Reaction of Iodonium Nitrate with Alkenes

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Summary Iodonium nitrate in chloroform–pyridine adds to alkenes at room temperature to form (i) iodo-aliphatic nitrate esters, (ii) iodo-alkane pyridinium nitrates, or (iii) alkene pyridinium iodides depending on the substrate.

FOLLOWING the recently reported study by one of us on the use of iodonium nitrate for the oxidation of alcohols,[1] we have examined the addition of this reagent to alkenes. The subject is of current interest in view of the recent report by Hassner *et al.*[2] of the reaction of a closely related compound, nitryl iodide with alkenes.

Iodonium nitrate (prepared *in situ* by the addition of an equimolar quantity of ICl to a solution of $AgNO_3$ in chloroform–pyridine†) readily adds to alkenes to form, (i) iodo-aliphatic nitrate esters, (ii) iodo-alkane pyridinium nitrates, or (iii) alkene pyridinium iodides depending on the substrate (see Table). The first five alkenes of the Table gave products of the type (i), according to equation 1. Only

Addition products of iodonium nitrate with alkenes[a]

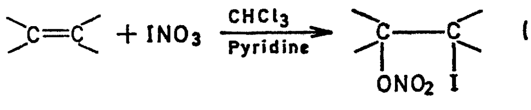
Entry	Alkene		Molecular ion	Yield %	B.p. (°)
1	Hex-1-ene	1-Iodo-hexan-2-ol nitrate	—	50	80/0·5 mm
2	*cis*-Pent-2-ene	(i) 3-Iodo-pentan-2-ol nitrate	197[b]	(70) } 75	45/0·2 mm[c]
		(ii) 2-Iodo-pentan-3-ol nitrate		(30)	
3	Cyclohexane	2-Iodocyclohexanol nitrate	271	61	113/1·3 mm
4	3,4-Dimethylhex-1-ene	(i) 1-Iodo-3,4-dimethylhexan-2-ol nitrate	301	(40) } 67	75/1·2 mm
		(ii) 2-Iodo-3,4-dimethylhexan-1-ol nitrate		(60)	
5	3,3-Dimethylbut-1-ene	2-Iodo-3,3-dimethylbutanol nitrate	211[b]	65	55/0·2 mm
					M.p (°)
6	2,3-Dihydro-4-pyran	*N*-(3-Iodotetrahydropyranosyl)pyridinium nitrate	—	65	113—116
7	Ethyl vinyl ether	*N*-[1-(1-Ethoxy-2-iodo)ethyl]pyridinium nitrate	—	75	65—68
8	2-Methylbut-2-ene	*N*-[2-(2-Methyl-3-iodo)butyl]pyridinium nitrate	—	74	105—108
9	Styrene	(i) *N*-[1-(1-phenylethenyl)]pyridinium iodide	—	(80) } 50	65—68
		(ii) 2-Iodo-1-phenylethanol nitrate	293	(20)	b.p.110°/1 mm[d]

[a] Satisfactory analytical data were obtained on all new compounds. Nitrate esters showed very intense i.r. absorptions at 1630 cm^{-1} (covalent $-ONO_2$, ref. 9); considerably reduced in intensity in the case of the ionic nitrates.

[b] $(M - ONO_2)$.

[c] Isomeric mixture.

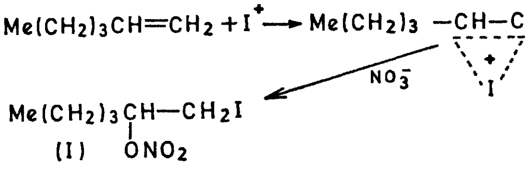
[d] Decomposes partially at the b.p.



$$>C{=}C< + INO_3 \xrightarrow[Pyridine]{CHCl_3} >\underset{ONO_2}{C}-\underset{I}{C}< \quad (1)$$

with hex-1-ene (entry 1) was the adduct predicted from considerations of carbonium ion stability (I) the sole product in the reaction (equation 2). In the assignment of structures to (I) and to similar compounds in this study by n.m.r. spectroscopy it was noted that methine hydrogens α to an ONO_2 group absorb at about 1 p.p.m. downfield from hydrogens α to an I group.[3] The $-CH_2I$ protons also have a characteristic n.m.r. absorption at δ 4·3—4·0.[4]

cis-Pent-2-ene afforded a mixture of 3-iodopentan-2-ol and 2-iodopentan-3-ol nitrates (II) and (III). The n.m.r. spectrum showed signals at 5·2 [m, 8 lines, $CH(Me)-ONO_2$] and 4·7 [m, 5 lines, $CH(Et)-ONO_2$] in the ratio of (28 : 12), indicating an isomer ratio (II) : (III) of approximately 70 : 30 corresponding to preferential attack by the nitrate ion at the less hindered carbon of the iodonium ion intermediate. The multiplicities and relative intensities of the other signals in the spectrum are in accordance with these structural assignments which were confirmed by hydrogenolysis of (II) and (III) to the corresponding iodohydrins (IV) and (V) by (a) Zn–Cu couple in acetic acid or (b) electrolytic reduction in a buffer at pH 4·7 at −0·9 v *versus* S.C.E. at a Hg cathode. Reduction of (IV) and (V) with $LiAlH_4$ produced a mixture of the corresponding pentan-2- and -3-ols the composition of which (70 : 30) was



$$Me(CH_2)_3CH{=}CH_2 + I^+ \longrightarrow Me(CH_2)_3-CH-CH_2- \xrightarrow{NO_3^-} \underset{(I)}{Me(CH_2)_3\underset{ONO_2}{C}H-CH_2I} \quad (2)$$

determined by g.l.c. by comparison with mixtures of authentic pentan-2-ol and pentan-3-ol.

Iodonium nitrate with cyclohexene afforded 2-iodocyclohexanol nitrate the n.m.r. spectrum of which indicated a

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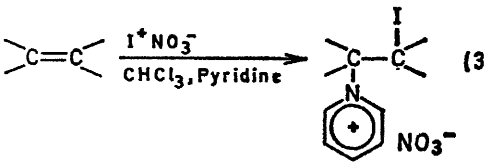
† The AgCl is collected and the alkene added at once to the filtrate. The reaction time for the additions is about 3 hr. at room temperature.

trans-addition[5] giving a *trans*-diequatorial conformation. The preferred conformation was completely insensitive to changes in solvent polarity ($CDCl_3$, CCl_4, C_6D_6, CD_3CN) as indicated by the n.m.r. spectrum.[6]

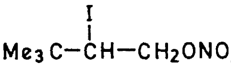
The adducts formed with 3,4-dimethylhex-1-ene and 3,3-dimethylbut-1-ene (entries 4 and 5) showed clearly the influence of steric hindrance *versus* substituent electronic effects. The products from 3,4-dimethylhex-1-ene was shown by n.m.r. spectroscopy to consist of a 40 : 60 isomeric mixture of 1-iodo-3,4-dimethylhexan-2-ol nitrate and 2-iodo-3,4-dimethylhexan-1-ol nitrate. Steric hindrance of the approach of the nitrate ion to the iodonium intermediate results in an attack at the ostensibly unfavourable primary position to the extent of 60%. Steric hindrance of the approach of the nitrate ion is the overriding factor in the case of the adduct of 3,3-dimethylbut-1-ene (entry 5) and the ester with the nitrate group of the primary position (VI) is the only product obtained as clearly demonstrated by the n.m.r. spectrum.

Addition of iodonium nitrate to the last four alkenes (entries 6—9) followed a different course in which iodo-pyridinium salts were formed‡ (equation 3). In all these examples the carbonium ion involved is either tertiary, benzylic, or α to an oxygen. Evidently in such cases the superior nucleophilicity of the pyridine[7] comes into play and it competes successfully with the nitrate ion for the iodonium ion. The reaction with 2,3-dihydro-4-pyran produced *trans*-diequatorial *N*-(3-iodotetrahydropyranosyl)-pyridinium nitrate (VII), the n.m.r. spectrum of which (anomeric proton) δ [Me_4Si, $(CD_3)_2SO$] 6·5 (d, 1H, $J_{1,2}$ 10 Hz), closely resembles that of similar substances reported by Lemieux and Morgan.[8] Similarly, ethyl vinyl ether afforded *N*-[1-(1-ethoxy-2-iodo)ethyl]pyridinium nitrate (VIII).



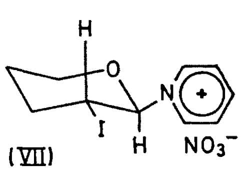
(3)

In contrast, styrene afforded *N*-[1-(1-phenylethenyl)]-pyridinium iodide (IX) as the major product (75—80%) together with a small amount of the iodo-nitrate ester (X) (20%). Treatment of (X) with an excess of pyridine at room temperature afforded (IX) in good yield, presumably by way of pyridine-catalysed elimination of HI from the intermediate (XI). This suggests but not proves that (VII), (VIII), (IX), and (XII) are formed by nucleophilic displacement of the nitrate ion by pyridine from the corresponding initially formed iodo-nitrate esters.

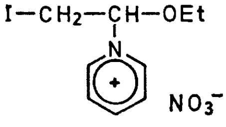


$Me_3C-\overset{I}{C}H-CH_2ONO_2$

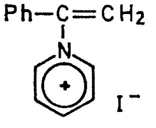
(VI)



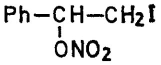
(VII)



(VIII)

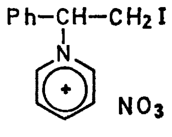


(IX)

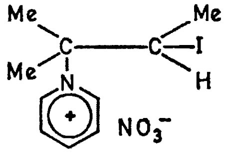


$Ph-\underset{ONO_2}{C}H-CH_2I$

(X)



(XI)



(XII)

In contrast to the previously described sensitivity of the attacking nitrate ion to steric hindrance effects, the formation of (VII), (VIII), and (IX) corresponds to the exclusive attack by the pyridine at the more hindered position corresponding to the more stable cation. The product of addition of iodonium nitrate to 2-methylbut-2-ene was assigned structure (XII) *N*-[2-(2-methyl-3-iodo)butyl]-pyridinium nitrate.

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‡ In these examples, after the addition is completed, the pyridinium salts are precipitated with ether, then recrystallised from $CHCl_3$–pyridine–ether. In the case of the reaction with styrene, the reaction mixture was poured into water and extracted with ether. The aqueous layer was evaporated, the residue taken up in ethyl acetate–ether–ethanol, the solid formed discarded, the solvents evaporated, the residue taken up in water and decolourized with charcoal, concentrated, and allowed to crystallize.

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[4] F. W. Fowler, A. Hassner, and L. A. Levy, *J. Amer. Chem. Soc.*, 1967, **89**, 2077.

[5] *trans*-Addition is a phenomenon encountered in closely related electrophilic additions to alkenes. See ref. 4 and R. G. Guy, R. Bonnett, and D. Lanigan, *Chem. and Ind.*, 1969, 1702.

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