and medium-intensity absorptions, especially in the 10,000–25,000-cm^{-1} range, again points to a system of electronic levels appropriate for a square-pyramidal $Co(CN)_5^{3-}$. At least two reasonable assignment schemes exist based on the splitting diagram shown in Figure 2.[10] Contrariwise, simple extrapolation of electronic levels from analogous trigonal bipyramidal complexes indicates that an approximately D_{3h} $Co(CN)_5^{3-}$ would not exhibit electronic bands between 8000 and 20,000 cm^{-1}.[11] Thus, the combined esr and optical spectral data require a square-pyramidal structure for $Co(CN)_5^{3-}$ in solution.

[10] We tentatively suggest the following assignments: 10,350 cm^{-1}, $^2A_1 \rightarrow {}^2B_1$ ($z^2 \rightarrow x^2 - y^2$); 16,200 cm^{-1}, doublet → quartet; 23,300 cm^{-1}, $^2A_1 \rightarrow {}^2B_2$ ($xy \rightarrow z^2$); 31,700 cm^{-1}, $^2A_1 \rightarrow {}^2A_2$ ($xy \rightarrow x^2 - y^2$). The intense bands at 35,700 and 43,300 cm^{-1} probably represent allowed $M \rightarrow \pi^*(CN^-)$ transitions.

[11] The observed ligand field bands in trigonal bypyramidal $Ni[PPh(OR)_2]_3(CN)_2$ complexes (B. B. Chastain, R. Pruett, E. A. Rick, and H. B. Gray, to be published) are at approximately 25,000 and 29,000 cm^{-1}. In addition, there is very little difference in the positions of the lowest ligand-field bands in $Ni(CN)_4^{2-}$ and $Ni[PPh_2(OR)]_2(CN)_2$. Thus, we may expect a trigonal bypyramidal $Co(CN)_5^{3-}$ to have an $e'' \rightarrow e'$ band below 8000 cm^{-1} and an $e' \rightarrow a_1'$ band at about 25,000 cm^{-1}.

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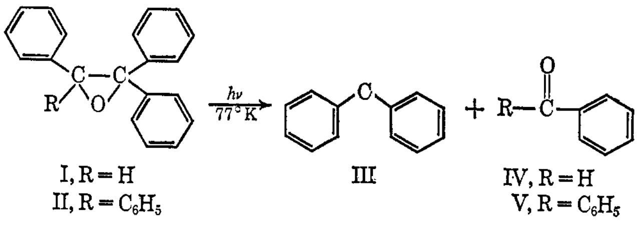
Direct Evidence for the Formation of Diphenylmethylene in the Photolysis of Triphenyl- and Tetraphenyloxirane

Sir:

Recent studies have shown that the photolytic reactions of oxiranes can give rise to products which have been interpreted in terms of carbene (methylene) intermediates.[1] We wish to report *convincing* direct evidence for the formation of diphenylmethylene (III) in the photolysis of triphenyloxirane (I) and of tetraphenyloxirane (II) (Scheme I).

Scheme I



Irradiations were carried out in methylcyclohexane glass at 77°K. Typically, a solution (10^{-4} *M*) of the oxirane was irradiated[2] with 2537-A light for 5–30 sec. The photolysis products were identified by a combination of epr and luminescence techniques.

The total luminescence spectrum[3] obtained after II was irradiated is shown in Figure 1. By use of a phosphoroscope it was possible to show that part of this luminescence was phosphorescence which corresponded closely with that of benzophenone, and the remaining luminescence was identified as the *fluorescence* previously reported for diphenylmethylene (III).[4]

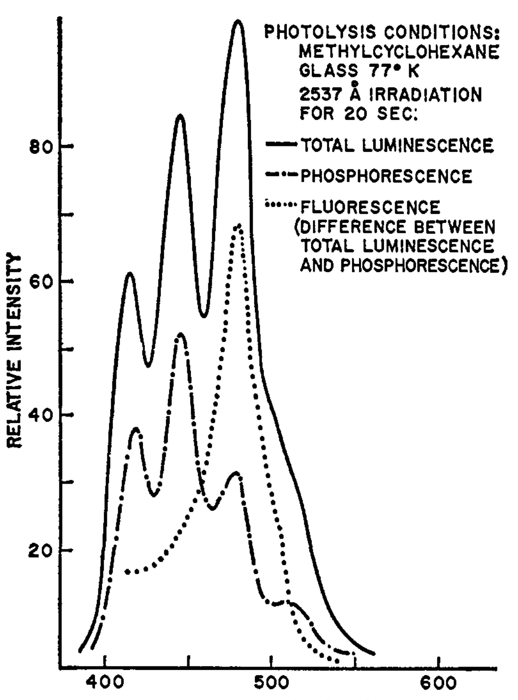


Figure 1. Photolysis of tetraphenyloxirane: luminescence of products.

Further confirmation for the presence of III was obtained from epr studies. The epr absorption spectrum of the same photolyzed solution which had been used in the luminescence measurements was attributed to a ground-state triplet molecule with zero-field parameters D/hc = 0.4053 cm^{-1}, E/hc = 0.0190 cm^{-1}. The comparable values for these parameters which had been obtained for III (in benzophenone) are: (a) randomly oriented sample:[5] D/hc = 0.4055 cm^{-1}, E/hc = 0.0194 cm^{-1}; and (b) single crystal:[6] D/hc = 0.40505 cm^{-1}, E/hc = 0.01918 cm^{-1}.

When a solution of I was photolyzed, the phosphorescence of benzaldehyde was detected as well as the fluorescence of III. The epr of III was detected with zero field parameters D/hc = 0.4056 cm^{-1}, E/hc = 0.0188 cm^{-1}. However, no epr absorption signals corresponding to those of phenylmethylene[7] were detected and no phosphorescence which could be ascribed to benzophenone was observed. This is to be contrasted with the results obtained in solution where products which could be derived from both phenyl- and diphenylcarbene were observed.[1a]

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[1] (a) H. Kristinnson and G. W. Griffin, *Angew. Chem. Intern. Ed. Engl.*, 4, 868 (1965); *Angew. Chem.*, 77, 859 (1965); (b) H. Kristinnson and G. W. Griffin, *J. Am. Chem. Soc.*, **88**, 1579 (1966); (c) H. Kristinnson, *Tetrahedron Letters*, 2343 (1966); (d) H. Kristinnson, R. A. Mateer, and G. W. Griffin, *Chem. Commun.*, 415 (1966); (e) G. W. Griffin and co-workers, unpublished work.

[2] An air-cooled Rayonet Chamber Reactor (Southern New England Ultraviolet Co., Middletown, Conn.) was used as the light source equipped with 16 8-w low-pressure mercury lamps.

[3] The luminescence spectra were recorded on an Aminco-Kiers spectrophotofluorometer (American Instrument Co., Silver Spring, Md.).

[4] (a) W. A. Gibbons and A. M. Trozzolo, *J. Am. Chem. Soc.*, **88**, 172 (1966); (b) A. M. Trozzolo and W. A. Gibbons, *ibid.*, **89**, 239, (1967).

[5] A. M. Trozzolo, E. Wasserman, and W. A. Yager, *J. Chim. Phys.*, **61**, 1663 (1964); E. Wasserman, A. M. Trozzolo, W. A. Yager, and R. W. Murray, *J. Chem. Phys.*, 40, 2408 (1964).

[6] R. W. Brandon, G. L. Closs, and C. A. Hutchison, Jr., *ibid.*, 37, 1878 (1962); R. W. Brandon, G. L. Closs, C. E. Davoust, C. A. Hutchison, Jr., B. E. Kohler, and R. Silbey, *ibid.*, **43**, 2006 (1965).

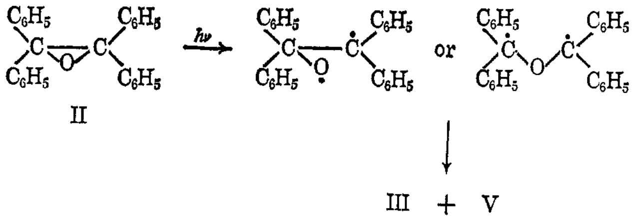
[7] A. M. Trozzolo, R. W. Murray, and E. Wasserman, *J. Am. Chem. Soc.*, **84**, 4990 (1962).

The effects of variations in wavelength and irradiation times also are noteworthy. Both I and II do not absorb light having a wavelength greater than 3000 A. However, when the sample was irradiated for only a short time ($\sim$5 sec) with 2537-A light, cleavage occurred with the production of III and the corresponding carbonyl compound (IV or V), and subsequent irradiation with 3500-A light caused further photolysis, suggesting that sensitization was occurring. Photosensitizers such as benzophenone and acetophenone appeared qualitatively to give increased yields of III over those obtained in unsensitized photolyses. Such effects had not been observed earlier in previous work in solution.[1e]

These experimental data, besides confirming the previous postulation that methylene intermediates may be produced upon photolysis of oxiranes, also show that oxiranes provide another set of precursors for the epr study of methylenes, in addition to the diazo compounds[8] and bisazides[9] which have been used previously.

The mechanism by which the methylene is formed in the photolysis of these oxiranes is of some interest. The present work does not exclude a two-step homolytic process such as that formulated in Scheme II.

Scheme II



However, in epr studies in the magnetic field region where monoradicals or triplets with smaller spin-spin interaction (such as would be anticipated for VI) might exhibit resonance absorption, only a relatively weak signal was observed. Thus, one is tempted to conclude that if VI or VII is formed in a rigid glass, it has a rather short lifetime, and either reverts to II or fragments to III and V. Furthermore, in view of recent observations[10] on the solvolytic photochemical cleavage of cyclopropanes (a reaction which competes with the fragmentation to carbene) we should consider an ionic intermediate perhaps formed by initial heterolytic cleavage or in a later step from VI or VII. Further studies on the mechanism of the photolysis of oxiranes are continuing.[11]

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(8) See ref 4b for bibliography.

(9) L. Barash, Abstracts of Papers, 150th National Meeting of the American Chemical Society, Atlantic City, Sept 1965, p 54S; L. Barash, E. Wasserman, and W. A. Yager, to be published.

(10) C. S. Irving, R. C. Petterson, I. Sarkar, H. Kristinsson, C. S. Aaron, G. J. Boudreaux, and H. W. Griffin, *J. Am. Chem. Soc.*, **88**, 5675 (1966).

(11) Note Added in Proof. According to P. Petrellis (unpublished results), diphenylcarbene is formed also in the photolysis of 2-methoxy-2,3,3-triphenyloxirane. The carbene was trapped in methanol as the methyl ether of benzhydrol. Methyl benzoate, the accompanying fragment, was isolated by glpc and compared with authentic material. The presence of III was detected by epr and luminescence studies. These data confirm and are consistent with the results of T. I. Temnikova and I. P. Stepanov, *Zh. Organ. Khim.*, **2**, 1525 (1966); *Chem. Abstr.*, **66**, 54820*y* (1967).

Inversion of Positional Reactivity Order and Two Mechanisms of Hydrogen–Deuterium Exchange for Pyridine

Sir:

Considerable confusion has existed regarding the positional reactivity order of hydrogen–deuterium exchange for pyridine. Relative rates of deprotonation at positions 4, 3,5, and 2,6 are reported to be 10^3, 10^2, and 1, respectively, in ND_3–$NaND_2$ (−25°).[1] These deprotonations were said to proceed by way of an anionic intermediate resulting from the addition of amide ion to substrate. By contrast, pyridine is reported not to exchange in D_2O, while in D_2O–NaOD (220°) exclusive deprotonation at the 2,6 positions is said to result.[2,3]

We wish to present a clarified picture of H–D exchange for pyridine. We have evidence for an inversion in the relative positional reactivity order in aqueous solution and for the existence of two mechanisms of deprotonation. In DCl or D_2O pyridine undergoes exchange at measurable rates only at the 2,6 positions. In NaOD the protons at all positions exchange, but in the order $4 > 3{,}5 > 2{,}6$.

For kinetic runs in acidic solution, pyridine and aliquots of DCl were mixed, sealed in glass tubes, and heated (218°). Analysis of the recovered pyridine by nmr showed exchange only at positions 2,6. The pseudo-first-order rate constants,[4] k, for this exchange are expressed as a function of acidity in Figure 1.[5] The resulting curve indicates that the rate of exchange at position 2 or 6 increases as the amount of unprotonated pyridine increases. The rate then levels and approaches that in neutral D_2O. We suggest that the mechanism for this exchange involves attack of deuterioxide ion on pyridinium ion to give ylide I. This ylide then captures a deuteron to produce exchanged pyridine (path 1). Support for this path is found in separate experiments with N-methylpyridinium chloride in D_2O. At 218° measurable exchange

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(1) I. F. Tupitsyn and N. K. Semenova, *Tr. Gos. Inst. Prikl. Khim.*, **49**, 120 (1962); *Chem. Abstr.*, **60**, 6721*c* (1964).

(2) Y. Kawazoe, M. Ohnishi, and Y. Yoshioka, *Chem. Pharm. Bull.* (Tokyo), **12**, 1384 (1964).

(3) We are unable to repeat these observations.

(4) Although deprotonation takes place consecutively at positions 2 and 6, for example, all rate constants in this work represent values for deprotonation at a single position. It follows from the usual kinetic treatment of consecutive, first-order reactions such as

$$\text{H-2, H-6} \xrightarrow{2k} \text{H-2, D-6} \xrightarrow{k} \text{D-2, D-6}$$

that the rate constant, k, for reaction at a single position is given by the expression $\ln ([\text{H-2, H-6}] + [\text{H-2, D-6}]/[\text{H-2, H-6}]_0) = -kt$. The concentration ratio in this expression was determined directly by nmr.

(5) That log [pyridine]/[pyridinium ion] provides a measure of solution acidity follows from the expression pD = log [pyridine]/[pyridinium ion] + pK_a. The pK_a value is known only approximately under the conditions of our experiments, but the ratio of free to protonated substrate is accurately known from the concentrations of pyridine and DCl employed.