

STABLE ISOBENZOFURAN ENDOPEROXIDE AND ITS USE FOR OXIDATION OF
OLEFINS AND AROMATIC COMPOUNDS¹

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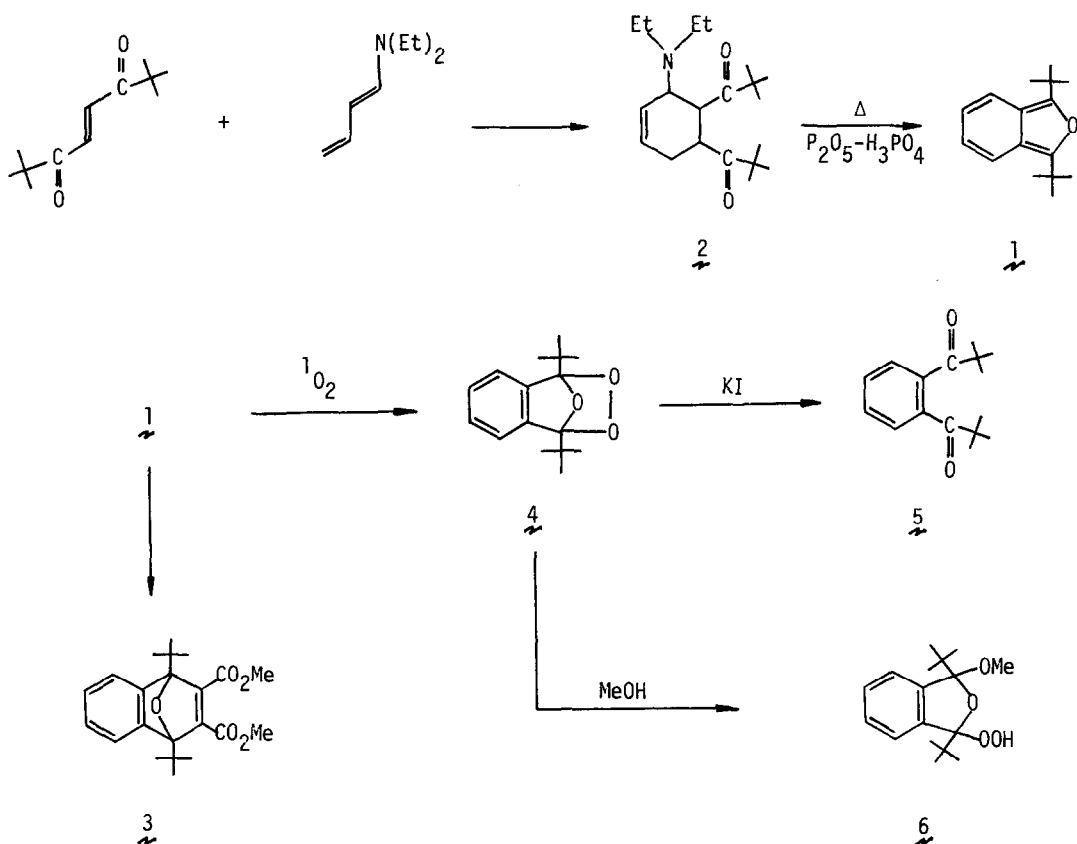
Summary: 1,3-Di-*tert*-butylisobenzofuran reacts with singlet oxygen with rate constant of $2.8 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$ to give stable endoperoxide **4**. Thermolysis of the endoperoxide (**4**) in the presence of norbornene and naphthalene gave the corresponding epoxide and naphthols, respectively. Addition of $\text{Pd}(\text{OAc})_2$ improved the yield of naphthols considerably.

1,3-Diphenylisobenzofuran (DPBF) is widely used as a singlet-oxygen acceptor because of its high reactivity toward singlet oxygen ($^1\text{O}_2$) and the unique fluorescent property.² However, the isolation of the endoperoxide is not easy, owing to its thermal lability.³ We report here that 1,3-di-*tert*-butylisobenzofuran reacts more rapidly with $^1\text{O}_2$ to give easily isolable endoperoxide and that the endoperoxide is capable of undergoing oxygen atom transfer to olefins and naphthalene probably via a carbonyl oxide intermediate.

Isobenzofuran⁴ and aryl-substituted isobenzofurans⁵ have been synthesized by several methods, whereas the synthesis of 1,3-di-alkylisobenzofurans has not been reported. We have prepared 1,3-di-*tert*-butylisobenzofuran (**1**) by using a modified method reported for the synthesis of 1,3-diarylisobenzofurans.⁶ Pyrolysis (120 °C) of the Diels-Alder adduct **2** in the presence of phosphorus pentoxide and phosphoric acid followed by vacuum distillation (90 °C/4 mmHg) provided **1** (51%). The structure of **1** was confirmed by spectral data⁷ and following reaction.⁸ Reaction of **1** with dimethyl acetylenedicarboxylate gave **3**⁷ quantitatively.

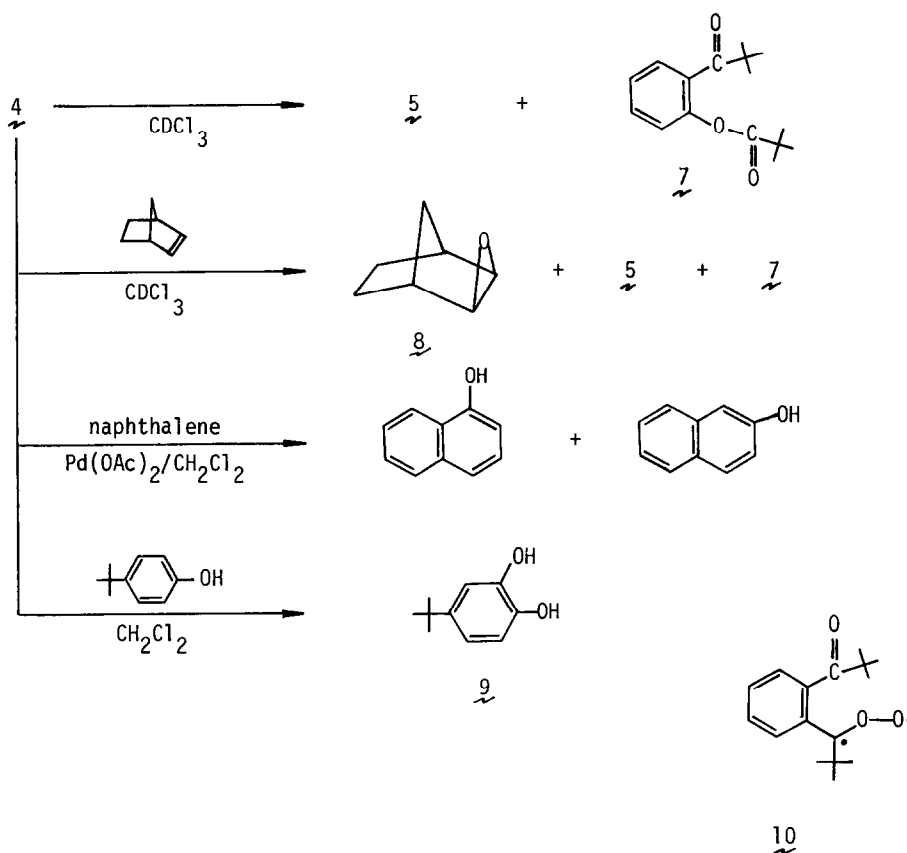
Photooxygenation (polymer-bound methylene blue, chromate filter) of **1** (0.04 M) in CFCl_3 at -70 °C rapidly absorbed an equimolar amount of oxygen to give a stable endoperoxide **4**⁷ (96%), which is readily isolable as a crystalline form simply by filtration of the insoluble sensitizer followed by evaporation of CFCl_3 below 20 °C. Reduction of **4** (KI-HCl-CFCl_3) gave **5** (95%),

whereas a solution of 4 in methanol at room temperature produced the methoxy hydroperoxide 6⁷ in quantitative yield. The rate constant for the reaction of 1 with $^1\text{O}_2$ determined by competition^{2b} with DPBF ($k_r = 7 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$) in CH_2Cl_2 is $2.8 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$, i.e., 1 appears to be the most reactive acceptor for $^1\text{O}_2$ so far reported.



Thermolysis of 4 (0.1 M) in CDCl_3 at 40°C (8 h) gave 5 (32%) and 7 (31%). However, when a solution of 4 (0.1 M) and norbornene (0.5 M) in CDCl_3 was stirred at 40°C under the above conditions, epoxide 8 (49%) was obtained in addition to 5 (73%) and 7 (9%). Apparently, the addition of norbornene increased the yield of 5 at the expense of 7, being accompanied with the formation of 8. A similar result has been obtained when 4 was decomposed in CH_2Cl_2 . When a solution of 4 (0.1 M) and naphthalene (0.5 M) in CH_2Cl_2 was stirred at 25°C under nitrogen atmosphere, α - and β -naphthols were obtained only in low yield (1.2%) with the ratio (79/21).¹⁰ However, the addition of $\text{Pd}(\text{OAc})_2$ (equimole to 4) to the reaction system increased the yield of naphthols (6.3%) with the ratio (79/21) being unchanged.¹¹ Likewise, thermolysis of 4 (0.1 M)

in the presence of 4-*tert*-butylphenol (0.5 M) gave a low yield (3%) of 4-*tert*-butylcatechol (9).



It has been reported that the isomerization of 1,2-naphthalene oxide in CH_2Cl_2 saturated with acetamide gave α - and β -naphthols with the (98/2 ~ 88/12) ratios under a variety of conditions,¹² whereas an intermediate formed in the photooxygenation of diphenyldiazomethane, probably a carbonyl oxide, was shown to oxidize naphthalene to α - and β -naphthols with the (85/15) ratio.¹³ The ratio observed here is close to the latter value, suggesting that a diradical type carbonyl oxide¹⁴ is involved as the reactive species in the present oxidation, whereas Adam and Rodriguez have proposed a dipolar oxidizing species for the epoxidation of olefins by furan endoperoxides.¹⁵

Owing to its extremely high reactivity toward various dienophiles including singlet oxygen, 1,3-di-*tert*-butylisobenzofuran (1) may be of considerable utility as a trapping reagent for reactive intermediates. Investigation of the mechanism and scope of the oxidation using 4 is currently underway.

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7. Selected spectral data follows. **1**: mp 43 - 45 °C; λ_{max} (cyclohexane) 339 nm (log ϵ 3.7), 347 (3.7), 356 (3.8), 376 (3.7); ^1H NMR (CDCl_3) δ 1.47 (s, 18 H), 6.53 (dd, 2 H, J = 7, 3 Hz), 7.37 (dd, 2 H, J = 7, 3 Hz); ^{13}C NMR (CDCl_3) δ 29.7, 34.8, 117.9, 120.2, 121.5, 150.1; Em 428 nm (excited at 360 nm). **3**: mp 133 - 134 °C; ^1H NMR (CDCl_3) δ 1.28 (s, 18 H), 3.68 (s, 6 H), 7.00 (dd, 2 H, J = 5, 3 Hz), 7.52 (dd, 2 H, J = 5, 3 Hz). **4**: mp 67 - 68 °C (decom); ^1H NMR (CDCl_3) δ 1.44 (s, 18 H), 7.16 - 7.66 (m, 4 H); ^{13}C NMR (CDCl_3) δ 25.6, 33.2, 115.9, 119.8, 127.2, 141.1. **6**: viscous oil; ^1H NMR (CDCl_3) δ 1.18 (s, 9 H), 1.24 (s, 9 H), 3.10 (s, 3 H), 7.20 - 7.67 (m, 4 H), 8.57 (br s, 1 H, OOH).
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