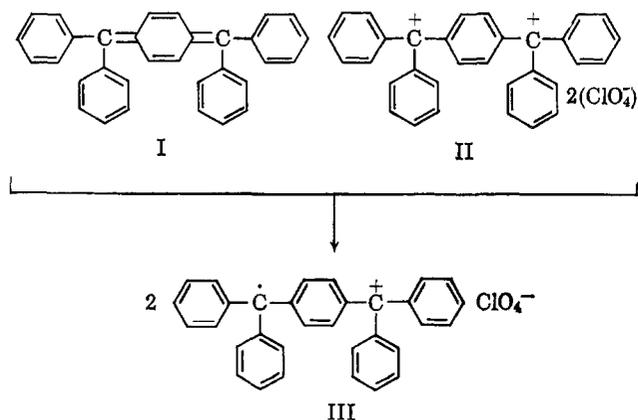


The latter color was presumably due to the formation of radical-ion III.³



Tetraphenyl-*p*-xylylene (I)⁴ in methylene chloride has a single absorption at 424 $m\mu$ ($\log \epsilon$ 4.68), whereas crystalline perchlorate II,⁵ in the same solvent, has maxima at 424 $m\mu$ ($\log \epsilon$ 4.50) and 463 $m\mu$ ($\log \epsilon$ 4.57). Upon mixing carefully degassed equimolar solutions of I and II, one obtains a dark red solution which has a new band at 580 $m\mu$, as well as maxima at 467 and 424 $m\mu$. If one assumes that this spectrum is due to III only, $\log \epsilon$ is 3.64, 4.23, and 4.17,⁶ respectively. The e.s.r. spectrum is shown in Fig. 1.⁷ Although a

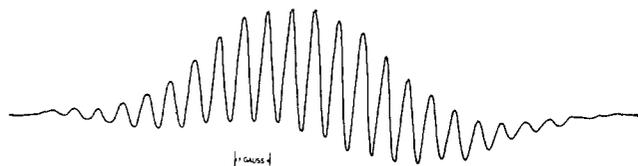


Fig. 1.—The e.s.r. spectrum of III at -90° ($4 \times 10^{-3} M$ solution in methylene chloride).

good signal was obtained at ambient temperature, resolution was improved by lowering the temperature. It is hoped that further experimentation with dilution, solvents, and temperature will improve the resolution, but 23 equally spaced lines with ΔH of 0.69 gauss are clearly visible.

Two syringes of equal size connected to separate arms of a capillary Y-tube were filled (argon atmosphere) with $10^{-3} M$ solutions of I and II. At this dilution, the solutions appeared pale yellow in the arms of the capillary tube. The plungers on the syringes were simultaneously and rapidly depressed; at the Y-juncture and 5 cm. beyond, the solution remained pale yellow, although it was dark red in the collection syringe attached to the third arm of the Y. When flow was

(3) In the nomenclature of the time, III was referred to as a meriquinoid salt. Presumably the same species was produced when the dichloride was treated with silver perchlorate or zinc chloride and I in benzene-chloroform. Other significant results in the earlier report² are (a) the solution is rapidly decolorized by oxygen; (b) it is converted by chlorine to the dichloride; and (c) the dichloride and I do not react in a nonpolar solvent.

(4) H. Staudinger, *Ber.*, **41**, 1355 (1908).

(5) Prepared from the dichloride and silver perchlorate in methylene chloride, and recrystallized at dry ice temperature from this solvent.

(6) Since I and II do not absorb at 580 $m\mu$, it is easy to show that the amount of species which absorbs at this wave length must be present at least to the extent of 64%; any concentration less than this would be meaningless in that it would require that the same species have a negative absorbance at 424 $m\mu$. It seems likely that the equilibrium between I + II and III lies largely, if not entirely, to the right.

(7) We are indebted to H. Kuska for assistance in obtaining this spectrum. The instrument was a Varian Model V-4500-10A e.p.r. spectrometer. Neither I nor II gives an e.s.r. signal.

stopped, the solution in the capillary beyond the juncture became dark red within 3 sec. Thus the half-life for production of the radical-ion is approximately 3 sec. and, if the reaction is bimolecular, its rate constant is roughly 300 l. mole⁻¹ sec⁻¹ at room temperature. Kinetic studies are therefore possible and are being undertaken.

When equal volumes of $10^{-3} M$ methylene chloride solutions of I and II were mixed and evaporated to dryness, a dark red residue was obtained which had an infrared spectrum (KBr pellet, prepared in an inert atmosphere) with several bands different from those of I or II. In particular, III had a sharp, intense band at 7.94 μ and a strong broad band at 12.25–12.50 μ .⁸ The solid gave a broad e.s.r. signal, but dissolution in methylene chloride led to e.s.r. and visible spectra identical with those described above.^{9–11}

(8) Also present were numerous sharp bands approximately common to I and II in the 3–4 and 6–7.4 μ regions and a broad intense band at 8.7–9.8 μ (perchlorate) present in II but not I.

(9) This work is being extended to various combinations of the 30–34 electron system on the tetraphenylxylyl framework. It is anticipated that suitable substitution should vary the electron-transfer rate and, in certain cases, lead to the transfer of more than one electron.

(10) It has recently been recognized (S. Hunig, H. J. Friedrich, D. Scheut-zow, and W. Brenninger, *Tetrahedron Letters*, 181 (1964)) that similar one-electron transfers can be accomplished in π -systems of the cyanine type; no rates are reported.

(11) We are indebted to the National Science Foundation, GP-71, for financial support of this work.

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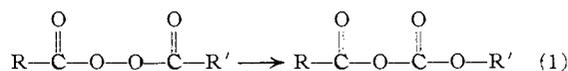
HAROLD HART
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RECEIVED FEBRUARY 27, 1964

Mechanisms of Decomposition of Diacyl Peroxides¹

Sir:

Thermal decomposition of diacyl peroxides is normally considered to proceed by a homolytic mechanism.² Exceptions are the rearrangement of unsymmetrical diacyl peroxides in polar solvents³ and decomposition catalyzed by Lewis acids⁴ (eq. 1).



The large body of detailed experimental work on aliphatic diacyl peroxides has been interpreted^{2,5} principally in terms of homolytic decomposition and/or direct conversion of peroxide to ester (frequently a major product).

We have ascertained that the *major* path of decomposition of the *symmetrical* aliphatic diacyl peroxide

(1) This work was supported in part by the Atomic Energy Commission under contract No. AT(30-1)-905.

(2) A. G. Davies, "Organic Peroxides," Butterworths, London, 1961; E. G. E. Hawkins, "Organic Peroxides, Their Formation and Reactions," E. and F. Spon Ltd., London, 1961; C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957.

(3) J. E. Leffler and C. C. Petropoulos, *J. Am. Chem. Soc.*, **79**, 3068 (1957); D. B. Denney, *ibid.*, **78**, 590 (1956); J. E. Leffler, *ibid.*, **72**, 67 (1950); D. B. Denney and D. Z. Denney, *ibid.*, **79**, 4806 (1957); W. Honsberg and J. E. Leffler, *J. Org. Chem.*, **26**, 733 (1961).

(4) (a) D. Z. Denney, T. M. Valega, and D. B. Denney, *J. Am. Chem. Soc.*, **86**, 46 (1964); (b) J. T. Edwards, H. S. Chang, and S. A. Samad, *Can. J. Chem.*, **40**, 804 (1962); (c) R. Huisgen and W. Edl, *Angew. Chem.*, **74**, 588 (1962); (d) J. K. Kochi, *J. Am. Chem. Soc.*, **85**, 1958 (1963).

(5) (a) M. S. Kharasch, J. Kuderna, and W. Nudenberg, *J. Org. Chem.*, **19**, 1283 (1954); H. J. Dauben, Jr., and H. T. Liang, *Hua Hsueh Hsueh Pao*, **25**, 136 (1959); *Chem. Abstr.*, **54**, 4365f (1960); (b) F. D. Greene, *J. Am. Chem. Soc.*, **77**, 4869 (1955); (c) D. F. DeTar and C. Weis, *ibid.*, **79**, 3045 (1957); (d) H. H. Lau and H. Hart, *ibid.*, **81**, 4897 (1959); (e) H. Hart and J. Chloupek, *ibid.*, **85**, 1155 (1963); (f) R. C. Lamb and J. G. Pacifici, *ibid.*, **86**, 914 (1964).

trans-4-*t*-butylcyclohexanecarbonyl peroxide^{5d} in *non-polar* media is *via* rearrangement to the carboxy inversion product, *trans*-4-*t*-butylcyclohexyl *trans*-4-*t*-butylcyclohexanecarbonyl carbonate (eq. 1, R = R' = *trans*-4-*t*-butylcyclohexyl), m.p. 102–103°, carbonyl absorption (CCl₄) 1800, 1750 cm.⁻¹, which has been isolated from the decomposition solution in carbon tetrachloride and found to be identical with an authentic sample prepared by an independent synthesis.^{6,7} Extensive purification of the carbon tetrachloride or a change of solvent to benzene, hexane, or isooctane did not alter the course of the reaction; in all cases the rearrangement of peroxide to inversion product was the primary reaction. Upon further heating, the "inversion product" is converted in high yield to the *trans*, *trans* ester.^{5d} In refluxing carbon tetrachloride substantially all of the peroxide (initial concentration 0.05 *M*) is consumed in the first 40 min. The resulting "inversion product" (approximately two-thirds of the product composition) is half destroyed (affording ester and carbon dioxide) after 1 day. Homolytic peroxide decomposition to alkyl radicals accounts for approximately one-third of the product composition in the form of a 2.7:1 ratio of *cis*- and *trans*-4-*t*-butylcyclohexyl chloride.⁸ Decomposition of the peroxide is first-order (determined over a 13-fold difference in initial peroxide concentration by following the change of optical density at 1775 cm.⁻¹); the rate of rearrangement increases as the solvent is changed from isooctane to carbon tetrachloride to benzene.

Ethylmethylacetyl peroxide^{4d,5a} (in addition to decomposition to alkyl radicals) is also observed (by nuclear magnetic resonance and infrared absorption) to undergo rearrangement to carboxy inversion product which in a subsequent, slower reaction is converted principally to ester.

The decomposition of peroxides *via* the intermediacy of an alkyl acyl carbonate provides an attractive explanation for the stereospecificity of ester formation observed in the past.⁵ We suspect that rearrangement (eq. 1) may be a major route of decomposition for other secondary aliphatic diacyl peroxides.⁹

A third example further delineates mechanistic complexities in this area. Decomposition of *p*-bromobenzoyl phenylacetyl peroxide in benzene at 30° is first-order, yields only 2% of radicals scavengeable by galvinoxyl,¹⁰ and affords benzyl *p*-bromobenzoate (45%), benzyl *p*-bromobenzoyl carbonate¹¹ (eq. 1, R = *p*-BrC₆H₄, R' = CH₂C₆H₅, 30%), *p*-bromobenzoic acid (13%), and diphenylmethane (10%). Extensive control experiments indicate that *in this case* ester is not formed from the inversion product under the mild reaction conditions; thus, for this particular unsymmetrical peroxide, a path for ester formation must be operative which does not involve the carboxy inversion product. Oxygen-18 labeling in the carbonyl carbon of the *p*-

bromobenzoyl portion of the peroxide becomes divided 55–45 in the carbonyl and alkyl oxygens of the ester; this excludes formation of the ester solely by a six-center transition state but is consistent with cage recombination (or a combination of six- and four-center reactions). Of principal significance here also is the simultaneous operation of different modes of decomposition of a diacyl peroxide in a nonpolar medium.

(12) National Institutes of Health Postdoctoral Fellow, 1963–1964.

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RECEIVED FEBRUARY 21, 1964

Isobenzofuran,* a Transient Intermediate

Sir:

We have found that 1,4-dihydronaphthalene-1,4-*endo*-oxide (**1a**), previously prepared by shaking a solution of *o*-fluorobromobenzene in furan with lithium amalgam (4 days),¹ is readily obtainable by aprotic diazotization of anthranilic acid² in the presence of furan. Use of 2,5-dimethylfuran as trapping agent affords **1b**.³ Having worked out improved procedures⁴ for the preparation of hexaphenylbenzene and 1,2,3,4-tetraphenyl-naphthalene from the purple reactive diene, tetraphenylcyclopentadienone (**2**), we were interested in the finding³ that **1a** is an effective Diels–Alder dienophile for simple dienes and decided to explore the reaction of **1a** with **2**. A solution of the reactants in diglyme was refluxed in the expectation that, at this temperature (165°), the adduct **3** would lose carbon monoxide and afford the tetrahydrotetraphenylanthracene *endo*-9,10-oxide **6**. A vigorous reaction occurred with gas evolution and with discharge of the purple color in 2 min. Dilution with water precipitated a colorless, crystalline product, m.p. 190°, characterized by the n.m.r. spectrum as having only aromatic hydrogens and found by elemental analysis to be a hydrocarbon. Initial ideas about the nature of the product were dismissed by the finding that the 1,4-dimethyl *endo*-oxide **1b** reacts with **2** to give the same aromatic hydrocarbon, and this eventually was identified as 1,2,3,4-tetraphenylbenzene (**9**).⁵ Since this hydrocarbon must arise by thermal decomposition of an intermediate, the reaction of **1a** with **2** was repeated in refluxing benzene. There resulted, in quantitative yield, a colorless product melting at 180–182° dec. and corresponding in analysis to the adduct **3**. This structure is confirmed by infrared carbonyl absorption at 1775 cm.⁻¹ and by the n.m.r. spectrum: a multiplet at τ 2.6–2.9 (10 protons of the phenyl groups at C-2 and C-3 and 4 protons of the *ortho*-disubstituted benzene ring), a singlet at 3.17 (10 protons from the phenyl groups at C-1 and C-4), a singlet at 4.72 (C-9 and C-10 protons), and a singlet at 7.09 (C-9a and C-10a

* For reasons set forth in L. F. Fieser and M. Fieser, "Style Guide for Chemists," Reinhold Publishing Co., New York, N. Y., 1960, L. F. F. strongly advocates the spelling isobenzofurane.

(1) G. Wittig and L. Pohmer, *Ber.*, **89**, 1334 (1956).

(2) L. Friedman and F. M. Logullo, *J. Am. Chem. Soc.*, **85**, 1549 (1963). See also M. Stiles and R. G. Miller, *ibid.*, **82**, 3802 (1960), and M. Stiles, R. G. Miller, and U. Burckhardt, *ibid.*, **85**, 1792 (1963).

(3) E. Wolthuis, *J. Org. Chem.*, **26**, 2215 (1961).

(4) Procedures submitted to *Org. Syn.* by L. F. Fieser, and by L. F. Fieser and M. J. Haddadin. See also L. F. Fieser, "Organic Experiments," D. C. Heath and Co., in press.

(5) W. Dilthey, W. Schomner, and O. Trösken, *Ber.*, **66**, 1627 (1933).

(6) Prepared by the procedure of D. S. Tarbell and E. J. Longosz, *J. Org. Chem.*, **24**, 774 (1959).

(7) Satisfactory combustion data and proof of structure have been obtained for all new compounds.

(8) F. D. Greene, C. C. Chu, and J. Walia, *J. Org. Chem.*, in press.

(9) Some data on bridgehead peroxides are also suggestive of the involvement of the carboxy inversion reaction [P. D. Bartlett and F. D. Greene, *J. Am. Chem. Soc.*, **76**, 1088 (1954)].

(10) P. D. Bartlett and T. Funahashi, *ibid.*, **84**, 3596 (1962); F. D. Greene, W. Adam, and J. E. Cantrill, *ibid.*, **83**, 3461 (1961).

(11) Melting point 67–67.5°, infrared absorption (CCl₄) in the carbonyl region: 1805, 1742 cm.⁻¹.