

ORGANIC PEROXIDES

Part VIII.—Reactions of Dibenzoyl Peroxide and *t*-Butyl Perbenzoate with Grignard Reagents and Phenyllithium

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Dibenzoyl peroxide and *t*-butyl perbenzoate are allowed to react with phenyllithium and several Grignard reagents. The yields of benzoyloxy substitution by these Grignard reagents varied between 15–44%. Phenyllithium appeared to be markedly inferior for similar substitution.

As an alternative to our previous method¹ for introducing the benzoyloxy group into aromatic nuclei, the reaction of benzoyl peroxide with aromatic magnesium/lithium compounds has been studied:



Gilman and Adams² reported a 30% yield of phenyl benzoate from the reaction of phenylmagnesium bromide with dibenzoyl peroxide. We have obtained 15–44% yields of benzoate esters from four different Grignard reagents. The yield of phenyl benzoate decreased when the reaction of phenylmagnesium bromide with peroxide took place in the presence of additional magnesium bromide.

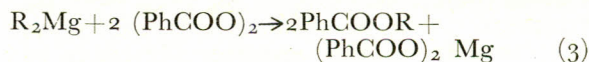
TABLE I.—YIELDS FROM REACTIONS OF DIBENZOYL PEROXIDE WITH GRIGNARD REAGENTS RMgBr .

R	Yields of ester (%) [*]	Yield of benzoic acid (%) [†]
<i>n</i> -Butyl	20	80
Cyclohexyl	44	71
Phenyl	23	72
<i>p</i> -Biphenyl	15	51

^{*}Based on equation 1. [†]Based on: $\text{Bz}_2\text{O}_2 \rightarrow 2\text{BzOH}$.

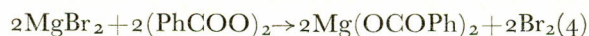
This finding and the high yields of benzoic acid have since received an explanation from the work of Lowesson and Yang,³ who found that Grignard reagent may react in two different ways:

1. to give benzoate ester and benzoic acid:



From this reaction the maximum yield of benzoic acid (based on $(\text{PhCOO})_2 \rightarrow 2\text{PhCO}_2\text{H}$) can only be 50%.

2. to give alkyl or aryl bromide and benzoic acid (maximum yield, 100%):



Thus the result with cyclohexylmagnesium bromide (Table I) indicates that in this case reaction 3 and reaction 6 are of almost equal importance, while that with *n*-butylmagnesium bromide indicates that with this reagent reaction 6 becomes more important than reaction 3.

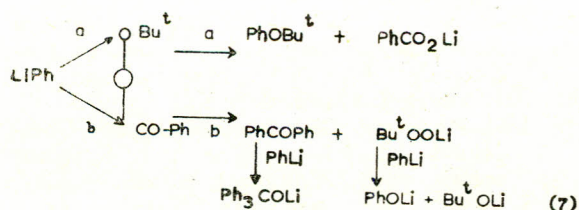
It was thought that with phenylmagnesium chloride reactions 4 and 5 might not take place, and that the yield of phenyl benzoate might consequently be increased; in fact, it decreased to 17%.⁴ The reaction of phenylmagnesium iodide and of butylmagnesium chloride with benzoyl peroxide failed to yield any benzoate esters.⁴

Because organolithium compounds are frequently easier to prepare than organomagnesium compounds, a few experiments were carried out

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with them, but they appeared to be markedly inferior for the present purpose. Phenyllithium reacted with dibenzoyl peroxide to give a 71% yield of triphenylcarbinol and 10% tribromophenol.

The reaction of phenyllithium with *t*-butyl perbenzoate at 0–5°C. afforded 41% of phenyl *t*-butyl ether, 41% of *t*-butyl alcohol, 28% of phenol, 28% of benzoic acid and 12% of triphenyl carbinol. Lowesson and Yang³ obtained 59% of phenyl *t*-butyl ether from this reaction run at –60°. It is evident that nucleophilic attack of phenyllithium may take place about equally readily either on the peroxide oxygen (reaction *a*) or on the carbonyl carbon (reaction *b*):



In the reaction of phenylmagnesium bromide route *a* is more favoured, yields of 67% of phenyl *t*-butyl ether and 85% of benzoic acid being obtained (about the same as the yields reported by Lawesson and Yang).³

Experimental

REACTIONS OF GRIGNARD REAGENTS WITH

(*a*) *Dibenzoyl Peroxide*.—The Grignard reagents were prepared according to Kharasch and Reinmuth⁵ by the addition of alkyl or arylbromide to a suspension of magnesium in ether under nitrogen, and estimated by titration of the base formed on adding an aliquot of the solution to water. The solution of organometallic compound was then added under nitrogen with stirring to a suspension of peroxide in dry ether, cooled to 0–4°. After addition, the reaction mixture was stirred for additional 30–60 minutes, followed by the addition of cold water and acidification by dilute hydrochloric acid. The ether layer was separated from the aqueous layer and extracted with sodium bicarbonate solution which on acidification gave benzoic acid. The ether layer was then extracted with 3–5% caustic potash solution to remove any phenol. After removal of acid and phenol, the ether layer was washed with water and dried by anhydrous sodium sulphate. The ether was removed by distillation and the residue was purified by crystallization, adsorption chromatography or vacuum distillation.

(*b*) *n*-Butylmagnesium Bromide.—From 24.2 g. (0.1 mole) of benzoyl peroxide and 0.1 mole of *n*-butylmagnesium bromide were obtained benzoic acid (19.4 g.; 80%) and butyl benzoate (3.6 g.; 20%) b.p. 119–120°/11 mm., n_D^{27} 1.4942 (reported⁶ n_D^{20} 1.4972; found for authentic butyl benzoate, n_D^{27} 1.4950), ν film max in cm^{-1} : 3050 (w), 2990 (m), 1725 (s), 1610 (w), 1458 (m), 1320 (m), 1280 (s), 1180 (w), 1115 (m), 1075 (m), 1030 (m), 940 (w), 840 (w), 710 (s), 690 (w). The infrared spectrum of an authentic specimen of butyl benzoate was identical.

(*c*) *Cyclohexylmagnesium Bromide*.—From 12.1 g. (0.05 mole) of benzoyl peroxide and (0.05 mole) of cyclohexylmagnesium bromide was obtained benzoic acid (8.55 g.; 71%) and cyclohexyl benzoate (4.49 g.; 44%), b.p. 164°/24 mm., n_D^{27} 1.5182, ν film max in cm^{-1} : 3040 (w), 2940 (s), 2870 (s), 1717 (s), 1690 (sh), 1605 (w), 1450 (s), 1435 (s), 1375 (w), 1318 (s), 1280 (s), 1180 (s), 1160 (m), 1110 (s), 1025 (m), 905 (m), 860 (m), 810 (w), 710 (s), 695 (m). An authentic specimen of cyclohexyl benzoate, b.p. 192–193°/61 mm., n_D^{27} 1.5178, showed an identical infrared spectrum.

(*d*) *Phenylmagnesium Bromide*.—From 24.2 g. (0.1 mole) of benzoyl peroxide and 0.1 mole of phenylmagnesium bromide were obtained 17.5 g. (72%) of benzoic acid and 4.6 g. (23%) of phenyl benzoate, which crystallized from the ether solution on concentration. Recrystallized from ligroin, phenyl benzoate had m.p. and mixed m.p. 68–69°.

(*e*) *p*-Biphenylmagnesium Bromide.—From 0.07 mole of *p*-biphenylmagnesium bromide and 17.8 g. (0.07 mole) of peroxide were obtained 0.9 g. (9%) of quarterphenyl, m.p. and mixed m.p. 309° (reported⁷ m.p. 315°), as an ether insoluble solid; 8.6 g. (51%) of benzoic acid; and 2.87 g. (15%) of colourless needles of *p*-biphenyl benzoate, m.p. and mixed m.p. 149° (reported⁸ m.p. 150°). Calc. for $\text{C}_{19}\text{H}_{14}\text{O}_2$: C, 83.21; H, 5.11%. Found: C, 83.25; H, 5.19%.

REACTION OF DIBENZOYL PEROXIDE WITH PHENYLLITHIUM

To 12.1 g. (0.05 mole) of benzoyl peroxide in ether, 0.05 mole of phenyllithium was added. An yield of 8.47 g. (70%) of benzoic acid was obtained. A caustic potash (5%) extract of the ether solution gave on acidification a product which crystallized from ethanol and was identified

as tribromophenol (0.42 g.; 10%) m.p. 93° alone or when mixed with an authentic specimen. The residue left after the evaporation of ether crystallized from ligroin (b.p. 60-70°) as needles of triphenylcarbinol (3.2 g.; 71%), m.p. and mixed m.p. 160°.

REACTION OF TERT-BUTYL PERBENZOATE WITH PHENYLMAGNESIUM BROMIDE

From the reaction of 19.4 g. (0.1 mole) of *t*-butyl perbenzoate and 0.1 mole of phenylmagnesium bromide were obtained 10.8 g. (88%) of benzoic acid and 10.1 g. (67%) of phenyl *t*-butyl ether, b.p. 80°/20 mm. (reported⁹ b.p. 80°/20 mm.), n_D^{20} 1.4866 (reported⁹ n_D^{20} 1.4869), ν film max in cm^{-1} : 3044 (s), 2961 (s), 2890 (s), 1595 (s), 1500-1495 (s), 1250-1150 (s), 1069 (s), 1021 (s), 925-875 (s), 810 (s), 775 (s), 690 (s).

REACTION OF TERT-BUTYL PERBENZOATE WITH PHENYL LITHIUM

From 8.9 g. (0.046 mole) of perbenzoate and 0.092 mole of phenyllithium were obtained 1.6 g. (28%) of benzoic acid and 1.2 g. (28%) of phenol (characterized as tribromophenol). The ether solution of neutral products was distilled through a Nester-Faust spinningband

distillation column, and gave 1.4 g. (41%) of *t*-butanol, b.p. 83°, n_D^{20} 1.3872 (reported¹⁰ n_D^{20} 1.3878 and 2.85 g (51%) of *t*-butyl phenyl ether b.p. 80°/20 mm., n_D^{22} 1.4868. The residue from distillation was triphenylcarbinol (1.5 g., 12%), m.p. and mixed m.p. 160°.

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