about the molybdenum is octahedral and the Mo–P and Mo–N bonds lengths are typical of molybdenum dinitrogen complexes.[12] The small sulfur-donor group introduces an asymmetry in the molecule, which is expressed in a bending of the linear N_2 groups toward the sulfur (angles MoNN are 168 (3)°, 174 (3)°). The N–N distances (1.04 (3), 1.10 (3) Å) are not significantly different although two IR modes, $\nu(N_2)$, are observed for toluene solutions of I (2014 w, 1942 s cm^{-1}) whereas only one is observed for $Mo(N_2)_2(PMePh_2)_4$ (1928 s cm^{-1}). The small N_2 ligands fit snugly in pockets defined by the phenyl and methyl groups on the other ligands. Bonds to the chelate ligand (Mo–S, 2.483 (8), Mo–P3, 2.457 (9) Å) are shorter than corresponding bonds in $Mo(PPh_2CH_2CH_2SMe)(CO)_4$ (2.560 (1), 2.542 (1) Å).[9b] The phosphorus–sulfur ligand has a bite angle of 80.3 (3)° in complex I.

The ^1H NMR spectrum shows that the sulfur methyl protons are coupled to phosphorus P1 trans to sulfur ($^4J_{PH}$ = 1.0 Hz at 80 or 200 MHz).[10] This coupling is not present for the free ligand or the complex $Mo(PPh_2CH_2CH_2SMe)(CO)_4$ and its existence proves that the thioether, despite its poor donor properties,[13] is not dissociating on the NMR time scale.[14] The ^{31}P NMR resonances of complex I[10] can be unequivocally assigned by comparison with spectra for the complexes $Mo(N_2)_2(PMePh_2)_3(py)$[8d] and $Mo(N_2)_2(PMePh_2)_2(PPh_2CH_2CH_2PPh_2)$.[8a,b,15]

The chemistry of complex I resembles that of some molybdenum dinitrogen complexes coordinating by four phosphorus donors[16-18] in that it yields ammonia at 23 °C when it is treated with strong acid. When complex I is treated with 15 mol of H_2SO_4 in methanol at 23 °C then 1.1 mol of N_2, and 0.05 of mol H_2 are evolved over 18 h. After this time the solution is evaporated, treated with excess KOH (40%), and tested for ammonia and hydrazine according to literature procedures.[16] At this stage ca. 0.3 mol of N_2 and 0.7 of mol H_2 are evolved, and 0.3 mol of NH_3 and 0.0 mol of N_2H_4 are detected. The yield of ammonia is less than that observed for $Mo(N_2)_2(PMePh_2)_4$ (0.66 mol) and $Mo(N_2)_2(PMePh_2)_2(PPh_2CH_2CH_2PPh_2)$ (0.56 mol) under identical conditions.[16] Hydrogen (0.2 mol) was only detected for reactions with the latter complex.[16] This suggests that reducing equivalents are diverted from ammonia to hydrogen production in the reaction involving complex I. The contribution of the sulfur ligand to this apparent difference in reactivity is not clear but merits further study.

Attempts are now being made to isolate a hydrazido(2–) intermediate[19] and explain the reduced yield of ammonia. Other sulfur ligands are being examined but attempts to displace two phosphine ligands from $Mo(N_2)_2(PMePh_2)_4$ by use of $MeSCH_2CH_2SMe$ or $EtSCH_2CH_2SEt$ result in immediate displacement of all dinitrogen.

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Registry No. I, 89958-79-2; *trans*-$Mo(N_2)_2(PMePh_2)_4$, 33248-03-2; *trans*-$Mo(N_2)_2(PMePh_2)_2(PPh_2CH_2CH_2PPh_2)$, 65498-66-0; NH_3, 7664-41-7; N_2, 7727-37-9; H_2, 1333-74-0.

Supplementary Material Available: Listings of positional parameters (Table I), bond angles (Table II), bond distances (Table III), and the observed and calculated structure factors (Table IV) along with the ^1H NMR spectrum of I (Figure 2) and its preparation (13 pages). Ordering information is given on any current masthead page.

(12) (a) Carmona, E.; Marin, J. M.; Poveda, M. L.; Atwood, J. L.; Rogers, R. D. *J. Am. Chem. Soc.* **1983**, *105*, 3014; (b) *J. Organomet. Chem.* **1982**, *238*, C63. (c) Forder, R. A.; Prout, K. *Acta Crystallogr., Sect. B* **1974**, *30*, 3778. (d) Uchida, Y.; Uchida, T.; Hidai, M.; Kodama, T. *Ibid.* **1975**, *31*, 1197.

(13) (a) Sanger, A. R.; Day, R. W. *Inorg. Chim. Acta* **1982**, *62*, 99. (b) Kuehn, C. G.; Isied, S. S. *Prog. Inorg. Chem.* **1980**, *27*, 153. (c) Rigo, P.; Bressan, M.; Basato, M. *Inorg. Chem.* **1979**, *18*, 860.

(14) (a) Abel, E. W.; Bhatti, M. M.; Orell, K. G.; Sik, V. *J. Organomet. Chem.* **1981**, *208*, 195. (b) Abel, E. W.; Booth, M.; Orrell, K. G.; Pring, G. M.; Cameron, T. S. *J. Chem. Soc., Chem. Commun.* **1981**, 29.

(15) *trans*-$Mo(N_2)_2(PMePh_2)_2(PPh_2CH_2CH_2PPh_2)$. ^{31}P NMR (THF, reference 85% H_3PO_4, 81 MHz) 63.3 (AA′, 2P, PPh_2CH_2), 22.0 ppm (XX′, 2P, $PMePh_2$), $^2J_{AX'}$ (trans) = 105.8, $^2J_{AX}$(cis) = −16.0, $^2J_{AA'}$ = 2.2, $^2J_{XX'}$ = 12.6 Hz.

(16) Chatt, J.; Pearman, A. J.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1977**, 1852.

(17) (a) George, T. A.; Koczon, L. M. *J. Am. Chem. Soc.* **1983**, *105*, 6334. (b) Baumann, J. A.; George, T. A. *Ibid.* **1980**, *102*, 6153.

(18) Takahashi, T.; Mizobe, Y.; Sato, M.; Uchida, Y.; Hidai, M. *J. Am. Chem. Soc.* **1980**, *102*, 7461 and references therein.

(19) (a) Bossard, G. E.; George, T. A.; Howell, D. B.; Koczon, L. M.; Lester, R. K. *Inorg. Chem.* **1983**, *22*, 1968. (b) Anderson, S. N.; Chatt, J.; Fakley, M. E.; Richards, R. L. *J. Chem. Soc., Dalton Trans* **1981**, 1973 and references therein.

Photoenolization of α-(2,4,6-Triisopropylphenyl)acetophenone

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Hart and Giguere just reported indirect evidence for the transient photochemical production of ketones from several stable enols.[1] We wish to report the photointerconversion of keto and enol forms of a similarly congested ketone via a biradical intermediate.

We have already reported that several α-(*o*-tolyl)acetophenones photocyclize quantitatively and in high quantum efficiency to 2-phenyl-2-indanols.[2] We have also studied the title compound (TipAP).[3] When a 0.025 M benzene solution of this ketone is irradiated at 313 nm with a 450-W mercury arc, it cyclizes to the corresponding 2-phenyl-2-indanol derivative, which was isolated and identified by its spectra.[5] Packed column and capillary GC analysis at elevated temperatures both indicated a quantitative yield of this product in a quantum yield of only 0.04. Since the other α-tolylacetophenones studied all cyclize in high quantum yields,[2] we felt that the unusually low efficiency for TipAP might indicate competitive formation of enol, as already observed for acyclic 1,5-biradicals.[6]

^1H NMR spectra of cyclopentane solutions of TipAP irradiated with 300-nm Rayonet lamps showed a weak vinyl proton resonance at δ 6.1 during the early stages of reaction. However, by the time all ketone had reacted, no vinyl signal remained and the NMR spectrum was the same as that of isolated indanol. A deaerated dioxane-d_8 solution 0.2 M in TipAP was irradiated with Rayonet 350-nm lamps until no methylene signal at δ 4.6 was visible in the NMR spectrum. The spectrum was entirely different from that of indanol product. There were two vinyl proton singlets at δ 6.10 and 5.93 in a 4:1 ratio. We assign these to the *Z* and *E* enols; the rest of the NMR spectrum is consistent with these structures.[7] From the relative intensities of the vinyl resonances and that due to the indanol methyl at δ 0.78, we estimate a 15:1 ratio of enols/indanol.

(1) Hart, H.; Giguere, R. J. *J. Am. Chem. Soc.* **1983**, *105*, 7775.

(2) Meador, M. A.; Wagner, P. J. *J. Am. Chem. Soc.* **1983**, *103*, 4484.

(3) The acronym recognizes Fuson's use of "tip" as an abbreviation for 2,4,6-triisopropylphenyl in his pioneering studies of stable enols and of TipAP itself.[4]

(4) Fuson, R. C.; Armstrong, L. J.; Chadwick, D. H.; Kneisley, J. W.; Rowland, S. P.; Shenk, W. J., Jr.; Soper, Q. F. *J. Am. Chem. Soc.* **1945**, *67*, 386.

(5) Of particular interest here are the proton NMR resonances for the OH at δ 2.14 and for the ring methyls at δ 1.36 and 0.78.

(6) Wagner, P. J.; Chiu, C. *J. Am. Chem. Soc.* **1979**, *101*, 7134.

(7) Hart and Giguere found similar chemical shifts for similar enol ethers.[1] The only other major NMR resonances were at δ 2.7 (s, 1 H, a readily exchangeable OH), 1.37 and 1.44 (2 overlapping d, 18 H, J = 10 Hz), 3.30 (septet, 3 H, J = 10 Hz), and 6.9–8.0 (complex, 7 H).

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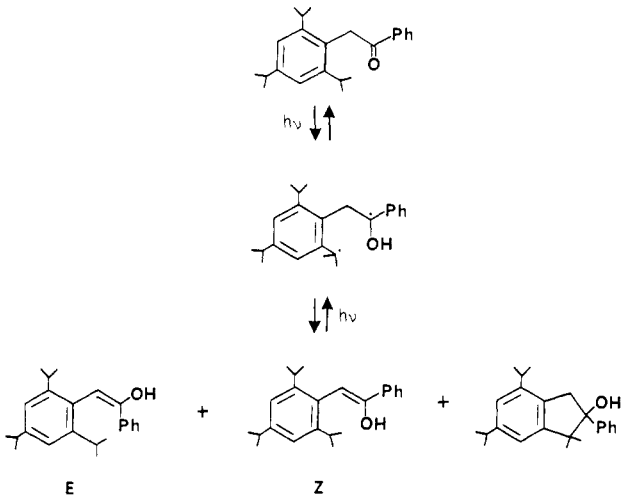
Scheme I



The sample was allowed to sit for 24 h, after which time the smaller vinyl signal had disappeared and been replaced by the ketone methylene signal at δ 4.6. The more stable enol did not disappear upon addition of 4 drops of acetic acid-d_4. The solution was then treated with 1 drop of HCl, neutralized with excess bicarbonate, evaporated, and redissolved in CCl_4. This treatment regenerated starting ketone quantitatively (Scheme I).

There are several intriguing aspects of these results. An explanation is required for the fact that the enol is a stable product at long-wavelength irradiation but not at shorter wavelengths. The solution containing only *Z* enol showed strong UV absorption below 330 nm, with λ_{max} at 270 nm, and strong fluorescence, as expected for a stilbene derivative. A portion of this solution was irradiated for 2 h with the 300-nm lamps. This process produced a complicated NMR spectrum, which included the readily identifiable singlets at δ 4.6 and 5.93 for ketone and *E* enol. The *Z* enol obviously undergoes efficient photoisomerization to *E* enol and ketone, with indanol formation being slow and irreversible.

We originally assumed that indanol formation proceeds through 1,5-biradicals formed by triplet-state δ-hydrogen abstraction.[2] We have verified the intermediacy of the expected 1,5-biradicals by laser flash spectroscopy.[8] Quenching studies indicate that triplet TipAP reacts in less than 1 ns. Since no physical decay of ketone triplets occurs so rapidly, the low quantum yield of cyclization must be due to predominant reversion of the biradical to starting ketone. In dioxane the quantum yield of enolization is very high. However, in hydrocarbon solvents the biradical apparently also returns directly to ketone. Such behavior has good precedent in the behavior of other 1,5-biradicals generated from ketones, in which hydrogen bonding to solvent impedes reketonization.[6,9]

We had considered the possibility of similar enol formation with the other α-arylacetophenones that we studied[2] and therefore reinvestigated α-mesitylacetophenone. Both capillary GC and NMR analysis of irradiated solutions revealed just indanol product, with no enol. This ketone cyclizes in a much higher quantum yield than TipAP, 0.54 with 0.5 M pyridine present. The 46% inefficiency represents biradical disproprotionation to both ketone and enol. The less hindered mesityl enol is expected to be much less stable with respect to the ketone;[4] any that may be formed apparently is too short lived to detect. The extent to which the increased steric hindrance in TipAP increases the enolization–cyclization ratio of the 1,5-biradical is remarkable, given what appears to be a not very ideal geometry for internal hydrogen transfer.

Apart from being another example of photogeneration of otherwise inaccessible enols,[10] these results put a new perspective on Hart and Giguere's results.[1] They suggested that the very low quantum yield rearrangement of the enol of α,α-dimesitylacetophenone to a mesityl vinyl ether proceeds from the ketone following enol to ketone rearrangement. Unfortunately, they did not consider the rapid and highly efficient indanol formation from mesitylacetophenone, which we had just published. Our present results indicate that their neglect of the cyclization probably does not detract from their conclusions. The increased steric hindrance afforded by a second mesityl group would not prevent triplet ketone from abstracting a δ-hydrogen but might very well prevent the resultant biradical from undergoing any significant cyclization to indanol. A steady state favoring enol probably is established rapidly, with enol ether than forming slowly, probably from ketone as suggested.[1]

Finally, the significant difference in stability between *Z* and *E* enols warrants comment. It is not surprising that the more congested *E* isomer ketonizes relatively rapidly. Fuson long ago determined that the enol from TipAP is unstable with respect to the ketone.[4] However, the congestion about the α carbon afforded by the triisopropylphenyl group obviously makes protonation of the *Z* enol quite slow, a fact that is disguised by the thermodynamics and that makes such compounds likely candidates for kinetic studies of enol acid–base reactions.[11,12]

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(8) Scaiano, J. C.; Wagner, P. J. *J. Am. Chem. Soc.*, submitted for publication.
(9) Wagner, P. J.; Scaiano, J. C., paper in preparation.
(10) Hart, H. *Chem. Rev.* **1979**, *79*, 515.
(11) Haspra, P.; Sutter, A.; Wirz, J. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 617. Chiang, Y.; Kresge, A. J.; Tang, Y. S.; Wirz, J. *J. Am. Chem. Soc.* **1984**, *106*, 460.
(12) Biali, S. E.; Rappoport, Z. *J. Am. Chem. Soc.* **1984**, *106*, 477.

Thermodynamic Control of Electron Transfer of Flavoproteins by Substrate Binding[1]

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Flavoproteins are unique in their ability to transfer either a single electron or two electrons. In fact, the same enzyme can catalyze both modes of electron transfer.[2,3] The current hypothesis is that noncovalent binding forces from the apoprotein active site regulate the redox potentials of the flavin and control the flavoprotein reactivity.[4] However, the measured redox potentials of the flavoproteins are often inconsistent with the known catalytic mechanism, e.g., lactate oxidase, L-amino acid oxidase, and electron transferring flavoprotein.[5-7] We postulate these enzymes

(1) Abbreviations: DAAO, D-amino acid oxidase; LAAO, L-amino acid oxidase; EFl_{ox}, oxidized D-amino acid oxidase; $EFl^{\cdot}$, anion radical D-amino acid oxidase; $EFl_{red}H^-$, two-electron-reduced D-amino acid oxidase unprotonated; EFl_{ox}:Benz, benzoate-bound enzyme; $EFl^{\cdot}$:Benz, one-electron-reduced benzoate-bound enzyme; $EFl_{red}H^-$:Benz, two-electron-reduced benzoate-bound enzyme unprotonated; Fl_{ox}, oxidized flavin; $Fl^{\cdot}$, one-electron-reduced flavin; $Fl_{red}H^-$, two-electron-reduced flavin unprotonated; E, apoprotein. All potentials are reported vs. the standard hydrogen electrode.
(2) Hemmerich, P.; Massey, V.; Heinrich, M.; Schug, C. "Biochemistry—Structure and Bonding"; Clark, M. T.; Ed.; Springer-Verlag: Berlin, 1982; Vol. 48 pp 93–123.
(3) Massey, V.; Hemmerich, P. *Biochem. Soc. Trans.* **1980**, *8*, 246–257.
(4) Hemmerich, P.; Massey, V. "Oxidases and Related Redox Systems"; King, T. E., Ed.; Pergamon Press: Oxford, 1982; pp 379–405.
(5) Stankovich, M.; Fox, B. *Biochemistry* **1983**, *22*, 4466–4472.
(6) Stankovich, M.; Fox, B. *Biochim. Biophys. Acta*, in press.
(7) Husain, M.; Stankovich, M.; Fox, B. *Biochem. J.*, in press.

0002-7863/84/1506-3685$01.50/0