undistorted structure. Actually the fully optimized structure for X = F has the C–C–Ti angle of 88.0°. A large $|\Delta E|$ suggests that the CF_3 complex might have an ethyl group even more distorted than has been found in the Cl complex, or possibly might rearrange to be a β-elimination product. An analysis shows that $|\Delta E|$ becomes larger, as Ti d_{xy} containing unoccupied orbitals come lower in energy, facilitating the electron delocalization from the CH^β bond. As neither σ nor π orbitals of the axial ligands can mix with the Ti d_{xy} orbital, this lowering of unoccupied orbitals has to be purely inductive.

As will be reported elsewhere, in the course of theoretical study of reaction pathways of palladium complexes,[6] we have also found a distorted ethyl group in an electron-deficient, coordinatively unsaturated three-coordinate d^8 complex $Pd(H)(C_2H_5)(PH_3)$. Its optimized geometry has an ethyl structure quite similar to that in **1**. Though such unsaturated intermediates may not be easily detectable experimentally, our theoretical finding suggests that an intramolecular CH···M interaction may be taking place more commonly than has been established.

Acknowledgment. Numerical calculations were carried out at the Computer Center of IMS. We are grateful to Professor M. L. H. Green for sending a preprint before publication.

Registry No. 1, 91084-14-9; **4**, 91084-15-0; **5**, 91084-16-1; **6** (X = H), 91084-17-2; **6** (X = F), 91084-18-3; **6** (X = CF_3), 91084-19-4.

---

(6) Obara, S.; Koga, N.; Kitaura, K.; Morokuma, K., to be published.

Excited-State Chemistry of a 1,5-Biradical: Laser-Induced Ejection of a 1,3-Biradical

J. C. Scaiano*[‡,1] and Peter J. Wagner*[†]

Division of Chemistry, National Research Council
Ottawa, Canada K1A 0R6
Chemistry Department, Michigan State University
East Lansing, Michigan 48824

Received April 3, 1984

We recently reported some new photocyclizations of α-(*o*-tolyl)acetophenones which were concluded to involve 1,5-biradical intermediates.[2] We have studied these biradicals by laser flash spectroscopy and have observed that additional products resulting from excitation of the biradicals are formed under intense laser irradiation. Although there are several examples of the photochemistry of cryogenically isolated biradicals,[3] demonstrations of discrete photochemistry of transient intermediates in solution are rare.[4,5]

The compounds that we have examined most closely are α-(2,4,6-trimethylphenyl)acetophenone (MesAP) and α-(2,4,6-triisopropylphenyl)acetophenone (TipAP). When dilute (0.02–0.20 M) solutions of these ketones are irradiated with conventional lamps, they isomerize quantitatively to mixtures of the corresponding 2-phenyl-2-indanol derivatives[2] and, in the case of TipAP, enol.[6] The products formed under low-intensity conditions are just those expected from a 1,5-biradical in thermal equilibrium with its surroundings.[7]

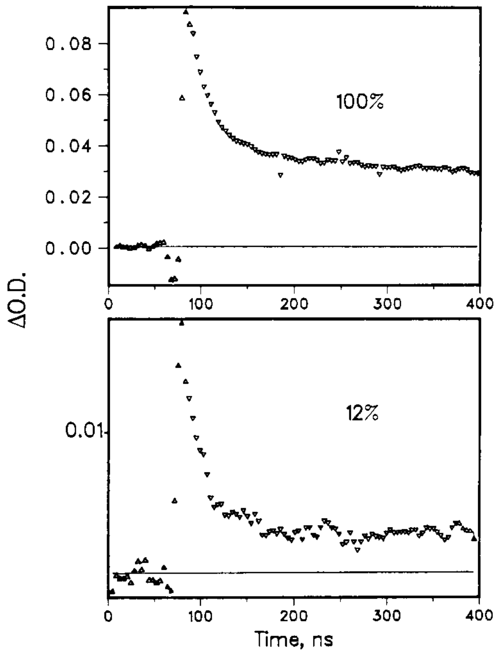


Figure 1. Computer-averaged biradical decay traces for TipAP in cyclopentane, monitored at 320 nm. Both samples were irradiated with the 308-nm excimer laser: the top one with no filter, the bottom one with a 12% neutral density filter. Note the differences in ratios of residual to maximum signal and the slow decay of the residual in the upper trace.

Quenching studies indicate triplet lifetimes shorter than 1 ns for both ketones.[2] Therefore the triplet ketones should be invisible to nanosecond flash spectroscopy.[8] Indeed they are, but the transient decay profiles observed depend strongly on laser power and wavelength. With nitrogen laser excitation at 337 nm (~10 mJ/8-ns pulse), both compounds produce transients which exhibit clean first-order decay and lifetimes in various solvents of 40–50 ns for TipAP and 15 ns for MesAP. The spectra and lifetimes of these transients are similar to those of many other phenyl ketone derived biradicals that have been reported previously, with maxima at 415 (weak) and 310–330 nm. Moreover, the transients reduce paraquat with rate constants $\geq 10^9\ M^{-1}\ s^{-1}$ in methanol, as expected for biradicals containing a ketyl radical center.[10] Therefore we are confident in assigning the 1,5-biradical structure to these transients.

When a more powerful excimer laser (~80 mJ/4-ns pulse) is used to produce 308-nm excitation, the transient absorption below 400 nm no longer decays to the preexcitation level (Figure 1). New transients with lifetimes $>10^{-5}$ s can be observed, and the relative amount of long-lived transient increases with excitation intensity. Final/total intensity ratios at 320 nm of 0.15, 0.21, 0.27, 0.36, and 0.42 were measured with neutral density filters of 12%, 25%, 40%, 70%, and 100% transmission, respectively. Time-resolved spectra of the long-lived transient absorption in cyclopentane indicate that it has two discrete components. Spectra recorded after a 10-μs delay show a sharp maximum at 329 (MesAP) or 334 nm (TipAP) characteristic of benzylic radical centers[11] and a broader underlying absorption with a maximum $\leq$300 nm. The broad band is much more prominent for TipAP than for MesAP, is the predominant absorption at delays $>100\ \mu$s, and has a profile identical with that of the enol form of TipAP.[6]

The linear increase in the fractional contribution of long-lived transient as a function of excitation intensity indicates that some biphotonic process occurs under these irradiation conditions to produce new transients. In order to see whether this biphotonic

---

[†] Michigan State University.

[‡] National Research Council.

(1) Issued as NRCC Contribution 23385.

(2) Meador, M. A.; Wagner, P. J. *J. Am. Chem. Soc.* **1983**, *105*, 4484.

(3) (a) Muller, J.-F.; Muller, D.; Dewey, H. J.; Michl, J. *J. Am. Chem. Soc.* **1978**, *100*, 1629. (b) Schmidt, S. P.; Pinhas, A. R.; Hammons, J. H.; Berson, J. A. *Ibid.* **1982**, *104*, 6822.

(4) One apparent example is: Wang, Y.; Sitzmann, E. V.; Novak, F.; Dupuy, C.; Eisenthal, K. B. *J. Am. Chem. Soc.* **1982**, *104*, 3238.

(5) The phenomenon is more common in the gas phase; see: Gooden, R.; Brauman, J. T. *J. Am. Chem. Soc.* **1977**, *99*, 1977. Hetherington, W. M., Jr.; Korenowski, G. M.; Eisenthal, K. B. *Chem. Phys. Lett.* **1981**, *77*, 275 and references therein.

(6) Wagner, P. J.; Meador, M. A. *J. Am. Chem. Soc.* **1984**, *106*, 3684.

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

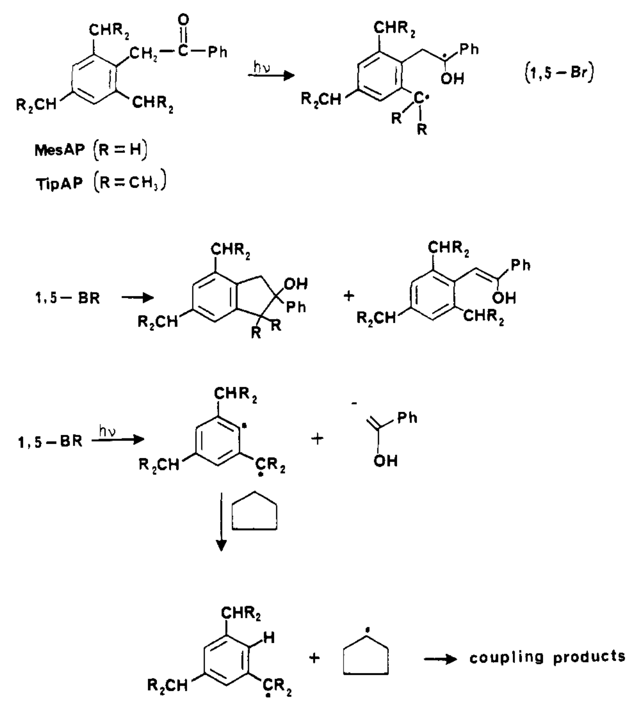
(8) The instrument used has been described elsewhere: Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7747.

(9) Small, R. D., Jr.; Scaiano, J. C. *Chem. Phys. Lett.* **1977**, *50*, 431.

(10) Small, R. D., Jr.; Scaiano, J. C. *J. Phys. Chem.* **1977**, *81*, 2126.

(11) (a) Chatgilialoglu, C.; Ingold, K. U.; Lusztyk, J.; Nazran, A. S.; Scaiano, J. C. *Organometallics* **1983**, *2*, 1332. (b) Porter, G.; Windsor, M. W. *Nature* (*London*) **1957**, *180*, 187.

Scheme I



process produces any new permanent products, we subjected 2-mL samples of deaerated cyclopentane solutions 0.02 M in ketone to 10 min of 308-nm laser excitation (6000 pulses). Capillary GC-MS analysis revealed much different product distributions from those obtained at low intensities. Several lower molecular weight products were formed from both ketones, most of which were easily identified from their MS spectra. Acetophenone was formed from both ketones. Triisopropylbenzene, tetraisopropylbicumyl, and a $C_{15}H_{22}$ product (probably 3,5-diisopropyl-1-propenylbenzene) were the major new products formed from TipAP, in total yields of 30% relative to indanol. Mesitylene, bimesityl, and mesitylcyclopentane were formed from MesAP in yields of 1–2% relative to indanol.

As summarized in Scheme I, we believe that these additional products all result from excitation and cleavage of the 1,5-biradical. It is not surprising that a biradical with an extra 90 kcal/mol of excitation energy might undergo fragmentation reactions inaccessible to the ground-state biradical. The actual fragmentation products appear to arise from the same sort of radical β-cleavage that gives Norrish type II elimination products from 1,4-biradicals.[12] Acetophenone enol presumably is formed in both cases. However, elimination of a benzyl–aryl 1,3-biradical from these 1,5-biradicals requires substantial additional excitation energy beyond that needed for a 1,4-biradical to eliminate a ground-state alkene. Given the high reactivity of aryl radicals,[13] the resulting 1,3-biradicals would be expected to abstract hydrogen rapidly from solvent to give substituted cumyl or benzyl radicals which then disproportionate and couple as usual. Our laser flash experiments indeed demonstrate the formation of benzyl radicals.

We ascribe the ability of these ketones to undergo this laser-specific photochemistry primarily to their short triplet lifetimes. The duration of the excimer laser pulses is 4–5 ns. With the triplet ketones reacting in less than 1 ns, and with the biradical products absorbing strongly at 308 nm, many of the biradicals formed by each laser pulse are also excited by the same pulse. These results are the first solution photochemistry of which we are aware in which a single light pulse sequentially excites first the reactant and then the metastable product formed from that reactant. As such, it exploits a combination of several characteristics unique to pulsed lasers, unlike other "laser vs. lamp" comparisons which utilize only high intensity[14] or monochromaticity.[15]

With MesAP, several apparent radical coupling products containing duryl, cyclopentyl, and benzoyl fragments are formed in 1% total yield with low-intensity lamps. This yield rises to 10% under excimer laser excitation. It appears that the laser pulse also excites triplet MesAP to an upper triplet which undergoes Norrish type I cleavage more efficiently than the lowest triplet. Biphotonic photochemistry involving upper excited states of reactants is well-known[16] and distinct from biradical excitation.

We are now studying other biradical systems to see how general this phenomenon may be. Two obvious questions involve the nature of the excitation and the necessity for a second benzylic center. We are also attempting to trap the postulated 1,3-biradicals, as Closs was able to do with the intermediates observed upon irradiation of 3*H*-indazoles.[17]

Acknowledgment. PJW thanks the National Science Foundation for continuing support of his research, the John Simon Guggenheim Foundation for a fellowship which facilitated this collaboration, and the National Research Council of Canada for its hospitality.

---

[12] (a) Yang, N. C.; Yang, D.-H. *J. Am. Chem. Soc.* **1958**, *80*, 2913. (b) Wagner, P. J.; Kelso, P. A.; Zepp, R. G. *Ibid.* **1972**, *94*, 7480.

[13] Scaiano, J. C.; Stewart, L. C. *J. Am. Chem. Soc.* **1983**, *105*, 3609.

[14] (a) Turro, N. J.; Aikawa, M.; Butcher, J. A., Jr.; Griffin, G. W. *J. Am. Chem. Soc.* **1980**, *102*, 5127. (b) Turro, N. J.; Aikawa, M.; Gould, I. R. *Ibid.* **1982**, *104*, 856. (c) Adam, W.; Hannemann, K.; Hossel, P. *Tetrahedron Lett.* **1984**, *25*, 181.

[15] (a) Malatesta, V.; Willis, C.; Hackett, P. A. *J. Am. Chem. Soc.* **1981**, *103*, 6781. (b) Dauben, W. G.; Phillips, R. B. *Ibid.* **1982**, *104*, 355, 5780. (c) Wilson, R. M.; Wunderley, S. W.; Walsh, T. F.; Musser, A. K.; Outcalt, R.; Geiser, F.; Gee, S. K.; Brabender, W.; Yerino, L., Jr. *Ibid.* **1982**, *104*, 4429.

[16] (a) Siegel, S.; Eisenthal, K. *J. Chem. Phys.* **1965**, *42*, 2494. (b) Brocklehurst, B.; Gibbons, W. A.; Lang, F. T.; Porter, G.; Savadatti, M. I. *Trans. Faraday Soc.* **1966**, *62*, 1793. (c) Muralidharan, S.; Ferraudi, G. *J. Phys. Chem.* **1983**, *87*, 4877.

[17] Closs, G. L.; Riemenschneider Kaplan, L.; Bendall, V. I. *J. Am. Chem. Soc.* **1967**, *89*, 3376.

Structure of Phenyllithium in Solution

L. M. Jackman* and L. M. Scarmoutzos

Department of Chemistry
The Pennsylvania State University
University Park, Pennsylvania 16802

Received March 19, 1984

Two X-ray crystallographic structures have been reported for phenyllithium. The first report is for the structure of the tetramethylethylenediamine (TMEDA) solvate, which is found to be a dimer with a planar arrangement of the C(1) and Li atoms.[1] Very recently, Hope and Power[2] have shown the existence of a tetrameric diethyl ether solvate in which the C(1) and Li atoms are at the eight corners of a distorted cube. It has been claimed,[3–5] on the basis of colligative methods, that the species in diethyl ether and tetrahydrofuran solution are dimers although there may be some indication of more extensive aggregation at high concentration (~0.8 M) in the former solvent.[6] Kinetic analyses of certain reactions of phenyllithium in the concentration range 0.005–2 M in tetrahydrofuran are consistent with a dimer, rather than a higher aggregate, in equilibrium with low concentrations of monomers.[7] Unequivocal evidence for the existence of the dimer in THF at −120 °C comes from the multiplicity of the

---

[1] Thoennes, D.; Weiss, E. *Chem. Ber.* **1978**, *111*, 3157.

[2] Hope, H.; Power, P. P. *J. Am. Chem. Soc.* **1983**, *105*, 5321.

[3] Wittig, G.; Meyer, F. J.; Lange, G. *Justus Liebigs Ann. Chem.* **1951**, *571*, 167.

[4] Talalaeva, T. V.: Rodionov, A. N.; Kocheshkov, K. A. *Dokl. Chem. (Engl. Transl)* **1964**, *154*, 47.

[5] West, P.; Waack, R. *J. Am. Chem. Soc.* **1967**, *89*, 4395.

[6] West, P. In "MTP International Reviews of Science"; Vol. 4, B. Aylett, J., Ed.; University Park Press: Baltimore, 1972; Inorganic Chemistry, Ser. One, p 1, and references cited therein.

[7] Waack, R.; West, P.; Doran, M. A. *Chem. Ind. (London)* **1966**, 1035.

0002-7863/84/1506-4627$01.50/0