abundance) line, which serves as a useful internal standard in the mass 36 region. The intensity ratio of the lines at masses 28 ($^{14}N_2^+$) and 32 ($^{16}O_2^+$) in the blank agrees with that of an air sample. Based on this ratio we correct for the air contamination effect on the line intensity at mass 32 ($^{16}O_2^+$) of the photolysis sample spectrum. The resulting pattern for the observed isotopic distribution of molecular oxygen is in excellent agreement with the expected pattern (see Figure 2). The photolytic sample was measured after 20 min of illumination. The electrolysis was carried out by passing a 20-mA current for 5 s. Calibrating the line intensities at masses 34 ($^{16}O^{18}O^+$) and 36 ($^{18}O_2^+$) of the photolytic sample against the corresponding intensities of the electrolytic sample, we arrive at a water splitting rate of 10^{-5} mol/h.[12] From the same calibration, using the line intensity at mass 28 (N_2^+) and the known mass intensity ratio of 28 (N_2^+):32 ($^{16}O_2^+$) for air, we estimate that atmospheric contamination in the photolytic sample amounts to 3×10^{-7} mol of $^{16}O_2$, approximately an order of magnitude lower than the 2.5×10^{-6} mol of molecular oxygen, occurring variously in the forms of $^{16}O_2$, $^{16}O^{18}O$, and $^{18}O_2$, produced in 20 min of the light-induced water splitting reaction.

The incident irradiance of photons ("white light") focused on the Pt–Chl a electrode was 1.74 W cm^{-2}. An energy storage efficiency of 0.04%, given by the ratio of the rate of chemical free energy stored (in the form of H_2 and O_2) and the incident irradiance, was thus obtained for the observed rate ($\sim 10^{-5}$ mol/h) of water photolysis employing 10^{17} Chl a molecules. We estimate that <1% of the light was effectively engaged in the photoreaction.[13] It seems reasonable to suppose that, by increasing the number of Chl a molecules engaged in the photoreaction, it should be possible to enhance the energy storage efficiency by two orders of magnitude.

The enclosure of the sample cell to minimize air contamination precluded direct temperature measurement during the light reaction. Gaseous evolution was evident in bubble formations over the brilliantly blue Chl a coating under illumination. In the absence of Chl a no gaseous bubbling off the platinum was observed under comparable illumination conditions, suggesting that the sample was well below the boiling point of water. In control experiments, we observed that at $T \gtrsim 90$ °C the platinized (Chl a·$2H_2O)_n$ film visibly disintegrates over a period of several hours. The Chl and purity before and after the light reaction was checked in the usual manner.[11b] Demetalation of Chl a to pheophytin was observed after light experiments performed under acidic conditions. In corresponding experiments at pH ≥ 7 no degradation of the chlorophyll was detected after extended usage of the Pt–Chl a samples.

In view of the observed photoreactivity of (Chl a·$2H_2O)_n$ with water in the absence of Pt,[4] we believe that the experimental effects described in the present work are attributable, in part at least, to the intrinsic photochemical properties of the chlorophyll. In water splitting work on inorganic semiconductors[6-8] the indispensable role[7] of the platinum black was interpreted in terms of a mechanism that relates properties of the semiconductor with those of the platinum.[7] However, we have evidence that the platinum itself may be partially responsible for our observations in the UV wavelength region.

The Chl a water splitting reaction in vivo provides the sustenance of life on this planet. The photochemical properties of (Chl a·$2H_2O)_{n\geq2}$ reported here and elsewhere[3-5] suggest possible clues to the origin of this remarkable reaction.

References and Notes

(1) The work described in this communication was presented in the In Vitro Photosynthesis Symposium of the 13th Informal Photochemistry Conference, Clearwater Beach, Fla., Jan 4–7, 1978, and in the Inorganic Compounds with Unusual Properties. II. Molecular Catalysis and the Conversion, Production, and Storage of Energy Symposium of the 1978 American Chemical Society Inorganic Chemistry Meeting, Athens, Ga., Jan 31–Feb 3, 1978.
(2) A detailed description of a pyrolytic analysis of the water splitting reaction reported here will appear in the Proceedings of the 1978 American Chemical Society Inorganic Chemistry Meeting; see L. Galloway, D. R. Fruge, and F. K. Fong, *Adv. Chem. Ser.*, in press.
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(12) The agreement between the various photolysis rate determinations may be fortuitous. Sample film quality is expected to play a role. The effect of acid–base buffer solutions on the rate of water photolysis is a subject of current investigation in this laboratory. The question of H_2O_2 being a possible product intermediate is also being considered.
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Osmium-Catalyzed Vicinal Oxyamination of Olefins by *N*-Chloro-*N*-argentocarbamates

Sir:

We have previously reported two[1,2] procedures for the vicinal oxyamination of olefins, One method employs stoichiometric amounts of preformed *tert*-alkyl imido osmium compounds (**1a**).[1] The other method is catalytic in osmium and

1a, R = *tert*-alkyl
1b, R = Ts
1c, R = R'OCO

relies on Chloramine-T (TsNClNa) for the in situ regeneration of the imido osmium species **1b**;[2] this procedure produces vicinal hydroxy *p*-toluenesulfonamides. The relative difficulty of removing sulfonamide protecting groups provided incentive for developing a catalytic method which would place a more easily removed group on the nitrogen. The successful outcome of this search is reported here.
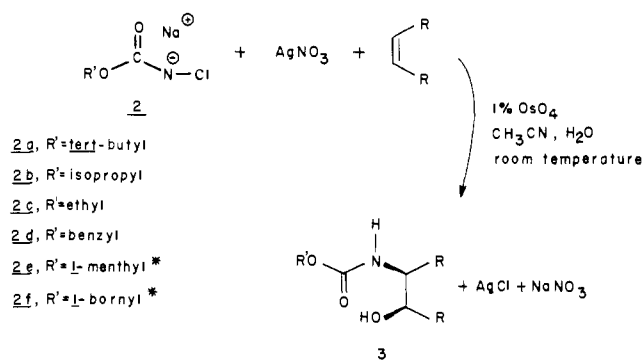
N-Chloro-*N*-argentocarbamates[3] are generated in situ by reaction of the corresponding *N*-chlorosodiocarbamates (**2**) with silver nitrate in acetonitrile. Addition of the olefin, some water and 1% of osmium tetroxide catalyst to the resulting suspension, affords the vicinal hydroxycarbamates (**3**) in generally good yields (Scheme I and Table I). As revealed in Scheme I the process is very general with respect to the structure of the carbamate.[4] The *N*-chlorosodiocarbamates (**2a** through **2f**) were prepared from the carbamates according to a convenient method developed by Johnson in the laboratory of Professor Malcolm M. Campbell.[5] In this way[5] the *N*-chlorosodiocarbamates **2a**, **2b**, **2c**, and **2d** were prepared and isolated.[6] However, when isolation of *N*-chlorosodiocarbamates with larger organic groups (e.g., **2e** and **2f**) was attempted, decomposition[8] sometimes occurred. Fortunately, the crude *N*-chlorosodiocarbamates (i.e., after evaporation of the methanol but before trituration with ether) from the

Table I[a]

Example	Olefin	Reaction time, h	% yield of vicinal hydroxycarbamate product (mp, °C)[b]	
			Primary aza isomer	Secondary aza isomer
1	Styrene	2	68.5 (122–123)	12 (141–142)
2	Styrene[c]	2	64 (114–115)	11 (83–84.5)
3	Styrene[d]	2	63 (85.5–87)	12 (62–63)
4	1-Decene	6	61	9
5	(E)-Stilbene	10	87 (137–138)[e]	
6	Cyclohexene	40	61 (103–104)[f]	
7	Dimethyl fumarate	10	51[e]	
8	(Z)-5-Decene	40	59 (99–100)[e,g]	
9	(E)-5-Decene	40	36[e,g]	

[a] All reactions were performed on 1 mmol of the olefin (except example 4 which was on a 3-mmol scale) as described in detail under the general procedure. The chloramine salt derived from *tert*-butyl carbamate was used in all cases except examples 2 and 3. [b] All yields are for isolated pure substances and are based on the initial moles of olefin. For solid products the melting points are given after the yields. [c] In this case the chloramine salt derived from benzyl carbamate was used in place of the *tert*-butyl analogue. [d] In this case the chloramine salt derived from ethyl carbamate was used. [e] In those cases where stereoisomers are possible the product is assumed to be that resulting from cis addition of the hydroxyl and carbamate moieties to the olefin. This presumed stereoselectivity was proven only in the case (example 6) of cyclohexene. [f] In a separate experiment utilizing the chloramine salt derived from ethyl carbamate, the product was shown to be exclusively the cis isomer by comparison with an authentic sample of the trans isomer. The trans isomer was prepared by reaction of *trans*-2-aminocyclohexanol with ethyl chloroformate. [g] These erthyro and threo isomers have different TLC mobilities.

Scheme I

2a, R'=*tert*-butyl
2b, R'=isopropyl
2c, R'=ethyl
2d, R'=benzyl
2e, R'=*l*-menthyl *
2f, R'=*l*-bornyl *

* Negligible (<5 % e.e.) asymmetric induction was observed when these chiral reagents were employed for oxyamination of α-methyl styrene

Johnson–Campbell preparation[5,6] are sufficiently pure for direct use in our procedure.[7] However, since the crude (i.e., not ether washed) salts gave somewhat lower yields, the following *general procedure* calls for use of the isolated *N*-chlorosodiocarbamate salts (2). A one-necked, round-bottomed flask (25 mL) equipped with a magnetic stirrer is charged with 1.5 mmol of the desired *N*-chlorosodiocarbamate (2), 0.51 g (3 mmol) of silver nitrate,[9] and 10 mL of reagent grade acetonitrile. After the mixture was stirred at room temperature for ~5 min, a slightly yellow suspension results. To this suspension is added 81 μL (4.5 mmol) of water, 1 mmol of olefin, and 2.54 mg (0.01 mmol) of OsO₄ as a solution in *tert*-butyl alcohol,[10] A milky brown suspension is usually obtained and it is stirred at room temperature until (see Table I for times) the olefin has been consumed (disappearance of olefin is monitored by TLC or GLC). When the reaction is complete, 0.25 mL (1.5 mmol) of saturated sodium chloride solution is added (to precipitate the remaining silver ion), and the solid salts are removed by filtration. The filtrate is refluxed with 4 mL of 2.5% aqueous sodium bisulfite for 3–6 h.[11] The resulting mixture is concentrated and the largely aqueous residue is extracted with three 10-mL portions of methylene chloride. The organic phase is dried (MgSO₄) and concentrated to give the crude hydroxycarbamate (3). When mixtures were formed, chromatography on silica gel was used to separate the regioisomers. When only one hydroxycarbamate was produced, recrystallization of the crude reaction product was the preferred method of purification.

The regioselectivity of this new procedure toward terminal olefins (examples 1–4) is considerably better than that realized with the earlier catalytic oxyamination procedure[2] based on Chloramine-T. However, neither of these catalytic procedures can compete with the regiospecificity exhibited by the stoichiometric *tert*-alkyl imido osmium reagents.[1]

This new catalytic procedure shows a different range of reactivity in comparison with the Chloramine-T based procedure.[2] The new method is more effective with electron deficient olefins such as dimethyl fumarate (Table I, example 7). On the other hand, trisubstituted olefins are, so far, less readily oxyaminated[12] than with the earlier[2] procedure. However, this carbamate-based procedure seems amenable to further improvement. For example, it was recently found that addition of 1 equiv of Et₄NOAc·4H₂O (in place of the extra equivalent of AgNO₃) to the reaction mixture in the case of (E)-5-decene raised the yield to 68%.[13] This is almost double the yield (36%, Table I, example 9) observed with the original procedure.

This new procedure for vicinal, cis addition of an oxygen and a nitrogen to an olefinic bond constitutes a major improvement over the earlier methods.[1,2] *The nitrogen is now introduced bearing an easily removed protecting group*. The most commonly used protecting groups for amines are benzyloxycarbonyl (BOC) and *tert*-butoxycarbonyl (*t*-BOC). As mentioned earlier,[9] both benzyl *N*-chloro-*N*-argentocarbamate and *tert*-butyl *N*-chloro-*N*-argentocarbamate are among the most effective oxidants in this new oxyamination process.

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(4) Ethyl and benzyl carbamate were obtained from Aldrich. Menthyl, bornyl, *tert*-butyl, and isopropyl carbamate were synthesized following the procedure of B. Loev, M. F. Kormendy, and M. M. Goodman, "Organic Syntheses", Collect. Vol. V, Wiley, New York, N.Y., 1973, p 162. Although Table I deals principally with *tert*-butyl carbamate, all of the carbamates which were tried gave good results.

(5) Graham Johnson, Ph.D. Thesis, Heriot-Watt University, Edinburgh, Scotland, Aug 1975, p 206.
(6) To an ice-cold, stirred solution or suspension of 50 mmol of the carbamate (ROCONH₂) in 40 mL of reagent grade methanol was added 5.63 mL (5.4 g, 50 mmol) of *tert*-butyl hypochlorite (Frinton Laboratories). After 15 min a methanolic solution (25 mL) of sodium hydroxide (2.0 g, 50 mmol) was added dropwise over a period of several minutes. The ice bath was removed and stirring was continued for 10 min. Then the solvent was removed on a rotary evaporator (bath <45 °C) and the resulting white solid residue⁷ was triturated with dry ether, isolated by filtration, and washed with dry ether to afford the *N*-chloro-*N*-sodiocarbamate (ROCONClNa). The *N*-chlorosidiocarbamates prepared and isolated in this way are quite hygroscopic and should be stored in a desiccator in a freezer (ca. −20 °C). When stored in this way at low temperature these reagents are stable for at least 2 months.
(7) This crude salt can be used directly, in which case the entire oxyamination procedure is carried out in one reaction vessel. Application of this procedure, using *tert*-butyl carbamate, to (*E*)-stilbene afforded an 83% yield of the vicinal hydroxycarbamate. This compared favorably with the 87% yield realized with the ether-washed salt (Table I, example 4). However, in the few cases so far tried the crude salt modification appears to result in slower reactions and in some cases poorer yields than the method using the ether-washed salts. To demonstrate that the reaction can be performed on a moderate scale the crude salt (2c) of ethyl carbamate was prepared on a 200-mmol scale and was used directly to transform 24.16 g (134 mmol) of (*E*)-stilbene to 29.4 g (77%) of the oxyaminated product (mp 122–123 °C).
(8) *Warning:* It was noted early in this work that salts 2e and 2f derived from menthyl and bornyl carbamates were unstable and were therefore best used directly after removal of the methanol. More recently, the stability of salts 2 from even the simpler carbamates has become a concern to us. On one occasion, when EtOCONClNa was prepared on a 250-mmol scale, it decomposed rapidly (but not explosively), turning dark and releasing heat and gases. However, we had twice earlier prepared this same chloramine salt on a 100-mmol scale without incident. There are conflicting statements in the literature³ about the stability of these *N*-chlorosodiocarbamates. For the present, *we recommend that salts 2 never be prepared on greater than a 200-mmol scale.* We are now developing in situ procedures in which the entire reaction sequence is carried out in acetonitrile, obviating the need for dealing with the dry *N*-chlorocarbamate salts (2). These modifications will be described in a future publication.
(9) Note that this general procedure calls for use of 2 equivalents (based on salt 2) of silver nitrate. The extra equivalent of silver nitrate was found to accelerate the reaction. However, the magnitude of this effect was very dependent on the structure of the carbamate. It was most noticeable with ethyl carbamate, which took 18 h to reach completion when only 1 equiv (1.5 mmol) of silver nitrate was used, while with 2 equiv of AgNO₃ present, the reaction was over in 2 h (Table I, example 3). In spite of the rate differences there was no significant difference in the final yields. The other carbamates shown in Scheme I gave rapid reactions even with only 1 equiv of AgNO₃. We speculate that this might be due to better solubility imparted by the larger organic moieties. Thus the extra equivalent of silver nitrate is not essential, but may in some cases give faster reactions.
(10) Recipe for OsO₄ catalyst solution: 1 g (3.94 mmol) of OsO₄, 199 mL of reagent grade *tert*-butyl alcohol, and, as a stabilizer, 1 mL of 70% or 90% *tert*-butyl hydroperoxide (Aldrich); each milliliter contains 5 mg (~0.02 mmol) of OsO₄. The resulting catalyst solution is stored in a brown bottle at room temperature.
(11) The purpose of this bisulfite treatment is to reduce, and thereby remove, the small amount of osmium that may be bound to the organic products. If a molecule were sensitive to this step, then it could be omitted. Thus far all the hydroxycarbamates we have obtained were stable to this bisulfite treatment.
(12) E. Herranz, unpublished results.
(13) The beneficial effect of nucleophiles (e.g., Et₄NOAc and Et₄NOH) on osmium catalyzed reactions of olefins has been observed previously: K. B. Sharpless and K. Akashi, *J. Am. Chem. Soc.*, **98**, 1986 (1976); K. Akashi, R. E. Palermo and K. B. Sharpless, *J. Org. Chem.*, in press.
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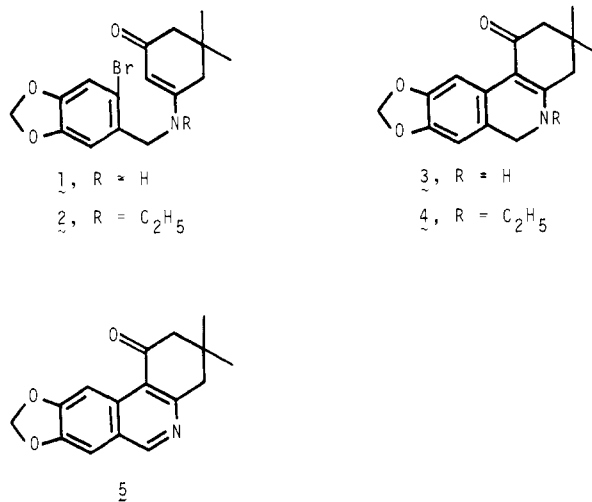*Cambridge, Massachusetts 02139*

An Intramolecular Cyclization of Enaminones Involving Benzyne Intermediates and Application to the Synthesis of γ-Lycorane and Related Compounds

Sir:

The area of reactivity and versatility of the enaminone[1] ($>N_c$—C_e=C_b—C_d=O_a) possessing three nucleophilic sites (a, b, and c) and two electrophilic sites (d and e) is of current interest[2] particularly in heterocyclic chemistry, which shows diverse and sometimes complicated reactivity. Although many and increasing examples concerning reactions of enaminones have been reported,[2] a search of the literature indicates that no work has been done on the arylation of enaminones. The purpose of this communication is to demonstrate a new intramolecular arylation of enaminones and the use of this reaction for the synthesis of γ-lycorane and related compounds. Our procedure represents the crucial ring closure of enaminones utilizing an intramolecular reaction of benzyne intermediates which was hinted by a cyclization reaction[3] involving electrophilic attack by alkynes on enaminone systems.

Condensation of 5,5-dimethylcyclohexa-1,3-dione with 2-bromo-4,5-methylenedioxybenzylamine, prepared by Gabriel synthesis from the corresponding benzyl chloride, gave the bromoenaminone **1** in 83% yield: mp 223–224 °C. Treatment of **1** with lithium diethylamide in THF at room temper-

ature for 2 h gave the 3,4-dihydro-1(2*H*)-phenanthridone **5** in 26% yield: mp 175–177 °C; NMR (CDCl₃) δ 7.06, 8.73, and 8.86 (each s, 1 H, ArH). This compound may have arisen from initial intramolecular arylation of **1** yielding the 3,4,5,6-tetrahydro-1(2*H*)-phenanthridone **3** as an intermediate followed by oxidative aromatization.

N-Alkylation of **1** with ethyl iodide was carried out in refluxing toluene in the presence of NaH to give **2** in 80% yield: mp 167–169 °C. In a similar manner to that described for **1**, **2** was treated for 30 min to yield the 3,4,5,6-tetrahydro-1(2*H*)-phenanthridone **4** in 55% yield: mp 123–124 °C; NMR (CDCl₃) δ 6.40 and 8.80 (each s, 1 H, ArH).

The synthetic utility of this cyclization reaction was demonstrated by the synthesis of γ-lycorane and related compounds. The requisite haloenaminones were conveniently available by a one-step synthesis as follows. Upon heating the iminoenol ether **6**,[4] prepared by Birch reduction of 6-methoxyindoline in quantitative yield, with 2-bromo-4,5-methylenedioxybenzyl chloride (**7a**) in refluxing toluene, N-benzylation occurred predominantly to give the desired