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EPOXIDATION OF 2,3-DIMETHYL-2-BUTENE BY SUBSTITUTED BENZYLAZOBENZENE α-HYDROPEROXIDES IN C_6D_6

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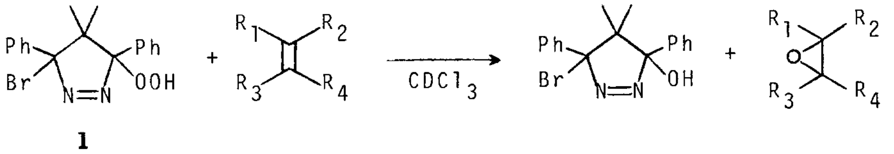
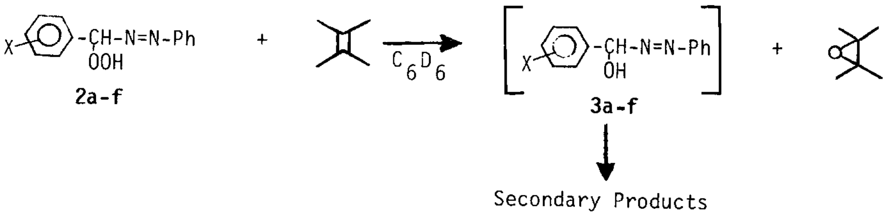
Summary: The reaction of substituted benzylazobenzene α-hydroperoxides, **2a-f**, with 2,3-dimethyl-2-butene in C_6D_6 at 34° produced tetramethyloxirane in ~90% yield; was of the first order in ROOH and in alkene; and exhibited an excellent LFER vs. sigma values (ρ=1.1 ± 0.1).

Alkenes can undergo epoxidation, without the requirement of added catalyst,[1] with hydroperoxides like triphenylsilyl hydroperoxide,[2] 2-hydroperoxyhexafluoro-2-propanol,[3] and α-substituted hydroperoxides.[4] Recently, 3-bromo-4,5-dihydro-5-hydroperoxy-4,4-dimethyl-3,5-diphenyl-3H-pyrazole (**1**) was shown to epoxidize alkenes in $CDCl_3$ under mild conditions (Reaction 1).[5,6] Cyclic α-azohydroperoxide, **1**, has also been shown to be of unusual reactivity[7] in S- and N-oxidations (similar to that of flavin 4a-hydroperoxides). Acyclic α-azohydroperoxides (benzylazobenzene α-hydroperoxides) have been shown to hydroxylate[8] benzene by a radical pathway. Acyclic α-azohydroperoxides have been shown[9] to be effective reagents for S-oxidation in aprotic media. The oxygen-atom transfer reactions of acyclic α-azohydroperoxides with alkenes have not been investigated. We report here the uncatalyzed reaction of 2,3-dimethyl-2-butene with a series of substituted benzylazobenzene α-hydroperoxides, **2a-f**, in C_6D_6 at 34° to produce tetramethyloxirane and the unstable α-azohydroxides (**3a-f**) in approximately 90% yield (Reaction 2).



(1)



(2)

The epoxidation studies were carried out as follows: 100μl of 2,3-dimethyl-2-butene (835μmol) were added, via syringe, to a solution of the α-azohydroperoxide[10] (35-120μmol) in 400μl of C_6D_6 (MSD, 1% TMS) in a new 5-mm NMR tube. Anisole (10.0μl) had been previously added as an internal standard. Reaction progress, at 34°, was followed by electronic integration. Final product yields were determined relative to the internal standard. The primary products, benzylazobenzene α-hydroxides (**3a-f**), although detected by ^1H NMR spectroscopy, could not be isolated. Compounds **3a-f** were observed to undergo decomposition to yield secondary products: hydrazides, Ar-CO-NHNHPh (30-40%), and aldehydes, ArCHO[60-70% (PhN_2H was not isolated)]. Tetramethyloxirane and the aldehydes were isolated by preparative gas chromatography and identified by comparison of spectral data with those of authentic samples. The hydrazides were isolated by filtration of the reaction mixture, recrystallized from benzene-pentane, and identified by comparison of spectral data with those of authentic samples.

The epoxidation reaction was found to be of the first order with respect to both alkene and α-azohydroperoxide. Pseudo-first-order plots of hydroperoxide concentration vs. time were linear for at least two half-lives (Figure 1). A two-fold variation in the concentra-

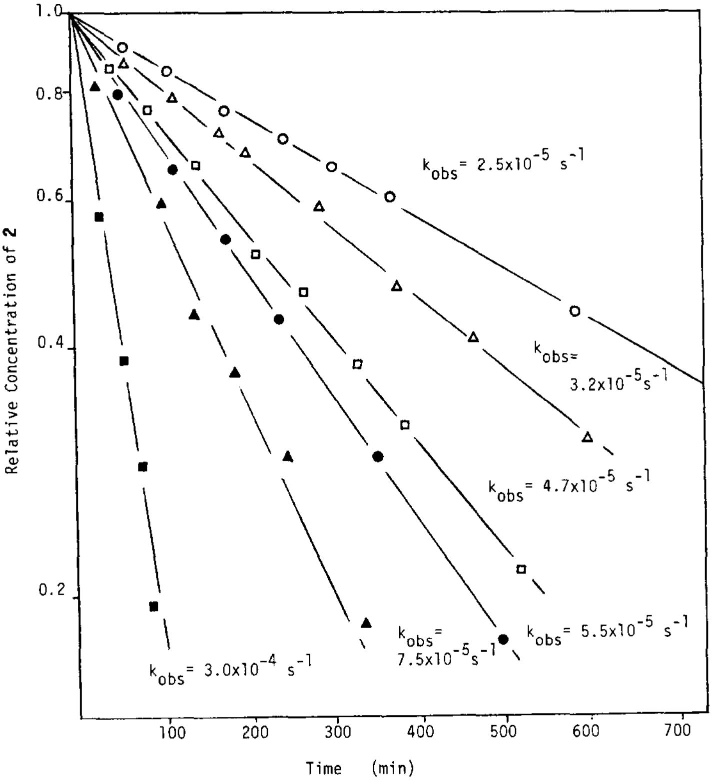


Figure 1. Pseudo-First Order Plots for the Reaction of 2,3-Dimethyl-2-butene (1.67 M) with X-Ar-CH(OOH)-N=N-Ph in C_6D_6: ○ ,$[p\text{-MeO}]_o$=0.18M; △ ,$[p\text{-Me}]_o$=0.13M; □ ,$[H]_o$=0.11M; ● ,$[p\text{-F}]_o$= 0.071M; ▲ ,$[p\text{-Br}]_o$=0.085M; ■ ,$[m\text{-NO}_2]_o$=0.11 M.

tion of hydroperoxide in the presence of a large excess of the alkene did not affect the observed pseudo-first order rate constants. Variation of the alkene concentration under pseudo-first order conditions resulted in the expected change in the value of k_{obs}. The rate of appearance of epoxide was found to correspond to the rate of disappearance of α-azohydroperoxide. The presence of electron-withdrawing substituents on the hydroperoxide increased the rate of oxygen-atom transfer significantly while electron-donating substituents had the opposite effect. The rate data and final product yields for the reaction of **2a-f** with 2,3-dimethyl-2-butene are listed in Table 1.

Table 1 Rate Data and Yields of Tetramethyloxirane for the Reaction of 2,3-Dimethyl-2-butene (1.67*M*) with X-Ar-CH(OOH)-N=N-Ph (**2a-f**) in C_6D_6 at 34°C.

ROOH	X-	[ROOH] M	k_{obs} s^{-1}	k_2 $M^{-1}s^{-1}$	% Yield of Epoxide[a]
2a	*p*-MeO	0.18-0.35	2.5×10^{-5}	$1.5 \pm 0.1 \times 10^{-5}$	92
2b	*p*-Me	0.11-0.13	3.2×10^{-5}	$1.9 \pm 0.1 \times 10^{-5}$	94
2c	H	0.11-0.24	4.7×10^{-5}	$2.8 \pm 0.1 \times 10^{-5}$	87
2d	*p*-F	0.061-0.18	5.5×10^{-5}	$3.3 \pm 0.1 \times 10^{-5}$	90
2e	*p*-Br	0.085-0.11	7.5×10^{-5}	$4.5 \pm 0.2 \times 10^{-5}$	86
2f	*m*-NO_2	0.11 0.11[b]	3.0×10^{-4} 1.7×10^{-4}	$1.8 \pm 0.3 \times 10^{-4}$ $2.0 \pm 0.3 \times 10^{-4}$	96

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a) Average from two experiments; determined by ^1H NMR spectroscopy relative to internal standard. b) 0.85 *M* = [alkene].

The reactivity of the acyclic α-azohydroperoxides seems similar to those of α-hydroperoxy esters and hydroperoxy ketals.[4] Acyclic α-azohydroperoxide, **2c**, was found to be approximately 10^{+2} times less reactive toward the oxidation of 2,3-dimethyl-2-butene in C_6D_6 than that of cyclic α-azohydroperoxide, **1**, in $CDCl_3$. Unfortunately, the acyclic α-azohydroperoxides are not stable in $CDCl_3$[9,10a]. Peracid epoxidations have been shown to be sensitive to solvent effects[11a] (the epoxidation of cyclohexene by perbenzoic acid is 3 times faster in $CHCl_3$ than in benzene). It seems likely that solvent effects account for a portion of the large difference in reactivity between the acyclic and cyclic α-azohydroperoxides. The decreased reactivity of acyclic α-azohydroperoxides relative to that of **1** is likely to be due to a combination of the following factors. The basicity of the anti azo function of **2** is less than that of the syn azo group of **1**. The azo function in **2** is mobile while that of **1** is fixed. Intramolecular hydrogen bonding in **2** can occur with either nitrogen atom of the azo function while that in **1** can occur only with one of the nitrogen atoms.

The Hammett-type plot of the second-order rate constants for the reaction of 2,3-dimethyl-2-butene with **2a-f** vs. sigma values showed a good LFER with a rho value of +1.11±0.12 (r=0.996). The rho value observed for epoxidation by **2a-f** is similar to those obtained[11] for epoxidations with substituted perbenzoic acids in aprotic media. The oxidation of sulfides with benzylazobenzene $\underline{\alpha}$-hydroperoxides also exhibited[9] excellent LFERs vs. sigma values (rho = +1.0 with BzSMe and +0.9 with PhSMe). Epoxidations with **1** were found[6] to show similar selectivity to peracid epoxidations. These clearly show that the mechanism for epoxidation by $\underline{\alpha}$-azohydroperoxides is similar to that of peracids[11a,12] and to that of peroxy ketals[4]. The transition state for the epoxidation reaction should involve partial intramolecular transfer (or hydrogen bonding) of the peroxy proton to a nitrogen atom during the nucleophilic attack of the alkene on the terminal oxygen atom.

Work is in progress to further evaluate the structural features required for oxygen-atom transfer reactions in $\underline{\alpha}$-azohydroperoxides.

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