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CATALYTIC ACTIVITY IN THE REVERSION OF AN ENERGY STORING VALENCE PHOTOISOMERIZATION

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Valence photoisomerization of <u>endo</u>-tricyclo(5.2.1.0^{2,6})-deca-4,8-diene-3-one gives a cage structure in quantitative chemical yield and with a quantum efficiency of 0.4 (350 nm). The efficiency of storage of electronic excitation energy as chemical potential energy is 8%. The photoisomer is thermally quite stable but can be reverted to dienone in the presence of Rh(I) complexes at 140-180°. Catalyst instability prohibits significant recycling of the system. Rate studies bear significantly on the mechanism of Rh(I) catalyzed valence isomerizations.

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CATALYTIC ACTIVITY IN THE REVERSION OF AN ENERGY STORING VALENCE PHOTOISOMERIZATION

by

G. Jones, II and B.R. Ramachandran

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ABSTRACT

The quantum yield of valence photoisomerization of *endo*-tricyclo($5.2.1.0^{2,6}$)-deca-4,8-diene-3-one (1) to cage isomer 2 is 0.35 - 0.40 in several solvent. Upon irradiation at 330 - 380 nm the chemical yield of isomer 2 is essentially quantitative. Cage isomer 2 is thermally stable to 295° where slow decomposition occurs to give a mixture of products. Upon treatment with catalytic amounts of complexes of Rh(I) at 140 - 180°, 2 may be reverted to 1 in high yield. Catalysis kinetics are well behaved and first order in Rh(I) complex and substrate 2 during the initial stages of isomerization, after which the rate of reaction slows precipitously due to catalyst instability. Initial isomerization rates establish relative catalytic activity: $Rh_2(CO)_4Cl_2 > Rh_2(NOR)_2Cl_2 \sim Rh(PPh_3)_3Cl$ (NOR = norbornadiene). The slow rate of catalyzed isomerization for 2 is striking in comparison with that for quadricyclenes, hexamethylprismane, cubanes, and homocubanes especially in view of the exothermicities for these reactions which are similarly large. A crude ordering of substrate activity (40°) obtains: quadricyclenes $\sim$ prismane $\sim$ cubanes > homocubanes > 2 (a 1,8,4,7-bishomocubane). Relative rates are rationalized on the basis of nucleophilic character in the organic substrate and electrophilic character in the Rh(I) complex. The strained cage systems then depend for their reactivity modestly on substituent electronics and steric factors and more on the degree of local bond angle deformation. The system $1 \rightarrow 2$ (ΔH = 16 kcal/mol) stores 8% of absorbed electronic excitation energy as chemical potential energy.

Although the capability to produce thermodynamically unstable molecules in organic photochemical reactions has been so widely exploited to be even taken for granted, a systematic quantitative assessment of the extent to which electronic excitation energy can be converted to chemical potential energy has not been made. Such a survey that might extend over many classes of photochemical reaction has direct relevance to possible photochemical conversion of solar energy and gains theoretical importance upon recognition of the intimacy of ground and excited state potential surfaces for highly endoergic photoreactions which are potentially thermally reversible. Important among criteria[1] for an efficient energy storage system employing an interconversion of isomers A and B

$$A \underset{\Delta}{\overset{h\nu}{\rightleftarrows}} B$$

are (1) system photochromism; *i.e.*, a change in light absorption properties during photoreaction such that for certain wavelengths of excitation a photostationary state rich in B is assured; (2) a large positive ground state enthalpy A → B; (3) a quantum efficiency for A → B approaching unity; (4) a kinetic stability for B which matches the objective of energy storage (*e.g.*, synthesis or energy conversion, normally significant stability for B somewhat above room temperature). We assess here the excitation energy storage capability of one system, **1** → **2**, with focus on the mode of retrieval of latent heat in the thermal back reaction which is catalyzed by transition metal complexes and for which several important structure-reactivity relationships are apparent.

RESULTS AND DISCUSSION

Dienone 1 was prepared and photolyzed as previously reported[2] and cage isomer 2 was obtained on a preparative scale as sole product in good yield. Irradiation of 1, which displays an n,π* maximum at 340 nm, using a Rayonet chamber reactor and RUL 3500 lamps (330 - 380 nm), was followed as a function of time. Monitoring of absorbance of 1 and 2 revealed an isosbestic point at 310 nm, and glc analysis of photolysis mixtures confirmed that the photoisomerization was remarkably clean. With 330 - 380 nm excitation the "photostationary"[3] mixture consisted of > 99% isomer 2.[4] The material balance during irradiation of 1 vs. a glc internal standard was > 98%. Quantum yields for photoisomerization in several solvents using valerophenone actinometry,[5] are shown in Table I. The progress of photoisomerization at constant lamp intensity is shown in Figure 1, indicating that the yield is undiminished as a function of time to very high conversion for moderately concentrated samples.

Table I. Quantum Yields for photoisomerization 1 → 2[a]

Solvent	Quantum yield[b]
acetonitrile	0.37 ± 0.02
benzene	0.38 ± 0.02
diglyme	0.40 ± 0.02

[a] 0.07 M samples, 330 - 380 nm, 30 ± 1°C. [b] Valerophenone actinometer (ϕ = 0.33, ref 5).

Figure 1. Irradiation mixtures as a function of time starting with 1 (lower graph) and 2 (upper graph), 1.7 M in diglyme at constant lamp intensity (330 - 380 nm).

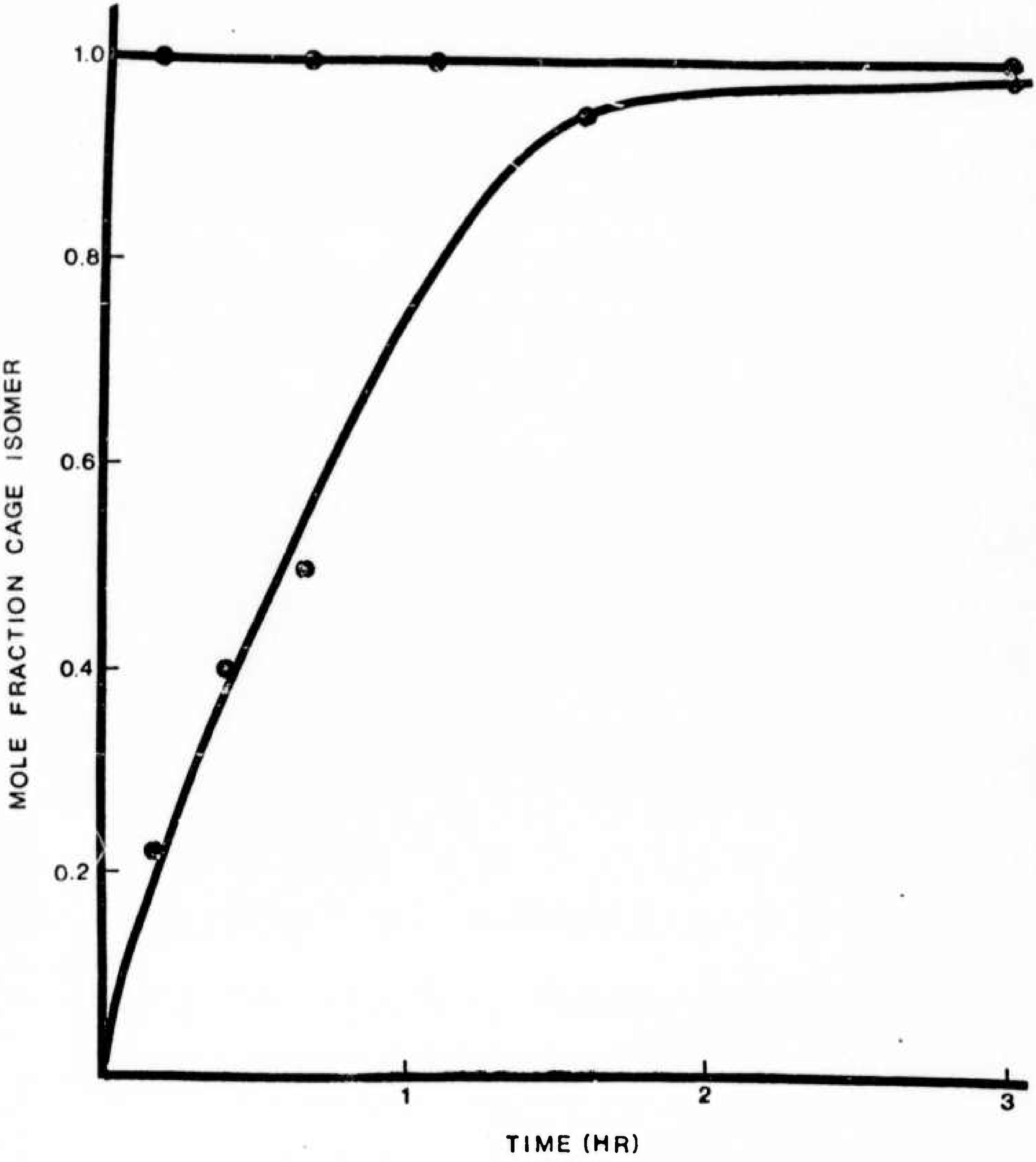

Figure 1

The assessment of energy storage capability follows with the simple calculation of "Q value", as suggested by Calvert:[1a]

$$Q = \frac{(\phi)(\Delta F)(100)}{E(h\nu)_{avg}}$$

where ϕ, ΔF, and $E(h\nu)_{avg}$ are quantum yield, the ground state free energy change (kcal/mol) for the photoreaction, and the average energy/photon absorbed (kcal/Einstein), respectively. We may confine our attention to the amount of energy stored only as latent, recoverable heat and replace ΔF with ΔH (**2** → **1**), or -16.4 kcal/mol determined by combustion calorimetry.[6] With $\phi = 0.4$ and $E(h\nu)_{avg} = 80$ kcal/Einstein (350 nm), Q = 8%. Thus, storage of electronic excitation energy as chemical potential energy in the **1**,**2** couple is appreciable (particularly in view of the relatively high excitation energy involved) and compares favorably with the capabilities noted for inorganic systems[1a] (Q generally < 10%).

Sealed-tube pyrolysis of **2** in diphenyl ether (DPE) at 295° led to slow decomposition. The production of some tarry material was apparent, and nmr analysis showed that a mixture of products was obtained. This mixture was not identified but presumed to be akin to the products (including **1**) reported[7] for the flow pyrolysis of **2** at very high temperatures. The rate of decomposition of **2** was estimated ($k = 1 \times 10^{-4}$ sec^{-1}).

The thermal isomerization of **2** → **1** could be carried out more respectably in the presence of transition metal catalysts at moderately high temperatures. For example, 5 mol% of $Rh_2(CO)_4Cl_2$ affected virtually quantitative reversion to **1** in diglyme-d_{14} (DG) or diphenylether (DPE) at 140°. While nmr analysis indicated a > 95% organic material balance, the separation of a gray-black metallic material (unidentified) during isomerization suggested catalyst instability. In a control experiment, $Rh_2(CO)_2Cl_2$ slowly deposited a gray-black substance on heating in solvents alone, at 140°. At high catalyst concentrations (~5 mol%) the rate of isomerization could be followed (nmr) over two half-lives and shown to be first order in substrate. At low catalyst concentrations (~0.5 mol%) first order substrate disappearance plots were linear initially but deviated at about one half-life, with catalyzed isomerization finally coming to an end before completion. Under these circumstances the **1**,**2** pair could not be "cycled" through sequential photolysis-pyrolysis steps. Attempts to bring about isomerization using $Pd(PhCN)_2Cl_2$, $AgClO_4$, Rh/C, Pd/C, K_2PtCl_4, $CuSO_4$, and p-toluenesulfonic acid under a variety of heterogeneous and homogeneous conditions at elevated temperatures were unsuccessful.

The catalysts which uniformly brought about isomerization **2** → **1** were the complexes of Rh(I). A ranking of these catalysts was attempted using initial disappearance rates for **2**. First order plots were quite good at 10 - 40% conversion, giving rate constants which along with initial catalyst concentrations produced second order rate constants as shown in Table II. That a classical second order catalytic rate law was obeyed is supported by experiments in which initial catalyst and substrate concentrations were varied. Thus, plots of the first order rate constants for disappearance of **2** *vs*. $[Rh_2(CO)_4Cl_2]$ (10 fold range) was linear, and in experiments with $Rh_2(NOR)_2Cl_2$ (NOR = norbornadiene) a nearly three-fold change in substrate concentration did not affect the calculated first and second order rate coefficients. Apparently the catalyst destruction which mitigated high conversion and cycling experiments was slow enough at the required temperatures (perhaps requiring an induction period) that the initial portion of the catalyzed isomerization was kinetically well behaved. Within the range of substrate concentration used, we did not observe Michaelis-Menten type kinetic behavior (denoting a rapid preequilibrium of substrate and catalyst) which has been documented in several transition metal catalyzed valence isomeri-

Table II. Kinetic Data[a] for the Catalyzed Isomerization 2 → 1.

Substrate Conc. (M)	Catalyst (Conc., M)	Solvent	Temp (°C)	k ($M^{-1}sec^{-1}$)
1.7	$Rh_2(CO)_4Cl_2$ (0.02 - 0.21)	DG	140	1.0×10^{-2}[b]
1.3	$Rh_2(CO)_4Cl_2$ (0.005)	DG	180	4.9×10^{-1}
1.7	$Rh_2(CO)_4Cl_2$ (0.007)	DPE	180	1.0×10^{-1}
1.0 - 2.6	$Rh_2(NOR)_2Cl_2$ (0.061)	DG	180	1.8×10^{-3}
1.7	$Rh(PPh)_3Cl$ (0.007)	DPE	180	3.0×10^{-3}

[a] Obtained from pseudo first order rates at low conversion. Estimated rate constant error = ± 20%. [b] Obtained graphically from plot of first order rate constant for appearance of 1 and vs. catalyst concentration.

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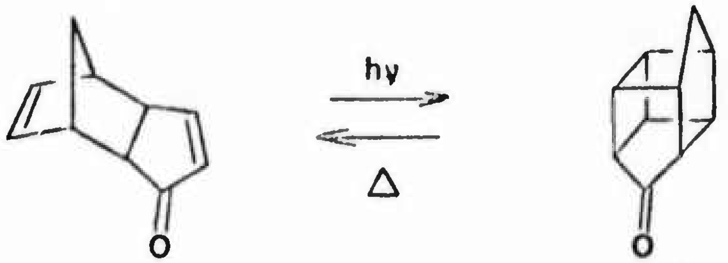
zation systems.[8]

The extreme reluctance of 2 to isomerize is somewhat surprising in view of the facile catalyzed ring openings of quadricyclenes (3,4) to norbornadienes, hexamethylprismane (5) to hexamethyldewarbenzene, and cubanes (6,7) and homocubanes (8) to their tricyclic diene isomers.[9] In order to make a semiquantitative comparison of the organic substrates we have calculated relative rates for valence isomerization ctalyzed by $Rh_2(NOR)_2Cl_2$ at 40°, a temperature for which rate data for 6 - 8 were available (Table III). For 2 - 5 the rates at 40° were obtained by extrapolation from data at other temperatures. Since activation parameters for these systems are not available, we have used for the extrapolation a frequency factor (log A = 7) similar to those reported for relevant



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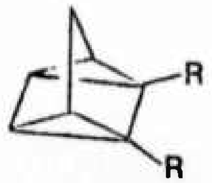

3, R = H
4, R = CO_2Me

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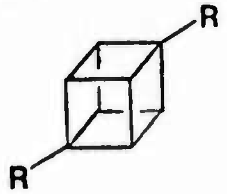
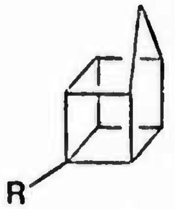


6, R = H
7, R = CO_2Me



8, R = H
9, R = CO_2Me

valence isomerizations catalyzed by Rh(I) complexes.[14] To relate the reactivities in terms of activation energy differences alone is admittedly an oversimplification, but the extrapolations in rate are not enormous (except for 2) and our conclusions at any rate will largely depend on order of magnitude relative reactivities.

For comparison rate and heat of reaction data for the *uncatalyzed* pyrolysis of 2 - 6 are found in Table IV. Relative rates for isomerization of 3 - 4 at 295° (where 2 underwent measureable decomposition, *vide supra*) were computed by extrapolation of rate data at lower temperatures, using the activation parameters reported. The enthalpies of valence isomerization were derived from heat of combustion or differential scanning calorimetric measurements.

Several structure-reactivity relationships are striking. (1) Relative reactivities in metal catalyzed and uncatalyzed (presumably homogeneous) pyrolyses, where comparison can be made, bear no resemblance. Neither the spread nor order of rate constants match. One concludes that rates for catalyzed isomerization do not depend on homolytic bond dissociation energies.[18] (2) A rate retardation of about two orders of magnitude[19] results from substitution by the $-CO_2Me$. (Compare 3 and 4, 6 and 7, and relate the rate for 8 to the fact that 9 undergoes decomposition only at 150°.[9d]) This deceleration has been noted previously for the quadricyclene[14a] and cubane[13] series and has been rationalized (with particular reference to the homocubane series) in terms of electronic and steric factors.[9d] (3) Comparison among ring types reveals the relative reactivity order, quadricyclenes $\sim$ prismane $\sim$ cubanes > homocubanes > 2 (a 1,8,4,7-bishomocubane) (compare 3, 5, 6 with 8 and in the carbonyl-substituted series, 4, 7, with 9 and 2). Ring strain release might have been important, as suggested by early theories concerning transition metal catalyzed valence isomerization.[20] However, the measured or calculated enthalpies of isomerization (Table IV) for 2 - 6 are simi-

Table III. **Comparative Kinetic Data for Valence Isomerization of Cage Compounds Catalyzed by $Rh_2(NOR)_2Cl_2$**

Cage Substrate	$k_{observed}$ ($M^{-1}sec^{-1}$)	Temp (°C)	Solvent	Reference	k (40°)[a] ($M^{-1}sec^{-1}$)	k_{rel} (40°)
2	1.8×10^{-3}	(180)	DG	This work	3.2×10^{-8}	1
3	5.5×10^{-2}	(-26)	$CDCl_3$	10	3.2	1×10^{8}
4	2.8×10^{-2}	(60)	$CDCl_3$	11	7.9×10^{-3}	3×10^{5}
5	9.7×10^{-3}	(-30)[b]	$CHCl_3$	12	1.0	3×10^{7}
6	14	(40)	$CDCl_3$	13	14	4×10^{8}
7	1.1×10^{-1}	(40)	$CDCl_3$	13	0.11	3×10^{6}
8	1.4×10^{-2}	(40)	C_6H_6	9a	0.014	4×10^{5}

[a] Except for **6** - **8** extrapolated to 40°, using the Arrhenius equation and log A = 7. [b] Calculated from the reported half-life.

Table IV. Relative Rates and Heats of Isomerization (Uncatalyzed Pyrolysis)

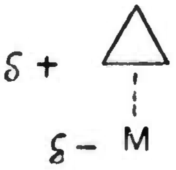
Starting Material	Pyrolysis Temp (°C)	Reference	k (295°)[a] (sec^{-1})	k_{rel} (295°)	ΔH (kcal/mol)
2	295	This work	(1.0×10^{-4})[b]	1	-16.0[c]
3	150	15	0.10	10^3	-21.2[d]
4	150	15	7.9	10^5	-18.5[d]
5	105	12	190	10^6	-31.7[e]
6					-16.7[f]

[a] Extrapolated from lower temperatures, using activation parameters reported, ref 12 and 15. [b] Rate constant for total decomposition (product includes 1, see text and ref 7. [c] From heats of combustion, ref 6. [d] From DSC measurements, ref 15. [e] From DSC measurements, ref 16. [f] From MINDO/3 calculations of heats of formation, ref 17.

lar, all indicating large exothermicities. In addition the bond-switch rearrangements of cubane derivatives catalyzed by silver ion likewise show little dependence on incremental strain effects.[21] The dramatic disregard for stabilizing influences in product suggests at one extreme a very early transition state involving monodentate edgewise coordination by rhodium which leads an overall concerted decomposition (*e.g.*, 10 and 11 for coordination at cyclopropane and cyclobutane rings, respectively), and at the other extreme formation of an intermediate (*e.g.*, 12 - 15 for interaction with a cyclobutane ring) which is rate determining in consecutive reactions leading to isomerization or which controls the position of a preequilibrium[8] between substrate and catalyst.

Although *overall* molecular strain (and its potential release) appears not a rate determining factor, the degree and kind of *local* bond deformation must influence the reactivity order. Thus, as models show that the bond angle requirements become less severe in the series, cubane > homocubane > bishomocubane (the cyclobutane rings begin to pucker increasingly), so do the relative rates of rhodium catalyzed decomposition vary for **6**, **8**, and **2** (or compare **7** and **2** with the low reactivity reported for **9**[9d]) with a rate retardation of $\sim 10^3$ per replacement of a zero carbon bridge with a one carbon bridge. This dependence on the degree of local bond angle deformation (and on the number of deformed bonds) is no doubt related to the ability of the strained ring to act as a base (**12**),[9e,22] an oxidizing agent (**13**),[13,23] a nucleophile (**14**),[24] or as an electron donor (**15**),[22] types of interaction of strained sigma bonds with metals which have been considered. The significance of pi character for strained sigma bonds has been considered important since the earliest report[10] of catalyzed valence isomerization, and this feature is manifest in other ways. Thus, for quadricyclene edge association in solution phenomena is apparent in ir and nmr studies,[25] high p character for sigma bonds has been supported by ^{13}C coupling constant data,[26] and low ionization potentials (7.4[27] and 8.3[28] eV) have been reported. Similarly, cubane has a pronounced tendency to act as a nucleophile,[29] exhibits pi character in its sigma bonds as indicated by ^{13}C-H coupling constants and by atomic orbital overlap calculations,[30] and has a low ionization potential (8.7 eV).[30] Likewise, hexamethyl prismane (5) shows phenomenal reactivity with conventional Lewis acids (electrophiles) for a saturated hydrocarbon,[31] and atomic orbital overlap calculations indicate sp^4 hybridization at carbon for the $C_2 - C_6$ and $C_3 - C_5$ bonds.[32]

Thus, **2** is less reactive by a factor of 10^8 than model cage compounds



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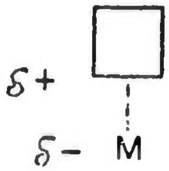

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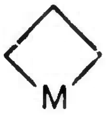

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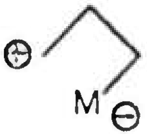

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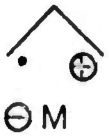

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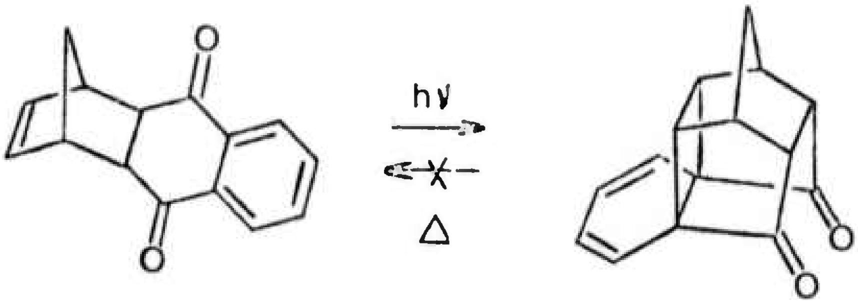

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(**3**, **5**, **6**) in reaction with Rh(I) complexes due to the effect of the carbonyl group which accounts for perhaps two orders of magnitude in the rate diminution[33] and to an effect related to the enforcement of bond angles in the cage structure which is surprisingly large (10^6x). These factors combine to make **2** much less nucleophilic (basic)[34] than the model systems, destabilizing a transition state such as **11** or reducing the binding in an intermediate such as **12** or **13**.[35] That the important interaction of metal and substrate is one of electrophile and nucleophile (Lewis acid - Lewis base) is supported by the order of reactivity of the Rh(I) complexes (Table II). Thus $Rh_2(CO)_4Cl_2$ in which Rh is more electron-deficient is a more potent catalyst (10^2x) than those with the less electron demanding norbornadiene and PPh_3 ligands.[36] Maitlis has previously pointed out the importance of Lewis acidity among metal ions and complexes which catalyze the valence isomerization of 1,2,5-*tri*-*tert*-butylprismane.[22] Concerning the structure **12** - **15** which describe a possible intermediate for catalyzed isomerization (whether they be contributors to a resonance hybrid or a set of equilibrating valence isomers), fully charge-separated species **14** and **15** lose importance in light of the substituent effects, the electronic portion of which is modest (*vide supra*) for catalysis by Rh(I).[9d] Finally the remarkable reactivity of caged saturated substrates with metals may be confined to a rather small group of compounds,[38] **2** (or 1,8,4,7 bishomocubanes) representing a limit of sorts to practical reactivity.

We have examined the reversibility of one other system capable of storing electronic excitation energy. For the photochromic isomerization of **16**[39] (350 nm), one can estimate an impressively large energy storage efficiency (Q = 25%) from the reported quantum yield ($\phi = 1$)[39a] and an estimate[40] of the heat of reaction **17** → **16** ($\Delta H \sim -20$ kcal/mol). Dione **17** is thermally stable to 150° and resists catalytic reversion to **16** at elevated temperatures in the presence of $Rh_2(CO)_4Cl_2$, $Rh(PPh_3)_3Cl$, $Pd(PhCN)_2Cl_2$ or p-toluenesulfonic acid despite a large potential exothermicity. The reverse valence isomerization is no doubt mitigated by those same inductive and steric substituent effects and reduced bond angle deformation effects already discussed for **2** and other cage substrates.

Finally, Dewar and Ramsden have recently suggested[41] that the selection rules governing stereochemistry and rate for reactions which are potentially pericyclic may break down in cases where large exothermicities are involved (due to the diminished contribution of the canonical form corresponding to product to a delocalized antiaromatic transition state hybrid). An inference that might be drawn is that for a series of "forbidden" reactions which assume similar topologies and basically similar electronics, higher rates (lower activation energies) would be correlated with increasing exothermicity. The data in Table IV indicate that **2** - **5** do not decompose with impressive regard for this factor.

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Experimental Section

Melting points were determined on a Fisher-Johns hot stage melting point apparatus and are uncorrected. Proton magnetic resonance spectra were recorded with a Joelco C-60-HL spectrometer. Gas chromatography was performed on a Varian Aerograph 1400 instrument (FI detector) equipped with a disc integrating recorder.

Thiophene-free benzene was washed with sulfuric acid until no further coloration of the acid layer appeared, then with aqueous $NaHCO_3$ solution and distilled water, and finally distilled over phosphorous pentoxide. Valerophenone (Aldrich) and diglyme were distilled under reduced pressure. Acetonitrile (spectroquality, Matheson, Coleman, and Bell), dodecane (spectrophotometric grade, Aldrich), diglyme-d_{14} (DG) (Merck), $Rh_2(CO)_4Cl_2$ (Alfa), and anhydrous and hydrated rhodium tichloride (Alfa) were used without further purification.

$Pd(PhCN)_2Cl_2$,[42] $Rh_2(NOR)_2Cl_2$[43] and $Rh(PPh_3)_3Cl$[44] and tricyclo(5.2.1.0^{2,6})-deca-4,8-dien-3-one (1)[45] were prepared according to literature procedures.

The 1,4-naphthoquinone-cyclopentadiene adduct 16 was prepared and photolyzed to give 17 as previously described.[39]

Preparative Irradiation of Dienone 1.[2] A nitrogen purged solution of 1 (1.0 g, 6.8 mmol) in 330 ml of acetonitrile was irradiated with a 450 W Hanovia medium pressure lamp (Pyrex filter). Over 250 min of irradiation, an isosbestic point at 305 nm and a "photostationary"[3] state (some 10% of 1 remaining) developed (uv analysis). Removal of solvent invacuo gave a viscous oil which was crystallized from light petroleum. The waxy solid was sublimed (2 mm) to give 750 mg of 2 (75%), mp 118 - 121° (lit mp 124 - 126°); λ_{max} 295 nm (ϵ 22).

Quantum Yield Determinations. Solutions containing known concentrations of dienone 1 and dodecane (internal standard for glc analysis) were prepared for irradiation in 15 mm Pyrex tubes. The solutions were deoxygenated by bubbling nitrogen for 30 min through long syringe needles inserted through rubber serum caps. The Rayonet RS Photochemical Reactor was fitted with four RUL 3500 lamps. The temperature in the reaction chamber was maintained at 30 ± 1° by means of a fan which circulated air from the bottom of the chamber. A Merry-Go-Round unit (Southern New England Ultraviolet) provided a sample tube mounting for parallel irradiation.

The conversion of valerophenone to acetophenone[5] ($\phi = 0.33$) in irradiations in parallel with **1** was monitored for actinometric purposes. Small differences in absorbance for actinometer and **1** over the lamp emission range (330 - 380 nm) were calculated using solution % transmittence values and lamp relative intensity (data from the supplier) at intervals of 2 - 5 nm. Glc analysis (8' x $\frac{1}{8}$" 3% FFAP on 80 - 100 Chrom W column at 90 - 150°) of actinometer and sample product (vs. dodecane) provided relative conversion values which were corrected for differential detector response.

Catalyzed Pyrolysis of 2. Solutions of **2**, catalyst, solvent, and diphenylmethane (nmr internal standard) were prepared in heavy-wall nmr tubes (Wilmad) which had been washed with acid, base, distilled water, and acetone, and dried. The sample tubes were evacuated through several freeze-thaw cycles and sealed. Pyrolyses were carried out in an oil bath insulated and thermoregulated (± 0.5°) using an I^2R Therm-o-watch as described previously.[46] Pyrolysis tubes were totally immersed in the well stirred baths and examined periodically after quenching in ice water.

Nmr analysis for the appearance of **1** (vinyl protons) vs. diphenylmethane (methylene protons) provided conversion data (generally 10 - 40%) from which rate constants could be calculated using the integrated first order rate equation. Second order rate constants derived from these values and catalyst concentrations.

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(33) The exact retardation relative to that experienced for **4** and **7** is uncertain. The ketone relative to ester carbonyl is somewhat more electron withdrawing; *e.g.*, the pK_a's of alpha hydrogens for ketones and ester are around 20 and 24, respectively, and sigma substituent constants follow the same trend; see C.D. Johnson, "The Hammett Equation," University Press, Cambridge, 1973, p. 14. On the other hand, the ester groups would provide more steric difficulty and they are two in number.

(34) The distinction betweeen nucleophilicity and basicity as primarily electrostatic phenomena diminishes for nucleophiles (such as strained sigma bonds) which do not possess diffuse, easily polarized electron clouds.

(35) The direct evidence[13,23a] concerning formation of **13** with Rh(I) complexes involves the isolation of a Rh(III) adduct in which a -CO ligand has inserted

into a carbon C-Rh bond. This side reaction which operates in lieu of valence isomerization could have been responsible for the fall off in rate (catalyst destruction) observed for **2** in the presence of $Rh_2(CO)_4Cl_2$. However, the untoward kinetic behavior at high conversion was general for all the Rh(I) catalysts, and $Rh_2(CO)_4Cl_2$ has been used successfully in other isomerization systems[11,22] presumably without trapping of the Rh(III) intermediate through insertion. The partitioning of a putative Rh(III) intermediate (**13**) between CO insertion, and decomposition to either valence isomer must be extremely subtle (perhaps temperature dependent) or else the CO insertion products are not *generally* stable.

(36) Dauben[37] has proposed a more subtle dependence for the rate of catalysis on the sigma donor, pi acceptor ability and polarizability of the metal ligands which does not readily rationalize the activity in our system of $Rh_2(CO)_4Cl_2$.

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