equals ca. $\langle d_{yz}|l_z|d_{xz}\rangle$. Converting to the complex basis in which l_z is diagonal, and since l_z operates only on $\Phi(\phi)$, we obtain eq 4. Similarly, for transition $\sim d_{xz}, d_{yz}$ Cr → $\sim d_{x^2-y^2}$ Cr, we obtain

$$\langle e_x|l_z|e_y\rangle \simeq -\langle d_{yz}|l_z|d_{xz}\rangle = -\Bigg\{\frac{2^{1/2}}{2}i\Bigg(\langle 2,1| - \langle 2,-1|) \times |l_z|\frac{2^{1/2}}{2}(|2,1\rangle + |2,-1\rangle\Bigg)\Bigg)\Bigg\}\langle R(r,d_{yz})|R(r,d_{xz})\rangle = i \quad (4)$$

$A/D = -{}^1/{}_2\beta$. The sign difference of the A terms for $^1A_1 \rightarrow {}^1E$ will therefore differentiate between transitions to the two different orbital types. This applies to the present data as follows.

The dominant optical band II, and the one of great photochemical interest,[8-12] at ~400 nm of each compound has a distinct MCD A term of positive sign (Figure 1). These bands are therefore directly assignable to $^1A_1 \rightarrow {}^1E_1$. Additionally, the orbital character can be assigned, from the *sign* of the A term, e.g., to e^4 ($\sim d_{xz}$, $\sim d_{yz}$ Cr) → $e^3\,a_1{}^1$ ($\sim d_{z^2}$ Cr) (A/D positive), ruling out the $\sim d_{xz}, d_{yz}$ Cr → $\sim d_{x^2-y^2}$ Cr assignment (A/D negative). Thus, excited state *and* excited orbital assignments are made directly for this photochemically important band II.

Bands III at 350 (Cr) and ~340 nm (Mo and W) are tentatively assigned to the vibronically allowed transition $^1A_1 \rightarrow {}^1A_2$ (T_{1g} [$t_{2g}{}^5e_g{}^1$]) since (i) for the first time fine structure is observed here at 80 K, and (ii) their intensities decrease in going from room temperature to 80 K.

Band types I and III are clearly and distinctly present only in the $W(CO)_5A$ complexes, band I is present weakly in $Mo(CO)_5A$ and absent in $Cr(CO)_5A$, and band II′ is absent in Cr and Mo complexes. Therefore, band I is assigned to the spin-forbidden transition $^1A_1 \rightarrow {}^3E$ of the e^3 ($\sim d_{xz}, d_{yz}$) $a_1{}^1$ ($\sim z^2$) excited orbital origin. Since the appearance of band II′ (blue shoulder of band II) follows that of band I, band II′ is also attributed to a spin–orbit-allowed transition, perhaps of $^1A_1 \rightarrow {}^3A_2$ origin, whose spin-allowed partner would be band III. Such assignments were offered for similar molecules.[8,9]

The main conclusion is that MCD directly assigns band II, the band of great photochemical interest.[8-12] Our measurements were carried out as previously described.[13]

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(8) M. Wrighton, G. S. Hammond, and H. B. Gray, *J. Am. Chem. Soc.*, **93**, 4336 (1971).

(9) (a) M. Wrighton, *Inorg. Chem.*, **13**, 905 (1974); (b) *J. Am. Chem. Soc.*, **98**, 4105 (1976).

(10) M. Dahlgren, Ph.D. Dissertation, The University of California, Los Angeles, 1978.

(11) G. Schvenzer, M. Y. Darensbourg, and D. J. Darensbourg, *Inorg. Chem.*, **11**, 1967 (1972).

(12) F. A. Cotton, W. T. Edwards, F. C. Rauch, M. A. Graham, R. N. Perutz, and J. J. Turner, *J. Coord. Chem.*, **2**, 247 (1973).

(13) D. J. Hamm and A. F. Schreiner, *Chem. Phys. Lett.*, **32**, 322 (1975).

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Received June 6, 1979

Organic Photochemistry with 6.7-eV Photons: Rigid Homoallylic Alcohols. An Inverse Norrish Type II Rearrangement

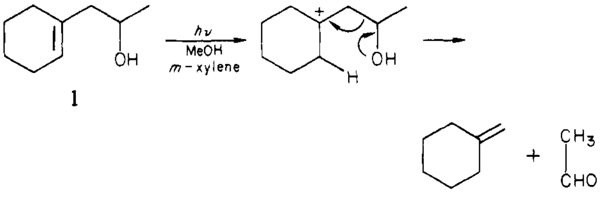
Sir:

There are numerous examples of the photoprotonation of six- and seven-membered cyclic alkenes, which takes place on sensitized photolysis in an appropriate solvent.[1] Kropp and co-workers,[2-4] who have studied this process extensively, have proposed that photoprotonation is preceded by a light-induced cis → trans isomerization of the olefin, and protonation occurs as a secondary ground-state reaction of the highly strained trans olefin. In the case of homoallylic alcohols,[5] this reaction proceeds as in eq 1.[6]

Table I. Rates and Compositions of Aldehydic Products from Homoallylic Alcohols 2-5[a]

reactant	ratio 6/7	ratio 8/9	total rate of aldehyde formation, mol/L/min
2	1.6		7.0×10^{-6}
3	1.0		5.3×10^{-6}
4		2.1	3.2×10^{-6}
5		1.0	1.4×10^{-6}

[a] For reaction conditions, see ref 9.

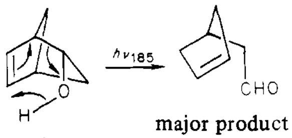


1

(1)

On direct irradiation with an unfiltered mercury arc, a homoallylic alcohol with a cyclohexene group underwent a similar fragmentation, but one with a cyclopentene group did not.[7] These results will be discussed later.

In this communication, we show that direct irradiation of homoallylic alcohols which incorporate the olefinic group in a rigid, bicyclic framework results in an intramolecular process which leads to an isomeric, monocyclic, unsaturated aldehyde. In the case of bicyclo[2.2.1]hept-5-en-2-ol (**2**), this reaction can be represented as in eq 2. Since this reaction formally involves the abstraction

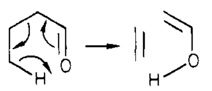


major product

2

(2)

of a hydrogen from a hydroxyl group by an olefin possibly via a six-membered cyclic intermediate to yield a carbonyl group, it can be viewed as the inverse of the Norrish type II process (compare eq 2 to eq 3).[8]



(3)

The homoallylic alcohols **2–5** exhibit ultraviolet absorptions (solvent: pentane) which are indistinguishable from those of the

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(1) For reviews, see (a) P. J. Kropp, C. Ouannes, and R. Beugelmans in "Elements de Photochimie Avancée", P. Courtot, Ed., Hermann, Paris, 1972, pp 229–288; (b) P. J. Kropp, *Mol. Photochem.*, **9**, 39 (1978–1979).

(2) P. J. Kropp, *J. Am. Chem. Soc.*, **88**, 4091 (1966).

(3) P. J. Kropp and H. J. Kraus, *J. Am. Chem. Soc.*, **89**, 5199 (1967).

(4) An initial report was also published by J. A. Marshall and R. D. Carroll, *J. Am. Chem. Soc.*, **88**, 4092 (1966).

(5) P. J. Kropp and H. J. Kraus, *J. Am. Chem. Soc.*, **91**, 7466 (1969).

(6) In the case of cholesterol in which the –OH group is bound to the cyclohexene by a fused ring, a similar reaction leads predominantly to oxetanes which are derived by the intramolecular addition of the aldehyde to the exo methylene olefin [Y. Kondo, J. A. Waters, B. Witkop, D. Guenard, and R. Beugelmans, *Tetrahedron*, **28**, 797 (1972)].

(7) P. J. Kropp, E. J. Reardon, Jr., Z. L. F. Gaibel, K. F. Willard, and J. H. Hathaway, Jr., *J. Am. Chem. Soc.*, **95**, 7058 (1973).

(8) A purely formal view can be confusing as there is also a thermal reaction of homoallylic alcohols which is formally similar to reaction 2 [R. T. Arnold and G. Smolinsky, *J. Am. Chem. Soc.*, **82**, 4918 (1960)]. The deuterium labeling experiments which are described later in this communication show that the view of reaction 2 as the inverse of the Norrish type II process is not merely a formalism but duplicates the latter in detail.

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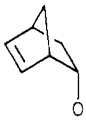
corresponding olefins [λ_{max} **2** or **3** 192 nm (ϵ_{max} 6000); λ_{max} **4** or **5** 196 nm (ϵ_{max} 4000)]. Irradiation[9] of each of these alcohols



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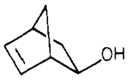

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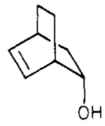

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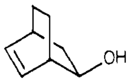
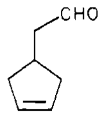


5

at 185 nm in pentane solution gave mixtures of isomeric aldehydes which were isolated by GC and identified by comparison of their spectra to those of authentic material. Both **2** and **3** gave rise to the same pair of unsaturated aldehydes **6** and **7**[10,11] while **4** and



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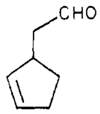

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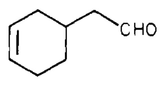

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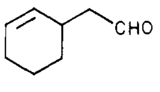
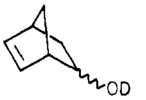


9

5 gave another pair of unsaturated aldehydes, **8** and **9**.[12,13] At low conversions, no other product was detected, but in preparative scale (0.5–1.0 g) irradiations, the yields of the aldehydes were only ~35%. Secondary photolytic decomposition of the primary products accounted for the reduced yield. The relative rates of formation of the four products from the appropriate reactants are given in Table I. These rates were reproducible to ±5%.

Although reaction 2 resembles 1 in its outcome, it was established that the mechanism of the former was quite different from that of the latter from the following deuterium-labeling experiments: (i) The irradiation of bicyclo[2.2.2]oct-5-en-2-ol (80% endo, **4**, 20% exo, **5**) was conducted in perdeuteriocyclohexane as solvent. The aldehydes **8** and **9** that were obtained were found to be entirely free from any excess deuterium over the normal abundance from their mass and IR spectra. This showed that reaction 2 does not involve the participation of a solvent molecule. A similar experiment with bicyclo[2.2.1]hept-5-en-2-ol (79% endo, **2**, 21% exo, **3**) in perdeuteriocyclohexane did not result in the incorporation of deuterium in the aldehydic products, **6**, and **7**. (ii) A sample of bicyclo[2.2.1]hept-5-en-2-ol (79% endo, 21% exo) was exchanged repeatedly with D_2O until >90% of the hydroxyl position (according to NMR) was –OD, as in **10**. On photolysis



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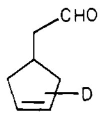

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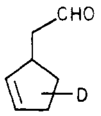
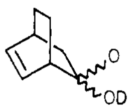


12

in pentane, the aldehydic products **11** and **12** were found to contain one D atom each (parent ion at M = 111). The position of the D atom could also be determined to be in the cyclopentene ring from the mass spectrum of the material. The intense peaks in the spectra of **6** and **7** are at M – 44 (=66), corresponding to the McLafferty rearrangement,[14] and M – 43 (=67), corresponding to the loss of $-CH_2CHO$. These peaks had shifted to masses 67 and 68 in **11** and **12**, thus demonstrating the intramolecular nature of the hydrogen (or D) shift.[15] (iii) Photolysis of the alcohol **13** (74% endo, 26% exo)[16] in pentane gave the aldehydes **14** and **15**.



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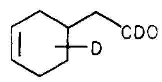

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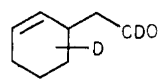

15

The mass spectra of both aldehydes showed that they each contained 2 D atoms. The intense peaks were at 80 (M – CH_3CDO) and 81 (M – CH_2CDO) instead of the normal values of 79 and 80. It is therefore reasonable to represent the structures of these compounds as in **14** and **15** with one D atom on the ring and the other on the aldehyde group. The NMR spectrum confirmed the absence of a proton on the aldehyde group.

These data fully justify the depiction of reaction 2 and the corresponding process in the bicyclo[2.2.2]oct-5-en-2-ols as an intramolecular process. The failure in such rigid systems to promote the formation of a trans olefin by a photoreaction was noted by Kropp and his co-workers.[7] It is therefore conceivable that the intramolecular rearrangement (reaction 2) is observable only when stereoisomerization is blocked by the rigidity of the cycloalkene. But one also has to consider the possibility that in a nonrigid homoallylic alcohol such as **1** the fragmentation that was observed on direct irradiation[7] proceeds by an intramolecular mechanism similar to reaction 2. Since no mechanistic studies had been carried out previously, this is entirely possible.

The effect of variations in the solvent on the photolysis of **1**, **2** + **3**, and **4** + **5** at two wavelengths was examined. These results are summarized in Table II. Photolysis of **1** at 185 nm in pentane solution was a complex reaction which gave rise to eight products in comparable amounts. Methylenecyclohexane, the presence of which was used to measure the fragmentation reaction 1, accounted for less than 14% of **1** that disappeared. But the addition of progressively increasing concentrations of methanol up to 10^{-1} M gradually eliminated the products other than methylenecyclohexane. The mass balance improved at the same time. The *rate* of formation of methylenecyclohexane was seen to accelerate by 50% which can be considered a minimum since the methanol absorbed some of the radiation at 185 nm.

In contrast, the addition of 10^{-1} M methanol to a solution of **2** + **3** was seen to decrease the rate of formation of **6** + **7**. An

Table II. Solvent Effects on Rates of Aldehyde Formation

reactant	solvent	concn, M	rate of product formation, mol/L/min
irradiation wavelength: 185 nm			
bicyclo[2.2.1]hept-5-en-2-ol[a] (**2** + **3**)	pentane	1.50×10^{-2}	4.3×10^{-6}
	pentane/ 10^{-1} M methanol	1.50×10^{-2}	2.2×10^{-6}
3-(1′-cyclohexenyl)-2-propanol (**1**)	pentane	0.86×10^{-2}	1.7×10^{-6}
	pentane/ 10^{-1} M methanol	0.86×10^{-2}	2.5×10^{-6}
irradiation wavelength 214 nm			
bicyclo[2.2.1]hept-5-en-2-ol (**2** + **3**)	pentane	0.94×10^{-2}	20×10^{-6}
	methanol	1.17×10^{-2}	3.3×10^{-6}[d]
bicyclo[2.2.1]oct-5-en-2-ol[c] (**4** + **5**)	pentane	0.69×10^{-2}	3.5×10^{-6}
	methanol	0.99×10^{-2}	0.53×10^{-6}[d]
3-(1′-cyclohexenyl)-2-propanol (**1**)	pentane	0.76×10^{-2}	6.2×10^{-6}[b]
	methanol	0.98×10^{-2}	14×10^{-6}[d]

[a] A mixture of endo (79%) and exo (21%) isomers. [b] Measured as methylenecyclohexane. [c] A mixture of endo (80%) and exo (20%) isomers. [d] Not corrected for absorption of the radiation by the solvent (see text).

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(9) Irradiations were carried out in pentane solution (~4 × 10^{-2} M) by using a Hanovia low-pressure Hg resonance lamp filtered by an Acton 185-N band-pass filter (quantitative runs) or a 35-W hot cathode low-pressure Hg lamp without a filter (preparative experiments).

(10) P. Yates and R. O. Loutfy, *Acc. Chem. Res.*, **8**, 209 (1975).

(11) W. C. Agosta, *J. Am. Chem. Soc.*, **97**, 456 (1975); W. C. Agosta and S. Wolff, *ibid.*, **99**, 3355 (1977); A. G. Singer, S. Wolff, and W. C. Agosta, *J. Org. Chem.*, **42**, 1327 (1977).

(12) We thank Professor W. C. Agosta for kindly providing the spectra of authentic cyclohexenylacetaldehydes.

(13) An authentic sample of **8** was prepared by the oxidation of Δ^3-cyclohexenylethanol [J. C. Collins and W. W. Hess, *Org. Synth.*, **52**, 5 (1972)].

(14) For a review, see A. Frigerio, "Essential Aspects of Mass Spectrometry", Spectrum Publications, New York, 1974, p 61.

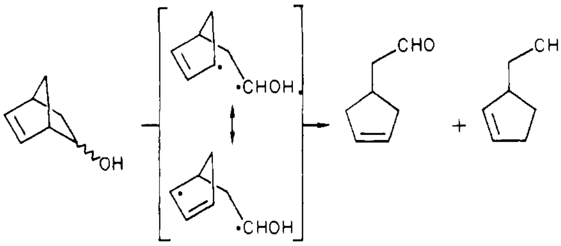
(15) Attempts to locate the precise site of the D atom by 220-MHz NMR spectroscopy were frustrated by the complexity of the midfield region of the spectrum.

(16) The alcohol was prepared by the reduction of the corresponding ketone with lithium aluminum deuteride.

accurate value of the extinction coefficient of methanol in solution at 185 nm is not available.[17] If the value is between that of the vapor and the liquid, the decrease in the rate can be largely attributed to the fraction of the light that is absorbed by the methanol.

In order to obtain more extensive data, the photolysis of these homoallylic alcohols was extended to monochromatic radiation at 214 nm.[18] It was possible to use methanol as a solvent although it absorbed ~60% of the radiation in the path length that was used.[19] The results (Table II) show that in **1** methanol speeds up the fragmentation to give methylenecyclohexane by a factor of more than five (after correction for absorption by the solvent) whereas in the rigid bicyclic alcohols it *slows* the rate to about 30–40% (corrected) of its value in pentane. The acceleration of the former would be in keeping with the protonation mechanism that was suggested by Kropp and his co-workers[5,7] which would be favored when a hydroxylic species is available to capture the trans olefin. The decelerating effect on the reactions of the bicyclic alcohols clearly rules out a common mechanism for these two classes of compounds.

Some mechanistic details such as the differences in behavior between exo and endo alcohols and formation of both Δ^2- and Δ^3-aldehydes deserve comment. If the excitation of an endo alcohol such as **2** led to a concerted process as depicted in eq 2, only the Δ^3-aldehyde would be formed. Such a concerted reaction is obviously not feasible in the exo isomers. It is therefore necessary to postulate a diradical path as well which is shown in eq 4.[20] The diradical pathway alone would not explain the differing ratios of aldehydes from the exo and endo isomers. Note that the endo alcohols which have two routes for reaction according to this hypothesis also react faster than the exo alcohols. The slowing down of these reactions in methanol is an intriguing phenomenon. The type II process in a variety of ketones is known to be speeded up in hydroxylic solvents.[21] At first sight, it seems reasonable that the inverse of this process should be slowed down by a hydroxylic solvent. But since no epimerization of the starting compounds was detected, there is no reason to believe that the intermediate biradical reverts to the starting material. The effect of the hydroxylic solvent may therefore be on the starting material rather than on the intermediate.



(4)

The photoreactions seen in these rigid, bicyclic ene alcohols at 185 nm are not characteristic of olefins which usually react via carbene intermediates.[22] Alcohols do undergo a variety of scission processes at 185 nm,[17] but in the present examples the reaction paths seem few and narrowly channelled. Thus, some interaction between the olefin and alcohol chromophores in the excited state can be inferred even if it is not evident from the ultraviolet spectra.

Acknowledgment. We thank V. Mayne-Banton for her skilled technical assistance.

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[17] C. von Sonntag and H. P. Schuchmann, *Adv. Photochem.*, **10**, 59 (1977).

[18] The source was a Phillips 93106E zinc lamp. It was surrounded by an annulus which contained the solution to be photolyzed.

[19] "UV Atlas of Organic Compounds", Plenum Press, New York, 1966, Vol. I, M-1.

[20] The epimerization **2** ⇄ **3** or **4** ⇄ **5** under the influence of light was not observed. Further fragmentation of the diradicals to give cyclopentadiene and acetaldehyde is seen in the mass spectrum but cannot be taken as an indication of stepwide cleavage.

[21] P. J. Wagner, *J. Am. Chem. Soc.*, **89**, 5898 (1967); R. D. Rauh and P. A. Leermakers, *ibid.*, **90**, 2246 (1968); P. J. Wagner, P. A. Kelso, and R. G. Zepp, *ibid.*, 94, 7480 (1972).

[22] (a) P. J. Kropp, H. G. Fravel, Jr., and T. R. Fields, *J. Am. Chem. Soc.*, 98, 86 (1976), and earlier references therein; (b) Y. Inoue, S. Takamuku, and H. Sakurai, *J. Chem. Soc., Perkin Trans. 2*, 1635 (1977); (c) R. Srinivasan and K. H. Brown, *J. Am. Chem. Soc.*, **100**, 4602 (1978).

Quenching of Emission and of Photochemistry of Pentacarbonyl(4-cyanopyridino)tungsten(0)

Sir:

Several complexes of the general formula $W(CO)_5L$, where L is an *n*-electron donor, have been found to luminesce at 77 K either as the pure solid or in rigid glasses.[1,2] The emission has been assigned to either a $^3E \rightarrow {}^1A_1$ ligand-field (LF) transition or a W → L charge-transfer (CT) transition, depending on the nature of L. As L becomes more electron withdrawing, the CT state lowers in energy, and for various 4-substituted pyridines as L has been inferred to be the lowest lying state.[3] $W(CO)_5L$ complexes have not been thought to luminesce in room temperature solution, presumably because of rapid ligand dissociation and nonradiative relaxation to ground state.[2,4] We report here what appears to be the first observation of emission from a $W(CO)_5L$ complex in room temperature solution. The finding makes possible quenching studies, and results are reported for anthracene as quencher.

$W(CO)_5(4\text{-CNpyr})$ (cyanopyridine) was prepared via the tetrahydrofuran complex, $W(CO)_5(THF)$, according to a literature procedure.[3,5] Purification was achieved by chromatography on alumina, followed by recrystallization from toluene/isooctane solution. Anthracene was recrystallized from benzene prior to use. The solvent methylcyclohexane was purified by several distillations, to remove emitting or quenching impurities. Laser pulse excitation was at 353 or 530 nm, using a 20-ns pulse from a Nd glass laser.[6] The photomultiplier was an RCA 7265. Conventional photolyses were carried out with light from an interference filtered Hg lamp, and quantum yields were determined by means of Reineckate actinometry.[7]

Either 353- or 530-nm excitation of $W(CO)_5(4\text{-CNpyr})$ (5×10^{-5} to 1×10^{-4} M) in argon-flushed[8] methylcyclohexane produced a relatively weak emission (comparable in intensity to that found for various Cr(III) ammines in room temperature solution[9]). The decay time, τ, is 360 ± 30 ns at 25 °C, and the emission is in the 600–700-nm region with an uncorrected peak intensity at about 630 nm (reported values in EPA at 77 K are 33 μs and 602 nm[3]). On correction, using the manufacturers response data, the emission maximum shifts slightly, to 640 nm; the emission is broad and unstructured. The emission temperature dependence was determined both in the above solvent and with added 0.1 M ethanol (which has no detectable effects). Points for seven temperatures from 0 to 30 °C give good Arrhenius behavior, the least-squares line being $1/\tau = 3.56 \times 10^7 \exp(-1520/RT)$, R in cal; the apparent activation energy is thus small, and may relate to that of solvent viscosity. It might be noted that we see weak emission

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