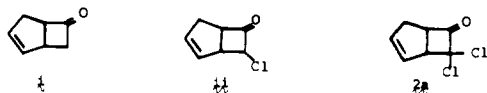considerably higher than those obtainable using other methods. In addition, the mild reaction conditions should permit the presence of additional functionality in the substrate. Furthermore, and most importantly, the highly versatile intermediates in this synthesis offer the possibility of effecting a myriad of other synthetically important transformations in conjunction with those discussed above. For example, the α,α-dichlorocyclobutanones are transformed regioselectively and in high yield to α-substituted cyclopentanones (eq 3),[15] and the readily prepared α-chlorocyclopentanones can be easily converted to pure enones (eq 4)[16] and olefins (eq 5).[17] Of course, there are also numerous other possibilities.[18]

Extensions and applications of this work will be the subjects of future reports.

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(10) For example, treatment of 11-nor-PGE₂ methyl ester with diazomethane in Et₂O-MeOH cleanly produced a ca. 2:1 mixture of methyl 15α-hydroxy-10-oxoprosta-5,13-dienoate and 11-deoxy-PGE₂ methyl ester, respectively, in 75% isolated yield.[8] In contrast to certain literature reports,[11a,b] we have found that, in general, diazomethane can quite effectively produce cyclopentanones from cyclobutanones in yields after purification of up to 75%.
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Cyclization of Olefinic Tosylhydrazones under Acidic Conditions. A Facile Synthesis of Bicyclic Azo Compounds

Sir:

Bicyclic azo compounds have attracted a great deal of interest during the past few years since they have been found to serve as stable analogues of prostaglandin endoperoxides,[1] to exhibit unusual electronic absorption properties,[2] and to serve as precursors for a wide variety of theoretically intriguing and synthetically useful biradicals.[3] We have become interested in bicyclo[*n*.2.1] azo compounds as starting materials for the synthesis of unusual bicyclic peroxides.[4] This report describes a facile synthesis of symmetrical and unsymmetrical azo compounds via a unique reaction of tosylhydrazones.

A particularly appealing route to bicyclo[*n*.2.1] azo compounds (**1**) would seem to be the intramolecular 1,3-dipolar cycloaddition of diazoalkenes (**2**) (Scheme I). However, previous workers[5] have only been able to realize dipolar additions of this type in low yields and then have only observed the bicyclo[*n*.3.0] adducts **1'**, rather than the desired bicyclo[*n*.2.1]
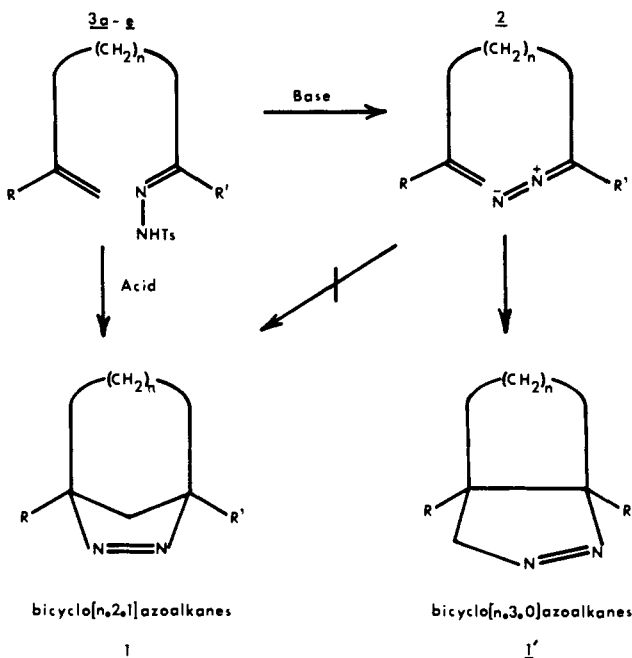
Scheme I

bicyclo[n.2.1]azoalkanes   bicyclo[n.3.0]azoalkanes

1   **1'**

Table I. Methods and Results of Tosylhydrazone Cyclizations

tosylhydrazone	method of tosylhydrazone preparation[a]	cyclization conditions	yields[b] (%)	azo absorption properties, λ_{max}, nm (ϵ)[c]
3a (n = 3; R,R' = CH$_3$)	A	Et$_2$O-BF$_3$; CH$_2$Cl$_2$; 0 °C-RT; 2.5 h	**1a** (87)	351 (192)
3b (n = 3; R = CH$_3$; R' = H)	A	Et$_2$O-BF$_3$; CH$_2$Cl$_2$; 0 °C; 0.5 h	**1b** (46)	349 (140)
3c (n = 3; R,R' = H)	B	Et$_2$O-BF$_3$; CH$_2$Cl$_2$; 0 °C-RT; 24 h	**1c** (14)	347 (305)
3d (n = 2; R,R' = CH$_3$)	C	Et$_2$O-BF$_3$; PhH; reflux; 6 h	**1d** (43), **4** (39)	347 (174)
3e (n = 2; R = CH$_3$; R' = H)	B	Et$_2$O-BF$_3$; CH$_2$Cl$_2$; reflux; 18 h[d]	**1e** (55)	344 (135)
3f (n = 2; R,R' = H)	B	Et$_2$O-BF$_3$; variety of conditions	**1f** (0)	341 (420)[e]

[a] The carbonyl compounds used to prepare the tosylhydrazones were obtained as follows: method A, (1) 1,2 addition of allyl Grignard reagents to α,β-unsaturated carbonyl compounds, (2) oxy-Cope rearrangement;[8] method B, pyridinium chlorochromate oxidation of the alcohol;[9] method C, commercially available. [b] All yields are of material isolated. [c] All spectra were determined in n-pentane. [d] High-dilution conditions used. [e] Reference 2; determined in hexane.

Scheme II
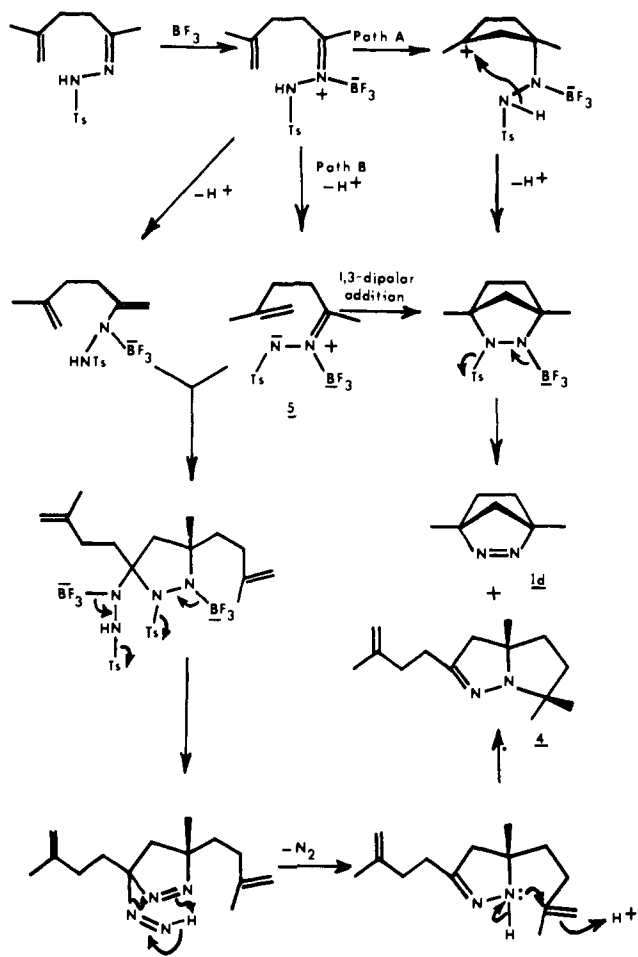
adducts **1**. Apparently, these reactions require polar or strained alkenes in order to proceed in satisfactory yields.[6]

We have now observed that, when tosylhydrazones (**3**) are decomposed under acidic conditions, the desired bicyclo-[n.2.1]azo isomers (**1**) are formed exclusively (Scheme I). While the yields of azo compounds from these acidic reactions are somewhat variable (see Table I), the azo compounds can be isolated in high purity from the crude reaction mixture by a simple trap-to-trap distillation.[7]

From these results it is evident that the bicyclo[3.2.1] systems **1a–c** are formed much more readily than the bicyclo[2.2.1] systems **1d–f**. In fact, the formation of **1f** has not been realized under a variety of conditions. Methyl substitution of the olefinic moiety enhances the ease with which cyclization takes place as the unsubstituted azo compounds either are not formed (n = 2, **1f**) or are formed with the greatest difficulty

in a given series (n = 3, **1c**).

In several of these reactions it was necessary to use high-dilution conditions (addition of a solution of the tosylhydrazone over several hours with a syringe pump) in order to suppress the formation of intermolecular condensation products. In the hope that the structure of these condensation products might provide additional information bearing on the mechanism of the formation of the azo compounds, we have characterized the intermolecular condensation product formed in the reaction of **3d** with itself.[10] This material has an empirical formula of C$_{14}$H$_{24}$N$_2$, exhibits a band in the infrared at 1644 cm^{-1} (>C=N–), and the loss of CH$_3$ and CH$_2$C (=CH$_2$)(CH$_3$) as the major fragmentation products in the mass spectrum. The 300-MHz NMR spectrum (δ, CDCl$_3$) displays three >NCCH$_3$ signals [1.16 and 1.32 ppm, the latter resolvable into two singlets in CDCl$_3$–C$_6$D$_6$ (1:1)], and three allylic CH$_2$ groups are clearly discernible [doublet of doublets, 2.24 ppm, J = 8 and 7 Hz; overlapping doublet of triplets, 2.43 ppm, J = 7 and 5 Hz; AB system, 2.47 and 2.69 ppm, J = 17 Hz]. The latter two CH$_2$ groups display magnetically nonequivalent hydrogens due to proximate asymmetric centers. These data are consistent with the proposed hydrazone structure **4** (Scheme II).

Either of two mechanistic types might account for these transformations: a carbocation mechanism (Scheme II, path A) or a 1,3-dipolar cycloaddition mechanism involving azo-methine imine intermediates such as **5** (Scheme II, path B).[11] Azo formation results from simple intramolecular addition to the olefin. If this intramolecular reaction is retarded owing to the introduction of ring strain or the lack of olefin substituents, as mentioned above, the hydrazone can undergo isomerization to the enamine tautomer, which serves as a highly reactive olefin substrate for intermolecular addition reactions.[12] The final products of these reactions are determined by a number of yet not fully understood alterations in the nitrogen functional groups. These seem to include the elimination of toluenesul-finate to produce azo linkages and substituted diimides,[13] the tautomerization of azo compounds to hydrazones, and the reductive extrusion of nitrogen from diimides.[14] Examples of some of these processes are shown in Scheme II.

In view of the extensive work that has been done with tos-ylhydrazones under basic conditions,[15] it is indeed suprising that virtually nothing has been reported dealing with tos-ylhydrazone chemistry under acidic conditions.[16] The pre-liminary results reported here indicate that the addition of tosylhydrazones to olefins under acidic conditions provides a versatile new type of carbon–carbon bond-forming reaction.

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Applications of Light-Induced Electron-Transfer Reactions. Coupling of Hydrogen Generation with Photoreduction of Ruthenium(II) Complexes by Triethylamine

Sir:

The photoinduced splitting of water to hydrogen and oxygen using visible or near-UV light continues to be the subject of intensive investigation.[1-9] Potential light-absorbing catalysts that have been particularly well-studied include chlorophyll,[1] several dyes and transition metal complexes such as tris(2,2'-bipyridine)ruthenium(II) (**1**), and related compounds.[5-9] Very recently it has been shown that several one-electron oxidizing or reducing agents can be coupled to produce the oxidation or reduction, respectively, of water through the use of heterogeneous catalysts such as PtO_2 or IrO_2[6,8,10-12] or in photoelectrochemical cells.[13] Previously we found that certain hydrophobic ruthenium(II) complexes can be photoreduced efficiently by amines using visible light in nonaqueous solution.[14] In the present paper we report the coupling of this reaction with the reduction of water in a net process leading to hydrogen evolution in good quantum efficiency with a high turnover in terms of moles of hydrogen produced/mole of light-absorbing metal complex.

Although many light-induced electron-transfer reactions result in no net chemistry due to energy-wasting back electron transfer,[15] we recently found that for some hydrophobic ruthenium(II) complexes such as **2** (RuL_3^{2+}, where L = 4,4'-dicarboxy-2,2'-bipyridine diisopropyl ester) photolysis in the presence of certain oxidants[16,17] or reductants[14] in nonaqueous solutions can lead to the isolation of one of the primary one-electron transfer products. Thus, irradiation of **2** with visible light in dry acetonitrile containing triethylamine leads to a net photoreduction of **2** with a quantum efficiency, $\phi \simeq$ 0.4 (eq 1):[14]

$$2RuL_3^{2+} + 2Et_3N \xrightarrow[\sim500\ nm]{h\nu} 2RuL_3^+ + Et_3NH^+$$
$$+ Et_2N^+{=}CHCH_3 \quad (1)$$
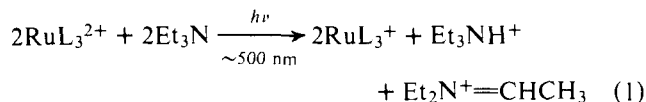
When the reaction is carried out in the presence of water, acetaldehyde is formed as a product,[18] but there is no accumulation of the reduced metal complex, RuL_3^+. The involvement of water evidently occurs after the excited-state quenching process, since water does not quench the luminescence of **2** but has been found to react rapidly with RuL_3^+ in acetonitrile.[14] The details of the interaction between water and RuL_3^+ are currently under investigation. Prolonged irradiation of **2** in aqueous acetonitrile containing triethylamine leads to a slow decomposition of the metal complex.

We now find that irradiation of solutions containing **1** or **2** in the presence of a small amount of Adams' catalyst (PtO_2) results in a net photostability of the metal complex with a steady evolution of hydrogen gas. In typical experiments an argon deaerated solution of **2** (6×10^{-5} M) in acetonitrile with 0.3 M triethylamine and 25% water was stirred with ca. 5 mg of PtO_2 and irradiated with visible light.[19] The gas above the solution was analyzed by gas chromatography and mass spectrometry; the major product formed during several hours irradiation was found to be hydrogen.[19] Replacement of water with deuterium oxide led to the production of D_2; comparison of the isotopic distribution resulting from the photolysis (by mass spectrometry) with that produced by electrolysis of a sample of the same D_2O indicated that water is the source of the hydrogen produced in the photolysis. Experiments omitting separately the light, PtO_2, triethylamine, ruthenium complex, and water all resulted in no generation of hydrogen. The quantum yield for hydrogen production using monochromatic 436-nm light from a 1000-W mercury–xenon lamp was determined to be 0.3;[20] a turnover number of 300 mol of H_2 per mol of **2** was obtained for moderate irradiation periods in which the hydrogen was allowed to collect above the stirred solution. Prolonged irradiation of stirred solutions leads to a slow decrease in the content of hydrogen in the volume above the solution; presumably this is caused by a PtO_2-catalyzed reaction with unsaturated products generated in the photolysis. Experiments with **1** led to similar results; with the same amount of catalyst present, a quantum yield of 0.37 was obtained at 436 nm.[20]

The results are most consistent with a mechanism (eq 2–6) in which photochemically generated RuL_3^+ reacts with a source of protons (water in the net sense) in the presence of PtO_2 to give RuL_3^{2+} and H_2. However, the neutral radical **3** is also a strong reducing agent,[21,22] and in the absence of reaction 4 (which may be unfavorable for **1**) it may be directly involved in the generation of H_2 (e.g., eq 6). Since we also observe oxidation of RuL_3^+ produced by irradiation of **2** in the presence of NEt_3 and PtO_2 when water is excluded (eq 7), it is unclear whether RuL_3^+ reacts first with water and then with PtO_2, or whether RuL_3^+ acts as a simple electron-transfer carrier (eq 7). The relatively high quantum efficiencies obtained are noteworthy, since the stoichiometry indicated by eq 2–5 suggests that ϕ_{max} for the production of RuL_3^+ should be twice that for hydrogen evolution. The higher than expected value may reflect a higher initial yield of free ions in the more polar aqueous acetonitrile mixture, since our studies have indicated lower efficiencies for reduction in nonpolar solvents.[14]

$$RuL_3^{2+*} + Et_3N: \rightarrow RuL_3^+ + Et_3N^+\cdot \quad (2)$$

$$Et_3N^+\cdot + Et_3N: \rightarrow Et_3NH^+ + CH_3CH-NEt_2 \quad (3)$$
$$\mathbf{3}$$

$$\mathbf{3} + RuL_3^{2+} \rightarrow RuL_3^+ + CH_3{=}NEt_2^+ \quad (4)$$