JOURNAL OF CATALYSIS 31, 438-443 (1973)

Metal-Catalyzed Epoxidation of Olefins with Organic Hydroperoxides

II. The Effect of Solvent and Hydroperoxide Structure

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Received March 13, 1973

The relatively unreactive olefins 1-octene and allyl chloride have been epoxidized with *tert*-butyl hydroperoxide in the presence of $Mo(CO)_6$ or TiO_2-on-SiO_2, in a variety of solvents. The rates and selectivities are highest in polychlorinated hydrocarbons, slightly lower in hydrocarbon solvents, and very poor in coordinating solvents such as alcohols, ethers, etc.

In addition, the selectivities to epichlorohydrin obtained in the epoxidation of allyl chloride with several organic hydroperoxides have been compared. The low selectivities observed with alkylaromatic hydroperoxides are due to their facile heterolytic decomposition under the reaction conditions. Competition from this reaction is diminished when the hydroperoxide contains electron-attracting groups. A further complication in the epoxidation with alkylaromatic hydroperoxides is the metal-catalyzed dehydration of the co-product alcohol.

I. INTRODUCTION

A wide variety of solvents has been claimed (*1*) to be suitable for metal-catalyzed epoxidations of olefins with organic hydroperoxides. Of these, hydrocarbons such as benzene, toluene or cyclohexane have generally been the solvent of choice for these reactions (*2*).

Similarly, a wide variety of organic hydroperoxides has been claimed (*1*) to be effective in metal-catalyzed epoxidations. The relevant literature (*3*) suggests that the choice of hydroperoxide is the least critical factor in these reactions. *tert*-Butyl hydroperoxide has been widely used in mechanistic studies (*2*). Comparative studies with various hydroperoxides have previously been carried out (*3*) with relatively reactive olefins, such as 2-octene or cyclohexene, which may have masked the differences between the hydroperoxides. It was of interest, therefore, to compare hydroperoxides in the epoxidation of the unreactive olefin allyl chloride where differences are expected to be more pronounced.

II. EXPERIMENTAL METHODS

Materials

Allyl chloride and 1-octene were distilled and passed through a column of basic alumina prior to use.

Cumene, ethylbenzene and tetralin hydroperoxides were prepared from the corresponding hydrocarbons by autoxidation according to standard procedures (*4*). The products were purified by vacuum distillation or via their sodium salts. *o*-Chlorocumene hydroperoxide was synthesized by reaction of the corresponding alcohol with hydrogen peroxide (*5*). All of these hydroperoxides were at least 99% pure by iodometric titration. A solution (12.8 %w) of dichlorocumene hydroperoxide in dichlorocumene was prepared by autoxidation of

TABLE 1

$Mo(CO)_6$-CATALYZED EPOXIDATION OF 1-OCTENE WITH *tert*-BUTYL HYDROPEROXIDE IN VARIOUS SOLVENTS AT 90°C[a]

Solvent	Reaction time (min)	*tert*-BuO_2H conversion (%)	Epoxide selectivity[b] (%)
Tetrachloroethene	120	97	76
1,1,2,2-Tetrachloroethane	180	91	76
Chlorobenzene	180	90	65
Benzene	180	88	64
Carbon tetrachloride	180	83	68
Methylcyclohexane	240	89	63
tert-Butanol	240	10	50
Cyclohexanone	100	>97	<10
Dimethylformamide	240	<10	nd
Tetrahydrofuran	240	<10	nd
Dioxane	240	<10	nd
Diisopropyl ether	240	<10	nd

[a] 5 mmol 1-octene + 5 mmol *tert*-BuO_2H + 0.05 mmol $Mo(CO)_6$ in 25 ml of solution.

[b] Based on *tert*-BuO_2H consumed.

the latter (a mixture of 2,4- and 3,5-dichlorocumenes) and used as such.

Procedure for Allyl Chloride

A quantity of 25 ml of a solution containing the hydroperoxide (0.01 mol), allyl chloride (0.1 mol), an internal standard (chlorobenzene) and the catalyst (13.2 mg $Mo(CO)_6$ or 1.0 g 2% TiO_2-on-SiO_2) was allowed to react at 80°C (bath temperature). The formation of epichlorohydrin was followed by glc analysis (2 m Carbowax 20M column) and the disappearance of hydroperoxide by iodometric titration of reaction aliquots. All other products were determined by glc analysis (Carbowax 20M) at the end of the reaction.

Procedure for 1-Octene

The procedure for 1-octene has been described previously (*2*).

III. RESULTS

The results of the epoxidation of 1-octene with *tert*-butyl hydroperoxide, in the presence of $Mo(CO)_6$ at 90°C, in various solvents are shown in Table 1. The reactions were carried out at a low olefin/hydroperoxide molar ratio (1:1) in order to accentuate the differences among the various solvents. At higher olefin/hydroperoxide ratios (10:1) the selectivities to epoxide based on hydroperoxide converted, were nearly quantitative, for example, in benzene as the solvent.

The epoxidation of allyl chloride with *tert*-butyl hydroperoxide, in the presence of $Mo(CO)_6$ and TiO_2-on-SiO_2, was studied only in hydrocarbon and chlorinated hydrocarbon solvents at 80°C (Table 2). In

TABLE 2

EPOXIDATION OF ALLYL CHLORIDE WITH *tert*-BUTYL HYDROPEROXIDE IN VARIOUS SOLVENTS AT 80°C[a]

	$Mo(CO)_6$		TiO_2-on-SiO_2	
Solvent	$t_{1/2}$ (hr)[b]	Selectivity (%)[c,d]	$t_{1/2}$ (hr)[b]	Selectivity (%)[e,d]
1,1,2,2-Tetrachloroethane	1	78 (40)	3	76 (71)
Tetrachloroethene[f]	1	75 (73)	3	74 (67)
o-Dichlorobenzene	1	73 (42)	3.5	70 (65)
Ethylbenzene	1.5	62 (53)	4	68 (67)
sec-Butylbenzene	1.5	66 (54)	4	66 (68)
Benzene	2.5	59 (37)	6	67 (65)
Methylcyclohexane	2.5	64 (30)	5	66 (68)

[a] See text for conditions.

[b] Approx time for 50% *tert*-BuO_2H conversion.

[c] For 100% *tert*-BuO_2H conversion.

[d] Figures in parentheses are selectivities for reactions in the absence of Ionol.

[e] For 80–95% *tert*-BuO_2H conversion.

[f] Containing *N*-methylpyrrole, morpholine and phenol as stabilizers.

order to obtain reasonably high selectivities to epichlorohydrin it was necessary to employ an olefin/hydroperoxide ratio of 10:1 (4 and 0.4 *M*, respectively).

The reactions with allyl chloride were carried out both in the presence and in the absence of the radical inhibitor 2,6-di-*tert*-butyl-4-methylphenol (Ionol). Ionol, by scavenging *tert*-butoxy and *tert*-butylperoxy radicals, suppresses the radical chain decomposition of the hydroperoxide via reactions (*1*) and (*2*).*

The presence of Ionol had a far greater effect on epichlorohydrin selectivities when $Mo(CO)_6$ was the catalyst than when TiO_2-on-SiO_2 was used (Table 2). This is consistent with the much lower rate of homolytic decomposition of *tert*-butyl hydroperoxide observed (*2*) in the presence of the latter catalyst.

In the presence of Ionol the two catalysts afforded roughly the same selectivity (based on hydroperoxide) to epichlorohydrin. The highest selectivities (ca. 75%) were obtained in the polychlorinated hydrocarbons 1,1,2,2,-tetrachloroethane and tetrachloroethene. Slightly lower selectivities (ca. 65%) were observed in hydrocarbon solvents (benzene, alkylbenzenes and methylcyclohexane). It should be noted that no attempt was made to optimize selectivities with respect to other reaction parameters such as temperature, and concentrations of catalyst and reactants.

The selectivities to epichlorohydrin found in the $Mo(CO)_6$- and TiO_2-on-SiO_2 catalyzed epoxidations of allyl chloride with various hydroperoxides, at 80°C in *o*-dichlorobenzene, are compared in Table 3. Cumene and tetralin hydroperoxides gave very low selectivities (<10%) with both catalysts. Ethylbenzene hydroperoxide gave moderate (40%) whereas *o*-chlorocumene hydroperoxide afforded a low value (22%) with $Mo(CO)_6$ and a high value (79%) with TiO_2-on-SiO_2. With dichlorocumene hydroperoxide an even higher selectivity was attained (92% at 90% hydroperoxide conversion; TiO_2-on-SiO_2 as the catalyst). That the low selectivities were not a consequence of an increased rate of homolytic decomposition of the hydroperoxide was demonstrated by the observation that Ionol had little effect on the selectivities (Table 3). It was evident from the nature of the products (Table 4) derived from the hydroperoxide that the low selectivities were due to competing heterolytic decomposition of the hydroperoxide. Thus, in the reactions with cumene hydroperoxide high yields of phenol obtained and little α-cumyl alcohol was found. Similarly, in the reaction with *o*-chorocumene hydroperoxide in the presence of $Mo(CO)_6$ (marked by a low selectivity to epichlorohydrin), *o*-chlorophenol was formed in high yield.

Another side reaction in the epoxidations with alkylaromatic hydroperoxides was

$$tert\text{-BuO}\cdot + tert\text{-BuO}_2\text{H} \rightarrow tert\text{-BuO}_2\cdot + tert\text{-BuOH}, \quad (1)$$

$$2\ tert\text{-BuO}_2\cdot \rightarrow 2\ tert\text{-BuO}\cdot + O_2. \quad (2)$$

TABLE 3

EPOXIDATION OF ALLYL CHLORIDE WITH VARIOUS HYDROPEROXIDES IN *o*-DICHLOROBENZENE AT 80°C[a]

Hydroperoxide	Catalyst	Epichlorohydrin selectivity (%)[b] No Ionol	Ionol added[c]
tert-Butyl	$Mo(CO)_6$	42	73
	TiO_2-on-SiO_2	65	71
Dichlorocumene[d]	TiO_2-on-SiO_2	92	nd
o-Chlorocumene	$Mo(CO)_6$	15	22
	TiO_2-on-SiO_2	69	79
Cumene	$Mo(CO)_6$	1	2
	TiO_2-on-SiO_2	6	8
Ethylbenzene	$Mo(CO)_6$	38	40
	TiO_2-on-SiO_2	46	55
Tetralin	$Mo(CO)_6$	5	7
	TiO_2-on-SiO_2	4	7

[a] See text for conditions.

[b] Based on Ro_2H reacted (85–100%).

[c] 100 mg Ionol added.

[d] Dichlorocumene used as the solvent.

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* In the reactions with 1-octene the olefin itself is a reasonably good radical scavenger for the *tert*-butoxy radicals.

TABLE 4
PRODUCTS DERIVED FROM THE HYDROPEROXIDE IN THE EPOXIDATION OF ALLYL CHLORIDE WITH ALKYLAROMATIC HYDROPEROXIDES

Hydroperoxide	Catalyst	Products (%)		
		Phenol	Alcohol	Olefin
Cumene	$Mo(CO)_6$	70	0.5[a]	8[b]
	TiO_2-on-SiO_2	67	4[a]	3[b]
Ethylbenzene	$Mo(CO)_6$	5	56[c,d]	nd
	TiO_2-on-SiO_2	8	55[c,d]	nd
o-Chlorocumene	$Mo(CO)_6$	70[e]	29[f]	<1[g]
	TiO_2-on-SiO_2	4[e]	90[f]	<1[g]
Dichlorocumene	TiO_2-on-SiO_2	0	>95	0

[a] Cumyl alcohol.
[b] α-Methylstyrene.
[c] 1-Phenylethanol.
[d] Acetophenone (ca. 20%) also found.
[e] o-Chlorophenol.
[f] o-Chloro-α-cumyl alcohol.
[g] o-Chloro-α-methylstyrene.

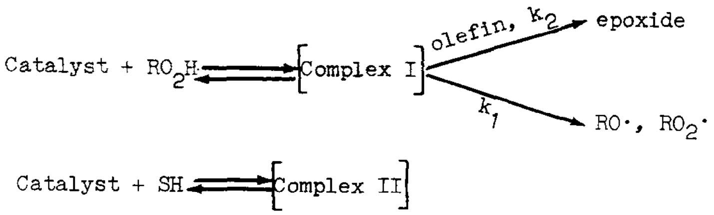
the catalytic dehydration of the co-product alcohol. Thus α-methylstyrene was present among the products of the reaction of cumene hydroperoxide with allyl chloride (Table 4). Similarly, in epoxidations with tetralin hydroperoxide only trace amounts of α-tetralol were found together with considerable quantities (15–30%) of 1,2-dihydronaphthalene. The corresponding epoxides (α-methylstyrene and 1,2-dihydronaphthalene epoxides) may also have been formed in these reactions (mixtures were not analyzed for these products). *o*-Chlorocumene hydroperoxide, on the other hand, gave high yields of *o*-chlorocumyl alcohol and only small amounts of *o*-chloro-α-methylstyrene. Thus, compared with cumene hydroperoxide *o*-chlorocumene hydroperoxide has the advantage of giving both a lower rate of heterolytic decomposition and a lower rate of dehydration of the co-product alcohol. There was no formation of dichloro-α-methylstyrene observed in epoxidations with dichlorocumene hydroperoxide. Separate experiments confirmed that α-cumyl alcohol is readily dehydrated in the presence of TiO_2-on-SiO_2 or Mo(VI) compounds at 80°C, whereas *tert*-butanol does so only at temperatures higher than 110°C.

In contrast to the low selectivities observed in the reaction of allylchloride with cumene hydroperoxide, the selectivities obtained in the epoxidations of the much more reactive cyclohexene with this hydroperoxide in the presence of $Mo(CO)_6$ and TiO_2-on-SiO_2 were high (100 and 93%, respectively, at 99% conversion of hydroperoxide).

IV. DISCUSSION

The Effect of Solvent

It has been proposed (*2*) that metal-catalyzed epoxidations involve the reaction of a catalyst–hydroperoxide complex with the olefin via a cyclic transition state. By-products arise from decomposition of the catalyst–hydroperoxide complex into radicals. In coordinating solvents (alcohols, ethers, etc.) the catalyst can also form complexes with the solvent (SH) and this will hinder the formation of the catalyst–hydroperoxide complex and, hence, lower the rate of epoxidation. In addition, unlike the rate of decomposition of the complex (k_1),



the rate at which the catalyst–hydroperoxide complex reacts with the olefin (k_2) may be expected to be lowered by coordinating solvent molecules. Thus, the ratio k_2/k_1 and, hence, the selectivity are also expected to decrease.

Table 1 shows that the rates and selectivities in coordinating solvents such as alcohols, ethers, dimethylformamide, etc., are relatively low. The effect of alcohols has been discussed previously (*2*) with regard to the autoretarding effect of the co-product alcohol in metal-catalyzed epoxidations.

The best solvents were polychlorinated hydrocarbons such as 1,1,2,2-tetrachloroethane, which suggests that the desired solvent should be polar but of low coordinating power. These solvent effects closely parallel those observed in epoxidations with organic peroxy acids (*6*).

The Effect of Hydroperoxide Structure

The low epoxide selectivities obtained with cumene hydroperoxide are due to facile heterolytic decomposition into acetone and phenol:

$$PhC(CH_3)_2O_2H \rightarrow PHOH + (CH_3)_2C{=}O. \quad (3)$$

Valendo and Norikov (*7*) showed that transition-metal-oxide catalysts for the decomposition of cumene hydroperoxide can be divided into two types: firstly, the basic and amphoteric oxides which catalyze the homolytic decomposition into a mixture of α-cumyl alcohol and acetophenone, and secondly, the acidic oxides MoO_3, TiO_2, V_2O_5 and WO_3, which, in addition, catalyze reaction (*3*). Among the catalysts of the second type MoO_3 was the most effective for reaction (*3*).

The acid-catalyzed decomposition of hydroperoxides has been extensively studied (*8*) and is known to be much more facile with alkylaromatic hydroperoxides than with *tert*-butyl hydroperoxide. When the alkylaromatic hydroperoxide contains electron-attracting substituents (such as chloro) the rate of heterolytic decomposition is diminished (*5*). The high yields of epichlorohydrin obtained in the reactions of *o*-chlorocumene and dichlorocumene hydroperoxides with allyl chloride in the presence of TiO_2-on-SiO_2 are in accordance with this effect. A lower selectivity was observed (with *o*-chlorocumene hydroperoxide) when $Mo(CO)_6$ was used as the catalyst. This is consistent with the fact that Mo(VI) compounds—formed via oxidation of $Mo(CO)_6$ with the hydroperoxide (*9*)—are stronger Lewis acids than TiO_2-on-SiO_2, as is demonstrated by the more facile dehydration of α-cumyl alcohol with $MoO_2(acac)_2$ than with TiO_2-on-SiO_2.

An electron-attracting substituent in the ring of the alkylaromatic hydroperoxide also stabilizes the alcohol produced against acid-catalyzed dehydration. Thus, little or no dehydration of the co-product alcohol was observed in epoxidations with *o*-chlorocumene and dichlorocumene hydroperoxides (Table 4).

In addition to reducing the rates of the above-mentioned side reactions electron-attracting substituents in the hydroperoxide are also expected to increase the rate of epoxidation. Electron-attracting substituents enhance the electrophilic nature of the hydroperoxide and facilitate electrophilic attack by the catalyst–hydroperoxide complex on the olefin. In agreement with this, the relative rates of epoxidation of allyl chloride (TiO_2-on-SiO_2 catalyst) with cumene, *o*-chlorocumene and dichlorocumene hydroperoxides were found to be 1:2.3:5.

In conclusion, the structure of the hydroperoxide can play an important role in determining the selectivities in metal-catalyzed epoxidations. That this is not apparent from previously published data is due to the fact that the relevant comparative studies had been made with reactive olefins.

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