

Communications TO THE EDITOR

A Modification of Free Radical Reactions

Sir:

It has been observed that certain additives modify the course of free radical reactions. In the present communication we wish to describe the marked effect of trace amount of copper salts on both the rates and products of well known free radical reactions.

In the presence of 1 mole % of copper chloride benzoyl peroxide, *tert*-butyl peroxide, *tert*-butyl perbenzoate,¹ *tert*-butyl hydroperoxide, and α -cumyl hydroperoxide undergo a fast induced decomposition in solvents, whereas in the absence of copper chloride, these compounds normally undergo a slow first-order decomposition or no decomposition whatever. The products of the regular (R) and modified (M) reactions are quite different as illustrated in the following examples:

Decomposition of *tert*-butyl peroxide (1 mole) in benzaldehyde (7 moles) at 140°: (M) *tert*-butyl benzoate, 83%; benzpinacol dibenzoate, less than 5%. (R) only benzpinacol dibenzoate.²

Decomposition of benzoyl peroxide (1 mole) in cumene (10 moles) at 80°: (M) α -cumyl benzoate, 30% (b.p. 110°/0.1 mm., n_D^{20} 1.5560. *Anal.* Calcd. for C₁₆H₁₆O₂: C, 79.97; H, 6.7. Found: C, 80.15; H, 6.9. The infrared spectrum and the hydrolysis products are in agreement with the structure proposed); isopropyl biphenyls, 20%; no dicumene. (R) dicumene, 35%; isopropyl biphenyls, 24%.³

Decomposition of *tert*-butyl perbenzoate (1 mole) in cumene (10 moles) at 90° (perbenzoate was added dropwise to the cumene containing 0.01 mole of copper chloride): (M) α -cumyl benzoate, 40%.

Decomposition of benzoyl peroxide (1 mole) in octene-1 (8 moles) at 90°: (M) high mol. wt. polymers, 7 g; benzoic acid 72%; phenyloctene, 8%; 1:1 adduct (one benzoyloxy to one octene), 35%; 1:2 adduct, 34%. The 1:1 adduct is mostly 1-benzoyloxy octene-2, mixed with benzoyloxyoctane and 3-benzoyloxy-1-octene. It is unsaturated to the extent of 77%. Its infrared spectrum has a strong band at 975 cm.⁻¹ (trans double bond) and a weaker band at 930 cm.⁻¹ (established to be characteristic of terminal double bonds in this type of compounds). (R) polymers, 340 g. (average mol. wt., 600); benzoic acid, less than 6%.

(1) A separate investigation of the copper-catalyzed decomposition of *tert*-butyl perbenzoate by M. S. Kharasch and G. Sosnowsky is in press.

(2) F. F. Rust, F. H. Seubold, and W. E. Vaughn, *J. Am. Chem. Soc.*, **70**, 3258 (1948).

(3) D. H. Hey, B. W. Pengilly, and G. H. Williams, *J. Chem. Soc.*, 1463 (1956).

Decomposition of benzoyl peroxide (1 mole) in octene-2 (8 moles) at 90°: (M) 1:1 adduct, 80% (completely unsaturated); only traces of higher polymers. (R) 1:1 adduct, 85% (only 60% unsaturated); 1:2 adduct, 13%.

Decomposition of benzoyl peroxide (1 mole) in a solution of valeraldehyde (2 moles) in carbon tetrachloride: (M) benzoic acid, one mole, acid anhydrides, one mole; no attack on carbon tetrachloride. (R) chloroform, 1 mole; hydrochloric acid, 1 mole; acid anhydrides, 2 moles (due to the reaction between the initially formed acid chloride and benzoic acid).⁴

Pyrolysis of dicumene in bromobenzene at 250°: (M) 70% of dicumene is recovered unchanged after 20 hr. (R) all the dicumene disproportionates into cumene and α -methylstyrene.

We wish to propose the formation of unstable copper organic complexes as intermediates in these reactions.

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(4) S. Winstein and F. H. Seubold, *J. Am. Chem. Soc.* **69**, 2916 (1947).

(5) Deceased.

(6) Prepared the manuscript.

A New Method of Introducing Peroxy Groups into Organic Molecules

Sir:

We wish to report the discovery of a new reaction. We find that in the presence of trace amounts of copper, cobaltous or manganous salts, alkyl and aralkyl hydroperoxides react readily with organic molecules containing a slightly activated hydrogen, replacing it with a peroxy group.¹ For example, *tert*-butyl hydroperoxide reacts with cumene in the presence of a metal salt to give *tert*-butyl- α -cumyl peroxide. This method appears as effective in introducing a peroxy group as *N*-bromosuccinimide is in

(1) W. Pritzkow and K. A. Muller [*Ann.*, **597**, 167 (1956) and *Ber.*, **89**, 2321 (1956)] are the most recent to report that Cu, Co, and Mn salts catalyze the decomposition of hydroperoxides. But neither they, nor any previous author, reported any peroxides among the products.

introducing a bromine atom. The similarity does not hold where the bromination proceeds by an ionic mechanism, *e.g.*, the bromination of dimethyl aniline with *N*-bromosuccinimide. In such cases, a different hydrogen atom, the one most activated for free radical attacks, will be replaced by the peroxy group. The peroxydation of olefins, with cobaltous naphthenate as a catalyst, was already observed by Kharasch, Pauson, and Nudenberg.² These authors used a much larger amount of the catalyst, thus failed to obtain a reaction with cumene, and concluded that the reaction was only applicable to olefins. Using 0.2 mole % cobaltous 2-ethylhexoate or small amounts of cuprous or manganous salts (the reaction is less sensitive to excess of these catalysts) and warming to 60–70° the solution of the hydroperoxide and the substrate in a solvent, we observe that the reaction proceeds smoothly and rapidly. The reaction is 70% completed in less than 12 hr. Benzene, chloroform, heptane, *tert*-butyl alcohol, pyridine, acetic acid, nitrobenzene, and ethyl acetate are found to be suitable solvents. The use of excess substrate also favors the reaction. (Attention is drawn to the fact that nitrobenzene, an unsuitable solvent for regular free radical reactions, does not inhibit a modified radical reaction.)

The following peroxides have been prepared by this method (reaction temperature 70°, reaction time 24 hr.): α -cumyl-*tert*-butyl peroxide; yield 90%; physical constants and infrared spectrum identical with those of the known compound.³ 2-methyl-2-*tert*-butylperoxycyclohexanone; yield 90%; b.p. 66°/2 mm.; n_D^{20} 1.4431. *Anal.* Calcd. for $C_{11}H_{20}O_3$: C, 65.97; H, 10.07; mol. wt. 200. Found: C, 65.9; H, 9.9; mol. wt., 189. The infrared spectrum indicates that the peroxy group is α to the carbonyl.

2-*tert*-Butylperoxycyclohexanone; yield, 20%; b.p. 52°/0.15 mm.; n_D^{20} 1.4500. *Anal.* Calcd. for $C_{10}H_{18}O_3$: C, 64.5; H, 9.74; mol. wt., 186. Found: C, 64.0; H, 9.5; mol. wt., 176. The infrared spectrum indicates that the peroxy group is α to the carbonyl. Decomposes on standing to yield large amounts of adipic acid.

α -Cumylperoxycyclohexene; yield, 90% b.p. 98°/0.1 mm.; n_D^{20} 1.5238. *Anal.* Calcd. for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68; mol. wt., 232. Found: C, 77.8; H, 8.8; mol. wt., 220.

The preparation of *tert*-butylperoxycyclohexene and 1-*tert*-butylperoxy-2-octene have been previously described.¹ A more careful investigation shows that the reaction of 1-octene with *tert*-butyl hydroperoxide yields equal amounts of 1-*tert*-butylperoxyoctene-2 and 3-*tert*-butylperoxyoctene-1. (B.p. 57°/2.5 mm.; n_D^{20} 1.4243.) *Anal.* Calcd. for $C_{12}H_{24}O_2$: C, 71.95; H, 12.08. Found: C, 72.0; H,

12.2. Infrared spectrum, bands at 920 cm^{-1} and 990 cm^{-1}

The general applicability of this new method is readily demonstrated by the preparation of *N*-methyl-*N*-*tert*-butylperoxymethylaniline, in 95% yield, from dimethyl aniline at room temperature in benzene as solvent. This peroxide can be titrated iodometrically in acetic acid, but is not decomposed after 24 hr. refluxing in benzene. (B.p. 75°/0.1 mm.; n_D^{20} 1.5160. *Anal.* Calcd. for $C_{14}H_{19}O_2N$: C, 68.86; H, 9.15; N, 6.70; mol. wt., 209. Found: C, 69.1; H, 8.9; N, 7.0; mol. wt., 212. The infrared spectrum indicated no nuclear substitution whatever.)

Investigation of the use of other possible metal salts as catalysts, other type of substrates⁴ and other hydroperoxides and hydrogen peroxide for the synthesis of peroxides is in progress.

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(4) Interesting examples of replacement of labile hydrogen atom by a *tert*-butylperoxy group have been observed by M. S. Kharasch and G. Sosnowsky in the course of the investigation of autoxidation of nitriles, and by the present authors in the peroxidation of xylenes, dioxane, etc. Results of these studies will be the subject of forthcoming publications.

(5) Deceased.

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Radical Substitution Reactions

Sir:

We wish to describe free radical reactions in which a hydrogen atom is replaced by a benzoyloxy or a phthalimido group.

If *tert*-butyl hydroperoxide (one mole) and benzoic acid (one mole) are added to cyclohexene (10 moles) and the reaction mixture is warmed to 80° in the presence of 0.2 mol % cuprous chloride, there is obtained cyclohexenyl benzoate in over 90% yield. (B.p. 103°/0.15 mm., n_D^{20} 1.5380. *Anal.* Calcd. for $C_{13}H_{14}O_2$: C, 77.29; H, 6.89; mol. wt., 202. Found: C, 77.50; H, 7.1; mol. wt., 203. Unsaturation, 100% by ozonolysis.) Using only a slight excess of cyclohexene, benzene, *tert*-butyl alcohol, and nitrobenzene were found suitable solvents for this reaction.

With octene-1 as the substrate and solvent, 3-benzoyloxyoctene-1 is isolated in 50% yield. (B.p. 105°/0.2 mm., n_D^{20} 1.4920. *Anal.* Calcd. for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68; mol. wt., 230. Found: C, 77.23; H, 8.81; mol. wt., 235.) The infrared spectrum indicates the presence of terminal double bonds only. The product is thus different from the one obtained by the action of benzoyl peroxide on

(2) M. S. Kharasch, P. Pauson, W. Nudenberg, *J. Org. Chem.*, **18**, 322 (1953).

(3) M. S. Kharasch, A. Fono, W. Nudenberg, *J. Org. Chem.*, **15**, 753 (1950).