Catalytic Activity in the Reversion of an Energy Storing Valence Photoisomerization

Guilford Jones, II,* and B. R. Ramachandran

Department of Chemistry, Boston University, Boston, Massachusetts 02215

Received September 16, 1975

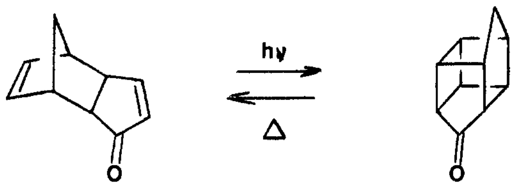
The quantum yield of valence photoisomerization of *endo*-tricyclo[5.2.1.$0^{2,6}$]deca-4,8-dien-3-one (1) to cage isomer 2 is 0.35–0.40 in several solvents. Upon irradiation at 330–380 nm the chemical yield of isomer 2 is essentially quantitative. Cage isomer 2 is thermally stable to 295 °C where slow decomposition occurs to give a mixture of products. Upon treatment with catalytic amounts of complexes of Rh(I) at 140–180 °C, 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 owing 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 °C) obtains: quadricyclenes ~ prismane ~ cubanes > homocubanes > 2 (a 1,8,4,7-bishomocubane). The system 1 → 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 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.

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

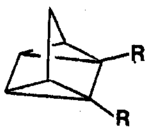
Results and Discussion

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 (valerophenone actinometry[5]) are shown in Table I. The progress of photoisomerization at constant lamp intensity revealed that the yield is undiminished as a function of time to very high conversion for moderately concentrated samples.

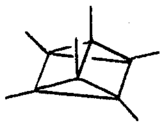


1

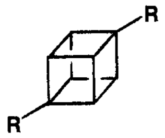
2



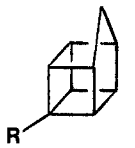
3, R = H
4, R = CO_2Me



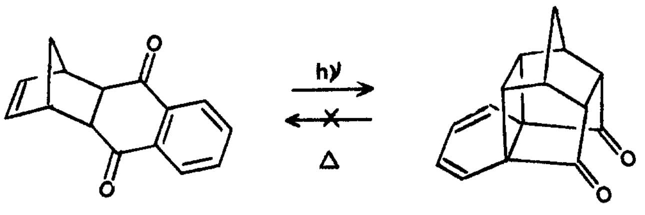
5



6, R = H
7, R = CO_2Me



8, R = H
9, R = CO_2Me



10

11

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

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

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).

where ϕ, ΔF, and $E(h\nu)_{av}$ 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 $E(h\nu)_{av} = 80$ 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 diphenyl ether (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 °C. At high catalyst concentrations (~5 mol %) the rate of isomerization could be followed (NMR) over 2 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 1 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. (See paragraph at end of paper regarding supplementary material.) That a classical second-order catalytic rate law was obeyed is supported by experiments in which initial catalyst and substrate concentrations were varied. Thus, a plot of the first-order rate constants for disappearance of **2** vs. $[Rh_2(CO)_4Cl_2]$ (sevenfold range) was linear, and in experiments with $Rh_2(NOR)_2Cl_2$ (NOR = norbornadiene) a nearly threefold 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 isomerization systems.[8]

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

Substrate concn, M	Catalyst (concn, M)	Solvent	Temp, °C	k, M^{-1} sec^{-1}
1.7	$Rh_2(CO)_4Cl_2$ (0.02–0.14)	DG	140	1.0×10^{-2} [b]
1.3	$Rh_2(CO)_4Cl_2$ (0.005)	DG	160	7.1×10^{-2}
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	$Rh(PPh_3)_3Cl$ (0.07)	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 vs. catalyst concentration.

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 hexamethyl(Dewar benzene), and cubanes (**6**, **7**) and homocubane (**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 catalyzed by $Rh_2(NOR)_2Cl_2$ at 40 °C, a temperature for which rate data for **6–8** were available (Table III). For **2–5** the rates at 40 °C 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 valence isomerizations catalyzed by Rh(I) complexes.[14] Also included for reference in Table III are enthalpies of valence isomerization. Reasons for the markedly low reactivity of **2** in comparison with a family of caged substrates are not readily apparent. The presence of the carbonyl group in **2** might be responsible for a rate retardation of only about two orders of magnitude.[18] This deceleration has been noted previously for the quadricyclene (compare **3** and **4**)[14a] and cubane (compare **6** and **7**)[13] series and has been rationalized (with particular reference to the homocubane series, **8** vs. **9**) in terms of electronic and steric factors.[9d] Solvent effects are not likely a significant contributor to rate differences in view of the modest acceleration in more polar solvent noted for catalyzed isomerization of **4**.[11]

Early theories concerning transition metal catalyzed valence isomerization[19] suggest a role for ring strain release in determining rate. However, the measured or calculated negative enthalpies of isomerization for **2–6** are similarly large. Comparison among ring types reveals the relative reactivity order, quadricyclenes ~ prismane ~ 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**). Although *overall* molecular strain appears not to be 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 cubanes > homocubane > bishomocubane (the cyclobutane rings begin to pucker in-

Table III. Comparative Kinetics and Heat of Reaction Data for Valence Isomerization of Cage Compounds Catalyzed by $Rh_2(NOR)_2Cl_2$

Cage substrate	k_{obsd}, M^{-1} sec^{-1} (temp, °C)	Solvent	Ref	k_{rel} (40 °C)[a]	ΔH, kcal/mol
2	1.8×10^{-3} (180)	DG	This work	1	−16.0[c]
3	5.5×10^{-2} (−26)	$CDCl_3$	10	1×10^8	−21.2[d]
4	2.8×10^{-2} (60)	$CDCl_3$	11	3×10^5	−18.5[d]
5	9.7×10^{-3} (−30)[b]	$CHCl_3$	12	3×10^7	−31.7[e]
6	14 (40)	$CDCl_3$	13	4×10^8	−16.7[f]
7	1.1×10^{-1} (40)	$CDCl_3$	13	3×10^6	
8	1.4×10^{-2} (40)	C_6H_6	9a	4×10^5	

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

creasingly), so do the relative rates of rhodium-catalyzed decomposition vary, with a rate retardation of ~10^3 for each 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,[9e,20] an oxidizing agent,[13,21] a nucleophile,[28] or as an electron donor,[20] types of interaction of strained σ bonds *with metals which have been considered. We wish to* emphasize that the remarkable reactivity of caged saturated substrates with metals may be confined to a rather small group of compounds.[23] High energy content is insufficient ground for reactivity while an effect related to the enforcement of bond angles in the cage structure is largely rate determining.

We have examined the reversibility of one other system capable of storing electronic excitation energy. For the photochromic isomerization of **10**[25] (350 nm), one can estimate an impressively large energy storage efficiency (Q = 25%) from the reported quantum yield ($\phi = 1$)[25] and an estimate[26] of the heat of reaction **17** → **16** ($\Delta H \sim -20$ kcal/mol). Dione **11** is thermally stable to 150° and resists catalytic reversion to **10** 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 bond angle deformation effects already discussed for **2** and other cage substrates.

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 phosphorus 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 trichloride (Alfa) were used without further purification.

$Pd(PhCN)_2Cl_2$,[27] $Rh_2(NOR)_2Cl_2$,[28] and $Rh(PPh_3)_3Cl$[29] and tricyclo[5.2.1.$0^{2,6}$]deca-4,8-dien-3-one (**1**)[30] were prepared according to literature procedures. The 1,4-naphthoquinone–cyclopentadiene adduct **16** was prepared and photolyzed to give **17** as previously described.[25]

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 in vacuo 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 °C (lit. mp 124–126 °C), 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 °C 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 percent transmittance values and lamp relative intensity (data from the supplier) at intervals of 2–5 nm. GLC analysis (8 ft × 0.125 in. 3% FFAP on 80–100 Chromosorb W column at 90–150 °C) 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 °C) using an I^2R Therm-o-watch as described previously.[31] 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. (See supplementary material.)

Acknowledgments. This research was supported by the Advanced Research Projects Agency of the Department of Defense and was monitored by the Office of Naval Research under Contract N00014-67-A-0280. We thank Professors Warren P. Giering and K. W. Barnett for helpful discussions and Mr. Allen H. Pachtman for technical assistance.

Supplementary Material Available. Tables of rate data for catalyzed isomerization of **2** (3 pages). Ordering information is given on any current masthead page.

Registry No.—**1**, 5530-96-1; **2**, 15584-52-8.

References and Notes

(1) (a) J. G. Calvert in "Introduction to the Utilization of Solar Energy", A. M. Zarem, Ed., McGraw-Hill, New York, N.Y., 1993, p 190; (b) F. Daniels, "Direct Use of the Sun's Energy", Yale University Press, New Haven, Conn., 1964, p 299; (c) R. J. Marcus, *Science*, **123**, 399 (1956).

(2) (a) R. C. Cookson, J. Hudec, and R. O. Williams, *J. Chem. Soc. C,* 1382 (1967). (b) The sensitized isomerization has also been reported; see R. O. Campbell and R. S. H. Liu, *J. Am. Chem. Soc.*, **95,** 6560 (1973).
(3) Photochemical isomerization **2** → **1** was unobserved both at 350 and 254 nm.
(4) The isomerization **1** → **2** was driven on a small scale cleanly but slowly likewise to >99% conversion by Pyrex filtered direct December sunlight (Boston, Mass.).
(5) P. J. Wagner, P. A. Kelso, and R. G. Zepp, *J. Am. Chem. Soc.*, **94,** 7480 (1972).
(6) R. C. Cookson, E. Crundwell, R. R. Hill, and J. Hudec, *J. Chem. Soc.*, 3062 (1964).
(7) R. C. Cookson, J. Hudec, and R. O. Williams, *J. Chem. Soc. C,* 1382 (1967).
(8) (a) L. A. Paquette, J. S. Ward, R. A. Boggs, and W. B. Farnham, *J. Am. Chem. Soc.*, **97,** 1101 (1975); (b) L. A. Paquette and J. S. Ward, *Tetrahedron Lett.*, 4909 (1972); (c) H. Hogeveen and B. J. Nusse, *ibid.*, 159 (1974); (d) L. A. Paquette, S. E. Wilson, R. P. Henzel, and G. R. Allen, Jr., *J. Am. Chem. Soc.*, **94,** 7761 (1972).
(9) For a compilation of references on valence isomerizations catalyzed by transition metal complexes, see ref 8a and (a) L. A. Paquette and R. S. Beckley, *J. Am. Chem. Soc.*, **97,** 1084 (1975); (b) L. A. Paquette, R. S. Beckley, and W. B. Farnham, *ibid.*, **97,** 1089 (1975); (c) L. A. Paquette, R. A. Boggs, W. B. Farnham, and R. S. Beckley, *ibid.*, **97,** 1112 (1975); (d) L. A. Paquette, R. A. Boggs, and J. S. Ward, *ibid.*, **97,** 1118 (1975); (e) R. Noyori, I. Umeda, H. Kawauchi, and H. Takaya, *ibid.*, **97,** 812 (1975).
(10) H. Hogeveen and H. C. Volger, *J. Am. Chem. Soc.*, **89,** 2486 (1967).
(11) H. Hogeveen and B. J. Nusse, *Tetrahedron Lett.*, 159 (1974).
(12) H. Hogeveen and H. C. Volger, *Chem. Commun.*, 1133 (1967).
(13) L. Cassar, P. E. Eaton, and J. Halpern, *J. Am. Chem. Soc.*, **92,** 3515 (1970).
(14) (a) H. Hogeveen and B. J. Nusse, *Tetrahedron Lett.*, 3667 (1973); (b) H. C. Volger and H. Hogeveen, *Recl. Trav. Chim. Pay-Bas,* **86,** 830 (1967).
(15) D. S. Kabakoff, J.-C. G. Bunzli, J. F. M. Oth, W. B. Hammond, and J. A. Berson, *J. Am. Chem. Soc.*, **97,** 1510 (1975).
(16) J. F. M. Oth, *Recl. Trav. Chim. Pays-Bas,* **87,** 1185 (1968); for a somewhat different enthalpy value and activation parameters, see W. Adam and J. C. Chang, *Int. J. Chem. Kinet.*, **1,** 487 (1969).
(17) R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, **97,** 1294 (1975).
(18) Hogeveen has calculated a larger substituent deceleration (5000 ×).[14a] However, the extrapolated rate for **3** apparently derived from previously reported[10] Eyring parameters ($\Delta H^{\ddagger}$ = 21 kcal/mol, $S^{\ddagger}$ = 45 eu) which appear dubious.
(19) F. D. Mango, *J. Am. Chem. Soc.*, **93,** 1123 (1971); *Tetrahedron Lett.*, 505 (1971).
(20) K. L. Kaiser, R. F. Childs, and P. M. Maitlis, *J. Am. Chem. Soc.*, **93,** 1270 (1971).
(21) (a) L. Cassar and J. Halpern, *Chem. Commun.*, 1082 (1970); (b) T. J. Katz and S. Cerefice, *J. Am. Chem. Soc.*, **91,** 2405 (1969).
(22) For a suggestion of electrophilic ring opening by Ag^+, see ref 8a and 9b.
(23) 1,3-Bishomocubane appears to react with Rh(I) more sluggishly than **6** or **8**[24] only at the site of fusion of small rings in line with a dependence on local bond angle deformation.
(24) J. Blum, C. A. Zlotogorski, and A. Zoran, *Tetrahedron Lett.*, 1117 (1975).
(25) (a) N. Filipescu and J. M. Menter, *J. Chem. Soc. B,* 616 (1969); (b) A. S. Kushner, *Tetrahedron Lett.*, 3276 (1971).
(26) The isomerization of the *p*-benzoquinone–cyclopentadiene adduct analogous to **16** to its cage isomer is *exothermic* as calculated from heat of combustion data ($\Delta H = -11.3$ kcal/mol).[6] For the heat of reaction **17** → **16** this value must be substracted from ~30 kcal/mol, the resonance energy difference between benzene and cyclohexadiene, to obtain ΔH(**17** → **16**) = −20 kcal/mol.
(27) M. S. Kharasch, R. C. Seyler, and F. R. Mayo, *J. Am. Chem. Soc.*, **60,** 882 (1938).
(28) E. W. Abel, M. A. Bennett, and G. Wilkinson, *J. Chem. Soc.*, 3178 (1959).
(29) M. A. Bennett and P. A. Longstaff, *Chem. Ind.* (*London*), 846 (1965).
(30) L. A. Paquette and J. S. Ward, *J. Org. Chem.*, **37,** 3569 (1972).
(31) G. Jones, II, M. E. Fantina, and A. H. Pachtman, *J. Org. Chem.*, **41,** 329 (1976).

Conformational Control by Carbinyl Hydrogens. Implications and Applications

William H. Pirkle* and J. R. Hauske

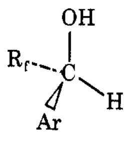
School of Chemical Sciences, University of Illinois, Urbana, Illinois 61801

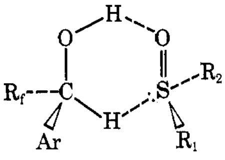
Received July 9, 1975

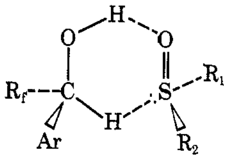
"Acylation shifts" and $Eu(fod)_3$ gradients of the carbinyl hydrogens of a variety of esterlike derivatives of secondary alcohols are substantially enhanced when the carbinyl carbon bears a trifluoromethyl group. This enhancement is not steric in origin and is attributed to weak intramolecular bonding between the carbinyl hydrogen and the carbonyl oxygen which populates conformations placing the carbinyl hydrogen near to and approximately in the plane of the magnetically anisotropic carbonyl. Here, this hydrogen may be deshielded (acylation shift) or shifted downfield (gradient) upon coordination of the carbonyl oxygen to $Eu(fod)_3$. The concept of conformational control by carbinyl hydrogen bonding can be used to account for prior instances of chemical behavior such as chromatographic properties, NMR chemical shifts, and asymmetric induction.

Prior papers dealing with chiral NMR solvents have explained the ability of these solvating agents to cause the spectra of enantiotopic solutes to become nonequivalent as a consequence of the formation of transient diastereomeric solvates.[1–6] Further, it has been proposed that these solvates assume conformations which place enantiomeric solute nuclei in different orientations with respect to a magnetically anisotropic substituent of the chiral solvating agent. Accurate knowledge of the conformational behavior of these diastereomeric solvates would enable one to directly relate the observed spectral differences to the stereochemical differences of the solvates.[7] For chiral solvents of known absolute configuration, this type of spectral interpretation would amount to *simultaneous determination of the absolute configuration and enantiomeric purity of the solute.* Clearly, an understanding of the factors underlying the conformational behavior of the transient diastereomeric solvates is essential to the successful employment of this technique.

Specific solvation models have been advanced[1,2] to account for the NMR nonequivalence shown by enantiomeric sulfoxides or enantiomeric tertiary amine oxides in the presence of chiral type 1 alcohols. After initial intermolecular hydrogen bonding, a weaker but intramolecular bonding between the carbinyl hydrogen of 1 and a second basic site in the solute is postulated to afford chelatelike conformations exemplified by **2a,b** and **3a,b.** Such conformations would place enantiomeric solute nuclei (R_1 or R_2) in different orientations with respect to the aromatic substituent of chiral alcohol 1. Hence, the resultant average chemical shift


1


2a


2b