The solid-state structure of Pt(dien)[d(ApGpA)-*N*7(2)] differs from the solution structure for the nonplatinated part, as one would expect for such a compound where intermolecular packing, stacking, and hydrogen bonds are likely to predominant in the solid.

Comparison between the solid-state structure and the solution structure reveals first of all that the solid-state structure is mainly determined by intermolecular interactions, with hardly any intramolecular interactions present. In the solution structure, on the other hand, intramolecular effects are more important.

Pt(dien)[d(ApGpA)-*N*7(2)] simulates the structure of the intermediate in the chelate formation of cDDP to DNA. The changes found in this adduct probably direct the DNA backbone, for instance by hydrogen bonding of the platinum amino groups to the phosphates and bases, to a better position for the chelation step.

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Supplementary Material Available: Listing of atomic fractional coordinates and isotropic thermal parameters and tables with intermolecular hydrogen bond information (11 pages); listing of *F*(obs) and *F*(calc) for the title compound (18 pages). Ordering information is given on any current masthead page.

Use of Excited-State and Ground-State Redox Properties of Polyoxometalates for Selective Transformation of Unactivated Carbon–Hydrogen Centers Remote from the Functional Group in Ketones

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Abstract: Two types of processes are described which involve the selective transformation of unactivated carbon–hydrogen bonds in a ketone, *cis*-2-decalone, *cis*-**1**, which possesses conventionally far more reactive bonds. The first type of process involves irradiation of decatungstate, $W_{10}O_{32}^{4-}$ in the presence of *cis*-**1** producing, *trans*-2-decalone, *trans*-**1**, the product resulting from epimerization of an unactivated tertiary C–H bond remote from the carbonyl group, in high selectivity at high conversion of substrate, eq 1. The second type of reaction involves irradiation of the heteropolytungstate, α-$P_2W_{18}O_{62}^{6-}$ or α-$PW_{12}O_{40}^{3-}$, in the presence of *cis*-**1** producing two monounsaturated ketones (octalones) in high selectivity with the nonthermodynamic isomer, **2**, in comparable or greater quantity than the conventional thermodynamic (conjugated) isomer, **3**, eq 2. Both types of processes are independent of wavelength over the principal range of absorption of the complexes (250–380 nm). The reactions are first order in $W_{10}O_{32}^{4-}$ under optically dilute conditions. The primary kinetic isotope of the corresponding decalin hydrocarbons evaluated under the same reaction conditions as eq 1, $k_{cis\text{-decalin-}H_{18}}/k_{cis\text{-decalin-}D_{18}} \sim 2$, and the solvent kinetic isotope effect, $k_{CH_3CN}/k_{CD_3CN} = 1.0$. The photochemical reaction of decatungstate with $\alpha,\alpha,\alpha',\alpha'$-$D_4$-*cis*-**1** leads exclusively, even at moderate conversion of substrate (25%), to $\alpha,\alpha,\alpha',\alpha'$-$D_4$-*trans*-**1**. These data, an isotope crossover experiment in which decatungstate was irradiated in the presence of a 50/50 molar mixture of deuterated and protiated *cis*-decalin in CD_3CN, reactions of *cis*-**1** and *cis*-decalin with an authentic localized ground-state radical, *t*-BuO$^\bullet$, and a number of other experiments are consistent with initial H atom abstraction in all cases. The dramatically different products seen with the different polyoxometalate systems are dictated by the relative rates of epimerization, oxidation, and escape of the cisoid tertiary bridgehead radicals in the initial radical cage and, to a lesser extent, by the rates of conventional radical–radical reactions and other processes.

Introduction

Some classes of early transition-metal–oxygen anion clusters, or polyoxometalates, exhibit a unique combination of physical and chemical properties that make them attractive for probing a number of problems either long standing in chemistry or associated with emerging technological issues.[1-9] The systematic exploitation of the extensive redox properties of the ground and/or excited states of some polyoxometalates has already lead to new processes

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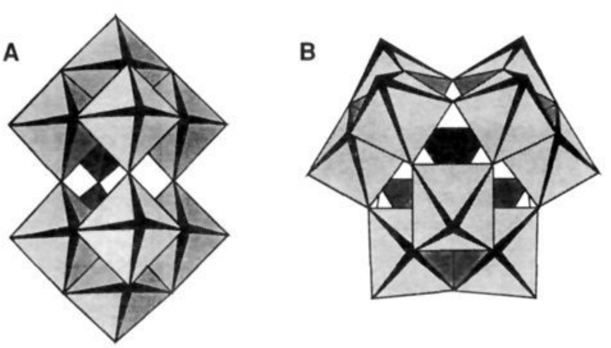
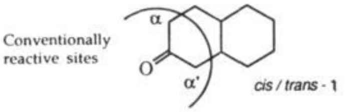


Figure 1. Polyhedral representations of the two polyoxotungstates used as catalysts in this study: (A) the isopolytungstate, decatungstate, $W_{10}O_{32}^{4-}$, (D_{4h} point group symmetry) and (B) the heteropolytungstate, dodecatungstophosphate, α-$PW_{12}O_{40}^{3-}$, (T_d point group symmetry). In polyhedral notations, each octahedron represents one W atom surrounded by six O atoms; the vertices define the center of the oxygen and nuclei, and the central metal atoms are not directly seen. In each WO_6 octahedron, the W atom is displaced from the center of the unit toward the one terminal oxo group.

for the catalytic functionalization of alkanes,[2-5] microlithography,[6] catalytic dehalogenation of halocarbons and other environmental toxins,[7,8] and other processes.

We report here a study that utilizes the redox and other properties of isopolytungstates and heteropolytungstates to address two substantive issues in the catalysis of functionalization of unactivated C–H bonds that have been minimally discussed or elaborated to date.[1-14] The first is the catalytic replacement of unactivated C–H bonds in molecules which bear activated (and conventionally more reactive) C–H bonds. The second is the *catalytic* transformation of unactivated C–H bonds which proceed simultaneously with high selectivity at high substrate conversion. We report here reactions of $W_{10}O_{32}^{4-}$, a representative isopolytungstate, and α-$PW_{12}O_{40}^{3-}$, a representative heteropolytungstate (Figure 1) with the exemplary substrate, *cis*-2-decalone, *cis*-**1**, that exhibit both of these features. The ketone *cis*-**1** was selected for investigation as it bears traditionally activated C–H bonds, those α to the ketone (marked α and α'), and an extensive unactivated carbocyclic skeleton. In addition, many of its chemical and physical properties have been thoroughly documented.[15] The products in these reactions vary dramatically with the physical properties of the polyoxometalate. The products and other unusual or unprecedented aspects of these processes are probed using the energetic and mechanistic information also presented here.



Experimental Section

Materials. The acetonitrile was Burdick and Jackson glass-distilled grade and was stored under argon in Aldrich Sure-Seal bottles and subsequently used with no further purification. The deuterated solvents and decalins were purchased from Aldrich and used with no further purification. The *cis*- and *trans*-decalin, purchased from Fluka, had purities of 99+% by gas chromatography and were used as is. *cis*-2-Decalol was obtained from Columbia Organics, Inc. and used as received. The catalysts, $Q_3PW_{12}O_{40}$,[16] $Q_4W_{10}O_{32}$ (Q refers to n-Bu_4N^+),[17] $Na_4W_{10}O_{32}$,[3] and $(NH_4)_6P_2W_{18}O_{62}$[18] were prepared and purified by literature procedures, and their purities were established by infrared, UV–vis, ^{183}W NMR spectroscopy, and elemental analysis. All other organic and inorganic materials were commercially available, reagent grade and used without further purification.

Methods. The ^{183}W NMR spectra were recorded on an IBM WP-200-SY spectrometer using a probe specifically designed and fabricated for this application by Cryomagnetic Systems, Inc. The ^{183}W NMR spectra were recorded at 8.34 MHz in 15-mm i.d. NMR tubes with a probe temperature of ~25 °C. The spectra were referenced to 2.0 M Na_2WO_4 in D_2O by the sample replacement method. ^1H NMR and ^{13}C NMR spectra were recorded on a General Electric QE-300 operating at 300 and 75.5 MHz, respectively, in 5-mm i.d. NMR tubes with a probe temperature of ~25 °C. The infrared spectra were recorded on a Perkin-Elmer Model 1430 infrared spectrophotometer as KBr pellets (2–4 wt % of compound in KBr). The electronic absorption spectra were obtained on a Hewlett-Packard Model 8451A multidiode array instrument. Microanalyses were performed by Atlantic Microlabs, Atlanta, GA (C, H, N) and by Galbraith Laboratories, Knoxville, TN (P, W).

The gas chromatographic (GC) analyses of the organic products were performed on a Hewlett-Packard 5890 instrument, equipped with flame ionization detectors and a 25-m × 0.2-mm (i.d.) 5% phenyl methyl silicone fused-silica capillary column, utilizing a variety of temperature programs. Nitrogen was the carrier gas, and products were quantified on a Hewlett-Packard 3390A electronic integrator by the internal standard technique (typically bromobenzene was used as the standard). Gas chromatography–mass spectrometric (GC/MS) analyses of the organic materials were performed on a Finnigan 4000 or a VG 70S instrument at Emory University, Atlanta, GA or on a Hewlett-Packard 5890A GS/MS instrument at Wan Technologies of Atlanta, GA.

Irradiation of the reaction solutions was performed with either an Oriel 1000-W Xe lamp equipped with a variety of cut-off and interference filters or a 450-W Hanovia medium-pressure Hg arc lamp. Sample solutions were irradiated in either a 1-cm cylindrical quartz cuvette or a 25-mL Pyrex Schlenk, each of which was fitted with an airtight Teflon stopcock. In the experiments elaborated below involving different polyoxometalates, different light sources were used to achieve similar rates while always maintaining selective polyoxometalate absorption (polyoxometalate absorbing at least 99% of the incident light). As long as the

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Synthesis of *cis*-2-Decalone, *cis*-1. Chromic acid oxidation[19] of the *cis*-2-decalol precursor afforded the desired decalone product. Further purification by passing a toluene solution of the product mixture through a column of neutral activity grade I alumina and subsequent high vacuum distillation (0.01 mmHg, ketone collected at 65–66 °C) afforded highly purified 2-decalone (99+% overall 2-decalone purity which consisted of 98.3% *cis*- and 1.7% *trans*-2-decalone based on GC analysis): $^{13}C\{^1H\}$ NMR (CD_3CN)[20] δ (ppm) 23.3, 24.1, 28.6, 29.0, 29.1 (methylene), 35.2, 39.0 (tertiary, bridgehead carbon atoms), 39.5, 45.6 (methylene carbon atoms α to the carbonyl), 212 (carbonyl); UV–visible, CH_3CN, λ, nm (ϵ, M^{-1} cm^{-1})[21] 292 (16); MS, *m/z* (rel intensity)[22] 152.15 (M^+, 90%).

Synthesis of the 1,1,3,3-Tetradeuterio-*cis*-2-decalone. The deuterated ketone was prepared according to the literature procedure:[23] $^{13}C\{^1H\}$ NMR (CD_3CN)[20] δ (ppm) 23.2, 24.0, 28.5, 28.8, 29.0, 35.1, 38.8, 212 (assignments are the same as those given for *cis*-**1** immediately above); the resonances representing the deuterated carbons (~39.5 and ~45.6 ppm) were not observed due to the extensive signal splitting resulting from C–D coupling; MS, *m/z* (rel intensity) 156.15 (M^+, 98%).

Synthesis of $\Delta^{9,10}$-2-Octalone and $\Delta^{1,9}$-2-Octalone. Synthesis of the 2-octalone mixture (octalones **2** and **3**) was according to the literature procedure.[24] Separation of the isomers was achieved by passage of the octalones (hexane/ethyl acetate, 10:1) through a column of silica gel (100–200 mesh) followed by room temperature evaporation of the solvent. The contents of the fractions were monitored by GC. Spectral characteristics of the nonconjugated ("remote") octalone, $\Delta^{9,10}$-2-octalone, **2**: ^1H NMR, (CD_3CN)[25] δ (ppm) 2.7 (s, 2 H); MS, *m/z* (rel intensity) 150 (M^+, 45%), 122 ($M^+ - CO$, 100%). Spectral characteristics of the conjugated octalone, $\Delta^{1,9}$-2-octalone, **3**: ^1H NMR, (CD_3CN)[26] δ (ppm) 5.8 (s, 1 H); MS, *m/z* (rel intensity) 150 (M^+, 15%), 136 ($M^+ - CH_2$, 100%).

Synthesis of Di-*tert*-butyl Peroxyoxalate. Di-*tert*-butyl peroxyoxalate, DTBO, was synthesized according to the literature procedure[27] and stored in a flask, under argon, at −10 to −20 °C. **Caution: DTBO is a contact explosive and, when dry, easily detonates when struck by a hard object.** Consistent with this danger, all manipulations of DTBO were done very carefully and with a rubber policeman: ^1H NMR (C_6D_6) δ (ppm) 1.12 (s, only signal observed); $^{13}C\{^1H\}$ NMR (C_6D_6) δ (ppm) 25.7, 85.4, no signal observed for the carbonyl carbon.

Dehydrogenation of *cis*-1. In a typical experiment, 10 mL of a CH_3CN solution of *cis*-**1** (150 mM) and the polyoxotungstate catalyst (catalyst concentration, range of UV–visible irradiation (nm): 5.6 mM $Q_3PW_{12}O_{40}$, $\lambda > 290$, or 6.5 mM $(NH_4)_6P_2W_{18}O_{62}$, $\lambda > 305$) were placed in a 25-mL Schlenk flask containing a stir bar. The polyoxometalate concentration was determined by calculation of the minimum amount necessary to absorb >99% of the incident radiation at the specified wavelength and thus suppress the formation of products arising from photochemical excitation of the ketone chromophore. The solution was thoroughly degassed and placed under an atmosphere of argon. The colorless reaction mixture was irradiated by utilizing the 1000-W Xe lamp and the appropriate cut-off filter ($\lambda > 290$ and 305 nm for the reactions catalyzed by $Q_3PW_{12}O_{40}$ and $(NH_4)_6P_2W_{18}O_{62}$, respectively). Throughout the irradiation period the solutions were stirred and maintained at 25 °C by immersion in a water bath. The irradiation times required to achieve a specific number of turnovers (turnovers were defined as the moles of organic product/moles of polyoxometalate catalyst) varied from one catalyst to the next but were fairly consistent for a given polyoxotungstate system. Typically, the rate of generation of octalone products in the reactions with the Wells–Dawson complex, $(NH_4)_6P_2W_{18}O_{62}$, were an order of magnitude slower than the analogous reactions with $Q_3PW_{12}O_{40}$. Therefore, in order to minimize the irradiation time, the former reaction was taken to a much lower turnover number than the latter. However, the observed product selectivities (remote versus conjugated octalone and octalones versus all other products) were similar for the two catalysts. The product solutions after irradiation were analyzed by GC to determine the extent and selectivity of the reaction. The catalyst could be regenerated (reoxidized) by exposing the solution to air for a few moments until the blue color ($\lambda_{max} \approx 740$ nm) of the photoreduced polyoxotungstate complex disappeared. The solution was once again degassed and placed under an inert atmosphere before irradiation was resumed. Catalyst regeneration methods were employed only for those cases in which the maximum possible number of turnovers of the catalyst was being assessed.

Equilibration of the 2-Octalones (2 and 3). To determine the thermodynamic ratio of remote to conjugated octalone under the conditions of the experiment, the following room temperature equilibration was performed. A CH_3CN solution of a 50/50 mixture of the two octalones was placed over a bed of AG-50(X8) resin (strong acid form, swollen with CH_3CN) and gently stirred at room temperature throughout the experiment. The octalone ratio was analyzed periodically by GC until no further change was observed (8 days). Likewise, a CH_3CN solution containing only the conjugated octalone was allowed to equilibrate over resin until no further change was observed. The same product distribution was obtained in both cases; at equilibrium, the ratio of **2** (remote octalone) to **3** (conjugated octalone) was 13:87.

Isomerization of *cis*-1. Reaction conditions were identical to those in the dehydrogenation of *cis*-**1** except for the following points: (i) the polyoxotungstate catalyst used in these transformations was decatungstate, $W_{10}O_{32}^{4-}$, (ii) the concentration of the substrate was 150 mM and that of the catalyst was 1.5 mM, and (iii) a 360-nm cut-off filter was used in these experiments. There was no net oxidation of the substrate, and hence, as long as the solution was irradiated, the epimerization reaction continued. On termination of the irradiation the solution remained blue, however, indicating a net reduction of the decatungstate catalyst. This observation is discussed in the text subsequently.

Isomerization of Decalin. The conditions used were identical to those described above for the epimerization of *cis*-**1**. Although the substrate did not absorb appreciably in the spectral region of interest, for consistency, a 360-nm cut-off filter was used nonetheless.

Collection of Relative Rate Data (Table III). The relative rate data were acquired using both comparative kinetics methods (separate reactions) and competitive kinetics methods (two substrates competing in each reaction). Although competitive kinetics methods usually generate rate data that are more internally consistent, this is not necessarily the case when there is substantial reaction of intermediates with substrates under the reaction conditions, as is shown below to be the case in some of these polyoxometalate-facilitated photochemical functionalization reactions investigated here. The rates of cis-to-trans isomerization for a number of substrates were calculated relative to that of the parent, *cis*-2-decalone, system. In the parent system, a 2-mL CH_3CN solution consisting of 150 mM *cis*-**1** and 1.5 mM decatungstate was placed in a cuvette of 1-cm pathlength which contained a small stir bar. The reactions were run at 23 °C under an atmosphere of argon. A 360-nm cut-off filter was employed for the irradiation (1000-W Xe lamp) of each system in this experiment. The formation of organic product (the trans isomer) as a function of time was monitored by GC through sampling of the solution at specified time intervals (0, 30, 60, 90, and 120 s of total irradiation). The parent system was given a relative rate of 1.0 ($-d[cis\text{-}\mathbf{1}]/dt = 4.1 \times 10^{-3}$ mM/s, which corresponds to ~9.8% conversion or ~9.8 turnovers of the catalyst per hour based on the formation of *trans*-**1**). The next two systems analyzed were identical to the previous one except that the deuterated solvent, CD_3CN, was used instead of the protiated analogue in one case, and in the other, *cis*-decalin was the substrate instead of *cis*-**1**. A deuterium isotope effect was determined by measuring the relative rate of epimerization of *cis*-decalin-H_{18} versus *cis*-decalin-D_{18} (k_H/k_D). In this system, and in the one described immediately below, equimolar concentrations of the substrates were used (75 mM each) such that the total substrate concentration, 150 mM, was still 100 times that of the catalyst. To determine the competitive rates of epimerization of the two substrates, the final system analyzed in this experiment was that of an equimolar mixture of *cis*-**1** and *cis*-decalin in CH_3CN.

Isotope Crossover Experiment. A CD_3CN solution (2 mL) of *cis*-decalin-H_{18}, *cis*-decalin-D_{18} (90 mM each) and the sodium salt of decatungstate (1.8 mM) were placed in a Schlenk flask, degassed, placed under argon, and irradiated (1000-W Xe lamp, 360-nm cut-off filter) at room temperature (H_2O bath, 25 °C) for 2 h. After irradiation, 7.4 and 4.5% of the protiated and deuterated *cis*-decalin isotopomers, respectively, had been converted to *trans*-decalin. The irradiated and nonirradiated solutions were analyzed by GC/MS.

Reaction of *cis*-1 with DTBO. One milliliter of a CH_3CN solution of *cis*-2-decalone (0.15 mmol) was placed in a 5-mL round-bottomed Schlenk flask equipped with a small magnetic stir bar. In another small Schlenk flask was placed 35 mg (0.15 mmol) of DTBO. Both flasks were thoroughly degassed and left under argon. The contents of the former vessel were transferred via cannula under a flow of argon to the latter

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(26) Scott, J. W.; Banner, B. L.; Saucy, G. *J. Org. Chem.* **1972**, *37*, 1664.

(27) Bartlett, P. D.; Benzing, E. P.; Pincick, R. E. *J. Am. Chem. Soc.* **1960**, *82*, 1762.

Table I. Selective Transformations Involving Unactivated Carbon–Hydrogen Centers in *cis*-2-Decalone (*cis*-**1**) and *cis*-Decalin by Polyoxotungstates[a]

rxn	organic substrate	catalyst[b]	convn, %[c]	product yields, % turnovers[d]		
					octalones[e]	
				trans isomer	**2**	**3**
1	*cis*-**1**	$W_{10}O_{32}^{4-}$[f]	81	~100 (20)	0	0
2	*cis*-**1**	α-$PW_{12}O_{40}^{3-}$[g]	6	0	68 (0.75)	32 (0.35)
3	*cis*-**1**	α-$PW_{12}O_{40}^{3-}$	12	0	52 (1.2)	48 (1.1)
4	*cis*-**1**	α-$P_2W_{18}O_{62}^{6-}$[h]	<2	0	45 (0.045)	55 (0.05)
5	*cis*-decalin	$W_{10}O_{32}^{4-}$	4	80 (32)[i]		
6		H^+ equilibration of two octalones at 25 °C			13	87

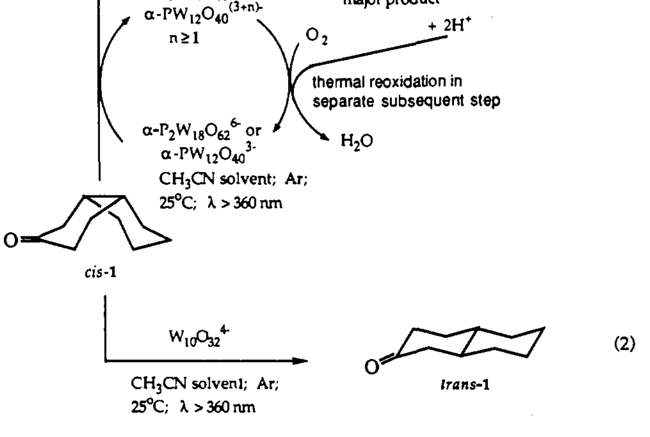
[a] See Experimental Section for the reaction conditions. No products were observed when either the light or the polyoxometalate (when $\lambda > 360$ nm) was excluded. [b] n-Bu_4N^+ salt unless otherwise indicated. [c] Conversion = total moles organic products/moles organic substrate. Reactions **2**–**5** were done under pseudo-first-order conditions (large excess of hydrocarbon substrate and hence low conversions) to simplify analysis of the product distributions. [d] Turnover = moles organic product/moles polyoxometalate catalyst. Product yields = % of total observed organic products. [e] **2** = $\Delta^{9,10}$-2-octalone (remote) and **3** = $\Delta^{1,9}$-2-octalone (conjugated). [f] Na^+ salt used to eliminate photodegradation of Q^+, a competing side reaction which becomes significant at long irradiation times. [g] Reaction **2** was treated with air after one turnover to reoxidize the catalyst and then degassed again (argon) before continuing irradiation and collecting data for reaction **3**. [h] NH_4^+ salt. [i] Bridgehead methyl ketone is the primary other product.

flask which was then placed in an oil bath at 60 °C for 2 h. The solution changed from colorless to amber to brown over the course of the reaction. The progress of the reaction was monitored by GC; after 2 h there was no further change in the appearance of the GC trace of the reaction mixture so the reaction was assumed to be complete. The organic products were analyzed by GC and GC/MS.

Ceric Ion Titration of Reduced Decatungstate. A 0.1 N Ce^{IV} solution composed of 0.1 M $(NH_4)_2Ce^{IV}(NO_3)_6$ and 0.1 M H_2SO_4 was used as the standard in the anaerobic titration of reduced decatungstate. The product solution was obtained by irradiation of 5 mL of an acetonitrile solution consisting of 3 mM $Na_4W_{10}O_{32}$ and 54 mM *cis*-**1** until 81% conversion to *trans*-**1** had been achieved. This represents ~15 turnovers of the polyoxotungstate catalyst based on the formation of *trans*-**1**. The actual titrations were carried out by adding the degassed standard solution of ceric ammonium nitrate by gas-tight syringe to the reaction vessel containing reduced polyoxotungstate and organic oxidation products under an argon atmosphere. The end points were readily detected, and the values obtained were very reproducible.

Results and Discussion

General Characteristics of the Processes. Table I summarizes the products generated from the photochemical reactions of *cis*-2-decalone, *cis*-**1**, with three polyoxotungstates varying greatly in ground- and excited-state redox potentials, $W_{10}O_{32}^{4-}$, α-$PW_{12}O_{40}^{3-}$, and α-$P_2W_{18}O_{62}^{6-}$ (first ground-state reduction potentials: −1.27, −0.670, −0.780 V vs Ag/Ag$^+$(CH$_3$CN), respectively).[3] The tetra-n-butylammonium (Q) salt of α-$PW_{12}O_{40}^{3-}$ or the ammonium salt of α-$P_2W_{18}O_{62}^{6-}$ stoichiometrically photodehydrogenates *cis*-**1** to the monounsaturated ketones (common name = octalones), eq 1 (reactions 2–4, Table I). These reactions are noteworthy not only with respect to the exclusive formation of not only two enones, **2** and **3**, among the many possible dehydrogenation products but also with regard to the higher selectivity for the production of the thermodynamically less stable "remote" olefin, the $\Delta^{9,10}$-2-octalone, **2**. The data given in Table I indicate a substantially higher percentage of remote olefin production from the heteropolyoxotungstate-catalyzed kinetically controlled reactions (up to at least 75% with $PW_{12}O_{40}^{3-}$) than under conditions of acid equilibration of the octalones (~13%). This dehydrogenation process may be rendered catalytic with the aerobic reoxidation of the photoreduced polyoxotungstate in a separate step (eq 1). In stark contrast, the Q or sodium salt of $W_{10}W_{32}^{4-}$ in acetonitrile solution catalyzes the photochemical isomerization (epimerization) of *cis*-2-decalone, *cis*-**1**, to the corresponding trans isomer, *trans*-**1**, with virtually quantitative selectivity even at high conversion of *cis*-**1**, eq 2 (reaction 1, Table I). This epimerization involves exclusive reaction of the unactivated tertiary C–H bonds remote from the ketone group. No other *cis*-**1**-derived products are detected in either eqs 1 or 2 (<3% yield)! The product distributions in eqs 1 and 2 are independent of wavelength as long as the polyoxometalate in each reaction is absorbing effectively all (≥99%) of the incident light.



There are two side reactions in eq 2 that, unlike eq 2, are net redox processes resulting in production of reduced decatungstate and oxidized organic products. Of these processes, the first involves photooxidation of the n-Bu_4N^+ (Q) cation (in the case of the Q salt of decatungstate) producing 1-butene, tributylamine, and $W_{10}O_{32}^{5-}$, and the second involves photooxidation of acetonitrile solvent producing succinonitrile. The first process is a facile,[28] undesirable side reaction under these conditions and lowers the overall product selectivity. As a consequence, the sodium salt of decatungstate was used in the high yield epimerization reactions. The second process is more than an order of magnitude less prevalent than the first (maximum yields of succinonitrile ~2%).

Two lines of evidence argue against the involvement of ketone excited states in either the catalytic epimerization or dehydrogenation reactions whether the ketone excited state is generated by direct absorption of light or from quenching of the polyoxometalate excited state. The first is that organic products typically arising from ketone excited states were not observed in these reactions. Indeed, irradiation ($\lambda > 290$ nm) of a CH$_3$CN solution of the substrate, *cis*-**1**, in the absence of polyoxometalate, led to ketone excited state products derived from Norrish-type α-cleavage reactions[29] (principally aldehydes); no *trans*-**1**, **2**, or **3** were produced whatsoever. Second, the electronic absorption spectra of *cis*-**1** and the polyoxometalates argue against substantial quenching of excited states of the latter by the carbonyl group of the former (Figure 2).

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(28) Yamase, T.; Takabayashi, N.; Kaji, M. *J. Chem. Soc., Dalton Trans.* **1984**, 793.

(29) Recent reviews on organic photochemistry: (a) Coyle, J. D. *Introduction to Organic Photochemistry*; John Wiley and Sons: 1986; Chapter 4. (b) Coxon, J. M.; Halton, B. *Organic Photochemistry*, 2nd ed.; Cambridge University Press: 1987; Chapter 3.

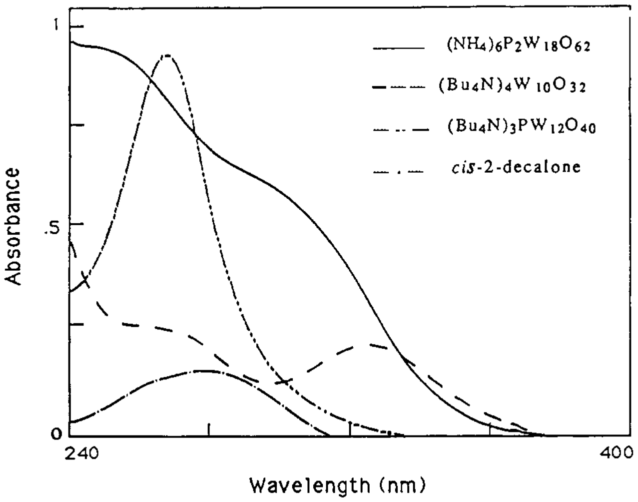

Figure 2. Relative absorbances of the three polyoxotungstates of this study versus that of *cis*-**1** in CH_3CN: [polyoxotungstate] ≈ 1.8×10^{-2} mM and [*cis*-**1**] ≈ 18 mM which represent concentrations ~100 and ~10 times, respectively, less concentrated than in a typical reaction.

Scope and Mechanism of Catalytic Epimerization and Dehydrogenation Reactions. No other known reactions involving unactivated C–H bonds in ketones proceed with such high selectivities as eqs 1 and 2. In defining the scope and mechanism of these processes, several points from the literature and the results of other experiments in this study pertain.

The first point is that most reactivities of *cis*-**1** either documented or predicted based on established reactivities would lead to products derived principally, if not exclusively, from attack at the activated C–H bonds. The carbon atoms α to the carbonyl group are the sites of reaction in alkylation, Michael addition, and all other electrophilic substitution processes under either acidic conditions (likely enol intermediates) or basic conditions (enolate anion intermediates).[30] The high conversion, high selectivity oxidative cleavage of ketones by polyoxometalates of vanadium and molybdenum has recently been reported. These thermal transformations, however, involve attack at the conventional activated α C–H bonds by a mechanism, which, although not yet satisfactorily established, is clearly distinct in important respects to the ones operable in the chemistry here (eqs 1 and 2).[31] In addition, few literature preparations exist for the synthesis of remote enones such as octalone **2**, from the parent conjugated or parent enone. The only systematic production of remote versus conjugated enones involves kinetic protonation of the conjugate anion formed upon deprotonation of the conjugated enones by strong base (KOH in aprotic media, *t*-BuO$^-$ in *t*-BuOH, hydrides, or amide anions).[32] Deconjugation of the α,β-unsaturated compound, **3**, over solid KOH leads to a product mixture enriched in the β,γ-octalone, **2** (3.3:1 ratio of remote to conjugated octalone). To our knowledge, the reactions in eq 1 and Table I represent the first examples of formation of a remote enone such as **2** under neutral conditions.[33]

The second point concerns two known reactions that involve epimerization of saturated hydrocarbon centers, namely, electrophilic reaction by strong Lewis acids and reaction at high temperatures over some hydrogenation catalysts.[34] The former process is of marginal relevance in elucidating the mechanisms of the title transformations (eqs 1 and 2) as the chemoselectivity and regioselectivity exhibited by the products as well as the reaction conditions in eqs 1 and 2 make electrophilic mechanisms very unlikely for these reactions. The problem with the heterogeneous high-temperature isomerization reactions is that the mechanisms for these processes are not understood in their entirety.[34]

Table II. Reactions of *cis*-2-Decalone (*cis*-1) with Di-*tert*-butyl peroxyoxalate (DTBO)[a]

cis-**1**/DTBO/P_{ox}[b] (P_{ox})	convn of *cis*-**1**, %	organic product yield,[c] %			
		trans-**1**	**2**	**3**	acetamides
1:1:0	8	16	13	19	0
1:1:0.02 (PW_{12})	10	0	21	26	~31
1:1:0.02 (W_{10})	12	28	21	21	0
1:1:0.10 (W_{10})	11	19	28	23	0
1:1:0.20 (W_{10})	11	20	20	22	0
1:1:0.60 (W_{10})	9	21	21	40	0

[a] CH_3CN solvent, [*cis*-**1**] = [DTBO] = 0.15 M, argon atmosphere, 2 h at 60 °C, analyzed by GC and GC/MS. No products were detected in the control reactions of *cis*-**1** in the absence of DTBO. [b] P_{ox} = polyoxometalate, PW_{12} = α-$(Bu_4N)_3PW_{12}O_{40}$, W_{10} = $(Bu_4N)_4W_{10}O_{32}$. [c] *trans*-**1** = *trans*-2-decalone, **2** = $\Delta^{9,10}$-2-octalone (remote) and **3** = $\Delta^{1,9}$-2-octalone (conjugated), acetamides = two different *N*-alkyl acetamide derivatives derived from *cis*-**1**; the exact position isomers of these products were not established. Product yield = % of total observed organic products.

The third point concerns the current knowledge regarding the mechanism of C–H bond photooxidation by polyoxometalates.[2-5,9] Considerable evidence from a range of spectroscopic, product distribution, kinetics, and other studies indicate that the initial process involving the organic substrate and the polyoxometalate excited state may well vary with the type of substrate and polyoxometalate. However, this initial process in the case where the substrate is an alkane and the polyoxometalate is a polyoxotungstate is hydrogen atom abstraction by the polyoxometalate excited state. Furthermore, this mechanism appears to be operable for a range of polyoxotungstates varying in structure, protonation state, and redox potential (ground and excited state).[2-5] The great diversity of observed products in polyoxometalate facilitated photochemical transformations of alkanes is dictated by the relative rates of subsequent coupled thermal processes effected principally by the ground-state polyoxometalates: (1) rapid oxidation of radicals leads to carbonium ions, which, in turn, lead to thermodynamic olefins, and, under some conditions, acetamides; (2) radical–radical dismutation, seen under reaction conditions devoid of competitive trapping agents, leads to nonthermodynamic olefins; (3) radical reduction by reduced polyoxometalates with very negative potentials leads to carbanions and thus to carbanion products including methyl ketones.[3-5] Portions of these mechanisms must be considered as reasonable for the reactions in eqs 1 and 2.

Fourth, three other studies substantiate the validity of attack by radicals at remote unactivated C–H bonds in the presence of C–H bonds activated by carbonyl groups.[35,36] Such processes should also be possible, in principle, for triplet carbenes,[37] triplet nitrenes,[38] and other species that have substantial radical character in their ground electronic states. Radical atom abstraction reactivity generally parallels the homolytic bond strengths (bond dissociation energies) of the bonds being cleaved. As the homolytic bond strengths of tertiary aliphatic (i.e., $(CH_3)_3C$–H) and α carbonyl (i.e., acetone) C–H bonds are typically ~91 and ~92 kcal/mol, respectively,[39] one would anticipate competitive initial

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(30) For example, see: House, H. O. *Modern Synthetic Reactions*; Benjamin: Menlo Park, CA, 1972; Chapters 9 and 10.

(31) (a) El Ali, B.; Brégeault, J. M.; Martin, J.; Martin, C. *New J. Chem.* **1989**, *13*, 173. (b) Ali, B. E.; Brégeault, J.-M.; Mercier, J.; Martin, J.; Martin, C.; Convert, O. *J. Chem. Soc., Chem. Commun.* **1989**, 825.

(32) D'Incan, E.; Viout, P. *Tetrahedron* **1984**, *40*, 3421.

(33) Haag, W. O.; Pines, H. *J. Am. Chem. Soc.* **1960**, *82*, 387, and references cited therein.

(34) Eliel, E. L.; Allinger, J. L.; Angyal, S. J.; Morrison, G. A. *Conformation Analysis*; Wiley: New York, 1965; pp 58–62ff, and references cited therein.

(35) Russel, G. A. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Chapter 7.

(36) Relative C–H and O–H bond energies and rates in radical autoxidation of alkanes: Tolman, C. A.; Druliner, J. D.; Nappa, M. J.; Herron, N. reference 11a, Chapter X.

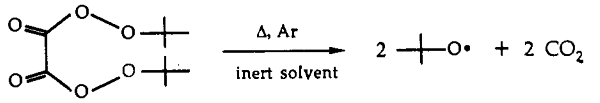
(37) Kirmse, W. *Carbene Chemistry*; 2nd ed.; Academic Press: New York, 1971.

(38) *Nitrenes*; Lwowski, W., Ed.; Interscience: New York, 1970.

(39) Kerr, J. A. *Chem. Rev.* **1966**, *66*, 465.

attack at both types of C–H bonds by radical species. There is evidence that this happens in these three studies based supposedly on radical processes.

The first study was conducted in our laboratory and involves the reactions of *cis*-**1** with a conventional ground-state localized radical, $(CH_3)_3CO^{\bullet}$ (*tert*-butoxyl), generated thermally from di-*tert*-butyl peroxyoxalate (DTBO), eq 3. This radical and the



(3)

method of its generation were carefully chosen as one of the most unequivocal sources of atom abstraction chemistry. Table II gives the kinetic products from this reaction and those from the same reaction in the presence of either α-$PW_{12}O_{40}^{3-}$ or $W_{10}O_{32}^{4-}$. All reactions were carried out to conservative conversions to minimize masking of the inherent kinetic selectivities by subsequent reactions by other radical species generated in situ in the course of the reactions. Even at these conversions, reaction of *cis*-**1** with $(CH_3)_3CO^{\bullet}$ was far less selective than for any of the reactions with *cis*-**1** and polyoxotungstates alone (Table I). Although all three of the principal products observed in the polyoxometalate reactions, *trans*-**1** and the octalones, **2** and **3**, are produced by thermal reaction with $(CH_3)_3CO^{\bullet}$, they were produced in comparable quantities unlike any of the polyoxometalate photochemical reactions. Also in sharp contrast to any of the polyoxometalate reactions, the $(CH_3)_3CO^{\bullet}$ reactions produced over 20 additional organic products detectable by GC, collectively constituting >52% of the organic products. No acetamides, indicative of carbonium ion intermediates, were produced whatsoever in the $(CH_3)_3CO^{\bullet}$ reactions. The affect of polyoxometalate additives on the thermal $(CH_3)_3CO^{\bullet}$ reactions yields more useful mechanistic information. While the addition of the weakly oxidizing complex, $W_{10}O_{32}^{4-}$, has little affect on the product distribution, the addition of a small amount of α-$PW_{12}O_{40}^{3-}$, a polyoxotungstate known to rapidly oxidize aliphatic organic radicals to carbonium ions,[3] completely suppresses production of *trans*-**1** and facilitates production of the acetamides. These results are consistent with some points: (1) α-$PW_{12}O_{40}^{3-}$ but not $W_{10}O_{32}^{4-}$ oxidizes the radicals derived from the ketone substrate under these reaction conditions. (2) Carbonium ions are not involved to a significant extent in the unactivated C–H bond epimerization, and (3) they are involved exclusively in acetamide formation. Given the available data, the most likely product-determining processes in the dehydrogenation of *cis*-**1** to octalones **2** and **3** are oxidation of the organic radical and then rapid deprotonation by the polyoxometalate while still in the solvent cage (vide infra). There is no evidence that reduced polyoxometalate species function as reductants outside the solvent cage in the formation of any products except the methyl ketones.

A second ketone reaction with radical character involves irradiation of $HgBr_2$ in the presence of ketones containing unactivated carbocyclic centers.[40] These reactions effect epimerization in yields as high as 90% but are effectively stoichiometric in $HgBr_2$. Control experiments indicate that neither free bromine atoms, the abstracting agent of choice based on the classical radical literature, nor excited Hg atoms, a viable abstraction agent given the recent radical alkane oxidation work of Crabtree and co-workers,[14h] are apparently the actual hydrogen-abstracting agent in these processes.[40] The third study of pertinence involves epimerization of unactivated tertiary C–H bonds upon irradiation of appropriate hydrocarbons in acetone solution. The authors noted that although epimerization is effected, appreciable dehydrogenation, and sensitizer adduct product formation renders these reactions of marginal preparative interest.[41] The principal mechanistic caveat here is that in hydrogen abstractions by triplet excited-state ketones there is some degree of electron-transfer character in the C–H cleavage transition state.[42]

Table III. Relative Rates of *cis*- to *trans*-Epimerization[a]

substrate	solvent	relative rate[b]	comments
	Values from Comparative Kinetics		
cis-**1**	CH_3CN	1.0	parent system
cis-**1**	CD_3CN	1.0	$k_{CH_3CN}/k_{CD_3CN} = 1.0$
cis-decalin	CH_3CN	0.59	
	Values from Competitive Kinetics		
cis-decalin and	CH_3CN	0.41	$k_H/k_D = 2.0$
cis-decalin-D_{18}[c]		0.21	
cis-**1** and	CH_3CN	1.2	
cis-decalin[d]		0.46	

[a] 150.5 mM substrate and 1.50 mM $(n\text{-}Bu_4N)_4W_{10}O_{32}$, 1000-W Xe lamp, 360-nm cut-off filter, 1-cm cell, Ar atmosphere, 25 °C. Analysis of organic product formation as a *f*(time) monitored by GC. Polyoxometalate absorbing >99% of the incident light. [b] $-d[cis\text{-2-decalone}]/dt = 4.1 \times 10^{-2}$ mM s^{-1}. [c] $[C_{10}D_{18}] = [C_{10}H_{18}] = 75.25$ mM. [d] [Decalin] = [decalone] = 75.25 mM.

The fifth point defining the scope and mechanism of the title processes concerns the relative thermodynamic stabilities of the various isomers of the substrates. Equilibration of the cis and trans isomers of 2-decalone at high temperatures (459–516 K), over a palladium catalyst and over a period of several days, has established that the enthalpy of the trans isomer is 2.5 kcal/mol more negative than that of the cis isomer at these temperatures.[15] This is in agreement with results found by Hueckel through heat of combustion measurements.[43] Similarly, both direct equilibration experiments and heat of combustion measurements have established the enthalpy of *trans*-decalin to be 2.7 kcal/mol more negative than the cis isomer.[44] Therefore, it would appear that the thermodynamic preference of the trans over the cis isomer is approximately equal in both the 2-decalone and the decalin systems. This legitimates to a great extent the use of the decalins, which are commercially available in deuterated form, as models for the 2-decalones in the subsequently described experiments that principally address the epimerization processes.

The sixth area defining scope and mechanism involves rate behavior. The photochemical epimerization of *cis*-**1** by $W_{10}O_{34}^{4-}$ is first order in $W_{10}O_{34}^{4-}$ under optically dilute conditions further ruling out rate-determining oxidation of intermediate radicals to carbonium ions by $W_{10}O_{34}^{4-}$. The primary kinetic isotope effect, $k_{cis\text{-decalin-H}_{12}}/k_{cis\text{-decalin-D}_{12}} = 2.0$, is a value in accord with rate-determining atom abstraction. Substantially different values would be expected if the initial process were either hydride transfer or electron transfer. The reaction is quite fast (~9.8 turnovers per h) and very selective (~100%) for the epimerization process (Table III). Likewise, the analogous reaction with *cis*-decalin is also quite selective, at early reaction times, for the production of *trans*-decalin. However, after several turnovers of decatungstate in the latter reaction, a bridgehead methyl ketone of decalin, a new product consistent with carbanion capture by acetonitrile,[5] is formed (Table I). However, even at low turnovers when the selectivity for *trans*-decalin formation is ~100%, the rate of epimerization is slower for *cis*-decalin (~5.8 turnovers per h) than that for *cis*-**1**. The higher rate of formation of *trans*-**1** relative to that of *trans*-decalin probably derives from an increased stabilization of the tertiary radical in the former case via through-space interactions with the π electrons of the carbonyl group of 2-decalone. This stabilization effect may be enough to lengthen the lifetime of the radical sufficiently to allow the decalone radical to diffuse from the immediate vicinity of the reduced decatungstate

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(40) (a) Gorodetsky, M.; Kogan, D.; Mazur, Y. *J. Am. Chem. Soc.* **1968**, *90*, 6540. (b) Gorodetsky, M.; Mazur, Y. *J. Am. Chem. Soc.* **1970**, *92*, 1094. (c) Kogan, D.; Mazur, Y. *Tetrahedron Lett.* **1971**, 2401.

(41) Salomon, R. G.; Kochi, J. K. *Tetrahedron Lett.* **1973**, *44*, 4387. The specific yields of neither the dehydrogenation nor the sensitizer adduct products were given in this paper.

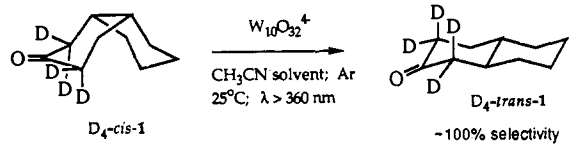
(42) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings: 1978; Chapter 10.

(43) Hueckel, W. *Justus Liebigs Ann. Chem.* **1926**, *451*, 109.

(44) Eliel, E. L.; Allinger, B. L.; Morrison, G. A.; Angyal, S. J. *Conformational Analysis*; Interscience-Wiley: New York, NY 1965; p 231.

and undergo an interconversion to the planar radical conformation from which the trans isomer is thought to be derived, vide infra. In addition, preassociations via hydrogen bonding, ion–dipole, or other interactions between the substrate and the polyoxometalate prior to C–H cleavage would be more facile for the decalone substrates than for the decalins. Indeed, analysis of the competitive rates of formation of the trans isomers from 2-decalone and decalin demonstrated that *cis*-**1** was more reactive toward excited-state decatungstate than *cis*-decalin, (Table III).

The seventh area involved isotope labeling studies. In the first experiment, 1,1,3,3-tetradeuterio-*cis*-2-decalone (*cis*-**1** with all activated α positions deuterated) was prepared, purified, and photochemically epimerized by $W_{10}O_{34}^{4-}$ in CH_3CN under the regular conditions (Table I). The exclusive product was 1,1,3,3-tetradeuterio-*trans*-2-decalone (eq 4). The complete retention of the deuterium label established that (1) epimerization resulted from exclusive reaction at the tertiary carbon atom(s) (C9 or C10) remote from the carbonyl group, (2) abstraction of a hydrogen atom α to the carbonyl group with subsequent oxidation of the resulting radical followed by rearrangement, although defensive as a possible mechanism, is not operable here, and (3) an olefinic intermediate is highly unlikely.

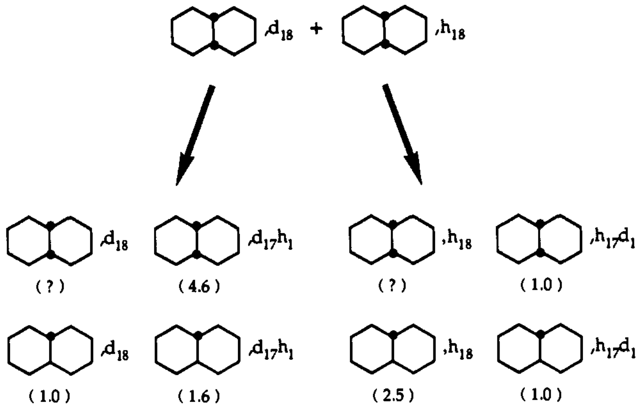


(4)

In a second labeling experiment, the loss of deuterium isotope from *cis*-decalin-D_{18} in irradiated CH_3CN solutions of decatungstate (Na^+ salt) was analyzed. At 4% conversion (four turnovers) to the trans isomer, the loss of label was significant, and the hydrogen atom incorporation was as follows: *cis*-decalin 90% H_0, 10% H_1 and *trans*-decalin 9% H_0, 85% H_1, and 6% H_2. The results of this experiment confirmed three aspects of this transformation: (1) hydrogen atom abstraction from the solvent by the decalyl radical can be significant, (2) the cis tertiary radical may lead to cis as well as trans product, and (3) some of the decalin molecules live long enough to undergo several encounters with reactive species, leading to loss of deuterium label at both tertiary carbons. Interestingly, the analogous experiment performed with protiated decalin (or *cis*-**1**) in *deuterated* acetonitrile did not lead to any observable deuterium incorporation into the bicyclic molecule as analyzed by GC/MS. Importantly recall that there was no solvent isotope effect found in the relative rate of epimerization of protiated *cis*-**1** or *cis*-decalin (Table III).

For completeness, a third isotope labeling experiment was conducted. This isotope crossover experiment was devised to address the possibility of interaction of intermediate decalyl radicals with molecules of decalin. Such radical–molecule reactions can be quite significant in determining products in conventional radical reactions and are often ignored. Such reactions were not addressed in the two radical-like C–H abstraction reactions involving ketones and related molecules cited above: the $HgBr_2$/light system of Y. Mazur and co-workers[40] and the acetone/light system of J. Kochi and co-workers.[41] Irradiation of a CD_3CN solution consisting of decatungstate and a 50/50 molar mixture of *cis*-decalin-D_{18} and *cis*-decalin-H_{18} produced some interesting results (Scheme I). The numbers in parentheses represent the number of turnovers of the decatungstate catalyst. Reaction conditions and controls are given in the Experimental Section. There was a significant amount of isotope scrambling between the two isotopomers indicating hydrogen (deuterium) atom transfer to the decalyl radical from either (1) another molecule of decalin or (2) the inorganic species $H(D)W_{10}O_{32}^{4-}$ (deuterium transfer from the solvent was ruled out as a major process based on control experiments which indicated minimal deuterium incorporation into protiated *cis*-**1** or *cis*-decalin upon epimerization in CD_3CN and the solvent kinetic isotope effect of 1.0). Analysis of the products by GC/MS indicated greater than 50% of the isotope loss was on a secondary carbon. This is in accord with the statistical probability of a freely diffusing, nonselective decalyl radical abstracting a hydrogen atom from one of the eight possible secondary carbons versus the two possible tertiary carbons in the decalin molecule.[45] The earlier observation that decalyl radicals may incorporate hydrogen from a solvent donor such as CH_3CN also implies that a small percentage of the caged radicals escape the solvent cage. It should be noted that the epimerization of *cis*-decalin-D_{18} in CH_3CN leads to a loss of isotope at primarily the tertiary carbon atoms, supporting the initial generation of a tertiary versus a secondary decalyl radical. Therefore, the dominant if not the only way to induce isotope scrambling at a secondary carbon of decalin is by interaction of a tertiary decalyl radical with another molecule of decalin. Subsequent reaction of the secondary radical with $H(D)W_{10}O_{32}^{4-}$ would produce *nonepimerized* decalin (most likely *cis*-decalin since it is in higher concentration at initial times) and $W_{10}O_{32}^{4-}$, respectively. Moreover, energetics would favor the decalyl (tertiary or secondary) radical abstracting a hydrogen atom from the protiated decalin versus a deuterium atom from deuterated decalin. This phenomenon, coupled with the seemingly higher barrier to ring inversion of the fully deuterated *cis*-decalin (see below), may explain the unusually high production of *cis*-decalin-$D_{17}H_1$. However, hydrogen atom abstraction from $HW_{10}O_{32}^{4-}$ must be competitive since, remarkably, no olefins (resulting from dehydrogenation of decalin) or succinonitrile (resulting from coupling of acetonitrile radicals) are produced in the observed organic products. Therefore, both mechanisms must be operable to some extent.

Scheme I. Isotope Crossover Experiment



Typically, stereoisomeric compounds give rise to identical product mixtures from either isomer. In contrast, Bartlett and co-workers have studied the thermal decomposition (50 °C, anaerobic, cumene solvent) of 9-carbo-*tert*-butylperoxydecalin which yields the tertiary 9-decalyl and the *tert*-butoxy radicals.[46] The fate of the radical includes hydrogen atom transfer from the solvent to generate the cis and trans isomers of decalin and hydrogen atom transfer to a *tert*-butoxy radical to produce the tetra- and trisubstituted olefins of decalin and *tert*-butyl alcohol. The relative quantities of these decomposition products is identical from either perester. The initial 9-decalyl radicals have a short stereochemical "memory" of their origin (*cis*- versus *trans*-perester). However, it was demonstrated in this study that the ratio of cis to trans product (9-decalyl hydroperoxide) from the decomposition of the *cis*-perester could be slightly increased by increasing the pressure of O_2. It should be noted that hydrogen atom transfer to decalyl radicals from various hydrocarbon solvents or *p*-thiocresols was not fast enough to trap the initial radicals, although the bulkiness of the solvent did influence the *cis*-decalin/*trans*-decalin ratio. Several conclusions were drawn from this experiment, most notably, that initial nonplanar radicals, similar to the conformation of the parent perester, are quickly converted to a planar radical from which cis and trans products arise (Scheme

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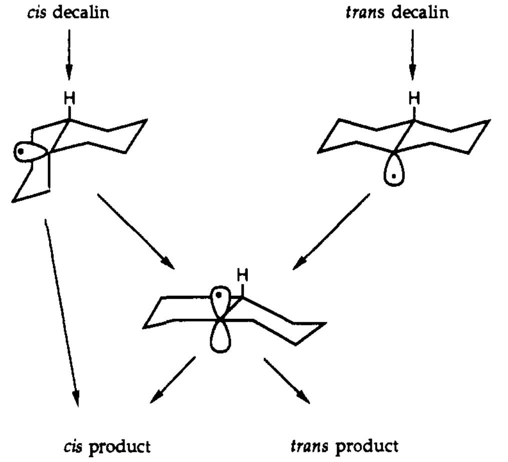
(45) A referee pointed out that decalyl radical is quite hindered, and thus one would expect less secondary H abstraction from decalin with a less bulky radical having the same intrinsic reactivity.

Scheme II. Conformational Interconversion of *cis*- and *trans*-Decalyl Radicals via a Common Planar Radical Intermediate[46]



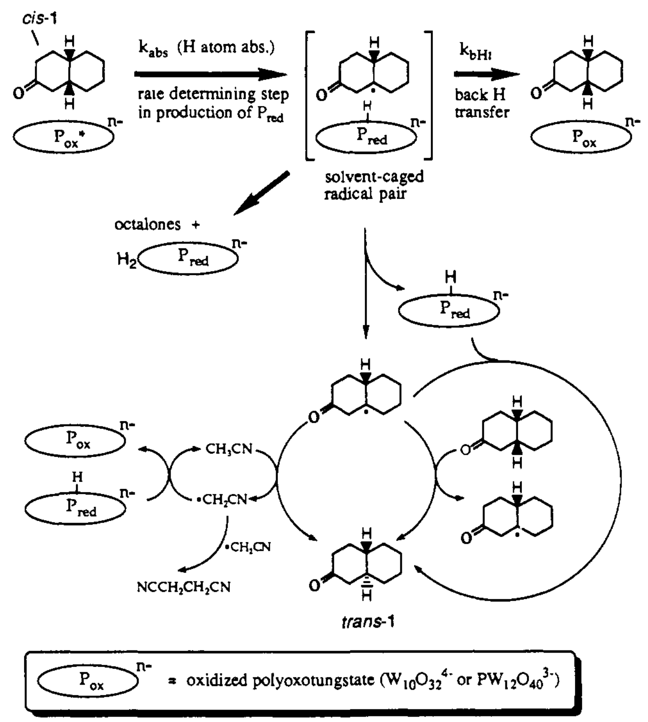
II). The activation parameters for the formation of the decalyl radical from either perester are similar; differences in energy of the transition state must account for the increased cis product at high pressures of O_2. Indeed, a slight flexing of the trans structure enables this species to readily form the planar radical, while the analogous *cis*-9-decalyl radical must undergo an inversion of one of the chair-form rings to adopt the planar conformation.

Anet and co-workers have observed that deuterium substitution can cause a significant shift in the equilibrium between the rapidly equilibrating conformers of a compound such as *cis*-decalin.[47] This "steric isotope effect" results primarily from changes in the vibrational frequencies of the molecule.[48] The C–D vibration has a lower zero point energy and thus is raised less in energy relative to that of the corresponding C–H vibration. These results, coupled with those of Bartlett[46] and those observed in the isotope crossover experiment described above, allow the following conclusion to be made concerning the relative rates of conversion of the deuterated and protiated *cis*-9-decalyl radical to the planar form. On transforming from the cis to the planar radical, some relief from steric repulsion should be realized. The H(D)···H(D) interactions are greater in the protiated species such that this radical would benefit the most on converting to the planar form. In other words, the deuterated decalyl radical has a higher barrier to conversion to the planar conformer than does the protiated analogue. This may serve as another explanation of the unusually high percentage of deuterium label lost from *cis*-decalin-d_{18} in the isotope crossover experiment. With the relatively high barrier for conversion to the planar radical, much of the deuterated species stays in the cis conformation long enough to react with a hydrogen atom source.

Conclusions

The exemplary moderately oxidizing polyoxotungstates, α-$PW_{12}O_{40}^{3-}$ and α-$P_{12}W_{18}O_{62}^{6-}$, facilitate the homogeneous selective photochemical production of the enones (octalones), **2** and **3**, with the remote or nonthermodynamic isomer, **2**, predominating. In dramatic contrast, the exemplary weakly oxidizing polyoxotungstate, $W_{10}O_{32}^{4-}$, catalyzes epimerization of the remote and unactivated tertiary C–H bond in high selectivity at high conversion of substrate. The epimerization process takes place without perturbing the activated C–H bonds α to the carbonyl group at all. The former reactions produce no epimer, *trans*-**1**, while the latter reactions produce no dehydrogenation products (octalones **2** and **3**). These selectivities exhibited in both types of reactions are novel.

Scheme III. Principle Mechanistic Features[a]



Based on the experimental evidence, which lead to the observed organic products (*trans*-**1** and octalones) from the reaction of *cis*-**1** with the excited states of $W_{10}O_{32}^{4-}$ or $PW_{12}O_{40}^{3-}$, respectively. Major paths with heavy arrows.

Scheme III summarizes several of the mechanistic conclusions regarding these reactions that follow from all the data. The major paths are designated with heavy arrows. Although the rate law does not distinguish between several possibilities for the initial rate-determining C–H cleavage process, substantial data allow us to rule out several mechanisms for this step. The kinetic selectivities manifested in the product distributions obtained over a range of reaction conditions (both chemoselectivities and regioselectivities represented in these products), the isotope effects, labeling experiments, and data from other reactions rule out deprotonation and hydride abstraction for this first step. They make electron transfer very unlikely. An initial electron transfer cannot be unequivocally ruled out, however, as there are no thoroughly investigated bona fide examples of ketone oxidation by inorganic species that proceed by this mechanism, and thus key bases of comparison are lacking. All data are consistent, however, with initial hydrogen abstraction forming a solvent-caged radical pair. This initial step is rate-determining but not product determining. Epimerization takes place predominantly by a thermal back hydrogen transfer.

On the basis of the various polyoxotungstate redox potentials and all the reactions of *cis*-**1**, including the labeling studies, with excited polyoxotungstates and various radical species, it is very unlikely that epimerization involves radical oxidation at any point along the reaction coordinate. The mechanism for generation of the octalones most consistent with all the data involves oxidation and subsequent deprotonation in the initially generated radical pair. Not surprisingly, the complexes that facilitate the selective generation of the octalones are those that are not only readily reduced (quite positive ground-state potentials) but also readily reduced by two electrons and readily doubly protonated (e.g., α-$PW_{12}O_{40}^{3-}$ and α-$P_2W_{18}O_{62}^{6-}$). The preferential generation of the nonthermodynamic nonconjugated octalone regioisomer, **2**, most likely reflects kinetic control of the deprotonation of the carbonium ion in the cage. Production of the acetamide byproducts appear to arise principally by capture of intermediate freely

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(46) Bartlett, P. D.; Pincock, R. E.; Rolston, J. H.; Schindel, W. G.; Singer, L. A. *J. Am. Chem. Soc.* **1965**, *87*, 2590.

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(48) Deuterated species, such as CD_2, behave as though they are "smaller" than their protiated analogues. This may be viewed more accurately as a perturbation of the potential surface for the C–H(D) vibration by the H(D)···H(D) interactions. This perturbation results in an increase in the vibrational frequency and hence the zero point energy of the C–H(D) of the cisoid species.[47]

diffusing carbonium ions by acetonitrile solvent followed by hydrolysis (the Ritter reaction starting from an unactivated C–H bond). The other minor byproducts including those derived from photooxidation of the tetra-*n*-butylammonium cations and the acetonitrile solvent as well as a small percentage of the epimerization product arise from freely diffusing intermediate radicals.

Not shown in Scheme III are the processes involving reoxidation of the reduced [or photoreduced] polyoxotungstates. Reoxidation can be facilitated by (1) reaction with O_2 and protons, evolved from the dehydrogenation reactions, to form H_2O, (2) reaction solely with protons to form H_2, or (3) in some circumstances, by reaction with other oxidants. These processes, although peripheral to the novel chemistry in the complex redox processes which we have elaborated in this paper, are nevertheless significant for they limit the overall rate of catalytic turnover.

The substantial degree to which the first and second redox potentials, protonation states, and other characteristics of the polyoxometalates that affect the relative rates of the key processes in Scheme III and analogous processes in other reactions can be systematically altered through rational syntheses of polyoxometalates suggests potential applications of these complex inorganic molecules to transformations of organic materials in synthesis and various technologies.

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Registry No. *cis*-**1**, 1579-21-1; *trans*-**1**, 16021-08-2; **2**, 13837-12-2; **3**, 1196-55-0; DTBO, 1876-22-8; $Q_3PW_{12}O_{40}$, 53749-37-4; $(NH_4)_5P_2W_{18}O_{62}$, 110294-54-7; $Q_4W_{10}O_{32}$, 68109-03-5; $Na_4W_{10}O_{32}$, 126752-51-0; D_2, 7782-39-0; *cis*-decalin, 493-01-6; *trans*-decalin, 493-02-7.

Influence of Geometry on the Emitting Properties of 2,3-Naphthalimides

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Abstract: The luminescence properties of 2,3-naphthalimides have been studied using picosecond and nanosecond spectroscopies. In acetonitrile solution *N*-phenyl-2,3-naphthalimide (**3**) is found to emit dual fluorescence with emission maxima at 385 and 490 nm, respectively. The short-wavelength emission corresponds to the known fluorescence of the naphthalimides and is demonstrated for **3** to originate from a molecular conformation in which the phenyl substituent and the naphthalimide skeleton are orthogonal to each other. The long-wavelength emission is assumed to originate from a singlet excited state formed by a ca. 90° rotation of the phenyl group so that the two moieties are coplanar. Only a small dipole moment change is found between this excited state and the ground state. Only short-wavelength emission is observed with a lifetime in the nanosecond range as in the case of **1** and **2** when phenyl rotation is blocked with a bulky ortho *tert*-butyl group (compound **4**). Increasing the viscosity of a glycerol/ethanol medium enhances both the efficiency and the lifetime of the short-wavelength emission of **3**. It appears that at 77 K the emission originates directly from the Franck–Condon state. At room temperature, the other two emitting species are shown to arise from the Franck–Condon state by competitive intramolecular geometrical relaxation processes. Structures **5** and **6** are tentatively put forward to explain the formation of naphthazepinedione **8** by a $2\pi + 2\pi$ photochemical cycloaddition reaction.

1. Introduction

The photochemistry of imides has received much attention during the last two decades,[1-4] especially their inter- and intramolecular photoreduction reactions[5-10] and their photoadditions to alkenes which leads to oxetanes, thus illustrating the reactivity of their carbonyl n,π* state. In addition, phthalimides and naphthalimides show typical photoreactivity with olefins leading to dihydrobenzazepinedione-type molecules[11-17] following insertion of the alkene into the N–C bond of the imide function. Photoreductions, involving the abstraction of an allylic hydrogen atom of the olefin followed by the coupling of the resulting two radicals, have been shown[17] to depend upon the redox potential of the alkene and to arise from photoinduced electron transfer. On the other hand, benzazepinedione formation has been postulated to occur through a $2\sigma + 2\pi$ concerted cycloaddition.[13,14] Extension of the π conjugation using naphthalimides has shown a fundamental difference in reactivity depending on the position of the imide moiety in the molecule.[5,11,17] Thus, irradiation of 2,3-naphthalimides in the presence of olefins in methanol solution yields oxetanes, naphthazepinedione, and solvent-trapped adducts,[5,11] while the 1,8-naphthalimides give only tetracyclic imides

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