Novel Synthesis of γ-Hydroxy-α-nitro-olefins

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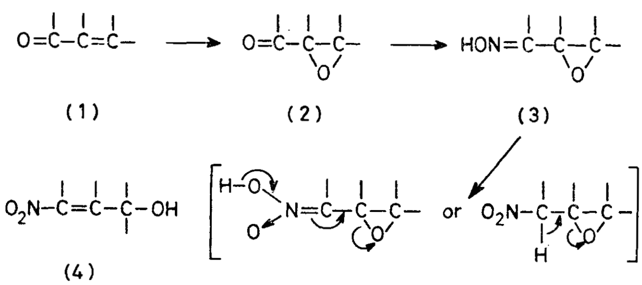
Summary Treatment of α-unsubstituted αβ-epoxyketoximes with trifluoroperoxyacetic acid affords the corresponding γ-hydroxy-α-nitro-olefins in high yields.

The nitro group is important in organic synthesis since it activates a neighbouring C–H bond for aldol or Michael reactions and can also be converted into useful functions such as NH_2 or C:O.[1] In addition, the nucleophilic α-carbon atom of nitroalkanes is essentially equivalent to an electrophilic carbonyl carbon atom when the conversion *C*-nitro → carbonyl under mild conditions is available.[2] It is thus important to develop procedures for the ready interconversion of nitro and carbonyl functions.

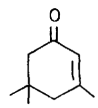
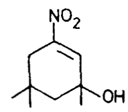
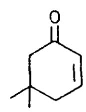
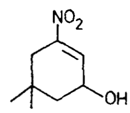
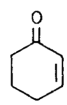
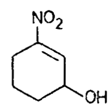
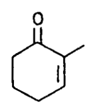
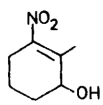
Emmons *et al.* have reported[3] the oxidative conversion of isolated carbonyl groups into nitro functions *via* oximes using trifluoroperoxyacetic acid, and we have applied this method successfully to carbohydrates.[4] We now report a novel method for the transformation of αβ-unsaturated carbonyl compounds to γ-hydroxy-α-nitro-olefins using this oxidation procedure at the final step of the sequence in the Scheme.



Scheme

The chromatographically and spectroscopically homogeneous oximes (**3**) obtained from the αβ-epoxyketones† (**2**) in 90—95% yields by Corey's procedure[5] were treated with trifluoroperoxyacetic acid[3] (1·5—3 equiv.) in acetonitrile in the presence of $NaHCO_3$ (6 equiv.) and urea (0·3 equiv.) at 0 °C for 30 min to give the γ-hydroxy-α-nitro-olefins (**4**) in high yields (Table). The products (**4a**—**f**) gave satisfactory microanalytical data, i.r. absorption bands at

Table

	Enone (1)	Product (4)	% Yield[a]	M.p. or b.p./°C
a			86	99–99·5
b			77	94–96 at 0·1 mmHg
c			75	b
d	MeC(O)CH=CMe_2	O_2NCMe=$CHCMe_2OH$	84	115 at 21 mmHg
e	MeC(O)CH=CHPh	O_2NCMe=CHCHPhOH	88	b
f			*ca.* 5[c]	b

[a] Isolated yields from the oximes (**3**). [b] Liquid; purified by silica gel column chromatography. [c] Minor product; see text.

† Epoxidation of the αβ-unsaturated ketones (**1**) was carried out by reaction with alkaline hydrogen peroxide according to the reported procedure: *Org. Synth.*, 1963, Coll. Vol. 4, 552.

3300 (OH) and 1520 cm^{-1} (NO_2) and a characteristic ^1H n.m.r. signal in the conjugated olefinic region with small long-range coupling constants and an alcoholic proton (disappeared on addition of D_2O). The possible nitro-epoxide or nitronic acid intermediates shown in the Scheme could not be detected spectroscopically or chromatographically.

Oxidation of the α-substituted oxime (**3f**) was complicated, however, and the main product, which has not yet been purified, showed NO_2 and CF_3CO i.r. absorptions (1550 and 1780 cm^{-1}, respectively).

Further examination of α-substituted derivatives is thus necessary, but, apart from such compounds, the method appears to be generally applicable to αβ-unsaturated carbonyl compounds.

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[1] For a review of the chemistry of nitro groups, see 'The Chemistry of Nitro and Nitroso Groups,' ed. H. Feuer, Interscience, New York, Part 1, 1969, Part 2, 1970.
[2] J. E. McMurry and J. Melton, *J. Org. Chem.*, 1973, **38**, 4367; T.-L. Ho and C. M. Wong, *Synthesis*, 1974, 196; A. McKillop and R. J. Kobylecki, *Tetrahedron*, 1974, **30**, 1365; R. Kirchhoff, *Tetrahedron Letters*, 1976, 2533, and references cited therein.
[3] W. D. Emmons and A. S. Pagano, *J. Amer. Chem. Soc.*, 1955, **77**, 4557.
[4] T. Takamoto and R. Sudoh, *Bull. Chem. Soc. Japan*, 1975, **48**, 3413, and other papers in this series.
[5] E. J. Corey, L. S. Melvin, Jr., and M. F. Haslanger, *Tetrahedron Letters*, 1975, 3117.