plexes or as H_3^- complexes of Ir(III). In this situation the designation of the formal oxidation state is dependent on the extent of back donation from the metal to the ligand.

The observed coupling constants in **1**–**3** are highly temperature dependent. In complex **3**, J_{H-H} = 376 Hz at 176 K, increasing steadily to J_{H-H} = 570 Hz at 189 K. Similar trends are seen in **1** and **2** (see Supplementary Material). The origin of this pronounced temperature dependence remains obscure. Very recently, Chaudret and co-workers[23] have reported similar observations of large, temperature dependent H–H couplings in closely related *neutral* ruthenium complexes. Further studies to elucidate the structures of **1**–**3** and related complexes are in progress.

Acknowledgment. We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for their support of this research. We acknowledge receipt of a Cottrell grant-in-aid from the Research Corporation. A generous loan of iridium trichloride from Johnson-Matthey, Inc. is appreciated.

Registry No. 1, 113161-52-7; **2**, 113161-54-9; **3**, 113180-40-8; $(\eta^5\text{-}C_5H_5)Ir(PMe_3)H_2$, 113161-55-0; $(\eta^5\text{-}C_5H_5)Ir(PPh_3)H_2$, 113161-56-1; $(\eta^5\text{-}C_5H_5)Ir(AsPh_3)H_2$, 113161-57-2.

Supplementary Material Available: X-ray structure data for **1**, including details of data collection and refinement, experimental (^{1}H and ^{1}H {^{31}P}) NMR spectra and computer-simulated spectra for **1** and **2** at various temperatures, and a table of J_{H-H} as a function of temperature for **1**–**3** (10 pages); table of observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

---

(21) Nageswara Rao, B. D.; Anders, L. R. *Phys. Rev.* **1965**, *140*, A112.

(22) Neronov, Yu. I.; Barzakh, A. E. *Zh. Eksp. Teor. Fiz.* **1977**, *72*, 1659.

(23) Arliguie, T.; Chaudret, B.; Devillers, J.; Poilblanc, R. *C. R. Acad. Sci. Paris* **1987**, *305* (series II), 1523.

Stereochemistry and Mechanism of [4 + 2] Photocycloaddition of Pummerer's Ketone to Furan

Mladen Mintas and David I. Schuster*

Department of Chemistry, New York University
New York, New York 10003

Paul G. Williard

Department of Chemistry, Brown University
Providence, Rhode Island 02912

Received November 12, 1987

On the basis of the stereochemistry of photoaddition of MeOD to Pummerer's ketone (PK) **1**, Hart and co-workers[1] suggested that "an excited state or intermediate in which the C=C bond is twisted more than 90°" might be the chemically reactive intermediate. The reaction course was suggested to be syn addition to the "trans" double bond, by analogy to the reaction course followed on photoaddition of MeOD to derivatives of cycloheptenone and cyclooctenone.[2] We have recently presented kinetic data which suggest that [2 + 2] photocycloaddition of alkenes to nonconstrained cyclohexenones may proceed via *trans*-cyclohexenones.[3] Photoaddition of reactive 1,3-dienes to cycloheptenones and cyclooctenones[4] as well as 1-acetylcycloalkenes (n = 6–8)[5] gives trans fused [4 + 2] cycloadducts, which has generally been ascribed to capture by the diene of a ground-state *trans*-enone. This conclusion has been confirmed in eight-ring systems by formation of the same adduct(s) on excitation of the enone at low temperature followed by dark reaction with added diene.[5] Because of our interest in *trans*-cyclohexenones as possible reaction intermediates in the photochemistry of *cis*-cyclohexenones,[3] we have investigated the photoaddition of PK to furan.

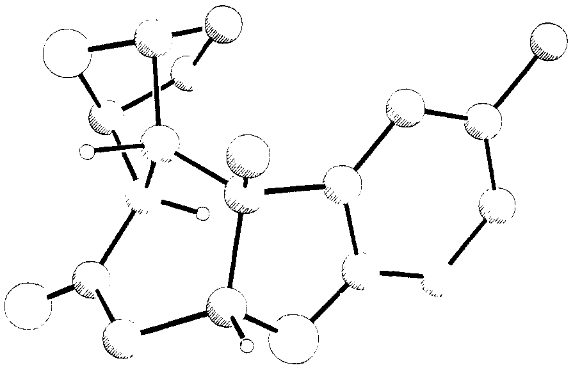


Figure 1. X-ray crystal structure of the cycloadduct **2**.

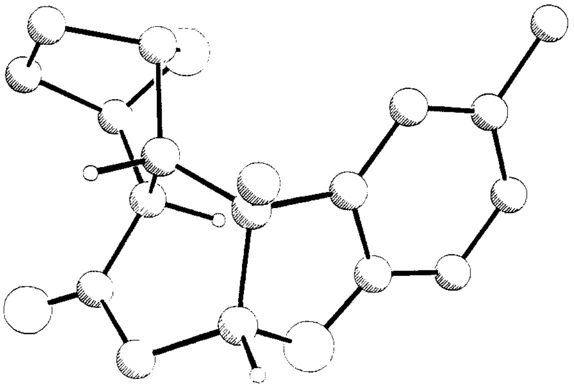
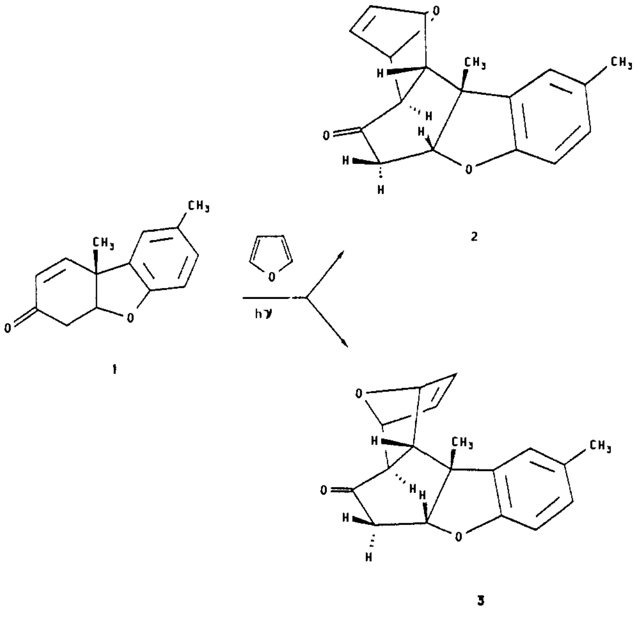


Figure 2. X-ray crystal structure of the cycloadduct **3**.

Scheme I



Irradiation of a 0.005 M solution of PK in neat furan at room temperature through Pyrex led to isolation of two PK–furan adducts, **2** (mp 219–220 °C) and **3** (mp 208–209 °C) (Scheme I). The assignment of trans stereochemistry to the ring junction protons was made from completely decoupled 300 MHz ^{1}H NMR spectra (see Supplementary Material) and was confirmed by X-ray crystallography (see Figures 1 and 2 for the crystal structures of **2** and **3**). Both **2** and **3** crystallized in the centrosymmetric, monoclinic space group $P2_1/c$, with unit cells parameters as

---

(1) Dunkelblum, E.; Hart, H.; Jeffares, M. *J. Org. Chem.* **1978**, *43*, 3409.

(2) Dunkelblum, E.; Hart, H. *J. Am. Chem. Soc.* **1977**, *99*, 644. Hart, H.; Dunkelblum, E. *J. Am. Chem. Soc.* **1978**, *100*, 5141.

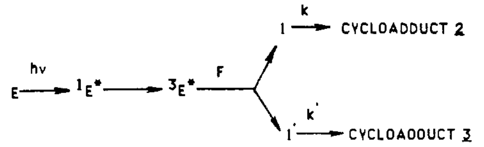
(3) Schuster, D. I.; Brown, P. B.; Capponi, L. J.; Rhodes, C. A.; Scaiano, J. C.; Weir, D. *J. Am. Chem. Soc.* **1987**, *109*, 2533.

(4) Corey, E. J.; Tada, M.; LeMahieu, R.; Libit, L. *J. Am. Chem. Soc.* **1965**, *87*, 2051. Eaton, P. E.; Lin, K. *J. Am. Chem. Soc.* **1965**, *87*, 2052. Eaton, P. E.; Lin, K. *J. Am. Chem. Soc.* **1964**, *86*, 2087.

(5) Eaton, P. E. *Acc. Chem. Res.* **1968**, *1*, 50.

0002-7863/88/1510-2305$01.50/0

Scheme II



follows: **2**, $a = 7.701$ (2), $b = 16.593$ (3), $c = 12.041$ (3) A; **3**, $a = 7.722$ (2), $b = 16.631$ (4), $c = 11.741$ (3) A. Final agreement factors were $r = 0.0479$ for **2** and 0.0485 for **3**.[6] Although these results appear to confirm the photochemical generation of *trans*-PK,[1] subsequent results indicate this is probably not the case. No reaction between PK and furan occurs on heating at 150–155 °C for up to 48 h.

Laser flash photolysis of PK at 308 nm in acetonitrile using pulses from an excimer laser leads to the formation of an intermediate with a lifetime of ca. 15 ns with absorption centered at 270–277 nm.[7] This very short lifetime, at the limit of the time resolution of this flash system, precluded quenching studies to fully characterize this transient species. However, by analogy with previous laser flash studies of cyclohexenones[8] and other cyclic enones,[9] we assign this absorption to a highly twisted triplet excited state of PK; a general correlation of triplet lifetimes of cyclohexenones with structure has been observed, in which the lifetime is inversely correlated with the ability to twist around the C=C bond.[8-10] Consistent with these findings is that methylnaphthalene (MN) (E_T 61 kcal/mol) in concentrations up to 0.86 M (PK 0.013 M, furan 0.05 M) does not quench the formation of **2** and **3**. However, the free radical tetramethyl-1-piperidinyloxy (TEMPO) quenches formation of **2** and **3**, with Stern–Volmer quenching constants $k_q\tau$ of 12.5 ± 0.6 and 6.6 ± 0.3 M^{-1}, respectively, where k_q is the quenching rate constant and τ is the lifetime of the intercepted intermediate. Quenching by oxygen was also observed, with $k_q\tau = 438 \pm 8$ and 132 ± 5 M^{-1}, respectively.

Differential quenching by TEMPO and O_2 is consistent only with a nonconcerted photocycloaddition mechanism, as shown in Scheme II, in which the highly twisted triplet of PK reacts with furan (F) to give two distinct quenchable intermediates, I and I′, which are direct precursors of **2** and **3**, respectively. Since the adducts have lost conjugation, the possibility that I and I′ could be adduct triplet states can be eliminated on energetic grounds. It seems more likely that I and I′ are short-lived triplet biradicals, interceptable by TEMPO and O_2 but not by MN. The quantum efficiency for formation of **2** and **3**, 0.062 ± 0.005 and 0.065 ± 0.005, suggests that reversion to ground states of PK and F may occur from I and I′ as well as PK*. The observed stereochemistry suggests that reaction occurs on only one face of the twisted triplet of PK but indiscriminately exo and endo to the oxy bridge of furan. Since Diels–Alder addition of ground state *trans*-PK to furan should be concerted mechanistically even if nonsynchronous,[11] quenching of this process by TEMPO or O_2 is not expected.[12]

Mechanistic examination of [4 + 2] photocycloaddition reactions of dienes to cyclic enones[13] and to other systems in which strained trans ground state intermediates have been proposed[14] appear warranted.

Acknowledgment. This study was supported by grants from the National Science Foundation (CHE-8320154) and the Petroleum Research Fund of the American Chemical Society, to the donors of which we are grateful. We are also grateful to Dr. J. C. Scaiano, NRC, Ottawa, for the flash study of PK and to Dr. Martyn Price for helpful discussions regarding the NMR spectra. M.M. is grateful to the University of Zagreb in Yugoslavia for the grant of a sabbatical leave.

Supplementary Material Available: Tables consisting of 300-MHz ^{1}H NMR spectral data, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters, details of the structure determination, and a computer-generated plot with atom labels for **2** and **3** (9 pages); tables of observed and calculated structure factors for **2** and **3** (18 pages). Ordering information is given on any current masthead page.

---

[6] The full NMR and X-ray data are provided as Supplementary Material.

[7] These data were kindly obtained by Dr. J. C. Scaiano at the National Research Council, Ottawa, Canada.

[8] Schuster, D. I.; Bonneau, R.; Dunn, D. A.; Joussot-Dubien, J. *J. Am. Chem. Soc.* **1984**, *106*, 2706. Dunn, D. A. Ph.D. Dissertation, New York University, 1985.

[9] Bonneau, R. *J. Am. Chem. Soc.* **1980**, *102*, 3816.

[10] Schuster, D. I.; Dunn, D. A.; Brown, P. B.; Bonneau, R., unpublished data.

[11] Dewar, M. J. S.; Olivella, S.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1986**, *108*, 5771.

[12] No one has ever observed quenching by radical traps of a thermally induced Diels–Alder reaction, to the best of our knowledge. Dewer (ref 11) goes to great pains to distinguish between a concerted, nonsynchronous, two-stage mechanism in which the two bonds are formed to different extents at the transition state and two-step nonconcerted addition via biradical *intermediates*. In the absence of experimental and theoretical evidence for a two-step mechanism in *any* ground-state Diels–Alder process, we cannot accept the possibility raised by a referee that Diels–Alder reactions of a ground-state *trans*-cyclohexenone might be uniquely quenchable. See, also: Tolbert, L. M.; Mahfuza, B. A. *J. Am. Chem. Soc.* **1984**, *106*, 3806.

[13] For examples of photocycloaddition of dienes to cyclohexenone and cyclopentenone, see: Cantrell, T. S. *J. Org. Chem.* **1974**, *39*, 3063.

[14] Dauben, W. G.; van Riel, H. C. H. A.; Hauw, C.; Leroy, F.; Joussot-Dubien, J.; Bonneau, R. *J. Am. Chem. Soc.* **1979**, *101*, 1901.

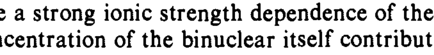
Ionic Strength Dependence of Intervalence Transition Bands in Electron Tunnelling Processes

Nita A. Lewis* and Yaw S. Obeng

Department of Chemistry, University of Miami
Coral Gables, Florida 33124

Received August 17, 1987

We wish to report the first study of the effect of ionic strength on an intervalence transition band (IT band). It is apparent that not only is the nature of the anion present important in determining the position of the IT band[1] but also the present work shows that there can be a strong ionic strength dependence of the band so that the concentration of the binuclear itself contributes to the band position as does the concentration of the oxidant or reductant used to generate the mixed-valence species. The ruthenium binuclear used in this investigation was the μ-2,6-dithiaspiro[3.3]heptanedecaamminediruthenium(II,III) species studied earlier (complex I);[2] electron transfer in this molecule is known to be



I

significantly nonadiabatic.[3,4] The oxidant employed was $[Fe(bpy)_3](PF_6)_3$. The ionic strength was controlled to the desired values by the addition of tetra-*n*-butylammonium hexafluorophosphate (TBAH). For ion-pairing in optical electron transfers, the Guntelberg[5] modification of the Debye–Huckel equation may be expressed as

$$E_{op} = E_{op}{}^{\circ} + \frac{2z_1z_2A\sqrt{\mu}}{1+\sqrt{\mu}}$$

where z_1 and z_2 are the charges of the ions, μ is the ionic strength, A is a Debye–Huckel constant, E_{op} is the energy of the IT band, and $E_{op}{}^{\circ}$ is the energy of the IT band at infinite dilution. The ionic strength dependence of complex I was studied in two solvents, dimethyl sulfoxide and *N*-methylformamide; the results are graphically displayed in the figure, where the lines shown are

---

[1] Chang, J. P.; Fung, E. Y.; Curtis, J. C. *Inorg. Chem.* **1986**, *25*, 4233.

[2] Stein, C. A.; Taube, H. *J. Am. Chem. Soc.* **1981**, *103*, 693.

[3] Stein, C. A.; Lewis, N. A.; Seitz, G. *J. Am. Chem. Soc.* **1982**, *104*, 2596.

[4] Stein, C. A.; Lewis, N. A.; Seitz, G.; Baker, A. D. *Inorg. Chem.* **1983**, *22*, 1124.

[5] Guntelberg, E. *Z. Phys. Chem.* **1926**, *123*, 199.

0002-7863/88/1510-2306$01.50/0