

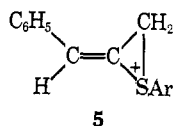
Table I. Second-Order Rate Constants for the Reaction of Deuteriophenylallenes^a

| Allene | $10^4 k_2$, $M^{-1} \text{ sec}^{-1}$ | k_H/k_D |
|-------------------|---|---------------------------------|
| $C_6H_5CH=C=CH_2$ | 9.79 ± 0.08 | |
| $C_6H_5CD=C=CH_2$ | 9.68 ± 0.18 | 1.01 ± 0.03 |
| $C_6H_5CH=C=CD_2$ | 11.67 ± 0.14 | 0.84 ± 0.02 (0.92 per D) |

^a [2] = 0.08 M; [allene] = 0.04–0.06 M; in acetic acid at 30°.

determining step. Furthermore, rate-enhancing effects by deuteration is interpreted in terms of the partial hybridization change of the carbon atom in question ($sp^2 \rightarrow sp^3$)⁸ and thus the formation of a bridged episulfonium ion. Similar secondary isotope effects have recently been observed in the sulfenylation of styrene- α -d.⁹

In conclusion, in contrast to the hydrochlorination,³ the addition of 2 to 1 takes place through the rate-determining attack on the terminal 2,3 double bond of 1 by electrophilic sulfur from the side of the phenyl group to form an episulfonium ion 4. The reason for a favorable formation of 4 as compared with an isomeric intermediate 5 is not obvious at present and further investigations will be needed. Particularly, extension of the study for other sulfenyl halides would be useful.



Acknowledgment. We wish to thank Mr. Y. Kawashima for his partial assistance in the experimental work.

(8) E.g., E. A. Halevi, *Progr. Phys. Org. Chem.*, **1**, 109 (1963).

(9) C. L. Wilkins and T. W. Reguiski, *J. Amer. Chem. Soc.*, **94**, 6016 (1972).

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On the Mechanism for Photoreduction of Benzophenone in Benzene. Evidence for Self-Quenching of Benzophenone Triplets in Solution and for H Abstraction from Benzophenone Ground State¹

Sir:

In earlier papers,² we reported on the basis of flash experiments that the relatively rapid rate of decay of benzophenone triplets ($^3\text{Ph}_2\text{CO}^*$), in solution in benzene and substituted benzenes at room temperature, is primarily due to interaction of $^3\text{Ph}_2\text{CO}^*$ with the aromatic to give a complex which ultimately decays to ground state Ph_2CO and the aromatic.

This decay mechanism is in competition with an inefficient photoreaction in these media which leads mainly to benzpinacol^{3–6} and, in the case of benzene

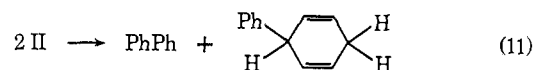
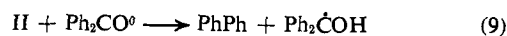
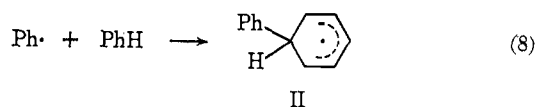
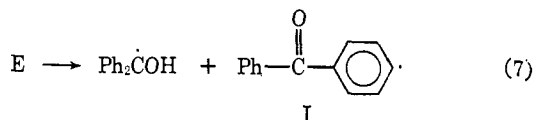
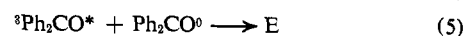
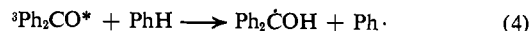
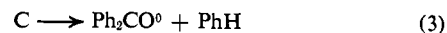
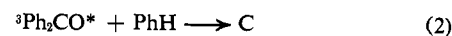
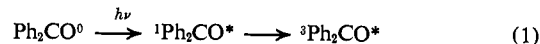
(1) Part XXXVIII of Photochemistry of Ketones in Solution. Part XXXVII: D. I. Schuster and M. D. Goldstein, *J. Amer. Chem. Soc.*, **95**, 986 (1973).

(2) (a) D. I. Schuster, T. M. Weil, and M. R. Topp, *Chem. Commun.*, 1212 (1971); (b) D. I. Schuster, T. M. Weil, and A. M. Halpern, *J. Amer. Chem. Soc.*, **94**, 8248 (1972).

(3) E. J. Bowen and E. L. A. E. de la Praudiere, *J. Chem. Soc.*, 1503 (1934).

solvent, biphenyl.^{4–7} The quantum yield for benzpinacol⁶ in aromatic solvents decreased as the lifetime of $^3\text{Ph}_2\text{CO}^*$ decreased.⁸ We report here the results of a detailed kinetic investigation on the formation of benzpinacol and biphenyl in benzene, which reveal interesting features of this fundamental reaction⁹ not previously disclosed.^{2–5,7}

Absolute and relative quantum yields for formation of benzpinacol and biphenyl⁶ as a function of benzophenone concentration [B⁰] over the range 0.01–3.0 M were measured in benzene purified by the Saltiel-Metts photochlorination procedure.^{8,10} Whereas biphenyl formation is strongly quenched by benzophenone, benzpinacol yields are barely affected.¹¹ The following mechanistic scheme is proposed.



Assuming the steady-state approximation holds for all reaction intermediates, the following relationships can be derived, if step 11 is excluded.^{12,13} The rate

(4) J. Saltiel, H. C. Curtis, and B. Jones, *Mol. Photochem.*, **2**, 331 (1970).

(5) J. Dedinas, *J. Phys. Chem.*, **75**, 181 (1971).

(6) Quantitative determination of benzpinacol yields was by rearrangement to benzpinacolone using iodine in acetic acid and analysis for the latter by gas-liquid partition chromatography (glpc) with internal standards. Analysis by glpc for biphenyl was made on the original photolysate.

(7) J. A. Bell and H. Linschitz, *J. Amer. Chem. Soc.*, **85**, 528 (1963).

(8) Full details and data, not included because of space limitations, will be given in the full publication. See also T. M. Weil, Ph.D. Dissertation, New York University, 1973.

(9) See N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1965; J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966.

(10) J. Saltiel and L. Metts, private communication of unpublished results. See also J. Saltiel, H. C. Curtis, and B. Jones, *Mol. Photochem.*, **2**, 331 (1970). This method of purification of benzene is the best of many tried by us, as indicated by the fact that it gives the longest measured lifetime of $^3\text{Ph}_2\text{CO}^*$.²

(11) Dedinas⁵ made the same observation over a much more limited concentration range. He also found very small yields ($\sim 10^{-4}$) of 4-biphenyldiphenylcarbinol.

(12) This assumes that phenylcyclohexadienyl radical (II) reacts exclusively with benzophenone⁵ and that the disproportionation reaction (11)¹³ plays little role. If step 11 were important at low [B], the yield of $\text{Ph}_2\dot{\text{C}}\text{OH}$ and derived pinacol would fall below the extrapolated line from high [B], which is not observed. The absence of tetrahydroquaterphenyls suggests dimerization of II is also not important, at least over the range [B] = 0.002–0.05 M.⁵ The fate of I is not yet defined.

(13) E. L. Eliel, S. Meyerson, Z. Welvart, and S. H. Wilen, *J. Amer. Chem. Soc.*, **82**, 2936 (1960); D. F. De Tar, R. A. J. Long, J. Rendleman, J. Bradley, and P. Duncan, *ibid.*, **89**, 4051 (1967).

constants refer to the above steps, respectively, $B = \text{benzophenone}$ and $\text{PhH} = \text{benzene}$.

$$1/\Phi_{\text{biphenyl}} = 1 + \frac{k_2}{k_4} + \frac{k_3[B]}{k_4[\text{PhH}]} \quad (\text{I})$$

$$1/\Phi_{\text{pinacol}} = \frac{1 + \frac{k_2}{k_4} + \frac{k_3[B]}{k_4[\text{PhH}]}}{1 + \frac{k_5}{2k_4(k_6 + k_7)} \frac{[B]}{[\text{PhH}]}} \quad (\text{II})$$

$$\frac{\Phi_{\text{pinacol}}}{\Phi_{\text{biphenyl}}} = 1 + \frac{k_5}{2k_4(k_6 + k_7)} \frac{[B]}{[\text{PhH}]} \quad (\text{III})$$

Equation II predicts little dependence of Φ_{pin} on $[B]$, as observed. Plots of $1/\Phi_{\text{biphenyl}}$ and $\Phi_{\text{pinacol}}/\Phi_{\text{biphenyl}}$ vs. $[B]/[\text{PhH}]$ indeed give excellent linear correlations as predicted by eq I and III.⁸ From the least-squares slopes and intercepts of the linear plots and the absolute value for k_2 determined by flash methods ($k_2 = 9.0 \times 10^3 \text{ M}^{-1} \text{ sec}^{-1}$),^{2,14} absolute values of the rate constants k_4 and k_5 and the ratio k_7/k_6 can be determined. The results are $k_4 = 16.4 \text{ M}^{-1} \text{ sec}^{-1}$, $k_5 = 1.26 \times 10^5 \text{ M}^{-1} \text{ sec}^{-1}$, and $k_7/k_6 = 10^{-2}$. The value for H abstraction from benzene by ${}^3\text{Ph}_2\text{CO}^*$, k_4 , agrees very well with the value of $19 \text{ M}^{-1} \text{ sec}^{-1}$ deduced by Saltiel, *et al.*,⁴ from lifetime data and trapping of $\text{Ph}\cdot$ by CCl_4 .

We have also directly measured the lifetime of benzophenone triplets in benzene at room temperature as a function of benzophenone concentration $[B^0]$. The single photon counting technique was utilized,^{2b} in which the phosphorescence lifetime was directly determined in purified benzene¹⁰ using highly purified benzophenone.¹⁵ The results fit the equation

$$1/\tau_{\text{obsd}} = 1/\tau^0 + k_{\text{sq}}[B^0] \quad (\text{IV})$$

where $1/\tau^0$ is the limiting decay rate in the absence of quenchers including ground-state benzophenone, and k_{sq} is the rate constant for self-quenching. The data provide values of $1/\tau^0 = (1.0 \pm 0.1) \times 10^5 \text{ sec}^{-1}$ and $k_{\text{sq}} = 1.6 \times 10^5 \text{ M}^{-1} \text{ sec}^{-1}$ in benzene.^{8,16} We have observed self-quenching of ${}^3\text{Ph}_2\text{CO}^*$ in many other solvents; *e.g.*, in purified carbon tetrachloride¹⁴ self-quenching occurs with $1/\tau^0 = 1.14 \times 10^4 \text{ sec}^{-1}$ and $k_{\text{sq}} = 3.25 \times 10^5 \text{ M}^{-1} \text{ sec}^{-1}$. Ledger and Porter¹⁷ recently reported for benzophenone in water that $k_{\text{sq}} = (1.20 \pm 0.2) \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$.¹⁸

The value of k_{sq} in benzene from the lifetime studies is in gratifying agreement with the value for k_5 (above) for reaction of ${}^3B^*$ with B^0 in benzene from quantum yield determinations. We envisage interaction of triplet- and ground-state benzophenone to give a triplet excimer E, which then partitions between deactivation (step 6) and transfer of an H atom (step 7). By analogy to other H abstraction and decay rate

(14) D. I. Schuster and T. M. Weil, *Mol. Photochem.*, **4**, 447 (1972).

(15) Benzophenone from Aldrich was purified by recrystallization, sublimation and distillation at reduced pressure, the middle fraction being collected. Analysis by glpc under a variety of conditions invariably gave only a single peak. The maximum possible level of impurities seems too low to account for the self-quenching effects.

(16) A preliminary report of self-quenching of ${}^3\text{Ph}_2\text{CO}^*$ in benzene, as determined using laser flash photolysis, has been given by L. A. Singer, R. E. Brown, and J. Parks, 163rd National Meeting of the American Chemical Society, Boston, Mass., April 1972, Abstract ORGN 23. They find $1/\tau^0 = 1.3 \times 10^5 \text{ sec}^{-1}$ and $k_{\text{sq}} = (4.4 \pm 0.1) \times 10^5 \text{ M}^{-1} \text{ sec}^{-1}$.

(17) M. B. Ledger and G. Porter, *J. Chem. Soc., Faraday Trans. 1*, **3**, 539 (1972).

(18) The possible contribution of dioxetane formation to self-quenching, as documented for acetone by Yang, *et al.*, will be examined using suitably labeled compounds; see N. C. Yang, W. Eisenhardt and J. Libman, *J. Amer. Chem. Soc.*, **94**, 4030 (1972).

constants, the experimental value of k_7/k_6 is reasonable. It should be noted that no direct spectroscopic evidence for triplet excimers was obtained in this study, and that the results do not require the intermediacy of an excimer.¹⁹

The proposed reaction of Ph_2CO with itself is confirmed by the following. Benzpinacol is formed on irradiation of high concentrations of Ph_2CO in CCl_4 , wherein Φ_{pin}^{-1} is a linear function of $[B^0]^{-1}$, and self-quenching of the triplet is also observed. Furthermore, irradiation of degassed molten neat Ph_2CO gives benzpinacol and other as yet unidentified products.

These observations also have important consequences in energy transfer experiments, *i.e.*, where benzophenone or other ${}^3n, \pi^*$ ketones are used as triplet sensitizers in benzene. In the case where $[B^0] \gg [A^0]$, the experimental arrangement recommended to minimize light absorption by the substrate and complications due to direct photolysis of A, self-quenching may compete with energy transfer. Even if the efficiency of triplet formation of a reactive triplet of A on direct photolysis is 100%, Φ_{sens}^A will often be less than Φ_{direct}^A . Observed inefficiencies on sensitization need not be due to the relative triplet excitation energies of B and A, nor to the efficiency of intersystem crossing of A, but rather may be due to the competing self-quenching process, as is well documented in the case of ${}^3\pi, \pi^*$ sensitizers.^{1,20} Thus, extending the warning given by Chapman,²⁰ the results of triplet sensitization experiments using ${}^3n, \pi^*$ or ${}^3\pi, \pi^*$ sensitizers, particularly in "inert" solvents such as benzene, must be interpreted with great caution. Furthermore, considerable revision may be required of interpretations of sensitization data already in the literature.

Acknowledgment. The authors thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for a grant in support of this work. They also thank Professor Arthur Halpern of this department for permission to use his single photon counting apparatus and for assistance with the experiments.

(19) Analogously, the interaction of ${}^3\text{Ph}_2\text{CO}^*$ with benzene could also be described formally in terms of partitioning of an exciplex between decay and H transfer, equally consistent with the kinetics.

(20) O. L. Chapman and G. Wampfler, *J. Amer. Chem. Soc.*, **91**, 5390 (1969). See also P. S. Engel and B. M. Monroe, *Advan. Photochem.*, **8**, 245 (1971); D. R. Kemp and P. de Mayo, *J. Chem. Soc., Chem. Commun.*, 233 (1972).

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Generalized Frontier Orbitals of Alkenes and Dienes. Regioselectivity in Diels-Alder Reactions

Sir:

Applications of perturbation molecular orbital theory^{1,2} to reactivity in cycloadditions have evolved from

(1) E. Heilbronner and H. Bock, "Das HMO-Modell und Seine Anwendung," Verlag Chemie, GmbH, Weinheim/Bergstr., Germany, 1968; M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969; R. Hoffmann, *Accounts Chem. Res.*, **4**, 1 (1971).

(2) K. Fukui, *Fortschr. Chem. Forsch.*, **15**, 1 (1970); *Accounts Chem. Res.*, **4**, 57 (1971).