[CONTRIBUTION FROM THE INSTITUTE OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF CHICAGO]

New Metal Salt-Induced Homolytic Reactions. II. Modification of Free Radical Reactions by Copper Salts[1]

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Received October 2, 1958

The following reactions are profoundly influenced by small quantities of cuprous salts: (1) the pyrolysis of dicumene; (2) the decomposition of benzoyl peroxide in octene-1 and octene-2; (3) the decomposition of benzoyl peroxide in cumene; (4) the decomposition of benzoyl peroxide in a mixture of valeraldehyde and carbon tetrachloride; (5) the decomposition *tert*-butyl peroxide in benzaldehyde; (6) the decomposition of *tert*-butyl peroxide in cumene. The influence of copper salts is discussed.

It is well established that the course of ionic reactions can be altered by catalysts. The aim of this work was to show that there are compounds, which if present in catalytic amounts, can drastically change the course of free radical reactions. This publication deals with the effect of copper salts on some well known homolytic reactions. Future publications will deal with some new homolytic reactions, which can be carried out while using copper and other metal salts as catalysts. There were several considerations which directed us to copper salts as the most promising catalysts to alter homolytic reactions.

Many metal salts are capable of initiating homolytic reactions by acting as one-electron oxidizing and reducing agents, for example, the reactions of hydroperoxides initiated by iron, copper, cobalt, and manganese salts.[4]

Metal salts can also initiate homolytic reactions if advantage is taken of the property that in their most stable form, the valence of some metals is different in organometallic compounds than in some salts. For example, if potassium cyanide is added to cupric salts, the initially formed cupric cyanide is unstable and breaks down into cuprous cyanide and cyanogen.[5] In a similar fashion, certain

$$CuSO_4 + 2KCN \longrightarrow Cu(CN)_2 + K_2SO_4 \qquad (1)$$

$$2Cu(CN)_2 \longrightarrow 2CuCN + (CN)_2$$

salts such as cuprous, cobaltous, and manganous salts initiate the formation of free radicals and Grignard reagents.[6] Depending on the nature of

$$RMgBr + CoCl_2 \longrightarrow RCoCl + MgBrCl \qquad (2)$$

$$RCoCl \longrightarrow R\cdot + CoCl$$

the salt, the reaction takes a different course. The reaction between *tert*-butylmagnesium bromide and ethyl bromide, with cobaltous chloride as catalyst yields as disproportionation products isobutane and isobutylene exclusively. The same reaction with manganous chloride as catalyst yields 43% of the dimerization product, hexamethylethane. On the basis of these findings, it was expected that the presence of metal salts would alter other homolytic reactions, reactions which are usually carried out in the absence of any metal salt.

The copper-catalyzed Ullmann reaction, condensation of an aromatic amine with an aromatic halide, is widely used in the vat-dyestuff industry. Its homolytic nature has long been suspected, notwithstanding the fact that some of its characteristics, like the advantage of using nitrobenzene as a solvent, would appear to bear evidence to the contrary. Similarly, it has been suggested several times that the Meerwein and Sandmeyer reactions are free radical in nature. As a starting place, it was decided to study the effect of copper salts on homolytic reactions.

Pyrolysis of dicumene. If a solution of dicumene in bromobenzene is heated in a sealed tube to 255° for 10 hours, all of the dicumene will have disappeared. After distilling off the lower boiling material, only a tarry material weighing 12% of the dicumene charged remains. At an elevated temperature, dicumene is expected to disassociate, to some extent into α-cumyl radicals (Equation 3), which will induce a decomposition into cumene and α-methylstyrene (Equation 4). In the presence

$$[C_6H_5(CH_3)_2C]_2 \longrightarrow 2C_6H_5(CH_3)_2C\cdot \qquad (3)$$

$$C_6H_5(CH_3)_2C\cdot + [C_6H_5(CH_3)_2C]_2 \longrightarrow C_6H_5(CH_3)C{=}CH_2 + C_6H_5(CH_3)_2CH + C_6H_5(CH_3)_2C\cdot \qquad (4)$$

of two mole percent of cuprous bromide, 70% of the charged weight of the high-boiling material remained, even after heating at 255° for 24 hours. After recrystallization, 37% of pure dicumene could be isolated. The melting point was 119°, undepressed by the starting material.

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[1] *Cf.* M. S. Kharasch and A. Fono, *J. Org. Chem.*, **23**, 324 (1958).

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[4] M. S. Kharasch and A. Fono, *J. Org. Chem.* **24**, 72 (1959).

[5] G. Jacquemin, *Bull. Soc. Chim.*, (2) **43**, 556 (1885).

[6] M. S. Kharasch, T. W. Hancock, W. Nudenberg, and P. O. Tawney, *J. Org. Chem.*, **21**, 322 (1956). M. S. Kharasch, D. W. Lewis, and W. B. Reynolds, *J. Am. Chem. Soc.*, **65**, 493 (1943).

Reaction of benzoyl peroxide with octene-1 in the presence and the absence of cuprous salts. It is claimed that substances having the physical consistency of vaseline are formed when benzoyl peroxide is heated with octene-1, dissolved in organic solvents.[7] Unfortunately, the chemical nature of the products formed were not investigated, as the authors were primarily interested in producing "lubricants of high viscosity and low pour point".

In our study, the matter of primary concern was the modification induced by cuprous salts on the decomposition of benzoyl peroxide in the presence of simple olefins. The strong effect of trace amounts of such salts (one mole percent on the basis of the peroxide used) on the distribution of the products formed, when benzoyl peroxide is decomposed in octene-1 is shown in Table I.

TABLE I

PRODUCTS FORMED BY THE DECOMPOSITION OF BENZOYL PEROXIDE (1 MOLE) IN OCTENE-1 (8 MOLES) AT 100° IN THE PRESENCE AND ABSENCE OF CUPROUS CHLORIDE (1 MOLE %)

Without Additive	Cu_2Cl_2
1. Benzoic acid (6 mole %)	1. Benzoic acid (72 mole %)
2. 1:1 adduct (20 mole %)[a] Unsaturation in adduct (30%)	2. 1-Phenyloctene-2 (8 mole %)
3. 1:2 adduct (25 mole %) Unsaturation in adduct (30%)	3. 1:1 adduct (34 mole %) Unsaturation in adduct (77%)[b]
4. High mol. wt. adduct (average mol. wt., 600; containing four octenes to one benzoyloxy group (57 mole %). Total wt. on peroxide used—340 g. Unsaturation—(60%)	4. 1:2 adduct (34 mole %) Unsaturation in adduct (100%)
5. CO_2 (80 mole %)	5. High mol. wt. adduct—negligible (only about 7 g.). Since only 0.2 mole of peroxide was used, the amount of the material formed was too small for further work (1.4 g.)
	6. CO_2 (42 mole %)

[a] On the basis of the infrared spectrum and analyses of this material (after hydrolysis) it is estimated that it contains about 40% of a phenyloctane. [b] Probably the low unsaturation in this adduct (77%) is caused by the very low solubility of the cuprous chloride; note also that this salt was not finely powdered.

The important difference in the decomposition of benzoyl peroxide in octene-1 in the presence, and in the absence of cuprous salts is not in the products formed, but in the relative amounts of the products. First: only seven grams of high molecular weight products are formed in the presence, 340 grams in the absence, of cuprous salts. Second: a higher amount of unsaturation is found in the 1:1 and 1:2 adducts (1 benzoyloxy group to 2 octenes) formed in the presence of cuprous salts. Third: A large amount of benzoic acid (72 mole %) is formed in the reaction with cuprous salts; a small amount (6 mole %) is formed in their absence. Fourth: 42 mole % of carbon dioxide is evolved in their presence; approximately 80 mole % is evolved in the absence of cuprous salts.

All of these products, according to their infrared spectra contain a *trans* double bond, and with the exception of the benzoyloxyoctene (1:1 adduct) formed in the presence of copper salts, there is no indication of a terminal double bond in any of these adducts. The benzoyloxyoctene contains about 30% terminal double bond.

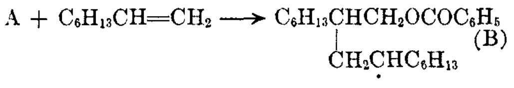
The decomposition of the peroxide in the absence of cuprous salt can be described by the following reaction scheme, in agreement with other well known radical reactions.

$$(C_6H_5COO)_2 \xrightarrow{\Delta} 2C_6H_5COO\cdot \qquad (5)$$

$$C_6H_5COO\cdot + C_5H_{11}CH_2CH{=}CH_2 \longrightarrow C_5H_{11}CH_2\underset{\cdot}{C}HCH_2OCOC_6H_5 \qquad (6)$$

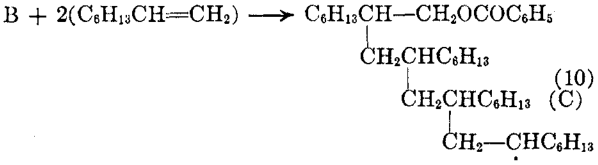
(A)

$$2A \xrightarrow{\text{Disp.}} C_5H_{11}CH_2CH_2CH_2OCOC_6H_5 + C_5H_{11}CH{=}CHCH_2OCOC_6H_5 \text{ (1:1 adducts)} \qquad (7)$$



$$A + C_6H_{13}CH{=}CH_2 \longrightarrow \begin{array}{l} C_6H_{13}CHCH_2OCOC_6H_5 \\ \quad | \\ \quad CH_2\underset{\cdot}{C}HC_6H_{13} \end{array} \text{(B)} \qquad (8)$$

$$2B \xrightarrow{\text{Disp.}} B_{+H} + B_{-H} \text{ (1:2 adducts)} \qquad (9)$$



$$B + 2(C_6H_{13}CH{=}CH_2) \longrightarrow \begin{array}{l} C_6H_{13}CH{-}CH_2OCOC_6H_5 \\ \quad | \\ \quad CH_2CHC_6H_{13} \\ \qquad\quad | \\ \qquad\quad CH_2CHC_6H_{13} \quad \text{(C)} \\ \qquad\qquad\quad | \\ \qquad\qquad\quad CH_2{-}\underset{\cdot}{C}HC_6H_{13} \end{array} \qquad (10)$$

$$2C \longrightarrow C_{+H} + C_{-H} \qquad (11)$$

(High molecular weight material)

The radical C may disproportionate with itself as in Equation 11 to give 50% unsaturation in the "high molecular weight material"; or it may disproportionate with the free radicals A and B. Since the 1:1 and 1:2 adducts are less than 50% unsaturated, while the "high molecular weight material" is 60% unsaturated, it is reasonable to assume that the radicals A and B, when they disproportionate with C, capture a hydrogen atom.

In the presence of cuprous salts, very little "high molecular weight material" is formed. The unsaturation in the 1:1 and 1:2 adducts is very much higher than the unsaturation in the adducts formed in the absence of cuprous salts. This suggests that cuprous salts must facilitate the termination reaction. This conclusion is substantiated by the large amount of benzoic acid (78 mole %) formed in the reaction in the presence of cuprous salts and the very small amount of benzoic acid (6 mole %) formed in the absence of these salts.

The reaction of benzoyl peroxide with octene-1 took a similar course, when instead of a large excess of octene, ethyl acetate was used as a solvent. Using an aromatic solvent, (benzene, chlorobenzene,

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(7) F. M. Seger, Pittman, W. Garwood, Haddonfield, and A. N. Sachanen, U. S. Patent 2,551,641.

xylene) the reaction takes a somewhat different course. No 1-phenyloctene-2 is formed. The main reaction product is 1-phenyloctene-1, in 45% yield, n_D^{20} 1.5225,[8] absorption peak in the ultraviolet at 247 millimicrons (characteristic of styrenes). The benzoyloxyoctenes (1:1 adduct) formed in 23% yield. Judging their composition from the infrared absorption spectra, they contained mainly 1-benzoyloxyoctene-2, but also some 1-benzoyloxyoctene-1, indicated by a peak at 1778 cm.$^{-1}$ (characteristic for vinyl esters) and approximately 20% 3-benzoyloxyoctene-1. 15% of a 1:2 adduct was also isolated (1-benzoyloxy group for 2 octene groups).

Reaction of benzoyl peroxide with octene-2 in the presence and absence of cuprous salts. Examination of Table II will indicate that the decomposition of benzoyl peroxide in the presence and absence of cuprous salts is somewhat similar to the thermal decomposition of the peroxide in octene-1. The differences observed in the yields of the various products (namely large amounts of 1:1 adduct, and very small amounts of higher adducts) as compared with the products formed when octene-1 is used were attributed to the lower reactivity of the double bond in octene-2.

TABLE II

Products Formed by the Decomposition of Benzoyl Peroxide (1 mole) in Octene-2 (8 moles) at 95° in the Presence and Absence of Cuprous Chloride (1 mole %)

Without Additives	Cu_2Cl_2
1. Benzoic acid (29 mole %)	1. Benzoic acid (69 mole %)
2. 1:1 adduct (85 mole %) Unsaturation in adduct (60%)	2. 1:1 adduct (73 mole %)[a] Unsaturation in adduct (93%)
3. 1:1 adduct (13 mole %)	3. High boiling residue (7.5g.) Mol. wt., 350
4. High boiling residue (20g.) Mol. wt., 380	

[a] This product contains approximately 5 per cent of a phenyloctene.

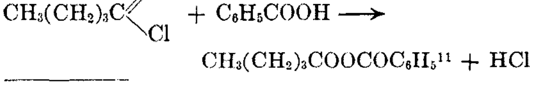
Reaction of benzoyl peroxide with cumene in the presence and absence of cuprous chloride. The decomposition of benzoyl peroxide in cumene has been studied by a number of investigators. The products which have been isolated are listed in Table III. For comparison purposes, the products formed when benzoyl peroxide is decomposed in cumene, in the presence of cuprous chloride are included in the same table.

The data recorded in Table III suggest two mechanisms for the decomposition of benzoyl peroxide in cumene. By one of these, a hydrogen atom is removed from cumene to give a free cumyl radical. The second is the phenylation of cumene, which leads to various isopropyl biphenyls.[9]

The effect of minute amounts of cuprous salts on the decomposition of benzoyl peroxide in cumene is quite remarkable. In the presence of the cuprous salt, (see Table III), the yield of dicumene is practically negligible, less than 2%. However, α-cumyl benzoate is formed in an amount nearly equivalent to the dicumene formed in the absence of the cuprous salt. A second striking effect is that cuprous salts have practically no effect on the yield of the isopropylbiphenyls. Hence, in the decomposition of the peroxides in solvents, cuprous salts have apparently a pronounced effect only on the reactions which involve very unreactive radicals; and only a minor effect on reactions involving reactive radicals.

There is evidence however, that cuprous salts play a role in the formation of isopropylbiphenyls. The decomposition of the benzoyl peroxide in toluene, in the presence of cuprous salts gives products similar to those formed in the absence of the same salts. Yet, the rate of the decomposition of the peroxide is considerably greater and an appreciably less high molecular weight oil is formed.

The decomposition of benzoyl peroxide in a mixture of valeraldehyde and carbon tetrachloride in the presence of cuprous chloride. It has been established that isovaleroyl chloride and chloroform are formed[10] when a mixture of isovaleraldehyde and carbon tetrachloride, in the presence of benzoyl peroxide (10 mole %) is refluxed for 24 hours. Similarly, when a mixture of valeraldehyde (one mole), benzoyl peroxide (0.5 mole), carbon tetrachloride (5–6 moles) is heated to 76° for six hours, the reaction products are chloroform, hydrogen chloride, and valeroyl benzoyl anhydride, and a mixture of the two unsymmetrical anhydrides. The mixed anhydride is undoubtedly formed in this instance from the valeroyl chloride and the benzoic acid.



$$CH_3(CH_2)_3C(=O)Cl + C_6H_5COOH \longrightarrow CH_3(CH_2)_3COOCOC_6H_5{}^{11} + HCl \quad (12)$$

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(8) S. Reich, R. Van Wijck, and C. Waelle, *Helv. Chim. Acta*, **4**, 242 (1921) prepared what they thought to be pure 1-phenyloctene-1 from phenylheptylcarbinol and reported refractive index n_D^{17} 1.50728. Because of the method used, it may have contained 1-phenyloctene-2. The refractive index reported by us is similar to those of other long chain vinylbenzenes. 1-Phenylpentene n_D^{18} 1.5302, T. Levy, Dvoleitska, and Gombinska, *Bull. Soc. Chim.*, (4) **49**, 1765 (1931). 1-Phenylhexene n_D^{25} 1.5377, C. S. Marvel, F. D. Hager, and D. D. Coffman, *J. Am. Chem. Soc.*, **44**, 2323 (1927).

(9) As to the respective yields of isopropylbiphenyl, the results obtained by Dannley and Zaremsky (see Table III), although somewhat low are comparable to those obtained by the other investigators. The exceptionally low yield of dicumene obtained by Dannley and Zaremsky cannot readily be dismissed. Prof. Dannley mentioned in private discussions that it is possible that his reaction mixture contained a trace amount of copper salts.

(10) S. Winstein and F. H. Seubold, *J. Am. Chem. Soc.*, **69**, 2916 (1957).

(11) Since mixed anhydrides are thermally unstable, and break down into two symmetrical anhydrides, it is not surprising that some of these symmetrical anhydrides were also obtained during the distillation of the unsymmetrical anhydride.

TABLE III

DECOMPOSITION OF BENZOYL PEROXIDE IN CUMENE AT 80°

Investigator	[a]	[b]	[c]	Kharasch, Fono[d]
Reagents in moles				
Benzoyl peroxide	1.0	1.0	1.0	1.0
Cumene	16.0	—	80.0	10.0
Cuprous chloride (1 mole %)	Absent	Absent	Absent	Present
Products				
CO_2	1.1	—	—	1.0
Benzoic acid	0.78	0.41	0.60	0.45
Isopropylbiphenyls	0.18	0.27	0.24	*ca.* 0.20
Dicumene	0.08	0.31	0.35	Less than 0.02
α-Cumyl benzoate	None	None	None	0.33
Residue in gr.	76.0	Not given	66.0	70.0
Moles of benzoic acid formed upon hydrolysis of the crude reaction mixture	Not given	Not given	0.09	0.50

[a] R. L. Dannley and B. Zaremsky, *J. Am. Chem. Soc.*, **77**, 1588 (1955). [b] C. S. Rondestvedt, Jr., and H. S. Blanchard, *J. Am. Chem. Soc.*, **77**, 1769 (1955). [c] D. H. Hey, B. W. Pengilly, and G. H. Williams, *J. Chem. Soc.*, 1463 (1956). [d] M. S. Kharasch and A. Fono. In addition to the products cited, there is formed (in the presence of cuprous salts) about 13 mole % of a mixture of α-cumyl alcohol and acetophenone. The mechanism of formation of these products will be discussed in detail in a forthcoming publication.

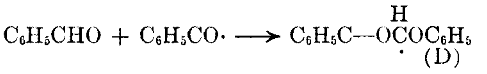
When one mole percent of cuprous chloride was added to a mixture of benzoyl peroxide (0.5 mole), valeraldehyde (1 mole) and carbon tetrachloride, and the mixture heated to 76°, the peroxide completely decomposed in approximately 30 minutes. Under these conditions, no hydrogen chloride or chloroform was formed. The major reaction products were benzoic acid (0.64 mole), the mixed anhydride, benzoyl valeroyl anhydride and the two symmetrical anhydrides. In this reaction, the mixed anhydride must be formed by a mechanism different from the one indicated in Scheme 12.

Reaction of tert-butyl peroxide with benzaldehyde in the presence and absence of copper salts. It is well established that the chief reaction products formed by decomposing *tert*-butyl peroxide in benzaldehyde are equal quantities of the *meso* and racemic forms of benzpinacol dibenzoate.[12] The same products were obtained by Kharasch and McBay by decomposing acetyl peroxide in benzaldehyde.[13] In their investigation, Rust, Suebold, and Vaughan isolated the *meso* compound in crystalline form. They assumed that the oil which they obtained was the racemic form.

The racemate could be crystallized by us from a mixture of ether and ligroin (b.p. 30–35°). It melts at 115° in an evacuated tube. The rate of the reaction of the benzaldehyde and the *tert*-butyl peroxide is first order, with respect to the peroxide used, and is quite slow.[12] After 30 hours at 130°, only about 70% of the peroxide decomposes. The following mechanism was proposed to account for the products formed in this reaction.

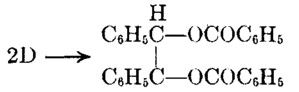
$$(CH_3)_3COOC(CH_3)_3 \xrightarrow{\Delta} 2(CH_3)_3CO\cdot \qquad (13)$$

$$C_6H_5CHO + (CH_3)_3CO\cdot \longrightarrow (CH_3)_3COH + C_6H_5CO\cdot \qquad (14)$$



$$C_6H_5CHO + C_6H_5CO\cdot \longrightarrow C_6H_5\overset{H}{\underset{\cdot}{C}}\text{—}OCOC_6H_5 \qquad (15)$$

(D)



$$2D \longrightarrow \begin{array}{l} C_6H_5\overset{H}{C}\text{—}OCOC_6H_5 \\ \quad\ \ \vert \\ C_6H_5C\text{—}OCOC_6H_5 \end{array} \qquad (16)$$

(E) meso and racemic forms

An entirely different reaction takes place when *tert*-butyl peroxide is decomposed in benzaldehyde in the presence of small amounts of cuprous salt (chloride or benzoate). Instead of a practically quantitative yield of E, benzopinocol dibenzoate, on the basis of the peroxide used, only a negligible yield (5%) was obtained. However, there is a very high yield (83%) of *tert*-butyl benzoate. It is pertinent that as far as the mechanism is concerned, the decomposition of *tert*-butyl peroxide in benzaldehyde is very much faster in the presence than in the absence of copper salts. Where only 70% of the peroxide was decomposed when heated to 140° for 18 hours, in benzaldehyde, complete decomposition occurred after 6 hours at 140°, in the presence of cuprous salts. Further, the decomposition of the *tert*-butyl peroxide, in benzaldehyde, in the presence of cuprous chloride appeared to be a zero order reaction, rather than the first order reaction which occurred in the absence of a cuprous salt.

At this point, we should indicate that when cuprous bromide is used, some of the benzoyl-radicals are oxidized and the yield of the *tert*-butyl benzoate decreases.

Reaction of tert-butyl peroxide in cumene, in the presence and absence of cuprous chloride. A *tert*-butyl peroxide (1 mole) and 10 fold cumene, heated to 145° gives dicumene, methane, acetone (0.4 mole), and *tert*-butyl alcohol (1.1 mole).

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[12] F. F. Rust, F. H. Seubold, and W. E. Vaughan, *J. Am. Chem. Soc.*, **70**, 3258 (1948).

[13] Unpublished work.

The rate of decomposition is first order.[14] The rate of the reaction, in the presence of the cuprous chloride is much faster, almost O order. In the latter reaction, less acetone (0.4 mole) and more *tert*-butyl alcohol (1.6 moles) is formed.

DISCUSSION

A mechanism is sought which explains how copper salts modify homolytic reactions. Many mechanisms can be proposed for each individual reaction. Instead of carefully studying an individual reaction, the authors chose to study the effect of copper salts on a large variety of different reactions, trying to find a mechanism which is consistent with all the observations: a mechanism which explains why copper salts act in some reactions as free radical inhibitors, in others only as deactivators and yet in others, promote induced decomposition of peroxides. The mechanism has to be able to account for the increased solvent effect in homolytic reactions catalyzed by copper salts. In addition to the arguments given in the previous publication of this series, more evidence is presented here to substantiate the hypothesis that free radicals are not completely free in many homolytic reactions, in either the presence or the absence of copper salts.

Copper salts are capable of inhibiting some free radical chain reactions. It was found that chloroform can be brominated with *N*-bromosuccinimide to bromotrichloromethane, using light or benzoylperoxide as an initiator. This reaction can be completely inhibited when one mole percent cuprous chloride is added to the reaction mixture.[15] Copper salts do not affect all reactions of *N*-bromosuccinimide in the same fashion. The bromination of octene-1 with *N*-bromosuccinimide is slowed down, but not inhibited by the presence of copper salts.[16]

$$(C_6H_5CO_2)_2 \longrightarrow C_6H_5CO_2\cdot \qquad (17)$$

$$C_6H_5CO_2\cdot + CHCl_3 \longrightarrow C_6H_5COOH + \cdot CCl_3$$

$$\cdot CCl_3 + Su > NBr \longrightarrow BrCCl_3 + Su > N\cdot$$

$$Su > N\cdot + CHCl_3 \longrightarrow Su > NH + \cdot CCl_3$$

These observations indicate that copper salts are capable of deactivating some radicals. For example, copper salts deactivate trichloromethyl radicals to the extent that they are unable to abstract a bromine from *N*-bromosuccinimide. We propose that the trichloromethyl radical reacts with a cuprous cation to give an unstable organocupric compound, as a reaction intermediate. Two of these trapped radicals, similar to the metal salt catalyzed Grignard reagent, will react with each other to give hexachloroethane in a chain ending step. We propose the name "free radical trapper" for substances which are capable of modifying homolytic reactions, through their ability to form loosely bound compounds with free radicals.

$$\cdot CCl_3 + Cu^+ \rightleftarrows Cu^+CCl_3 \qquad (18)$$

$$2Cu^+CCl_3 \longrightarrow 2Cu^+ + Cl_3C{-}CCl_3$$

A similar mechanism accounts for the observation that if the pyrolysis of dicumene is carried out in the presence of copper salts, the initially formed cumyl radicals do not disproportionate. They are trapped on the copper salt and subsequently dimerize.

A trapped "free radical" does not necessarily retard or inhibit a reaction. Free radicals trapped on cuprous salt readily cause an induced decomposition of peroxides. The peroxides decompose in less time, at lower temperatures, in the presence of copper salts than they do in the absence of them. Careful rate studies were not made, but experimental observation indicates lower than first order rate, a characteristic of induced decompositions. The nature of the reaction products is further evidence in favor of induced decomposition.

When benzoyl peroxide is decomposed in octene-2, both in the presence and the absence of copper salts, the initial reaction is the addition of a benzoyloxy radical to the double bond.

$$(C_6H_5CO_2)_2 \longrightarrow 2C_6H_5CO_2\cdot \qquad (19)$$

$$C_6H_5CO_2\cdot + C_8H_{16} \longrightarrow \underset{(F)}{C_6H_5CO_2C_8H_{16}\cdot}$$

In the absence of a metal salt, radical F, for the most part disproportionates into a saturated and an unsaturated compound. In the presence of copper salts, radical F is reversibly trapped on a cuprous salt, and can readily attack a peroxide molecule.

$$\begin{aligned} C_6H_5CO_2C_8H_{16}\cdot Cu^+ + (C_6H_5CO_2)_2 \longrightarrow \\ C_6H_5CO_2C_8H_{15} + C_6H_5CO_2H + \\ C_6H_5CO_2\cdot + Cu^+ \quad (20) \end{aligned}$$

No disproportionation occurs, indicated by the observation that no saturated compound is formed. In agreement with the proposed mechanism, benzoyloxyoctene and benzoic acid are formed in about equimolar quantities.

As an alternate mechanism, the benzoyloxy radical formed in Equation 19 oxidizes cuprous to cupric, in turn, the cupric oxidizes radical F to benzoyloxyoctene. The relative importance of these two mechanisms can be discerned by studying the decomposition of benzoylperoxide in cumene, in the presence of copper salts. The cumyl radicals in this reaction may either be trapped on the cuprous salts and attack the benzoylperoxide causing an induced decomposition, or they may be further oxidized by a cupric ion. The reactions lead to two different reaction products as indicated in the following equations:

$$C_6H_5(CH_3)_2C\cdot + Cu^+ \rightleftarrows C_6H_5(CH_3)_2C\cdot Cu^+ \qquad (21)$$

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[14] J. H. Raley, F. F. Rust, W. E. Vaughan, *J. Am. Chem. Soc.*, **70**, 1336 (1948).

[15] M. S. Kharasch and S. Lemberg, unpublished work.

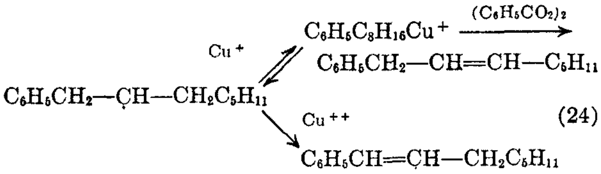
[16] R. Malec, Ph.D. thesis, University of Chicago, 1957.

$$C_6H_5(CH_3)_2C{\cdot}Cu^+ + (C_6H_5CO_2)_2 \longrightarrow C_6H_5(CH_3)_2CO_2CC_6H_5 + C_6H_5CO_2{\cdot} + Cu^+ \quad (22)$$

$$C_6H_5(CH_3)_2C{\cdot} + Cu^{++} \longrightarrow \text{Cumyl alcohol and acetophenone} \quad (23)$$

The reaction products indicate that Equation 22 is about three times more important than Equation 23.

It is of no importance if the catalytic amounts of copper salts added are cuprous or cupric, as both oxidizing and reducing agents are always present. If the equilibrium in Equation 21 is shifted to the right or to the left depends on the nature of the solvent. It is expected that homolytic reactions, carried out in the presence of copper salts will show an unusually strong solvent effect. An interesting example of this may be made by comparing the nature of the phenyloctenes formed, when benzoylperoxide is reacted with octene-1, in the presence of copper salts in either aromatic or aliphatic solvents. In an aliphatic solvent, only 1-phenyloctene-2 is formed. In an aromatic solvent, 1-phenyloctene-1 is predominately formed.



$$C_6H_5CH_2{-}\dot{C}H{-}CH_2C_5H_{11} \underset{}{\overset{Cu^+}{\rightleftharpoons}} C_6H_5C_8H_{16}Cu^+ \xrightarrow{(C_6H_5CO_2)_2} C_6H_5CH_2{-}CH{=}CH{-}C_5H_{11}$$

$$C_6H_5CH_2{-}\dot{C}H{-}CH_2C_5H_{11} \xrightarrow{Cu^{++}} C_6H_5CH{=}\dot{C}H{-}CH_2C_5H_{11} \quad (24)$$

Equation 22 postulates that the reaction between an organo copper compound and a peroxide is homolytic. Indirect evidence in favor of this hypothesis is in the nature of the products formed when the peroxide used is *tert*-butyl perbenzoate. The copper salt catalyzed decomposition through an organo copper intermediate introduces the benzoyloxy group. The ionic reaction of *tert*-butyl perbenzoate, with a Grignard reagent introduces the *tert*-butoxy group.[17]

A good example of the induced decomposition of the peroxides in the presence of copper salts is the decomposition of *tert*-butyl peroxide, in benzaldehyde, in the presence of cuprous chloride. This was the first time that the induced decomposition of *tert*-butyl peroxide was observed. The initially formed benzoylradical is trapped on the cuprous salt. It is unable to add to another benzaldehyde. However, it can readily attack the *tert*-butyl peroxide.

$$C_6H_5CO{\cdot} + CuCl \longrightarrow C_6H_5COCuCl$$

$$C_6H_5COCuCl + (CH_3)_3COOC(CH_3)_3 \longrightarrow C_6H_5CO_2C(CH_3)_3 + (CH_3)_3CO{\cdot} + CuCl \quad (25)$$

In the presence of cuprous chloride, there is practically no oxidation of the intermediate radical by a cupric salt. In future publications, we shall show that oxidation would lead through intermediately formed benzoic acid to benzoic anhydride.

However, the decomposition of benzoyl peroxide in benzaldehyde is an induced decomposition, even in the absence of copper salts. The only difference to observe in these reactions is that in the absence of copper salts both benzopinacol dibenzoate and benzoic anhydride will form: in the presence of copper salts, only benzoic anhydride will form. The mechanism is similar to the one outlined.

The mechanism of the decomposition of benzoyl peroxide in a solution of valeraldehyde in carbon tetrachloride, in the presence of cuprous chloride is again similar. The copper salts play a dual role. In part they prevent any chain reaction in which trichloromethyl radicals would participate. Trapped trichloromethyl radicals are very inactive, as seen in the bromination of chloroform. Copper salts promote the reaction between the trapped valeryl radical and the peroxide.

Previously, we have shown that carbon free radicals can readily form radical complexes with hydroperoxides and with organic acids.[4,18]

$$R{\cdot} + R'OOH \longrightarrow R{\cdot}\overset{H}{O}OR' \quad (26)$$

(free radical complex)

The radical complexes are the postulated intermediates in the formation of peroxides and esters. The peroxide, and especially the ester formation is greatly enhanced in the presence of copper salts. This suggests that cuprous salts can trap not only free radicals, but even more readily, free radical complexes, thus promoting reactions which proceed through free-radical complex intermediates.

In the reactions just discussed, it was not important that it was the copper salt that trapped the free radical or free radical complex. The complexing agent could have been another substrate molecule or the solvent.

The experimental observation that cuprous chloride causes an induced decomposition of *tert*-butyl peroxide without effecting the formation of dicumene forces us to the hypothesis that the reaction proceeds through a free radical complex. The mechanism envisaged for this reaction is:

$$(CH_3)_3COOC(CH_3)_3 \longrightarrow 2(CH_3)_3CO{\cdot}$$

$$(CH_3)_3CO{\cdot} + C_6H_5(CH_3)_2CH \longrightarrow C_6H_5(CH_3)_2C{\cdot} + (CH_3)_3COH$$

$$C_6H_5(CH_3)_2C{\cdot} + C_6H_5(CH_3)_2CH + CuCl \longrightarrow \underset{(G)}{C_6H_5(CH_3)_2C{\cdot}\overset{H}{C}(CH_3)_2C_6H_5CuCl}$$

$$(G) + (CH_3)_3COOC(CH_3)_3 \longrightarrow C_6H_5(CH_3)_2CC(CH_3)_2C_6H_5 + (CH_3)_3COH + (CH_3)_3CO{\cdot} + CuCl \quad (27)$$

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[17] S. O. Lawson, unpublished work.

[18] M. S. Kharasch and A. Fono, *J. Org. Chem.*, **23**, 324 (1958).

[19] M. S. Kharasch, A. Fono, and W. Nudenberg, *J. Org. Chem.*, **16**, 105 (1951).

The *tert*-butoxy radical formed in this reaction has a different origin than the one formed from the first order decomposition of *tert*-butyl peroxide. Therefore it was expected that the ratio of the *tert*-butyl alcohol to acetone would be different.[19] The existence of complex G would predict that in the presence of copper salts, a cumyl radical could abstract a hydrogen from another cumyl radical.

Cadogan, Gold, and Satchell[20] have shown that free radicals formed from xylene can abstract a hydrogen from another xylene molecule, *i.e.* that reactions of the type in Equation 28 do occur.

$$\mathrm{RH} + \mathrm{R}\cdot \longrightarrow \mathrm{R}\cdot + \mathrm{RH} \tag{28}$$

Eliel, Wilken, Fang, and Wilen[21] repeated this work, but their experimental results contradicted those of the former authors.

Considering the influence of copper salts on homolytic reactions, we are forced to the hypothesis that at least in the presence of copper salts, a carbon radical can form a free radical complex, not only with an oxygen, hydrogen, or nitrogen bond, but even with a carbon hydrogen bond.

$$\mathrm{R}\overset{\mathrm{H}}{\cdot}\mathrm{R'Cu^{+}} \tag{29}$$

The chemical bond in this free radical complex is probably a resonance hybrid of a hydrogen bond, and of a charge transfer complex.[22] A more direct proof for the existence of such a free radical complex would be, if it could be shown, that the difference between the experiments of Eliel and his co-workers, and Cadogan and his co-workers was due to the presence of trace amounts of metal salt impurities.

EXPERIMENTAL

Reagents and procedure. The reagents were distilled prior to use. Commercial (Eastman) benzoyl peroxide was used in all experiments. The air in the apparatus was always displaced by nitrogen gas. Moisture (and air) were rigidly excluded. The gases generated during the reaction were collected over a saturated solution of sodium chloride in water, saturated with carbon dioxide. No reaction was considered complete unless the reaction mixture gave a negative test for the peroxides. The infrared spectra measurements were made on a Perkins-Elmer Model 21, double beam spectrophotometer. The molecular weights of the compounds were determined cryoscopically (benzene). The extent of the unsaturation in the compounds was determined either by ozonolysis, or by a bromate-bromide titration, or by both methods.

Pyrolysis of dicumene in bromobenzene. A mixture containing dicumene (3 g.) and bromobenzene (24 g.) was heated in a bomb tube at 255° for 10 hr. After distilling out the low boiling materials, there remained only 0.35 g. of a residue which could not be crystallized from methylalcohol.

We repeated the same experiment, adding 0.05 g. of cuprous bromide. The mixture was heated for 24 hr. After distillation, we obtained 2.1 g. of a higher boiling residue. This recrystallized from methyl alcohol yielding 1.1 g. of dicumene, m.p. 119°, giving no depression with the starting material.

Reaction of benzoyl peroxide in octene-1 in the presence and absence of cuprous chloride. (a) A mixture of octene-1 (0.7 mole) and benzoyl peroxide (0.083 mole) was heated to 100°. A strong exothermic reaction followed and all of the peroxide was consumed in approximately 1 hr. Carbon dioxide (0.066 mole) was evolved during the reaction.

The reaction mixture was washed with a dilute solution of sodium carbonate to remove benzoic acid (0.0055 mole). The organic layer was washed with water, and dried with sodium sulfate. The drying agent was collected on a filter and the filtrate distilled at reduced pressure to remove the unreacted octene-1. The boiling point, index of refraction and the infrared spectrum indicated that the distillate was pure octene-1. No isomerization of the octene-1 to octene-2 took place during the course of the reaction.

After removing the octene-1, the Residue I was distilled at reduced pressure, and the fraction boiling at 85–90°/0.1 mm. was collected (Fraction I). The remaining material was transferred to a molecular still and the material distilling at 100–105°/10^{-4} mm. was collected (Fraction II). The Residue (II) remaining after this distillation was a semi-solid material of the consistency of vaseline (26 g.).

Fraction I (0.017 mole; n_{D}^{20} 1.4916; mol. wt. 222) was shown by analyses and infrared spectrum to be a mixture of 60% of the 1:1 adducts, [($C_5H_{11}CH_2CH_2CH_2OCOC_6H_5$) and ($C_5H_{11}CH{=}CHCH_2OCOC_6H_5$)], and 40% of phenyloctene. The unsaturation (30%) in this same material was determined by ozonolysis and bromate-bromide titration.

Fraction II (0.021 mole; n_{D}^{20} 1.4900; mol. wt. 335) was presumed an impure 1:2 adduct. The unsaturation (30%) in this material was determined by ozonolysis.

Residue II could not be distilled. Lower boiling materials were removed from it in a molecular still. The material appeared to be an adduct containing one benzoyloxy unit to four octane units, or a mixture of adducts having a similar ratio of benzoyloxy and octene units.

Residue II. *Anal.* $C_{89}H_{68}O_2$ (60%) + $C_{39}H_{70}O_2$ (40%). Calcd. for: C, 82.15; H, 12.23; mol. wt. 570. Found: C, 82.5; H, 11.7; mol. wt. 605.

The unsaturation of Residue II (60%) was determined by ozonolysis. Residue II was quite soluble in petroleum ether, ether, chloroform and ethyl acetate. It was readily soluble in benzene. A solution of Residue II in alcoholic potassium hydroxide, when heated, gave sodium benzoate and an oil. Examination of the infrared spectrum of the oil established that it did not contain benzoyloxy or aromatic groups.

The yields of the various fractions are given in Table I.

Reaction of benzoyl peroxide with octene-1 in the presence of cuprous salts. Cuprous bromide (1 mole % on the basis of the peroxide used) was added to a solution of benzoyl peroxide (0.25 mole) in octene-1 (2 moles) and heated to 100°. A rapid exothermic reaction followed and no peroxide could be detected in the reaction mixture after 15 min. Carbon dioxide (0.11 mole) was evolved during the reaction.

The reaction mixture was shaken with a water solution of sodium carbonate and the extracted benzoic acid (0.18 mole) was recovered from the alkaline solution. The organic layer was dried over sodium sulfate. After removal of the inorganic salt, the organic layer was distilled at reduced pressure. The unchanged octene was collected first. The residue was then distilled at low pressure and the following fractions collected: Fraction I: b.p. 83–84.5°/1 mm., d_4^{23} 0.871; n_{D}^{23} 1.4932. Fraction II: b.p. 90–100°/0.1 mm., n_{D}^{23} 1.4985. Residue I.

Fraction I (0.02 mole) was a somewhat impure mixture of phenyl octane and a phenyl octene, containing a small quantity of benzoyloxy octene.

Calcd. for phenyl octene: $C_{14}H_{20}$: C, 89.3; H, 10.7, mol. wt. 188. Found: C, 88.2; H, 11.0, mol. wt. 192.

The infrared spectrum of this material indicated the presence of a *trans* double bond.

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(20) J. J. Cadogan, W. Gold, and D. P. N. Satchell, *J. Chem. Soc.*, 561 (1955).

(21) E. L. Eliel, P. H. Wilken, F. T. Fang, and S. H. Wilen, *J. Am. Chem. Soc.*, **80**, 3303 (1958).

(22) R. S. Mulliken, *J. Chim. Phys.*, **51**, 341 (1954).

Fraction II (0.09 mole) was shown to be a mixture of the benzoyloxyoctane and benzoyloxyoctene.

Calcd. for benzoyloxyoctene: $C_{15}H_{20}O_2$: C, 77.5; H, 8.7; mol. wt. 232. Found: C, 77.0; H, 8.8; mol. wt. 226.

Ozonolysis of this material indicated that it contained 75% double bonds. This value was in excellent agreement with a bromate-bromide titration (78%). The infrared spectrum of this same material showed about 70% trans double bond and 30% terminal double bonds.

Residue I was transferred to a molecular still and the material which distilled at 100–110°/10^{-4} mm. was collected (Fraction III).

Fraction III (0.9 mole, n_D^{23} 1.4950) was evidently an adduct containing one double bond for one benzoyloxy unit and two octene units. The infrared spectrum indicated only non-terminal double bonds.

Calcd. for: $C_{23}H_{36}O_2$: C, 80.2; H, 10.5; mol. wt. 334. Found: C, 80.6; H, 10.5; mol. wt. 325.

Ozonolysis of Fraction III indicated that there was one double bond per molecule.

After removing Fraction III from the molecular still, there remained 3.8 grams of a material, probably a high-addition-polymerization adduct of the type previously discussed. It was not investigated.

Reaction of benzoyl peroxide in octene-1, in the presence of benzene as solvent. A mixture of benzoyl peroxide (0.1 mole), octene (0.5 mole), cuprous chloride (1 mole % on the basis of the peroxide used) was warmed in benzene (2 moles) at 65° for 12 hr. To complete the reaction, it was heated to 80° for an additional 5 hr. The reaction mixture was worked up as in the previous case. We isolated benzoic acid (0.092 mole): Fraction I; b.p. 70–71°/0.15 mm., n_D^{20} 1.5225: Fraction II; b.p. 95–100°/0.1 mm., n_D^{20} 1.5070: and, a residue; (5 g.) n_D^{20} 1.5050.

Fraction I was almost pure 1-phenyloctene-1 (45%).

Calcd. for $C_{14}H_2O$: C, 89.3; H, 10.7. Found: C, 89.6; H, 10.4.

A comparison of its infrared spectrum with that of 1-phenyloctene-2 showed that absorption peaks at 740 cm.$^{-1}$ and 3000 cm.$^{-1}$ are much stronger. Instead of a single peak at 1500 cm.$^{-1}$, Fraction I had a double peak, 1500 cm.$^{-1}$ and 1478 cm.$^{-1}$ The ultraviolet adsorption showed a maximum at 247 millimicrons.

Fraction II, benzoyloxyoctene (23%). Infrared spectrum showed about half as much terminal double bond, as the 1:1 adduct obtained in excess octene. Fraction II had an additional medium peak at 1778 cm.$^{-1}$ After alkaline hydrolysis, the infrared spectrum indicated the presence of an aldehyde (peaks at 2700 cm.$^{-1}$ and 1725 cm.$^{-1}$). Fraction II gave a dinitrophenylhydrazone, m.p. 106°,[23] (caprilic aldehyde).

Reaction of benzoyl peroxide with octene-2. A mixture of benzoyl peroxide (0.04 mole) and octene-2 (0.32 mole) was slowly heated to 95° and maintained at that temperature for 2 hr. A strong exothermic reaction ensued and most of the carbon dioxide (0.019 mole) was liberated in the first 10 min. The reaction mixture was shaken with a water solution of sodium carbonate to remove the benzoic acid (0.012 mole) formed during the reaction. The organic layer was dried and the unchanged octene-2 was removed by distillation. The residue was distilled at reduced pressure and the following fractions were collected: Fraction I: b.p. 87–93°/0.2 mm. Fraction II: b.p. 120–125°/0.2 mm. Residue: 1 gram.

Fraction I (0.035 mole; n_D^{20} 1.4825) was a mixture of the saturated (40%) and unsaturated (60%) adducts of one benzoyloxy unit to one octene unit. The molecular weight of this material was 225 as compared with a calculated value of 232.

Fraction II (0.0054 mole; n_D^{20} 1.4930) was presumed to be a mixture of adducts (saturated and unsaturated) consisting of one benzoyloxy unit to two units of octene. The molecular weight of this material was 330 as compared with a calculated value of 324.

Reaction of benzoyl peroxide with octene-2 in the presence of cuprous salts. Cuprous chloride (2 mole % on the basis of the peroxide used) was added to a solution of benzoyl peroxide (0.041 mole) in octene-2 (0.28 mole). The mixture was heated to 95°. A fast exothermic reaction followed, and the carbon dioxide (0.02 mole) was liberated in 10 min. The heating was continued for 1 hr. longer. The reaction mixture was then washed with a water solution of sodium carbonate. The layers were separated, and the benzoic acid (0.028 mole) was isolated from the alkaline solution.

The organic layer was dried with anhydrous sodium sulfate and the drying agent collected on a filter. The octene-2 was then distilled off from the filtrate. The residue was distilled at reduced pressure and collected.

Fraction I (b.p. 93°/0.2 mm.; 0.03 mole; n_D^{20} 1.4957) was a mixture of saturated (7%) of unsaturated (93%) adducts of one benzoyloxy unit and one octene unit. The molecular weight of the material (cryoscopic in benzene) was 226 as compared with a calculated value of 230.

Anal. Calcd. for $C_{15}H_{20}O_2$: C, 77.5; H, 8.7. Found: C, 77.9; H, 9.0.

Fraction I was hydrolyzed with alcoholic potassium hydroxide and the benzoic acid formed during the reaction was removed by the usual procedure. The infrared spectrum of the non-acidic material (mostly octenol) showed a weak band at 700 cm.$^{-1}$, indicating the presence of no more than 5% of the phenylated octene.

The residue (1.5 g.) most probably consisted of higher addition-polymerization product. It was not investigated.

Decomposition of benzoyl peroxide in cumene, in the presence of copper salts. Benzoyl peroxide (0.1 mole) was dissolved in cumene (1.5 moles), in the presence of cuprous chloride (0.0006) and was heated to 85°, under vigorous stirring. The peroxide decomposed in an exothermic reaction in approximately 10 min., accompanied by the evolution of 0.1 mole of CO_2. The crude reaction mixture was washed with dilute sodium carbonate solution. After acidification, benzoic acid (0.05 mole) was recovered from the aqueous layer. The organic layer was dried over anhydrous sodium sulfate, filtered, and distilled in vacuo. After collecting the unreacted cumene, three fractions were separated, leaving 7 grams of residue.

The first fraction, b.p. 50–60°/0.2 mm. was acetophenone, containing a α-cumyl alcohol (0.013 mole). The second fraction, b.p. 90–95°/0.10 mm. consisted of a mixture of isopropylbiphenyls (0.02 mole). The third fraction, b.p. 110–112°/0.10 mm. was shown to be α-cumyl benzoate, 0.03 mole, n_D^{20} 1.5560.

Anal. Calcd. for $C_{16}H_{16}O_2$: C, 79.97; H, 6.7; mol. wt. 240. Found: C, 80.15; H, 6.9; mol. wt. 231.

The infrared spectrum indicated a monosubstituted benzene ring in the 700–900 cm.$^{-1}$ region, and a benzoyloxy group on the side chain, adsorption peak at 1715 cm.$^{-1}$ Alkaline hydrolysis gave benzoic acid and α-cumyl alcohol, identified as its thioglycolic acid derivative. Pyrolysis yielded benzoic acid and α-methylstyrene dimers.

All fractions were tested for dicumene, by attempted crystallization in both alcohol and nitromethane, at −80°. Dicumene, even 2% by weight would have been detected, were it present. The infrared spectra of the isopropyl biphenyls indicated the same composition as that which occurred in the absence of copper salts. The α-cumyl benzoate was identical with an authentic sample. The residue had a molecular weight of 290 and its infrared spectra suggested it to be mostly phenyl α-cumyl benzoate.

Reaction of tert-butyl perbenzoate in cumene, in the presence of copper salts. Tert-butyl perbenzoate (0.068 mole) was added, dropwise, to a well stirred suspension of cuprous chloride (0.0006 mole) in cumene (0.7 mole) over a period of 6 hr. The reaction was worked up in the usual manner. We isolated benzoic acid (0.034 mole), 50%; a mixture of

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(23) H. Stephen, *J. Chem. Soc.*, **127**, 1874 (1925).

acetophenone and carbinol (approx. 0.02 mole), 30%; and α-cumyl benzoate (0.07 mole), 40%.

Reaction of valeraldehyde, benzoyl peroxide, and carbon tetrachloride in the presence and absence of cuprous salts. (a) A mixture of valeraldehyde (0.0475), benzoyl peroxide (0.0246 mole) and carbon tetrachloride (0.25 mole) was heated at 76° for 6 hr. At the end of that time, all gas evolution (0.02 mole) had ceased. The benzoic acid (0.003 mole) formed in the reaction was separated by the usual procedure. The chloroform formed in the reaction was separated by distillation and identified. The formation of hydrogen chloride during the course of the reaction was also demonstrated.

The major reaction product was a mixture (0.29 mole) of the unsymmetrical benzoyl valeroyl anhydride and the two symmetrical anhydrides.

(b) A mixture of valeraldehyde (0.1 mole), benzoyl peroxide (0.05 mole), carbon tetrachloride (0.3 mole) and cuprous chloride (0.2 gram) was heated to 76° for less than 1 hr. The gas evolution (carbon dioxide 0.017 mole) ceased at the end of 30 min. The benzoic acid (0.032 mole) formed during the reaction was separated by the usual procedure. Under the conditions described in (a), no chloroform and hydrogen chloride (volatile acid) were formed in the reaction. The reaction product (0.05 mole) appeared to be valeroyl benzoyl anhydride (b.p. 100°/15 mm., n_D^{20} 1.4835) and a mixture of the two symmetrical anhydrides.

Reaction of tert-butyl peroxide in benzaldehyde in the presence and the absence of cuprous salts. (a) A mixture of benzaldehyde (0.47 mole) and *tert*-butyl peroxide (0.068 mole) was heated at 140° for 24 hr. The evolved methane gas (0.0043) was collected. The low boiling materials (benzaldehyde and unreacted peroxide) were removed by distillation at reduced pressure. The residue (0.054 mole, calculated on the basis that it was a mixture of the *meso* and racemic forms of benzopinacol dibenzoate) was crystallized from methanol. The *meso* form of benzopinacol dibenzoate (0.015 mole) obtained melted at 244°. The methanol filtrate was evaporated, leaving an oily residue. Repeated crystallization of this residue material from a mixture of ether and petroleum ether gave a solid material (0.018 mole), which melted quite sharply in an evacuated melting point tube at 115°. This solid was presumed to be the racemic form of benzopinacol dibenzoate.

Anal. Calcd. for $C_{28}H_{22}O_4$: C, 79.6; H, 5.3; mol. wt. 422. Found: C, 79.8; H, 5.5; mol. wt. 440 (camphor).

(b) A mixture of benzaldehyde (0.45 mole), *tert*-butyl peroxide (0.072 mole) and cuprous chloride (0.7 g.; 0.001 mole) was heated at 140° for 6 hr. The reaction mixture was worked up in the usual way. The major reaction product (83%) was *tert*-butyl benzoate (b.p. 92°/10 mm.; n_D^{20} 1.4915). *Tert*-butyl benzoate is known to boil at 94°/10 mm.[24]

Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.1; H, 7.9. Found: C, 74.3; H, 7.9.

The minor reaction products were the *meso* and racemic forms of benzopinacol dibenzoate (5%).

The infrared spectrum of the *tert*-butyl benzoate obtained with peaks at 1710 cm.$^{-1}$ (benzoate), and 1375 cm.$^{-1}$ and 1395 cm.$^{-1}$ (*tert*-butyl group) was in agreement with the structure assigned to this compound. *Tert*-butyl benzoate was stable when warmed in an alcoholic solution of potassium hydroxide. However, an acetic acid solution of the ester was rapidly hydrolyzed by strong acids.

Acknowledgment. The authors are indebted to Otto B. May, Inc. for the financial support which made this work possible.

CHICAGO, ILL.

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(24) V. R. Stimson, *J. Chem. Soc.*, 2673 (1955) states that *tert*-butyl benzoate boils at 50°/0.5 mm. (n_D^{20} 1.4900).

[CONTRIBUTION FROM SOUTHERN REGIONAL RESEARCH LABORATORY[1] UNITED STATES DEPARTMENT OF AGRICULTURE]

Reaction of Epichlorohydrin with Cyclohexylamine

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Received October 27, 1958

The addition of epichlorohydrin to cyclohexylamine through the epoxide group has been reinvestigated. Two chlorohydrins, *N*-(3-chloro-2-hydroxypropyl)cyclohexylamine and *N,N*-bis(3-chloro-2-hydroxypropyl)cyclohexylamine, have been isolated. These compounds have been converted to their respective epoxides and hydrochlorides.

Modern research[3,4,5] has shown various amines react with epichlorohydrin to form *N*-(3-chloro-2 hydroxypropyl)amines. In view of these findings it seemed advisable to reconsider the earlier investigation of Wedekind and Bruch.[6] These latter investigations showed that when cyclohexylamine was treated with epichlorohydrin (3.5 to 1 mole ratio of amine to epoxide) on a water bath, small yields of 1,3-bis(cyclohexylamino)-2-propanol were obtained, in addition to considerable quantities of cyclohexylamine hydrochloride and unidentified tars. We have confirmed this observation, since the reaction easily gets out of hand even when the correct ratio of amine to epoxide is used. However, this investigation has demonstrated that a slow, smooth reaction, which gave the desired products, occurred when mutual solvents were used at room temperature.

In order to prepare the mono- and diepichlorohydrin derivatives of cyclohexylamine, increasing mole ratios of epichlorohydrin to amine were in-

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