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# REACTION OF EPOXIDES WITH MERCAPTANS

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Epoxides react with a variety of anions such as mercaptide, alkoxide, and phenoxide, and with a number of molecular species possessing unshared electron pairs such as mercaptans, alcohols, phenols, ammonia, and amines. In general, two modes of addition are possible in the reaction of an unsymmetrical epoxide with any of these reactants, the reaction of epichlorohydrin, 1-chloro-2, 3-epoxypropane, with a mercaptan, for example, conceivably yielding either a 1-alkylthio-3-chloro-2-propanol or a 2-alkylthio-3-chloro-1-propanol:

$$RSH + ClCH_2\text{-}CH\text{-}CH_2 \rightarrow ClCH_2\text{-}CHOH\text{-}CH_2\text{-}SR \textit{ or}$$
$$\qquad\qquad\quad O$$
$$ClCH_2\text{-}CH(SR)\text{-}CH_2OH$$

This reaction was first investigated by Nenitzescu and Scarlatescu (1), who concluded that the secondary alcohol is formed. Their conclusion was based upon the observation that dehydrohalogenation of the addition product yields the same product obtained directly from epichlorohydrin and a mercaptide, i.e.,

$$RSH + ClCH_2\text{-}CH\text{-}CH_2 \rightarrow RS\text{-}CH_2\text{-}CHOH\text{-}CH_2Cl \xrightarrow{KOH}$$
$$\qquad\qquad\quad O \qquad\qquad\qquad\qquad\qquad\qquad (I)$$
$$RSK + ClCH_2\text{-}CH\text{-}CH_2 \rightarrow RS\text{-}CH_2\text{-}CH\text{-}CH_2 \leftarrow$$
$$\qquad\qquad\quad O \qquad\qquad\qquad\quad O$$
$$(II)$$

Gilman and Fullhart (2) observed that the above sequence does not necessarily preclude the primary alcohol structure. They then demonstrated conclusively that addition of a mercaptan to styrene oxide yields a secondary alcohol structure. However, the proof of addition to styrene oxide is not necessarily valid when applied to epichlorohydrin. The secondary alcohol structure postulated by Nenitzescu and Scarlatescu was verified, however, by hydrolysis of the addition product and subsequent periodic acid oxidation of the resulting glycol (3).

$$RS\text{-}CH_2\text{-}CHOH\text{-}CH_2Cl + H_2O \rightarrow RS\text{-}CH_2\text{-}CHOH\text{-}CH_2OH + HCl$$

Periodic acid is a specific reagent for the cleavage of vicinal dihydroxy compounds and this reagent reacted smoothly with the glycol to yield formaldehyde by fission. Had the addition product been of the primary alcohol structure, hydrolysis would have yielded a 2-alkylthio-1,3-propanediol and periodic acid oxidation would not have occurred.

The 1-alkylthio-2, 3-epoxypropane (II) obtained by dehydrolhalogenation of (I) provided additional opportunity for study of addition at an epoxide bond. Reaction of (II) with a mercaptan again yielded a secondary alcohol, a 1,3-bis(alkylthio)-2-propanol (III) as shown by the behavior of the oxidation product of (III), a 1,3-bis(alkylsulfonyl)-2-propanol (IV), on hydrolysis.

$$RSH + RS\text{-}CH_2\text{-}CH\text{-}CH_2 \rightarrow RS\text{-}CH_2\text{-}CHOH\text{-}CH_2\text{-}SR \xrightarrow{H_2O_2} RSO_2\text{-}CH_2\text{-}CHOH\text{-}CH_2\text{-}SO_2R$$

(II) (III) (IV)

A disulfone of the type illustrated by (IV) would be expected to undergo virtually no hydrolysis according to Stuffer's rule (4) and relatively little hydrolysis was observed experimentally. The alternative structure, 2,3-bis(alkylthio)-1-propanol on oxidation would yield a so-called gamma disulfone which would characteristically undergo hydrolysis according to the above rule.

Addition of an alcohol to (II) paralleled the addition of a mercaptan and a secondary alcohol is formed.

$$ROH + RS\text{-}CH_2\text{-}CH\text{-}CH_2 \rightarrow RS\text{-}CH_2\text{-}CHOH\text{-}CH_2\text{-}OR$$

(V)

The structure of (V) was proved by demonstrating its identity with the substance obtained by reaction of a potassium mercaptide with a 1-alkoxy-3-chloro-2-propanol of established structure (5).

Since both alkylthio and alkoxy groups are necessarily situated on primary carbon atoms, the hydroxy group is present on a secondary carbon atom.

$$RO\text{-}CH_2\text{-}CHOH\text{-}CH_2Cl + KSR \rightarrow RO\text{-}CH_2\text{-}CHOH\text{-}CH_2\text{-}SR$$

(V)

## REFERENCES CITED

(1) Nenitzescu and Scarlatescu: Ber., *68*, 589 (1936).
(2) Gilman and Fullhart: J. Am. Chem. Soc., *71*, 1478 (1949).
(3) Todsen, Pollard, and Rietz: J. Am. Chem. Soc., *72*, 4000 (1950).
(4) Stuffer: Ber., *23*, 3232 (1890).
(5) Rietz, Todsen, Leon, and Pollard: J. Am. Chem. Soc., *74*, 1358 (1952).