Table I. Yields of Products Obtained from Reaction of 1 with $Mo(CO)_6/Al_2O_3$

R	yield of 2,[a] %	R	yield of 2,[a] %
p-$CH_3OC_6H_4$	60	p-$C_6H_5C_6H_4$	73
p-ClC_6H_4	83	1-adamantyl	88
p-BrC_6H_4	71	2-naphthyl	80

[a] Yields are of pure materials. Products were identified by comparison of melting or boiling points and spectral data (IR, NMR) with authentic samples.[4]

particularly by Posner and co-workers,[1] have clearly demonstrated the utility of alumina as a support.

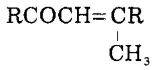
Comparatively little work has been done in the area of organic reactions effected by organometallic compounds supported on alumina. Molybdenum hexacarbonyl on alumina can catalyze olefin disproportionation and isomerization reactions.[2] The nature of the molybdenum species adsorbed on alumina (at different temperatures) is a subject of some controversy.[3] We now report a simple and mild dehalogenation reaction effected by $Mo(CO)_6$ on alumina.

Treatment of molybdenum hexacarbonyl, adsorbed on alumina, with an α-halo ketone (1) in tetrahydrofuran at room temperature for 18 h gives the monoketone (2) in 60–88% yield (eq 1). Product yields for several R groups

$$\underset{1}{RCOCH_2Br} + Mo(CO)_6/Al_2O_3 \xrightarrow{THF} \underset{2}{RCOCH_3} \quad (1)$$

are listed in Table I. Bromides are more reactive than chlorides. 2-Bromo-4′-phenylacetophenone (1, R = p-$C_6H_5C_6H_4$) was recovered unchanged when exposed to alumina in the absence of the metal carbonyl.

There are genuine advantages of this method when compared with conditions needed for the homogeneous reaction previously described by Alper and DesRoches.[4] Reaction of an α-halo ketone with $Mo(CO)_6$ in refluxing 1,2-dimethoxyethane (~82 °C), for 48 h, afforded the α,β-unsaturated ketone 3 in addition to 2. Using $Mo(CO)_6/Al_2O_3$ enables one to effect the dehalogenation under very gentle conditions, avoiding the formation of the condensation byproduct 3. Furthermore, the reaction is faster than that using homogeneous conditions, and the yields of 2 are consistently higher (e.g., 2, R = 1-adamantyl, is formed in 88% yield by $Mo(CO)_6/Al_2O_3$ but in only 14% yield by $Mo(CO)_6$ under homogeneous conditions).



$$RCOCH{=}\underset{\displaystyle CH_3}{C}R$$

3

Experimental Section

Spectral data were recorded with a Unicam SP-1100 infrared spectrometer and Varian T-60 or HA-100 proton magnetic resonance spectrometers. Solvents were dried by standard methods. Molybdenum hexacarbonyl and all α-halo ketones were commercial products. All reactions were run under a dry nitrogen atmosphere.

General Procedure for Reaction of α-Halo Ketones with $Mo(CO)_6/Al_2O_3$. Alumina (30 g, Fisher A-540) was dried overnight at 300 °C. After cooling to room temperature, it was suspended in hexane (180 mL) containing $Mo(CO)_6$ (2.64 g, 10.0 mmol). The hexane was removed by rotary evaporation, and $Mo(CO)_6/Al_2O_3$ was then heated at 100 °C (oil-bath temperature) for 1 h. To the cooled solid was added the α-halo ketone (1, 3.0 mmol) in tetrahydrofuran (60 mL), and the reaction mixture was stirred at room temperature for 18 h. Workup, after filtration, was effected according to the procedures described for the homogeneous reaction.[4]

Acknowledgments. We are grateful to the National Research Council of Canada for support of this research.

Registry No. 1 (R = p-$CH_3OC_6H_4$), 2632-13-5; 1 (R = p-ClC_6H_4), 536-38-9; 1 (R = p-BrC_6H_4), 99-73-0; 1 (R = p-$C_6H_5C_6H_4$), 135-73-9; 1 (R = 1-adamantyl), 5122-82-7; 1 (R = 2-naphthyl), 613-54-7; 2 (R = p-$CH_3OC_6H_4$), 100-06-1; 2 (R = p-ClC_6H_4), 99-91-2; 2 (R = p-BrC_6H_4), 99-90-1; 2 (R = p-$C_6H_5C_6H_4$), 92-91-1; 2 (R = 1-adamantyl), 1660-04-4; 2 (R = 2-naphthyl), 93-08-3; $Mo(CO)_6$, 13939-06-5; Al_2O_3, 1344-28-1.

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Epoxidation of Alkenes with O-Ethylperoxycarbonic Acid Generated in Situ in an Alkaline Biphasic Solvent System

Robert D. Bach,* Michael W. Klein, Rose A. Ryntz, and Joseph W. Holubka

Department of Chemistry, Wayne State University, Detroit, Michigan 48202

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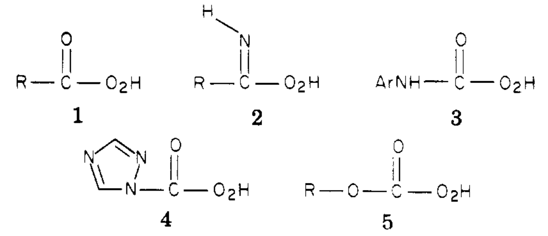
The direct oxidation of an alkene to its 1,2-epoxide is most typically accomplished by an organic peracid[1] (1)



such as m-chloroperbenzoic acid (MCPA).[2] Alternate procedures based upon the utilization of hydrogen peroxide as the oxidant have also been developed, most notably by Payne.[3] Although hydrogen peroxide itself is not sufficiently reactive to epoxidize a nonconjugated carbon–carbon double bond, its reactivity can be markedly enhanced by placing the OOH moiety in conjugation with a multiple bond as exemplified by structures 1–5. A synthetically useful adaptation of this principle has been accomplished by the in situ formation of a peroxyimidic acid (2) by the addition of H_2O_2 to a nitrile.[4] Both acetonitrile[3a,5] and benzonitrile[3b] have been employed as a coreactant in the epoxidation of a variety of alkenes. Peroxybenzimidic acid (2, R = C_6H_5) has been shown to be a more reactive but less discriminating epoxidizing reagent than MCPA in its reactions with polyunsaturated substrates.[6] N-Arylperoxycarbonic acids (3), derived from the addition of H_2O_2 to aryl isocyanates, have also found

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application in oxirane syntheses.[7] More recently, Rebek[8] has developed several peroxycarbamates related to **3** and **4** that exhibit a high reactivity toward alkenes and form oxiranes under very mild conditions.[9]

Our objective in the present study was to develop a method of preparing peroxycarbonic acids (**5**) from readily available starting materials that could be utilized without isolation. We now describe a new method of epoxidizing alkenes that utilizes *O*-ethylperoxycarbonic acid (**6**) which is formed in situ by the reaction of H_2O_2 with ethyl chloroformate.

Although dialkyl esters of peroxycarbonic acid ($ROCO_3R'$)[10a] and peroxydicarbonates ($(ROCOO)_2$)[10b] are stable isolable compounds, an *O*-alkylperoxycarbonic acid (**5**) has only recently been reported.[11] *O*-Benzylperoxycarbonic acid was prepared from dibenzylperoxydicarbonate and alkaline H_2O_2 in methanol solvent. It was shown to be considerably less stable than a peroxycarboxylic acid (**1**) and had a half-life of about 61 h at room temperature in benzene solvent. However, it is an effective epoxidizing reagent and exhibited a reactivity toward *trans*-stilbene that was intermediate between that of peroxybenzoic acid and MCPA in benzene.[11]

Our procedure utilizes a biphasic solvent system that allows us to take advantage of the use of 30% H_2O_2 in an aqueous layer and CH_2Cl_2 as a second phase since the rate of epoxidation of alkenes is maximized in nonpolar solvents. *O*-Ethylperoxycarbonic acid (**6**) is produced at the interface by the reaction of H_2O_2 with ethyl chloroformate (eq 1).

$$\mathrm{EtOCOCl} + H_2O_2 \rightarrow \underset{\mathbf{6}}{\mathrm{EtOCOO_2H}} + \mathrm{HCl} \qquad (1)$$

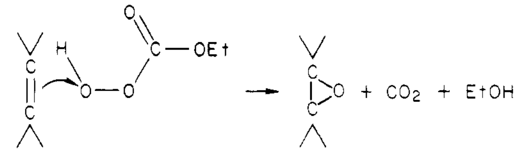
The epoxidizing reagent should be formed in the presence of a buffer to neutralize the HCl produced since the decomposition of the CO_3H functional group is catalyzed by both acids and bases. When Na_2HPO_4 was used as a buffer, the reaction medium was slightly acidic (method A) and the pH was observed to decrease from 6.8 to 4.5 during the course of the reaction. Alternatively, if alkaline conditions are desired, because of an acid-sensitive alkene or epoxide, Na_3PO_4 may be used as the buffer and the pH maintained within a range of 9.5–8.8 (method B). Obviously, the pH can be varied by the choice of the proper buffer system. There have been only two other examples of alkaline biphasic epoxidation and both procedures utilized MCPA.[12,13] Our procedure offers a distinct advantage in chemoselectivity with polyfunctional substrates over more commonly used oxidants like MCPA. The attempted Baeyer–Villiger reaction with **6** and cyclohexanone did not produce a detectable amount of caprolactone in 16 h at ambient temperature.

Table I. Two-Phase Epoxidation of Alkenes with *O*-Ethylperoxycarbonic Acid[a]

alkene	method	reacn time, h	isolated yield of epoxide[b]
cyclohexene	A[c]	24	48 (77)
	B[d]	24	55 (84)
	B	3	(65)
1-methylcyclohexene	B	3	59 (80)[e]
norbornene	A	24	79
	B	17	82 (94)
	B	3	(77)
cyclooctene	A	24	85 (95)
	B	24	85 (94)
	B	1.5	(90)
1-nonene	A	48	15 (33)
	B	28	7 (12)

[a] Unless otherwise specified all experiments utilized 0.03 mol of alkene, 50 mL of 30% H_2O_2 and 50 mL of CH_2Cl_2. [b] The yields given in parentheses were determined by gas chromatography. [c] Method A utilized 8.5 g of Na_2HPO_4 which afforded a pH range of 6.8–4.5 for the initial and final reaction conditions. [d] Method B utilized 23 g of $Na_3PO_4\cdot 12H_2O$ which gave a pH range of 9.5–8.8. [e] The product was partially rearranged to 2-methylcyclohexanone during GLPC analysis.

Although the formation of **6** seems fairly straightforward, its structure is only inferred and is based upon the prior knowledge that peroxycarbonic acids such as **5** afford epoxides[11] and that in the present study we have "activated" H_2O_2 as evidenced by the observation of facile oxirane formation (eq 2).



(2)

The overall procedure is extremely clean and epoxide formation is accompanied by only two innocuous byproducts. Good to excellent yields of epoxides were obtained with all alkenes with the exception of 1-nonene (Table I). Terminal carbon–carbon double bonds typically react more slowly than more highly substituted alkenes with peroxycarboxylic acids. For such slow reactions self-decomposition of the oxidizing agent may become competitive with formation of the desired product. Reaction times of 24 h were chosen for convenience and can be reduced substantially if desired (Table I). As noted earlier,[11] the mechanism for product formation with **6** probably does not differ significantly from that with peroxycarboxylic acids which involves[14] S_N2 displacement by the π bond (HOMO) on the low-lying σ^* –O–O– orbital (LUMO) of the peracid.

This synthetic method offers the advantages of the in situ generation of a relatively inexpensive oxidant under *either* mildly acidic *or* basic conditions. It precludes handling an organic peroxide and utilizes a simple procedure that affords products of high purity uncontaminated by residual byproducts. Peroxycarbonic acids have considerable synthetic potential in oxygen-transfer reactions and should be competitive with existing methods.

Experimental Section

In a typical experiment (method B) 22.8 g (60 mmol) of $Na_3PO_4\cdot 12H_2O$ was dissolved in 50 mL of 30% H_2O_2. A second phase consisting of 2.40 g (30 mmol) of cyclohexene and 5.43 g (50 mmol) of ethyl chloroformate in 50 mL of CH_2Cl_2 was added and the reaction was stirred at room temperature for 24 h. The phases were separated and the aqueous layer was extracted with CH_2Cl_2. The combined organic fractions were washed with 0.2

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M $NaHSO_3$ (or metabisulphite), dried ($MgSO_4$), and concentrated. Distillation at 52 °C (29 mm) afforded 1.57 g (55%) of cyclohexene oxide. A reduction in the amount of H_2O_2 and buffer by as much as one-half did not have a deleterious effect on the yields. The use of either ethyl ether or toluene as solvent resulted in a substantial reduction in yield.

Acknowledgments. We are grateful to the National Institutes of Health for support of this work through Grant ES 00761-07. R.D.B. thanks Professor Roald Hoffmann for his generous hospitality during his sabbatical leave at Cornell where this paper was written.

Registry No. 6, 70288-43-6; cyclohexene, 110-83-8; 1-methylcyclohexene, 591-49-1; norbornene, 498-66-8; cyclooctene, 931-88-4; 1-nonene, 124-11-8; cyclohexene epoxide, 286-20-4; 1-methylcyclohexene epoxide, 1713-33-3; norbornene epoxide, 278-74-0; cyclooctene epoxide, 286-62-4; 1-nonene epoxide, 28114-20-7; 2-methylcyclohexanone, 583-60-8; H_2O_2, 7722-84-1; ethyl chloroformate, 541-41-3.

Synthesis and Thermal Solid-State Polymerization of a New Diacetylene: 2,4-Hexadiynylene Bis(*p*-fluorobenzenesulfonate)

K. C. Yee*

Corporate Research Center, Allied Chemical Corporation, Morristown, New Jersey 07960

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Of all the diacetylenes ($RC\equiv C-C\equiv CR$) reported to date, PTS (R = p-$CH_3C_6H_4SO_3CH_2$)[1] is the most investigated system. PTS monomer has been used as a model compound to study the kinetics and mechanism[2-6] of solid-state polymerization of diacetylenes. The resulting PTS polymer has also been used as a prototype for studying the electrooptical properties[7-20] of a pseudo-one-dimensional organic polymer. Thus far, no large single crystals of diacetylene sulfonates isomorphous with PTS have been available for a comparative investigation. It has been shown that the solid-state reactivity of diacetylene monomers is governed by their spatial arrangement in the crystal lattice as well as by their functional groups.[21] A closely related compound, 2,4-hexadiynylene bis(*p*-chlorobenzenesulfonate), has recently been reported to be inactive in the solid state.[22]

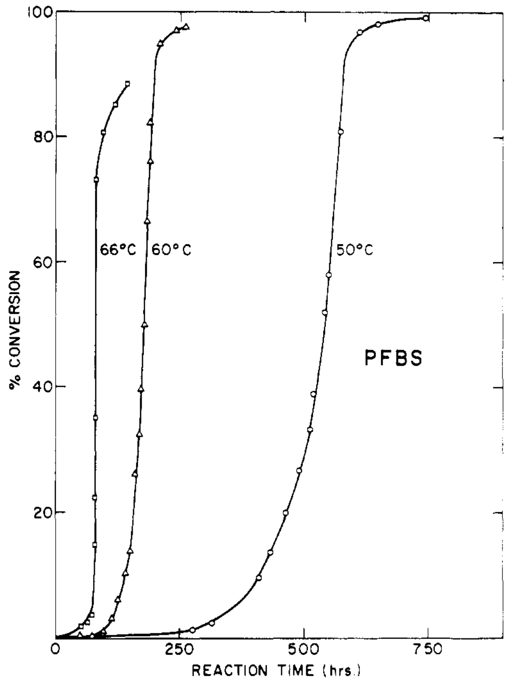


Figure 1. Thermal polymerization of PFBS at 50, 60, and 66 °C. Percent conversion is determined as the insoluble polymer fraction after extraction with acetone at room temperature.

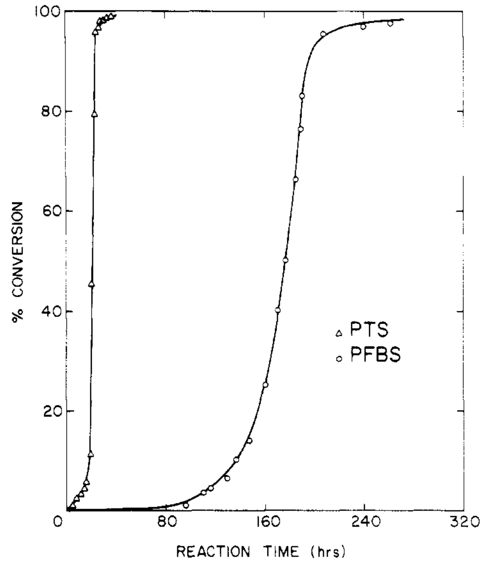
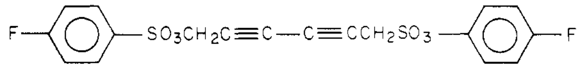


Figure 2. Time–conversion curves for PTS and PFBS at 60 °C. Data for PTS are from ref 23.

The most interesting induction period followed by an autocatalytic behavior observed in the thermal polymerization of PTS has been attributed[2,23] to the large mismatch (~5%) between monomer and polymer repeat units along the chain direction. Our recent findings on the solid-state polymerization of DCHD (R = $CH_2N(C_6H_4)_2$)[24] which shows an S-shaped conversion–time curve upon thermal or γ-ray polymerization have provided supporting evidence that the autocatalytic effect in PTS is due to an increase in chain propagation length. Theoretically, the autocatalytic effect in PTS has been related to the strain energy associated with the monomer–polymer solid solution by Baughman's model.[25] However, any direct comparison between PTS and DCHD must be regarded with caution since they differ in functional groups. This paper reports on the synthesis and solid-state thermal polymerization of the new diacetylene 2,4-hexadiynylene bis(*p*-fluorobenzenesulfonate) (hereafter referred to as PFBS). The structure of the monomer is



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* Address correspondence to the author at Sandoz, Inc., Route 10/Bldg. 520, East Hanover, N.J. 07936.

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