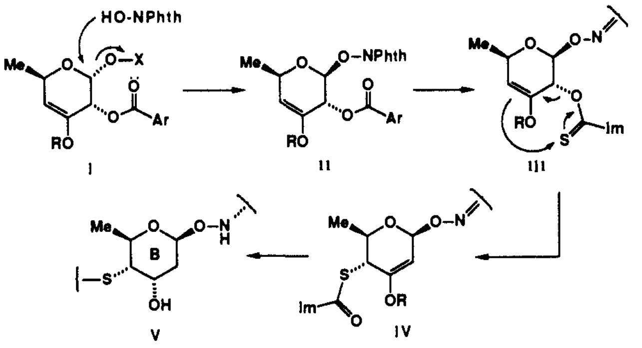
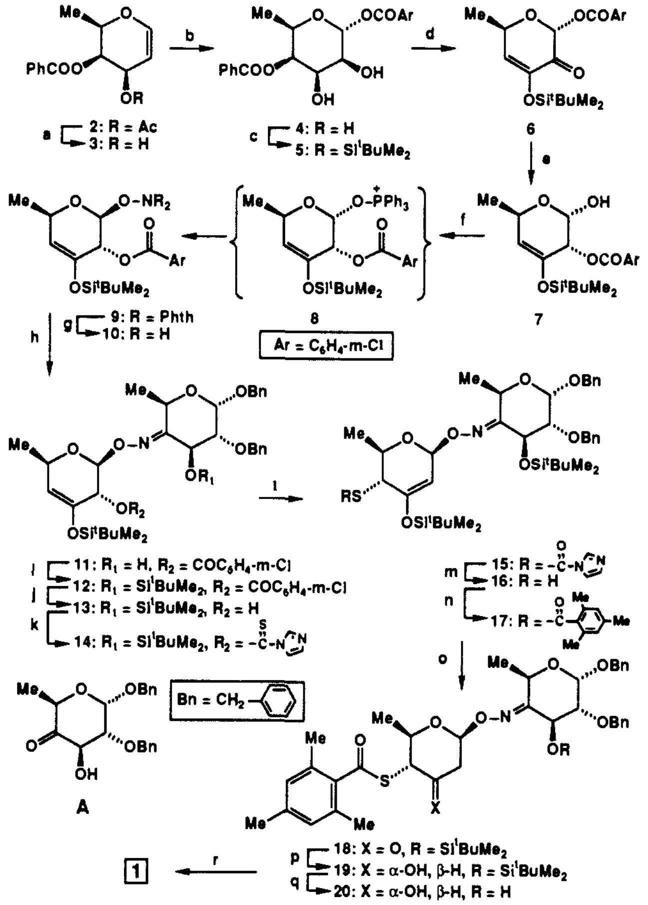
Scheme I. Synthetic Design for the Construction of the Central Ring of the Calicheamicin $\gamma_{1\alpha}{}^1$ Oligosaccharide Fragment



Scheme II. Synthesis of Compound 1^a



^{a}Reagents and conditions: (a) 1.0 equiv of DIBAL, CH_2Cl_2, −78 °C, 2.5 h, 72%, plus 15% recovered **2**; (b) 2.5 equiv of 55% MCPBA, $MgSO_4$, CH_2Cl_2, 0 °C, 0.5 h, 55%; (c) 1.5 equiv of ^{t}BuMe$_2$SiCl, 2.0 equiv of imidazole, CH_2Cl_2, 25 °C, 30 h, 67%; (d) 1.5 equiv of (COCl)$_2$, 2.0 equiv of DMSO, 5 equiv of Et_3N, CH_2Cl_2, −78 to 25 °C, 88%; (e) 1.2 equiv of $Zn(BH_4)_2$, 0.5 equiv of NH_4Cl, ether, 0 °C, 20 min; (f) 1.1 equiv of HO-NPhth, 1.2 equiv of diisopropyl azodicarboxylate, 1.2 equiv of Ph_3P, THF, 25 °C, 0.5 h, 53% overall from **6**; (g) 1.0 equiv of N_2H_4, MeOH, 25 °C, 10 min; (h) 1.2 equiv of A, 0.1 equiv of PPTS, PhH, 25 °C, 3 h, 92% overall from **9**; (i) 1.5 equiv of ^{t}BuMe$_2$SiOTf, 2.5 equiv of 2,6-lutidine, −25 to 0 °C, 0.5 h, 99%; (j) 2.5 equiv of DIBAL, CH_2Cl_2, −78 °C, 1 h, 91%; (k) 1.0 equiv of thiocarbonyldiimidazole, CH_3CN, 25 °C, 20 h; (l) $PhCH_3$, 110 °C, 1 h, 85% overall from **13**; (m) 6.0 equiv of DIBAL, CH_2Cl_2, −78 °C, 2 h; (n) 2.0 equiv of 2,4,6-trimethylbenzoyl chloride, 10 equiv of Et_3N, 0.35 equiv of DMAP, CH_2Cl_2, 25 °C, 8 h, 91% overall from **15**; (o) 1.0 equiv of TBAF, THF–H_2O–HOAc (100:25:1), 0 °C, 20 min; (p) 2.5 equiv of K-Selectride, DME, −78 °C, 1.5 h, 74% overall from **17**; (q) 1.2 equiv of TBAF, THF, 0–25 °C, 45 min, 100%; (r) 6 equiv of $BH_3 \cdot NH_3$, 6 equiv of PPTS, 25 °C, 4 h, 85%.

thiocarbonyldiimidazole for 20 h at 25 °C gave a mixture of the thioimidazolide **14** and **15**, the latter resulting from a stereospecific [3,3]-sigmatropic rearrangement[12] of **14**. Refluxing the mixture for 1 h in toluene completed the rearrangement in 85% overall yield from **13**. Generation of the free thiol group in **15** using DIBAL resulted in the formation of **16**, which was immediately reacted with 2,4,6-trimethylbenzoyl chloride under basic conditions, to afford the desired thioester **17**. Selective desilylation was achieved with a stoichiometric amount of nBu_4NF leading to ketone **18** in good yield. As expected, stereoselective reduction of the carbonyl group of ring B with a bulky reagent (K-Selectride) led to compound **19** (74% overall yield from **17**). Desilylation of **19** led to dihydroxy compound **20** in quantitative yield. Finally, stereoselective reduction of the oxime in **20** was secured with $BH_3 \cdot NH_3$–pyridinium *p*-toluenesulfonate (PPTS), furnishing the targeted ABC system **1** in 85% yield.[13] The stereochemistry of the stereogenic centers generated in this sequence (C-4, C-1′, C-3′ and C-4′) was evident from NMR data (see supplementary material).

The described chemistry provides stereocontrolled solutions to the crucial bond constructions of the calicheamicin $\gamma_{1\alpha}{}^1$ oligosaccharide fragment and makes available the interesting subfragment **1** for DNA binding studies and other investigations in this area. Furthermore, the reported sequence is expected to facilitate the synthesis of the complete oligosaccharide fragment of these antibiotics.

Acknowledgment. We express our many thanks to John Ramphal for NMR spectroscopic assistance and Andrew Altman of VG Instruments for mass spectra. This work was financially supported by the National Institutes of Health and Hoffmann LaRoche, USA.

Supplementary Material Available: Schemes with reagents and conditions for the synthesis of compounds **2** and A and listing of selected R_f, $[\alpha]_D$, ^{1}H NMR, and mass spectrometric data for compounds A, **1**, **2**, **4**, **6**, **9**, **11**, **13**, **15**, **17**, **19**, and **20** (10 pages). Ordering information is given on any current masthead page.

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[12] (a) For a rearrangement of an allylic xanthate in a carbohydrate derivative see: Ferrier, R. J.; Vethauiyasar, N. *J. Chem. Soc. D* **1970**, 1385. (b) For a rearrangement of an allylic xanthate in a 2-substituted cyclohexene derivative, see: Trost, B. M.; Hiemstra, H. *J. Am. Chem. Soc.* **1982**, *104*, 886.

[13] The precise mechanism for the axial delivery of hydride in this stereoselective process is not well understood at present.

Tellurapyrylium Dyes as Catalysts for the Conversion of Singlet Oxygen and Water to Hydrogen Peroxide

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The development of methods for light-to-chemical energy conversion is important for application to solar-energy storage schemes. While the major emphasis in such research has been water splitting for the production of hydrogen,[1-6] the photopro-

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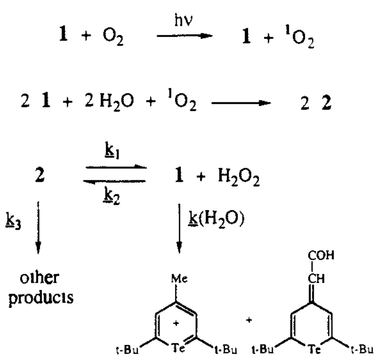
[1] For Ru(2,2′-bipyridine)$_3^{2+}$/methylviologen systems: (a) Kalyanasundaram, K. *Coord. Chem. Rev.* **1982**, *46*, 159. (b) *Photogeneration of Hydrogen*; Harriman, A., West, M. A., Eds.; Academic: London, 1982. (c) *Energy Resources through Photochemistry and Catalysis*; Gratzel, M., Ed.; Academic: New York, 1983. (d) Prasad, D. R.; Khoffman, M. Z. *J. Am. Chem. Soc.* **1986**, *108*, 2568.

0002-7863/90/1512-4086$02.50/0

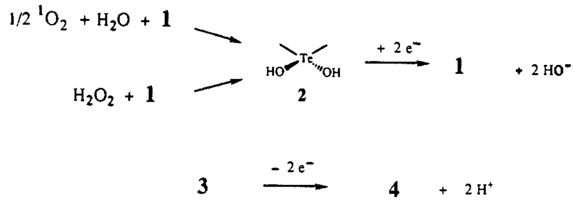
Scheme I

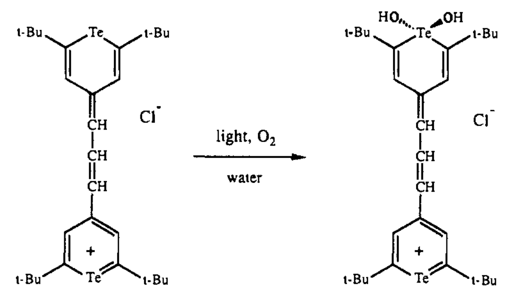


duction of other energy-rich compounds such as hydrogen peroxide has also received attention.[1c,7–9] In metal-based systems for the production of either hydrogen or hydrogen peroxide as well as in dye-mediated systems for the production of hydrogen peroxide, a sacrificial electron donor is required to minimize electron back-transfer to the sensitizer from the electron relay.

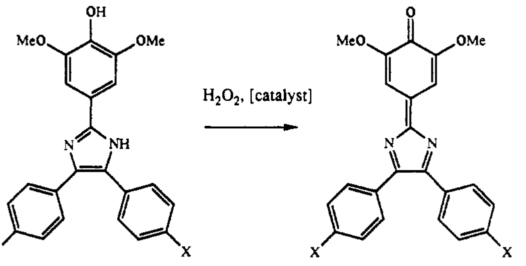
We report novel, catalytic reactions of tellurapyrylium dye **1** that utilize tellurium(IV) species **2** as an intermediate. In one reaction, the formation of **2** mediates the reduction of singlet oxygen to hydrogen peroxide in the presence of water. In a second reaction, the formation of **2** leads to a two-electron reduction of hydrogen peroxide to water with concomitant oxidation of leucodyes **3** to dyes **4**. In both systems, a tellurium(II)–tellurium(IV)–tellurium(II) cycle avoids the use of a sacrificial electron donor.

Scheme II





1   **2**



3a, X=OMe
3b, X=NMe$_2$

4a, λ_{max} = 515 nm
4b, λ_{max} = 660 nm

Compound **2** undergoes a thermal, reductive elimination of hydrogen peroxide in various combinations of methanol and water. The first-order rate constant (k_1) for reductive elimination of hydrogen peroxide from **2** increases by more than 500-fold at 310 K as the solvent is made less polar by going from water [k_1 = (2.24 ± 0.03) × 10^{-5} s^{-1}] to 99% methanol [k_1 = (1.10 ± 0.005) × 10^{-2} s^{-1}].

From the temperature-dependent values of k_1 in 99% methanol,[10] $\Delta H^\ddagger$ was calculated to be 18.5 ± 0.5 kcal mol^{-1} (R^2 = 0.999); $\Delta S^\ddagger$, to be 15.3 ± 0.1 cal K^{-1} mol^{-1}; $\Delta G^\ddagger_{298}$, to be 13.9 kcal mol^{-1}; and the Arrhenius parameters were calculated (R^2 = 0.999) to be 19.1 ± 0.5 kcal mol^{-1} for E_a and 24.40 ± 0.04 for A, consistent with a dissociative process producing hydrogen peroxide and **1** from **2**. These values can be compared with a $\Delta H^\ddagger$ of 19.1 ± 0.5 kcal mol^{-1}, $\Delta S^\ddagger$ of 11.9 ± 0.1 cal K^{-1} mol^{-1}, and $\Delta G^\ddagger_{298}$ of 15.6 kcal mol^{-1} for the thermal dissociation of **2** in 50% aqueous methanol[11] and a $\Delta H^\ddagger$ of 20.9 ± 0.1 kcal mol^{-1}, $\Delta S^\ddagger$ of 10.9 ± 0.1 cal K^{-1} mol^{-1}, and $\Delta G^\ddagger_{298}$ of 17.6 kcal mol^{-1} in water.[12] These data suggest that the mechanism of peroxide generation is similar in various combinations of methanol and water and that solvent polarity influences the transition state leading to reductive elimination.

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(10) The temperature-dependent values of k_1 in 99% methanol were found to be (2.38 ± 0.06) × 10^{-3} s^{-1} at 295.9 K, (5.38 ± 0.15) × 10^{-3} s^{-1} at 303.0 K, (1.100 ± 0.005) × 10^{-2} s^{-1} at 310.0 K, and (2.03 ± 0.02) × 10^{-2} s^{-1} at 316.9 K. These values were measured by following the disappearance of the 510-nm band of **2**.

(11) The temperature-dependent values of k_1 in 50% methanol were found to be (1.515 ± 0.005) × 10^{-4} s^{-1} at 296.0 K, (2.946 ± 0.006) × 10^{-4} s^{-1} at 303.0 K, (5.55 ± 0.08) × 10^{-4} s^{-1} at 310.0 K, (1.43 ± 0.04) × 10^{-3} s^{-1} at 317.0 K, and (2.50 ± 0.02) × 10^{-3} s^{-1} at 324.0 K.

(12) The temperature-dependent values of k_1 in water were found to be (2.24 ± 0.03) × 10^{-5} s^{-1} at 310.0 K, (9.15 ± 0.02) × 10^{-5} s^{-1} at 323.0 K, and (2.51 ± 0.05) × 10^{-4} s^{-1} at 333 K.

Tellurapyrylium dye **1** reacts with singlet oxygen[13] in the presence of water to give oxidized dye **2** with a second-order rate constant that varies from 9×10^6 M^{-1} s^{-1} in 99% methanol to 8×10^8 M^{-1} s^{-1} in water at ambient temperature.[14] The stoichiometry for the reaction of singlet oxygen with **1** was determined from studies employing an oxygen electrode. For five independent runs, the concentration of oxygen was lowered $(4.0 \pm 0.3) \times 10^{-5}$ M in air-saturated aqueous solutions of **1** (9.3×10^{-5} M) upon irradiation with filtered light (630–850 nm) from a quartz-halogen source. After 100 s of irradiation, no further decrease in oxygen concentration and complete oxidation of **1** to **2** were observed. The observed loss of oxygen corresponds to 2.3 ± 0.2 molecules of **1** oxidized for each oxygen molecule consumed.

In 99% methanol at 310 K, $\leq 10^{-7}$ M **2** is detected following irradiation (630–850 nm) of air-saturated, 1.0×10^{-5} M solutions of **1** for 900 s (**1** is depleted). However, following 2-fold dilution with an aqueous solution of leucodye **3a** (10^{-3} M) and addition of horseradish peroxidase to a concentration of 10^{-12} M, 3.7×10^{-5} M dye **4a** (ϵ 45 000 L mol^{-1}) was formed. Thus, 7.4 mol of hydrogen peroxide was produced from each mole of **1** in solution.

The catalytic cycle for the production of hydrogen peroxide from singlet oxygen and water with **1** is summarized in Scheme I. Catalyst lifetime is determined by chemical and photochemical reactions of the catalyst. For **1** at 1.0×10^{-5} M in 99% methanol, the quantum yield for self-sensitized scavenging of singlet oxygen was measured to be 1.1×10^{-4} while the quantum yield for photochemical loss of **1** was measured to be 1.5×10^{-5}. The rate constant for hydrolysis of **1**, $k(H_2O)$, was measured to be $\leq 5 \times 10^{-7}$ s^{-1} at 310 K in 99% methanol. Similarly, the rate constant, k_3, for other thermal reactions of **2** was measured to be $\leq 6 \times 10^{-5}$ s^{-1} at 310 K in 99% methanol by monitoring the thermal recovery of **1** ($\approx$99%). Under pseudo-first-order conditions, **1** (1.0×10^{-5} M) reacts with hydrogen peroxide (1×10^{-3} M or 1×10^{-4} M) to give **2** with a second-order rate constant, k_2, of $(1.29 \pm 0.06) \times 10^{-2}$ M^{-1} s^{-1} at 310 K in 99% methanol. In 50% aqueous methanol and in water, k_2 is larger, with values of 0.33 M^{-1} s^{-1} and 2.0 M^{-1} s^{-1}, respectively, at 298 K.[14]

At 298 K in distilled water, **3b** (10^{-3} M) is oxidized by **2** (1×10^{-5} M) with a second-order rate constant of (44.1 ± 2.0) M^{-1} s^{-1}, producing **4b** and **1**. This suggests that **1** should function as a catalyst for the two-electron oxidation of **3** to **4** with either singlet oxygen or hydrogen peroxide as shown in Scheme II.

As illustrated in Figure 1 in 99% methanol, an initial concentration of **1** of 3.0×10^{-6} M will oxidize 1.56×10^{-4} M **3a** (initially 10^{-3} M) to **4a** in air-saturated 99% methanol upon irradiation (630–850 nm) before the catalyst is consumed ($\approx$900 s). Similarly, 5.13×10^{-5} M **3b** (initially 10^{-3} M) is oxidized to **4b** upon irradiation of air-saturated, 99% methanol solutions containing 1.0×10^{-6} M **1** for 900 s. These numbers represent turnovers of ≥ 50 for the catalyst **1**. In rigorously degassed 99% methanol solutions of **1** and **3**, no oxidation is observed upon irradiation.

In aqueous solutions (pH 6.8) containing 1×10^{-4} M leucodye **3** and 0.01 M hydrogen peroxide, dyes **4** are formed with pseudo-first-order rate constants of 7.04×10^{-8} s^{-1} for **3a** and 1.57×10^{-7} s^{-1} for **3b** at 298 K. The addition of 1.0×10^{-6} M **1** (1 mol %) gave accelerated (>2000-fold larger) pseudo-first-order rate constants of $(1.74 \pm 0.02) \times 10^{-4}$ s^{-1} for oxidation of **3a** at 298 K and $(3.34 \pm 0.03) \times 10^{-4}$ s^{-1} for oxidation of **3b** at 298 K. In both cases, concentrations of **4** approached 10^{-4} M with catalyst turnover numbers of 100.

Analogues of **1** containing either two sulfur atoms or two selenium atoms in place of tellurium do not catalyze the conversion of singlet oxygen and water to hydrogen peroxide and do not catalyze the oxidation of leucodyes **3** to **4** with hydrogen peroxide. We are currently investigating other tellurapyrylium dyes as catalysts to optimize hydrogen peroxide production and catalyst lifetime and to increase the scope of oxidations with species such as **2**.

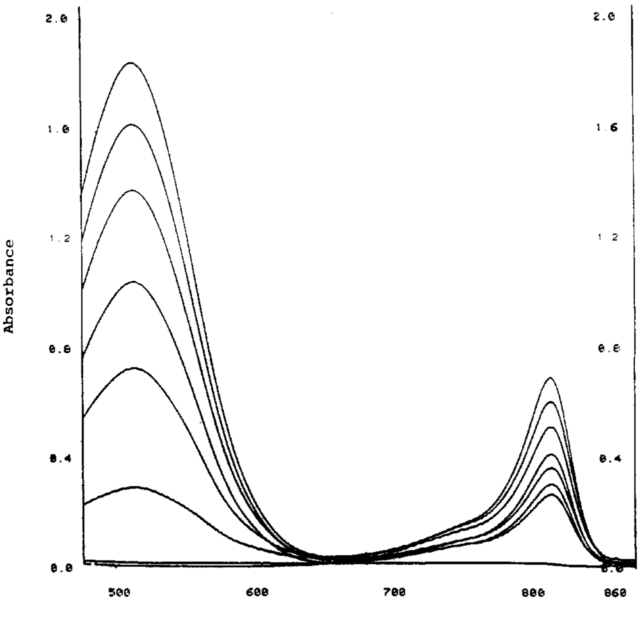

Figure 1. Photochemical oxidation of **3a** (5×10^{-3} M) to **4a** (λ_{max} 515 nm) in 99% aqueous methanol upon irradiation of **1** (λ_{max} 810 nm, 3.0×10^{-6} M) with filtered (630–850-nm) light from a quartz-halogen source. The irradiation was stopped every 60 s to generate the absorption curves shown (0–360 s). After 900 s, the optical density was 7.02 (measured by 10-fold dilution, curve not shown). The blank trace was for the leucodye **3** in air-saturated 90% aqueous methanol irradiated for 20 min without catalyst.

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[13] This reaction was observed with singlet oxygen generated from irradiation of a variety of sensitizers in air-saturated aqueous methanol including rose bengal [$\Phi(^1O_2) = 0.76$; Gollnick, K.; Schenck, G. O. *Pure Appl. Chem.* **1964**, *9*, 507], methylene blue [$\Phi(^1O_2) = 0.52$; Nemoto, M.; Kokubun, H.; Koizumi, M. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 1223, 2464], and self-sensitized generation of singlet oxygen from **1** [$\Phi(^1O_2) = 0.12$, ref 14].

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General Approach to the Synthesis of Macroline-Related Alkaloids. Stereospecific Total Synthesis of (−)-Alstonerine

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In the last several years, approximately 30 macroline-related alkaloids have been isolated from *Alstonia macrophylla* Wall, *Alstonia muelleriana* Domin, and other species of *Alstonia*;[1-3] macralstonine (**1**),[1a,b] alstonerine (**2a**),[2a] and alstophylline (**2b**)[2b] serve as representative examples. The recent biomimetic interconversions by LeQuesne et al.[3] have served to establish that the absolute configurations of alstonerine (**2a**), alstophylline (**2b**) and macroline **4** (**3a** → **4**)[3a] are identical with those of N_a-methylsarpagine, the non-macroline portion of the bisindole alkaloid macralstonidine.[3] Moreover, macroline (**4**) and alstophylline (**2b**) have been condensed to provide the hypotensive

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