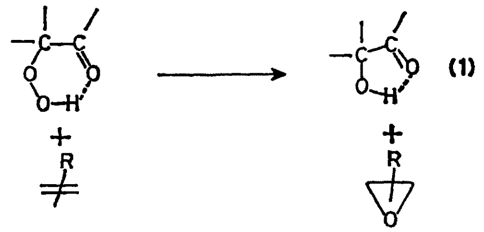
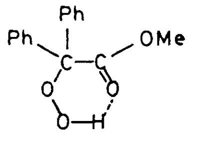
Olefin Epoxidation with α-Hydroperoxides of Esters, Amides, Ketones, and Nitriles

By Julius Rebek, Jr.,* Russell McCready, and Raymond Wolak
(*Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania* 15260)

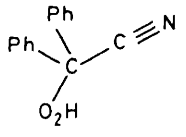
Summary A number of α-substituted hydroperoxides are capable of olefin epoxidation; unusual *cis–trans* selectivities are observed in reactions with olefins substituted with phenyl-groups.

Mild oxygenations of enolizable carbonyl-compounds have made accessible α-hydroperoxy-acids,[1] esters,[2] ketones,[3] amides,[4] and nitriles.[5] While a number of studies have discussed the decomposition of these substances under acidic, basic, and pyrolytic conditions[6] none has dwelt on their reaction with olefins. However, the curious instability of α-hydroperoxides of *olefinic* acids (compared with their saturated counterparts) has been noted.[1] This instability can now be explained; we find that α-hydroperoxycarbonyl-compounds are effective reagents for olefin epoxidation, equation (1). Specifically, the hydroperoxides (**1**)—(**4**) were tested for their ability to epoxidize

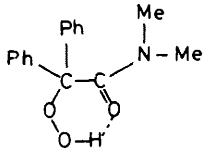




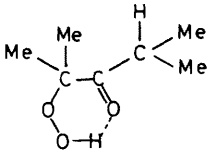
(1)



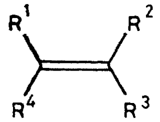
(2)

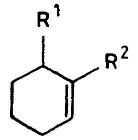


(3)



(4)





(5) $R^1=R^2=R^3=R^4=Me$
(6) $R^1=R^3=H$, $R^2=Me$, $R^4=Ph$
(7) $R^1=R^2=R^3=H$, $R^4=n\text{-}C_6H_{13}$

(8) $R^1=H$, $R^2=Me$
(9) $R^1=R^2=H$
(10) $R^1=OH$, $R^2=H$

olefins. All proved active, but the highest yields were obtained with (**1**) and (**2**), (Table 1), on warming (60 °C) a 0·3 M solution of (**1**) or (**2**) with the olefin for 24 h followed by g.l.c. analysis.

Kinetic studies established that the reaction is first order with respect to the olefin and hydroperoxide and that the epoxidation is cleanly stereospecific. As for peroxy-acids [of which (**1**) may be considered a homologue] an intramolecular hydrogen-bonding is observed and epoxidation rates are slower in Et_2O than in CH_2Cl_2. Moreover, a preference for *syn*-epoxidation of cyclohexenol is found and the Baeyer–Villiger reaction of cyclopentanone with (**1**) occurs. However, unlike with peroxy-acids, an unusual selectivity between *cis*- and *trans*-stilbenes (**14**) was detected (Table 2). Typically peroxy-acids show a marginal preference for the *cis*-isomer,[7] but (**1**) [and, to a lesser extent, (**2**)] react more rapidly with *trans*-stilbene.

TABLE 1. % Yields of epoxides obtained in the reaction of (**1**) or (**2**) with the olefins (**5**)—(**10**) ($CHCl_3$, 60 °C, 24 h)

	(5)	(6)	(7)	(8)	(9)	(10)
(1)	99	85	3	84	63	30[a]
(2)	99	86	12	97	87	39[b]

[a] *syn* : *anti* = 7 : 3 [b] *syn* : *anti* = 6 : 4

$R^1CH{=}CHR^2$
(**11**) *cis* or *trans*, $R^1=Me$, $R^2=n\text{-}C_6H_{13}$
(**12**) *cis* or *trans*, $R^1=Et$, $R^2=Bu^t$
(**13**) *cis* or *trans*, $R^1=Me$, $R^2=Pr^i$
(**14**) *cis* or *trans*, $R^1=R^2=Ph$

TABLE 2. Selectivity (k_{cis}/k_{trans}) in epoxidations of *cis*- and *trans*-olefins (**11**)—(**14**)

	k_{cis}/k_{trans}				
Reagent	(11)	(12)	(13)	(14)	$k(9)/k(6)$
McPBA[a]	1·6	1·1	1·4	1·5	2·8
(1)	0·92	1·0	0·58[b]	<0·05	<0·05
				0·54[c,d]	0·26[c]
(2)	1·2	1·6	1·2	0·46	0·75
				0·55[c]	0·95[c]

[a] *m*-Chloroperoxybenzoic acid. [b] 25 °C, CH_2Cl_2. [c] 60 °C, C_6H_6. [d] Some epoxide is converted into benzaldehyde.

Competition studies with aliphatic olefin pairs showed little such general selectivity, but *trans*-β-methylstyrene (**6**) was epoxidized much faster than cyclohexene (**9**). The selectivity is much diminished when benzene is used as a solvent, which implies that the unusual selectivity in $CHCl_3$ is due to attractive forces between the aromatic rings of the reagent and substrate.

We are grateful to the National Institutes of Health for financial support of this work.

(*Received, 26th March* 1980; *Com.* 325.)

---

[1] D. A. Konen, L. S. Silbert, and P. E. Pfeffer, *J. Org. Chem.*, 1975, **70**, 3253.
[2] M. Avramoff and Y. Sprinzak, *J. Am. Chem. Soc.*, 1963, **85**, 1655.
[3] H. R. Gersmann, H. J. W. Niewenhuis, and A. F. Bickel, *Proc. Chem. Soc. London*, 1962, 279.
[4] H. Wasserman and B. Lipshutz, *Tetrahedron Lett.*, 1975, 1731, 4611.
[5] S. J. Selikson and D. S. Watt, *J. Org. Chem.*, 1975, **40**, 267.
[6] For example, see Y. Sawaki and Y. Ogata, *J. Am. Chem. Soc.*, 1975, 6983.
[7] D. Swern, *J. Am. Chem. Soc.*, 1947, **69**, 1692; W. Stumpf and K. Rombusch, *Justus Liebigs' Ann. Chem.*, 1965, **687**, 136; D. Swern, 'Organic Peroxides,' Wiley Interscience, New York, 1971, Vol. II, p. 355.