Preparation and Separation of the Isomeric 1,2,1′,2′-Bis(α-ketotetramethylene)-ferrocenes XIVa and XIVb.—Ferrocene-1,1′-dibutyric acid (XIII, 0.45 g.) was added to 5.0 g. of trifluoroacetic anhydride at −70°. The orange suspension was swirled in an ice-bath for 30 minutes, allowed to come to room temperature during 1 hour, and finally poured over ice-sodium hydroxide. The aqueous solution was extracted with ether and the ether extract was washed, dried, filtered and transferred to an alumina column. Elution with 5% acetone in ether removed 5.6 mg. (1%) of 1,2-(α-ketotetramethylene)-ferrocene (IIIc) from monoacid impurity in the starting di-acid, while elution with 20% acetone in ether gave 0.176 g. (47%) of a mixture of isomeric diketones XIVa and XIVb.

Recrystallization of the product from ether–acetone gave 31.6 mg. of material melting 153–161° dec., which after two further recrystallizations from ether–acetone had constant m.p. 167–168°. The infrared spectrum (potassium bromide pellet) has bands at 3100, 2970, 1678, 1480, 1455, 1350, 1290, 1253, 1175, 1025, 985 and 840 cm.$^{-1}$, while the ultraviolet spectrum has λ_{max} 232 mμ (ε 19,400) and λ_{max} 269 mμ (ε 17,400).

Anal. Calcd. for $C_{18}H_{18}FeO_2$: C, 67.10; H, 5.63; Fe, 17.33. Found: C, 66.99; H, 5.61; Fe, 17.37.

The mother liquor from the first crystallization was concentrated and the acetone–ether was displaced by hexane. Crystallization at −70° gave 104.6 mg. of orange–red crystals, m.p. 134.0–135.5°. Repeated recrystallization from hexane gave 69.4 mg. of the pure isomer, m.p. 135.0–135.5°. The infrared spectrum contains essentially the same bands as those given for the other isomer, while the ultraviolet spectrum has λ_{max} 227 mμ (ε 22,700) and λ_{max} 268 mμ (ε 17,400).

Preparation of 1,2-(α-Ketopentamethylene)-ferrocene (IIId). A. Polyphosphoric Acid Method.—A mixture of a small amount (500 mg.) of δ-ferrocenylvaleric acid (Id)[3] and polyphosphoric acid stood for 4 hours with occasional manual stirring. It was then poured over ice and extracted with ether, which was in turn washed with sodium carbonate and water, dried and concentrated to small volume. The remaining solution was chromatographed over alumina (Merck, basic). Elution with benzene gave a single band, which on concentration under reduced pressure gave 70 mg. (14%) of red crystals, m.p. 61–63°.

Anal. Calcd. for $C_{15}H_{16}FeO$: C, 67.19; H, 6.02. Found: C, 66.99; H, 6.18.

B. Trifluoroacetic Anhydride Method.—To 10 ml. of trifluoroacetic anhydride was added slowly 0.30 g. (0.001 mole) of δ-ferrocenylvaleric acid (Id).[3] The reaction mixture was cooled to 5°, allowed to stand for 16 hours with occasional shaking, and finally poured over ice. Workup as in method A gave 80 mg. (28%) of 1,2-(α-ketopentamethylene)-ferrocene (IIId) as red crystals, m.p. 57–58°, infrared spectrum nearly identical to that of the product from method A.

Reaction of ε-Ferrocenylcaproic Acid with Polyphosphoric Acid.—A purple mixture of 1.09 g. of ε-ferrocenylcaproic acid and 21 g. of polyphosphoric acid was stirred occasionally for 10 hours at room temperature and 4 hours at 56°, then cooled and poured over ice. The product–acid mixture was extracted successively with ether and methylene chloride; there remained undissolved an orange precipitate in the aqueous layer. This was filtered, washed with water, and digested with acetone, then dried for 24 hours at 1 mm. and room temperature; yield, 0.12 g. (11%). The orange solid did not melt below 200°, but decomposed slowly above that temperature. Its analytical values and infrared spectrum (strong ketone carbonyl at 1660 cm.$^{-1}$ and weak carboxyl carbonyl at 1725 cm.$^{-1}$) indicated that it was an intermolecular condensation product.

Anal. Calcd. for $(C_{16}H_{18}FeO)n$: C, 68.14; H, 6.43; Fe, 19.80. Calcd. for $C_{16}H_{20}FeO_2$: C, 64.03; H, 6.72; Fe, 18.61. Calcd. for $H(C_{16}H_{18}FeO)_2OH$: C, 66.0; H, 6.53; Fe, 19.2. Calcd. for $H(C_{16}H_{18}FeO)_3OH$: C, 66.8; H, 6.49; Fe, 19.4. Found: C, 66.7; H, 6.58; Fe, 18.09, 18.30.

Both the original ether and methylene chloride extracts were worked up in the same way: washed with water, sodium carbonate, water, dried, evaporated, chromatographed over alumina. From the ether extract were obtained two small neutral chromatographic bands, while the major portion of the methylene chloride extract appeared to be recovered, starting acid and only very little neutral material was found.

Acknowledgments.—Financial assistance was provided in part by the Materials Laboratory, Wright Air Development Division, Wright–Patterson Air Force Base, Ohio. The work also was supported in part by grants from the Research Corporation and from the Petroleum Research Fund, administered by the American Chemical Society. Grateful acknowledgement is hereby made to the donors of this fund.

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY, HARVARD UNIVERSITY, CAMBRIDGE 38, MASS.]

Peresters. IX. Di-*t*-butyl Monoperoxycarbonate

BY PAUL D. BARTLETT AND HIDEKI SAKURAI

RECEIVED APRIL 30, 1962

Di-*t*-butyl monoperoxycarbonate (IV) decomposes at 100° in cumene to yield a mole of carbon dioxide, 0.06 mole of methane, 0.82 mole of bicumyl and *t*-butyl alcohol and acetone in a ratio of about 15 to 1. For the decomposition of this perester $\Delta H^{\ddagger} = 35.4$ kcal. and $\Delta S^{\ddagger} = 14.6$ e.u. It is about 100 times faster than di-*t*-butyl peroxide at 100°, and about 10^5 times slower than di-*t*-butyl diperoxyoxalate (I) at 45°. The absence of di-*t*-butyl peroxide in the decomposition products of the peroxycarbonate, and of the latter in the decomposition products of the diperoxyoxalate, shows that there is no cage effect in either of these decompositions.

Introduction

In the decomposition of di-*t*-butyl diperoxyoxalate (I) in cumene at 25–45° the only products are *t*-butyl alcohol and carbon dioxide[1] and there is no cage effect.[2] The corresponding monoperoxyoxalate, (II) however,[3] yields 37–44% di-*t*-butyl carbonate (III) and only about half of the radicals are scavengeable. From these results it is clear that two *t*-butoxy radicals do not recombine with a low enough activation energy for their coupling to be diffusion controlled. To explain the nonoccurrence of di-*t*-butyl monoperoxycarbonate (IV) among the products from I there were two possibilities: (1) the monoperoxycarbonate was not formed because the carbo-*t*-butylperoxy radical V, unlike the carbo-*t*-butoxy radical VI, did not survive even the few collisions necessary for cage recombination; or (2) the monoperoxycarbonate

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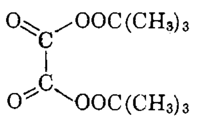
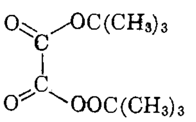
[1] P. D. Bartlett, E. P. Benzing and R. E. Pincock, *J. Am. Chem. Soc.*, **82**, 1762 (1960).

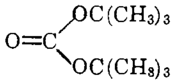
[2] P. D. Bartlett and T. Funahashi, *ibid.*, **84**, 2596 (1962).

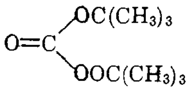
[3] P. D. Bartlett, B. A. Gontarev and H. Sakurai, *ibid.*, **84**, 3101 (1962).

IV was formed but was itself more unstable than the diperoxyoxalate I. We assume that the radicals V and VI cannot be extremely different in their coupling rates with *t*-butoxy radical. To decide


I


II


III


IV

$O{=}\dot{C}{-}OOC(CH_3)_3$
V

$O{=}\dot{C}{-}OC(CH_3)_3$
VI

this point we have prepared di-*t*-butyl monoperoxycarbonate (IV) and studied the rate and products of its decomposition. Since IV turns out to be completely stable under the conditions of the decomposition of I, the first of the two explanations above is the correct one.

Experimental

Di-*t*-butyl **Monoperoxycarbonate**.—Phosgene (22 g.) and *t*-butyl hydroperoxide (11.5 g.) were allowed to react together at 0° for 5 hours. The phosgene and hydrogen chloride were then removed in a stream of nitrogen at room temperature. *t*-Butyl alcohol (12 g.) and pyridine (20 g.) in 40 ml. of pentane were added dropwise at 3–5°. After 30 minutes the solution was washed with a 5% solution of sulfuric acid, then with water, 10% sodium bicarbonate and water again. The solution was dried over anhydrous magnesium sulfate and the pentane was distilled off. The product was distilled through a short Vigreux column at 46–47° (0.47 mm.) in a yield of 5.32 g. Redistillation yielded 2.17 g. of a colorless thick oil with the same boiling range, n^{25}_D 1.4075.

Anal. Calcd. for $C_9H_{18}O_4$: C, 56.83; H, 9.54. Found: C, 56.01; H, 9.04.

The perester carbonyl peak at 5.59 μ was characteristic and could be used to follow quantitatively the decomposition of the perester.

The kinetic and product studies were carried out as previously described.[1]

Results

Table I lists the products of decomposition of di-*t*-butyl monoperoxycarbonate in cumene solution at 99.98°. The evolution of carbon dioxide is quantitative, and the tertiary butyl groups are fully accounted for (104%) in the sum of the assays for *t*-butyl alcohol and acetone. In addition, the possible product of geminate recombination, di-*t*-butyl peroxide, was specifically looked for by infrared spectroscopy and vapor chromatography, and shown not to be present in detectable amount.

TABLE I

DECOMPOSITION PRODUCTS OF DI-*t*-BUTYL MONOPEROXYCARBONATE IN CUMENE AT 99.98°

Compound	Amount (millimoles)	Moles per mole of perester
Original perester	2.28	1
Carbon dioxide		
by weight	2.27	0.996
by volume	2.25	.988
Methane	0.14	.06
t-Butyl alcohol	4.41	1.93
Acetone	0.296	0.13
Bicumyl	1.87	0.82

Table II lists the rate determinations made at 100–122°. It is immediately evident that this perester is not in a class with the peroxyoxalates, nor with the peroxydicarbonates,[4] as to speed of decomposition.

TABLE II

RATE CONSTANTS FOR DECOMPOSITION OF DI-*t*-BUTYL MONOPEROXYCARBONATE IN CUMENE

Temp., °C.	Concn., *M*	$k \times 10^5$, sec.$^{-1}$
99.98	0.0223	2.19
110.21	.0223	9.05
110.21	.235	8.45
121.90	.0223	32.63

A plot of log (k/T) against $(1/T)$ yields a value of 35.4 kcal./mole for $\Delta H^{\ddagger}$ and 14.6 cal./degree mole for $\Delta S^{\ddagger}$. The measured rate constant at 100° is about 100 times as fast as that of di-*t*-butyl peroxide; the extrapolated rate constant at 45° is less than that of di-*t*-butyl diperoxyoxalate by five powers of ten; and at 50° its extrapolated rate constant is one-three thousandth of that of diisopropyl peroxydicarbonate.[4] These relations are normal if di-*t*-butyl monoperoxycarbonate decomposes by simple O–O bond fission. Its relation to di-*t*-butyl peroxydicarbonate would be like that of *t*-butyl perbenzoate to benzoyl peroxide, the unconcerted decomposition of the latter proceeding some 500 times as fast at 60° as that of the related *t*-butyl ester.[5]

The rate constant for decomposition of IV in cumene at 100° is within 35% of that calculated by applying a statistical factor of $^1/_2$ to the constant reported by Martin[6] for the unconcerted decomposition of di-*t*-butyl diperoxycarbonate under the same conditions.

The perester IV completes a series of three initiators, all of which decompose with quantitative yields of the tertiary butoxy radical, but at rates covering a range of a million-fold. The insensitivity of the decomposition kinetics of di-*t*-butyl peroxide to reactive and unreactive solvents was an early indication[7] that no important amount of geminate recombination of *t*-butoxy radicals was occurring as a part of the process. This conclusion was made certain by the fact that 100% of the *t*-butoxy radicals from the decomposition of di-*t*-butyl diperoxyoxalate (DBPO) could be scavenged by the stable radical galvinoxyl.[2] Now that di-*t*-butyl monoperoxycarbonate is found to be entirely stable at the decomposition temperature of DBPO, it is clear that the peroxycarbonate also cannot be a transient cage product in the decomposition of the peroxyoxalate. Since the carbo-*t*-butoxy radical is readily scavenged, we believe that this would also be the case with the carbo-*t*-

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[4] F. Strain, W. E. Bissinger, W. R. Dial, H. Rudoff, B. J. DeWitt, H. C. Stevens and J. H. Langston, *J. Am. Chem. Soc.*, **72**, 1254 (1950).

[5] P. D. Bartlett and R. R. Hiatt, *ibid.*, **80**, 1398 (1958), in Table I include a comparison of these rates, with references. There is an error in the table: for 3 × 10^4 read 3 × 10^5.

[6] M. Martin, *ibid.*, **83**, 2871 (1961).

[7] J. H. Raley, F. F. Rust and W. E. Vaughan, *ibid.*, **78**, 1336 (1948).

butylperoxy radical if it did not undergo immediate fission into carbon dioxide and *t*-butoxy radical. In order not to be scavenged at all, it must cleave within the time of a very few collisions, faster than the acetoxy radical to which Herk, Feld and Szwarc assign a lifetime of the order of 10^{-9} to 10^{-10} second.[8]

These experiments afford no indication as to possible cage return of the radical pair to which the ester IV dissociates, since the products of such return would be identical with the starting material. However, we have thus far no evidence that pairs of oxygen radicals ever recombine within the solvent cage,[9] although C–O, C–C and C–N couplings do occur under such conditions.

Acknowledgment.—This work was supported by a grant from the National Institutes of Health.

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[8] L. Herk, M. Feld and M. Szwarc, *J. Am. Chem. Soc.*, **83**, 2998 (1961).

[9] A surmise of ours to the contrary (T. G. Traylor and P. D. Bartlett, *Tetrahedron Letters*, **No. 24**, 36 (1960)) has been rendered improbable by further experiments on the autoxidation of cumene to be described in a forthcoming paper.

[CONTRIBUTION FROM EMERYVILLE RESEARCH LABORATORIES, SHELL DEVELOPMENT CO., EMERYVILLE, CALIF., AND DEPARTMENT OF CHEMISTRY, CASE INSTITUTE OF TECHNOLOGY, CLEVELAND 6, OHIO]

Oxidation of Allylic Radicals by Electron Transfer: Effect of Complex Copper Salts[1]

BY JAY K. KOCHI

RECEIVED MARCH 10, 1962

The oxidation of allylic radicals by complex cupric salts of 1,10-phenanthroline and α,α'-bipyridyl affords a mixture of allylic isomers. The composition of the allylic mixture is the same as those obtained from conventional carbonium ion processes. Thus, the specificity previously described for the oxidation of allylic radicals by *simple copper salts* of oxyanions to terminally unsaturated products is destroyed. Oxidation of allylic radicals by copper complexes is postulated to proceed *via* an electron transfer process to produce allylic carbonium ions as intermediates. The role of copper complexes as catalysts in the reactions of peroxides and unsaturated substrates is discussed.

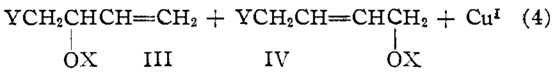
Introduction

Previous studies[2,3] have shown that *t*-butyl peresters, *t*-butyl hydroperoxides and peroxides react with cuprous salts to produce *t*-butoxy radicals (1). In the presence of alkenes these alkoxy radicals produce allylic radicals I by hydrogen abstraction (2); and with conjugated dienes such as butadiene, isoprene and styrene they react by addition (3) to form such adducts as the allylic *t*-butoxybutenyl radicals II. Allylic radicals produced either by hydrogen abstraction or addition react in the same manner with cupric salts of oxyanions, such as carboxylates, alkoxides, sulfates and perchlorates, to afford a mixture of allylic isomers III and IV (reaction 4). The compositions of these mixtures of isomers are strikingly independent of the reaction conditions. Neither the temperature of the reaction nor the constitution of the solvent affects the ratio between these allylic isomers. For example, butenyl radicals produced from any of the normal butene isomers are oxidized by these cupric salts to a mixture of α-methallyl and crotyl derivatives in which the secondary (α-methallyl) isomer is invariably the major constituent (85–95%). The same is true of *t*-butoxybutenyl radicals from butadiene and *t*-butoxy radicals: the secondary or 1,2-adduct (III, Y = *t*-BuO) always predominates (75–85%) over the primary or 1,4-adduct (15–25%).

$$t\text{-BuO}_2\text{X} + \text{Cu}^{\text{I}} \longrightarrow t\text{-BuO}\cdot + \text{Cu}^{\text{II}}\text{OX} \qquad (1)$$

$$t\text{-BuO}\cdot + \text{C}_4\text{H}_8 \longrightarrow t\text{-BuOH} + \underset{\text{I}}{\text{C}_4\text{H}_7\cdot} \qquad (2)$$

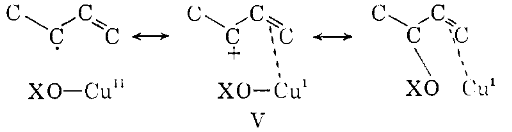
$$t\text{-BuO}\cdot + \text{C}_4\text{H}_6 \longrightarrow \underset{\text{II}}{t\text{-BuOC}_4\text{H}_6\cdot} \qquad (3)$$



$$\text{YC}_4\text{H}_6\cdot + \text{Cu}^{\text{II}}\text{OX} \longrightarrow \underset{\text{III}}{\text{YCH}_2\underset{\text{OX}}{\text{CH}}\text{CH}{=}\text{CH}_2} + \underset{\text{IV}}{\text{YCH}_2\text{CH}{=}\text{CH}\underset{\text{OX}}{\text{CH}_2}} + \text{Cu}^{\text{I}} \qquad (4)$$

X = RCO, H, R; Y = *t*-BuO, H

The study of the products arising from the partitioning of an allylic moiety is a convenient method for studying competitive reactions of reactive intermediates. Thus, the formation of a secondary derivative (III) as a major isomer from allylic free radical or carbonium ion intermediates is an unusual phenomenon. Chain transfer reactions with butenyl radicals usually produce the primary crotyl products.[2] Solvolysis of butenyl halides and esters or the deamination of butenylamines, reactions which proceed *via* carbonium ion or incipient carbonium ion intermediates, produce a mixture of allylic isomers which are approximately evenly distributed between crotyl and α-methallyl derivatives. Neither of these reaction types can be used to account for the predominance of the α-methallyl isomer in the mixture obtained from the oxidation of butenyl radicals by cupric salts of oxyanions. We have interpreted these reactions in valence bond designation as oxidation processes which proceed *via* transition states V comprised of electron transfer and ligand transfer components.[2,3] The importance of the electron transfer or carbonium ion contribution to these transition states has been stressed when copper salts of oxyanions are involved.[3] Implicit



V

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[1] Part V, The Copper Salt-Catalyzed Reactions of Peroxides.

[2] J. K. Kochi, *J. Am. Chem. Soc.*, **83**, 3162 (1961); **84**, 1572 (1962); *Tetrahedron*, **18**, 483 (1962).

[3] J. K. Kochi, *J. Am. Chem. Soc.*, in press.