aldehyde b. p. 85–95°, $n^{20}D$ 1.4025–28, 2,4-dinitrophenylhydrazone m. p. 189–190°; methyl *t*-butyl ketone b. p. 105°, $n^{20}D$ 1.3970, 2,4-dinitrophenylhydrazone m. p. 125°; ethyl *t*-butyl ketone b. p. 120–125, $n^{20}D$ 1.4051, 2,4-dinitrophenylhydrazone 144°, 2,4-dinitrophenylhydrazone 95°. All derivatives were checked with mixed m. p. of known samples.

The products from the decarboxylation of isobutyric acid were analyzed only for diisopropyl ketone, b. p. 123°, $n^{20}D$ 1.4000, semicarbazone m. p. 157°, mixed m. p. 157°, and *n*-propyl isopropyl ketone b. p. 135–140°, $n^{20}D$ 1.4060–1.4070, semicarbazone m. p.119°, mixed m. p. 119°.

Preparation of *t*-Butyl Isobutyl Ketone.—A 2.2 mole preparation of *t*-butylmagnesium chloride was made in 60% yield. The Grignard reagent was removed to a separatory flask by pumping with nitrogen pressure. Over a period of four hours the reagent was added to 1.3 moles of methyl isovalerate, $n^{20}D$ 1.3920, dissolved in 0.5 liter of anhydrous ether.

A mixture of *t*-butyl isobutyl ketone and *t*-butylisobutylcarbinol b. p. 153–165° 33 g., was isolated and oxidized in the following manner: The alcohol–ketone mixture (33 g.) was added slowly with stirring to the oxidizing mixture (36 g. of $Na_2Cr_2O_7$, 290 ml. of water, 49 g. of concd. H_2SO_4), the temperature not exceeding 50°. After stirring for two hours, the reaction mixture was refluxed for one-half hour and then steam distilled. The yield of *t*-butyl isobutyl ketone was 80%, b. p. 155°, $n^{20}D$ 1.4135, 2,4-dinitrophenylhydrazone m. p. 94°.

Decomposition of *t*-Butyl Isobutyl Ketone.—Twenty-three grams of *t*-butyl isobutyl ketone was passed over aerogel thoria catalyst at 490° and 20 g. of liquid condensate collected, 87%. Better than 90% of the product was unchanged *t*-butyl isobutyl ketone. Of the 10% which reacted approximately 10% was pinacolone, identified by b. p. and its 2,4-dinitrophenylhydrazone derivative.

Summary

1. The ketonic decarboxylation of trimethylacetic acid over thoria catalyst at 490° was found to yield *t*-butyl isobutyl ketone and a variety of products resulting from the decomposition of this ketone.

2. A mechanism is proposed to explain this product. This mechanism has been applied to the ketonic decarboxylation of isobutyric acid, and the formation of *n*-propyl isopropyl ketone in addition to diisopropyl ketone was confirmed.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, LOS ANGELES]

The Reaction of Grignard Reagents with Di-*t*-butyl Peroxide[1]

BY TOD W. CAMPBELL,[2] WELTON BURNEY[3] AND THOMAS L. JACOBS

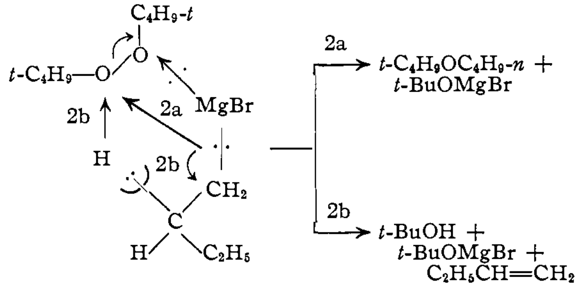
The reaction of dialkyl peroxides with Grignard reagents has not been examined extensively because most of these peroxides are unstable. However, it has been shown[4] that phenylmagnesium bromide and diethyl peroxide give a 35% yield of phenetole and 18% of biphenyl. This is similar to the reaction of Grignard reagents with disulfides[5]

$$\text{RSSR} + \text{R'MgX} \longrightarrow \text{RSR'} + \text{RSMgX} \quad (1)$$

and diselenides.[6]

The availability of the relatively inert di-*t*-butyl peroxide in large amounts,[7] has made possible investigations of the chemistry of organic peroxides heretofore impossible or very difficult. In this paper are presented the results of an investigation of the reaction of this compound with a series of Grignard reagents, including phenylmagnesium bromide as well as primary, secondary and tertiary aliphatic bromomagnesium compounds. Little or no reaction occurred in the case of the *t*-aliphatic and phenyl Grignard reagents; steric hindrance may be important in the first of these. The Grignard reagents from the primary and secondary halides reacted readily to yield as significant products a *t*-butyl alkyl ether, which would be predicted on the basis of equation (1), an olefin derived from the Grignard reagent, and *t*-butyl alcohol. The coupling product from the Grignard reagent was also formed in low yield.

It is possible and appears attractive to postulate a course for the reaction of aliphatic Grignard reagents with the hindered peroxide similar to that for the reduction of a hindered ketone by a β-hydrogen atom in a Grignard reagent.[8] Thus, the reaction between butylmagnesium bromide and di-*t*-butyl peroxide might involve the initial complex A, which could, by appropriate electronic shifts, decay by either path 2a or 2b to give the experimentally observed products.



According to this formulation the moles of *t*-butyl alcohol should be equal to the moles of ether plus twice the moles of olefin. This was found to be true within experimental error.

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[1] Taken from the thesis submitted by Welton Burney in partial fulfillment of the requirements for the M.S. degree in Chemistry, June, 1949.

[2] Western Regional Research Laboratory, Albany, California.

[3] Lockheed Aircraft, Burbank, California.

[4] Gilman and McCracken, THIS JOURNAL, **45**, 2462 (1923).

[5] Wuyts, *Bull. soc. chim.*, **35**, 166 (1906).

[6] Campbell and McCullough, THIS JOURNAL, **67**, 1965 (1945).

[7] We wish to thank the Shell Development Co., Emeryville, California, for a generous gift of this compound.

[8] Whitmore and George, THIS JOURNAL, **64**, 1239 (1942).

Experimental

Materials.—Di-*t*-butyl peroxide was obtained as a gift from the Shell Development Co., Emeryville, California. It was distilled before use, b. p. 111° (758 mm.).

Halides.—Bromobenzene, butyl bromide, and hexyl bromide were Eastman Kodak Co. white label products, redistilled before use. The 2-bromoöctane was synthesized by the method of Shriner and Young,[9] and 3-ethyl-3-bromopentane was made by treating triethyl carbinol[10] with phosphorus tribromide. The product boiled at 41° (15 mm.).

Anal. Calcd. for $C_7H_{15}Br$: C, 46.94; H, 8.44. Found: C, 46.60; H, 8.72.

General Procedure.—The Grignard reagent was prepared by standard methods from 0.5 m. of halide and 0.5 g. atoms of magnesium in 500 ml. of ether. To the cooled ethereal solution of the Grignard reagent was added 0.5 m. of di-*t*-butylperoxide at a rate to cause gentle refluxing of the ether, provided reaction occurred. When the peroxide was all added, the reaction mixture was refluxed one hour, and hydrolyzed with saturated ammonium chloride solution. The phases were separated, the aqueous layer extracted with two 100-ml. portions of ether, and the ether phases combined and dried over anhydrous potassium carbonate. After removal of the ether, the residue was examined as described below, for the individual Grignard reagents.

Phenylmagnesium Bromide.—No noticeable reaction occurred, so refluxing was continued for twenty-four hours. After hydrolysis, all of the added peroxide was recovered unchanged. A 10% yield of biphenyl was not considered significant, since this amount was recovered from a preparation of phenylmagnesium bromide which had not been treated with peroxide.

***n*-Butylmagnesium Bromide.**—A vigorous reaction occurred on addition of the peroxide. After decomposition of the reaction mixture, distillation gave three fractions. Fraction 1, b. p. below 0°, absorbed hydrogen bromide readily to give *s*-butyl bromide and was probably 1-butene; fraction 2, 7.4 g., b. p. 82.1°, m. p. 25.5°, was *t*-butyl alcohol; fraction 3, 14 g., b. p. 124°, was found to be inert to most reagents. By refluxing with 57% hydriodic acid for two hours it gave 6 g. of *n*-butyl iodide, b. p. 130° and 4.1 g. of a hydrocarbon, b. p. 125°, presumably *n*-octane resulting from the coupling of the Grignard reagent. Fraction 3 was thus a mixture of *n*-octane and *n*-butyl *t*-butyl ether, b. p. 124°.

On the basis of this experiment, Grignard reagents with at least six carbons were chosen for further work and another primary compound was investigated.

***n*-Hexylmagnesium Bromide.**—After hydrolysis of the reaction mixture, the following products were isolated and identified.

	B. p.,		Yield,
	°C.	Mm.	moles
1-Hexene	64	760	0.15
t-Butyl alcohol	82	760	.24
t-Butyl *n*-hexyl ether[a]	64	21	.10
Dodecane[b]	81	17	.03

[a] *Anal.* Calcd. for $C_{10}H_{22}O$: C, 75.86; H, 14.02. Found: C, 76.10; H, 14.25. [b] *Anal.* Calcd. for $C_{12}H_{26}$: C, 84.60; H, 15.40. Found: C, 84.45; H, 15.61.

The residue consisted of a viscous red tar.

2-Octylmagnesium Bromide treated as above gave

	B. p.,		Yield,
	°C.	Mm.	moles
1-Octene	121	760	0.15
t-Butyl alcohol	82	760	.31
t-Butyl 2-octyl ether[a]	78	11	.10
7,8-Dimethyltetradecane[b]	141	10	.03

[a] *Anal.* Calcd. for $C_{12}H_{26}O$: C, 77.35; H, 14.07. Found: C, 77.15; H, 14.14. [b] *Anal.* Calcd. for $C_{16}H_{34}$: C, 84.86; H, 15.14. Found: C, 84.70; H, 15.10.

Again, the residue was a dark tar.

3-Ethylpentyl-3-magnesium Bromide.—Reaction with *t*-butylperoxide was mild. Distillation of the reaction mixture gave 0.3 mole of 3-ethylpentene-2, but no other identifiable products except unreacted peroxide.

Summary

The reaction of primary and secondary alkylmagnesium bromides with di-*t*-butyl peroxide yields *t*-butyl alcohol, alkyl *t*-butyl ethers, olefins corresponding to the Grignard reagents and the coupling products from the Grignard reagents. The reaction producing the ether and alcohol may be formulated like the normal addition reactions of Grignard reagents, and the reaction leading to olefin and alcohol may be formulated like the reducing action of the reagents. Phenylmagnesium bromide and a *t*-alkyl Grignard reagent failed to react with the peroxide.

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(9) Shriner and Young, THIS JOURNAL, **52**, 3332 (1930).

(10) Moyer and Marvel, "Organic Syntheses," Coll. Vol. II, 602 (1943).