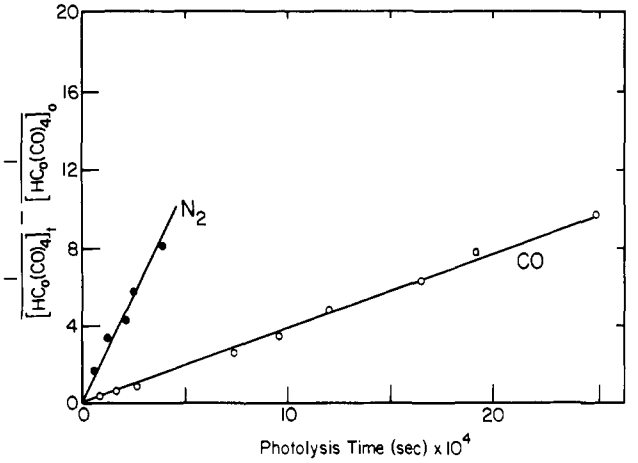

Figure 2. Second-order plot for disappearance of $HCo(CO)_4$ in the photochemical decomposition, under N_2 atmosphere and under 1 atm of CO.

agreement with previous work, that the reaction rate is inversely dependent on [CO].

The kinetics of the photochemical reaction have not been previously reported. Upon irradiation at 366 nm at room temperature decomposition is much faster than the thermal process. All of the absorbance at 366 nm is due to traces of $Co_2(CO)_8$; $HCo(CO)_4$ has negligible absorbance at this wavelength. Because absorption under the experimental conditions is essentially total, the rate of photodecomposition of $HCo(CO)_4$ is independent of added $Co_2(CO)_8$. The rate of photodecomposition is second order in $[HCo(CO)_4]$, and is inhibited by addition of CO at 1 atm (Figure 2).

Our results are not readily accounted for by a mechanistic scheme that involves CO loss from $HCo(CO)_4$ as a preequilibrium in the thermal reaction or primary photoprocess in the photochemical reaction. We propose the following mechanism:

$$Co_2(CO)_8 \rightleftarrows 2Co(CO)_4\cdot \quad (2)$$

$$Co(CO)_4\cdot \rightleftarrows Co(CO)_3 + CO \quad (3)$$

$$Co(CO)_3 + HCo(CO)_4 \rightleftarrows HCo_2(CO)_7\cdot \quad (4)$$

$$HCo_2(CO)_7\cdot + HCo(CO)_4 \rightarrow H_2Co_2(CO)_7 + Co(CO)_4\cdot \quad (5)$$

$$H_2Co_2(CO)_7 \rightarrow H_2 + Co_2(CO)_7 \quad (6)$$

$$Co_2(CO)_7 + CO \rightarrow Co_2(CO)_8 \quad (7)$$

The mechanism involves an initial formation of $Co(CO)_4\cdot$ radicals. The thermal reaction involves a homolytic preequilibrium; in the photochemical reaction, facile rupture of the Co–Co bond occurs via excitation of the σ–σ^* transition for $Co_2(CO)_8$. The labile $Co(CO)_4\cdot$ radicals lose CO;[8b,12] there follows an oxidative addition preequilibrium, a slower hydrogen atom transfer, and then reductive elimination of H_2. When the rate expression for the thermal reaction is integrated, recognizing that the reaction is autocatalytic in $Co_2(CO)_8$ via preequilibrium 2, one obtains

$$F([HCo(CO)_4]_t) = \frac{(K - \frac{1}{2}[HCo(CO)_4]_t)^{1/2}}{K[HCo(CO)_4]_t} + \frac{1}{4K^{3/2}} \log \frac{\{(K - \frac{1}{2}[HCo(CO)_4]_t)^{1/2} + K^{1/2}\}^2}{[HCo(CO)_4]_t} = kt \quad (8)$$

where $K = [Co_2(CO)_8]_0 + \frac{1}{2}[HCo(CO)_4]_0$. This function is displayed in Figure 1b for the same data shown in 1a. The fit is satisfactory through 2 half-lives.

The proposed mechanism leads to the following expression for the rate of $HCo(CO)_4$ loss in the photochemical decomposition:

$$-\frac{d[HCo(CO)_4]}{dt} = \frac{\kappa I_a[HCo(CO)_4]^2}{[CO]} \quad (9)$$

I_a represents the flux of photons, and κ is a collection of rate constants relating to equilibria 2–4 and rate-determining step 5. Although we have not tested the dependence of photochemical rate on I_a, we have observed the expected dependences on $[HCo(CO)_4]$ and [CO].

The commonly accepted mechanism for thermal decomposition or substitution of $HCo(CO)_4$ involves a presumed facile loss of CO to form $HCo(CO)_3$.[10,11] There is, however, little independent evidence that such a thermal process exists. The observation of rapid substitution of $HCo(CO)_4$ by a phosphine[13] is not supportive evidence, because such a substitution probably proceeds via a now well-established radical chain mechanism.[8,14] Compounds of the form $XCo(CO)_4$, where $X = Sn(C_6H_5)_3$, CF_3, and others, all undergo slow substitution at room temperature.[12,15] Only when X is a strongly cis-labilizing ligand such as $-C(O)R$[16] is substitution reasonably rapid at room temperature. Hydride is not expected to be a cis-labilizing ligand.[17,18]

Our present results thus strongly suggest a common radical mechanism for both the photochemical and thermal decomposition of $HCo(CO)_4$. These results also carry the implication that radical intermediates could be plausibly involved in much of the catalytic reaction chemistry involving $HCo(CO)_4$, $Co_2(CO)_8$, or related compounds.[19]

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Adamantyl Allenic Rhodopsin. Leniency of the Ring Binding Site in Bovine Opsin

Sir:

We had previously shown[1] that bovine opsin not only binds to the 9-cis and 9,13-dicis isomers of 6,7-didehydro-5,6-dihydroretinal (**1**)[2] but is also capable of accepting all four diastereomers and enantiomers. In view of the high specificity usually encountered in binding sites, this lenient property of

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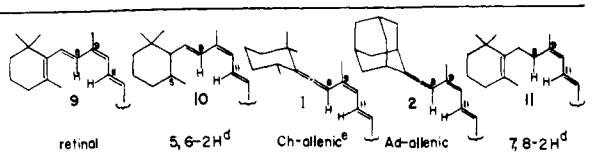
Table I. Chemical Shifts of Adamantyl Allenic Retinals[a]

retinal	8-H	9-Me	10-H	11-H	12-H	13-Me	14-H	15-H
all-trans	5.69	~1.8[b]	5.77[c]	6.88	6.14	2.19	5.77[c]	9.95
9-cis	5.86	~1.8[b]	5.78[c]	6.90	6.13	2.18	5.78[c]	9.97
9-13-dicis	5.89	~1.8[b]	5.89	6.96	7.09	2.01	5.70	10.1

[a] 80 MHz, $CDCl_3$. [b] Buried under methylene resonances. [c] Not resolved.

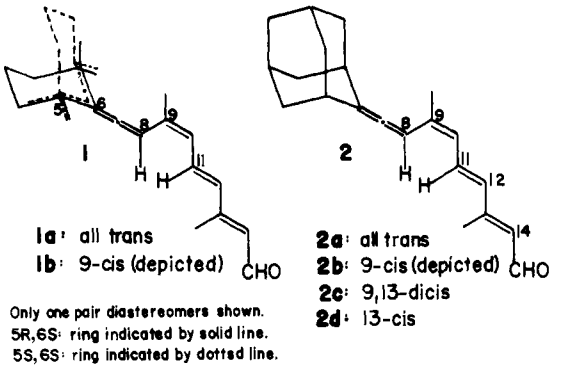
Table II. Absorption Data of Retinals, Protonated Schiff Bases, (SBH^+), and 9-*cis*-Rhodopsins[g]

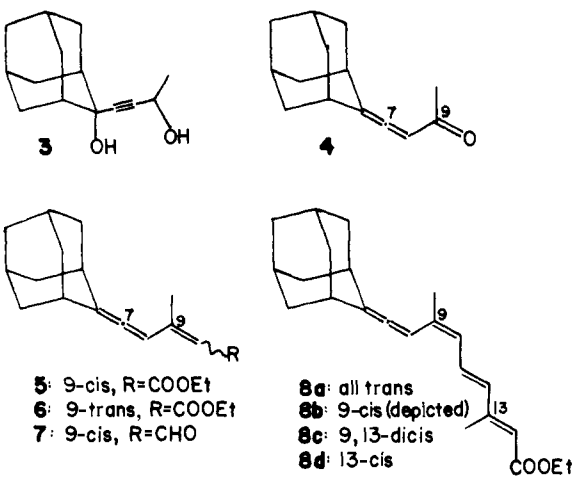


trans-ald[a]	369	356[f]	353[f]	355[f]	320[f]
9-cis-ald.[a]	362	347[f]	351[f]	335[f]	321[f]
SBH^+[b]		425	430	398	392
9-cis-rhod[c]	485	460	460	410	425

[a] Hexane. [b] Methanol. [c] 1.5% Triton X-100. [d] Reference 8. [e] The electronic spectra of the two diastereomeric pairs are almost superimposable. [f] Fine structure. [g] The retinals are represented by their 9-cis forms for the sake of convenience.

the apoprotein was quite unexpected. It may be argued, however, that the manner in which the retinal is depicted in **1** exaggerates the diastereomeric difference (solid and dotted rings) and that conformational changes could make the stereoisomers adopt very similar overall shapes. To investigate whether the "β-ionone binding site"[3] can actually accept the open "crocodile jaws" (see **1**), we have synthesized adamantyl allenic retinals and carried out binding studies with bovine opsin.





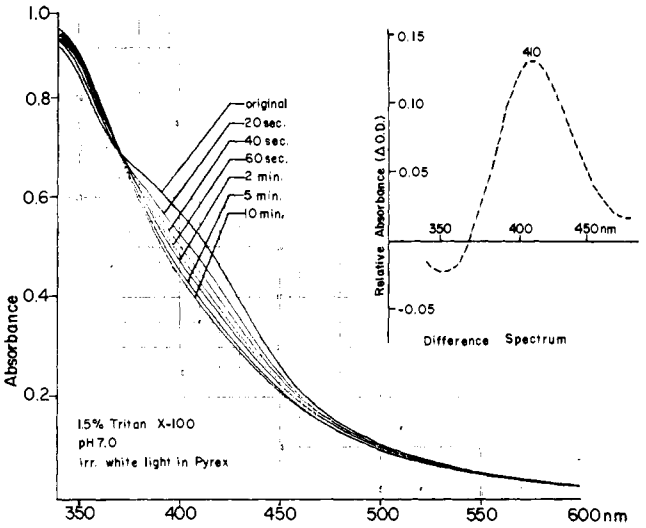


Figure 1. Bleaching of adamantyl allenic pigment in 1.5% Triton X-100, 67 mM phosphate buffer, pH 7.0, 25 °C. The solution was irradiated with a 100-W tungsten lamp (>310 nm) and the spectra were measured at suitable time intervals. The inset shows the difference curve between the "original" and "10-min" spectra.

Condensation of 2-adamantanone with 2 equiv of 3-butyn-2-ol afforded the yne-diol **3** (87%), which upon treatment with 20 molar excess of lithium aluminum hydride,[4] followed by MnO_2 oxidation, gave the allenic ketone **4** (45%). Condensation of ketone **4** with triethylphosphonoacetate (NaH, THF, 25 °C, 6 h) gave a 4:1 mixture of esters **5** and **6** (1,2 adducts) in the low yield of 13%, the major product (85%) being the 1,4 adduct. This contrasts to the results of the cyclohexyl allenic counterpart where the desired 1,2 adduct was the major product (84%);[1] in this case the 1,4 adduct was not formed, presumably owing to the steric blocking at C-7 by the 1- and 5-Me groups.

The 9-cis ester **5** was isolated by flash chromatography[5] (2% EtOAc in petroleum ether), reduced with Dibal (−78 °C, ether), and oxidized with MnO_2 (room temperature, ether) to give 9-cis aldehyde **7**; condensation of **7** with triethylphosphonosenecioate gave retinyl esters **8b** and **8c** in 48% overall yield from ester **5**. After separation of the esters by nonaqueous reverse-phase LC (Whatman ODS-2, MeOH), each was reduced (Dibal, −78 °C) and oxidized (MnO_2, ether, 4 °C) to give 9-cis aldehyde **2b** and 9,13-dicis aldehyde **2c**, respectively. Similarly, the 9-trans ester **6** yielded the trans aldehyde **2a** and the 13-cis aldehyde **2d**. Double-bond configurations are based on comparisons of ^1H NMR data (Table I) with those of retinals[6] and allenic retinals.[1]

Schiff bases (SB) with *n*-butylamine were made as previously described.[7,8] The protonated Schiff bases (SBH^+) were obtained by titrating the methanol or hexane solution of SB to an UV end point with MeOH saturated with dry HCl gas. Addition of a threefold excess of HCl solution caused no change in spectra (Table II).

The 9-cis and 9,13-dicis isomers were incubated for 5 h at 25 °C, pH 7.0, with bovine opsin in suspension, the suspension was centrifuged, the pellets were triturated repeatedly with hexane at −20 °C to remove excess unbound chromophore, and the absorption was measured in Triton X-100 (Figure 1). The difference spectrum shows a clear maximum at 410 nm. This peak is accompanied by a positive CD Cotton effect, $\theta \times 10^3/A_{max} = 2.5°$, the intensity of which is ~50% of that of the cyclohexyl allenic pigments;[1] another very weak positive band is present at ~370 nm (CD measured at 0 °C). This evidence indicates that the 9-cis chromophores **2b** and **2c** indeed form pigments. The fact that these adamantyl chromophores and 9-*cis*-retinal occupy the same binding site in opsin was secured by incubating first with 9-cis allenic aldehydes **2b** or **2c**, and

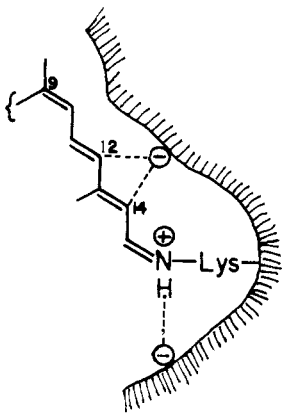


Figure 2. External point-charge model for the binding site of bovine rhodopsin. The dotted lines represent interactions over distances of ~3 Å. The negative charge near C-12/C-14 could be a member of a charge pair in a salt bridge or the negative end of a dipolar group.

then with 9-*cis*-retinal; comparisons of the absorptions at 410 vs. 485 nm (for 9-*cis*-rhodopsin, Table II) showed that formation of 9-*cis*-rhodopsin was ~3% for both **2b** and **2c**. Furthermore, submission of the hexane-washed pellet to the CH_2Cl_2-denaturation extraction procedure[9] regenerated the original retinal, thus proving that the chromophore had not changed upon binding. The chromophores **2a** and **2d** with 9-trans bonds failed to give pigments.

The 9-cis and 9,13-dicis adamantyl allenic retinals, despite their cage structures, thus bind to bovine opsin. This result proves the earlier deduction[1] that the β-ionone binding site is quite lenient. However, there is considerable difference in terms of stability between the cyclohexyl (Ch) and adamantyl (Ad) series, the latter being much less stable. Cyclohexyl-9-*cis*-rhodopsin underwent only 3, 10, and 20% decomposition when kept in 0.5% digitonin,[10] 1.5% Triton X-100, and 2% A-LO,[11] respectively, for 1 h at 25 °C in the dark. In contrast, adamantyl-9-*cis*-rhodopsin was completely destroyed after 2 h in digitonin, after 35 min in Triton, and immediately in A-LO. It is also not stable in 0.1 M hydroxylamine (Triton, pH 7.0). However, the stability of the pigment in Triton X-100 is not affected by change in pH from 5.2 to 8.3. In the form of pellets, adamantyl-9-*cis*-rhodopsin could be stored for at least 1 month without appreciable decomposition if kept at −20 °C, but 50% was destroyed after 3 h at 25 °C.

The data in Table II point to several interesting aspects. The maxima of trans aldehydes **1a** and **2a** are similar to that of *all-trans*-5,6-dihydroretinal (356) and are red shifted in comparison with *all-trans*-7,8-dihydroretinal (320) as expected. The 9-cis chromophores are at ~8 nm shorter wavelengths than the trans chromophores in retinals **9** and **10**, presumably owing to steric interaction between 8-H and 11-H. This difference in the cyclohexyl analogue is only 2 nm, but in the adamantyl analogue it is much larger, i.e., 20 nm. Examination of CPK molecular models allows one to suggest the following to account for these results. In **1b**, the 9-ene is locked into conjugation with the allenic 7-ene owing to steric hindrance between the 9-Me and the annular equatorial Me groups despite the steric interaction between 8-H/11-H. In contrast, in **2b**, which has no ring Me groups, the 8–9 single bond is free to rotate, and hence the 8-H/11-H interaction moves the 9-ene considerably out of conjugation with the allenic 7-ene. The λ_{max} (335 nm) thus falls between those of 5,6-dihydro- and 7,8-dihydroretinals, **10** (347 nm) and **11** (321 nm); a similar tendency is seen in the three protonated Schiff bases, i.e., 398 nm vs. 425 and 392 nm.

The instability of the adamantyl allenic pigment relative to the cyclohexyl allenic pigment is probably due to the spheric shape of the adamantyl moiety. It is to be noted that the 410-nm absorption maximum of the adamantyl pigment is only 12 nm red shifted from the SBH^+ value, and is at a shorter wavelength even than that of 7,8-dihydrorhodopsin. We have proposed[12,13] that external charges within the binding site are responsible for wavelength regulation in visual pigments. Namely, in the external point-charge model for bovine rhodopsins (Figure 2), the point-charge located at ~3 Å from C-12/C-14 is responsible for the red shifts of bovine visual pigments relative to their SBH^+. The short-wavelength absorption of the adamantyl allenic pigment implies that in the present case C-12/C-14 are farther away from this point charge.

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Nonradical Intermediates in the Photolysis of Decacarbonyldimanganese

Sir:

Many metal–metal-bonded complexes are thought to react photochemically via homolytic cleavage of the metal–metal bond to form metal-centered radicals.[1] The following scheme is proposed[1a] for reaction of $Mn_2(CO)_{10}$ with carbon tetrachloride:[2]

$$Mn_2(CO)_{10} \overset{h\nu}{\rightleftharpoons} Mn_2(CO)_{10}^* \quad (1)$$

$$Mn_2(CO)_{10}^* \rightarrow 2Mn(CO)_5 \quad (2)$$

$$Mn(CO)_5 \xrightarrow[k_3]{CCl_4} ClMn(CO)_5 \quad (3)$$

$$2Mn(CO)_5 \xrightarrow[k_4]{} Mn_2(CO)_{10} \quad (4)$$

Kinetic studies fully consistent with such a scheme are conspicuously rare, almost all observations[1,3] being of limiting quantum yields that do not help to define the nature of the intermediates. Only when $[CCl_4]$ is low enough for reaction 4 to compete with 3 is kinetic evidence positively in favor of the

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