has been suggested by others,[9a,14] the ratio of methyl ether to hydrocarbon might be related to the relative energies of the cation and radical. In the 1-adamantyl case, the ratio is about 95:5;[14] in the 1-norbornyl system, 76:12.[9a] We find that on irradiation of cubyl iodide in methanol under similar conditions, the ratio of methoxycubane to cubane is >95:5.[15] *The trend from adamantyl to norbornyl to cubyl is not in agreement with expectation from simple geometric and electronic arguments.* What is needed now is a more quantitative picture, both from experiment and theory, of the relative energies of the radical and cation species involved.

Experimental Section

1,4-Diiodocubane. This procedure is derived from that in the literature for monoiodocubane.[5] *tert*-Butyl hypochlorite (3.8 g, 35 mmol) was added with stirring to a mixture of mercuric iodide (7.95 g, 17.5 mmol) and Freon 113 (25 mL) held at 0 °C. The precipitated mercuric chloride was removed after 2 h. The filtrate was added to a stirred suspension of 1,4-dicarboxycubane[16] (1.34 g, 7.0 mmol) in the same solvent (20 mL), and the mixture was irradiated overnight at 40 °C with a 200-W tungsten lamp. The mixture was then filtered, and the residue washed with acetone. The combined filtrate and wash was taken to dryness on a rotary evaporator under vacuum, keeping the bath temperature below 20 °C. The residue was dissolved in a small volume of methylene chloride. The solution was washed with aqueous 10% sodium thiosulfate solution to remove iodine and then dried ($MgSO_4$). The solvent was removed; the residue was purified by chromatography on silica gel, eluting with hexanes, to give the white, crystalline diiodide (1.79 g, 72%): mp 227–228 °C dec (lit.[3] mp 226–227 °C dec); ^{1}H NMR ($CDCl_3$) δ 4.37 (s); ^{13}C NMR ($CDCl_3$) δ 57.4 (d), 35.6 (s). Some higher iodides are also formed.[4]

4-Methoxyiodocubane and 1,4-Dimethoxycubane. 1,4-Diiodocubane (71 mg) was kept suspended in dry methanol (6.0 mL) under nitrogen in a 10-mL quartz tube with a magnetic stirrer. The tube, centered in a Rayonet (The Southern New England Ultraviolet Co.) RPR-204 reactor equipped with 2537-Å low-pressure lamps, was irradiated at ambient temperature (ca. 40 °C). The progress of the irradiation was monitored by GLC (flame detection; OV-101) at 1-h intervals (removing HI before injection). After 6 h about 32% of the soluble product mixture was 4-methoxyiodocubane. Further irradiation gave significant conversion to 1,4-dimethoxycubane. After 12 h the reaction was stopped. A few drops of aqueous 10% Na_2CO_3 solution was added, and the solvent was removed under reduced pressure. The crude product was dissolved in 5 mL of dichloromethane; the solution was absorbed onto a silica gel column (10 g). This was eluted with hexane (100 mL) to remove residual diiodocubane and then with toluene (50 ml) to get 4-methoxyiodocubane (5 mg, 10%): mp 86–87 °C; IR (KBr) ν 2996, 1352, 1316, 1305, 1130, 1118, and 1019 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.32 (3 H, s, OMe), 4.03 (3 H, m), 4.30 (3 H, d of d); MS (EI), *m/e* 217 (5), 204 (51), 165 (4), 152 (4), 118 (95), 89 (base), 77 (68).

Elution with 9:1 toluene/ethyl acetate (50 mL) gave 17 mg (52%) of 1,4-dimethoxycubane: mp 79–80 °C; IR (KBr) ν 2990, 1470, 1323, 1211, 1132, 1024 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.32 (6 H, s, OMe), 3.9 (6 H, s); ^{13}C NMR ($CDCl_3$) δ 46.1 (d), 51.6 (q), and 92.9 (s); MS (EI), *m/e* 149 (11), 133 (11), 121 (28), 108 (58), 91 (30), 78 (base).

4-Iodoacetamidocubane and 1,4-Diacetamidocubane. 1,4-Diiodocubane (1.2 g, 3.3 mmol) was suspended under nitrogen in 250 mL of ACS grade acetonitrile in a 300-mL, quartz, round-bottomed flask equipped with magnetic stirrer. Water (2 mL) was added, and the flask placed in a Rayonet apparatus (as above) and irradiated. The course of the reaction was monitored at 8-h intervals by thin-layer chromatography on silica gel. After 48 h, the starting material was essentially gone. The acetonitrile was removed under reduced pressure. The black gummy residue was washed with saturated aqueous solutions of sodium thiosulphate and potassium carbonate, leaving a brown powder. TLC on silica gel showed two major components. The crude was absorbed onto a silica gel column. Elution with chloroform gave 4-iodoacetamidocubane (113 mg, 12%): mp 210–213 °C dec; ^{1}H NMR (DMSO-d_6) δ 1.88 (3 H, s, $COCH_3$), 4.15 (3 H, d, cubyl H) 4.2 (3 H, d, cubyl H), 8.5 (1 H, s, NH); ^{13}C NMR (DMSO-d_6) δ 22.39 (q), 39.7 (s), 52.4 (d), 52.6 (d), 62.7 (s), 168.8 (s); IR (KBr) ν 3250 (s, N—H), 1650 (s, C=O) 1505 (m), 1375 (m), 1345 (w), 1306 (m) cm^{-1}. Elution with chloroform/methanol (9:1) gave 1,4-diacetamidocubane (370 mg, 50%): mp 276–281 °C dec; ^{1}H NMR (DMSO-d_6) δ 1.80 (6 H, s, CH_3), 3.80 (6 H, s, cubyl CH), 8.5 (s, 2 H, NH); ^{13}C NMR (DMSO-d_6) δ 22.17 (q), 47.1 (d), 66.08 (s), 168.3 (s); IR (KBr) ν 3250 (s, N—H), 1650 (s, C=O), 1555 (m) cm^{-1}.

Acknowledgment. Principal funding for this research was provided by the Army Research, Development and Engineering Center and Geo-Centers, Inc. The National Science Foundation and the National Institutes of Health, the latter through The University of Chicago Cancer Research Center (Grant CA 14599), contributed substantially to the departmental instrument facility. P.E. thanks the Alexander von Humboldt Foundation for a U.S. Senior Scientist Award during whose tenure this paper was drafted at Universität Köln, FRG, a most gracious host institution. D.S.R. is grateful to Geo-Centers, Inc., for a leave of absence permitting his work at The University of Chicago.

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Preparation and Utilization of a Macromolecular Analogue of *N-tert*-Butyl-*N*-ethylamine as a Reusable Amide Base

James R. Blanton* and Robert E. Salley

Department of Chemistry, The Citadel, Charleston, South Carolina 29409

Received August 24, 1988

Recently, examples of synthetically useful aldol and related reactions in which the stabilized carbanion intermediates were generated by polymeric analogues of strong bases have been reported. In particular, the polymeric species that were employed as bases involve alkali-metal derivatives of polystyrene or KF adsorbed on basic alumina.[1-4] Of specific interest to our work were the examples of the derivatized polystyrenes, which have been prepared by several procedures. Included among these procedures were the deprotonation of pendant aryl rings by *n*-BuLi–TMEDA, metal–halogen exchange between *n*-BuLi and halogenated polystyrenes, transmetalation reactions of alkyllithium reagents and mercurated polystyrenes, and deprotonation of polymer-bound weak acids. Of the metalated derivatives that have been prepared, the use of weak acids as precursors for regenerable bases were the ones that were synthetically useful in forming stabilized carbanions. Specific examples of such species included

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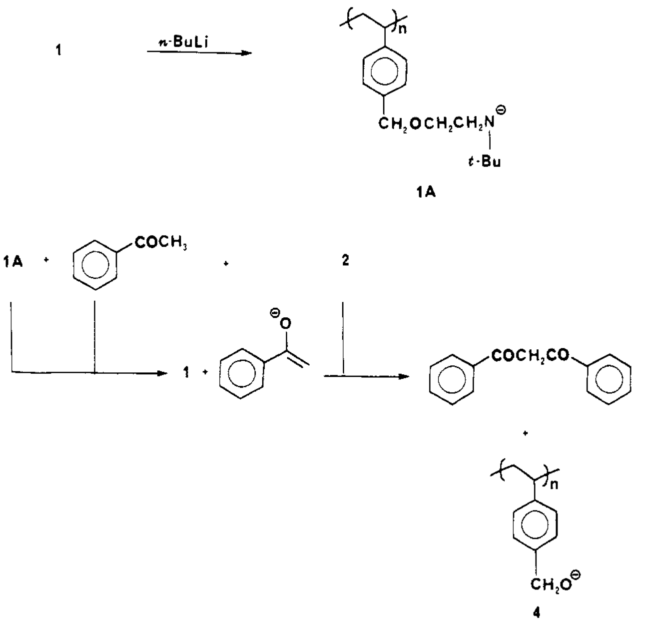
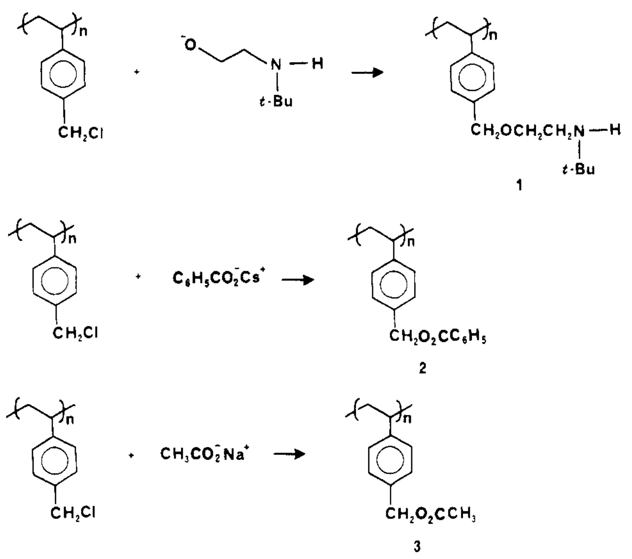
Scheme I



Scheme II



macromolecular analogues of diphenylmethane, triphenylmethane, and diisopropylamine.[5]

In this report we describe the preparation and use of a polymeric analogue of *N-tert*-butyl-*N*-ethylamine as a precursor in forming a regenerable amide base. As a means of studying the effectiveness of the amide derivative in generating stabilized carbanions, we chose to use the novel "Wolf and Lamb" reaction reported by Patchornik as a model reaction.[1] Basically, the Wolf and Lamb synthesis is a process in which incompatible reagents are attached polymeric supports forming mutually unreactive species. Because these reagents cannot successfully come into contact with one another, reactions requiring multiple steps may be carried out in the same reaction vessel.[6]

Since the immobilized reagents used in a Wolf and Lamb reaction cannot interact with one another, reactions such as Aldol condensations, enolate alkylations, and Claisen condensations may be conveniently carried out in a reaction vessel that simultaneously contains the base, the carbonyl substrate, and the electrophile. Patchornik successfully conducted examples of these reactions using macromolecular analogues of triphenylmethyllithium and lithium diisopropylamide as the bases. However, this project was initiated when we noted that the procedure for preparing the polymeric analogue of lithium diisopropylamide not only involved a potentially time-consuming, multistep process, but that the group containing the amide functionality was attached to the polymer by a more acidic methylene linkage.[1] Because this methylene linkage was essentially a diphenylmethyl group, the same unwanted side reactions previously reported for a polymeric analogue of diphenylmethyllithium could occur.[3]

Results and Discussion

To briefly summarize the one-pot, multistep reaction that was employed, we chose to use Patchornik's Wolf and Lamb Claisen condensation reaction as a model. As illustrated in Scheme I, conducting a reaction by this procedure involved deprotonating the amine functionality of **1** to form the amide base, **1A**. After the polymeric amide base was formed, both the polymer containing an electrophilic site (e.g. an ester group) and the soluble weak acid were added to the reaction. Since the functional groups attached to the polymers were mutually unreactive, only the soluble species could interact with both polymers. Initially, the soluble carbonyl compound was deprotonated by the amide base to form an enolate as an intermediate. This intermediate then underwent a nucleophilic substitution reaction with the electrophilic polymer to form the Claisen product. Once the reaction was complete, the polymers were removed by filtration to yield the product upon removal of the solvent.

In preparing the polymers for this study, we found that the macromolecular-supported amine, **1**, could be conveniently formed by a substitution reaction involving 1% divinylbenzene cross-linked chloromethylated polystyrene (Merrifield resin) and sodium 2-(*tert*-butylamino)ethoxide (Scheme II). The identity of the polymer was ascertained by subjecting the product that was isolated by both IR and titrimetric analyses. By use of these techniques, it was noted that the chloromethyl signal at 1260 cm^{-1} had disappeared with the concurrent appearance of a new signal at 3400 cm^{-1}. This new signal was taken to be the nitrogen–hydrogen stretch of the amino unit. Additionally, the loading of the active sites on the deprotonated polymer was determined by quenching a known amount of **1A** with methanol and titrating the methoxide base that was formed. It was found that the average loading of active sites on the polymer was 0.73 mequiv of base/g of polymer after allowing for the residual methylene cross-links found in Merrifield resin.[7] Complementary to these results, it was found that 1.0 g of the suspected amide base, **1A**, would deprotonate 0.70 mequiv of triphenylmethane. Since the pk_a of triphenylmethane is ca. 31, this indicated that the active site on the deprotonated polymer was a very strong base. While we cannot exclude the possibility of other organometallic species from being present, the data presented here was consistent with **1** and **1A** being the identities of the polymer-bound amine and amide, respectively.

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(5) For review articles concerning polymer-supported amines and other macromolecular-bound species, see: *Polymer-Supported Reactions in Organic Synthesis*; Hodge, P., Sherrington, D. C., Eds.; Wiley: New York, 1980. Mathur, N. K.; Narang, C. K.; Williams, R. E. *Polymers as Aids in Organic Chemistry*; Academic: New York, 1980. Akelah, A.; Sherrington, D. C. *Chem. Rev.* **1981**, *81*, 557–587.

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Table I. Claisen Condensation Reactions Using a Sterically Hindered Amide Base

substrate	product	% yield[a,b]
acetophenone[c]	dibenzoylmethane	92 (48)
acetone[c]	1-benzoylacetone	88
γ-butyrolactone[c]	α-benzoyl-γ-butyrolactone	92 (31)
acetophenone[d]	1-benzoylacetone	90
acetone[d]	2,4-pentanedione	87

[a] The products were isolated and characterized by ^{1}H NMR spectroscopy. [b] The numbers in parentheses signify the yields previously reported when the reactions were carried out in solution, see ref 1. [c] The reaction was conducted with **2** as the macromolecular electrophile. [d] The reaction was carried out with **3** as the polymeric electrophile.

Since a macromolecular-bound ester was chosen as the electrophilic species in this process, we found it convenient to prepare the desired substrate by a known procedure.[8] As illustrated in Scheme II, polymers **2** and **3** were synthesized by allowing an alkali-metal carboxylate to react with 1% divinylbenzene cross-linked Merrifield resin. In both cases the disappearance of the signal for the chloromethyl unit at 1260 cm^{-1} and the appearance at 1735 cm^{-1} for the ester functionality in the IR spectra confirmed the identities of the products.

The preliminary results obtained during this study indicated that **1A** was an effective base for generating enolates from ketones and lactones. As illustrated in Table I, the yields of the acylated products were excellent when **1A** was used as the base. It should also be noted that the yields of the products presented in Table I were the isolated yields. The identities of these products were confirmed by ^{1}H NMR analysis. Furthermore, when the results of these reactions were compared to those of previously reported reactions conducted with soluble reagents, it was found that the yields of acylated products increased as much as 3-fold. Additionally, it was previously reported that self-condensation products were the major components of the product mixture when such soluble species were employed; in contrast to these findings, we found no noticeable evidences of any self-condensation products forming in our system.

In summary, on the basis of this preliminary report, we have developed a hindered amine attached to a polymeric support, which may be employed as a precursor to a synthetically useful amide base. Because of these findings, work is under way to extend the utility of this base to include enolate-alkylation reactions, reactions with hydrazone derivatives, and studies involving physical properties of stabilized carbanions.

Experimental Section

Melting points were determined by using a Hoover-Thomas melting point apparatus and are uncorrected. The ^{1}H NMR spectra were obtained with a Varian 360A NMR spectrometer utilizing Me_4Si as the internal standard. The IR spectra were acquired with a Perkin-Elmer Model 1430 IR spectrometer. The THF was distilled over sodium metal and benzophenone prior to use.[9]

Preparation of *N-tert*-Butyl-*N*-(2-(polystyrylmethoxy)ethyl)amine, 1. To a 500-mL round-bottomed flask equipped with a stirring bar and a reflux condenser was added 50 g (1 mequiv of Cl$^-$/g of polymer) of 1% divinylbenzene cross-linked Merrifield resin, 100 mmol of sodium 2-(*tert*-butylamino)ethoxide, and 200 mL of DMF. The reaction was then carried out with rapid stirring for 48 h at 140 °C. After the reaction was complete, the polymer was isolated by filtration and washed with methanol until no DMF was detected (via IR) in the washes. The polymer was then dried in vacuo for 12 h to yield 51 g of an off-white solid: IR (KBr) 3400, 1200–1000 cm^{-1}; loading (mequiv of amide base/g of polymer) 0.73.

Preparation of Polystyrylmethyl Benzoate, 2. By use of a published procedure, 10 g of 1% divinylbenzene cross-linked Merrifield resin (1 mequiv of Cl$^-$/g of polymer) was allowed to react with 20 mmol of cesium benzoate. Isolation of the product by filtration afforded 10.5 g of the desired product:[8] IR (KBr) 1735, 1200–1000 cm^{-1}.

Preparation of Polystyrylmethyl Acetate, 3. By use of a published procedure, 10 g of 1% divinylbenzene cross-linked Merrifield resin (1 mequiv of Cl$^-$/g of polymer) was allowed to react with 20 mmol of sodium acetate. Isolation of the product by filtration afforded 10.5 g of the desired product:[8] IR (KBr) 1735, 1200–1000 cm^{-1}.

General Procedure for Wolf and Lamb Reactions. To a dry two-necked 250-mL round-bottomed flask equipped with a stirring bar, septum, and pressure equalizing funnel was added 5.0 g (3.65 mmol) of **1**. The polymer was then swollen with ca. 75 mL of dry THF, and the reaction mixture was cooled to −78 °C. The addition funnel was charged with 7.0 g (7 mmol) of either **2** or **3**, ca. 2–3 mmol of the soluble substrate, and 50 mL of dry THF. Prior to the initiation of the reaction, the entire system was purged with nitrogen.

To the swollen polymer was added 2.5 mL (4 mmol) of 1.6 M *n*-BuLi via syringe, and the mixture was allowed to stir for 30 min. Upon completion of this step, the reddish-brown polymer was washed with dry THF (cooled to −78 °C) until no soluble base was detected in the washes. At this point the contents of the funnel were rapidly added to the round-bottomed flask, and the reaction was allowed to proceed for 2 h with the flask gradually coming to room temperature. After the polymeric byproducts were removed by filtration, the solvent was removed to yield the final product.

Polymer Recovery. The mixture of polymeric reagents that were isolated at the end of the Wolf and Lamb reaction was separated by selective flotation. This was accomplished by swelling the mixture in toluene and slowly adding chloroform to the mixture until a noticeable partition between the two polymers was observed. The polymer from each layer was then analyzed by IR to determine if complete separation had occurred. A minimum of three such cycles were required to satisfactorily separate the two polymers. The composition of the solvent mixture was ca. 53:47 (v/v) of chloroform–toluene.

Analysis of Polymer 1. The loading of organometallic species on the polymer was estimated on the basis of the amount of soluble base detected by an acid–base titration of a methanol quench of a known amount of the polymer. Such an analysis was carried out by adding *n*-BuLi to a 1-g sample of the polymer that was swollen in dry THF and maintained at −78 °C under a nitrogen atmosphere. After being stirred for 30 min, the reddish-brown polymer was washed with dry THF until no soluble base was detected in the washes. The deprotonated polymer was then quenched with 10 mL of methanol and allowed to stir for 30 min. The resulting off-white solid was washed with THF until the washes were no longer basic. The methoxide base in the combined washes was then titrated to a phenolphthalein end point.

Preparation of Dibenzoylmethane. This reaction was carried out on a 2.5-mmol scale with acetophenone as the limiting reagent. Polymer **2** was employed as the electrophilic reagent. Isolation of the product as previously described afforded 0.51 g (92%) of the desired product as an off-white solid: ^{1}H NMR (60 MHz, $CDCl_3$) δ 8.3–8.1 (m, 4 H), 7.9–7.5 (m, 6 H), 7.1 (s, 2 H); mp 78–79 °C.

Preparation of 2,4-Pentanedione. This reaction was conducted on a 2.6-mmol scale as previously described with acetone as the limiting reagent. Polymer **3** was used as the electrophilic reagent. Removal of the solvent afforded 0.23 g (87%) of a clear liquid: ^{1}H NMR (60 MHz, $CDCl_3$) δ 5.5 (s, 2 H), 2.1 (s, 6 H).

Preparation of 1-Benzoylacetone. This product was afforded by two different routes. By the first route, acetophenone 0.30 g (2.55 mmol) was allowed to react with **3** to yield 0.36 g (88%) of the desired product. The same product was obtained by a second pathway, which involved the use of 0.14 g (2.40 mmol)

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[8] Gisin, B. F. *Helv. Chim. Acta* **1973**, *56*, 1476–1482.

[9] Unexceptional inert-atmosphere techniques were used in all reactions involving organometallic reagents; cf.: Brown, H. C. *Organic Syntheses via Boranes*; Wiley-Interscience: New York, 1975.

acetone and 2 as substrates to yield 0.35 g (90%) of an off-white solid: ^{1}H NMR (60 MHz, $CDCl_3$) 8.1–7.9 (m, 1 H), 7.7–7.4 (m, 4 H), 6.2 (s, 2 H), 2.1 (s, 3 H); mp 56–58 °C.

Preparation of α-Benzoyl-γ-butyrolactone. This reaction was conducted on a 3.0-mmol scale with γ-butyrolacetone as the limiting species. Removal of the solvent afforded 0.52 g (92%) of a pale yellow oil: ^{1}H NMR (60 MHz, $CDCl_3$) δ 8.3–8.1 (m, 1 H), 7.7–7.4 (m, 4 H), 4.4 (t, 2 H), 3.6 (t, 1 H), 2.5 (m, 2 H).

Acknowledgment is made to the donors of The Citadel Development Research Fund, administered by The Citadel Development Foundation, for their generous funding of this project.

Chemical Sources of Singlet Oxygen. 3.[1] Peroxidation of Water-Soluble Singlet Oxygen Carriers with the Hydrogen Peroxide–Molybdate System

J. M. Aubry*

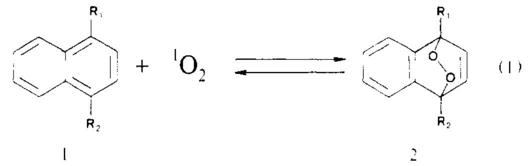
Laboratoire de Chimie Générale (UA 351), Faculté de Pharmacie de Lille, 59045 Lille Cedex, France

B. Cazin[2] and F. Duprat

Laboratoire de Recherches Organiques (UA 476), E.S.P.C.I., 75231 Paris Cedex 05, France

Received August 3, 1988

Naphthalenic endoperoxides 2 provide highly useful chemical sources of singlet oxygen ($^1O_2$, $^1\Delta_g$) for mechanistic studies as they split off known quantities of pure $^1O_2$ when warmed at moderate temperature (30–50 °C).[3] In particular, water-soluble derivatives have been used in aqueous media as singlet oxygen carriers[4-6] (eq 1) to assess the role of this species in inorganic reactions[5] and in photodynamic effect.[6]



a : $R_1 = (CH_2)_2COONa$, $R_2 = CH_3$
b : $R_1 = (CH_2)_2COOH$, $R_2 = CH_3$
c : $R_1 = R_2 = (CH_2)_2COONa$
d : $R_1 = R_2 = (CH_2)_2COOH$

However, endoperoxides 2 are secondary sources of $^1O_2$ as they must be prepared from a primary source. Up to now, only prolonged photooxidation at low temperature was able to generate the high flux of $^1O_2$ necessary to peroxidize the poorly reactive substrates 1.[3d,4a,5] In the present paper, we show that the newly discovered chemical source of $^1O_2$, H_2O_2/MoO_4^{2-}, is a simpler alternative to the usual photochemical method to peroxidize water-soluble substrates like 1.

Results and Discussion

Molybdate ions catalyze disproportionation of hydrogen peroxide in basic solution, providing $^1O_2$ in quantitative yield through the intermediacy of a diperoxomolybdate, MoO_6^{2-} (eq 2 and 3).[1]

$$2H_2O_2 + MoO_4^{2-} \rightleftarrows 2H_2O + MoO_6^{2-} \tag{2}$$

$$MoO_6^{2-} \rightarrow MoO_4^{2-} + {}^1O_2 \tag{3}$$

When a substrate A is present, singlet oxygen produced by reaction 3 at a rate v_f, is either quenched by water or A with rate constants k_d (eq 4) and k_q (eq 5) or reacts with A at a rate constant k_r (eq 6). The endoperoxide AO_2 thus obtained can undergo thermolysis at a rate constant k_t, giving back A and oxygen, a part of which is in a singlet state (eq 7).

$$^1O_2 + \text{water} \xrightarrow{k_d} {}^3O_2 \tag{4}$$

$$^1O_2 + A \xrightarrow{k_q} {}^3O_2 + A \tag{5}$$

$$^1O_2 + A \xrightarrow{k_r} AO_2 \tag{6}$$

$$AO_2 \xrightarrow{k_t} A + O_2 \tag{7}$$

Stationary concentration of singlet oxygen, $[^1O_2]_{st}$, may be calculated by neglecting $^1O_2$ coming from the slow dissociation of AO_2 (eq 7) compared with the one evolved by the disproportionation of hydrogen peroxide (eq 2 and 3).

$$[^1O_2]_{st} = v_f/\{k_d + (k_q + k_r)\}[A] \tag{8}$$

Reaction 1 shifts to the right as long as the peroxidation rate of A is higher than the decomposition of AO_2:

$$k_r[A][^1O_2]_{st} \geqslant k_t[AO_2] \tag{9}$$

substituting (8) into (9) we obtain

$$v_f \geqslant \frac{[AO_2]}{[A]}\frac{k_t}{k_r}\{k_d + (k_q + k_r)[A]\} \tag{10}$$

Since under our conditions, the main pathway for $^1O_2$ decay is the quenching by water ($k_d \gg (k_r + k_q)[A]$),[7] (10) reduces to

$$v_f \geqslant \frac{[AO_2]}{[A]}\frac{k_t k_d}{k_r} \tag{11}$$

If the reaction is performed at 20 °C under optimized conditions of pH (9.5–11.5) and H_2O_2 concentration ($[H_2O_2]/[MoO_4^{2-}]$ = 2–3), the rate of $^1O_2$ generation by reaction 3 is $v_f = (1.8 \times 10^{-3})[MoO_4^{2-}]$.[1] At the same

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[1] For paper 2, see: Aubry, J. M.; Cazin, B. *Inorg. Chem.* **1988**, *27*, 2013–2014.

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0022-3263/89/1954-0726$01.50/0 © 1989 American Chemical Society