A BASE-CATALYZED STEREOSPECIFIC EPOXIDATION WITH α-AZOHYDROPEROXIDES

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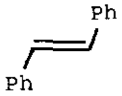
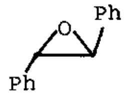
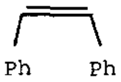
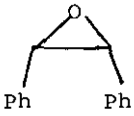
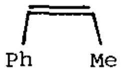
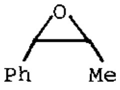
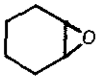
Abstract —— A new stereospecific epoxidation with the α-azohydroperoxide (1) is reported. α-Azohydroperoxides (1a - 1d) epoxidized cis- and trans-stilbenes stereospecifically in the reaction catalyzed by pyridine or sodium hydroxide. Similarly, cyclohexene, norbornylene, and cis-β-methylstyrene all were epoxidized by 1a - 1d in good to high yields in basic media. Reactive species of the epoxidation are discussed.

The base-catalyzed epoxidation by hydroperoxides or peracids is of interest from mechanistic and synthetic points of view.[1-3] Recently, we have reported that in the reaction catalyzed by pyridine, the α-azohydroperoxide (1a) generates dioxirane[4,5] or carbonyl oxide[6,7] (2a or 3a)[8] which epoxidizes cyclohexene and tetramethylethylene. However, the yield of epoxide is low. Being interested in the base-catalyzed epoxidation with hydroperoxides, we looked for the possibility of the α-azohydroperoxides (1) as an epoxidation reagent. We found that 1 epoxidizes olefin stereospecifically in basic media, and a high yield of epoxide is obtained under a highly-diluted condition.

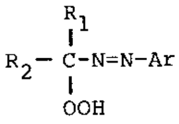
When a benzene or dioxane solution of 1 (10^{-2} - 10^{-4} M) and olefin (ca. 10 times) was stirred at room temperature or heated under reflux in the presence of pyridine or sodium hydroxide (ca. 5 times of 1), epoxide was formed in good to high yields (see Table 1).

The table indicates that the yield of epoxide depends on the concentration of 1 in the reactant. The best yield of epoxide was obtained when the reaction was carried out in a 10^{-4} M solution of 1. In general, the lower the concentration of the azohydroperoxide (1), the higher the yield of epoxide. An example

Table 1. Yield of epoxide

Olefin	Azohydroper-oxide 1 (M)	Base	Yield (%)[a]	Epoxide
	1a (10^{-4})	pyridine[b]	48	
	1b (10^{-4})	NaOH[b]	73	
	1c (10^{-4})	NaOH[b]	76	
	1d (10^{-4})	NaOH[b]	84	
	1b (10^{-4})	NaOH[b]	55	
	1b (10^{-3})	NaOH[b]	25	
	1b (10^{-2})	NaOH[b]	8	
	1c (10^{-4})	NaOH[b]	51	
	1d (10^{-4})	NaOH[b]	58	
	1a (10^{-4})	pyridine[b]	59	
	1b (10^{-4})	pyridine[c]	79	
	1b (10^{-4})	NaOH[b]	71	
	1a (10^{-3})	pyridine[b]	35	
	1b (10^{-4})	NaOH[b]	77	
	1a (10^{-3})	pyridine[b]	23	
	1b (10^{-4})	NaOH[b]	62	

a: yield based on 1 and determined by GLC; b: stirred at room temperature; c: heated under reflux



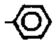
$$R_2-\overset{\displaystyle R_1}{\underset{\displaystyle OOH}{C}}-N=N-Ar$$

1

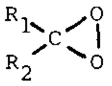
a: R_1= Ph; R_2= H; Ar= 

b: R_1= Ph; R_2= Me; Ar= 

c: R_1= R_2= Me; Ar= 

d: R_1= R_2= $-(CH_2)_5-$; Ar= 

is shown by the reaction of cis-stilbene with 1b in Table 1. The epoxidation is highly stereospecific. Both cis-stilbene and cis-β-methylstyrene gave the corresponding cis-epoxides stereospecifically. Phenyl and alkyl substituted olefins gave epoxides (Table 1). On the other hand, electron-deficient olefins such as mesityl oxide and cinnamic acid did not give epoxides. It is to be noted that sodium hydroxide is effective in the epoxidation with 1b - 1d, while



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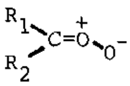

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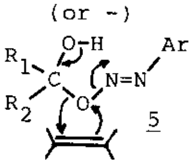

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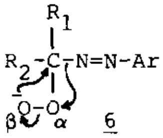

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it is not a good catalyst for 1a. This is probably due to the fact that the base-catalyzed dehydration of 1a, which gives rise to N-(4-bromophenyl)-N'-benzoyldiazene, occurs in competition with the epoxidation.[8]

Nevertheless, the azohydroperoxide (1) can be used as an epoxidizing reagent in anhydrous organic media with pyridine as a base. This has some advantage when compared with the base-catalyzed epoxidation of acid-sensitive compounds by hydroperoxides or peracids in aqueous solution.[1-3] The applicability of this reaction is under investigation.

The mechanism of this novel stereospecific epoxidation is of interest. The epoxidation by 1 occurred only in basic solution, and does not proceed through the direct oxygen transfer[9-11] from the hydroperoxides to olefin as reported previously.[8] The stereospecificity of the reaction rules out the stepwise mechanism intervening a carbanion of the type shown by 4.[1,2]

On the other hand, the mechanism involving dioxirane (2) as a reactive intermediate as proposed previously,[8] well accounts for the stereospecific epoxidation with 1 in basic media. However, it is worth noting that an oxenoid such as 5 also accounts for the epoxidation. 5 is derived from the peroxy anion of 1 by the Criegee-type rearrangement[12,13] of the azo group to the α-oxygen and the simultaneous attack of the β-oxygen at the aliphatic carbon (see 6).[14] Alternatively, the elimination of the azo group in 5 (or its anion) gives dioxirane (2) which epoxidizes olefin. We are investigating further the mechanism of this epoxidation in comparison with that of the caroate-acetone system in which dioxirane is proposed as a reactive oxenoid.[5] Details of our works will appear elsewhere.

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