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(23) Hydrogen peroxide reacts with cyclobutanone immediately to form an equilibrium concentration of 1-hydroperoxycyclobutanol. Since to a solution of cyclobutanone in dioxane first hydrogen peroxide and then benzenearsonic acid were added, it is believed that the observed oxidation of cyclobutanone proceeded via 1-hydroperoxycyclobutanol. WARNING! Addition of 90% aqueous hydrogen peroxide diluted by dioxane to a dioxane solution of cyclobutanone and benzenearsonic acid leads to a very exothermic and potentially explosive reaction!

(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 biphase 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 peroxo 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 accordingly only diols are isolated.[3] Only recently, application of substituted areneseleninic acids[4] and arsenic oxides[5] 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

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Table I. Epoxidation of Olefins in Biphase System[a]

olefin	catalyst	time, h	conversion, %		yield,[b] %
			epoxide	diol	
1-octene	polystyrene **3**	5	15	*c*	58
cyclohexene	polystyrene **3**	2	49	0	100
		5	69	5	90
		7.5	67	14	78
	4-$CH_3C_6H_4AsO_3H_2$	2	78	0	100
		5	72	15	73
	$PhAsO_3H_2$	2	79	0	89
	polystyrene **2**	4	47	22[d]	70
	(methanol)	7	16	57	18
norbornene	polystyrene **2**	1	56	0	100
		2.5	75	0	100
2,3-dimethyl-2-octene	polystyrene **2**	0.5	72	0	100
		5	100	0	100
allyl alcohol	polystyrene **3**	2	33	0	92
		5	57		96
	$PhAsO_3H_2$	2	46		82
		5	68		80
	As_2O_5	1.25	64		79

[a] Epoxidations were run at 80 °C in dioxane unless stated otherwise. The molar ratio of olefins:H_2O_2(90% aqueous):catalyst = 150:30:1. [b] The yield of epoxides (diols not included) is based on H_2O_2 consumed. [c] NMR of the residue after solvent evaporation suggests presence of polyethers formed from octene 1,2-oxide. [d] Mixture of 1,2-cyclohexanediol and 2-methoxycyclohexanol.

encountered in olefin epoxidation. It is the stability of the C–As bond[7] as compared with the C–Se bond,[8] weak acidity of arenearsonic acids (pK_a = 3.82 for toluenearsonic acid[9] compares well with the pK_a = 3.82 for *m*-chlorobenzoic acid[10]), easy separation of the arsonated polystyrenes from the reaction mixture, and a novel, facile route to arsonated polystyrenes[6] which influenced our choice. The results obtained by application of these catalysts to olefin epoxidation are summarized in this report.

Results and Discussion

Epoxidation of Olefins in a Biphase System.[11] In the biphase system, the arsonated polystyrenes **1**, **2**, and **3** (7%, 25%, and 50% of the phenyl groups are arsonated, respectively) proved to be excellent catalysts for epoxidation of a variety of olefins by 90% aqueous hydrogen peroxide (Table I). Dioxane is the solvent of choice since it is the best solvent for (a) swelling of functionalized polystyrene–divinylbenzene (1%) copolymers,[12] (b) Baeyer–Villiger oxidation of ketones by hydrogen peroxide catalyzed by the same arsonated polystyrenes,[6] and (c) olefin epoxidation by stoichiometric quantities of polystyrene functionalized by peroxycarboxylic groups.[12] Protonic solvents such as methanol can also be used. However, slower reaction rates[13] and extensive solvolysis of epoxides are inevitable (Table I).

The catalyst **3** was recycled five times (Table II) with no apparent decrease in catalytic activity which indicates little or no loss of arsenic. The monomeric analogues such as benzenearsonic (**4**) and toluenearsonic (**5**) acids are two to three times more active (Table I) than the arsonated polystyrenes. After the same time intervals, yields of epoxides obtained in the presence of **4** and **5** are the same. This indicates the insensitivity of the catalytic activity of arenearsonic acids to aromatic substitution. Therefore, the slower rates of epoxidations observed for arsonated polystyrenes should reflect only the effect of substrate diffusion into the pores of the polymer. A similar reduction in the reaction rate was previously observed for ketone oxidation.[6]

The ease of olefin epoxidation by hydrogen peroxide in the presence of arsonated polystyrene follows the trend observed in the case of peroxy acids, e.g., *m*-chloroperoxybenzoic acid: terminal < dialkyl < trialkyl olefins.[13] However, in contrast to organic peroxy acids,[14] the epoxidation of allyl alcohols in our system is faster than that of the corresponding alkenes (Table I).

Table II. Effect of Recycle on the Activity of Arsonated Polystyrene in the Biphase System[a]

cycle no.	conversion, %[b]		yield,[c] %
	epoxide	diol	
1	63	17	74
2	69	5	90
3	67	9	87
4	70	4	95
5	68	5	85

[a] Epoxidation of cyclohexene was run for 5 h at 80 °C in dioxane with polystyrene **3** as the catalyst and the molar ratio of olefin: H_2O_2(90% aqueous):catalyst = 150:30:1. [b] Based on the amount of hydrogen peroxide added to the reaction mixture. [c] Yield of epoxide only is based on hydrogen peroxide consumed.

The observed facile epoxidation of allyl alcohols suggested a close interaction of the hydroxy group of the alcohol with the arsonic groups of the catalyst resulting possibly in the formation of allyl arsonates.[15] This prompted a brief examination of the regio- and stereoselectivities in allylic alcohol epoxidations by hydrogen peroxide catalyzed by these novel catalysts. For comparison with other systems, geraniol and 2-cyclohexen-1-ol were chosen as the convenient substrates. The results summarized in Tables III and IV show that, in the presence of benzene- or toluenearsonic acid, geraniol is epoxidized predominantly to 2,3-epoxygeraniol (**6**) [6,7-epoxygeraniol (**7**) is the minor product] and that 2-cyclohexen-1-ol gives mainly *syn*-2,3-epoxycyclohexanol. Indeed the regio- and stereoselectivities observed in our system are approaching those achieved by $VO(acac)_2$ in epoxidations of the same substrates by *tert*-butyl hydroperoxide.[16] These high selectivities contrast sharply with low regio- and stereoselectivities introduced by substituted benzeneseleninic acids.[4] This finding, combined with the low stability of the C–Se bond of benzene-seleninic acid in the epoxidation mixture,[4] illustrates the advantages of the catalysts based on arsenic.

In contrast to either arsenic oxide or arenearsonic acids, the arsonated polystyrenes induce only moderate or low regio- and stereoselectivities. These results apparently reflect a relatively high local concentration of peroxyarsonic groups as well as a

Table III. Regioselectivity in Epoxidation of Geraniol[a]

catalyst	time, h	conversion, % 6	7	diepoxide	ratio 6:7	yield,[b] %
polymer **1**	3	46	9	8	5	78
polymer **2**	3	36	12	7	3	72
polymer **3**	5	26	14	7	1.9	67
polymer **3**[c]	4	25	14	3	1.8	55
$PhAsO_3H_2$	4	65	3	1	22	69
$V(O)(acac)_2$[d]					100	
$2,4-(NO_2)_2C_6H_3SeO_2H$[e]					0.5	
$3-ClC_6H_4CO_3H$[f]					0.6	

[a] Unless otherwise stated, the epoxidation was studied in dioxane at 80 °C with the molar ratio of geraniol:H_2O_2(90% aqueous):catalyst = 30:30:1. [b] The yields of epoxide are based on H_2O_2 consumed. [c] First recycle of the catalyst. [d] Reference 16; oxidant is *t*-BuOOH. [e] Reference 4. [f] The oxidation was run in dioxane at 50 °C for 3 h with the ratio of geraniol:peroxy acid equal to 1.

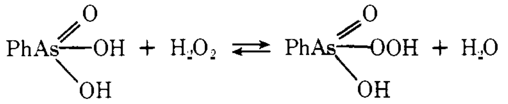
Table IV. Stereospecificity in Epoxidation of 2-Cyclohexene-1-ol[a]

catalyst	time, h	conversion to epoxide, % syn	anti	ratio syn:anti	yield,[b] %
polymer **1**	6	28	6	4.6	79
	9	35	8	4.4	74
polymer **2**	3	21	6	3.5	66
	6	31	8	3.9	57
polymer **3**	9	25	8	3.1	67
$4-CH_3C_6H_4AsO_3H_2$	2	40	2	20	78
$V(O)(acac)_2$[c]				49	
$2,4-(NO_2)_2C_6H_3SeO_2H$[d]				1.5	
m-$ClC_6H_4CO_3H$[e]				12	

[a] Unless otherwise stated, the epoxidation was studied in dioxane at 80 °C, with the molar ratios of 2-cyclohexen-1-ol:H_2O_2(90% aqueous): catalyst = 30:30:1. [b] The yields of epoxides are based on H_2O_2 consumed. [c] The oxidant is *t*-BuOOH, ref 16. [d] Reference 4. [e] The oxidation was run in refluxing dichloromethane with the ratio of the peroxy acid to 2-cyclohexen-1-ol equal to 1. A similar ratio (11.5) of syn to anti epoxides was reported in ref 16.

high mobility of the polymer chains in the swollen arsonated polystyrene beads. When diffused into the polymer, the double bonds of the allylic alcohol can interact not only with the peroxyarsonic groups to which the hydroxy group of the allylic alcohol is bonded ("intramolecular epoxidation"), but also with the peroxyarsonic groups not associated with the allylic alcohol ("intermolecular epoxidation"). This explanation requires an increase in the probability for the "intramolecular epoxidation" with decreasing concentration of the arsonic groups in the polymer. Indeed, the expected increase in the regio- and stereoselectivities with the decrease in the degree of substitution has been experimentally verified (Tables III and IV).

Water is the byproduct of olefin epoxidation by hydrogen peroxide. Unfortunately, water causes slow hydrolysis of the product epoxide and prolongs the reaction time by decreasing the amount of peroxyarsonic groups available for the epoxidation (equilibrium 1). This becomes critical mainly in the latter stages of the reaction when most of the hydrogen peroxide is consumed. Therefore, increase in the reaction rate is essential for optimal yields of epoxides. In solvents miscible with aqueous hydrogen peroxide, this can be achieved by increasing the concentration of olefin and by employment of 90% aqueous hydrogen peroxide. However, for prevention of epoxide hydrolysis and for effective utilization of hydrogen peroxide in the form of 30% aqueous solution, the separation of the aqueous and organic layers becomes necessary. For this reason, triphase catalysis has been developed for olefin epoxidation.



$$PhAs(=O)(OH)-OH + H_2O_2 \rightleftharpoons PhAs(=O)(OH)-OOH + H_2O \quad (1)$$

Triphase Catalysis. This system consists of water-insoluble organic solvent, aqueous hydrogen peroxide, and catalytic quantities of the arsonated polystyrene in the form of beads. No detailed study of the effect of the organic solvents has been carried out. However, preliminary results indicate that chlorinated hydrocarbons, such as chloroform, seem to be the best choice. The results summarized in Table V show that the ease of olefin epoxidation follows the same trend as that found in dioxane (biphase catalysis, Table I) and demonstrated for peroxycarboxylic acids: trialkyl > dialkyl > monoalkyl.[13] The loss of olefin can be fully accounted for by epoxide formation; no diols are detected. Except for 1-octene, the yields of epoxides

Table V. Epoxidation of Olefins by 30% Hydrogen Peroxide in the Triphase System[a]

olefin	catalyst	time, h	conversion, %[b] epoxide
1-octene	polymer **3**	31	11
cyclooctene	polymer **3**	21	69
		45	89
	$PhAsO_3H_2$	22	47
		43	67
	$4-CH_3C_6H_4AsO_3H_2$	29	91
	As_2O_5	57	24
2,3-dimethyl-2-octene	polymer **3**	10	78
		18	93
	$4-CH_3C_6H_4AsO_3H_2$	2	77
		6	98

[a] The epoxidation was run at 70 °C in a chloroform-30% aqueous H_2O_2 mixture enclosed in a glass pressure reactor with a molar ratio of H_2O_2:olefin:catalyst = 60:30:1. [b] The conversion is based on the starting amount of olefin used. The yield of epoxide and diol based on either the hydrogen peroxide or the olefin consumed is 100% except in the case of 1-octene where some decomposition of H_2O_2 takes place.

Table VI. Effect of Recycle on the Activity of Arsonated Polystyrene in the Triphase System[a]

cycle no.	time, h	conversion,[b] %
1	45	89
2	55	92
3	45	85
4	60	93
5	46	77

[a] Epoxidation of cyclooctene was run at 70 °C in a mixture of chloroform and 30% aqueous hydrogen peroxide with polystyrene **3** as the catalyst and the ratio of H_2O_2:cyclooctene:catalyst = 60:30:1. [b] The yield of epoxide based on either the hydrogen peroxide or the olefin consumed is 100%; no diol was detected.

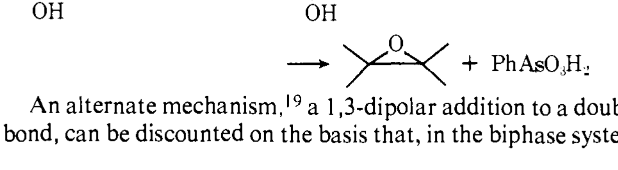
based on hydrogen peroxide consumed are also close to quantitative. These findings strongly suggest that the epoxidation takes place in the organic layer and that the microenvironment around the oxidant, polymer bound peroxyarsonic groups, must be predominantly or exclusively nonaqueous.

When compared with toluenearsonic acid, epoxidation of olefins catalyzed by the arsonated polystyrenes was found to be slower by a factor of 2 to 3. A similar decrease in the reaction rates was found in the biphase system. This suggests that the difference reflects the effect of the diffusion of the substrate and hydrogen peroxide into the polymer. Surprisingly, olefin epoxidation catalyzed by benzenearsonic acid is slower than that catalyzed by polymer **3** despite the fact that in dioxane benzene- and toluenearsonic acids were shown to be of comparable activity. The observed difference should be a reflection of the difference in the partition coefficients of the two acids or their peroxy acid forms between the organic and aqueous phases. Indeed, the solubility of toluenearsonic acid in the organic phase was found to be higher than that of benzenearsonic acid.

The arsonated polystyrenes can be separated from the reaction mixture by filtration and recycled (Table VI). A slight decrease in the activity was noticed only on the fourth recycle. This again demonstrates the stability of the C–As bond toward oxidation and hydrolysis.

Mechanism of Epoxidation. The initial step is a rapid equilibrium (eq 1) between hydrogen peroxide and the arenearsonic acids leading to peroxyarsonic acids. This is supported by the rapid ^{18}O exchange between $^{18}OH_2$ and arsonate ions[1] and by the finding that hydrogen peroxide is a better nucleophile than water by a factor of 500 to 1000.[17] The necessary byproduct of olefin epoxidation by hydrogen peroxide is water. Thus at the end of the reaction, water is present in a much higher concentration than hydrogen peroxide. Nevertheless, hydrogen peroxide can be utilized quantitatively for olefin epoxidation at least in the case of 2,3-dimethyl-2-octene (Table I). This finding and the analogy to the acid-catalyzed equilibrium between acetic acid and hydrogen peroxide[18] would suggest that the equilibrium (eq 1) lies on the side of peroxyarsonic acids.

The effect of the olefin structure on the ease of epoxidation corresponds to that found in the epoxidations of olefins by peroxycarboxylic acids, suggesting an analogous mechanism[13] for the rate-limiting step in both cases. The mechanism can thus be expressed by a concerted process (eq 2).



(2)

An alternate mechanism,[19] a 1,3-dipolar addition to a double bond, can be discounted on the basis that, in the biphase system (Table I), the rate of cyclohexene and norbornene epoxidation is very similar. The same argument was used for rejection of the 1,3-dipolar addition in the case of olefin epoxidation by peroxycarboxylic acids[20,21] and by molybdenum peroxides.[21]

Experimental Section

General Procedures. The spectra were recorded on the following instruments: ^1H NMR on Varian T-60, ^{13}C NMR on Varian CFT-20 using Me_4Si as internal standard, and GC–MS on Finnigan 3300. The samples were analyzed by GC on Perkin-Elmer 3920B or Hewlett-Packard 5710A chromatographs.

Materials. The following compounds were used as received. *Solvents and reagents:* dioxane and chloroform (Spectrophotometric Grade, Aldrich), acetonitrile (Matheson, Coleman and Bell), hydrogen peroxide 90% (FMC) and 30% (Baker), benzenearsonic (Alfa) and toluenearsonic acids (Pfaltz and Bauer, Inc.). *Olefins:* cyclohexene, cyclooctene, 2-cyclohexen-1-ol, 1-octene, allyl alcohol, geraniol, norbornene, and 2,3-dimethyl-2-octene (Chemical Samples Co.). *Epoxides:* cyclohexene oxide, 1,2-cyclohexanediol, cyclooctene oxide, glycidol (all from Aldrich). *Alcohols:* glycerol (Matheson, Coleman and Bell) and 1,2-octanediol (ROC/RIC).

Epoxidation[13] of 1-octene, geraniol, 2-cyclohexen-1-ol, 1-norbornene, and 2,3-dimethyl-2-octene by *m*-chloroperoxybenzoic acid in dichloromethane yielded 1,2-octane oxide, a mixture of 2,3-epoxygeraniol and 6,7-epoxygeraniol, a mixture of *syn*- and *anti*-2,3-epoxycyclohexanol, norbornene oxide, and 2,3-dimethyl-2,3-octene oxide, respectively.

Typical Procedure for Olefin Epoxidation in the Biphase Catalysis. Polymer **3** (0.50 mmol of As) was added to a solution of cyclohexene (6.15 g, 75 mmol) and biphenyl (0.205 g, 1.33 mmol) in dioxane (13 g). A 90% aqueous hydrogen peroxide solution in acetonitrile (30% solution, 15 mmol) was added to this solution at room temperature. The mixture was then stirred at 80 °C. Samples were taken at appropriate intervals. The content of epoxide was monitored by GC (6-ft column, 10% SE-30 on Chromosorb W) and the content of hydrogen peroxide by iodometric titration. The polymer was removed by filtration, washed with dioxane and diethyl ether, and then recycled. The solvent was evaporated in vacuo and the residue was analyzed by ^1H NMR.

Typical Procedure for Olefin Epoxidation in the Triphase Catalysis. A mixture of polymer **3** (0.25 mmol of As), cyclooctene (0.825 g, 7.5 mmol), biphenyl (0.10 g, 0.65 mmol), and chloroform (7 g) was placed into a glass pressure vessel. Aqueous 30% hydrogen peroxide (1.7 g, 15 mmol) was then added to the solution. The vessel was closed and heated at 70 °C. The progress of the reaction was monitored by GC (5-ft column, 5% Carbowax 20M on Chromosorb W) after appropriate intervals. After 45 h, the reaction was stopped and the polymer was filtered off. The water and chloroform layers were then separated. The organic layer was analyzed by ^1H NMR. The amount of hydrogen peroxide was determined by iodometric titration of the aqueous layer. The catalyst was thoroughly washed with dioxane and diethyl ether and then recycled.

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Studies of the Reactions of Molecular Fluorine with Methane, Acetylene, Ethylene, Allene, and Other Small Hydrocarbons in Matrices at Low Temperatures

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Abstract: Reactions of molecular fluorine with small hydrocarbons were studied in fluorine and argon-fluorine matrices. Certain hydrocarbons (methane, acetylene, benzene, ethane, etc.) could be condensed into a pure fluorine matrix without reaction. Ethylene and allene could also be condensed in fluorine without reaction, but did react when exposed to light in the wavelength region from 1 to 4 μ. The ethylene reaction produced either 1,2-*gauche*- and *trans*-difluoroethane or vinyl fluoride and hydrogen fluoride. Propylene, butadiene, and cyclohexene reacted (spontaneously) with molecular fluorine in low-temperature matrices.

Introduction

Fluorine is known to react explosively with hydrocarbons in the gas phase via a free radical chain mechanism.[1] As a result, molecular complexes and reaction intermediates of the fluorine molecule with hydrocarbons are difficult to study; however, they can be investigated at low temperatures in solid matrices of fluorine or mixtures of fluorine and argon. In low-temperature solids, reaction will occur primarily between nearest-neighbor molecules. In dilute matrices, where only one fluorine molecule is likely to be a nearest neighbor, reactions of a single fluorine molecule may be studied. Preliminary reports of our results have been published.[2,3]

Experimental Section

We have studied the reactions of small saturated and unsaturated hydrocarbons, e.g., CH_4, C_2H_4, C_2H_2, C_2H_6, and C_6H_6, with fluorine in pure fluorine matrices as well as in matrices of fluorine and argon.[2,3] A schematic of the equipment is shown in Figure 1. The reactants were not mixed until they condensed at the cold surface; condensations were carried out for a period of 1 h at a matrix gas rate of ~2 mmol/h on a polished copper surface held at 15 K. Spectra were taken with a Beckman I.R.-9 spectrometer. Fluorine (98%) was obtained from Linde. High-purity fluorine was obtained from the Chemical Engineering Division, Argonne National Laboratory. An attempt was also made to observe UV-vis-near IR spectra of an F_2-ethylene complex. The matrix was formed on a sapphire window and transmission spectra were taken with a Cary 14 spectrometer.

Results

Typical spectra for hydrocarbons isolated in a fluorine matrix are shown in Figure 2 and the observed bands listed in Table I. One sees from comparison of observed frequencies to gas-phase values that a fluorine matrix is a very nonperturbing matrix.

A list of the hydrocarbons studied and their behavior is given in Table II. It was found that the alkenes either reacted with F_2 during the trapping process or they could be caused to react by exposure to near-infrared radiation from the spectrometer light source after trapping. Neither the alkanes nor alkynes gave any indication of reaction when isolated in a fluorine matrix or as a result of prolonged exposure to the spectrometer light source. This was also the case for benzene. Reactions of the alkenes yielded a mixture of products with the major species resulting either from F_2 addition to the double bond or HF elimination with formation of monofluoro product. Thus, for ethylene, the major products are 1,2-difluoroethane and vinyl fluoride.

The reaction of ethylene with F_2 has been studied extensively and measured frequencies of the product species are given in Table III. Figures 3 and 4 illustrate the photolytic reaction of ethylene in a pure fluorine matrix and a mixed fluorine/argon matrix. The major difference between the two matrices appears to be in the relative amounts of 1,2-difluoroethane and vinyl fluoride formed. The F_2/Ar matrix enhances the formation of vinyl fluoride. The 1,2-difluoroethane is produced as both the trans and gauche isomers. Their identification is based on previously assigned argon matrix spectra.[5] As also observed

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