

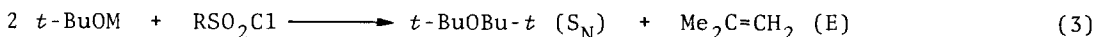
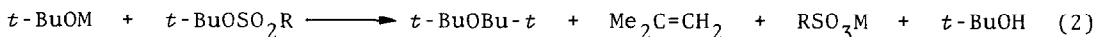
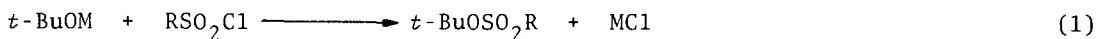
REACTIONS OF METAL *tert*-BUTOXIDES WITH AROMATIC SULFONYL CHLORIDES.  
A NEW SYNTHESIS OF DI-*tert*-BUTYL ETHER

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Summary: Di-*tert*-butyl ether was synthesized in good yields by the S<sub>N</sub> reactions of lithium *tert*-butoxide with tosyl and *p*-bromobenzenesulfonyl chlorides under mild conditions.

Di-*tert*-butyl ether has been prepared by the reaction of *tert*-butyl chloride with silver carbonate<sup>1</sup> or the other metal compounds,<sup>2</sup> by the reaction of *tert*-butyl perbenzoate with *tert*-butylmagnesium chloride,<sup>3</sup> and by the electrophilic alkylation of *tert*-butyl alcohol with trimethylcarbenium fluoroantimonate in the presence of amines.<sup>4</sup> However, the sterically hindered ether cannot be prepared by the Williamson synthesis using alkali metal *tert*-butoxides.

We now report a new convenient synthesis of the ether, which is interesting due to its stereochemistry and utility as a gasoline additive.<sup>4</sup> The reaction pathways were shown in Eqs. 1-3. Eq. 3 was derived from Eqs. 1 and 2, and summarized.



For example, a mixture of lithium (0.333 g, 48 mg-atom) and *tert*-butyl alcohol (60 cm<sup>3</sup>) was refluxed to give lithium *tert*-butoxide and cooled. There were then added *p*-toluenesulfonyl chloride (3.813 g, 20 mmol) and pentane (20 cm<sup>3</sup>). The mixture was stirred magnetically for 1 h at -10 °C, hydrolyzed, and extracted with pentane. The organic layer was washed with water, dried over sodium sulfate and fractionated to give 1.092 g (42%) of di-*tert*-butyl ether: bp 106 °C; IR (neat) 1384, 1363 (*t*-Bu), and 1173 cm<sup>-1</sup> (C-O-C); <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ=1.26 (18H, s, *t*-Bu). The corresponding small scale reaction was carried out to give 66% of di-*tert*-butyl ether and 34% of 2-methylpropene, which were

Table 1. Reactions of Metal *tert*-Butoxides with Aromatic Sulfonyl Chlorides

<i>t</i> -BuOM (mmol)	RSO <sub>2</sub> Cl <sup>a)</sup>	Solvent <sup>b)</sup> (vol/vol)	Temp. °C	Time h	Yield (%) of S <sub>N</sub> product <sup>c)</sup>
M=Li (12)	R=Me-Ph	<i>t</i> -BuOH	25	0.1	47
Li (12)	Me-Ph	<i>t</i> -BuOH-Pentane (3/1)	0	0.5	62
Li (12)	Me-Ph	<i>t</i> -BuOH-Pentane (3/1)	-10	1	66
Li (12)	Me-Ph	<i>t</i> -BuOH-Pentane (3/1)	-15	2	65
Li (15)	Me-Ph	Pentane	-10	2.5	43
Li (12)	Me-Ph	<i>t</i> -BuOH-DMSO (3/1)	-10	1	13
Na (12)	Me-Ph	<i>t</i> -BuOH-Pentane (3/1)	-10	1	14
Ba (6)	Me-Ph	<i>t</i> -BuOH-Pentane (3/1)	-10	1	39
Li (12)	Br-Ph	<i>t</i> -BuOH-Pentane (3/1)	-10	0.3	74
Li (12)	Br-Ph	<i>t</i> -BuOH-Pentane (3/1)	-15	0.5	73
Li (15)	Br-Ph	Pentane	-10	0.7	51

a) *p*-Toluenesulfonyl chloride (Me-PhSO<sub>2</sub>Cl) or *p*-bromobenzenesulfonyl chloride (Br-PhSO<sub>2</sub>Cl) 5 mmol used. b) Solvent 20 cm<sup>3</sup> used. c) Glpc theoretical yields of di-*tert*-butyl ether.

determined by glpc comparison with authentic samples using internal standards. The proportions of nucleophilic substitution (S<sub>N</sub>) to elimination (E) products were greatly influenced by the reaction conditions. The results of similar reactions were shown in Table.1. The yields of the ether formed by the reactions of metal *tert*-butoxides (*t*-BuOM) and *p*-toluenesulfonyl chloride decreased in the order M=Li>Ba>Na. Lower temperatures were much favorable for yielding the ether since the reaction intermediate, *tert*-butyl *p*-toluenesulfonate (*cf.* eq. 2), decomposed at about 0 °C.<sup>5</sup> *p*-Bromobenzenesulfonyl chloride reacted much more rapidly with lithium *tert*-butoxide to give the ether in better yields under comparable conditions. A mixed solvent, *tert*-butyl alcohol-pentane (3/1), was used to prevent the reaction mixtures from solidification at lower temperatures, and gave satisfactory results. When dimethyl sulfoxide was used instead of pentane in the above solvent system, the S<sub>N</sub>/E ratio decreased remarkably. As the reactions proceeded even in nonpolar pentane, the ether should be given by bimolecular nucleophilic substitutions.

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