*An Improved Synthesis of 1,3,5-Tri-t-butylbenzene**

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Various methods of preparing tri-*t*-butylbenzene have been reported in the literature[1], but the first positive mention of 1,3,5-tri-*t*-butylbenzene (I) is to be found in a paper by McCaulay and Lien[2]; the material was obtained by the disproportionation of *t*-butylbenzene with hydrogen fluoride and boron trifluoride at 0°C. The same substance has also been obtained by the Friedel-Crafts alkylation of *p*-di-*t*-butylbenzene (II)[3,4] or by other reactions[3,5,6].

Undoubtedly the procedure of Barclay and Betts[4], who showed that I was obtained from the aluminum chloride-catalyzed alkylation of II with a large excess of *t*-butyl chloride in

* This work was presented at the 13th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1960.

1) a) M. Senkowski, *Ber.*, **23**, 2412 (1890); b) F. Kunckell and G. Ulex, *J. prakt. Chem.*, **87**, 233 (1913); c) V. N. Ipatieff, B. B. Corson and H. Pines, *J. Am. Chem. Soc.*, **58**, 919 (1936).

2) D. A. McCaulay and A. P. Lien, ibid., **75**, 2411 (1953).

3) P. D. Bartlett, M. Roha and R. M. Stiles, ibid., **76**, 2349 (1954).

4) L. R. C. Barclay and E. E. Betts, *Can. J. Chem.*, **33**, 672 (1955).

5) W. Van Hartingsveldt, P. E. Verkade and B. M. Wepster, *Rec. trav. chim.*, **75**, 349 (1956).

6) U. Krüerke, C. Hoogzand and W. Hübel, *Chem. Ber.*, **94**, 2817 (1961).

TABLE I. *t*-BUTYLATIONS OF *m*-DI-*t*-BUTYLBENZENE

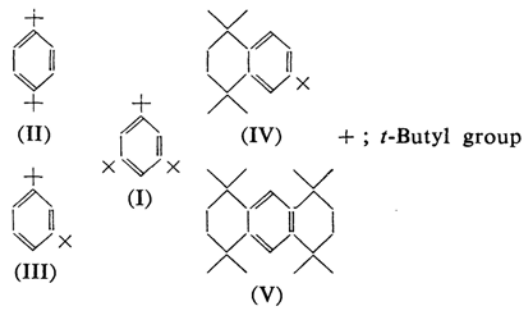
Exp. No.	1*	2	3	4	5	6	7
Reagents (mol.)							
m-Di-*t*-butylbenzene (III)	0.40	0.40	0.37	0.37	0.37	0.37	0.30
t-Butyl chloride	3.20	3.20	0.37	0.37	0.48	0.48	0.15
Aluminum chloride	0.20	0.20	0.022	0.022	0.03	0.03	0.005
($AlCl_3$, mol./mol. *t*-butyl chloride)	0.06	0.06	0.06	0.06	0.06	0.06	0.03
($AlCl_3$, mol./mol. aromatics (III)	0.5	0.5	0.06	0.06	0.08	0.08	0.02
Temp., °C	−8	−8	−8	30	30	30	25
Reaction time, hr.	1.0	1.0	1.0	1.0	2.0	4.0	6.0
Products, mol. %							
m-Di-*t*-butylbenzene (III)	—	—	94	37	35	9.5	67
1,3,5-Tri-*t*-butylbenzene (I)	76	76.5	—	56.5	57	79	21**
Total mol. %	76	76.5	94	93.5	92	88.5	88

* The method described by Barclay and Betts[4], *p*-di-*t*-butylbenzene (II) was used in spite of *m*-di-*t*-butylbenzene (III).
** Theoretical yield; 42%

the cold, is very attractive when large quantities of this compound are to be prepared.

However, *p*-di-*t*-butylbenzene has some undesirable properties for this purpose in comparison with *m*-di-*t*-butylbenzene (III); a large excess of *t*-butyl chloride[4] or of other organic solvents[3], such as carbon disulfide or ethylene dichloride, should be used to dissolve *p*-di-*t*-butylbenzene, while III is misible in *t*-butyl chloride in all proportions. The m. p. (76~77°C) of II is close to that (73.5°C) of I; furthermore, a rearrangement other than alkylation should be involved in the reaction steps.

Some unusual cyclialkylation products, such as IV[7], V[8] and others[3], have been isolated from a complex mixture as by-products of the preparation of I by the aluminum chloride-catalyzed alkylation of II with a large excess of *t*-butyl chloride in the cold. The mechanism of the formation of these by-products has been discussed by several workers[7-10].



An earlier communication[11] reported the formation of hydrocarbon II through a simple procedure from the alkylation of *t*-butylbenzene with *t*-butyl chloride in the presence of

TABLE II. DISPROPORTIONATIONS OF *m*-DI-*t*-BUTYLBENZENE

Exp. No.	8	9
Reagents (mol.)		
m-Di-*t*-butylbenzene (III)	0.25	0.37
Aluminum chloride	0.004	0.03
$AlCl_3$, mol./mol. III	0.02	0.08
Temp., °C	25	30
Reaction time, hr.	6.0	6.0
Products, mol. %		
t-Butylbenzene	6.0	8.0
m-Di-*t*-butylbenzene (III)	80.5	24.5
p-Di-*t*-butylbenzene (II)	4.0	40.0
1,3,5-Tri-*t*-butylbenzene (I)	2.0	9.0
Total mol. %	92.5	81.5

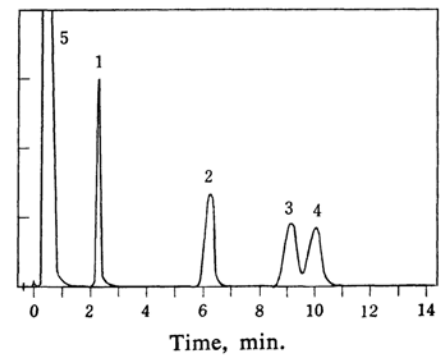


Fig. 1. Gaschromatogram of *t*-butylated benzenes.
1 *t*-Butylbenzene
2 *m*-Di-*t*-butylbenzene (III)
3 *p*-Di-*t*-butylbenzene (II)
4 1, 3, 5-Tri-*t*-butylbenzene (I)
5 Benzene (solvent)

7) P. C. Myhre and W. M. Schubert, *J. Org. Chem.*, **25**, 708 (1960).
8) L. R. C. Barclay and E. E. Betts, *J. Am. Chem. Soc.*, **77**, 5735 (1955).
9) L. R. C. Barclay and J. W. Hilchie, *J. Org. Chem.*, **22**, 633 (1957).
10) F. E. Condon, ibid., **21**, 761 (1956).
11) T. Kinugasa and S. Watarai, *J. Chem. Soc. Japan, Pure Chem. Sec. (Nippon Kagaku Zasshi)*, **83**, 333 (1962).

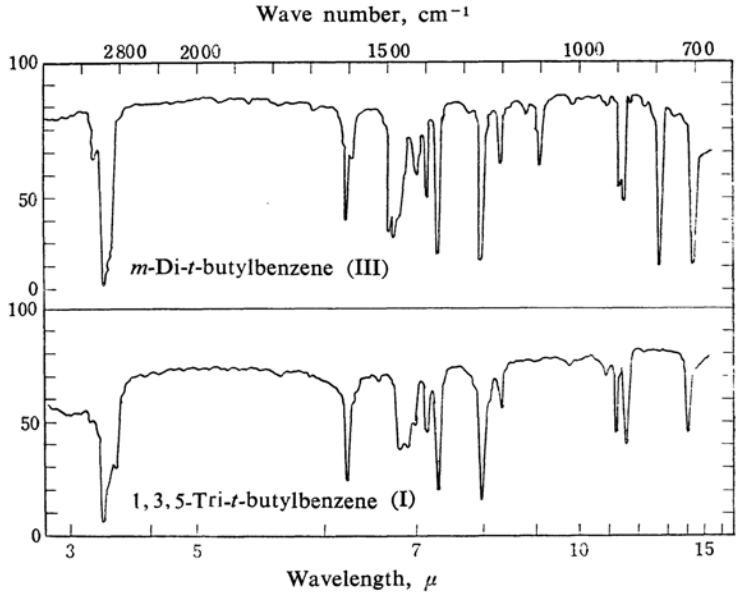


Fig. 2. Infrared spectra of compounds I and III.

rather a little aluminum chloride, and the preparative condition for this hydrocarbon was proposed.

In the present paper, the *t*-butylations of *m*-di-*t*-butylbenzene and an improved method of preparing 1, 3, 5-tri-*t*-butylbenzene are reported.

The experiments shown in Tables I and II were carried out under several conditions, which involved different amounts of the alkylating reagent and the catalyst, reaction times, and temperatures. The reaction products were fractionated, and each fraction was identified by its physical properties by means of gaschromatographic (Fig. 1) and spectrometric analysis (Fig. 2).

In these alkylations with a slight excess or a small amount of *t*-butyl chloride, the remarkable side-reactions previously reported in the literatures could not be observed, even under the influence of a prolonged reaction time at or over room temperature, although few boiling fractions higher than I were isolated.

At −8°C, *m*-di-*t*-butylbenzene (III) treated with the equivalent alkylating reagent was almost entirely recovered; on the other hand, when III was treated with a large excess of *t*-butyl chloride, it was alkylated rapidly into I in the same yield as in the case of II. However, at or over room temperature, I was formed from III using a very small amount of catalyst (Exp. No. 7), and the quantity was increased with the reaction time (Exp. No. 4—6). Thus, 1, 3, 5-tri-*t*-butylbenzene (I) was obtained in a good yield from *m*-di-*t*-butylbenzene (III) without using large excess of an alkylating reagent and a catalyst, which are apt to cause side-reactions.

The disproportionation of III shown in Table II was also examined under the same conditions as in the case of alkylation. From these experiments of alkylation and disproportionation, it was found that alkylation proceeds before the isomerization of III and that too many reaction times should be avoided, even in the case of III in the preparation of I.

The melting point of the 1, 3, 5-tri-*t*-butylbenzene (I) obtained in this manner was identical with that of the hydrocarbon obtained by Barclay's method (Exp. No. 1), and the mixed melting point was not depressed. The infrared spectra of the two materials were also identical.

Experimental*

Materials. — *m*-Di-*t*-butylbenzene[11]; b. p., 132°C (60 mmHg), 116°C (30 mmHg), n_D^{20} 1.4880, n_D^{25} 1.4874.

t-Butyl Chloride.—This was prepared essentially in the manner described in the literature[12], except that it was dried over phosphorus pentachloride and was used directly after filtration without further distillation.

Improved Synthesis of 1, 3, 5-Tri-*t*-butylbenzene. —Finely powdered anhydrous aluminum chloride (4.0 g., 0.03 mol.) was added in small portions to

* The melting points are uncorrected, and the infrared spectra were taken by the liquid film method or the KBr disk method. Gaschromatogaraphic analysis were carried out at 185°C with a Yanagimoto model GCG3D, using a 2m.×5mm.ϕ stainless steel tube packed with Celite 545, which was coated with Apiezon grease L and H_2-carrier gas; flow rate, 56 ml./min.

12) J. F. Norris and A. W. Olmsted, "Organic Syntheses", Coll. Vol. I, (1948) p. 144.

the stirred reaction mixture of *m*-di-*t*-butylbenzene (III, 70 g.. 0.37 mol.) and *t*-butyl chloride (44.5 g., 0.48 mol.) over a period of 1 hr. between 25 and 30°C. Hydrogen chloride was evolved, and the reaction mixture became brown. While the stirring was continued at 30°C, a crystalline material was obtained in the reaction mixture. After a total reaction time of 4 hr., the brown complex, on decomposition with cold diluted hydrochloric acid, formed a colorless semi-solid. This semi-solid layer was extracted with benzene, and the organic layer was separated, washed with ice-water, and with a 5% sodium carbonate solution. After evaporation of the solvent, the following fractions were obtained by distillation through a fractionating column 75 cm. in length and packed with Helipak No. 3.

Fraction	B. p. °C	Pressure mmHg	Wt. g.	Component
1[a)]	115~117	30	3.0	III
2[b)]	120~134	30	5.0	III, II and I
3	138~142	30	71.0	I
4[c)]	145~	30	—	

a) n_D^{20} 1.4877
b) This fraction, partially solid, was identified as a mixture of I, II and III by gaschromatographic analyses
c) Trace of yellow oil

Fraction 3, melting at 71~73°C, was practically pure, not needing further purification, and its infrared spectrum (Fig. 2) was identical with that of authentic I prepared in this laboratory by Barclay's method[4)] (Exp. No. 1). One recrystallization gave a sample melting at 73.5°C.

Found: C, 87.69; H, 12.33. Calcd. for $C_{18}H_{30}$: C, 87.73; H, 12.27%.

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