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Competition between Intramolecular Rearrangement of Free Radicals and Oxidation by Metal Salts[1,2]

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o-Phenylbenzoyloxy, o-benzylbenzoyloxy, δ-phenylbutyl, and ε-phenylpentyl radicals derived from the corresponding diacyl peroxides were examined for rearrangement and oxidation by cupric salts. In all cases, carbon radicals and those which result from rearrangement of aroyloxy radicals are efficiently oxidized by cupric salts at concentrations as low as 0.02 M. No cage or dimerization products from the decomposition of the peroxide or products of radical chain transfer reactions are observed in the presence of cupric salts. The ratio of the second-order rate constant for oxidation and the first-order rate constant for rearrangement, k_{Ox}/k_R, is estimated to be 1.3×10^3 and 4.0×10^3 l./mole for δ-phenylbutyl radical and ε-phenylpentyl radical, respectively.

Introduction

Intramolecular reactions, kinetically first order, offer a convenient method of obtaining information on the relative rates of reaction of reactive intermediates such as free radicals. In this paper we wish to compare the rates of intramolecular rearrangment of free radicals with their rates of oxidation by metal salts. Earlier studies[3] indicated that the oxidation of alkyl free radicals by cupric salts is an exceedingly efficient reaction.

Intramolecular rearrangement of free radicals can also be facile. Greene, et al.,[4] examined the rearrangement of o-benzylbenzoyloxy radical to o-carboxydiphenylmethyl radical and the cyclization of o-phenylbenzoyloxy radical to 3,4-benzhydrocoumaryl radical.

Intramolecular chain-transfer reactions of carbon free radicals have been examined by DeTar and Weis[5] and Grob and Kammüller.[6] The δ-phenylbutyl radical undergoes cyclization to hydrotetralyl radical and ε-phenylpentyl radical rearranges to α-phenylpentyl radical in a manner similar to the oxy radicals mentioned above.
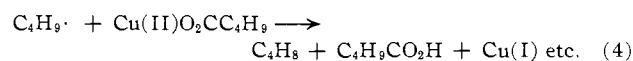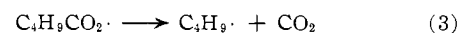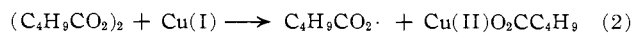
In each of these cases the free radical was generated from the corresponding diaroyl peroxide by thermolysis. Aroyl peroxides differ from the aliphatic analogs in that the initially formed aroxyloxy radicals[7] are less prone to decarboxylate,[8] and intramolecular reactions which occur subsequent[9] to homolysis are considered to arise directly from the aroyloxy radical and the alkyl radical, respectively. In many cases the identification of steps leading to products is made difficult by the formation of a variety of products. In a series of careful studies DeTar and co-workers[5] have shown how it is possible to obtain meaningful information from the complex processes[10] involved in the thermolysis of diacyl peroxides.

We have examined the metal salt-catalyzed[11] decomposition of a variety of peroxidic compounds at temperatures lower than those ordinarily required for thermolysis. Under these conditions the decomposition is smooth and the stoichiometry singularly uncomplicated. For example, cupric carboxylates in benzene, acetonitrile, or acetic acid catalyze the decomposition of n-valeryl peroxide according to reaction 1

$$(n\text{-}C_4H_9CO_2)_2 \xrightarrow{CuX_n} C_4H_8 + CO_2 + n\text{-}C_4H_9CO_2H \quad (1)$$
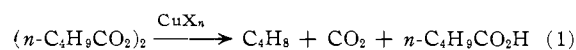
Other copper salts catalyze the decomposition in a similar manner[12] and we have presented evidence that these catalytic reactions proceed via a common mechanistic route involving the butyl (or valeryloxy)[13] radical as an intermediate. A similar scheme is applicable to aroyl peroxides (vide infra).

$$(C_4H_9CO_2)_2 + Cu(I) \longrightarrow C_4H_9CO_2\cdot + Cu(II)O_2CC_4H_9 \quad (2)$$

$$C_4H_9CO_2\cdot \longrightarrow C_4H_9\cdot + CO_2 \quad (3)$$

$$C_4H_9\cdot + Cu(II)O_2CC_4H_9 \longrightarrow$$
$$C_4H_8 + C_4H_9CO_2H + Cu(I) \text{ etc. } \quad (4)$$

Results

The decompositions of di-o-phenylbenzoyl, di-o-benzylbenzoyl, di-δ-phenylvaleryl, and di-ε-phenylcaproyl peroxides in the presence of catalytic amounts of copper salts differ markedly from those conducted thermally. In particular, the yields of carboxylic acids derived by the latter method are usually low, whereas in the catalytic decompositions a mole of acid usually accompanies the products derived from a corresponding mole of carboxy radical as indicated by eq. 2. Cage products[4,5] from the catalytic reaction are unimportant as shown below for each peroxide.

o-Phenylbenzoyloxy Radical.—Di-o-phenylbenzoyl peroxide[4] was decomposed in acetic acid and benzene solutions at 54° in the presence of catalytic amounts of cupric salts. The main products of the reaction are 3,4-benzcoumarin and o-phenylbenzoic acid formed in equimolar amounts. The neutral fraction remaining

(1) Part VII. Decompositions of Peroxides by Metal Salts.

(2) Presented in part at the 147th National Meeting of the American Chemical Society, Philadelphia. Pa., April, 1964.

(3) (a) J. K. Kochi, Tetrahedron, 18, 483 (1962); J. Am. Chem. Soc., 78, 4815 (1956); 79, 2942 (1957); (b) J. Kumamoto, H. E. DeLaMare, and F. F. Rust, ibid., 82, 1935 (1960); 85, 1437 (1963); (c) J. Kochi and F. Rust, ibid., 84, 3946 (1962).

(4) (a) F. D. Greene, G. R. Van Norman, J. C. Cantrill, and R. D. Gilliom, J. Org. Chem., 25, 1790 (1960); (b) G. W. Kenner, M. A. Murray, and C. M. B. Tylor, Tetrahedron, 1, 259 (1957); (c) D. B. Denney and R. P. Klemchuk, J. Am. Chem. Soc., 80, 3289 (1958).

(5) D. F. DeTar and R. C. Lamb, ibid., 81, 122 (1959); D. F. DeTar and R. A. J. Long, ibid., 80, 4742 (1958); D. F. DeTar and C. Weis, ibid., 79, 3045. 3041 (1957); 78, 4296 (1956).

(6) C. A. Grob and H. Kammüller, Helv. Chim. Acta, 40, 2139 (1957).

(7) G. S. Hammond and L. M. Soffer, J. Am. Chem. Soc., 72, 4711 (1950).

(8) Cf. L. Jaffe, E. J. Prosen, and M. Szwarc, J. Chem. Phys., 27, 416 (1957); H. J. Shine, J. Am. Chem. Soc., 85, 3613 (1963), and earlier papers; M. Szwarc, "Peroxide Mechanisms," J. Edwards, Ed., Interscience Publishers, Inc., New York, N. Y., 1962, p. 153 ff.

(9) There is no evidence for an anchimerically assisted decomposition in these cases, vide infra; also compare J. C. Martin, J. Am. Chem. Soc., 86, 1771 (1964), and earlier papers.

(10) Greene, et al., have recently shown that rearrangement by carboxy inversion is a common nonradical route which can complicate the interpretation of the thermolysis of diacyl peroxides (ibid, 86, 2080 (1964)).

(11) J. K. Kochi, ibid., 85, 1958 (1963).

(12) See following paper, Kochi, Graybill, and Kurz; unpublished results, R. Subramanian.

(13) Though we have been unable to obtain any evidence for an acyloxy radical as an intermediate in the catalyzed decomposition of aliphatic diacyl peroxides, we cannot yet eliminate the possibility that steps 2 and 3 occur simultaneously.

Run	Temp., °C.	Copper[a] salt, M	Peroxide, M	Solvent, ml.	3,4-Benzcoumarin, mole/mole peroxide	o-Phenylbenzoic acid, mole/mole peroxide
48	54.0–79.9	0.0	0.17	HOAc (20) C$_6$H$_6$ (10)	0.57 ± 0.03[b]	0.95
49	54.0–79.9	.0085 A	.17	HOAc (20) C$_6$H$_6$ (10)	.83 ± .01	.96
52	54.0	.022 A	.17	HOAc (20) C$_6$H$_6$ (10)	.89 ± .01	.90
53	54.0	.023 E	.17	C$_6$H$_6$ (30)	.91 ± .01	.89
Ref. 4b	80	.0	.086	HOAc	.83	.53
Ref. 4a	80	.0	.017	CCl$_4$	.77	.18

[a] A, cupric acetate hydrate; E, cupric 2-ethylhexanoate.   [b] Average deviation of duplicate analysis.

Run	Temp., °C.	Copper[a] salt, M	Peroxide, M	Solvent, ml.	3-Phenylphthalide, moles/mole peroxide	o-Benzylbenzoic acid, mole/mole peroxide
21	58.5–78	0.025A	0.52	HOAc, 20	1.01	0.98
23	59	.027E	.52	C$_6$H$_6$, 20	1.00	.96
Ref. 4a	80	.0	.036	C$_6$H$_8$	0.62[b]	.66
	80	.0		CCl$_4$	0.66[c]	.64

[a] A, cupric acetate hydrate; E, cupric 2-ethylhexanoate.   [b] In addition to 0.35 mole (0.70 equiv.) of dimer acid.   [c] In addition to 0.34 mole (0.68 equiv.) of dimer acid.

after a sodium bicarbonate extraction was almost pure benzcoumarin and it was possible to analyze for it in greater than 80% yield (Table I). The acid fraction crystallized to yield pure o-phenylbenzoic acid. This contrasts with the thermal reaction which yielded an acid fraction which was not crystalline and was probably contaminated with the dimer acid reported by Greene, et al.[4a] At 0.02 M cupric salt in benzene or acetic acid solutions, less than 2% carbon dioxide was formed. In the absence of copper salt the yield of carbon dioxide was 15–20% and in carbon tetrachloride a 53% yield[4a] has been reported at 80°.

The formation of benzcoumarin and o-phenylbenzoic acid in equal and good yields from o-phenylbenzoyl peroxide in the presence of copper salts is similar in principle to the stoichiometry found earlier[11] with the aliphatic diacyl peroxides, and the formulation of the sequence 5 to 7 is consistent with this stoichiometry.

$$(5)$$

$$(6)$$

$$(7)$$
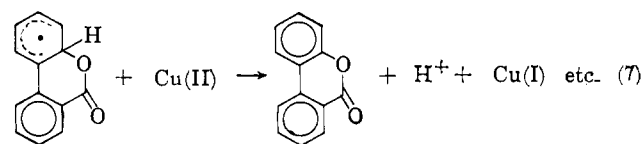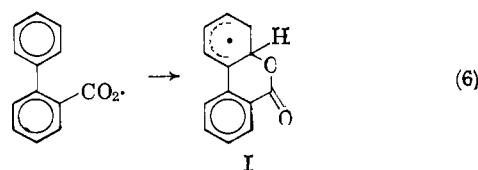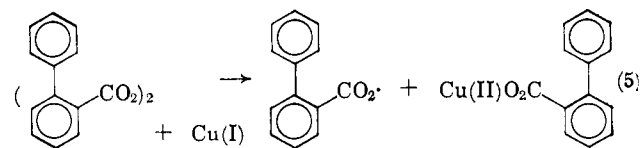
Benzcoumarin is also a major product[4] in the absence of cupric salts, though it is not formed there in as high a yield. Greene suggests that it arises by disproportionation of I or cross termination of I with other radical species. In the presence of cupric species, the oxidation reaction 7 is the preferred route for its formation. Although the possibility of disproportionation or the like contributing to the formation of benzcoumarin cannot be entirely ruled out, the presence of a catalytic effect characteristic[11] of cuprous species is indicative that a reaction such as 7 which generates cuprous ion is playing a major role. The decreased yields of carbon dioxide under these conditions compared to thermal reactions lend support to the hypothesis advanced earlier by Denney[4c] that the o-phenylbenzoyloxy radical is in equilibrium with the cyclized form I.[14]

o-Benzylbenzoyloxy Radical.—The decomposition at 58° of di-o-benzylbenzoyl peroxide[4a] in acetic acid and benzene solutions with 0.025 M cupric carboxylate yielded no carbon dioxide, but gave quantitative yields of 3-phenylphthalide and o-benzylbenzoic acid as shown in Table II.

The rapid intramolecular hydrogen transfer reaction of the o-benzylbenzoyloxy radical has been described by Greene.[4a] Although iodine can scavenge the o-benzylbenzoyloxy radical, intramolecular hydrogen transfer is much faster than decarboxylation, and the cupric salt reacts only with the rearranged o-carboxydiphenylmethyl radical II. The dimerization of this radical to the dimer acid, 1,2-di-o-carboxyphenyl-1,2-diphenylethane, formed in approximately 70% yield in the thermal decomposition,[4a] is completely suppressed by cupric salts in concentrations as low as 0.025 M.

Unfortunately, it could not be determined whether the oxidation of the benzhydryl radical II by cupric acetate proceeded by electron transfer[6] to form the benzhydryl carbonium ion followed by intramolecular collapse to the phthalide,[15] or by ligand transfer[16] to the benzhydryl acetate, since the latter readily lactonizes[17]

(14) It is still not clear whether I is a σ- or π-complex. This point is being pursued further.
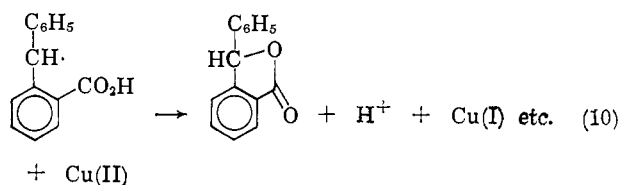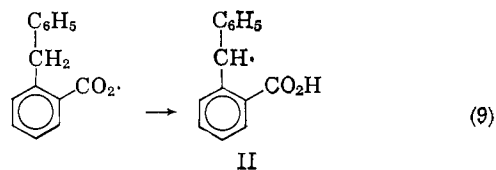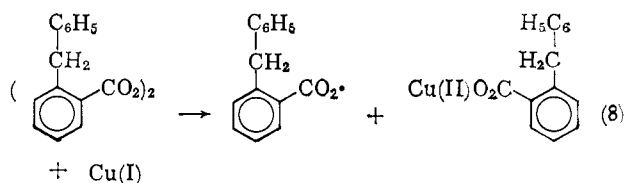(15) J. K. Kochi, J. Am. Chem. Soc., 84, 3271 (1962).
(16) J. K. Kochi, ibid., 84, 2121 (1962).

TABLE III

DECOMPOSITION OF DI-δ-PHENYLVALERYL PEROXIDE

Run	Temp., °C.	Copper[a] salt, M	Per-oxide, M	Solvent, ml.	4-Phenyl-butene-1, mole/mole peroxide	Phenyl-butane, mole/mole peroxide	Tetralin, mole/mole peroxide	PhC₄H₈ material balance, %	Ph-(CH₂)₄-COOH, moles/mole peroxide	$k_{OX}k_R$[b] × 10⁻⁸
26	54.5	0.025A	0.51	HOAc (20)	0.86 ± 0.01	0.042 ± 0.003	0.098 ± 0.002	100	1.0	0.35
31	48.8	.066E	.51	C₆H₆ (20)	.92	.012	.012	95	1.0	1.2
30	48.8	.013E	.50	C₆H₆ (20)	.89	.019	.048	95	1.0	1.4
32	48.8	.0023E	.49	C₆H₆ (20)	.71	.055	.222	99	0.86	1.4
33	48.8	.033E	.25	C₆H₆ (10) i-PrOH (10)	.84	.032	.104	97	1.1	
Ref. 5	80	0	0.0164	C₆H₆	.072	.046	.56	57[c]	0.079	

[a] A, cupric acetate hydrate; E, cupric 2-ethylhexanoate. [b] See text. [c] Material as phenylbutene, phenylbutane, and tetralin; other products formed.[5]

to the phthalide. In either case, the formation of 3-phenylphthalide under these conditions differs from that of the thermal reaction (by disproportionation) in that cuprous salt formed in the oxidation of the radical (step 10) is necessary for the catalytic reaction.[11]

$$\left(\begin{array}{c}C_6H_5 \\ CH_2 \\ \text{–}CO_2\end{array}\right)_2 \longrightarrow \begin{array}{c}C_6H_5 \\ CH_2 \\ \text{–}CO_2\cdot\end{array} + Cu(II)O_2C\text{–}\begin{array}{c}H_5C_6 \\ H_2C\end{array} \quad (8)$$

+ Cu(I)

$$\begin{array}{c}C_6H_5 \\ CH_2 \\ \text{–}CO_2\cdot\end{array} \longrightarrow \begin{array}{c}C_6H_5 \\ CH\cdot \\ \text{–}CO_2H\end{array} \quad (9)$$

II

$$\begin{array}{c}C_6H_5 \\ CH\cdot \\ \text{–}CO_2H\end{array} \longrightarrow \begin{array}{c}C_6H_5 \\ HC\text{–}O \\ \text{–}=O\end{array} + H^+ + Cu(I) \text{ etc.} \quad (10)$$

+ Cu(II)

δ-Phenylbutyl Radical. The decomposition of di-δ-phenylvaleryl peroxide in acetic acid, benzene, and isopropyl alcohol solutions is markedly accelerated by the addition of cupric salts, as shown in Fig. 1. The stoichiometry of these catalyzed reactions is the same as that with valeryl peroxide (eq. 2-4): each peroxide yields a phenylbutyl radical, carbon dioxide, and phenylvaleric acid. In the presence of 0.07 M cupric salt in benzene, virtually 97% of the phenylbutyl radicals were accounted for as 4-phenylbutene-1, and small amounts of 1-phenylbutane and tetralin. The latter two products arise from radical reactions with solvent

$$C_6H_5(CH_2)_3CH_2\cdot + Cu(II) \longrightarrow$$
$$C_6H_5(CH_2)_2CH=CH_2 + H^+ + Cu(I) \quad (11)$$

and disproportionation[5] since their yields increase as the cupric concentration is lowered as shown in Table III (however, see Discussion). Although 4-phenylbutene-1 can arise by disproportionation[5] of the δ-phenylbutyl radical, we do not consider this to be the route by which it is formed in the presence of cupric salts since DeTar[5]

(17) A. Singh, L. J. Andrews, and R. M. Keefer, *J. Am. Chem. Soc.*, **84**, 1179 (1962); T. Mole, *J. Chem. Soc.*, 2132 (1960).

has shown that it is formed in only 7% yield for the thermolysis of di-ε-phenylvaleryl peroxide under conditions where tetralin is formed in 56% yield. The yields of reduced products are slightly better in acetic acid and isopropyl alcohol than benzene. Since the
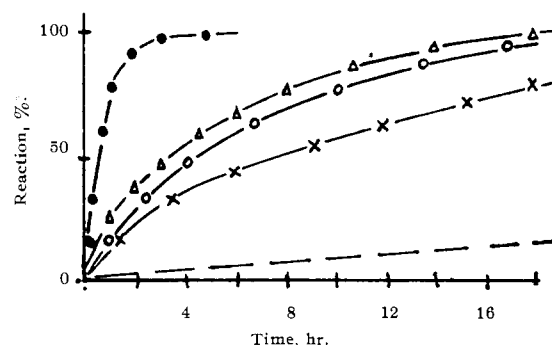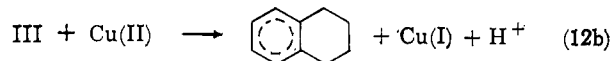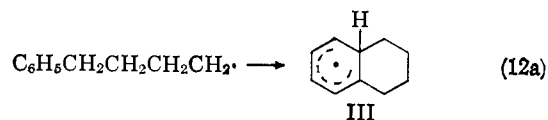

Fig. 1.—Decomposition of δ-phenylvaleryl peroxide at 48.8°: ●, 0.025 M cupric acetate in acetic acid; Δ, 0.066 M cupric octanoate in benzene–isopropyl alcohol; O, 0.013 M cupric octanoate in benzene; ×, 0.0023 M cupric octanoate in benzene; dashed line, no cupric salt.

yields of phenylbutane and tetralin vary significantly with experimental conditions, the δ-phenylbutyl radical exists independently of the closed form III; this conclusion is in accord with earlier work by Lapporte and Winstein.[18] The absence of 1-phenylbutene-1 or 1-

$$C_6H_5CH_2CH_2CH_2CH_2\cdot \longrightarrow \text{III} \quad (12a)$$

$$\text{III} + Cu(II) \longrightarrow \text{(tetralin)} + \cdot Cu(I) + H^+ \quad (12b)$$

phenylbutyl acetate indicates that 1,4- or 1,3-hydrogen transfer does not occur with this radical[5,19] under these conditions.

ε-Phenylpentyl Radical.—Crystalline di-ε-phenylcaproyl peroxide[6] was decomposed in acetic acid and benzene solutions. The rates of decomposition in the presence of approximately 0.025 M cupric salt are shown in Fig. 2. The products consisted of equal and stoichiometric amounts of carbon dioxide, 6-phenylhexanoic acid, and products derived from ε-phenylpentyl radical:

(18) S. Winstein, R. Heck, S. Lapporte, and R. Baird, *Experientia*, **12**, 138 (1956).

(19) O. A. Reutov and T. I. Shatkina, *Dokl. Akad. Nauk SSSR*, **133**, 381 (1960).

TABLE IV

DECOMPOSITION OF DI-ε-PHENYLCAPROYL PEROXIDE

Run	Temp., °C.	Copper salt,[a] M	Per- oxide, M	Solvent, ml.	5-Phenyl pentene-1, mole/mole	n-Amylbenzene, mole/mole	1-Phenyl- pentene-1, mole/mole	α-Phenyl- amyl acetate, mole/mole	5-Phenyl- amyl acetate mole/ mole	Ph- C_5H_{10}· mate- rial bal- ance,[b] %
56A	50.5	0.033E	0.23	HOAc (9)	0.93 ± 0.01	0.019 ± 0.002	0.034 ± 0.002	0.011 ± 0.002	0	99
50	48.8	.026A	.53	HOAc (20)	.81	.033	.072	....	0	91
56B	50.5	.0011A	.23	HOAc (9)	.39	.15	.190	0.075	0.024	83
56C	50.5	.0011A	.23	HOAc (9)	.37	.16	.195	.063	.023	81
56D	50.5	0	.23	HOAc (9)	.12	.17	.066	.022	.142	51
51	48.8	0.023E	.53	C_6H_6 (20)	.85	.013	.056	......	...	92
57A	50.5	.024E	.18	C_6H_6 (12)	.94	.008	.007	....	...	96
57B	50.5	.0020E	.18	C_6H_6 (12)	.73	.021	.058	....	...	81
57C	50.5	.00080E	.18	C_6H_6 (12)	.60	.038	.068	....	...	71
57D	50.5	0	.18	C_6H_6 (12)	.14	.28	.034	....	...	45

[a] A, cupric acetate; E, cupric 2-ethylhexanoate. [b] Assuming that 1 mole of peroxide yields 1 mole of PhC_5H_{10}· (see eq. 2 in text). Not true of decompositions in absence of cupric salt.

n-amylbenzene, 5-phenylpentene-1, 1-phenylpentene-1, and α-phenylpentyl acetate. As shown in Table IV, the distribution of products is highly sensitive to the cupric salt concentration. At concentrations of cupric salts greater than 0.03 M most of the ε-phenylpentyl
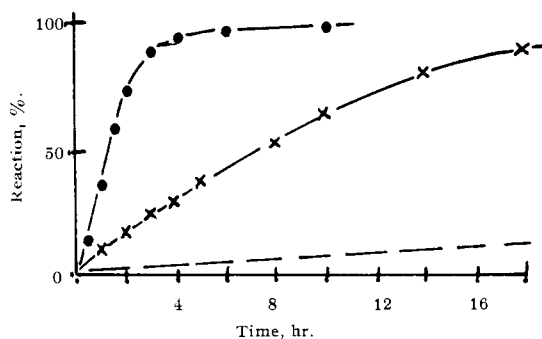

Fig. 2.—Decomposition of ε-phenylcaproyl peroxide at 48.8°: ●, 0.026 M cupric acetate in acetic acid; ×, 0.023 M cupric octanoate in benzene; dashed line, no cupric salt.
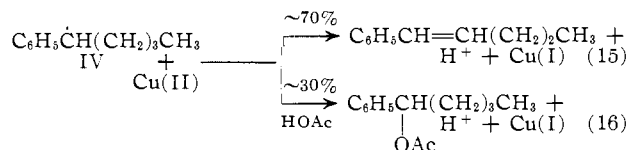
radicals are oxidized to 4-phenylpentene-1. As the cupric salt concentration is lowered, increasing amounts

$$C_6H_5(CH_2)_4CH_2\cdot + Cu(II) \longrightarrow C_6H_5(CH_2)_3CH=CH_2 + Cu(I) + H^+ \quad (13)$$

of products arising from the rearranged radical, α-phenylpentyl IV, are formed. In acetic acid these are primarily 1-phenylpentene-1 and α-phenylpentyl ace-

$$C_6H_5(CH_2)_4CH_2\cdot \longrightarrow C_6H_5\dot{C}H(CH_2)_3CH_3 \quad (14)$$
$$\text{IV}$$
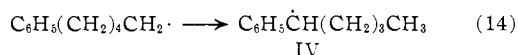
tate which result from the subsequent oxidation of IV by cupric species.

$$C_6H_5\dot{C}H(CH_2)_3CH_3 \xrightarrow[\text{Cu(II)}]{\sim70\%} C_6H_5CH=CH(CH_2)_2CH_3 + H^+ + Cu(I) \quad (15)$$
$$\text{IV} \quad +$$
$$\xrightarrow[\text{HOAc}]{\sim30\%} C_6H_5CH(CH_2)_3CH_3 + \\ | \quad H^+ + Cu(I) \quad (16) \\ OAc$$

These results are consistent with our earlier studies of the oxidation of alkyl radicals.[20] Even in the presence of acetic acid, oxidation of primary alkyl radicals by cupric acetate yields only α-olefins. The benzylic radicals IV are oxidized to a mixture of phenylalkenes

(20) H. E. DeLaMare, J. K. Kochi, and F. F. Rust, J. Am. Chem. Soc., 83, 2013 (1961); 85, 1437 (1963).

and aralkyl acetates in approximately 2–3 to 1 ratio similar to other aralkyl radicals. At the opposite extreme, allylic radicals are oxidized solely to allylic acetates.[21] At low cupric concentrations in acetic acid, small amounts of 5-phenylpentyl acetate is formed via the acid-catalyzed decomposition of the peroxide.[11] No evidence for benzsuberane or α-methyltetralin was found. At concentrations of cupric salt greater than 0.03 M the material balance for the phenylpentyl radical is good. Yields of dimeric products of the phenylpentyl radicals were not determined, and they probably account for the decreased material balance in those runs at lower cupric concentrations.

Experimental

Materials. Metal Salts.—Cupric acetate hydrate, $Cu(OAc)_2 \cdot H_2O$, Mallinckrodt analytical reagent; **cupric 2-ethylhexanoate,** $Cu(C_8H_{25}O_2)_2$, Shepherd Chemical Co., Cincinnati, Ohio.

Acids and Acid Chlorides. δ-Phenylvaleryl Chloride.—To a stirred solution of 13.8 g. of sodium and 96.0 g. of diethyl malonate was added 92.7 g. of 3-phenylpropyl chloride. After stirring 20 min., the mixture was refluxed for 5 hr. Water was added to dissolve the salt and the aqueous phase extracted with ether. After drying the ethereal solution over sodium sulfate and removal of the ether, distillation afforded 72.5 g., 44% of the ester, b.p. 195–203° at 19 mm., lit.[22] b.p. 189–194° at 13 mm. The ester with 70 g. of potassium hydroxide in 150 ml. of water was stirred and heated until homogeneous, then acidified and extracted with ether. The ethereal extract was washed with water, the ether removed, and the residue heated to 180° until evolution of gas ceased. It afforded 29.4 g., 64%, of the acid, m.p. 56–58°, lit.[22] m.p. 57°. Heating a 25.2-g. sample of the acid on the steam bath with 50 ml. of thionyl chloride for 105 min. followed by removal of excess thionyl chloride and distillation afforded 23.6 g., 88%, of the acid chloride, b.p. 110–111° at 3 mm., lit. b.p. 129–131° at 11 mm.

4-Phenylbutyric Acid.—Carboxylation of the Grignard of 3-phenylpropyl chloride afforded the crude acid in 93% yield, m.p. 42–47°, lit.[23] m.p. 46–48°.

o-Benzylbenzoyl Chloride.—A sample of o-benzoylbenzoic acid was prepared by the method of Fieser[24]; m.p. 127–129°, lit.[3] m.p. 127–128°. Ammoniacal zinc reduction of a portion of this by the method of Barnett, Cook, and Nixon[25] afforded o-benzylbenzoic acid in 71% yield, m.p. 115–116°; lit. m.p. 118°,[4] 115–117°.[5] The acid chloride was prepared by the method of

(21) J. K. Kochi, ibid., 84, 774, 1572, 2785 (1962).

(22) J. von Braun and O. Kruber, Ber., 45, 386 (1912).

(23) E. L. Martin, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 499.

(24) L. F. Fieser, "Experiments in Organic Chemistry," 3rd Ed., revised, D. C. Heath and Co., Boston, Mass., p. 160.

(25) E. de B. Barnett, J. W. Cook, and I. G. Nixon, J. Chem. Soc., 508 (1927).

Greene, et al.,[4a] and stored in petroleum ether at −20° until used.

o-Phenylbenzoyl Chloride.—A sample of o-phenylbenzoic acid was prepared from fluorenone by the procedure of Gutsche and Johnson[26]; m.p. 109–111°, lit.[6] m.p. 110–113°. The acid chloride was prepared by stirring a solution of 24 ml. of pyridine and 110 g. of the acid in anhydrous ether and adding 120 ml. of thionyl chloride slowly. Filtration, removal of the ether, and distillation afforded material of b.p. 143–145° at 2.8 mm., lit.[4a] b.p. 99.5–101° at 0.3 mm.

ε-Phenylcaproyl chloride was prepared in 60% yield from ε-phenylcaproic acid[27a] by the pyridine–thionyl chloride method; b.p. 128° at 1.9 mm. ε-Phenylcaproic acid was synthesized from 5-benzoylvaleric acid (Aldrich Chem. Co.) by the Wolff–Kishner reduction.[27b]

Hydrocarbons.—4-Phenylbutene-1 was prepared by coupling the Grignard of allyl chloride with benzyl chloride in 21% yield, b.p. 178–180.5°, n^{25}D 1.5100; lit.[5c] b.p. 178–179°, n^{25}D 1.5066.

5-Phenylpentene-1 was synthesized by treatment of the Grignard of 2-phenylethyl bromide with allyl bromide in 50% yield, b.p. 96–97° at 25 mm., lit.[28] b.p. 77–78° at 10 mm.

1-Phenylpentene-1 was prepared by the sulfuric acid dehydration of 1-phenylpentanol-1; b.p. 79.3–80.3° at 5.3 mm., lit.[29] b.p. 202–205°.

Amylbenzene was synthesized by hydrogenation of 5-phenylbutene-1 over Adams catalyst, b.p. 60° at 2.4 mm.

Esters, Lactones, and Alcohols. 4-Phenylbutyl Acetate.—The ethyl ester of 4-phenylbutyric acid was prepared by sulfuric acid-catalyzed esterification. Distillation afforded material of b.p. 143–144.5° at 20 mm., lit. b.p. 144–147° at 19 mm. Treatment of the ester with lithium aluminum hydride afforded the alcohol, b.p. 141–147° at ca. 20 mm., n^{27}D 1.5164; lit.[30] b.p. 125–126° at 8 mm., n^{20}D 1.5220. The acetate was prepared by treatment of the alcohol with an ethereal solution of acetyl chloride and pyridine. After filtration and removal of ether in vacuo, the residue was taken up in hexane and washed three times with aqueous sodium bicarbonate and then water.

1-Phenylpentyl Acetate.—Treatment of the Grignard reagent of 1-chlorobutane with benzaldehyde by the method of Conant and Blatt[31] afforded 1-phenylpentanol in 73% yield, b.p. 97–99° at 2 mm., lit.[31] b.p. 129–130° at 13 mm. The acetate was prepared by the acetyl chloride–pyridine method. Distillation afforded a heart cut of b.p. 107° at 2.3 mm.

3-Phenylphthalide was prepared from o-benzoylbenzoic acid in 68% yield by the method of Ullmann[32]; m.p. 114–115°, lit.[32] m.p. 114–115°.

3,4-Benzcoumarin was prepared by chromic acid oxidation of o-phenylbenzoic acid according to the method of Kenner, Murray, and Tylor[4b]; m.p. 92–93°, lit.[4a] m.p. 92–94°.

Peroxides.—o-Benzylbenzoyl peroxide was prepared in 51% yield from the acid chloride by the method of Greene, et al.[4a]; m.p. 74–75°, lit. m.p. 72.5–73°.

o-Phenylbenzoyl peroxide was prepared by the procedure of Kenner, Murray, and Tylor from the distilled acid chloride in 62% yield, m.p. 105–106° dec., lit.[4b] dec.p. 101.5–102.5°, 107–108°.[4b]

δ-Phenylvaleryl peroxide was synthesized by the method of DeTar and Weis in 88% yield, m.p. 31–32°, lit.[5] m.p. 33–34°.

ε-Phenylcaproyl Peroxide.—To a stirred mixture of 120 g. of ice and 120 cc. of water was added 18.4 g. of 94% sodium peroxide. To this was added by dropwise addition a solution of 26 g. of 6-phenylhexanoyl chloride in 70 cc. of anhydrous ether with cooling. After stirring for 20 min., the water layer was separated and washed with ether. The combined ether portions were washed with water, dried over sodium sulfate, and the ether removed in vacuo. The oily residue was dissolved in 30 cc. of chloroform and poured into 300 cc. of methanol. Upon cooling, the peroxide crystallized.　Recrystallization from

petroleum ether, b.p. 30–60°, followed by recrystallization from isopentane, afforded 16.2 g., 71%, of material, m.p. 26°, lit.[6] m.p. 27–28°. Iodometric titration indicated 98.3% purity.

Procedure for Decomposition of Peroxides.—The peroxides were decomposed in a magnetically stirred 50-ml. round-bottom flask maintained at constant temperature by an oil bath. In those reactions employing copper salts as catalysts, the salts were first dissolved in the solvent, the solution swept with nitrogen, and peroxide added under reverse nitrogen flow. The solution was swept for an additional 5 min. When no copper salt was used, the peroxide was dissolved in solvent and swept for 10 min. with nitrogen. The gas was collected over mercury and in all cases indicated only carbon dioxide by g.l.c. analysis. Upon completion of the decomposition, those reactions employing copper 2-ethylhexanoate as catalyst and benzene as solvent as well as those in benzene with no catalyst were diluted with aqueous HCl, extracted several times with an appropriate solvent, and the combined work-up solvent was extracted with aqueous sodium bicarbonate until no more gas evolved, and analyzed as described below. Acidification of the bicarbonate extract afforded the acids. These were dissolved in ether, dried over sodium sulfate, decanted, and the ether removed. The acids were weighed and melting points taken. Those reactions carried out in acetic acid with or without cupric acetate hydrate were diluted with water and worked up as described above.

o-Phenylbenzoyl Peroxide.—The extracting solvent used in these decompositions was benzene. The benzene solutions were analyzed by g.l.c. using a 5-ft., 5% SE30 on Chromosorb W column at 195°. The marker method was used with anthracene serving as the marker; all determinations were run in duplicate. Results are reported in Table I.

o-Benzylbenzoyl Peroxide.—The extracting solvent used in these decompositions was chloroform. After diluting run 21 to a known volume, the chloroform solution was analyzed for 3-phenylphthalide by infrared spectroscopy using the band at 1760 cm.$^{-1}$. Removal of the chloroform afforded a white solid, m.p. 112–114°; mixture m.p. with 3-phenylphthalide, 112–115°. Removal of the ether after extracting the bicarbonate solution afforded a white solid, m.p. 110–114°; mixture m.p. with o-benzylbenzoic acid, 111–116°; mixture m.p. with 3-phenylphthalide, 86–92°.

Run 23 afforded o-benzylbenzoic acid, m.p. 113–116°; mixture with authentic material, 113–116°. Results are reported in Table II.

δ-Phenylvaleryl Peroxide.—The extracting solvent used for these decompositions was hexane. The marker method of analysis by g.l.c. employed p-dichlorobenzene as a marker. Analysis was carried out in at least duplicate on a 7-ft., 20% Carbowax 4M terephthalate on Chromosorb W column at 195°. All of the acids isolated melted no lower than 54° and mixture m.p. with authentic 5-phenylvaleric acid showed no depression. Results are reported in Table III.

Hydrogenation of a portion of the products from runs 26 and 31 over Adams catalyst caused the g.l.c. peak identified as 4-phenylbutene-1 to coalesce with that identified as phenylbutane while the peak identified as tetralin showed no change. The ratio of 4-phenylbutene-1 to tetralin and to p-dichlorobenzene marker before hydrogenation and of phenylbutane to tetralin and p-dichlorobenzene after hydrogenation remained unchanged. This indicated that the peaks were pure and 4-phenylbutene was quantitatively hydrogenated to butylbenzene.

Refluxing a portion of the product mixture from run 32 with lithium aluminum hydride in ether for 3 days afforded no observable 4-phenylbutanol.

ε-Phenylcaproyl Peroxide.—These decompositions were treated exactly like those of δ-phenylvaleryl peroxide. Results are reported in Table IV. In order to ensure that the 5-phenylpentene-1-obtained from the oxidation was pure, it was hydrogenated quantitatively to amylbenzene in ethyl acetate over Adams catalyst. The reaction mixture containing tetralin as marker was also hydrogenated. The g.l.c. showed that both 5-phenylpentene-1 and 1-phenylpentene-1 was converted to n-amylbenzene. The combined ratio of the phenylpentene isomers to tetralin was the same as the ratio of amylbenzene to tetralin.

The value of k_{Ox}/k_R for δ-phenylbutyl radical listed in Table III was calculated by dividing the yield of 4-phenylbutene-1 (direct oxidation, eq. 11) by the yield of tetralin (rearrangement-oxidation, eq. 12) and dividing this ratio by the total cupric

(26) C. D. Gutsche and W. S. Johnson, J. Am. Chem. Soc., 68, 2239 (1946).

(27) (a) L. F. Fieser, ibid., 70, 3200 (1948); (b) Huang-Minlon, ibid., 68, 2487 (1946).

(28) J. von Braun and H. Deutsch, Ber., 45, 1255 (1912).

(29) J. von Braun and Z. Kohler, ibid., 51, 84 (1918).

(30) W. E. Truce and J. P. Millionis, J. Am. Chem. Soc., 74, 974 (1952).

(31) J. B. Conant and A. H. Blatt, J. Am. Chem. Soc., 50, 554 (1928).

(32) F. Ullmann, Ann., 291, 23 (1896).

(33) The latter appears unlikely since the alternative and more favorable bond cleavage would yield 2-carboxy-3'-acetoxybiphenyl which has not been found.

salt concentration. The assumptions made in applying this technique are discussed elsewhere.[34,35]

A similar method was applied to ε-phenylpentyl radical. 5-Phenylpentene-1 (direct oxidation, eq. 13) and 1-phenylpentene-1 and 1-phenylpentyl acetate (rearrangement–oxidation, eq. 15 and 16) were considered to be the products resulting from the oxidation of ε-phenylpentyl radicals.

Discussion

The procedure developed earlier[11] for the metal salt-catalyzed decomposition of valeryl peroxide is found to be applicable to the four diacyl peroxides used in this study. For both aroyl and acyl peroxides the catalyzed decomposition leads to 1 mole of acid together with 1 mole of aroyloxy radicals from aroyl peroxides and 1 mole of alkyl radicals and carbon dioxide from acyl peroxides, in accord with sequences (5), (8), and (2), respectively.

Oxy radicals are unaffected by cupric salts.[3a] Thus, only those radicals which result from rearrangement of aroyloxy radicals can be oxidized by these salts. The oxidation of the cyclized form I of o-phenylbenzoyloxy radical to 3,4-benzcoumarin (reaction 7) can proceed either by an intermediate carbonium ion[6] with subsequent loss of a proton,[20] or by transfer[16] of an acetate moiety to form a cyclohexadiene diester followed by loss of acetic acid and rearomatization.[33] The analogous oxidation of the cyclized form III of δ-phenylbutyl radical does not appear to be operative with cupric acetate, since the yield of tetralin falls to 1% at 0.07 M cupric salt in benzene compared to 56% in the absence of cupric salt. These apparently discordant results can be explained if one assumes that a primary alkyl radical such as a δ-phenylbutyl radical is more readily oxidized than it is cyclized to the cyclohexadienyl radical III. The relative rates of these reactions is given by k_{Ox}/k_R where k_R and k_{Ox} are the first-order rate constant for rearrangement and the second-order rate constant for oxidation, respectively. The ratio has a value of ca. 1.3×10^3 l./mole in benzene and is constant over a thirtyfold variation in cupric concentration, as shown in Table III.[34]
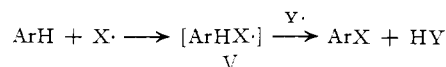
Homolytic aromatic substitution reactions are considered to proceed via addition to form a cyclohexadienyl radical intermediate V.[36] Such delocalized radicals as V are analogous to the cyclized forms I and III of o-phenylbenzoyloxy and 4-phenylbutyl radicals, respectively. We are presently examining the possibility

of generally effecting oxidation of such intermediates with metal salts.

$$ArH + X\cdot \longrightarrow [ArHX\cdot] \overset{Y\cdot}{\underset{V}{\longrightarrow}} ArX + HY$$

1-Phenylpentene-1 and 1-phenylpentyl acetate can be considered to be the only products of oxidation of the rearranged α-phenylpentyl radical derived from ε-phenylpentyl radical (eq. 14–16). The increasing amounts of 1-phenylpentene-1 and 1-phenylpentyl acetate as products of oxidation at low concentrations of cupric salt (Table IV) indicate that the intramolecular chain-transfer reaction (14) is competing significantly with the direct oxidation of ε-phenylpentyl radical to 4-phenylpentene-1 (eq. 13). The value of k_{Ox}/k_R can be determined from the yields of oxidation products in a manner similar to that applied to the δ-phenylbutyl radical. In benzene this value is approximately 4×10^3 l./mole and it is slightly larger than the corresponding value for the δ-phenylbutyl radical. Since it is expected that k_{Ox} will be the same for δ-phenylbutyl as its higher homolog, the indication is that the cyclization of δ-phenylbutyl radical is slightly faster than intramolecular hydrogen transfer of ε-phenylpentyl radical from its benzylic position. In both cases the rate of oxidation of ω-phenylalkyl radicals by cupric salts favorably competes with intramolecular rearrangement even at concentrations as low as 0.03 M cupric salt.

For both δ-phenylbutyl and ε-phenylpentyl radicals the value of k_{Ox}/k_x can be taken as a measure of the relative ease of oxidation of alkyl radicals generally by cupric salts.[37] These values which were calculated from the yields of products of oxidation of these radicals are inherently subject to question.[34,35] However, the order of magnitude for the rates of oxidation of alkyl radicals reflected in these values is significant. The yields of products of oxidation, furthermore, point out qualitatively the rapidity of these oxidation steps. Thus, less than 0.05 M cupric acetate is required to oxidize these phenylalkyl radicals efficiently to ω-phenylalkenes without significant incursion of the facile intramolecular rearrangement reactions.[5,6,38] Intermolecular reactions such as bimolecular hydrogen transfer or combination–disproportionation of these radicals were not observed even at concentrations less than 0.02 M cupric salt. We expect, therefore, that for specific oxidation of alkyl radicals, concentrations of cupric salt less than 0.02 M would be sufficient to cope with most intermolecular reactions since intramolecular reactions are generally slow.[39]

(34) An implicit assumption is, of course, that the rearrangement and oxidation are first- and second-order reactions, respectively. Furthermore, in the presence of cupric salt the further assumption is made that tetralin and only tetralin arises by oxidation of III and it does not arise via a disproportionation, or similar reactions (this assumption is less tenable, though the constancy of k_{Ox}/k_R at various cupric concentrations supports it).

(35) The values of k_{Ox}/k_R were calculated by assuming that all cupric species were active in the oxidation. Recent studies have shown that only monomeric cupric salts oxidize alkyl radicals. Since cupric acetate in benzene and glacial acetic acid is largely dimeric, the values of k_{Ox}/k_R are minimum values. They probably should be corrected by at least a factor of 10 (unpublished results, R. V. Subramanian).

(36) E. L. Eliel, S. Meyerson, Z. Welrart, and S. Wilen, J. Am. Chem. Soc., **80**, 3309 (1958); **82**, 2936 (1960); Tetrahedron Letters, 749 (1962); D. H. Hey, M. J. Perkins, and G. H. Williams, ibid., 445 (1963); D. F. DeTar and R. A. J. Long, J. Am. Chem. Soc., **80**, 4742 (1958).

(37) The remotely situated phenyl moiety should not affect the behavior of the alkyl radical (cf. M. M. Martin and G. J. Gleicher, ibid., **86**, 242 (1964)).

(38) K. Heusler and J. Kalvoda, Tetrahedron Letters, 1001 (1963).

(39) A. S. Gordon and J. R. McNesby, J. Chem. Phys., **33**, 1882 (1961); R. Kh. Friedlina, V. N. Kost, and M. Ya. Khorlina, Uspekhi Khim., **31**, 1 (1962).