*α-bromo ketals hold considerable promise as latent α-keto-vinyl anion equivalents.*[15]

With a viable route to **5** secured, we next directed our attention to the completion of our synthetic venture. Central here was elaboration of **13**, a *common* intermediate from which **1–3** could in turn be generated. To this end, cis-hydroxylation of **11**,[9] obtained from **5** in 77%[8] yield (1.1 equiv of *tert*-butyldi-

11

12

13 (R = H)
14 (R = Ac)

15
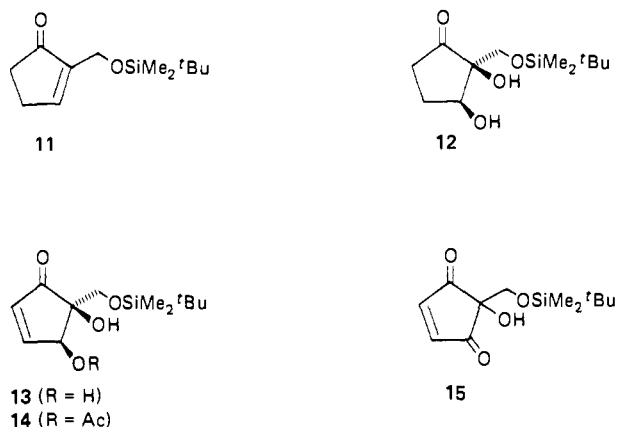
methylsilyl chloride/2.2 equiv of imidazole/DMF)[16] with 1.1 equiv of OsO₄ in pyridine,[17] followed by reductive cleavage (aqueous NaHSO₃) of the derived osmate ester, afforded cis diol **12**[9] in 95% yield.[8] Dehydrogenation of **12** was then conveniently effected via selenium dioxide oxidation[18] (SeO₂, *t*-BuOH, 7 days, reflux, followed by chromatography on silica gel). Under these conditions crystalline **13**[9] (mp 81 °C) was obtained in 53% yield: IR (CHCl₃) 3540 (s, br), 3025 (m), 1725 (s) cm⁻¹; NMR (220 MHz) δ 0.25, 0.29 (s, s, 6 H), 1.08 (s, 9 H), 3.80, 3.98 (br s, AB system, ν_{AB} = 25.6 Hz, J = 10 Hz, 4 H), 5.03 (br s, 1 H), 6.56 (d, J = 6 Hz, 1 H), 7.91 (m, 1 H).

With **13** in hand, conversion to **1–3** proceeded without event. In particular, hydrolysis of **13** (aqueous AcOH, THF, 80 h, room temperature)[16] afforded (±)-pentenomycin I (96%), while acetylation (Ac₂O, pyridine, 4 °C, 18 h), followed by a similar hydrolysis protocol of the derived monoacetate (**14**),[9] gave (±)-pentenomycin II (85%). Jones oxidation[19] of **13** (1.5 equiv, acetone, −10 °C) on the other hand led to the beautifully crystalline yellow enedione **15**[9] (61%, mp 65 °C) which upon hydrolysis afforded dehydropentenomycin I (74% yield[8] from **15**). That **1–3** were indeed identical with authentic pentenomycin I, pentenomycin II, and dehydropentenomycin I, respectively, was apparent from their spectroscopic properties (IR, 220-MHz NMR, and UV) as well as by direct comparison with published ¹H and, in the case of **3**, ¹³C NMR spectra. Finally, synthesis of **3** confirms the structure of dehydropentenomycin I.

Studies extending this route to the epimeric series of antibiotics (i.e., antibiotics C-2554 AI, AII, and B),[5] as well as to analogues of this novel class of pharmacologically active cyclopentenones, are currently in progress in our laboratory.

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i   ii   iii

properties and the spectroscopic properties of the derived triacetate, the latter apparently significantly different from those derived from pentenomycin I triacetate; see K. Hatano, T. Hasegawa, M. Izawa, M. Asai, and H. Kwasaki (Takeda Chemical Industries, Ltd.), Japan, Kokai 75, 70,597 (June 1975); *Chem. Abstr.*, **84**, 3287u (1976).
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(14) Hydroxyenone 5 is a white crystalline solid (mp 68–69 °C): IR (CHCl₃) 3620 (m), 3550–3350 (m, br), 1700 (sh), 1690 (s), 1645 (m) cm⁻¹; NMR (220 MHz) δ 2.46 (m, 2 H), 2.65 (m, 3 H), 4.38 (br s, 2 H) 7.71 (m, 1 H).
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Electrochemical Behavior and Standard
Potential of Au⁻ in Liquid Ammonia

Sir:

In a recent paper[1] spectroscopic evidence for the existence of the first transition metal anion, the auride ion (Au⁻), produced in liquid NH₃ solution containing cesium, rubidium, or potassium was reported. Preliminary electrochemical studies on the auride ion were described in this work but no detailed electrochemical data were given. We report here the electro-

Table I. Summary of Cyclic Voltammetric Data Obtained for the Oxidation of Au^- and Reduction of Gold(I) in Liquid NH_3 Containing 0.1 M KI at $-40\ °C^a$

scan rate, v, V/s	Au$^-$, c 2.54 mM		Au(I), c 6.3 mM	
	i_{pa} (μA)	$-E_{pa}$ (V vs. Ag)	i_{pc} (μA)	$-E_{pc}$ (V vs. Ag)
0.02	13	2.17	29	0.30
0.05	20	2.15	45	0.31
0.10	26	2.14	62	0.32
0.20	36	2.13	85	0.33
0.50^b	50	2.11	125	0.35
	$i_{pa}/v^{1/2}c = 32(\mu A\ s^{1/2}$ $L/V^{1/2}$ mmol)		$i_{pc}/v^{1/2}c = 31(\mu A\ s^{1/2}$ $L/V^{1/2}$ mmol)	

^{a} i_{pa} = anodic peak current, i_{pc} = cathodic peak current, E_{pa} = anodic peak potential, E_{pc} = cathodic peak potential. ^{b} There is a slight decrease in the current function at the higher scan rates which is primarily due to the difficulty in base-line estimation as well as response time of the recorder.

chemical generation and oxidation of Au^- in liquid NH_3 containing 0.1 M KI as the supporting electrolyte and an estimate of the standard potential of the Au/Au^- couple.

The electrochemical cell and apparatus used in these experiments has been previously described.[2-4] The working electrode consisted of a platinum disk (0.039 cm^2) sealed in soft glass. The quasi-reference electrode was a Ag wire isolated from the test solution by a fine-porosity glass frit. This reference electrode has been found to be stable in liquid NH_3 within ±15 mV for a series of experiments in a given solution. We purposely avoided using a standard reference electrode such as $Ag/AgNO_3$ redox couple to minimize any contamination of the test solution by silver(I). The potential of the reference electrode was calibrated against the potential of solvated electron (e_s^-), -2.69 V vs. $Ag/AgNO_3$ (0.1 M).[3]

A typical experiment consisted of the coulometric generation of excess solvated electrons followed by the introduction into the solution of a known amount of Au foil. The solution was kept at $-40\ °C$ using dry ice–2-propanol bath and stirred for at least 2 hours or until all of the gold dissolved. A cyclic voltammogram of this solution initiated at a potential where e_s^- is generated is shown in Figure 1. The first oxidation wave corresponds to the collection of e_s^- (~-2.5 V). The second oxidation wave, at -2.15 V vs. Ag, shows an anodic peak current (i_{pa}) proportional to $v^{1/2}$ (where v is the scan rate) and is attributed to oxidation of Au^-. On scan reversal a cathodic wave at -2.42 V, caused by reduction of the anodically deposited Au, occurs. This wave is not observed if the anodic scan does not encompass the wave at -2.15 V. The large potential difference between the peak potentials ($E_{pa} - E_{pc}$) of the two waves (~0.27 V) suggests some kinetic limitations in the electrode process. The dissolution of gold in liquid NH_3 caused by the presence of e_s^- probably leads to the formation of ion pairs (e.g., K^+Au^-) (and/or dimers). A recent paper suggested extensive dimerization and ion-pair formation of solvated electrons in liquid NH_3.[3] The peak potential, E_{pa}, of the anodic wave shifted in the positive direction by ~40 mV for each tenfold increase in scan rate. A summary of the cyclic voltammetric results is given in Table I. These results allow an estimation of the formal potential of the Au/Au^- redox couple, estimated as the mean of E_{pa} and E_{pc}:

$$Au + K^+ + e \rightarrow K^+Au^-$$
$$E^{°\prime} = -2.3 \pm 0.1 \text{ V vs. } Ag/AgNO_3 \text{ (0.1 M)}$$
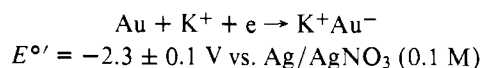
i.e., $E^{°\prime} = +0.4 \pm 0.1$ V vs. the solvated electron couple. Thus the $\Delta G^°$ for the reaction of solid gold with e_s^- to produce Au^- is estimated to be -9 kcal/mol.

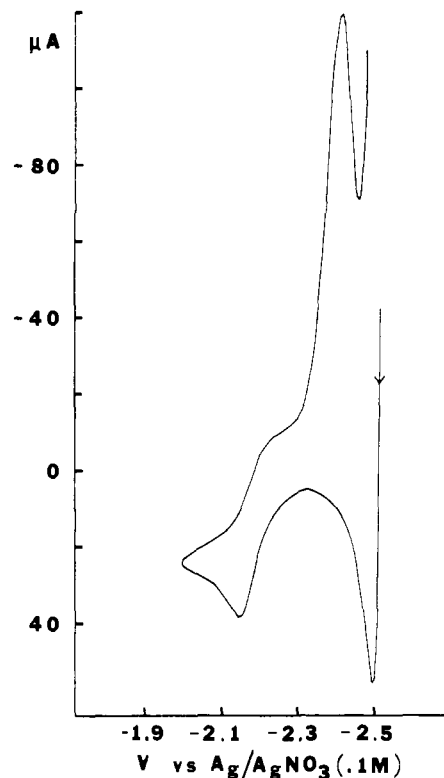To investigate the role of e_s^- in stabilizing the Au species

Figure 1. Cyclic voltammetric behavior of a 3.63 mM Au^- solution in liquid NH_3 containing 0.1 M KI at $-40\ °C$. Scan rate 0.1 V/s.

and to confirm the number of electrons consumed per Au atom, controlled potential oxidation following Au dissolution was carried out to remove excess e_s^-. The remaining solution was clear and exhibited cyclic voltammetric results identical with those obtained in the presence of excess e_s^-. A controlled potential electrolysis of this solution at a large Pt electrode at -2.0 V resulted in the passage of 0.92 faradays/mol of Au. A bright metallic coating was found on the platinum foil *anode*. Surface examination of the electrode by ESCA spectroscopy clearly indicated a strong signal for Au(0) with accompanying peaks observed at exactly the same binding energies found for gold foil.

Auride ion was also generated from solutions of Au(1) (added as gold(1) iodide). A cyclic voltammogram of a Au(1) solution in liquid NH_3 showed an irreversible wave ($E_{pc} = -0.33$ V vs. Ag) with an i_{pc} varying with $v^{1/2}$, corresponding to the reduction of Au(I) to Au(0) (Table I). When the scan was continued to more negative potentials, the reduction wave for production of Au^- and, on reversal, the anodic wave for Au^- oxidation, as shown in Figure 1, were observed. Controlled potential electrolysis at -0.5 V resulted in the formation of a layer of finely divided gold on the large Pt foil electrode. When the electrode potential was then stepped to the region for generation of e_s^-, the cathodic dissolution of Au occurred. A cyclic voltammogram of this solution showed the wave corresponding to the oxidation of Au^-.

These experiments show the electrochemical behavior of the first reported transition metal monoanion in liquid NH_3 and are consistent with the previously reported spectroscopic studies.[1] Moreover they demonstrate that Au^- is stable even in the absence of excess e_s^-. Further investigations of the properties of this anion as well as an extension of these studies to different metals in liquid ammonia and other solvents are in progress.[5]

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Table I. Photooxidation of Ⓟ-6-Methyl-5-heptenoate (**1a**) Sensitized by Ⓟ-Rose Bengal[a]

conditions	irradiation time, h	yield of **2** + **3**, %	$\tau(^1O_2)$, s
CCl$_4$	9	~0[b]	7×10^{-4} [c]
air, 760 mmHg	8	~0[b]	8.8×10^{-2} [d]
O$_2$, 25 mmHg	14	1–2	5.6×10^{-1} [d]
O$_2$, 10 mmHg	14	5–6	1.4[d]

[a] References 11 and 12. [b] ≪1 % could have been easily detected. [c] Reference 13. [d] Calculated from rate constant in ref 14.

Chemistry of Singlet Oxygen. 29. A Specific Three-Phase "Kautsky Test" for Singlet Oxygen[1]

Sir:

In 1933, Kautsky reported experimental evidence for a "metastable, reactive state of the oxygen molecule" by observing photochemical oxidation of leucomalachite green supported on dry silica gel which was intimately mixed with a separate batch of silica gel on which was adsorbed a sensitizer (trypaflavin).[2] Reaction was observed only over a rather limited range of pressures, with the maximal effect being found at 0.02 mmHg. This experiment provides strong evidence for a volatile reactive intermediate, but provides little information about its nature. Although this intermediate was probably singlet oxygen,[3] neither the sensitizer nor the acceptor[4] used have been much studied and the chemistry involved is obscure. Similar problems attend an analogous experiment carried out by Rosenberg and Shombert;[5] indeed, this experiment was used to suggest that a *vibrationally* excited oxygen molecule was the reactive intermediate.

Bourdon and Schnuriger carried out a related experiment in which oxidation of methoxynaphthalene, rubrene, or diphenylanthracene was photosensitized by methylene blue or eosin (separated from the acceptor by stearate layers).[6] This experiment is easier to interpret as singlet oxygen chemistry, but no product identification was reported.

Experiments in which a supported sensitizer is irradiated in a stream of O$_2$ and a downstream acceptor is oxidized have also been carried out, but give miniscule yields of product which often cannot readily be distinguished from that of autoxidation.[7]

Because of the central nature of this type of experiment to the singlet oxygen field, we wished to use a system in which both sensitizer and acceptor were well-characterized singlet oxygen reagents. We report the generation and trapping of $^1O_2$ in a "three-phase" system[8] using polymer-bound rose bengal[9] as acceptor and a polymer-bound olefin (6-methyl-5-heptenoate, **1a**) as acceptor.[10]

Photooxidation of polymer-bound ester **1a** or the methyl ester **1b** in methanol containing soluble rose bengal produced a mixture of the two allylic products (**2** and **3**, analyzed after reduction to alcohols) in 1:4 ratio.[11] The ratio of products was the same from **1a** and **1b** (but subject to analytical difficul-
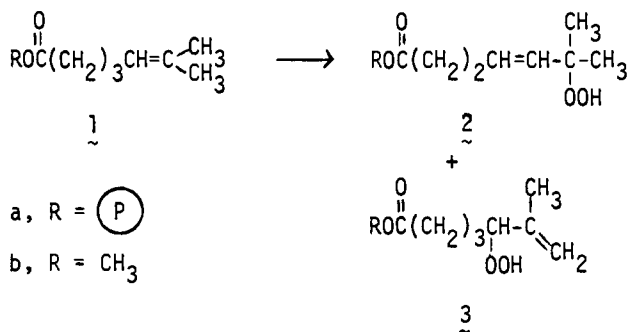
ties[11]). No oxidation of **1a** occurred in the absence of sensitizer.

Mixtures of bound sensitizer and bound acceptor were mixed and irradiated under various conditions. The results are summarized in Table I.[12] Substantial product formation occurred when photolysis was carried out at 25 mm of O$_2$, and more at 10 mm; in contrast, no product formation was observed in air or in CCl$_4$, a solvent in which $^1O_2$ has a comparatively long lifetime. The product ratio was the same as with the soluble photosensitized reaction with **1a** and **1b**.[11]

Although the exact efficiency of the $^1O_2$ trapping in this system cannot be calculated from the data, and, although the amount of $^1O_2$ formed would not be easy to make reproducible because of the variability of light adsorption associated with the inhomogeneous system, it is clear that singlet oxygen does not have sufficient lifetime to diffuse efficiently from one solid phase to the other through carbon tetrachloride ($\tau(^1O_2) = 700$ μs) or air (8.8×10^{-2} s), but that at 25 mm of O$_2$ (0.56 s) or 10 mm (1.4 s) measurable trapping occurs. Since the mean radius of diffusion of singlet O$_2$ during its lifetime varies from ~3 × 10^{-4} cm in CCl$_4$ to ~3 cm at 10 mm of O$_2$, and is ~0.1 cm in air, this experiment also sets some limits for the use of the "three-phase test" for trapping short-lived species.[8]

We believe the polymer-bound system used here may be of general utility for trapping $^1O_2$, both in gas-phase systems and in liquid media where $^1O_2$ is homogeneously generated. It does not appear to be useful in heterogeneous liquid $^1O_2$-generating systems such as the three-phase system because of the short diffusion radii for $^1O_2$ in solution.

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(11) Resin-bound products were reduced (NaBH$_4$) and subjected to ester interchange using NaOMe–dry CH$_3$OH. Products were gas chromatographed, and isolated samples characterized by IR, NMR, and mass spectral analysis.