

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

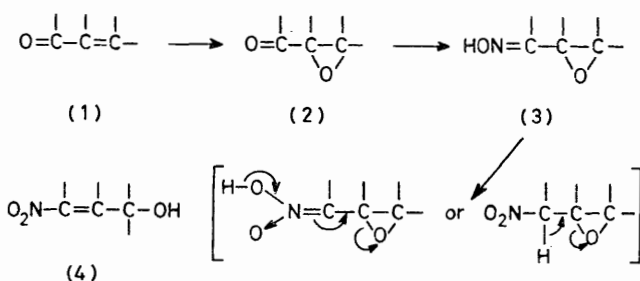
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Summary Treatment of α -unsubstituted $\alpha\beta$ -epoxyketoximes with trifluoroperoxyacetic acid affords the corresponding γ -hydroxy- α -nitro-olefins in high yields.

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 $\text{C}=\text{O}$.¹ In addition, the nucleophilic α -carbon atom of nitroalkanes is essentially equivalent to an electrophilic carbonyl carbon atom when the conversion $\text{C-nitro} \rightarrow \text{carbonyl}$ 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 reported³ 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 $\alpha\beta$ -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 $\alpha\beta$ -epoxyketones† (2) in 90–95% yields by Corey's procedure⁵ were treated with

trifluoroperoxyacetic acid³ (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	$\text{O}_2\text{NCMe=CHCMe}_2\text{OH}$	84	115 at 21 mmHg
e	MeC(=O)CH=CHPh	$\text{O}_2\text{NCMe=CHCHPhOH}$	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 $\alpha\beta$ -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 $\alpha\beta$ -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.