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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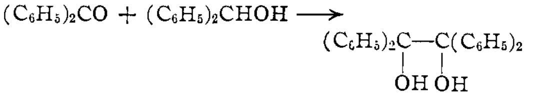
RECEIVED SEPTEMBER 25, 1959

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).



$$(C_6H_5)_2CO + (C_6H_5)_2CHOH \longrightarrow \underset{\mathrm{OH}}{(C_6H_5)_2C}\!-\!\underset{\mathrm{OH}}{C(C_6H_5)_2} \qquad (1)$$

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 $1/[\mathrm{BH_2}]$. 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.

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

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

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

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

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

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

From the slope of the plot of $1/\Phi$ *vs.* $1/[\mathrm{BH_2}]$, 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:

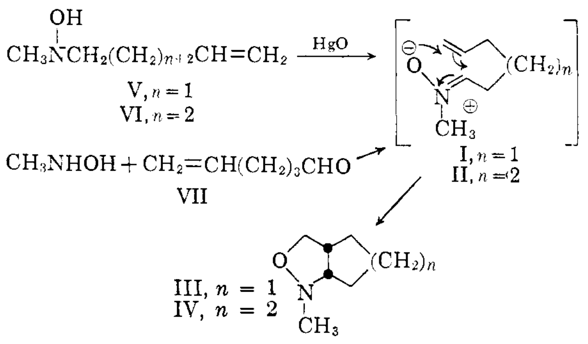
The isolation of *cis*-N-methyl-3-oxa-2-azabicyclo[3.3.0]octane (III) from the pyrolysis of a mixture of the isomeric N-methyl-α-pipecoline oxides[1] suggests that the unsaturated nitrone I may be an intermediate. We have therefore investigated the cyclization of I and a homolog.

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).



In addition, 5-hexenal (VII) was isolated and characterized as its 2,4-dinitrophenylhydrazone.

The oxidation of dialkylhydroxylamines proceeds through several intermediates to give nitrones.[2,3] Isolation of III and VII again demonstrates the preferential formation of the most highly substituted nitrone groups in such oxidations.[2]

In order to validate the occurrence of an intermediate nitrone (*e.g.*, as opposed to a radical anion),[3] we have investigated a second route to I and III. Nitrous acid deamination of a mixture of the 3-aminocyclohexanols[4] furnished 5-hexenal (VII) (38%), b.p. 118–121°. Equimolar quantities of VII and freshly prepared N-methylhydroxylamine gave after purification a 40% yield of the isoxazolidine III.

As additional structure proof, III was reduced with zinc and acetic acid to an oily aminoalcohol. The oxalate melted at 180–181° and did not depress the melting point of a sample of the oxalate of synthetic N-methyl-*cis*-2-hydroxymethylcyclopentylamine[1,5] (m.p. 181–181.5°).

When applied to the next higher homolog VI,[1] the mercuric oxide oxidation afforded *cis*-N-methyl-8-oxa-7-azabicyclo[4.3.0]nonane (IV) (18 %), b.p. 70–72° (15 mm.).[5] The infrared spectrum of IV was free of bands in the OH, NH, carbonyl or carbon–carbon double bond region. It formed a hydrogen oxalate, m.p. 95–95.8°.[5] Treatment with zinc and acetic acid produced an aminoalcohol, the infrared spectrum of which was identical with that of N-methyl-*cis*-2-hydroxymethylcyclohexylamine (m.p. 45–46°, hygroscopic)[5] prepared by lithium aluminum hydride reduction of the *N-cis*-2-carboxycyclohexylformamide,[5,6] m.p. 200–201°. Both the reduction product and the synthetic aminoalcohol formed hydrogen oxalates melting at 104–105° (m.m.p. 103–105°). From the crude oxidation mixture 6-heptenal as its 2,4-dinitrophenylhydrazone, m.p. 95.5–96°,[5] was isolated. Identity was established by reduction of its diethyl acetal and conversion to heptanal-2,4-dinitrophenylhydrazone.

In addition to applications to other systems,[7] we are investigating various oxidation procedures as preparative routes to the isoxazolidines themselves and the unsaturated aldehydes which can subsequently react with the appropriate monoalkylhydroxylamine.

Acknowledgment.—We are grateful to the Research Corporation for a generous grant in support of this work.

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[3] D. H. Johnson, M. A. T. Rogers and G. Trappe, *J. Chem. Soc.*, 1093 (1956).

[4] R. R. Burford, F. R. Hewgill and P. R. Jefferies, *ibid.*, 2937 (1957).

[5] Satisfactory analytical results have been obtained for all of the new compounds described herein.

[6] Prepared by formylation of *cis*-2-aminocyclohexanecarboxylic acid. We wish to thank Professor A. C. Cope for informing us of a procedure for the preparation of this acid *via* the reduction of anthranilic acid.

[7] We have been informed by Professor R. Huisgen (private communication) that he and his co-workers have effected the additions of certain stable nitrones to strained olefins such as norbornylene.

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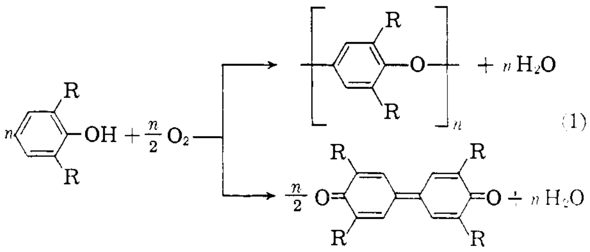
POLYMERIZATION BY OXIDATIVE COUPLING

Sir:

We wish to report the discovery of a new oxidative coupling reaction leading to the preparation of high molecular weight 2,6-di-substituted-1,4-phenylene ethers. In the past only low molecular weight 2,6-di-substituted-1,4-phenylene ethers have been prepared. Thus, Dewar and James[1] in an extension of earlier work reported by Süs and co-workers,[2] attempted the synthesis of poly-2,6-di-substituted-1,4-phenylene ethers by the thermal decomposition of substituted benzene-1,4-diazooxides but only with limited success. More recently, Staffin and Price[3] have extended earlier work reported by Hunter and co-workers,[4] and have prepared low molecular weight poly-2,6-dimethyl-1,4-phenylene ether by oxidative displacement of the bromine in 4-bromo-2,6-dimethylphenol.

Our reaction employs a 2,6-di-substituted phenol and is carried out at room temperature by merely passing oxygen through a solution of the phenol in an organic solvent containing an amine and a copper(I) salt as a catalyst. The stoichiometry is as shown in equation 1.



(1)

When the substituent groups are small, as in 2,6-dimethylphenol, carbon-oxygen coupling occurs and linear polyphenylene ethers with intrinsic viscosities up to 3.4 decil./g. have been obtained. With bulky groups, as in 2,6-di-*tert*-butylphenol, carbon–carbon coupling occurs and the diphenoquinone is the sole product. In intermediate cases

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[1] M. J. S. Dewar and A. N. James, *J. Chem. Soc.*, 917 (1958).

[2] O. Süs, K. Möller and H. Heiss, *Ann.*, **598**, 123 (1956).

[3] G. Staffin and C. C. Price, Fifth Joint Army-Navy-Air Force Conference on Elastomer Research and Development, October 15–17, 1958, Dayton, Ohio. See *Rubber World*, **139**, 408 (1958), for an abstract of this paper.

[4] W. H. Hunter and M. J. Morse, THIS JOURNAL, **55**, 3701 (1933), and earlier papers.