

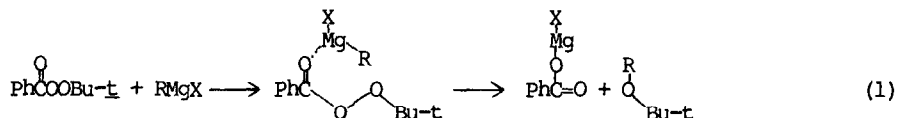
EVIDENCE FOR SINGLE ELECTRON TRANSFER IN THE REACTIONS OF  
ORGANOMETALLIC COMPOUNDS WITH 2,3,3-TRIMETHYL-2-BUTYL PEROXYBENZOATE

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**Abstract:** Utilization of a triptoxy radical probe in the reactions of organometallic compounds with 2,3,3-trimethyl-2-butyl peroxybenzoate indicates that the radical character of the reaction decreases in the order  $n\text{-BuLi} > n\text{-BuMgCl} > \text{PhMgBr}$ .

Peroxides may react with nucleophiles either by nucleophilic displacement ( $S_N2$ )<sup>1</sup> or single electron transfer (SET) mechanisms,<sup>2</sup> and these reactions thus provide a rich area in which to study the dichotomy between these two mechanisms. Many of the peroxide SET reactions reported recently have employed electron donors such as polynuclear aromatics,<sup>2a,b</sup> dimethoxybenzenes,<sup>2d,e</sup> and anispinacolone,<sup>2c</sup> which are relatively weak nucleophiles. In these cases  $S_N2$  would not be expected to compete with SET. The SET reaction between ethyllithium and tert-butyl peroxide is an example of a good nucleophile serving as an electron donor.<sup>4</sup> Evidently, SET is favored over  $S_N2$  because of the low reactivity of tert-butyl peroxide with nucleophiles. We are interested in studying the borderline region in which SET and  $S_N2$  mechanisms might compete or merge.<sup>2d,3</sup> We have found that the reactions of organometallic compounds with 2,3,3-trimethyl-2-butyl peroxybenzoate appear to be in this borderline region.

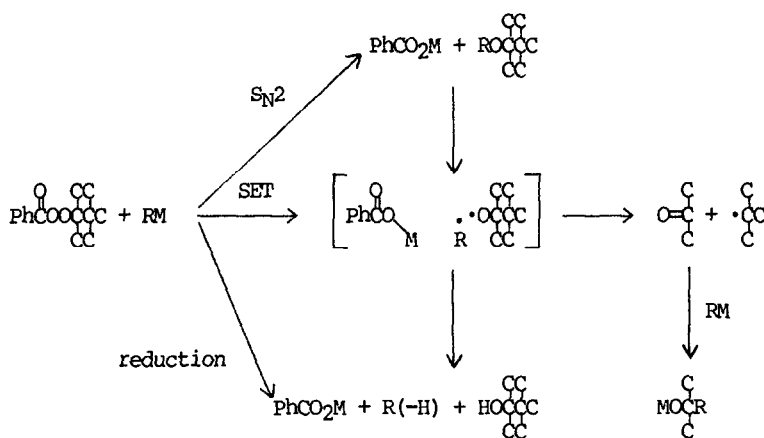
The reaction of tert-butyl peroxybenzoate with Grignard reagents was reported by Lawesson and Yang in 1959.<sup>4</sup> When the peroxyester was added to an excess of Grignard reagent in ether, the major products were benzoic acid and a tert-butyl ether. A nucleophilic displacement reaction was postulated, and a complexation between peroxyester and Grignard reagent prior to the displacement was suggested to explain nucleophilic attack at the alkoxy oxygen rather than at the carbonyl carbon (eq. 1).



Recent reports of SET reactions involving peroxyesters<sup>2b,9</sup> suggest that the peroxyester-Grignard reaction in eq. 1 may also follow an SET pathway. We have used a triptoxy radical probe to identify radical intermediates. Walling has shown that at 0°C the triptoxy radical undergoes  $\beta$ -scission at a rate >150,000 times faster than extraction of a hydrogen atom from cyclohexane.<sup>5</sup> This probe was successfully used by Kochi in the study of the ethyllithium-tert-butyl peroxide reaction.<sup>2h</sup>

Several possible pathways for the reaction of organometallic compounds with 2,3,3-trimethyl-2-butyl peroxybenzoate (TMBP) are shown in Scheme 1. Nucleophilic displacement at the alkoxy oxygen yields a *tert*-butyl ether and benzoate. Reduction by  $\beta$ -hydride transfer forms benzoate, alkene, and *tert*-butyl alcohol. An SET reaction produces benzoate, R $\cdot$ , and *tert*-butoxy radical intermediates which may undergo combination to yield ether, disproportionation to give alkene and *tert*-butyl alcohol, or  $\beta$ -scission to form acetone. In the presence of excess organometallic reagent, the acetone reacts further to produce a tertiary alcohol. Detection of this tertiary alcohol indicates the occurrence of radical intermediates in the reaction.

SCHEME 1



2,3,3-Trimethyl-2-butyl peroxybenzoate was prepared from benzoyl chloride and 2,2,3-trimethyl-2-butyl hydroperoxide.<sup>6</sup> The peroxyester was reacted with a two-fold excess of phenylmagnesium bromide, *n*-butylmagnesium chloride, or *n*-butyllithium in either diethyl ether or hexanes. The Grignard reagents were prepared from resublimed magnesium purchased from Alfa and the organolithium was obtained from Aldrich. A 10 mmol sample of the peroxyester was dissolved in ~5 ml of solvent under argon. About 20 mmol of the organometallic reagent was added dropwise to the stirred solution which was cooled in an ice bath. After two hours, the reaction was quenched by the addition of 0.5 ml water. Benzoic acid was extracted and weighed. Other reaction products were determined by g.l.p.c. using internal standards. Control experiments showed that acetone and *tert*-butyl alcohol, products of a Criegee rearrangement,<sup>6</sup> were not present in the initial samples of peroxyester and were not formed under the experimental conditions.

Table 1. Reactions of Organometallic Compounds with 2,3,3-Trimethyl-2-Butyl Peroxybenzoate<sup>a</sup>

R-M	PhCO <sub>2</sub> H	PhC(=O)R	PhC(OH)(R) <sub>2</sub>	ROOC(=O)C(=O)R	ROOC(=O)C(=O)OH	ROOC(=O)C(=O)C(=O)R
Ph-MgBr <sup>b</sup>	20	46	33	83	—	<0.1
n-BuMgCl <sup>c</sup>	101	2	9	86	1	14
n-Bu-Li <sup>d</sup>	50	36	26	22	30	30

<sup>a</sup>Percent yield based on complete reaction of the peroxyester.

<sup>b</sup>Reacted at room temperature overnight in diethyl ether.

<sup>c</sup>Reacted at 0°C for two h in diethyl ether.

<sup>d</sup>Reacted at 0°C for two h in hexanes.

The products from the reactions of the organometallic compounds with TMBP are shown in Table 1. Phenylmagnesium bromide gave a high yield of phenyl tert-butyl ether. The relatively low yield of benzoic acid is probably the result of a secondary reaction between benzoate anion and excess phenylmagnesium bromide which initially forms benzophenone and finally triphenylcarbinol.<sup>7</sup> No cumyl alcohol, which would result from reaction of acetone with phenylmagnesium bromide, was detected. For the *n*-butylmagnesium chloride reaction the benzoic acid yield was higher presumably because the shorter reaction time suppressed the formation of the secondary products valerophenone and di-*n*-butyl phenylcarbinol. The yield of ether was essentially the same as in the phenylmagnesium bromide reaction. However, a 14 percent yield of 2-methyl-2-hexanol was formed which indicates a substantial amount of intermediate triptoxy radicals.

*n*-Butyllithium gave a product distribution somewhat different from that of the Grignard reagents in that the yield of 2-methyl-2-hexanol was higher and the yield of tert-butyl ether was significantly smaller. (Control experiments showed that the ether does not react with *n*-butyllithium under the reaction conditions.) These product differences may be accounted for in three ways. First, since *n*-butyllithium is much more reactive than Grignard reagents, a nucleophilic displacement may be occurring at either the acyloxy oxygen to form *n*-butyl benzoate and triptyl alcohol, or at the carbonyl carbon to form valerophenone and triptyl hydroperoxide. In excess *n*-butyllithium these products are rapidly converted to di-*n*-butylphenylcarbinol and triptyl alcohol. In a related study both *n*-butyl benzoate and valerophenone were formed as primary products when *n*-butyllithium was reacted with excess tert-butyl peroxybenzoate.<sup>8</sup> A second explanation is that the radical intermediates may disproportionate rather than combine or undergo  $\beta$ -scission. The  $k_d/k_c$  ratio for the reaction of 2,3-dimethyl-2-butoxy radicals with ethyl radicals is about 0.25.<sup>9</sup> Therefore, the yield of

trityl alcohol formed by a free radical process should be approximately one-fourth of the ether yield. The third possibility is decrease of ether yield due to a reduction reaction. The reduction products are indistinguishable from disproportionation products. At this time we do not know which explanation applies or whether a combination of two or more apply. Work is currently in progress to answer this question.

Since it has been shown that free radicals can result from the homolysis of ionic intermediates formed in nucleophilic displacement reactions,<sup>1b,2a,10</sup> caution is required when attributing free radical intermediates to an SET pathway. However, the results in Table 1 concerning the yields of 2-methyl-2-hexanol indicate a large radical component in the reactions of both *n*-BuLi and *n*-BuMgCl with TMBP. If the radical intermediates in these reactions were the result of homolysis, we should observe free radical products in the PhMgBr reaction as well, since all of these reactions would have similar ionic intermediates. Although an SET reaction cannot be excluded for the PhMgBr reaction since the life time of the radical intermediates may be too brief for  $\beta$ -scission to occur, we believe that both the *n*-BuLi and *n*-BuMgCl reactions with the peroxyester do occur by an SET mechanism rather than by nucleophilic displacement.

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Acknowledgement: The authors wish to express their appreciation to the Robert A. Welch Foundation and to the O'Hara Chemical Sciences Institute of the University of Dallas for support of this research.

(Received in USA 15 January 1985)