the product. The sample was washed with ethyl ether to remove residual amounts of Me_2SO and then dried in a vacuum desicator: final yield, 0.257 g (95%); mp 128 °C (lit.[59] mp 132–134 °C); UV (H_2O) δ_{max} 267 nm, δ_{min} 235 nm. The NMR results are given in Tables V and VI.

Synthesis of [^{13}C]Methyl Methanesulfonate (MeMS). ^{13}C-labeled methyl methanesulfonate was prepared from the reaction of ^{13}C-labeled methanol (90% ^{13}C enriched, KOR Isotopes) and methanesulfonic anhydride as described in our previous publication.[17] [^{14}C]Methyl methanesufonate was obtained from Amersham Corp. with specific activity of 50 mCi/mmol and purified by distillation under vacuum after mixing with ^{13}C-labeled methyl methanesulfonate.

Methylation of Salmon Sperm DNA with [^{13}C]Methyl Methanesulfonate. (a) Three- and Six-Hour Reactions. An aqueous solution of salmon sperm DNA (0.202 g, 0.60 mmol) was treated at room temperature with a mixture of ^{13}C- and ^{14}C-labeled methyl methanesulfonate (50 μL, 0.60 mmol, 0.08 μCi). The pH of the reaction mixture was maintained at 7.00 ± 0.01 with an automatic titrator, using a 0.1 N sodium hydroxide solution. An aliquot of the reaction mixture (3.5 mL) was withdrawn after 3 h. The sample was dialyzed and its progress was monitored by radioactivity measurements. The methylated DNA sample was finally lyophilized. Six hours after the start of the methylation reaction, the remaining solution was treated following the same procedure, and the product was lyophilized.

(b) Twelve-Hour Reaction. An aqueous solution of salmon sperm DNA (0.250 g, 0.74 mmol) was treated at room temperature for 12 h with a mixture of ^{13}C- and ^{14}C-labeled methyl methanesulfonate (65 μL, 0.74 mmol, 2 μCi). The pH of the reaction was maintained at 7.00 ± 0.02. The sample was worked up as described above.

Chemical Transformation of Methylated Salmon Sperm DNA in Alkaline Solution. (a) ^{13}C NMR Study. A deuterium oxide solution of methylated salmon sperm DNA (3-h reaction with ^{13}C-enriched MeMS) was adjusted to pD 8.6 and allowed to stand at room temperature for a period of 32 h. The base treatment was quenched by readjusting the pD to 7.4, and the ^{13}C NMR spectrum was measured. This treatment was repeated, and ^{13}C NMR spectra were measured after incubating for 56 and 80 h. The final ^{13}C NMR sample was dialyzed against neutral water and then lyophilized.

(b) Reverse-Phase High-Performance Liquid Chromatographic Analysis of Dialysate. The dialysate was redissolved in 5 mL of double-distilled water and was analyzed by reverse-phase HPLC on a radial-compressed C_{18} (10 μm) column from Waters, Inc. eluted at 2 mL/min with a solution containing 0.004 M KH_2PO_4 (pH 5.1) and 8.5% CH_3CN. Preliminary analysis of a pure mixture containing adenine, guanine, 1-methyladenine, 3-methyladenine, and 7-methylguanine was also carried out for identification purposes.

Stability of Mononucleoside at pD 8.6. The decomposition of m^7dG, m^1dA, and m^3dC (5 mg/0.5 mL) in a weak alkaline solution (pD 8.6) was examined by ^{1}H NMR. Integration data of the aromatic as well as the *N*-methyl proton signals were obtained in order to study the course of the degradations taking place in each case, as a function of time.

Methylation of Alkaline Phosphatase Treated Salmon Sperm DNA with [^{13}C]Methyl Methanesulfonate. (a) Alkaline Phosphatase Treatment. Purified salmon sperm DNA (0.400 g, 1.2 mmol) in 5 mL of 0.1 N Tris buffer pH 8.0 was incubated for 1 h at 37 °C with 90 units of alkaline phosphatase type III. The product of this incubation was then extensively dialyzed initially against 100 mL of Tris buffer, pH 7.2 (2 × 3 h) and neutral water (3 × 3 h) and then lyophilized.

(b) Methylation with ^{13}C-Enriched MeMS. An aqueous solution (5 mL) of the alkaline phosphatase treated DNA (0.130 g, 0.39 mmol) was reacted at room temperature with ^{13}C- and ^{14}C-labeled MeMS (30 μL, 0.35 mmol, 6 μCi) for a period of 3 h. The reaction conditions and the product isolation were carried out as previously described.

Methylation of Salmon Testes DNA with [^{13}C]Methyl Methanesulfonate. An aqueous solution (10 mL) of salmon testes DNA (0.100 g, 0.30 mmol) was treated at room temperature for 78 h with a mixture of ^{13}C- and ^{14}C-labeled MeMS (26 μL, 3.30 mmol, 4 μCi). The pH of the reaction mixture was maintained at 7.0 ± 0.1. The sample was worked up as described above.

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Registry No. m^7dG, 28074-91-1; m^1dA, 60192-55-4; m^3dC, 5040-21-1; m^1dG, 5132-79-6; mP^2, 813-78-5; mP^3, 512-56-1; m^3T, 958-74-7; dT, 50-89-5; methyl methanesulfonate, 66-27-3; dC, 951-77-9; dA, 958-09-8; dG, 961-07-9; m^6dG, 964-21-6; m^6dA, 2002-35-9; m^1Ade, 5142-22-3; m^3dU, 24514-32-7.

(59) Miles, H. T. *J. Am. Chem. Soc.* **1957**, *79*, 2565–2568.

Polystyrene-Bound Phenylseleninic Acid: Catalytic Oxidations of Olefins, Ketones, and Aromatic Systems

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A new synthesis of polystyrene-bound phenylseleninic acid, from reaction of mercurated polystyrene and selenium dioxide, is described. A triphasic system of the polymer (in catalytic amounts), aqueous hydrogen peroxide, and dichloromethane is shown to be an effective medium for the conversion of olefins into trans diols and ketones into esters. A biphasic system of the polymer and *tert*-butyl hydroperoxide in refluxing chloroform effects the selective oxidation of benzylic alcohols to the carbonyl species. In a similar catalytic system hydroxy aromatic compounds can be converted into quinones. Conversion of 1,5-dihydroxynaphthalene into juglone can be realized in 70% yield.

The use of organoselenium reagents in organic synthesis has been developed to a great extent over the past several years.[1] While such reagents have been shown to be extremely versatile, they are also moderately expensive and quite toxic. The fact that the phenylselenyl group is the most frequently encountered organic moiety suggested that these reagents could be incorporated into polystyrenes. The use of functionalized polymers in this context would provide significant advantages,[2] including decreased vol-

(1) For a general review, see: Clive, D. L. J. *Tetrahedron* **1978**, *34*, 1049.

0022-3263/83/1948-5160$01.50/0

Table I. Oxidation of Olefins with Aqueous H_2O_2/1[a]

olefin	time, h	product	% yield (isolated)
1-hexene	120	1,2-hexanediol	41
2-methyl-1-pentene	120	2-methyl-1,2-pentanediol	57
cyclohexene	72	*trans*-1,2-cyclohexanediol	89[b]
2-methyl-2-butene	60	2-methyl-2,3-butanediol	84
2,3-dimethyl-2-butene	36	2,3-dimethyl-2-butene oxide	83

[a] Conducted at room temperature, with 1.5 mol % 1, CH_2Cl_2, and 1.8 equiv of H_2O_2. [b] No cis diol could be detected.

Table II. Oxidation of Ketones with Aqueous H_2O_2/1[a]

ketone	time, h	products	% yield (isolated)
cyclobutanone	3	γ-butyrolactone	96
cyclopentanone	72	δ-valerolactone	98
2-methylcyclopentanone	103	β-methyl-δ-valerolactone γ-methyl-δ-valerolactone	86[b]
cyclohexanone	96	6-hydroxyhexanoic acid	71
2,6-dimethylcyclohexanone	108	2,6-dimethylcaprolactone	92[c]
2-butanone	12	ethanol + acetic acid	90
pinacolone	60	*tert*-butyl acetate; acetic acid + *tert*-butyl alcohol	79[d]

[a] Conditions identical with those of olefin oxidations. [b] Approximately 1:1 ratio. [c] Mixtures of diastereomers were used. [d] Ratio 7.3:1 of ester to hydrolysis.

atility and ease of recovery and recycle of the spent reagent.

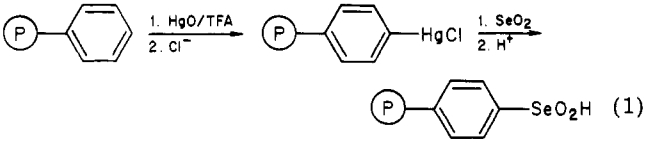
Polystyrene-bound phenylselenyl halides and anions have been investigated previously[3,4] and display reactivity similar to their homogeneous counterparts. Such divalent selenium species would normally be used in a stoichiometric fashion. Selenium(IV) reagents, however, can be used catalytically to afford net oxidations. Polymer-bound diphenyl selenoxide[3,4] has been used in such a way with fair results.

Phenylseleninic acid has been used as a catalyst for the epoxidation of olefins and the Baeyer–Villiger reaction of ketones.[5-7] Catalysis of the oxidation of allylic alcohols[8] has also has been reported as well as the oxidation of phenolic systems.[9] While polymer-immobilized phenylseleninic acid is known,[10] such catalytic reactions using this species have not been reported. Arsenated polystyrenes have been used in such reactions[11,12] and display acceptable reactivity, even in systems requiring triphase catalysis. Polymer-bound peracids have been used to carry out epoxidations of olefins[13,14] but not normally in a catalytic cycle.

We report herein a facile synthesis of polystyrene-bound phenylseleninic acid and our investigation of its catalytic effect in the oxidations of olefins, ketones, and aromatic systems.

Results and Discussion

Previous preparations of polystyrene-bound phenylseleninic acid have involved electrophilic substitutions of H_2SeO_4 (with Ag_2SeO_4), onto polystyrene. The resultant selenonic acid was reduced to the seleninic acid with chloride ion.[10] Since we had found that silylated[15] and mercurated[16] polystyrenes are substantially activated toward electrophilic substitution, the action of SeO_2 on these species was investigated. While the silylated polymer proved to be unreactive, the mercurated polymer underwent clean substitution (eq 1).



(1)

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To a sample of polystyrene–2% divinylbenzene copolymer beads that had been mercurated in a previously described fashion (HgO, TFA, Cl^-)[16-18] and swelled in THF was added excess selenium dioxide. After reflux for 120 h, a bright yellow polymer was isolated. Material isolated in this fashion was unsatisfactory for later reactions, due to subsequent decrease in selenium content. Attributing these losses to intercalated SeO_2, the polymer was treated with 30% hydrogen peroxide. Polymer derived from this treatment showed acceptable stability. In a typical experiment, a 49.9% mercurated polymer (elemental analysis 44.97% Hg) afforded a 20.8% selenated polymer (11.55% Se, degree of functionality assuming seleninic acid struc-

(2) For recent reviews on the use of functionalized polymers in organic synthesis, see: Akelahand, A.; Sherrington, D. C. *Chem. Rev.* **1981**, *81*, 557. Hodge, P., Sherrington, D. C. Eds. "Polymer-Supported Reactions in Organic Synthesis"; Wiley: London, 1980, Mathur, N. K.; Narang, C. K.; Williams, R. E. "Polymers as Aids in Organic Chemistry"; Academic Press: New York, 1980.

(3) Michels, R.; Kato, M.; Heitz, W. *Makromol. Chem.* **1976**, *177*, 2311.

(4) Kato, M.; Michels, R.; Heitz, W. *J. Polym. Sci., Polym. Lett. Ed.* **1976**, *14*, 413.

(5) Hori, T.; Sharpless, K. B. *J. Org. Chem.* **1978**, *43*, 1689.

(6) Grieco, P. A.; Yokoyama, Y.; Gilman, S.; Hishizawa, M. *J. Org. Chem.* **1977**, *42*, 2034.

(7) Grieco, P. A.; Yokoyama, Y.; Gilman, S.; Ohfune, Y. *J. Chem. Soc., Chem. Commun.* **1977**, 870.

(8) Kuwajima, I.; Shimizu, M.; Urabe, H. *J. Org. Chem.* **1982**, *47*, 837.

(9) Barton, D. H. R.; Magnus, P. D.; Rosenfeld, M. N. *J. Chem. Soc., Chem. Commun.* **1975**, 301. Clive, D. L. J. *Q. Rev.* **1968**, *22*, 435.

(10) Zundel, G. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 499 and references therein.

(11) Jacobson, S. E.; Mares, F.; Zambri, P. M. *J. Am. Chem. Soc.* **1979**, *101*, 6938.

(12) Jacobson, S. E.; Mares, F.; Zambri, P. M. *J. Am. Chem. Soc.* **1979**, *101*, 6946.

(13) Harrison, C. R.; Hodge, P. *J. Chem. Soc., Chem. Commun.* **1974**, 1009.

(14) Fréchet, J. M. J.; Haque, K. E. *Macromolecules* **1975**, *8*, 130.

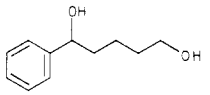
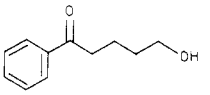
(15) Taylor, R. T.; Crawshaw, D. B.; Paperman, J. B.; Flood, L. A.; Cassell, R. A. *Macromolecules* **1981**, *14*, 1134.

(16) Taylor, R. T.; Cassell, R. A.; Flood, L. A. *Ind. Eng. Chem. Prod. Res. Dev.* **1982**, *21*, 462.

(17) Burlitch, J. M.; Winterton, R. C. *J. Organomet. Chem.* **1978**, *159*, 299.

(18) Janout, V.; Regen, S. L. *J. Org. Chem.* **1982**, *47*, 2212.

Table III. Oxidation of Alcohols with *t*-BuOOH/1[a]

alcohol	time, h	products	% yield (isolated)
p-nitrobenzyl alcohol	5	*p*-nitrobenzaldehyde	100
3,4,5-trimethoxybenzyl alcohol	22	3,4,5-trimethoxybenzaldehyde	94
benzyl alcohol	24	benzaldehyde	94
benzhydrol	24	benzophenone	100
benzoin	24	benzil	98
xanthen-9-ol	48	xanthone	100
	48		69
cinnamyl alcohol	63	cinnamaldehyde	100
3,4,5-trimethoxycinnamyl alcohol	70	3,4,5-trimethoxycinnamaldehyde	70
cis-1,4-butenediol		no reaction	
cyclopentanol		no reaction	

[a] Conducted in refluxing CCl_4, with 1.5 mol % 1 and 1.5 equiv of *t*-BuOOH.

ture). The IR spectrum was compatible with the previously reported material.[10]

With this material in hand, we examined reactions between olefins and hydrogen peroxide, as mediated by catalytic amounts of the polymer 1. Reactions were monitored by NMR spectroscopy and carried out at room temperature in a triphase system of olefin in dichloromethane, 30% aqueous hydrogen peroxide, and 1.5 mol % 1. Products were isolated by simple filtration and extraction. Results are summarized in Table I.

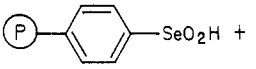
Upon mixture of hydrogen peroxide with the polymer, a marked loss of color was observed in the polymer. The recovered polymer, however, was indistinguishable from the original material.

Products were identified by comparison of spectral data (NMR, IR, MS) with those of the known compounds or by HPLC comparison with an authentic sample. In all cases, oxidation proceeded slowly at room temperature, usually affording 1,2-diols in moderate to high yield. The intermediacy of an epoxide is suggested by the oxidation of cyclohexene solely to the trans diol. Treatment of cyclohexene oxide under the same reaction conditions resulted in equivalent hydrolysis. Except for the case of tetramethylethylene (in which epoxide was the only observed species), such epoxides could not be observed, even when the solution was buffered. The observed reactivity pattern is consistent with formation of an electrophilic oxidizing agent.

In a similar fashion, oxidations could be carried out on a variety of ketones. With use of the same workup and characterization procedures, the products of Baeyer–Villiger reaction were generally obtained in good yield (Table II). Complications resulting from hydrolysis of the product were observed when appreciably water-soluble species were generated. Buffering of the solution was ineffective. Less water-soluble aliphatic ketones (2-heptanone, 3-isopropyl-2-heptanone) as well as aryl ketones (tetralone, indanone, acetophenone) were unreactive. More forcing conditions ($CHCl_3$, reflux) resulted in marked bleaching and loss of mechanical stability in the polymer. The reactivity pattern in these reactions is consistent with that normally described for Baeyer–Villiger reactions,[19] with strained ketones reacting fastest and migration of the more substituted group.

In all cases, the recovered polymer could be used in subsequent oxidations with no further treatment and no discernible loss of reactivity. Elemental analysis of a sample of catalyst that had been subjected to five reactions totalled 11.12% Se. Thus, over five reactions only 3.7% of the selenium content was lost.

The observed reactions can be rationalized on the basis of a rapid equilibrium between hydrogen peroxide and the polymer-bound peracid 2 (eq 2). Such species have been



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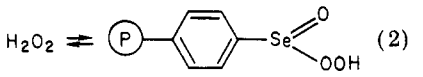

(2)

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invoked in homogeneous phenylseleninic acid reactions,[5-7] although the polymeric reactions are considerably slower since a triphasic system now operates. Although loss of selenium in such reactions with H_2O_2 has been observed,[5] this appears to be a problem only at elevated temperatures in our system.

It is interesting to compare our results with the analogous arsonated species.[11,12] Under triphase conditions, reactions required similar times although the reaction temperature was quite lower (room temperature vs. 70 °C) for the selenated polymer. The most significant difference between these two reagents was the amount of hydrolysis, presumably acid-catalyzed, in the selenium cases. Given the greater acidity of the arsonated species (pK_a of toluenearsonic acid = 3.82[20] vs. pK_a of tolueneseleninic acid = 4.88[21]), such results are initially surprising. While this result may indicate a more aqueous microenvironment (in accord with the greater reactivity of the more water-soluble ketones), it should also be recognized that oxidation at selenium is possible. While it has been shown that areneselenonic acids are incapable of promoting epoxidations,[22] a small conversion to the selenonic acid could lead to an increase in acid hydrolysis.

In accord with our expectations, no color change was observed when the polymer was treated with *tert*-butyl hydroperoxide. Since this particular reagent system would be appropriate for the catalytic oxidation of alcohols,[8] we examined these reactions. In a biphasic system of polymer (1.5 mol %), *t*-BuOOH (1.5 equiv), and alcohol in refluxing CCl_4, reaction with a variety of alcohols was carried out (see Table III).

(19) Hassall, C. H. *Org. React.* **1957**, 73.

(20) Pressman, D.; Brown, D. H. *J. Am. Chem. Soc.* **1943**, *65*, 542.
(21) McCullough, J. D.; Gould, E. S. *J. Am. Chem. Soc.* **1949**, *71*, 674.
(22) Faehl, L. G.; Kice, J. L. *J. Org. Chem.* **1979**, *44*, 2357.

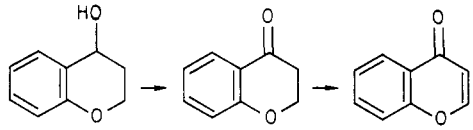
Table IV. Oxidations in Aromatic Species with *t*-BuOOH/1[a]

compd	time, h	products	% yield (isolated)
hydroquinone	0.3	*p*-benzoquinone	90
catechol	0.3	*o*-benzoquinone	65
1,3-cyclohexadiene	12	benzene	100
flavanone	216	flavone	95
1,3,5-cycloheptatriene	409	benzaldehyde	60
phenol		no reaction	
1,5-cyclooctadiene		no reaction	

[a] Conditions identical with those of alcohol oxidations.

As can be seen, benzylic alcohols are readily oxidized to the corresponding carbonyl compound. Overoxidation of aldehydes could not be observed. Unactivated allylic alcohols or aliphatic alcohols were generally unreactive. An increase in temperature led to decomposition of the peroxide.

Oxidation of 4-chromanol afforded further reaction (eq 3). After 62 hours under the above described conditions,

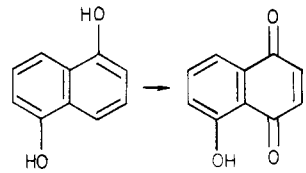


(3)

4-chromanone could be obtained in 93% yield. However, a small amount of another product could be observed in the NMR spectrum. Continuing the reaction for an additional 168 h afforded 4-chromone in 65% yield.

Since aromatization and phenol oxidations with Se(IV) compounds were precedented,[9] we examined under similar conditions a variety of dihydro aromatic and phenolic systems (see Table IV). As can be seen, dihydro aromatic systems oxidized readily. While phenol oxidation did not occur, dihydroxy species cleanly oxidized to the quinones.

With this data in mind, we carried out the oxidation of 1,5-dihydroxynaphthalene (eq 4). The reaction was carried out for 235 h. Filtration and Soxhlet extraction of the polymer afforded juglone in 70% isolated yield. The recovered polymer could be recycled in an equivalent fashion. Other methods for the formation of this key intermediate afford substantially lower yield or involve the use of quite expensive or toxic reagents.[23] This method is clean and can be carried out repetitively on a multigram scale.



(4)

Conclusion

By means of the treatment of mercurated polystyrene with selenium dioxide, a stable polymeric seleninic acid species can be generated. This material can be used in a catalytic fashion with H_2O_2, affording peracid oxidation, and with *t*-BuOOH as a selenium(IV) oxidant. The catalyst is stable to the reaction conditions and can be recycled with no apparent loss of activity.

Experimental Section

General Methods. IR spectra were recorded on a Perkin-Elmer Model 680 spectrometer and NMR spectra on a Varian EM-360 instrument. Mass spectra were measured on a Hitachi Perkin-Elmer RMU-6 spectrometer. HPLC comparisons were carried out on an IBM LC9533 instrument equipped with a 254-nm detector and C-18 column. Elemental analyses were determined by Galbraith Laboratories, Inc., Knoxville, TN.

Preparation of Polystyrene-Bound Phenylseleninic Acid (1). A two-necked, 500-mL flask was charged with 20.0 g of polystyrene-bound phenylmercuric chloride (prepared as previously described,[14] this lot having an analysis of 44.97% mercury, total of 44.84 mequiv) and 220 mL of THF. The slurry was allowed to swell for 60 min and then 1.5 g of Adogen 464 and 7.65 g (68.9 mmol) of selenium dioxide were added. The reaction mixture was heated to reflux and allowed to stir for 120 h. The polymer was filtered and then washed with 250 mL each of methanol, acetone, and chloroform.

The polymer was reswelled in THF, and 50 mL of 6 N HCl was added to facilitate demercuration. After stirring for 16 h the polymer was filtered and washed as before.

To the polymer was added 250 mL of dichloromethane and 50 mL of 30% H_2O_2. The slurry was stirred for 72 h and then filtered and washed with 500 mL of CH_2Cl_2, 200 mL of methanol, 200 mL of acetone, and 3 × 200 mL of chloroform. The bright yellow polymer was dried in an Abderhalden apparatus at 57 °C (0.1 torr).

For 1: IR ν (KBr) 3420, 3060, 3040, 3005, 2830, 1590, 1575, 1480, 1440, 1375, 1175, 1005, 820, 750, 690, 530 cm^{-1}. Anal. % Se, 11.55%.

General Procedure for H_2O_2 Oxidations. At 0 °C, a slurry of 1.0 g (1.46 mmol) of 1 in 18 mL of dichloromethane was allowed to swell, with stirring, for 10 min. To the slurry was added 100 mmol of the starting material followed by dropwise addition of 16.6 mL (180 mmol) of 30% H_2O_2. The slurry was stirred at room temperature until NMR analysis indicated the disappearance of starting material.

Workup proceeded following filtration. The polymer was washed with 25 mL of dichloromethane. The combined filtrate was separated and the aqueous layer washed three times with 25 mL of ether. The combined organics were washed with saturated sulfite and dried ($MgSO_4$). Evaporation of the solvent afforded the product, which was characterized by comparison with spectra of the authentic compound.

Filtered polymer could be used in the identical fashion. Elemental analysis of a sample that had been used in five separate reactions (total of about 400 h) showed a total of 11.12% Se.

General Procedure for *t*-BuOOH Oxidations. A 2.0-g sample of 1 was swelled in 30 mL of carbon tetrachloride at room temperature. To the slurry then were added 10 mmol of the starting material and 15 mmol (1.5 equiv) of 90% *tert*-butyl hydroperoxide. The solution was heated to reflux (80 °C) and stirred under nitrogen with monitoring of the reaction progress by ^1H NMR. After 2 days additional peroxide was periodically added to the reaction mixture. The reaction mixture was allowed to cool to room temperature and was filtered through a Büchner funnel to remove the polymeric reagent.

The filtrate was then treated with 100 mL of saturated sodium thiosulfate solution to remove excess *tert*-butyl hydroperoxide and *tert*-butyl alcohol. The organic layer was separated and dried overnight with $MgSO_4$. Flash evaporation of solvent afforded product material, which was then characterized by the usual methods.

Acknowledgment is made to the Faculty Research Committee, Miami University, for the support of this research. Funds for the purchase of the Perkin-Elmer Model 680 spectrometer were provided in part by the National Science Foundation through Grant TFI-8022902. The IBM LC9533 instrument was a gift from IBM Corp., which is gratefully acknowledged.

Registry No. Selenium dioxide, 7446-08-4; hydrogen peroxide, 7722-84-1; *tert*-butyl hydroperoxide, 75-91-2; 1-hexene, 592-41-6;

(23) For other syntheses of juglone, see: (a) Boeckman, R. K., Jr.; Sum, F. W. *J. Am. Chem. Soc.* **1982**, *104*, 4604. (b) Grundmann, C. *Synthesis* **1977**, 644. (c) Richey, F. A., Jr.; Bartley, W. J.; Fitzpatrick, J. F.; Kurtz, P. A. *J. Argic. Food Chem.* **1972**, *20*, 825. (d) Crouse, D. J.; Wheeler, M. M.; Goemann, M.; Tobin, P. S.; Basu, S. K.; Wheeler, D. M. S. *J. Org. Chem.* **1981**, *46*, 1814.

2-methyl-1-pentene, 763-29-1; cyclohexene, 110-83-8; 2-methyl-2-butene, 513-35-9; 2,3-dimethyl-2-butene, 563-79-1; cyclobutanone, 1191-95-3; cyclopentanone, 120-92-3; 2-methylcyclopentanone, 1120-72-5; cyclohexanone, 108-94-1; 2,6-dimethylcyclohexanone, 2816-57-1; 2-butanone, 78-93-3; pinacolone, 75-97-8; *p*-nitrobenzyl alcohol, 619-73-8; 3,4,5-trimethoxybenzyl alcohol, 3840-31-1; benzyl alcohol, 100-51-6; benzhydrol, 91-01-0; benzoin, 119-53-9; xanthen-9-ol, 90-46-0; 1-phenyl-1,5-pentanediol, 1011-61-6; cinnamyl alcohol, 104-54-1; 3,4,5-trimethoxycinnamyl alcohol, 1504-56-9; *cis*-1,4-but-2-enediol, 6117-80-2; cyclopentanol, 96-41-3; hydroquinone, 123-31-9; catechol, 120-80-9; 1,3-cyclohexadiene, 592-57-4; flavanone, 487-26-3; 1,3,5-cycloheptatriene, 544-25-2; phenol, 108-95-2; 1,5-cyclooctadiene, 111-78-4; 1,2-hexanediol, 6920-22-5; 2-methyl-1,2-pentanediol, 20667-05-4; *trans*-1,2-cyclohexanediol, 1460-57-7; 2-methyl-2,3-butanediol, 5396-58-7; 2,3-dimethyl-2-butene oxide, 5076-20-0; γ-butyrolactone, 96-48-0; δ-valerolactone, 542-28-9; β-methyl-δ-valerolactone, 1121-84-2; γ-methyl-δ-valerolactone, 3123-98-6; 6-hydroxyhexanoic acid, 1191-25-9; 2,6-dimethyl-ε-caprolactone, 55879-32-8; *p*-nitrobenzaldehyde, 555-16-8; 3,4,5-trimethoxybenzaldehyde, 86-81-7; benzaldehyde, 100-52-7; benzophenone, 119-61-9; benzil, 134-81-6; xanthone, 90-47-1; 5-hydroxy-1-phenyl-1-pentanone, 1011-62-7; cinnamaldehyde, 104-55-2; 3,4,5-trimethoxycinnamaldehyde, 34346-90-2; *p*-benzoquinone, 106-51-4; *o*-benzoquinone, 583-63-1.

Photolytic Dehydrochlorination of *N*-Chloro-*N*-alkyl Amides: Formation of *N*-(α-Methoxyalkyl) Amides

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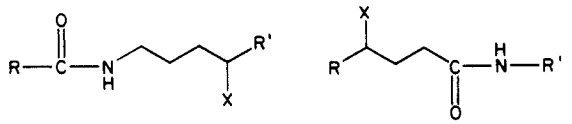
The photoinduced dehydrochlorination, in methanol, of *N*-chloro-*N*-alkyl amides with one substituent at the α position to nitrogen gave good yields of *N*-(α-methoxyalkyl) amides and the parent amides as secondary products. *N*-Chloro amides disubstituted at the α position gave mostly parent amides. In most cases no products resulting from 1,5 hydrogen transfer of amidyl radicals were observed. The quantum yields of decomposition of *N*-chloro-*N*-methylpentanamide (**1a**) were significantly greater than unity, indicative of a chain process for dehydrochlorination. The reaction was affected by the solvent, addition of base or radical inhibitors, concentration of *N*-chloro amide, light intensity, and irradiation wavelength.

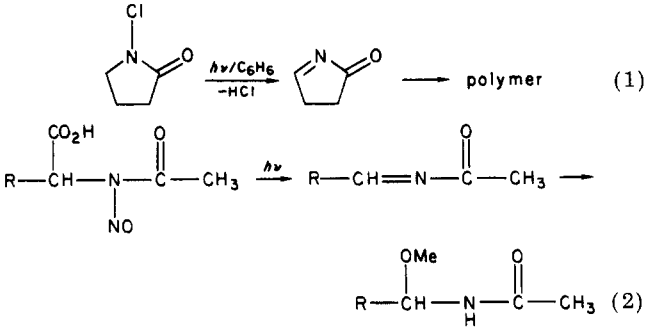
The photolysis of *N*-halo amides is known to give products arising from both amidyl radical and halogen atom intermediates.[1,2] Typical products of amidyl radical intermediates are δ-halo amides I and 4-haloacyl isomers II, which result from regiospecific 1,5 hydrogen abstraction



I II

from the *N*-alkyl moiety and the acyl chain, respectively.[2-6] When both the *N*-alkyl and acyl moieties of the *N*-halo amide are small, precluding normal 1,5 hydrogen transfer, a product arising from 1,4 hydrogen transfer has been observed.[2] Amidyl radicals also have been found to undergo efficient intramolecular addition to olefinic bonds.[7-9] All of these pathways are believed to involve amidyl radical chain processes with quantum yields greater than unity. In cases where intramolecular processes are impossible, such as with *N*-chloro-*N*-*tert*-butylacetamide, a slow intermolecular hydrogen abstraction predominates in solvents of poor hydrogen-donating ability.[3,6] In good hydrogen-donating solvents such as cyclohexane, an efficient radical-chain process produces the parent amide and chlorinated solvent.[2]

The photolysis in benzene of *N*-chloro amides bearing a hydrogen α to nitrogen, such as *N*-chloropyrrolidone, is complicated by the formation of gummy polymeric products.[6] These products are thought to result from polymerization of intermediate acyl imines derived from dehydrochlorination of *N*-chloro amides (eq 1). Although the



(1)

(2)

quantum yields were not reported, the dehydrochlorination is rapid and probably involves a radical-chain process. Products characteristic of intermediate acyl imines are also formed in the photolysis of *N*-chloro-*N*-methylcarbamates,[1c] *N*-nitroso-*N*-alkyl amides,[10-14] and *N*-acyl-*N*-nitroso-α-amino acids.[15,16] In the latter case, photolysis

(1) (a) R. S. Neale, *Synthesis*, 1 (1971); (b) P. Mackiewicz and R. Furstoss, *Tetrahedron*, 34, 3241 (1978); (c) J. Lessard, M. Mondon, and D. Touchard, *Can. J. Chem.*, 59, 431 (1981).
(2) R. A. Johnson and F. D. Greene, *J. Org. Chem.*, 40, 2186 (1975).
(3) Y. L. Chow and T. C. Joseph, *J. Chem. Soc., Chem. Commun.*, 490 (1969).
(4) A. L. J. Beckwith and A. Goodrich, *Aust. J. Chem.*, 18, 747 (1965).
(5) D. H. R. Barton, A. L. J. Beckwith, and A. Goosen, *J. Chem. Soc.*, 181 (1965).
(6) R. S. Neale, N. L. Marcus, and R. G. Schepers, *J. Am. Chem. Soc.*, 88, 3051 (1966).
(7) Y. L. Chow and R. A. Perry, *Tetrahedron Lett.*, 531 (1972).
(8) M. E. Kuehne and D. A. Horne, *J. Org. Chem.*, 40, 1287 (1975).
(9) Lessard et al. have shown that intramolecular addition to olefins by amidyl radicals also can be promoted with benzoyl peroxide initiation or chromous chloride reduction: P. Mackiewicz, R. Furstoss, B. Waegell, R. Cote, and J. Lessard, *J. Org. Chem.*, 43, 3746, 3750 (1978).
(10) Y. L. Chow and A. C. H. Lee, *Chem. Ind.*, 827 (1967).
(11) Y. L. Chow, N. S. Tam, and A. C. H. Lee, *Can. J. Chem.*, 47, 2441 (1969).
(12) Y. L. Chow and A. C. H. Lee, *Can. J. Chem.*, 45, 321 (1967).
(13) Y. L. Chow and N. S. Tam, *J. Chem. Soc. C*, 1138 (1970).
(14) O. E. Edwards, J. M. Paton, M. H. Benn, R. E. Mitchell, C. Watananda, and K. W. Vohra, *Can. J. Chem.*, 49, 1648 (1971).
(15) J. Polo and Y. L. Chow, *Heterocycles*, 11, 101 (1978).

0022-3263/83/1948-5164$01.50/0