18.[21-23] Nitrobenzene has been found to have a similar catalytic effect in substitution reactions of group 6b metal carbonyl amine derivatives.[5,6]

In ligand exchange reactions where coordinated water in aquocobalamin is displaced by other ligands, the kinetic data are consistent with a transition state in which both entering and leaving groups are loosely bound (I_d process).[24-29] If we extrapolate from the more inert model systems,[30] to aquocobalamins obeying the same rate law, it is logical to assume that the incoming ligand will compete with the solvent for the acidic protons of axially coordinated water in aquocobalamin.[31-33]

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(8) ν(NH) was observed to decrease as amines or other bases were added to $CDCl_3$ solutions of $CH_3Co(dmgH)_2NHC_5H_{10}$. It was necessary to use *N*-deuteriopiperidine as free amine in order to confirm the ν(NH···N) absorption due to the strong absorption due to association of piperidine in this frequency range.

(9) This surprising favorability in going from a bridging intramolecular hydrogen bond to an intermolecular interaction presumably results from the large strain energy expected for the bending of the hydrogen bond to align the proton with (O···O).[10,11] Supporting evidence for this intermolecular interaction comes from the observation that the bridging (O–H···O) protons undergo rapid exchange with free water.[12]

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(13) Specific interactions of the type described here may account for the competition ratios reported by Jensen and Kiskis,[1] e.g., pyridine (a better hydrogen bonding base than tri-*n*-butylphosphine) was observed to be much more reactive than $P(n\text{-}C_4H_9)_3$. These interactions would also account for the observed increase in this competition ratio as a function of excess pyridine concentration.

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(21) This may indeed occur via an I_a process since the free >N=O grouping is positioned favorably for electronic activation.

(22) The exceptional stability of the $P(OCH_3)_3$ derivative of methyl(cobaloxime) observed by Guschl and Brown[20] may be due to intramolecular hydrogen bonding of $P(OCH_3)_3$ to the diimine ligands. (See also, ref 23.)

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Photochemistry of Alkyl Halides. 3. Generation of Vinyl Cations[1]

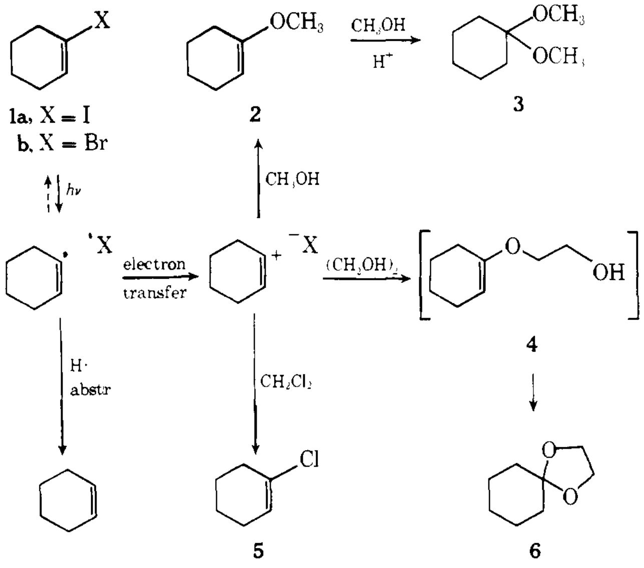
Sir:

Recent reports from these laboratories have shown that irradiation of alkyl bromides and, particularly, iodides in solution is a convenient, powerful method for the generation of carbocations.[1,2] The available data support a process involving initial homolytic cleavage of the carbon–halogen bond followed by electron transfer within the resulting radical pair to generate an ion pair.[1] We wish now to report that irradiation of vinyl iodides is a particularly facile route to the corresponding vinyl cations.

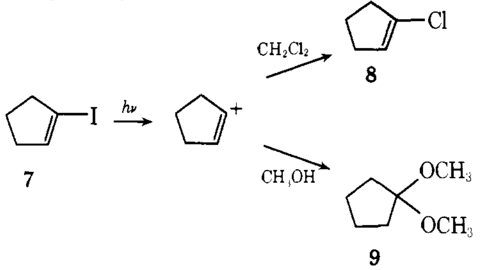
$$\begin{tikzcd} R{-}I \arrow[r, "h\nu"] & {[R^{\cdot}\ I^{\cdot}]} \arrow[r, "\text{electron}", "\text{transfer}"'] \arrow[d] & {[R^+\ I^-]} \arrow[d] \\ & \text{radical products} & \text{ionic products} \end{tikzcd}$$

Thus irradiation of 1-iodocyclohexene (**1a**) in methanol or methylene chloride solution at 40° in the presence of zinc as an iodine scavenger afforded principally the nucleophilic substitution product **2** or **5**, respectively, in 65% yield, each accompanied by minor amounts (19–27%) of the radical-derived reduction product cyclohexene.[3,4] In ethylene glycol the ketal **6** was obtained (77% yield), presumably via cyclization of the initially formed enol ether **4.** When the irradiation of **1a** in methanol was conducted in the absence of zinc, the ketal **3** was obtained as the principal product (70%), apparently via acid-catalyzed addition of methanol to the enol ether **2.** Similar behavior was exhibited by the bromide **1b,** which afforded ketal **3** (26%) and cyclohexene (62%); as noted previously in saturated alkyl systems,[1,2] bromides display less ionic behavior than the corresponding iodides. Reducing the temperature resulted in a significant increase in the amount of ionic product formed from **1a.** Thus at −20° the yields of ketal **3** and chloride **5** rose to 87 and 76%, respectively.[5]

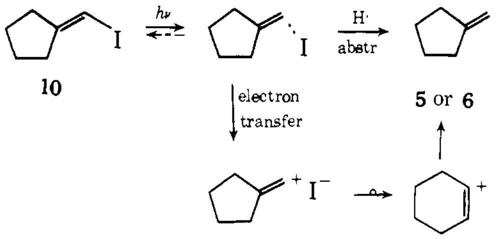
From these results it is clear that irradiation of **1a** or **b** results in formation of the 1-cyclohexenyl cation—in contrast to previous reports on the photochemical behavior of vinyl iodides,[6] in which it is concluded that only radical behavior is displayed. The results are of even more interest in that cyclic vinyl cations are difficult to form via the usual solvolytic methods because of the preferred linear geometry of vinyl cations.[7] Attempts to extend the photochemical method to generation of the even more highly strained 1-cyclopentenyl cation were initially unsuccessful. Irradiation of 1-iodocyclo-

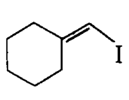


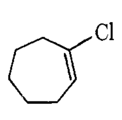
pentene (**7**) in methylene chloride at 40° afforded cyclopentene as the only detectable photoproduct (80%). However, at −25° the ionic product 1-chlorocyclopentene (**8**) was formed (18% yield) in addition. Similarly, irradiation in methanol at −25° afforded the ionic product 1,1-dimethoxycyclopentane (**9**, 13% yield). These are the first unequivocal examples of generation of the 1-cyclopentenyl cation.[8]

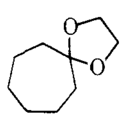


Irradiation of vinyl iodides has also afforded the first unequivocal route to the difficultly accessible primary vinyl cations.[9] Thus, for example, irradiation of (iodomethylene) cyclopentane (**10**) in methylene chloride or ethylene glycol afforded the ionic products **5** (23%) or **6** (30%), respectively, accompanied by the reduction product methylenecyclopentane (50%). Similar behavior was exhibited by the cyclohexyl analogue **11**, which afforded the chloride **12** and the ketal **13** (27%), along with reduced material.



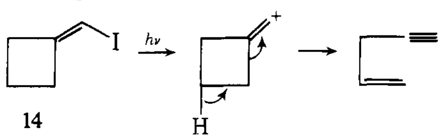






11 12 13

It is significant that the ionic products are ring expanded; apparently the cyclic cation, being secondary, is more stable despite the fact that it is constrained to be nonlinear. In an interesting contrast, the cyclobutyl analogue **14** principally underwent fragmentation to 1-penten-4-yne (60%) on irradiation in methylene chloride. In this case ring scission is more facile than isomerization to the secondary but highly strained 1-cyclopentenyl cation.



Thus photolysis of vinyl halides has afforded a number of vinyl cations not previously accessible. Further studies are in progress to elucidate the behavior of other vinyl cations prepared in this way.

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(5) The origin of the effect of temperature on the ratio of ionic to radical products is not clear at this time. It does not appear to be due principally to the increased viscosity of the medium at lower temperatures since vinyl iodides show no significant increase in yield of ionic products on going to highly viscous solvents such as ethylene glycol. Saturated alkyl halides, which exhibit increased ionic behavior in more viscous solvents,[1] do not exhibit a similar temperature effect.

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(9) Except for (halomethylene)cyclopropanes, which gain special stabilization from the cyclopropyl group, primary vinyl cations have not been generated solvolytically.[6] Although several primary vinyl cations have been proposed as possible intermediates from decomposition of diazonium ions, alternative mechanisms involving unsaturated carbenes or other intermediates are suspect; see M. S. Newman and A. Kutner, *J. Am. Chem. Soc.*, **73**, 4199 (1951); M. S. Newman and A. E. Weinberg, *ibid.*, **78**, 4654 (1956); M. S. Newman and C. D. Beard, *ibid.*, **91**, 5677 (1969); M. S. Newman and A. O. M. Okorodudu, *J. Org. Chem.*, **34**, 1220 (1969); M. S. Newman and C. D. Beard, *J. Am. Chem. Soc.*, **92**, 7564 (1970); and D. Y. Curtin, J. A. Kampmeier, and R. O'Connor, *ibid.*, **87**, 863 (1965).

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Thermolysis and Photochemistry of Cyclic Azo Compounds. A Novel Chemiluminescent Reaction and Alternate Route to Dewar Benzene

Sir:

The thermal,[1] direct photochemical,[2] and triplet sensitized decomposition[3] reactions of cyclic azo compounds are believed to yield hydrocarbons via diradical intermediates. These thermal and photochemical eliminations of nitrogen are considered to be general reactions of cyclic azo compounds.[4] However, there are a number of perplexing examples in which the loss of nitrogen failed.[5]

Understanding why the cyclic azo compounds studied unexpectedly resisted loss of nitrogen is important if nitrogen elimination reactions are to be employed rationally in organic synthesis. We report a study of the thermolysis, direct photolysis, and triplet sensitized photolysis of the tetracyclic azo compound **1**[4] which (a) has demonstrated that fluorescence characteristics may serve as a guide to when a cyclic azo compound will lose nitrogen with difficulty; (b) has uncovered a novel chemiluminescent reaction; (c) has resulted in the development of an alternate synthesis of Dewar benzene; (d) has revealed the first example of a cyclic azo compound to undergo cleavage of different bond types when excited to its singlet (C–N bond cleavage) and triplet (C–C bond cleavage) states; and (e) has provided direct evidence for oxygen assisted intersystem crossing.

Thermolysis of **1** in *n*-dodecane results in quantitative formation[6] of benzene and nitrogen (eq 1). The activation parameters for thermolysis (temperature range 130–150°) are $\Delta H^{\ddagger} = 35.6$ kcal/mol and $\Delta S^{\ddagger} = 7.8$ eu. The closeness of these values to those reported[7] ($\Delta H^{\ddagger} = 36.7$ kcal/mol, $\Delta S^{\ddagger} = 8.7$ eu) for 2,3-diazabicyclo[2.2.1]hept-2-ene, **2**, is consistent with the rate determining step being similar, presumably involving cleavage of a C–N bond.