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PREPARATION OF *tert*-BUTYL ARYL ETHERS

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The literature shows *tert*-butyl aryl ethers to be made only with considerable difficulty.

Lewis (1) was unable to prepare any *tert*-butyl phenyl ether by reacting the di-sodium salt of phenol sulfonic acid with *tert*-butyl chloride, followed by removal of the sulfonic acid group by steam-distillation. Smith (2) reported the preparation of *tert*-butyl phenyl ether only in very poor yield on reacting sodium phenoxide with *tert*-butyl chloride. Olsen, Hipsher, Buess, Goodman, Hart, Lamneck, and Gibbons (3) reacted phenol with *tert*-butyl alcohol in the presence of a large amount of 80% sulfuric acid at 49° to 51° for 1½ hours to obtain a 6.7% yield of *tert*-butyl phenyl ether. Natelson (4) reported the obtaining of *tert*-butyl phenyl ether (not isolated and no yields given) as an intermediate in the preparation of *p*-*tert*-butylphenol by passing one mole of isobutylene into one mole of phenol and one mole of concentrated H_2SO_4 at 0° and later warming the reaction product. McKinley (5) prepared *tert*-butyl *p*-tolyl ether, with a yield of 15.7% by preparing *p*-toloxymagnesium bromide from ethylmagnesium bromide and *p*-cresol, and reacting with *tert*-butyl chloride. Rosenwald (6) prepared the *tert*-butyl ethers of phenol, *p*-cresol, *p*-*tert*-butylphenol, 4-methoxyphenol, and 2-*tert*-butyl-4-methoxyphenol in yields up to 33% by reacting the phenols with isobutylene in an autoclave at 75°, using chloroacetic, oxalic, and trinitrobenzoic acid as catalysts.

It has been found in this laboratory (7) that *tert*-alkyl aryl ethers can be prepared in fairly high yields by simply passing isobutylene into the phenol at relatively low temperatures and in the presence of only a trace of sulfuric acid as the catalyst. In general, ether formation is discouraged and nuclear alkylation is encouraged by increasing the strength and amount of acid catalyst employed, and by increasing the reaction temperature.

A typical preparation, that of *tert*-butyl *m*-tolyl ether is given below:

Isobutylene was passed into a reactor containing 270 g. of *m*-cresol and 0.791 g. of 75.0% H_2SO_4 (0.00242 mole H_2SO_4/mole *m*-cresol) until an increase in weight of 139.9 g. was obtained. The isobutylene was added at the rate of maximum absorption, controlled by maintaining only a slight positive reading on a flow meter connected to the exit side of the apparatus. The system was vigorously agitated and held at 23° throughout the two hours needed to bring about the above isobutylene absorption. Temperature control was not difficult, for the ether-forming reaction is only mildly exothermic, much less so than that of nuclear alkylation of phenols. The *tert*-butyl aryl ether generally shows a boiling point close to that of its parent phenol, but the separation of the ether is simplified by dividing the reaction product into alkali-soluble and alkali-insoluble portions by repeated extractions with 10% aqueous NaOH. This treatment at the same time thoroughly neutralizes the product, a procedure that is necessary in order to prevent debutylation during the ensuing fractionation. To insure neutralization of the acid catalyst, one can add a slight excess of potassium ethoxide (made up in absolute alcohol) to the acidic alkylate before extracting

TABLE I

EFFECT OF VARYING STRENGTH OF ACID CATALYST

Strength H_2SO_4	96.0	75.0	60.0	40.0	10.0
Weight catalyst used, g.	0.556	0.791	0.372	0.646	2.350
m-Cresol, g.	270.0	270.0	109.6	107.7	108.0
Moles H_2SO_4/mole *m*-cresol	0.00230	0.00242	0.00228	0.00264	0.00240
Isobutylene added, g.	138.1	139.9	52.0	49.1	35.6
Alkali-soluble, g.	—	126.4	40.3	43.9	81.3
m-Cresol (101.0°/20 mm.)	64.1	104.7	36.5	40.7	75.4
4-*tert*-Butyl-3-methylphenol (153.0°/20 mm.)	0.0*	6.1	0.0*	0.0*	0.0*
Alkali-insoluble, g.	366.2	242.7	95.8	83.3	47.7
tert-Butyl *m*-tolyl ether (96.0°/20 mm.)	28.3	153.8	75.8	69.6	39.3
6-*tert*-Butyl-3-methylphenol (129.5°/20 mm.)	64.1	42.1	13.8	11.2	5.9
4,6-Di-*tert*-butyl-3-methylphenol (167.0°/20 mm.)	77.3	16.2	0.0*	0.0*	0.0*
m-Cresol consumed, g.	205.9	165.3	73.1	67.0	26.7
Yield of *tert*-butyl *m*-tolyl ether, %					
Based on *m*-cresol charged	6.7	37.5	45.6	42.4	24.2
Based on *m*-cresol consumed	9.7	61.2	68.4	68.1	80.2

* While the fractionations were run carefully, the 15-plate column used cannot be considered as a precision analytical instrument, and any component present in an amount less than the hold-up of the column could escape detection.

with the aqueous alkali. The alkali-insoluble portion, amounting to 242.7 g. was fractionated through a 24-inch column packed with ⅛″ glass helices (15 theoretical plates efficiency) to give 153.8 g. of *tert*-butyl *m*-tolyl ether, boiling at 96.0°/20 mm. (n_D^{20} 1.4892; d_{20} 0.9156). The calculated yield is 37.5% based on *m*-cresol charged and 61.2% based on *m*-cresol consumed

The yield of ether obtained is influenced greatly by the strength of acid used as the catalyst. In Table I are given the data obtained when using the same amount of H_2SO_4 in solutions of various strengths, with all alkylations carried out at 23°.

It is interesting to note that considerable ether formation took place even when sulfuric acid as dilute as 10% was employed as the catalyst. Some nuclear alkylation occurred with the 10% acid but no appreciable amount of di-alkylation on the nucleus was observed below acid strengths of 75%.

Ether formation can also be influenced by the amount of catalyst used, as is shown in Table II. The ether yield increases as the amount of catalyst is reduced. This same relationship was observed in a different series of experiments using various amounts of 10% acid at 23°.

The effect of temperature, both with concentrated and with 10% sulfuric acid is shown in Table III.

TABLE II

Effect of Varying Amount of Concentrated H_2SO_4 Catalyst

Amount of 96% H_2SO_4, g	0.556	0.142	0.069
m-Cresol, g	270.0	270.0	270.0
Moles H_2SO_4/mole *m*-cresol	0.00217	0.00054	0.00027
Temperature, °C	23.0	23.0	23.0
Isobutylene added, g	138.1	122.7	109.7
Alkali-soluble, g	—	—	128.8
m-Cresol	64.1	90.7	111.2
4-*tert*-Butyl-3-methylphenol	0.0	4.9	0.0
Alkali-insoluble, g	366.2	219.0	204.7
tert-Butyl *m*-tolyl ether	28.3	150.6	163.7
6-*tert*-Butyl-3-methylphenol	64.1	52.7	26.7
4,6-Di-*tert*-butyl-3-methylphenol	77.3	12.3	0.0
m-Cresol consumed, g	205.9	179.3	158.8
Yield of *tert*-butyl *m*-tolyl ether, %			
Based on *m*-cresol charged	6.7	38.0	40.0
Based on *m*-cresol consumed	9.7	57.3	68.0

TABLE III

Effect of Varying Temperature of Alkylation

	96% H_2SO_4				10% H_2SO_4		
Temperature, °C	−10	10	45	59	23	60	100
Amount H_2SO_4, g	0.1075	0.304	0.1105	0.1860	2.350	2.350	2.430
m-Cresol, g	109.3	270.0	110.1	186.9	108.0	108.0	109.2
Moles H_2SO_4/mole *m*-cresol	0.00106	0.00119	0.00106	0.00105	0.0024	0.0024	0.00246
Isobutylene added, g	72.2	133.0	53.0	84.9	35.6	42.9	43.1
Alkali-soluble, g	68.2	111.5	52.3	96.0	81.3	80.0	66.1
m-Cresol, g	65.6	87.0	47.9	77.1	75.4	63.6	32.9
4-*tert*-Butyl-3-methylphenol, g	0.0	7.1	0.0	13.9	0.0	10.8	3.3
Alkali-insoluble, g	58.6	246.5	83.0	162.3	47.7	63.6	70.8
tert-Butyl *m*-tolyl ether, g	55.2	146.2	31.6	3.9	39.3	16.1	0.0
6-*tert*-Butyl-3-methylphenol, g	0.0	72.2	47.2	79.3	5.9	22.1	71.3
4,6-Di-*tert*-butyl-3-methylphenol, g	0.0	0.0	0.0	70.6	0.0	18.2	17.9
m-Cresol consumed	43.7	183.0	62.2	109.8	32.6	44.4	76.3
Yield of *tert*-butyl *m*-tolyl ether, %							
Based on *m*-cresol charged	33.2	35.5	18.6	1.38	24.2	9.8	0.0
Based on *m*-cresol consumed	83.3	52.5	33.4	2.38	80.2	24.0	0.0

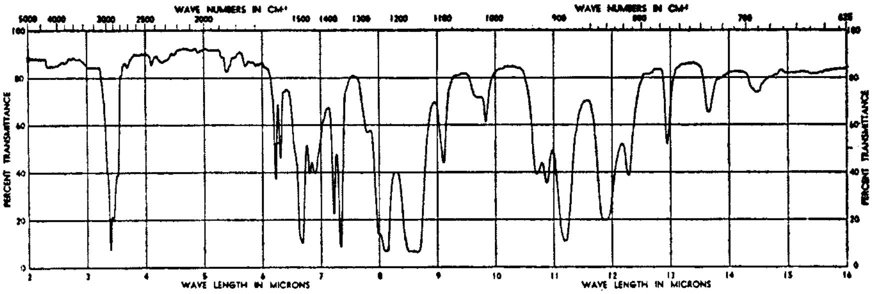

FIG. 1. INFRARED SPECTRUM OF *tert*-BUTYL-*p*-TOLYL ETHER

Varying the temperature materially affects the distribution of the alkylation products, a pronounced tendency toward nuclear alkylation showing up as the temperature rises, with both the strong and the weak sulfuric acid catalyst. It is interesting to note that at −10° very little, if any, nuclear alkylation takes place. An appreciable amount appears at 10°, and di-alkylation of the nucleus is noticed at a temperature between 45° and 59°. As would be expected, changes in distribution are greater with variation in temperature for the 95% acid than for the 10% acid, presumably a reflection of the differences in isomerization power of the two catalysts. Since in each of the above experiments the rate of isobutylene take-up had practically become zero at the time the experiment was stopped, conditions approaching ether-alkyl-phenol equilibrium probably existed.

In the alkylation made at −10°, the isobutylene was in the liquid state. Under this condition it acted as both reactant and solvent. It is possible in this manner to bring into solution many of the solid phenols which ordinarily would have offered alkylation difficulties.

Figure 1 shows the infrared spectrum of *tert*-butyl-*p*-tolyl ether. The intense absorption band near 1170 wave number (K) confirms the ether structure.

Other *tert*-butyl aryl ethers have been prepared by the above-described method. They have the following boiling points:

tert-Butyl Aryl Ether	*Boiling Point, °C./20 mm.*
tert-butyl phenyl ether	80.0
tert-butyl *m*-tolyl ether*	96.0
tert-butyl *o*-tolyl ether	95.0
tert-butyl *p*-tolyl ether	97.3
tert-butyl *p*-*tert*-butylphenyl ether	125–128
tert-butyl *p*-diisobutylphenyl ether	160.0

* Density = 0.9156/20°; Refractive index, n_D^{25} 1.4848.

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NOTICE TO AUTHORS

On and after September 1, 1955, the Journal will accept *Notes*; the Journal will accept *Communications to the Editor* received on or after November 1, 1955 for publication in Volume 21. See revised Notice to Authors for details.

Effective with Volume 21, the Journal will use a double column format with a page size approximately 6½″ by 9″. Authors should consider this in connection with graph sizes, and table compositions.