keeping with the *trans* nature[3] of the *cis*-aconitase system. The stereochemistry of the Krebs cycle from fumaric acid to isocitric acid may now be traced (Fig. 1) utilizing the finding[11,12] that the 3-monodeuterio-L-malic acid (from the fumarase re-reaction) gives, biochemically, isocitric acid lacking deuterium and utilizing our previously suggested[3] scheme for the *cis*-aconitase system.

[11] (a) S. Englard, *Fed. Proc.*, **18**, 222 (1959). (b) S. Englard, personal communication. We wish to thank Dr. Englard for sending us his manuscript prior to publication.

[12] The other results, Ref. 11, are also consistent with the scheme presented in Fig. 1.

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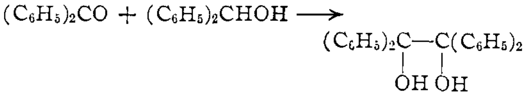
THE ROLE OF A TRIPLET STATE IN THE PHOTOREDUCTION OF BENZOPHENONE

Sir:

Irradiation of benzene solutions of benzophenone and benzhydrol with near ultraviolet light produces benzpinacol stoichiometrically according to equation (1).



$$(C_6H_5)_2CO + (C_6H_5)_2CHOH \longrightarrow (C_6H_5)_2\underset{OH}{C}-\underset{OH}{C}(C_6H_5)_2 \qquad (1)$$

Experiments were carried out using a collimated beam from a Westinghouse SAH800-C Mercury arc filtered to give a band having a maximum at 3660 Å. and a band pass of 500 Å. Photolysis rates were measured by spectrophotometric determination of residual benzophenone and by titration of the pinacol with lead tetraacetate.[1] Quantum yields were based upon uranyl oxalate actinometry although the reaction of benzophenone with 2-propanol[2] was used as a secondary standard. Solutions were degassed to 10^{-3} mm. A series of experiments was run using 0.1 *M* benzophenone and varying concentrations of benzhydrol.[3] Graphical analysis showed the $1/\Phi$ was a linear function of $1/[BH_2]$. This relationship indicates a simple competition between deactivation of the chemically active state and its reaction with benzhydrol. Since the intercept of the plot is one, physical quenching by benzhydrol must be negligible. The mechanism shown accounts for these facts.

$$B + h\nu \xrightarrow{n \rightarrow \pi} B^1 \text{ (singlet)} \qquad (2)$$

$$B^1 \longrightarrow B^3 \text{ (triplet)} \qquad (3)$$

$$B^3 \xrightarrow{k_d} B \text{ (all deactivation steps)} \qquad (4)$$

$$B^3 + BH_2 \xrightarrow{k_r} 2(C_6H_5)_2\dot{C}OH \longrightarrow \text{Benzpinacol} \qquad (5)$$

Application of steady state kinetics to the concentrations of excited states gives the rate law.

$$\frac{1}{\Phi} = 1 + \frac{k_d}{k_r[BH]_2}$$

From the slope of the plot of $1/\Phi$ *vs.* $1/[BH_2]$, the value of k_d/k_r is found to be 0.050. *Consideration of this number compels the conclusion that the triplet state is responsible for the chemical reaction.* The largest value that k_r can be imagined to have is 10^9 liter mole^{-1} sec.$^{-1}$, the diffusion controlled rate.[4] This gives an upper limit of 5×10^7 sec.$^{-1}$ for k_d. Fluorescence rate constants for singlet states[6] are believed to be of the order of 10^8 sec.$^{-1}$ Since benzophenone solutions have no visible fluorescence, the actual rate of non-radiative quenching of the lowest singlet state must be at least 10^{10} sec.$^{-1}$. It is clear that some longer lived state must be involved in the measured competition.

Reaction (5) actually must be much slower than diffusion-controlled since a substantial isotope effect is observed when α-deuteriobenzhydrol is used as the hydrogen donor. The value of $k_d/k_{r(D)}$ is 0.133, which indicates that $k_{r(H)}/k_{r(D)}$ is 2.7.

In summary, the results indicate that intersystem crossing to a triplet state must be complete, and that the triplet is responsible for chemical reaction.

Acknowledgments.—This work was supported by grants from the Film Department of the du Pont Company and from the National Science Foundation.

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[1] R. Criegee, *Ber.*, **64B**, 264 (1931).

[2] J. N. Pitts, R. L. Letsinger, R. P. Taylor, J. M. Patterson, G. Rechtenwald and R. B. Martin, THIS JOURNAL, **81**, 1068 (1959).

[3] Light absorption was essentially complete. Other experiments show that the quantum yields are independent of both light intensity and ketone concentration.

[4] Calculated by the method of Schultz[5] using a diffusion coefficient of 10^{-5} cm.^{2} sec.$^{-1}$ for benzophenone and benzhydrol in benzene.

[5] G. V. Schultz, *Z. physik. Chem.*, **8**, 284 (1956).

[6] M. Kasha, *Disc. Faraday Soc.*, **9**, 14 (1950). However, see J. W. Sidman, *Chem. Revs.*, **58**, 689 (1958), for a possible lower estimate.

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THE ADDITION OF NITRONES TO OLEFINS. A NEW ROUTE TO ISOXAZOLIDINES

Sir:

The isolation of *cis*-N-methyl-3-oxa-2-azabicyclo[3.3.0]octane (III) from the pyrolysis of a mixture of the isomeric N-methyl-α-pipecoline oxides[1] suggests that the unsaturated nitrone I may be an intermediate. We have therefore investigated the cyclization of I and a homolog.

Monofunctional aliphatic nitrones have not been reported, since their preparations generally lead to aldol-type dimers.[2] Nevertheless, the reactive nitrone linkage of I, generated *in situ*, might well undergo intramolecular addition to the terminal olefin group.

Oxidation of an ether solution of N-methyl-N-5-hexenylhydroxylamine (V)[1] with excess mercuric oxide afforded III, characterized as its hydrogen oxalate (m.p. and m.m.p. 82–82.5°) and by comparison of the infrared spectra,[1] in 24% yield.

[1] A. C. Cope and N. A. LeBel, Abstracts of Papers, 133rd Meeting, American Chemical Society, San Francisco, California, April 13–18, 1958, p. 62-N: THIS JOURNAL, in press.

[2] R. Bonnett, R. F. C. Brown, V. M. Clark, I. O. Sutherland and A. Todd, *J. Chem. Soc.*, 2094 (1959), present a summary of the various dimeric structures for nitrones including aldolization structures, and report the syntheses of several monomeric alicyclic nitrones. *Cf.* also R. F. C. Brown, V. M. Clark, I. O. Sutherland and A. Todd, *ibid.*, 2109 (1959); R. F. C. Brown, V. M. Clark, M. Lamchen, B. Sklarz and A. Todd, *Proceedings of the Chemical Society*, 169 (1959).