Addition of Iodine Nitrate to Olefins

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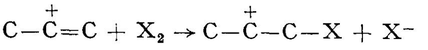
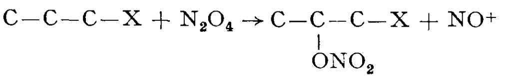
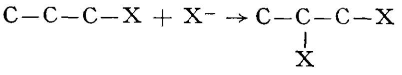
HALOGENOALKYL nitrates have been obtained by treating silver nitrate with iodine[2] or dinitrogen tetroxide with halogens[3,4] in the presence of olefins. Bachman and Logan[3] proposed the following mechanism for the latter reaction.



$$C{-}\overset{+}{C}{=}C + X_2 \rightarrow C{-}\overset{+}{C}{-}C{-}X + X^- \qquad (1)$$



$$C{-}C{-}C{-}X + N_2O_4 \rightarrow C{-}\underset{ONO_2}{\underset{|}{C}}{-}C{-}X + NO^+ \qquad (2)$$

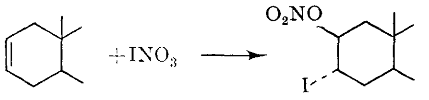


$$C{-}C{-}C{-}X + X^- \rightarrow C{-}\underset{X}{\underset{|}{C}}{-}C{-}X \qquad (3)$$

In looking for new ways to introduce nitrogen functions into organic molecules,[5] the stereochemistry of these additions was studied. The results obtained were inconsistent with this mechanism, and the reaction of olefins with I_2–N_2O_4 was shown to take two different pathways, one leading to nitro-compounds and one to nitrates, depending upon the conditions employed.

Silver nitrate reacted with iodine in the presence of cholest-2-ene, or with subsequent addition of cholest-2-ene, to give 3α-iodocholestan-2β-yl nitrate (I), m.p. 130—132° (79%). The n.m.r. spectrum of (I) shows half-width of 5 c./sec. for the C-2 and C-3 protons, implying *trans*-diaxial[6] addition consistent with the intermediacy

$$AgNO_3 + I_2 \quad AgI + INO_3 \qquad (4)$$

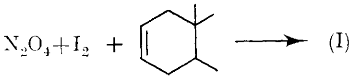


(I)

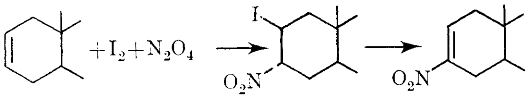
(5)

of a three-membered ring iodonium ion. This assignment is confirmed by the C-19 methyl signal at τ 9·10, which is shifted 0·19 p.p.m. relative to cholestane.†

When dinitrogen tetroxide was treated with iodine and cholest-2-ene was added, the same 3α-iodocholestan-2β-yl nitrate (I) was obtained (60%). However, if the order of addition is changed, and a solution of dinitrogen tetroxide is slowly added to a solution of iodine and cholest-2-ene, 2β-iodo-3α-nitrocholestane (III) [m.p. 141—143°, τ 8·99 (C-19 Me), 4·79 (C-3, $W_{1/2}$ 8), 5·16 (C-2, $W_{1/2}$ 8 c./sec.)] was obtained as the sole product (60%).‡ This product agrees with the mechanism which Stevens and Emmons[4] suggested for the trapping of the NO_2 radical addition product. As the dinitrogen tetroxide solution is added rapidly, a mixture of (II) and (III) results. Nitro-iodocholestane (III) was converted with silver oxide into 3-nitrocholest-2-ene (IV). The structure of (IV) was obvious from a zinc reduction to cholestan-3-one.



(6)



(III) (IV)

(7)

Since the mechanism[3] does not allow for the sole production of a nitro-iodide, the following reaction pathway is proposed. Dinitrogen tetroxide reacts with iodine to form iodine nitrate,

$$N_2O_4 + I_2 \longrightarrow INO_3 \qquad (8)$$

then addition to the double bond is observed as in reaction (5). The mixture of products observed upon rapid addition of the dinitrogen tetroxide solution can occur through localized formation of iodine nitrate and in competition with the formation of nitro-iodides.

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† If iodine was in the 2β-position, the C-19 methyl signal should have shifted[5] about 0·46 p.p.m. as seen for 2β-iodo-3α-nitrocholestane (III).

‡ For formation of nitro-compounds see A. Hassner in L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis", John Wiley, New York, 1967, p. 757; and W. A. Szarek, D. G. Lance, and R. L. Beach, *Chem. Comm.*, 1968, 356.

[1] For previous papers see A. Hassner, J. M. Larkin, and J. E. Dowd, *J. Org. Chem.*, 1968, **33**, 1733.
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[6] A. Hassner and C. H. Heathcock, *J. Org. Chem.*, 1965, **30**, 1748.