

Biphase and Triphase Catalysis. Arsonated Polystyrenes as Catalysts in the Baeyer–Villiger Oxidation of Ketones by Aqueous Hydrogen Peroxide

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Abstract: Arsonated polystyrene resins, prepared by a novel procedure, proved to be versatile catalysts for the Baeyer–Villiger oxidation of ketones by hydrogen peroxide. The insoluble beads of the catalyst can be quantitatively separated from the reaction mixture and recycled. Extensive hydrolysis of the lactone and ester products is prevented. In solvents miscible with aqueous hydrogen peroxide (biphase system), the catalysts facilitate oxidation of medium size cycloalkanones (C_4 – C_7) and their alkyl and aryl derivatives, steroid ketones, and branched-chain aliphatic ketones. Larger size cycloalkanones, acetophenone, and straight-chain aliphatic ketones react very slowly or not at all. The arsonated polystyrene beads are effective catalysts and phase transfer agents in solvents immiscible with aqueous hydrogen peroxide. This represents the first example of triphase catalysis in oxidations by hydrogen peroxide.

Replacement of carboxylic peroxy acids by a hydrogen peroxide–catalyst system has been of long-standing interest in the Baeyer–Villiger oxidation of ketones. This effort is important in view of the following considerations. Hydrogen peroxide is cheaper and more convenient than carboxylic peroxy acids (water is the only side product). The carboxylic acids resulting from peroxycarboxylic acids cannot be readily separated, and their equilibration with hydrogen peroxide is extremely slow.¹ Although this can be accelerated by catalytic quantities of strong acids, the presence of these acids results in hydrolysis of the product of the Baeyer–Villiger oxidation.¹ Therefore, in situ recycle of carboxylic acids is impossible. Thus, it becomes obvious that a good catalyst for the Baeyer–Villiger oxidation of ketones by hydrogen peroxide has to fulfill several requirements: (1) fast reaction with hydrogen peroxide resulting in hydroperoxy or metal peroxy species; (2) easy separation of the catalyst from the reaction mixture; and (3) low or no protonic or Lewis acidity.

Although several catalysts have been reported in the literature,^{2,3} they do not satisfy the above requirements and possess several shortcomings. We are now pleased to report the preparation and demonstration of a suitable catalyst based on polystyrene substituted by arsonic groups.

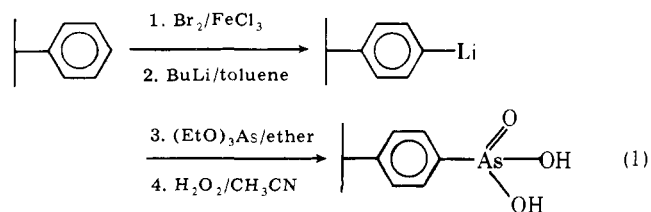
Results and Discussion

I. Catalyst Selection. The $OH/^{18}OH$ or OH/OOH exchange, and therefore formation of hydroperoxy and peroxy species, is known to be fast in oxides of groups 5, 5A, 6, and 6A elements.⁴ This fact has been employed in the preparation of benzeneperoxyarsenic acid in a two-phase system such as chloroform–aqueous hydrogen peroxide.⁵ The preformed benzeneperoxyarsenic acid dissolved in the organic solvent has then been used as a stoichiometric oxidant of cyclic ketones to lactones.⁵ Even more interesting are the patent literature reports² suggesting that selenium and arsenic oxides may be used as catalysts for the Baeyer–Villiger oxidation of ketones by hydrogen peroxide. In our work,³ similar properties have been demonstrated for molybdenum and tungsten peroxy complexes stabilized by pyridinecarboxylate ligands. Unfortunately, the above-mentioned catalysts cannot be easily separated from the reaction mixtures. Furthermore, selenium and arsenic oxides are toxic, and in the presence of aqueous hydrogen peroxide they exhibit protonic and Lewis acidity causing extensive solvolysis of lactones.⁶

Inspection of the literature revealed that the acidity of tolueneperoxyarsenic acid⁶ ($pK_a = 3.82$) is very close to that of *m*-chlorobenzoic acid⁷ ($pK_a = 3.82$), the peroxy form of which

is the most common reagent for conversion of cyclic ketones to lactones. Also, the C–As bond⁸ in benzenearsonic acid, unlike the C–Se bond⁹ in benzeneseleninic acid, is very stable toward nucleophilic and electrophilic reagents. Indeed, preliminary experiments indicated that benzenearsonic acid is an efficient catalyst for oxidation of cyclic ketones to lactones. Nevertheless, only bonding of the benzenearsonic acid group to an insoluble support would allow the separation of this catalyst from the product. Our interest therefore centered on polystyrene arsonated on the benzene ring since, from all the polymers modified by peroxycarboxylic groups, only those based on polystyrene have been found stable.¹⁰

II. Preparation and Characterization of the Catalyst. Previous attempts to derivatize polystyrene by arsonic groups have employed, as the key step, the Bart's reaction which involves interaction of the diazotized phenyl rings with alkaline metal arsenite.¹¹ The polystyrene derivatized by this method is contaminated^{11a,b} by a substantial number of phenyl groups bearing azo, amino, and hydroxy groups which are incompatible with hydrogen peroxide. Therefore, a new procedure has been developed which is summarized in eq 1:



Starting with polystyrene beads cross-linked by 1% of *p*-divinylbenzene, 7, 25, and 50% (polymers 1, 2 and 3, respectively) of the phenyl groups in the polymer beads have been arsonated. The procedure requires a few comments. The bromination¹² catalyzed by iron dust, or by iron trichloride, gives the para isomer exclusively.¹³ Quantitative removal of iron dust and iron ion is essential for the preparation of an active oxidation catalyst since even small quantities of iron left in the polymer cause fast decomposition of hydrogen peroxide to oxygen and water. Washing with a concentrated HCl–dioxane mixture gives the best results if iron dust is used as the bromination catalyst. Many washings with acetone are sufficient in the case of $FeCl_3$. In order to achieve complete replacement of bromine by lithium, the reaction of the brominated polymer with *n*-butyllithium has to be run in toluene and at an elevated temperature ($\sim 60^\circ C$). In other solvents such as ether, dioxane, and THF, only incomplete exchange is achieved regardless of the excess of *n*-butyllithium used. Similar observations were

Table I. Elemental Analyses of Substituted Polystyrenes^a

polymer	C, %	H, %	Br, %	As, %	deg of substitution	yield, %
1a	84.80 (84.86)	6.88 (7.02)	8.14 (8.11)		0.11	
1	85.17 (85.16)	7.07 (7.21)	0.31	4.60 (4.65)	0.07	64 ^b
2a	75.31 (75.59)	6.19 (6.21)	17.09 (17.20)		0.27	
2	71.28 (71.51)	6.94 (6.13)	0.003	13.24 (13.65)	0.25	93, 91 ^c
3a	64.38 (64.95)	5.28 (5.07)	29.88 (29.98)		0.55	
3^d	65.05 (64.51)	6.60 (6.75)		20.24 (20.04)	0.50	91

^a Calculated data are in parentheses. ^b May not be significant since at this low concentration a small error in the arsenic analysis will cause a substantial change in the yield. ^c Based on the alkalimetric titration of the arsonic groups. ^d Analyzed before hydrolysis and oxidation of the -As(OEt)₂ groups.

Table II. Effect of Recycle on the Activity of Catalysts Based on Arsonated Polystyrene^a

catalyst	cycle no.	ketone	time, h	conversion		As, % left in the polymer
				lactone, %	hydroxy acid, %	
polymer 1	1		9	39	14	4.24
	2		6	24		3.76
	3	cyclohexanone	6	26		4.28
	4		6	37		3.92
polymer 1	1	2-methylcyclohexanone	6	69	0	
	2	2-methylcyclohexanone	6	68	0	
	3	cyclohexanone	6	32	3	
	4	2-methylcyclohexanone	6	69	0	
polymer 3	1		7	34	24	
	2		7.5	42	7	
	3	cyclohexanone	7	37	10	
	4 ^b		8	40		

^a The oxidation is run in dioxane at 80 °C. The conversion is based on ketone. The yields of lactones and hydroxy acids are close to 100%. The ratio of ketone:H₂O₂:As is 40:40:1. ^b The molar ratio of ketone:H₂O₂:As = 51:26:1.

made by Farrall and Fréchet.¹⁴ In the third step (eq 1), an excess of triethoxyarsine is required in order to prevent substitution of more than one ethoxy group by the phenyl groups. In this way, after oxidation in the fourth step (eq 1), the presence of only arsonic groups can be assured and the content of the arsonic groups can be controlled by the amount of bromine employed in the first step (Table I). Scanning of the cross sections of the brominated and arsonated polystyrene beads by a microprobe suggests that the distribution of bromine throughout the brominated polymer and that of arsenic throughout the arsonated polymer is roughly constant without any "skin-core" effect (Figure 1). Alkalimetric titration of polymer 2 demonstrates that the content of the arsonic groups is within experimental error of that determined by the elemental analysis (Table I). This suggests that no structures analogous to diphenylarsinic acid and triphenylarsine oxide are present. Finally, the IR of polymer 3 exhibits broad bands at 3300 and 2900 cm⁻¹, associated with strongly hydrogen-bonded OH groups, and two bands at 820 and 890 cm⁻¹ assigned to symmetric and asymmetric As=O stretching vibrations, respectively.¹⁵ This IR spectrum, after subtraction of the bands belonging to polystyrene, is identical with that of benzenearsonic acid with the exception of the symmetric As=O stretching vibration which, in the case of benzenearsonic acid, appears at 780 cm⁻¹.

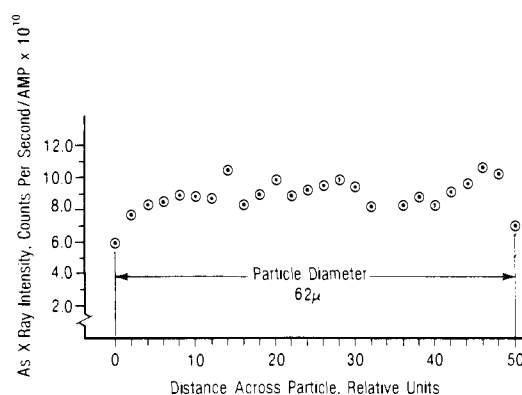


Figure 1. Scanning microprobe analysis of arsonated polystyrene bead of polymer 1.

III. Oxidation of Ketones in Solvents Miscible with Aqueous Hydrogen Peroxide (Biphasic System). A. Effects of Various Factors on the Efficiency of the Catalyst. The arsonated polystyrene beads 1 to 3 proved to be suitable catalysts for the Baeyer-Villiger oxidation of ketones by 90 and 30% aqueous hydrogen peroxide at 60–90 °C. The activities of the catalysts 1 to 3 per mole of As are practically identical (Table II).

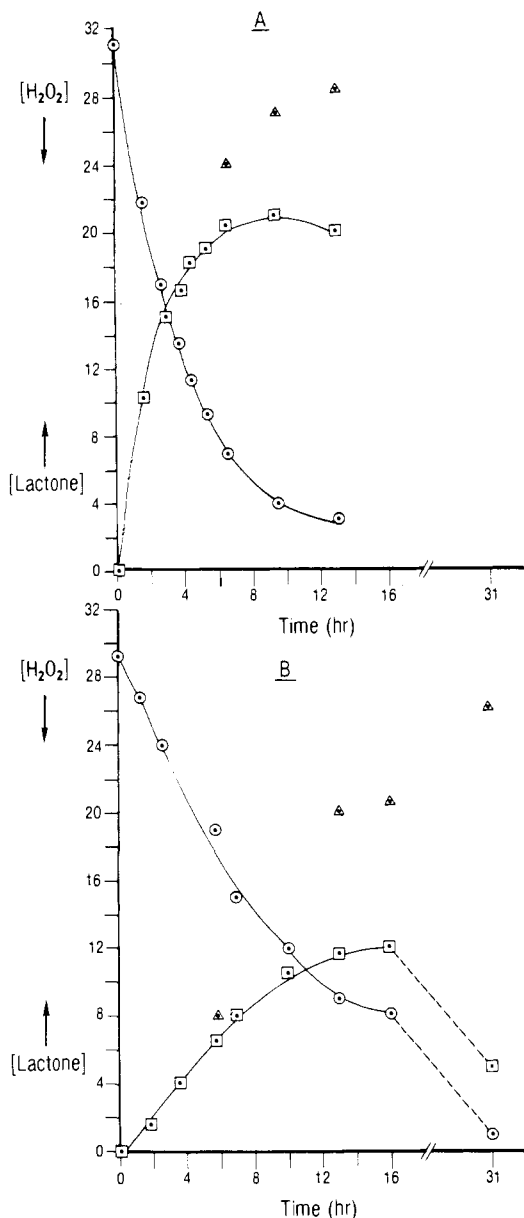


Figure 2. Oxidation of cyclohexanone in dioxane at 80 °C by 90% (A) and 30% (B) aqueous hydrogen peroxide in the presence of polymer 3. Plotted are H₂O₂ (○), caprolactone (◻), and combined caprolactone-6-hydroxycaproic acid (▲) concentrations (mmol).

However, due to different arsenic contents, the activity of **3** per gram of the catalyst is higher than that of **1** or **2**. Therefore, **3** was used in most of the runs. All of these catalysts can be filtered off and recycled without any apparent loss of activity (Table II). Furthermore, in the case of **1**, no significant change of the arsenic content is detected after each recycle.

The choice of solvent plays an important role. For one thing, the solvent is the main factor affecting the swelling of the catalyst beads. The extent of swelling, in turn, determines the ease of transport of the reagents and the products in and out of the polymer beads. The solvent should also be miscible with aqueous hydrogen peroxide. Indeed, the best results were obtained in dioxane in agreement with the observation that it is the best swelling solvent for the catalyst. Interestingly, THF and dioxane were also shown to be the best solvents in the epoxidation of olefins by either stoichiometric quantities of polystyrene derivatized by peroxy-carboxylic groups¹⁰ or by hydrogen peroxide in the presence of catalytic quantities of arsonated polystyrene.¹⁶ Protic solvents slow or stop the oxidation depending on their concentration and the structure of

the oxidized ketone. Thus, oxidation by 30% aqueous hydrogen peroxide is always slower (Figure 2) than that by equivalent quantities of 90% hydrogen peroxide. In methanol (Table III), only a slow oxidation of cyclohexanone by 90% hydrogen peroxide has been observed. However, under the same conditions, 2-phenyl- and 2-methylcyclohexanones are oxidized at a rate only slightly slower than in dioxane. Apparently, protic solvents capable of interaction with the arsonic groups decrease the equilibrium concentrations of intermediates **4** and **7** (Scheme 1) and, therefore, decrease the overall reaction rate. However, the main difference between the behavior of cyclohexanone and 2-methylcyclohexanone in methanol can best be explained by different tendencies of ketones to form ketals. Under the reaction conditions, formation of substantial amounts of cyclohexanone dimethyl ketal has indeed been observed, while ketals of 2-methyl- and 2-phenylcyclohexanones have not been detected. In these cases, a certain portion of the ketone is removed from the oxidation path leading to lactone.

For all ketones studied, the rates of oxidation catalyzed by the arsonated polystyrene are about three times slower than that in the presence of equivalent quantities of either benzene- or toluene-arsonic acids (Table IV). This suggests that the diffusion of the substrate into the polymer plays an important role in determining the overall rate of oxidation.

B. Scope and Limitation. In dioxane, a range of ketones was oxidized by 90% aqueous hydrogen peroxide at 80 °C. At the end of every run, the polymer was filtered off and recycled. The filtrate was analyzed for esters or lactones and the products of their hydrolysis. No polymerization of lactones to polyesters was observed. The results are summarized in Table V. The efficiency in the use of H₂O₂ for ketone oxidation to the products of the Baeyer-Villiger oxidation (e.g., lactones and ω -hydroxyalkanoic acids from cyclic ketones) is 90% or better except in very slow reactions (e.g., oxidation of acetophenone) where the efficiency decrease reflects a slow decomposition of hydrogen peroxide.

Most of the lactone hydrolysis occurs at the latter stage of the reaction when the concentration of H₂O₂ is low and the concentration of the byproduct water is high. In order to increase the oxidation rate in the latter stages of the reaction and minimize the hydrolysis of lactones, an excess of ketone is used in most of the runs.

Roughly, the ease of ketone oxidation follows that observed with peroxycarboxylic acids.¹⁷ Thus, aliphatic ketones are the most difficult to oxidize. Ketones with straight-chain alkyl groups such as 5-nonanone are not oxidized at all. Similarly, acetophenone can be oxidized only with difficulty and in a low yield. However, introduction of a better migrating group such as *tert*-butyl in pinacolone induces a relatively easy formation of *tert*-butyl acetate. Smaller cycloalkanones, C₄ to C₆, are oxidized much easier than the larger cycloalkanones. Steroid ketones (e.g., estrone-3-methyl ether) are oxidized more slowly than their monocyclic analogues. Oxidation of β,γ -unsaturated ketones such as 2-allylcyclohexanone leads to lactones rather than epoxides. In agreement with the chemistry of peroxy-carboxylic acids, α,β -unsaturated ketones such as 2-cyclohexenone and easily enolizable ketones such as alkyl cyclohexanone-2-carboxylates are not oxidized in our system.

In spite of the above similarities, there are significant differences between our system and peroxycarboxylic acids. Thus, the ease of cyclic ketone oxidation follows the order C₄ >> C₅ > C₆ >> C₇ which is in only partial agreement with the order of C₄ < C₅ < C₆ > C₇ observed for peroxycarboxylic acids.¹⁸ Oxidation of 2-methylcyclohexanone catalyzed by arsonated polystyrene is faster than that of cyclohexanone while the opposite is found for peroxybenzoic acid.^{17f} Oxidation of 2-chlorocyclohexanone in our system results only in adipic acid, in contrast to the reaction with peroxycarboxylic acids which

Table III. Effect of Methanol^a

catalyst	solvent	time, h	conversion, %		yield, ^b %	
			lactone	hydroxy ester		
cyclohexanone ^c PhAsO ₃ H ₂	CH ₃ OH	2	13		90	
		10	16		20	
	polymer 3	CH ₃ OH	2	13		100
			6	16		81
			24	30		
dioxane	3	47		99		
	7	79		80		
2-methylcyclohexanone ^c PhAsO ₃ H ₂	CH ₃ OH	1	40	13	100	
		3	52	13	73	
		5	55	19	73	
	dioxane	1.2	66	0	100	
		2.3	92	0	99	
2-phenylcyclohexanone ^d polymer 3	CH ₃ OH	2.7	40		97	
		6.5	60		90	
	dioxane	3	55		94	
		7	75		92	
		10	82		90	

^a The molar ratio of H₂O₂:As = 30. ^b Based on H₂O₂ consumed. The molar ratios of ketone:H₂O₂ are: ^c 5; ^d 1.

leads to satisfactory yields of 2-chlorocaprolactone.¹⁹ The reasons for the observed differences will emerge from the discussion of the reaction mechanism.

C. Mechanism. The mechanism of the ketone oxidation by hydrogen peroxide catalyzed either by benzene- and toluene-arsonic acids or by arsonated polystyrene is best described by Scheme I. First, hydrogen peroxide reacts with either the arsonic acids to form peroxyarsonic acids, or it adds to ketones to form vicinal hydroperoxyalkanols. Recent studies demonstrated that the rate of ¹⁸O exchange between the arsonate ion and ¹⁸OH₂ is strongly pH dependent.⁴ The oxygen exchange is relatively slow in basic solutions (pH ≥ 9–12) and it sharply increases as the acidity of the medium increases (pH 8 or lower). Thus, under the reaction conditions for ketone oxidation when very little or no arsonic acid is dissociated, the oxygen exchange should be fast. Since the nucleophilicity of H₂O₂²⁰ is much higher than that of water, it is expected that the formation of peroxyarsonic acids (step 1, Scheme I) is at least as fast as the ¹⁸O exchange⁴ and that the equilibrium of step 1 lies

heavily on the side of peroxyarsonic acid. This is supported by the fact that more than 95% of the H₂O₂ can be utilized in the ketone oxidation catalyzed by arsonated polystyrene beads and that the same beads are excellent catalysts for olefin epoxidation by H₂O₂.¹⁶

By analogy, it is assumed that the rate of perester **7** formation from peroxide **5** and arsonic acid (step 4 in Scheme I) is fast, approaching the rate of perarsonic acid formation in step 1. A support for this statement comes from an NMR study of the decomposition of 1-hydroperoxy-2-methylcyclohexanol (vide infra).

Even though it is well established²¹ that H₂O₂ reacts with ketones to form peroxides (steps 3 and 6 in Scheme I), no kinetic or equilibrium data for the peroxide formation are available. In order to establish the degree to which the peroxides contribute to the lactone formation, a short qualitative study of the rates and the equilibria of the peroxide formation in the absence and presence of either perchloric or benzenearsonic acids was undertaken. The reaction was followed

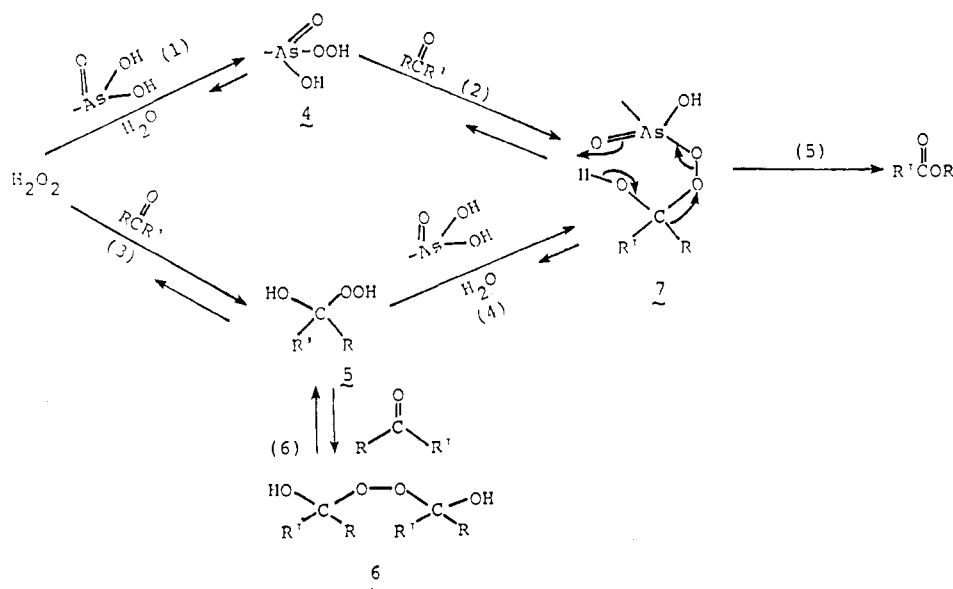
Scheme I. Mechanism of Ketone Oxidation by H₂O₂ Catalyzed by Arsonated Polystyrene

Table IV. Comparison of Catalytic Activity of Arsonated Polystyrenes with the Activity of Benzene- and Tolueneearsonic Acids^a

catalyst	time, h	conversion, %	yield of lactone, ^b %
2-methylcyclohexanone ^c polymer 1	1.8	38	100
	3.4	60	100
	4.7	79	100
PhAsO ₃ H ₂	1.2	66	100
	2.3	92	99
<i>p</i> -CH ₃ C ₆ H ₄ AsO ₃ H ₂	1.2	40	100
	2	88	94
pinacolone ^d polymer 2	1.5	15	80
	3.8	34	82
	8	55	84
	9.5	63	84
PhAsO ₃ H ₂	0.5	36	100
	1	54	100
	2.8	76	96
	6.5	87	95
<i>p</i> -CH ₃ C ₆ H ₄ AsO ₃ H ₂	0.5	33	100
	1	50	100
	2.5	75	100
	6	95	100
estrone-3-methyl ether ^e polymer 3	1.5	11	100
	3	21	100
	5	34	100
	PhAsO ₃ H ₂	0.5	27
1.5		41	
3		57	90
5		68	

^a The molar ratio of H₂O₂:As = 30. ^b Based on H₂O₂ consumed. The yield based on the oxidized ketone is better than 95%. The molar ratios of ketone:H₂O₂ are: ^c 5; ^d 10; ^e 1.

by ¹³C and ¹H NMR. The results (Table VI) show that the equilibria are affected by steric effects and, in the case of cyclic ketones, by the size of the ring. Although cyclohexanone exhibits the highest tendency of the cyclic ketones to form peroxides, the differences in the equilibrium concentrations of peroxides are small when compared with the effect of the ring size on the addition of other nucleophiles such as HCN.²² However, the rates at which the equilibria are approached differ dramatically from ketone to ketone and they show strong dependence on acid catalysis.

Thus, only cyclobutanone and cyclohexanone react with H₂O₂ in the absence of any acid at room temperature or at 80 °C. In the presence of a low concentration (~0.005 M) of a strong acid such as perchloric acid, all the ketones reach equilibrium with H₂O₂ immediately even at room temperature. In the presence of benzenearsonic acid (~3 mol %), the reaction pattern is more complex (Table VI). Detailed ¹H NMR study of the reaction mixtures at different temperatures and time intervals proved to be very instructive. Thus cyclobutanone is oxidized so fast that, even at room temperature, only butyrolactone can be detected immediately after mixing.²³ At room temperature, cyclohexanone and cycloheptanone reach the equilibrium concentration of peroxides in ~3 and 24 h, respectively. At 80 °C the equilibrium is established immediately and then lactones start to appear slowly. Furthermore, the rate of cyclohexanone oxidation as followed by the H₂O₂ consumption or by the caprolactone and 6-hydroxycaproic acid formation is not proportional to the cyclohexanone concentration. Instead it reaches a maximum at the ratio of cyclo-

hexanone:H₂O₂ of ~5:1 and approaches zero at the ratio of cyclohexanone:H₂O₂ of ~10:1 (Table VII). This behavior strongly suggests formation of the peroxide dimer **6** (Scheme I) which has to be dissociated before it can be converted to lactone via perester **7**. At a high ratio of cyclohexanone:H₂O₂, all H₂O₂ is thus channeled into **6** and the ketone oxidation stops. Due to the chemical shifts of C₁ in peroxides **5** (δ 102.8) and **6** (δ 102.0), the existence of the equilibrium (**6**) can be demonstrated by ¹³C NMR.²⁴ This is further supported by the observation that, under the reaction conditions, the dimer **6** is converted rapidly to caprolactone.²⁵ However, when the dimer is mixed with cyclohexanone in the ratio 1:8, simulating 1:10 ratio of cyclohexanone to H₂O₂, a very slow and low conversion to caprolactone is observed (Table VII).

In the course of pinacolone and 2-methylcyclohexanone oxidation, no peroxides can be detected either at room temperature or at 80 °C by NMR even though the Baeyer-Villiger type products, *tert*-butyl acetate and 6-methylcaprolactone, are formed. Furthermore, 1-hydroperoxy-2-methylcyclohexanol (peroxide of the type **5**) was prepared from 2-methylcyclohexanone and H₂O₂ in the presence of Amberlyst 15 used as a proton source. Addition of 3 mol % benzenearsonic acid to a solution of the peroxide in dioxane resulted in a fast (90% conversion in 3 min) conversion to 6-methylcaprolactone without any decomposition of the peroxide to 2-methylcyclohexanone and H₂O₂.

For cyclopentanone, ¹³C NMR was employed as the probe. In the presence of 3 mol % of either arsonated polymer or benzenearsonic acid, cyclopentanone reacts only slowly at room temperature to form relatively small amounts of peroxide, far from the equilibrium concentration (Table VI). Even at 80 °C only a low concentration of peroxides is present throughout the conversion to lactone.

It is assumed that the addition of peroxyarsonic acid to ketones (step 2, Scheme I) is of about the same rate as that of the H₂O₂ addition, and that it is also strongly dependent on the ketone structure and the acidity of the medium.

Finally, the rate of decomposition of the perester **7** (step 5, Scheme I) should, in analogy to the reactivity of analogous peresters of carboxylic acids,¹⁷ depend on the migratory aptitude of the migrating group, on the steric crowding, and in the case of cyclic ketones on the size of the ring.

Based on this information a general picture emerges for the mechanism of the ketone oxidation. There are two possible extremes. One is represented by cyclohexanone where the steps leading to the formation of perester **7** are in equilibrium and the decomposition of **7** (step 5, Scheme I) is the rate-determining step. Cycloheptanone and probably cyclobutanone also belong to this group. The other extreme is represented by sterically hindered ketones such as pinacolone and 2-methylcyclohexanone. In these cases, the rate-determining steps are thought to be the addition of H₂O₂ and perarsonic acid (steps 2 and 3, Scheme I) to ketones. All the remaining steps are fast. Cyclopentanone represents the intermediate between the two extremes. The results of the NMR study in the case of cyclopentanone can be explained only if it is assumed that steps 1 and 4 are fast and that the rates of the remaining steps are of about the same order of magnitude.

It is then mainly the importance of the route represented by steps 3, 4, and 5 (Scheme I) which is responsible for the observed differences between our system and the oxidation of ketones by peroxyarsonic acids. This fact also explains the behavior of 2-chlorocyclohexanone. It forms hydroperoxides of the type **5** readily.²⁶ However, the rate of rearrangement of the hydroperoxide to lactone is slower than that of cyclohexanone peroxide. Therefore, the hydroperoxide **5** has enough time to undergo decomposition to adipic acid which, in the case of hydroperoxides prepared from 2-halocyclohexanones, is facile and is independent of the catalyst.²⁶

Table V. Oxidation of Ketones by 90% Hydrogen Peroxide Catalyzed by Arsonated Polystyrene 3^a

substrate	time, h	ratio of ketone/H ₂ O ₂	conversion, ^b %	yield, % ^c		yield, % based ^d on H ₂ O ₂ consumed
				ester	acid	
cyclobutanone	0.5	5	98	100	0	100
cyclopentanone	8	1	39	99	1	62
	3.5	5	59	89	11	89
2-methylcyclopentanone	8	5	93	85	15	79
	11	1	58	92	8	70
cyclohexanone	30	1	84	76	24	70
	7.5	1	40	86	14	73
2-methylcyclohexanone	3	5	47	100	0	99
	7	5	79	80	20	80
2-phenylcyclohexanone	5	5	78	100	0	100
2-allylcyclohexanone	15	1	85	100	0	90
	4	5	87	100	0	88
cycloheptanone	23	5	31	29	71	11
2-allylcyclohexanone	9	1	65	70	30	52
estrone-3-methyl ether	24	1	60	100	0	71
pinacolone	25	5	83	100	0	89
acetophenone	29	5	11	100	0	14
	46	1	18	39	61	10
5-nonanone	32	5		no rxn		
2-cyclohexenone	23	5		no rxn		
methyl 2-cyclohexanonecarboxylate	26	1		no rxn		
2-chlorocyclohexanone	25	1		adipic acid		

^a The oxidations were run at 80 °C in dioxane with a molar ratio of H₂O₂:As equal to 30. ^b Conversion to the Baeyer-Villiger products is based on the hydrogen peroxide. ^c Ester represents also lactone and acid denotes also hydroxycarboxylic acids formed by hydrolysis of lactones. The yields are based on the ketone consumed. ^d Yield of lactone or ester based on the consumed hydrogen peroxide.

Table VI. Addition of Hydrogen Peroxide to Ketones^a

ketone	absence of acid, %	time, h	ketone converted to peroxides		
			0.005 M HClO ₄ , ^b %	0.09 M PhAsO ₃ H ₂ , %	time, h
cyclobutanone	33.3	<0.10	33.3	(lactone) ~100	~0.1
cyclopentanone ^c	0	>10	59.9	~20	12
				(lactone) 32	
cyclohexanone	61.0	~3	61.0	61.0	<0.1
cycloheptanone	0	>10	40.4	40.5	~10
2-methylcyclohexanone	0	>24	41.0	0 ^d	5.8
				(lactone) 10	
pinacolone	0	>24	14.5	0 ^d	0.6
				(ester) 11	1.3
acetophenone	0	>24	20.8	6.3	12

^a The reaction has been measured in dioxane at 36 °C starting with concentrations of H₂O₂ = 2.9 M and that of ketone = 3.0 M. ^b Equilibria established in time shorter than 1 min. ^c At 29 °C. ^d No peroxide found throughout the run followed at least to 60% conversion of the ketone to either lactone or ester.

IV. Triphase catalysis, introduced by Regen,²⁷ has so far been applied only to the phase transfer of nucleophiles such as cyanide, phenoxide, and hydroxide ions to effect either nucleophilic substitution of alkyl halides or formation of vicinal dichloropropanes from chloroform and olefins.²⁸

After the synthesis of arsonated polystyrene, we realized the potential for application of these catalysts to the triphase catalysis in oxidations by aqueous hydrogen peroxide. If successful, it would broaden the use of triphase catalysis in organic synthesis, allow us to use diluted aqueous hydrogen peroxide, prevent hydrolysis of lactones, and enable easy separation of the products from the phase transfer agent. The idea was briefly examined in a three-phase system containing 30% aqueous hydrogen peroxide, a chloroform solution of the ketone, and the arsonated polymer in quantities corresponding to 3 mol % of As relative to ketone. The results summarized in Table VIII suggest that, at least in the case of water insoluble ketones such as estrone-3-methyl ether **8** and 2-phenylcyclohexanone, the triphase system is a convenient synthetic

Table VII. Effect of the Ratio of Cyclohexanone to Hydrogen Peroxide on the Rate of Caprolactone Formation^a

catalyst	ketone/H ₂ O ₂	time, h	conversion, %
polymer 3	1	4	34
		7.5	40
polymer 3	5	3	47
		7	78
PhAsO ₃ H ₂	10	4.5	~2
		9.5	~6
(Ph) ₂ AsO ₂ H	peroxide 6	1	40
		3	60
PhAsO ₃ H ₂	ketone/ peroxide 6 = 8	3	14
		6.5	18

^a Dioxane, 80 °C; the molar ratio of H₂O₂:As = 30.

procedure. The corresponding lactones are obtained in high yields and the lactone hydrolysis is prevented.

Peroxides of type **5** (Scheme I) play an important role in the

Table VIII. Triphase Catalysis in Ketone Oxidation^a

substrate	time, h	temp, °C	catalyst	conversion ^b to lactone, %	recovered ^b ketone, %
estrone-3-methyl ether	48	80	PhAsO ₃ H ₂	80	20
	96	90	polymer 3	60	40
2-phenylcyclohexanone ^c	3	80	PhAsO ₃ H ₂	63	3
	14	80	polymer 3	63	28
cyclohexanone ^c	21	65	PhAsO ₃ H ₂	44	35
	27	80	polymer 3	30	44

^a Mixture of 30% aqueous H₂O₂ and chloroform. ^b Amount of ketone and lactone found in the chloroform layer. ^c Na₂SO₄ added.

overall oxidation of ketones in dioxane. It may be argued that even in the three-phase system hydrogen peroxide is transferred into the organic phase via a hydroperoxide of type **5** (Scheme I) rather than via peroxyarsonic acid bonded to the polymer. However, ¹H NMR (δ 0.87, s, CH₃ of estrone vs. δ 1.02, s, CH₃ of estrone peroxide) did not detect any peroxide during the oxidation of estrone **8**. Furthermore, estrone **8** does not react with hydrogen peroxide in the absence of acids. Therefore, peroxides of type **5** could be formed only on the water-organic layer interphase on the surface of or inside the catalyst beads. There, the local concentration of the arsonic groups (50% of phenyl group arsonated) is very high. However, for sterically hindered ketones such as estrone **8**, the addition of hydrogen peroxide to the ketone is a slow step while formation of peroxyarsonic acid is fast (see above). Finally, the same arsonated polymer is an excellent catalyst for olefin epoxidation where the polymer-bound peroxy acid can be the only oxidant. Therefore, we have concluded that at least in the case of estrone **8** and 2-phenylcyclohexanone a real triphase catalysis, characterized by hydrogen peroxide transfer from the aqueous layer into the organic layer via peroxyarsonic acid bound to the polystyrene polymer, is the prevailing, if not the exclusive, reaction path.

However, cyclohexanone behaves differently. The analyses of the organic layer never resulted in a complete material balance. The yields of caprolactone in the organic layer are only moderate even if sodium sulfate is added to the aqueous phase. This is caused by a relatively high solubility of caprolactone in water resulting in an extensive solvolysis of caprolactone to 6-hydroxycaproic acid which has been found in the aqueous layer. Furthermore, cyclohexanone is known to form peroxides even in the absence of acids. The peroxide **5** is water soluble. This would tend to increase the concentration of cyclohexanone in the aqueous hydrogen peroxide. Oxidation of cyclohexanone may then proceed in both phases increasing the possibility for direct oxidation to 6-hydroxycaproic acid.

Triphase catalysis is slower in comparison with a two-phase system containing a soluble phase transfer catalyst such as benzenearsonic acid (Table VII). Nevertheless, the triphase system may prove excellent for preparation of lactones insoluble in water. The potential of the triphase catalysis is made evident from the fact that, while estrone **8** does not react with *m*-chloroperoxybenzoic acid in chloroform,²⁹ it can be effectively oxidized in our triphase system with 30% aqueous hydrogen peroxide.

Experimental Section

I. General Procedures. IR spectra were recorded on a Perkin-Elmer 283 spectrophotometer. ¹H and ¹³C NMR were measured on Varian T-60 and Varian CFT-20 instruments, respectively, by using Me₄Si as internal standard. GLC-MS data were recorded on a Finnigan 3300. GLC analysis was carried out on either a Perkin-Elmer 3920B or a Hewlett-Packard 5710A chromatograph by using biphenyl as internal standard.

Electron microanalyses were carried out with a JEOL JXA-50A scanning electron microscope-microprobe. A beam of 15 kV at 1 × 10⁻⁴ μ A was used. X-ray intensities were measured from Br L α and As L α line emissions. X-ray intensities were taken as a measure of the relative density of a given element as a function of position within the bead. Beads were scanned by moving the bead across the X-ray beam and taking points at various intervals.

II. Materials. Spectrophotometric grade dioxane (Aldrich) was used as received. Aqueous hydrogen peroxide (90 and 30%) was obtained from FMC and Baker, respectively. Reagent grade tetrahydrofuran (Baker) and diethyl ether (Baker) were dried (over lithium aluminum hydride), distilled, and stored under vacuum until ready for use. Arsenic triethoxide, *n*-butyllithium (2.2 M in hexane), and benzenearsonic acid were obtained from Alfa and *p*-toluenearsonic acid from Pfaltz and Bauer, Inc. The starting styrene-1% divinylbenzene copolymers were obtained in the form of 200-400 mesh beads (Bio-Beads SX-1) from Bio-Rad Laboratories, Richmond, Calif.

A. Sources of Ketones. All ketones were obtained from Aldrich Chemical except those below. Cyclohexanone was received from Matheson, Coleman and Bell; 2-phenylcyclohexanone was from Chemical Samples, Inc.; estrone-3-methyl ether and 2-methylcyclopentanone were from Chemicals Procurement Laboratories, Inc.; and 2-cyclohexanonecarboxylate (mixture of methyl and ethyl esters) was from Research Organic/Inorganic Chemical Corp. All ketones were used without further purification.

B. Sources of Lactones, Esters, and Their Derivatives. Caprolactone was obtained from Research Organic/Inorganic Chemical Corp.; *tert*-butyl acetate, δ -valerolactone, and phenyl acetate were from Aldrich; and butyrolactone was from Matheson, Coleman and Bell. The rest of the lactones (6-allylcaprolactone, 6-methylcaprolactone, 5-methylvalerolactone, 6-phenylcaprolactone, and caprylactone) were prepared from the corresponding ketones by a standard oxidation with *m*-chloroperoxybenzoic acid in methylene chloride at 40 °C.³⁰ These lactones were characterized by elemental analyses, GLC-MS, and by ¹H and ¹³C NMR. 6-Methylcaprolactone, ¹H NMR (δ , CDCl₃): 1.35 [d, *J*_{H-H} = 6 Hz, 3 H, HC(CH₃)], 1.3-2.1 [m, 6 H, (CH₂)₃], 2.5-2.9 [m, 2 H, CH₂C(=O)], 4.2-4.7 [m, 1 H, (CH₃)-C(H)(O)]. Anal. Calcd for C₇H₁₂O₂: C, 65.6; H, 9.46. Found: C, 65.2; H, 9.28. 5-Methylvalerolactone, ¹H NMR (δ , CDCl₃): 1.35 [d, *J*_{H-H} = 6 Hz, 3 H, (H)C(CH₃)], 1.4-2.2 [m, 4 H, (CH₂)₂], 2.3-2.8 [m, 2 H, CH₂C(=O)], 4.2-4.7 [m, 1 H, (CH₃)C(H)(O)]. Anal. Calcd for C₆H₁₀O₂: C, 63.1; H, 5.31. Found: C, 62.9; H, 5.15. 6-Phenylcaprolactone, ¹H NMR (δ , CDCl₃): 1.2-2.2 [m, 6 H, (CH₂)₃], 2.4-3.1 [m, 2 H, CH₂C(=O)], 5.1-5.4 [m, 1 H, C(H)(C₆H₅)], 7.3 [s, 5 H, C₆H₅]. Anal. Calcd for C₁₂H₁₄O₂: C, 75.7; H, 7.44. Found: C, 75.8; H, 7.14. 6-Allylcaprolactone, ¹H NMR (δ , CD₃CN): 1.0-2.1 [m, 6 H, (CH₂)₃], 2.1-3.1 [m, 4 H, CH₂C=C and CH₂-C(=O)], 4.1-4.8 [m, 1 H, CH(O)], 4.8-5.4 [m, 2 H, CH₂=C], 5.5-6.3 [m, 1 H, CH=C]. Anal. Calcd for C₉H₁₄O₂: C, 70.1; H, 9.17. Found: C, 70.3; H, 9.32. Caprylactone, ¹H NMR (δ , CDCl₃): 1.3-2.1 [m, 8 H, (CH₂)₄], 2.3-2.7 [m, 2 H, CH₂C(=O)], 4.2-4.5 [m, 2 H, CH₂(O)].

An attempt was made to oxidize estrone-3-methyl ether to its lactone by *m*-chloroperoxybenzoic acid in an analogous manner to the ketones above. However, only the starting ketone was isolated after 48 h in refluxing chloroform. Therefore, estrone-3-methyl ether (1 g, 3.4 mmol) and the arsonic acid derivatized polymer **2** (3.15 g, 5.3 mmol of As) were reacted in a pressure tube at 80 °C for 19 h. The mixture was filtered to remove the insoluble polymer, and the white solid of pure 3-methoxy-D-homo-17 α -oxaestra-1,3,5(10)trien-17-one

was isolated after chloroform evaporation and wash with methanol (0.4 g, 1.4 mmol, 41% yield). ^{13}C NMR (δ , CDCl_3): 126.26 (C-1), 111.75 (C-2), 157.81 (C-3), 55.10 (OCH_3), 113.61 (C-4), 137.36 (C-5), 27.49 (C-6), 26.53 (C-7), 42.67 (C-8), 45.10 (C-9), 131.31 (C-10), 25.99 (C-11), 39.23 (C-12), 83.38 (C-13), 45.04 (C-14), 19.59 (C-15), 28.50 (C-16), 171.06 (C-17), 20.02 (C-18). The ^{13}C resonances were assigned by comparison of the chemical shifts and the off-resonance decoupled spectra with that of a similar steroidal lactone.³¹ The ^1H NMR, IR, and melting point correspond to those described elsewhere.³²

The solvolysis products of ϵ -caprolactone and δ -valerolactone were characterized by ^1H NMR. Methyl 6-hydroxycaproate was synthesized by sodium methoxide catalyzed solvolysis in refluxing methanol; ^1H NMR (δ , CDCl_3): 1.1–1.9 [m, 6 H, $(\text{CH}_2)_3$], 2.1–2.5 [m, 2 H, $\text{CH}_2\text{C}(=\text{O})$], 3.4–3.8 [m, 2 H, $\text{CH}_2\text{-OH}$], 3.65 [s, 3 H, OCH_3]. 6-Hydroxycaproic acid was recognized by characteristic ^1H NMR (δ , CDCl_3): 3.4–3.7 [m, 2 H, CH_2OH] which is distinguishable from the ^1H NMR (δ , CDCl_3): 4.1–4.4 [m, 2 H, $\text{CH}_2(\text{O})$] of ϵ -caprolactone and similar to methyl 6-hydroxycaproate. Hydrolysis of δ -valerolactone in a water/dioxane solution using a catalytic amount of polymer **3** (3 mol %) at 80 °C for 72 h results in 5-hydroxyvaleric acid [^1H NMR (δ , CDCl_3): 1.3–2.0 [m, 4 H, $(\text{CH}_2)_2$], 2.1–2.6 [m, 2 H, $\text{CH}_2\text{C}(=\text{O})$], 3.4–3.8 [m, 2 H, $\text{CH}_2\text{-OH}$] which is distinguishable from δ -valerolactone [^1H NMR (δ , CDCl_3): 4.2–4.6 [m, 2 H, $\text{CH}_2(\text{O})$]]. The other hydroxy acids reported were analyzed by integration of their characteristic ^1H NMR ($\text{CH}_2\text{-OH}$) multiplet using biphenyl as internal standard.

III. Preparation and Characterization of Ketone Peroxides. 1,1'-Dihydroxydicyclohexyl peroxide (analogous to **6**) was synthesized according to the literature procedure;²⁶ IR and mp (67–68 °C) correspond to literature values.²⁶ Anal. Calcd for $\text{C}_{12}\text{H}_{22}\text{O}_4$: C, 62.58; H, 9.63. Found: C, 62.70; H, 9.56. Its ^1H and ^{13}C NMR (δ , dioxane) indicated a mixture of cyclohexanone [^1H NMR 2.1–2.4 [m, 4 H, $\text{CH}_2\text{C}(=\text{O})$]], 1,1'-dihydroxydicyclohexyl peroxide [^1H NMR 1.2–2.0 [m, 10 H, $(\text{CH}_2)_5$]]; ^{13}C NMR 102.0 (C-1)], and 1-hydroxyperoxycyclohexanol [^{13}C NMR 102.8 (C-1)]. The assignments of the ^{13}C NMR C-1 resonance were made by adding an eightfold excess of cyclohexanone to the solution of 1,1'-dihydroxydicyclohexyl peroxide and observing the disappearance of the ^{13}C NMR C-1 resonance of 1-hydroxycyclohexanol due to the conversion of **5** to **6** (Scheme 1).

2-Methyl-1-hydroperoxycyclohexanol was synthesized from 2-methylcyclohexanone (20 g, 179 mmol), 30% aqueous hydrogen peroxide (21.2 g, 187 mmol), and 0.3 g Amberlyst 15 (Rohm and Haas) ion-exchange resin (prewashed with a solution of 90% aqueous hydrogen peroxide in acetonitrile at 60 °C). The reaction mixture was stirred at room temperature overnight. The volume was reduced by evaporation of volatiles in vacuo (0.01 mm) at 40 °C for 6 h until only an oil remained. Iodometric titration gave 6.5 mmol/g of active oxygen (calcd 6.84). ^1H NMR (δ , dioxane- d_8): 1.04 [d, $J_{\text{H-H}} = 7$ Hz, 3 H, $\text{CH}_3(\text{CH})$], 1.2–2.0 [m, 8 H, $(\text{CH}_2)_4$], 2.1–2.4 [m, 1 H, $\text{CH}(\text{CH}_3)$]. ^1H NMR of 2-methylcyclohexanone (δ , dioxane- d_8): 0.95 [d, $J_{\text{H-H}} = 6$ Hz, 3 H, $\text{CH}_3(\text{CH})$], 1.2–2.2 [m, 6 H, $(\text{CH}_2)_3$], 2.2–2.8 [m, 3 H, $\text{CH}-\text{C}(=\text{O})-\text{CH}_2$].

The remaining ketone peroxides were generated both by acidification of a mixture of ketone (3.0 M) and hydrogen peroxide (2.9 M) dissolved in dioxane with catalytic quantities of perchloric acid (0.005 M) and benzenearsonic acid (0.10 M). Their ^1H and ^{13}C NMR were observed in situ. The reaction was monitored by either the disappearance of the signals belonging to the carbonyl carbon and the protons of the methylene groups in the α position to the carbonyl function or the disappearance of the methyl group α or β to the carbonyl and the appearance of the signals of the methyl groups of the expected peroxides. The important chemical shifts which were used to monitor the concentration of the peroxides and ketones in equilibrium are given below. ^1H NMR (δ , dioxane): Pinacolone, 2.11 (s, CH_3); peroxide, 1.50 (s, CH_3); acetophenone, 2.61 (s, CH_3); peroxide 1.73 (s, CH_3); estrone-3-methyl ether, 0.87 (s, $\text{CH}_3\text{-C}$); peroxide, 1.02 (s, $\text{CH}_3\text{-C}$); 2-chlorocyclohexanone, 1.5–2.1 [m, 6 H, $(\text{CH}_2)_3$], 2.2–2.7 [m, 2 H, $\text{CH}_2\text{C}(=\text{O})$], 4.6–5.0 [m, 1 H, CH-Cl]; peroxide, 1.2–2.0 [m, 8 H, $(\text{CH}_2)_4$], 4.1–4.5 [m, 1 H, CH-Cl]. Cycloheptanone, 1.4–2.0 [m, 8 H, $(\text{CH}_2)_4$], 2.3–2.7 [m, 4 H, $\text{CH}_2\text{C}(=\text{O})$]; peroxide, 1.3–2.1 [m, 12 H, $(\text{CH}_2)_6$]. ^{13}C NMR (δ , dioxane) of cyclopentanone, 214 (C-1); peroxide, 121.36 (C-1). Monitoring by ^1H NMR was not possible with cyclopentanone because of overlap of the methylenes in the α position to the carbonyl with the remaining ones.

IV. Typical Procedure for Ketone Oxidation. Polymer **3** (2.67 mmol/g, 0.38 g, 1 mmol) was added to a solution of cyclohexanone (15 g, 153 mmol) and internal standard (biphenyl, 0.40 g, 2.6 mmol) in dioxane (10 mL). A solution of 90% aqueous hydrogen peroxide (31 mmol) was then added. The mixture was heated to 80 °C, samples were withdrawn at intervals, and the reaction was monitored by ^1H and ^{13}C NMR and by GC (employing a 5-ft column containing 5% Carbowax 20M on Chromosorb W). The content of hydrogen peroxide was monitored by iodometric titrations. The catalyst was then filtered off, thoroughly washed with dioxane and diethyl ether, dried in vacuo, and then recycled.

V. Analyses of Reaction Mixtures. Most of the samples were analyzed on a 5-ft GC column containing 5% Carbowax 20M on Chromosorb W at temperatures programmed from 85 °C (2 min) to 180 °C (8 min) at 16 °C/min. The same temperature program with a 6-ft column containing 10% SE-30 on Chromosorb W was used for 2-phenylcyclohexanone and for the mixture of methyl and ethyl 2-cyclohexanonecarboxylates. The reaction mixtures of acetophenone and pinacolone were analyzed with a 5-ft 5% Carbowax 20M on Chromosorb W in series with a 6-ft 10% FFAP on Chromosorb W at the same temperature program as above. The estrone-3-methyl ether oxidations were monitored by ^1H and ^{13}C NMR.

VI. Preparation of Arsonated Polystyrene Polymer. A. Bromination. In a typical bromination, 20 g of the resin beads and iron trichloride (2 g) or iron powder (1 g) were suspended in carbon tetrachloride (100 mL) and cooled to 0 °C. To this vigorously stirred slurry a solution of bromine (27 g, 168 mmol) in carbon tetrachloride (100 mL) was added slowly over a 2-h period with exclusion of light. The solution was left to stir at room temperature for 72 h. Unreacted bromine and solvent were removed by filtration and the resin was washed successively with acetone, 1:1 dioxane:water, dioxane, tetrahydrofuran, and finally diethyl ether. Each of these washings was done by stirring the resin 15–30 min in the appropriate wash solution. When iron powder is used as catalyst, it is first removed from the polymer beads with a magnet and then the polymer is prewashed with 1:1 dioxane:hydrochloric acid, water, and 1:1 water:ammonium hydroxide before the washing described above. This was followed by vacuum drying (25 °C, 0.1 Torr). The elemental analyses of this polymer **3** and the other bromide functionalized polymers are given in Table I.

B. Arsonation. The brominated polymer **3** (5 g) was suspended in 50 mL of dry toluene in the absence of oxygen. A solution of *n*-butyllithium in hexane (2.42 M, 60 mL, 145 mmol) was added under argon to another reaction compartment separated by a sintered glass filter from the polymer suspension. The hexane was removed under vacuum and replaced with dry toluene (60 mL). The solution of *n*-butyllithium was then slowly added to the polymer at –78 °C and let warm to room temperature. The solution was then heated to 60 °C for 3 h. The solvent was removed by filtration; the polymer was washed twice with toluene (30 mL) and finally suspended again in fresh toluene (30 mL).

Arsenic trioxide (22 g, 104 mmol) in 30 mL of diethyl ether was then slowly added under argon at –78 °C. The solution was allowed to warm to room temperature and the suspension was stirred overnight. The resin was then washed three times with anhydrous diethyl ether under argon. The beads were collected by filtration and washed with 1:1 dioxane:water (300 mL), water (200 mL), and finally dioxane (200 mL). The As(III) was oxidized to As(V) with 90% aqueous hydrogen peroxide dissolved in acetonitrile at 60 °C for about 2 h. The beads were then washed with acetonitrile, water, dioxane, and finally diethyl ether. This was followed by vacuum drying (25 °C, 0.1 Torr). The elemental analyses for all polymers are given in Table I.

An alkalimetric titration of polymer **2** was carried out in the following way to confirm the elemental analysis. Polymer **2** (0.5 g) was added to an excess (threefold) of 0.1055 N sodium hydroxide in 50 mL of THF. After several hours, the polymer was filtered and an aliquot of the solution was titrated with 0.1038 N hydrochloric acid to the phenolphthalein end point. Assuming one Na^+ per arsenic, the arsenic content (13%) is within experimental error of that obtained by elemental analysis (13.24%). The elemental analyses of all polymers are given in Table I.

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- (24) At 29 °C (temperature of ^{13}C NMR probe), the ratio of **6:5** is $>7:1$ for an 8:1 cyclohexanone:peroxide **6** ratio and 2:1 for the peroxide **6** itself.
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Biphase and Triphase Catalysis. Arsonated Polystyrenes as Catalysts for Epoxidation of Olefins by Aqueous Hydrogen Peroxide

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Abstract: Arsonated polystyrene resins have been found to be versatile catalysts for olefin epoxidation by aqueous hydrogen peroxide. In a biphasic system consisting of an organic solvent miscible with aqueous hydrogen peroxide and the insoluble resin, the catalysts are efficient for epoxidation of alkenes with internal double bonds and for regio- and stereoselective epoxidation of allylic alcohols. In order to prevent epoxide hydrolysis, 90% aqueous hydrogen peroxide and an excess of olefin are recommended. Olefins can also be epoxidized in a triphase system consisting of a water immiscible solvent, aqueous hydrogen peroxide, and the solid catalyst. The advantage of the triphase system is in the efficient utilization of hydrogen peroxide and prevention of epoxide hydrolysis even if 30% aqueous hydrogen peroxide is employed. In both systems, the catalyst can be quantitatively separated by simple filtration and recycled.

A practical route for direct epoxidation of olefins by aqueous hydrogen peroxide is a long-standing goal in oxidation chemistry. This can be achieved only with the help of suitable catalysts. The search for such a catalyst has centered around group 5a,b and 6a,b metal oxides known for their tendency to generate hydroperoxy and peroxy species by interaction with hydrogen peroxide.¹ Thus, high valent group 6b metal oxides, although inactive with alkenes, were found to catalyze epoxidation of olefinic alcohols to triols via epoxide intermediates.² Also, selenium dioxide, suitable as a catalyst for epoxidation of alkenes, does not avoid hydrolysis of epoxides and accord-

ingly only diols are isolated.³ Only recently, application of substituted areneseleninic acids⁴ and arsenic oxides⁵ resulted in high yields of epoxides. However, in neither of these cases is a convenient and quantitative separation and subsequent recycle of the homogeneous catalysts feasible. This is especially important for the arsenic and selenium based catalysts since they are environmentally detrimental even at low concentrations and cause epoxide hydrolysis during product isolation.

It appeared to us that arsonated polystyrenes, successful as catalysts for the Baeyer-Villiger oxidation of ketones by hydrogen peroxide,⁶ could circumvent the difficulties previously