) (VI)	123	2,3-Epoxy-1-iodo- 3-methyl butane (IX)	212	52/6
	2-Iodo-3,3-dimethyl- butyl (VII)	211	55/0.2	N-(2-Íodò-3,3-di methylbutyl) (VIII)	133			
50 50	2-Hydroxy-1-iodo- methylpentyl (XI) 3-Hydroxy-2-iodo- hexyl (XII)	289	90/0·1	N-(3-Hydroxy-2- iodohexyl) (XIII)	80—85	<b>3</b> -Iodo-2-propyl oxetan (XIV)	226	72/2
75	3-Hydroxy-1-iodo- methylpentyl (XVIII)	289	<b>6</b> 5/0·1	N-(5-Ethyltetra- hydrofuran-3-yl) (XX)	Oil	5-Ethyltetrahydro- furan-3-yl nitrate (XXI)	99	60/1
25	4-Hydroxy-2-iodo- hexyl (XVII) 3-Hydroxy-2-iodo- cyclohexyl (XXIV)	287	90/0.05	t í	166—168	. ,		
	50 50 50 55 25	<ul> <li>Alkyl nitrate</li> <li>2-Hydroxy-1-iodo- methylethyl (I)</li> <li>3-Hydroxy-2-iodo- propyl (II)</li> <li>3-Hydroxy-2-iodo- 3-methylbutyl (V)</li> <li>2-Iodo-3,3-dimethyl- butyl (VII)</li> <li>2-Hydroxy-1-iodo- methylpentyl (XI)</li> <li>3-Hydroxy-2-iodo- hexyl (XII)</li> <li>3-Hydroxy-1-iodo- methylpentyl (XVIII)</li> <li>4-Hydroxy-2-iodo- hexyl (XVII)</li> <li>3-Hydroxy-2-iodo- hexyl (XVII)</li> <li>3-Hydroxy-2-iodo- hexyl (XVII)</li> <li>4-Hydroxy-2-iodo- hexyl (XVII)</li> <li>3-Hydroxy-2-iodo- hexyl (XVII)</li> <li>3-Hydroxy-2-iodo- hexyl (XVII)</li> </ul>	<ul> <li>Alkyl nitrate M<sup>+</sup></li> <li>2-Hydroxy-1·iodo- methylethyl (I)</li> <li>3-Hydroxy-2·iodo- propyl (II)</li> <li>3-Hydroxy-2·iodo- 3-methylbutyl (V)</li> <li>2-Iodo-3,3-dimethyl- butyl (VII)</li> <li>2-Hydroxy-1·iodo- methylpentyl (XI)</li> <li>3-Hydroxy-1·iodo- hexyl (XII)</li> <li>3-Hydroxy-1·iodo- hexyl (XII)</li> <li>4-Hydroxy-2·iodo- hexyl (XVII)</li> <li>3-Hydroxy-2·iodo- hexyl (XVII)</li> <li>4-Hydroxy-2·iodo- hexyl (XVII)</li> <li>3-Hydroxy-2·iodo- hexyl (XVII)</li> <li>3-Hydroxy-2·iodo- hexyl (XVII)</li> <li>3-Hydroxy-2·iodo- hexyl (XVII)</li> <li>3-Hydroxy-2·iodo- hexyl (XVII)</li> <li>3-Hydroxy-2·iodo- hexyl (XVII)</li> <li>3-Hydroxy-2·iodo- hexyl (XVII)</li> </ul>	Isomer ratio Alkyl nitrate $M^+$ $M^+$ $M^+$ 80 2-Hydroxy-1-iodo- methylethyl (1) 20 3-Hydroxy-2-iodo- propyl (11) 211 55/0·2 butyl (VII) 211 55/0·2 butyl (VII) 211 55/0·2 butyl (XII) 50 2-Hydroxy-1-iodo- methylpentyl (XI) 50 2-Hydroxy-1-iodo- hexyl (XII) 75 3-Hydroxy-1-iodo- hexyl (XII) 75 3-Hydroxy-1-iodo- methylpentyl (XI) 289 65/0·1 methylpentyl (XII) 25 4-Hydroxy-2-iodo- hexyl (XVII) 3-Hydroxy-2-iodo- hexyl (XVII) 3-Hydroxy-2-iodo- hexyl (XVII) 3-Hydroxy-2-iodo- hexyl (XVII) 3-Hydroxy-2-iodo- hexyl (XVII) 3-Hydroxy-2-iodo- hexyl (XVII) 287 90/0·05	Isomer ratio Alkyl nitrate $M^+$ $mHg$ nitrate 80 2-Hydroxy-1-iodo- methylethyl (I) 20 3-Hydroxy-2-iodo- propyl (II) $N-(2-Hydroxy-1-iodomethylethyl)$ 3-Hydroxy-2-iodo- 3-methylbutyl (V) $N-(2-Hydroxy-1-iodomethylethyl)$ 2-Iodo-3,3-dimethyl- butyl (VI) $N-(3-Hydroxy-2-iodo-3,3-dimethylbutyl)$ 2-Hydroxy-1-iodo- butyl (VII) $N-(3-Hydroxy-2-iodo-3,3-dimethylbutyl)$ (VIII) 50 2-Hydroxy-1-iodo- methylpentyl (XI) 50 3-Hydroxy-2-iodo- hexyl (XIII) 75 3-Hydroxy-2-iodo- hexyl (XVII) $(XVII)$ 25 4-Hydroxy-2-iodo- hexyl (XVII) 25 4-Hydroxy-2-iodo- hexyl (XVII) N-(5-Ethyltetra-hydroxy-2-iodo-hexyl (XVII) (XII) $(XX)287 90/0-05 \dagger$		$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$

TABLE 3

† N.m.r. analysis does not provide enough information to decide if there are one or two isomers.

							*	101.15	x									
	Iodo-nitrate						Iodopyridinium salt					Cyclic ether						
	Calc. (%) Found (%)			%)	Calc. $(\%)$ Fo			ound (%)		Calc. (%)			Found (%)					
	С	H	N	С	н	N	С	H	N	С	Н	N	С	H	N	С	H	Ν
Allyl alcohol		<u>_</u>	5.7			5.9	29.45	3.4	8.6	30.2	3.18	8.8	~~~~~					
Hex-1-en-3-ol	24.95	$4 \cdot 2$	4.85	24.95	$4 \cdot 2$	4.7	35.9	4.65	$7 \cdot 6$	36.15	$4 \cdot 7$	$7 \cdot 2$	31.9	$4 \cdot 9$		31.75	4.75	
1,1-Dimethylallyl alcohol	21.85	3.65	$5 \cdot 0$	$22 \cdot 1$	3.7	4.55	33.9	4.25	$7 \cdot 9$	34.3	$4 \cdot 2$	7.65	28.3	<b>4</b> ∙3		$28 \cdot 5$	$4 \cdot 2$	
Cyclohex-2-en-1-ol	25.1	3.5	$4 \cdot 9$	$25 \cdot 3$	3.4	$4 \cdot 2$	36.1	4.1	7.65	$36 \cdot 1$	$4 \cdot 0$	8.0						
2-Methylprop- 2-en-1-ol							31.8	3.85	8.25	$32 \cdot 2$	<b>4</b> ∙0	8.5						
Hex-5-en-3-ol			4.85			$5 \cdot 0$	51.1	7.0	10.8*	50.85	6.5	10.6			8.7			8.1
3,3-Dimethylbut- 1-ene	S	ee ref.	2	Se	ee ref.	2	35.9	4.65	7.6	36.1	<b>4</b> ·7	$7 \cdot 6$						

TADLE A

\* Includes one molecule of water.

affording 2-propyloxetan (XV) (0.2 g, 66%), b.p. 100° at 700 mmHg (lit., 110—111° at 760 mmHg).

3-Hydroxy-2-iodocyclohexyl Nitrate (XXVII).—This was obtained from the reaction of cyclohex-2-enol with iodonium nitrate in chloroform–pyridine by a similar procedure to that described.<sup>2</sup> The n.m.r. spectrum showed  $\delta(CD_3CI)$  1.75 (4H, m), 2.3 (3H, m, CH<sub>2</sub> and OH), 3.8 (1H, m, HC·OH), 4.32 and 4.48 (1H, q, HCI,  $J_{1,2}$  8.5,  $J_{2,3}$  2.5 Hz), and 5.4 p.p.m. (1H, m, HC·O·NO<sub>2</sub>).

We thank Mr. T. M. Painter for technical assistance.

[1/674 Received, May 3rd, 1971]