

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).

octene-1 (described in a previous communication). Both 1-*tert*-butylperoxyoctene-2 and 3-*tert*-butylperoxyoctene-1 are formed as by-products.

The formation of α -cumyl benzoate from cumene, equimolar amounts of *tert*-butyl hydroperoxide and benzoic acid in the presence of trace amounts of copper salts proceeds less readily and shows a remarkable solvent effect. The highest yield, 20%, is obtained in excess cumene, in the presence of less than 0.2 mol % catalyst. Increased amounts of catalyst decrease the yield in favor of the α -cumyl *tert*-butyl peroxide, which is always the major product. When benzene or *tert*-butyl alcohol is used as a solvent, in the presence of 1.5 mole of cumene and 0.002 moles copper chloride, α -cumyl benzoate is formed in yields of only 11% and 6%, respectively. With nitrobenzene pyridine, acetic acid, or heptane as the solvent, no benzoate could be detected.

When *tert*-butyl hydroperoxide (one mole) was added over a period of 3 hours at 80° to a suspension of phthalimide (one mole) in a benzene (10 moles) solution of cyclohexene (1.5 moles) containing 0.002 mole cuprous chloride, *N*-cyclohexenyl phthalimide (0.14 mole) was isolated. (M.p., 114.5°, from alcohol. *Anal.* Calcd. for C₁₄H₁₃O₂N: C, 73.99; H, 5.77; N, 6.16; mol. wt., 227. Found: C, 73.96; H, 6.0; N, 6.16; mol. wt. 240. Unsaturation 100% by ozonolysis.) Its infrared spectrum is in agreement with the assigned structure. A solvent effect similar to the one observed with α -cumyl benzoate is found. Best solvents are benzene, xylene, acetonitrile, and ethyl acetate. Work in progress indicates that with *tert*-butyl peroxide as oxidizing agent this reaction is almost quantitative. It also indicates that saccharin and pyrimidine are also able to give *N*-substituted products.

Substitution is observed also in radical reactions of the conventional type. Decomposition of di-*tert*-butyl peroxide in cumene, in the presence of benzoic acid yields about equal amounts of dicumene and α -cumyl benzoate. However, addition of one mole per cent cuprous chloride inhibits completely the formation of dicumene but increases the yield of α -cumyl benzoate.

The solvent effect observed in these reactions indicates that the radicals form a loose complex with the solvent. The most suitable solvents are those which are known to give stable complexes with triphenyl methyl radicals.¹

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(1) M. Gomberg and L. H. Cone, *Ber.*, **38**, 1333 (1905).

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Disproportionation Reaction of Diphenylsilane in the Absence of Any Added Catalyst

Sir:

Disproportionation reactions of organosilicon compounds have been known for a long time, one of the early reactions¹ of this type being that in which triethylphenylsilane (itself formed in a sealed tube reaction at 175° from diethylzinc and trichlorophenylsilane) disproportionated into diethyldiphenylsilane and tetraphenylsilane. This disproportionation reaction occurred during either the sealed tube reaction or subsequent manipulations including distillation. It seems likely that the zinc chloride by-product from the original reaction acted as a Lewis acid type catalyst. What may be the first example of the disproportionation of a silicon hydride compound can be found in the silane experiments of Stock and Somieski.² During the course of their work, silane and dichlorosilane were allowed to react in a sealed tube with aluminum chloride at 100° for 7 days. Subsequent work-up yielded a significant amount of chlorosilane. No reaction was noted in the cold without added catalyst.

While such disproportionation reactions had been known, it remained for Calingaert, Beatty *et al.*³ to establish the identity of the "redistribution reaction," in which random distribution of all possible products is noted. There is ample proof that many such reactions do occur,^{3,4,5} but in some cases, such as the methylchlorosilanes^{6,7} and the ethoxychlorosilanes,⁸ the distribution is nonrandom. As noted previously a disproportionation reaction of a silicon hydride compound has been reported.² Other similar reactions are known. For instance, Benkeser, Landesman and Foster⁹ in several articles have reported the "apparent redistribution" reactions of phenylsilane and diphenylsilane in the

(1) A. Ladenburg, *Ber.*, **7**, 387 (1874). See also, C. Friedel and A. Ladenburg, *Ann.*, **143**, 124 (1867), and C. Friedel and J. M. Crafts, *Ann. chim. phys.*, (4) **9**, 5 (1866).

(2) A. Stock and C. Somieski, *Ber.*, **52**, 719 (1919).

(3) See G. Calingaert and H. A. Beatty in H. Gilman's *Organic Chemistry, An Advanced Treatise*, John Wiley and Sons, Inc., New York, N. Y., 2nd ed., 1943, pp. 1806-20 for a survey of work, including their own, on the redistribution reaction.

(4) H. H. Anderson, *J. Am. Chem. Soc.*, **66**, 934 (1944); **72**, 2091 (1950); **73**, 5800 (1951); G. S. Forbes and H. H. Anderson, *J. Am. Chem. Soc.*, **66**, 931 (1944); **67**, 1911 (1945).

(5) M. Kumada, *J. Inst. Polytech. Osaka City Univ., Ser. C*, **2**, 131 (1952); [*Chem. Abstr.*, **48**, 11303 (1954)].

(6) R. O. Sauer and E. M. Hadsell, *J. Am. Chem. Soc.*, **70**, 3590 (1948).

(7) P. D. Zemaný and F. P. Price, *J. Am. Chem. Soc.*, **70**, 4222 (1948).

(8) M. Kumada, *J. Inst. Polytech. Osaka City Univ., Ser. C*, **2**, 139 (1952); [*Chem. Abstr.*, **48**, 11303 (1954)].

(9) R. A. Benkeser, H. Landesman, and D. J. Foster, *J. Am. Chem. Soc.*, **74**, 648 (1952); R. A. Benkeser and D. J. Foster, *J. Am. Chem. Soc.*, **74**, 4200, 5314 (1952).