Nitratomercuriation of Alkenes

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Alkenes react rapidly and reversibly with mercury(II) nitrate to form β-nitratoalkylmercury(II) nitrates which undergo brominolysis to give β-bromoalkyl nitrates.

The recent report by Barluenga *et al.*[1] that β-halogenoalkyl nitrates may be prepared by treating alkenes with mercury(II) nitrate and halogen, prompts us to disclose our related findings in this area. We have shown that various simple alkenes undergo nitratomercuriation, *i.e.* they add mercury(II) nitrate to form β-nitratoalkylmercury(II) nitrates, and that these adducts react with bromine to give β-bromoalkyl nitrates.

Alkene (10 mmol or an excess where gaseous) was added to a well stirred suspension of $Hg(NO_3)_2 \cdot \frac{1}{2}H_2O$ (10 mmol; pre-dried by standing over P_2O_5) in dichloromethane (25 cm^3) at 0 °C. After 10—20 min, a clear solution was obtained which was decanted from a trace of oily residue. The solvent was then removed at water pump pressure to afford a near-quantitative yield of β-nitratoalkylmercury(II) nitrate (**1**) as a colourless oil.

$$R^1CH{=}CHR^2 + Hg(NO_3)_2 \rightleftarrows \underset{(\mathbf{1})}{R^1CH(ONO_2)CH(HgONO_2)R^2} \quad (1)$$

The oil was immediately dissolved in $CDCl_3$ and accumulation of the $\{^1H\}$-^{13}C n.m.r. spectrum commenced as quickly as possible. The spectral data so obtained for products from seven representative alkenes are shown in Table 1. Varying amounts of mercury(II) nitrate were precipitated during the spectrum accumulations which, typically, were over 40—50 min at 25 °C. All the spectra, except that of the product from norbornene, contained small peaks corresponding to the parent alkene, but showed no other absorptions. Similar attempts to characterise the adducts of ethylene, styrene, *Z*-but-2-ene, and cyclopentene were unsuccessful, apparently because dissociation occurred too readily.

^1H N.m.r. spectra were also consistent with the formation of adducts (**1**) [$\delta(CHONO_2)$ 4.9—5.6], and indicated that the stereochemistry of addition to cyclohexene is *trans* and to norbornene is *cis-exo*, as for other types of oxymercuriation.[2] Treatment of 2-nitratopropylmercury(II) nitrate (**1a**) with norbornene led to a quantitative displacement of propene and formation of the norbornene adduct (**1g**).

These results suggest that nitratomercuriation resembles trifluoroacetoxymercuriation,[3] where equilibria are established in which both addition and elimination reactions are fast. Although we have not yet measured equilibrium constants, the trends appear to parallel those for mercury(II) trifluoroacetate in that the adducts from styrene and cyclopentene are less stable that those from hex-1-ene and cyclohexene, and the norbornene adduct is much more stable than the others.

The one unusual feature of these oxymercuriations is that the adducts [(**1d**) and (**1e**)] from *E*-but-2-ene and *E*-hex-3-ene were obtained as mixtures of diastereoisomers, as revealed by the two sets of ^{13}C n.m.r. signals obtained for each (Table 1). For adduct (**1d**), a spectrum accumulated over 50 min, beginning 20 min after the product was isolated, indicated a ratio of isomers of 60:40, but this changed to 45:55 when a new spectrum was collected beginning 2 h later. This shows that isomerisation is occurring, and we believe that the initial addition is stereospecific since brominolysis (see below) of the freshly prepared adduct afforded only a single isomer of 2-bromo-3-nitratobutane. As yet, the mechanism of this intriguing isomerisation has not been established.

Treatment of a freshly prepared solution of nitratomercury(II) species (**1**) with bromine at 0 °C afforded β-bromoalkyl nitrates. Although the alk-1-ene adducts (**1a**—**c**) were single compounds, the derived β-bromoalkyl nitrates were mixtures of regioisomers (equation 2), which contained 20—25% of the 2-bromo-1-nitratoalkanes. *Z*-But-2-ene afforded a single diastereoisomer, which was different to that from *E*-but-2-ene.

$$\underset{(\mathbf{1a}\text{—}\mathbf{c})}{RCH(ONO_2)CH_2HgONO_2} \xrightarrow{Br_2} RCH(ONO_2)CH_2Br + RCH(Br)CH_2ONO_2 \quad (2)$$

Table 1. ^{13}C N.m.r. chemical shifts (δ) of adducts (**1**).

Alkene	C–ONO_2	C–Hg	R^1 and R^2
a Propene	80.6	29.2	22.1
b Hex-1-ene	83.8	36.2	28.1, 27.5, 22.4, 13.9
c Oct-1-ene	84.1	36.5	31.7, 29.1, 28.0, 25.4, 22.7, 14.1
d *E*-But-2-ene	84.3	46.3	20.1, 16.7
	85.1	46.7	
e *E*-Hex-3-ene	87.7	56.1	28.2, 24.2, 16.4, 9.7
	88.3	55.7	28.4, 25.8, 16.2, 14.1
f Cyclohexene	84.7	48.5	32.2, 30.6, 27.5, 22.7
g Norbornene	89.3	52.6	42.0, 40.3, 36.3, 29.7, 23.4

These results may be accommodated by the sequence of reactions shown in equations (3)—(5). Anion exchanges similar to that proposed in equation (3) have been observed before,[4] and the spontaneous stereospecific deoxymercuriation suggested in equation (4) is supported by the fact that treatment of the adducts (**1**) with aqueous KBr led to dissociation. Finally, it is known that bromine nitrate adds stereospecifically to *Z*- and *E*-but-2-enes and reacts with hex-1-ene to yield both 1-bromo-2-nitrato- and 2-bromo-1-nitratohexane.[5]

$$R^1CH(ONO)_2)CH(HgONO_2)R^2 + Br_2 \rightarrow R^1CH(ONO_2)CH(HgBr)R^2 + BrONO_2 \quad (3)$$

$$R^1CH(ONO_2)CH(HgBr)R^2 \rightarrow R^1CH{=}CHR^2 + O_2NOHgBr \quad (4)$$

$$R^1CH{=}CHR^2 + BrONO_2 \rightarrow R^1CH(ONO_2)CH(Br)R^2 + R^1CH(Br)CH(ONO_2)R^2 \quad (5)$$

Although our results for β-bromoalkyl nitrates agree with those obtained by Barluenga *et al.*,[1] it cannot be assumed that adducts (**1**) are necessarily intermediates in their reactions, since in their method the alkene is added last.

This work demonstrates that the hitherto unknown process of nitratomercuriation takes place readily under appropriate conditions. This may have important consequences for the future use of mercury(II) nitrate in synthesis, and renders more likely the validity of a recent postulate that nitratothalliation can occur.[6]

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References

1 J. Barluenga, J. M. Martinez-Gallo, C. Nájera, and M. Yus, *J. Chem. Soc., Chem. Commun.*, 1985, 1422.
2 A. J. Bloodworth and I. M. Griffin, *J. Chem. Soc., Perkin Trans. 2*, 1975, 531, and references therein.
3 H. C. Brown and M-H. Rei, *Chem. Commun.*, 1969, 1296.
4 A. J. Bloodworth and I. M. Griffin, *J. Chem. Soc., Perkin Trans. 2*, 1974, 688, and references therein.
5 J. L. Lown and A. V. Joshua, *Can. J. Chem.*, 1977, **55**, 508.
6 W. J. Layton, C. P. Brock, P. A. Crooks, S. L. Smith, and P. Burn, *J. Org. Chem.*, 1985, **50**, 5372.