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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_N 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[1] or the other metal compounds,[2] by the reaction of *tert*-butyl perbenzoate with *tert*-butylmagnesium chloride,[3] and by the electrophilic alkylation of *tert*-butyl alcohol with trimethylcarbenium fluoroantimonate in the presence of amines.[4] 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.[4] The reaction pathways were shown in Eqs. 1–3. Eq. 3 was derived from Eqs. 1 and 2, and summarized.

$$t\text{-BuOM} + \mathrm{RSO_2Cl} \longrightarrow t\text{-BuOSO}_2\mathrm{R} + \mathrm{MCl} \tag{1}$$

$$t\text{-BuOM} + t\text{-BuOSO}_2\mathrm{R} \longrightarrow t\text{-BuOBu-}t + \mathrm{Me_2C{=}CH_2} + \mathrm{RSO_3M} + t\text{-BuOH} \tag{2}$$

$$2\ t\text{-BuOM} + \mathrm{RSO_2Cl} \longrightarrow t\text{-BuOBu-}t\ (S_N) + \mathrm{Me_2C{=}CH_2}\ (E) \tag{3}$$

$$(\mathrm{M{=}Li,\ Na,\ Ba/2;\quad R{=}CH_3{-}Ph,\ Br{-}Ph})$$

For example, a mixture of lithium (0.333 g, 48 mg-atom) and *tert*-butyl alcohol (60 cm^3) 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^3). 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^{-1} (C–O–C); ^{1}H-NMR ($CDCl_3$) 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

t-BuOM (mmol)	RSO_2Cl[a]	Solvent[b] (vol/vol)	Temp. °C	Time h	Yield (%) of S_N product[c]
M=Li (12)	R=Me–Ph	*t*-BuOH	25	0.1	47
Li (12)	Me–Ph	*t*-BuOH–Pentane (3/1)	0	0.5	62
Li (12)	Me–Ph	*t*-BuOH–Pentane (3/1)	–10	1	66
Li (12)	Me–Ph	*t*-BuOH–Pentane (3/1)	–15	2	65
Li (15)	Me–Ph	Pentane	–10	2.5	43
Li (12)	Me–Ph	*t*-BuOH–DMSO (3/1)	–10	1	13
Na (12)	Me–Ph	*t*-BuOH–Pentane (3/1)	–10	1	14
Ba (6)	Me–Ph	*t*-BuOH–Pentane (3/1)	–10	1	39
Li (12)	Br–Ph	*t*-BuOH–Pentane (3/1)	–10	0.3	74
Li (12)	Br–Ph	*t*-BuOH–Pentane (3/1)	–15	0.5	73
Li (15)	Br–Ph	Pentane	–10	0.7	51

a) *p*-Toluenesulfonyl chloride (Me–$PhSO_2Cl$) or *p*-bromobenzenesulfonyl chloride (Br–$PhSO_2Cl$) 5 mmol used. *b*) Solvent 20 cm^3 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_N) 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.[5] *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_N/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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