links four anions together. The third potassium ion, K(2), is unusual because, while it is also coordinated to three outer oxalato oxygens, it is not coordinated to water but instead to four inner oxalato oxygens, three of which are in the same anion. K(2) is thus located directly above a triangular plane of the coordination octahedron of rhodium, resulting in a very short Rh–K distance of 3.480 Å. This distance may be compared to the average Rh–O distance to the outer oxygen atoms in the same anion of 3.957 Å. This phenomenon of K^+ penetrating into the coordination sphere of the anion had been observed previously in the structures of $K_3[Fe(C_2O_4)_3]\cdot 3H_2O$,[6] $K_3[Ir(C_2O_4)_3]\cdot 2H_2O$,[7] and $K_3[Rh(C_2O_4)_3]\cdot 2H_2O$.

The water molecules are tetrahedrally surrounded. There are five crystallographically independent water molecules in the structure, which can be differentiated into three kinds: (a) $H_2O(1)$ and $H_2O(3)$ are surrounded by two potassium ions and two oxygen atoms (or other water molecules); (b) $H_2O(2)$ and $H_2O(4)$ are surrounded by one potassium ion and three oxygen atoms (or other water molecules); and (c) $H_2O(5)$, which represents the 0.5 H_2O in the stoichiometric formula and is found to be statistically disordered, is surrounded by four water molecules.

The structure reported here is capable of providing an alternative interpretation of the nmr and dehydration results noted above, and the reaction kinetics of the complex can be explained[8] without the assumption of a monoaquated species preexisting in the solution.

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(6) P. Herpin, *Bull. Soc. Fr., Mineral. Cristallogr.*, **81**, 245 (1958).
(7) P. Herpin, *ibid.*, 81, 201 (1958).
(8) (a) L. Damrauer and R. M. Milburn, *Proc. Int. Conf. Coord. Chem., 1966*, **12**, 38 (1966); (b) submitted for publication.

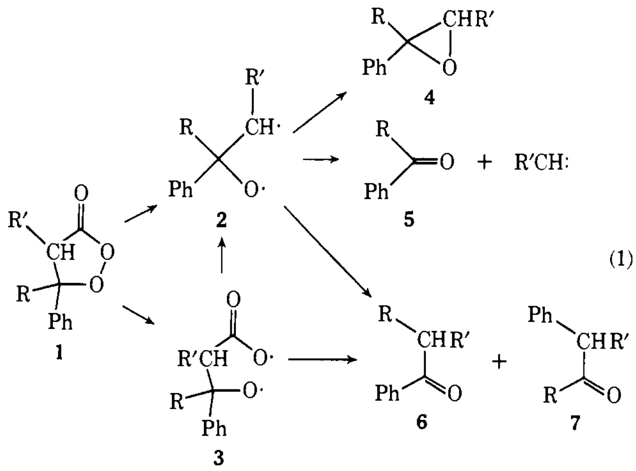
Bonita C. Dalzell, Klaas Eriks*
Department of Chemistry, Boston University
Boston, Massachusetts 02215

Received May 1, 1971

Cyclic Peroxides. VI.[1] Oxatrimethylene Diradicals *via* Photodecarboxylation of β-Peroxylactones[2]

Sir:

In view of the fact that photodecarboxylation of malonoyl peroxide[1] leads to α-lactones and mercury-sensitized photolysis of γ-butyrolactone[3] produces trimethylene diradicals which preferentially cyclize into cyclopropane, it was expected that β-peroxylactone **1** should photodecarboxylate to give the 1-oxatrimethylene diradical **2**. Diradical **2** should cyclize into epoxide **4**, but alternatively it could fragment into ketone **5** and methylene or rearrange into ketones **6** (alkyl migration) and **7** (phenyl migration), as illustrated in eq 1.[4] In this communication we report on the photolysis of peroxylactones **1a** (R = Me; R′ = H) and **1b** (R = Ph; R′ = Me) and show that indeed the oxatrimethylene diradical **2** is the precursor to the photoproducts rather than the 3-keto-1,5-dioxapentamethylene diradical **3**.[5]



(1)

The volatile products of the photolysis[6] of **1a** are summarized in Table I. Also, approximately 20% of unidentified residue was formed, providing a product balance of better than 96%. Control experiments showed that epoxide **4a** and ketones **5a**, **6a**, and **7a** were stable toward the photolysis conditions of **1a**, indicating that these photoproducts are primary products and do not interconvert during photolysis. Furthermore, photolysis of **1a** in the presence of each of the photoproducts did not alter the proportions of the products, suggesting that no photosensitized decomposition of **1a** by the products took place. Molecular oxygen had no effect on the product composition. When the photolysis was carried out in benzene which contained 1 *M* amounts of piperylene, the same products were formed (Table I).

The photolysis of (*S*)-(−)-**1b**, for which the preparation and configurational assignment were described previously,[5] gave 1,1-diphenylepoxypropane (**4b**), benzophenone (**5b**), α-methyldeoxybenzoin (**7b**), and benzhydryl methyl ketone (**8**), besides major amounts of intractable residue. It proved difficult to isolate epoxide **4b** and for that reason all volatile components were sublimed directly out of the photolysis mixture, the sublimate hydrolyzed with 0.1 *N* perchloric acid, and the 1,1-diphenyl-1,2-propanediol (**9**) isolated by fractional crystallization. Within experimental error, diol **9** and ketone **7b**, the only potentially optically active volatile photoproducts, showed zero rotation. For the purpose of control experiments to test the photostability of epoxide **4b**, the latter was prepared by converting (*R*)-(−)-*n*-butyl lactate to diol **9**, mp 92.5–93.5°, $[\alpha]^{26}D$ −150.2° in benzene (lit.[7] mp 92–93°, $[\alpha]^{26}D$ −149.8° in benzene) by treatment with excess phenylmagnesium bromide. The monobenzenesulfonate of diol **9** (mp 82–83°, $[\alpha]^{26}D$ −32.8° in benzene), prepared in 75% yield by treatment of **9** with benzenesulfonyl chloride in pyridine, on reaction with sodium hydride in dimethoxyethane gave a 76% yield of epoxide **4b** (mp 64–65°, $[\alpha]^{26}D$ +21.7° in benzene). To check the configuration and optical purity of **4b**, the latter

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(1) Part V: W. Adam and R. Rucktäschel, *J. Amer. Chem. Soc.*, **93**, 557 (1971).
(2) Presented at the "Cyclic Peroxide Symposium," Regional Meeting of the New York–New Jersey–Puerto Rico Sections of the American Chemical Society, Metrochem '71, San Juan, Puerto Rico, April 1971.
(3) I. S. Knull and D. R. Arnold, *Tetrahedron Lett.*, 1247 (1969).
(4) R. J. Cvetanovic, *J. Phys. Chem.*, 74, 2730 (1970); M. D. Scheer and R. Klein, *ibid.*, 74, 2732 (1970).
(5) W. Adam, Y. M. Cheng, C. Wilkerson, and W. A. Zaidi, *J. Amer. Chem. Soc.*, **91**, 2111 (1969); W. Adam and Y. M. Cheng, *ibid.*, **91**, 2009 (1969); F. D. Greene, W. Adam, and G. R. Knudsen, Jr., *J. Org. Chem.*, **31**, 2087 (1966).
(6) W. Adam and G. S. Aponte, Abstracts, 158th National Meeting of the American Chemical Society, New York, N. Y., 1969, No. ORGN-42.
(7) R. Roger, *Biochem. Z.*, **230**, 320 (1931).

Table I. Product Composition (Absolute Yields) of Peroxylactone **1a**

Mode of decomp	α-Methylstyrene oxide (**4a**)	Acetophenone (**5a**)	Propiophenone (**6a**)	Phenylacetone (**7a**)	Methyl to phenyl ratio[a]
Photolysis[b]	49.5 ± 1.9	11.5 ± 0.9	7.1 ± 0.2	7.6 ± 0.2	0.94
Piperylene-quenched photolysis	47.0 ± 1.3	5.6 ± 0.2	7.1 ± 0.4	15.9 ± 0.9	0.45
Thermolysis[c]	<0.5	7.6 ± 0.2	77.4 ± 1.0	13.8 ± 0.1	5.6

[a] Ratio of methyl (**6a**) to phenyl (**7a**) migration. [b] Irradiation of 1.0 *M* solution in benzene at 350 nm (Rayonet RPR-100) in Pyrex vessel for 24–30 hr. [c] Heating of a 1.0 *M* solution in benzene at 125° (ref 5).

was hydrolyzed with 0.1 *N* $HClO_4$ back to diol **9** (mp 93–93.5°, $[\alpha]^{26}\text{D}$ +138.9° in benzene). Since control experiments showed that diol **9** is optically stable under these hydrolytic conditions and since it is known that hydrolysis of epoxides by 0.1 *N* $HClO_4$ results in inverted diol with negligible racemization,[8] epoxide **4b** is 93% optically pure (2*S*)-(+)-1,1-diphenylepoxypropane. Additional control experiments indicated that (2*S*)-(+)-**4b** did not photoracemize under the photolysis conditions of **1b**, although prolonged photolysis converts **4b** into benzhydryl methyl ketone (**8**). Finally, no reacemization of **4b** could be provoked on irradiation in the presence of the individual photoproducts, a synthetic or authentic photoproduct mixture. In short, epoxide **4b** was produced in racemic form in the photolysis of optically active **1b** rather than photoracemized after its production.

The stereochemical results exclude formation of epoxide **4** directly from excited **1** *via* concerted photodecarboxylation. This mechanistic interpretation requires that optically active **1b** must lead to optically active **4b** with retained or inverted configuration.[9] Similarly, **4** cannot be derived from diradical **3**, since decarboxylation with concurrent cyclization must give optically active **4b** from active **1b**. Thus, the stereochemical results demand that the 1-oxatrimethylene diradical **2** serves as a precursor to epoxide **4** and that diradical **2** is sufficiently long-lived to racemize completely before cyclization into **4** takes place. Furthermore, fragmentation into ketone **5** and rearrangement into ketones **6** and **7** compete with cyclization (Table I) and, as expected, racemic **7b** is formed in the photolysis of (*S*)-(−)-**1b** since racemized diradical **2b** is the precursor to the photoproducts. On the contrary, in the thermolysis[5] of (*S*)-(−)-**1b** ketone **7b** was produced with quantitative inversion of configuration since diradical **3b**, the precursor to the thermoproducts, exclusively decarboxylates with concurrent migration of the β substituent. No epoxide is formed in the thermolysis.

It is of interest to compare the methyl–phenyl migratory aptitudes, *i.e.*, the ratio of rearrangement ketones **6a** (methyl migration) and **7a** (phenyl migration). In the last column of the table these data are summarized for the photolysis, piperylene-quenched photolysis, and thermolysis of peroxylactone **1a**. Clearly, in the photolysis of **1a** no differentiation between methyl and phenyl migration is made, yet in the thermolysis, methyl migration outweighs by a factor of 5.6 phenyl migration; however, in the piperylene-quenched photolysis phenyl predominates over methyl migration by a factor of 2.2. As already discussed,[5] the diradical 2-keto-1,5-dioxapentamethylene intermediate **3a** serves as precursor to the thermoproducts of **1a**, for which methyl migrates in preference to phenyl since β scission is the principal driving force for transposing the β substituent as **3a** decarboxylates. Probably in the unquenched photolysis a triplet 1-oxatrimethylene intermediate is the precursor which fails to discriminate between phenyl and methyl migration, while in the piperylene-quenched photolysis a singlet 1-oxatrimethylene intermediate intervenes. However, elaborate photomechanistic experiments are essential to settle the finer details of this novel reaction.

Acknowledgments. The financial assistance by the Petroleum Research Fund, the National Science Foundation, and the Sloan Foundation, as well as a study leave for G. S. A. from the Agricultural Experiment Station (Rio Piedras) are gratefully appreciated.

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(8) H. Audiei, J. F. Dupin, and J. Jullien, *Bull. Soc. Chim. Fr.*, 2811 (1966).

(9) R. B. Woodward and R. Hoffmann, *Angew. Chem.*, **81**, 797 (1969).

(10) M.S. Thesis, University of Puerto Rico, June 1970. Part of this work was presented by G. S. A. at the Fifth Junior Technical Meeting, administered by the Puerto Rico Section of the American Chemical Society (Aug 1970), and was awarded the first prize.

Waldemar Adam,* Generoso Santiago Aponte[10]
Department of Chemistry, University of Puerto Rico
Rio Piedras, Puerto Rico 00931

Received May 10, 1971

Partial Resolution of Racemic Tertiary Phosphines with an Asymmetric Palladium Complex

Sir:

Optically active tertiary phosphines can serve as key ligands in the transition metal catalyzed asymmetric hydrogenation of olefins.[1,2] They have been prepared through asymmetric syntheses[3–5] or by resolution of racemates,[6,7] most of which require tedious steps. Here we propose a simple method of resolving racemic tertiary phosphines through stereospecific reactions of an asymmetric palladium(II) complex.

Cope and Friedrich[8] reported the preparation of a chelated complex, di-μ-chloro-bis(*N*,*N*-dimethylbenzylamine-2-*C*,*N*)-dipalladium (**1**), from *N*,*N*-dimethylbenzylamine and lithium tetrachloropalladadate(II). A similar reaction of *N*,*N*-dimethyl-α-phenethylamine $[[\alpha]^{26}\text{D}$

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(1) W. S. Knowles and M. J. Sabacky, *Chem. Commun.*, 1445 (1968).

(2) L. Horner, H. Siegel, and H. Büthe, *Angew. Chem.*, **80**, 1034 (1968).

(3) L. Horner, H. Winkler, A. Rapp, A. Mentrup, H. Hoffmann, and P. Beck, *Tetrahedron Lett.*, 161 (1961).

(4) L. Horner, F. Schedlbauer, and P. Beck, *ibid.*, 1421 (1964).

(5) L. Horner and W. D. Balzer, *ibid.*, 1157 (1965).

(6) G. Wittig, H. J. Cristau, and H. Braun, *Angew. Chem.*, **79**, 721 (1967).

(7) T. H. Chan, *Chem. Commun.*, 895 (1968).

(8) A. C. Cope and E. C. Friedrich, *J. Amer. Chem. Soc.*, **90**, 909 (1968).