Synthesis and Octane Number of *tert*-Butyl Cyclohexane and 1,4-Di-*tert*-butyl Cyclohexane. Alkylation of Benzene with Isobutylene into *tert*-Butyl Benzene and *p*-Di-*tert*-butyl Benzene and their Hydrogenation.

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It is known that the octane number of naphthenic hydrocarbon generally decreases with the introduction of primary and secondary alkyl radical to the ring. For instance, cyclohexane has the octane number of 77(1), while methyl-, ethyl-, *n*-propyl-, *n*-butyl-, isobutyl-, isopropyl-, and *sec*-butyl cyclohexane have lower octane number.(2) However, only *tert*-butyl cyclohexane is reported to have high octane number of 99,(2) suggesting that the introduction of *tert*-butyl radical to the naphthenic ring increases its octane number.

In the present investigation, *tert*-butyl cyclohexane and 1,4- di-*tert*-butyl cyclohexane have been prepared by the reactions shown in the following schema, and their octane numbers have been measured.

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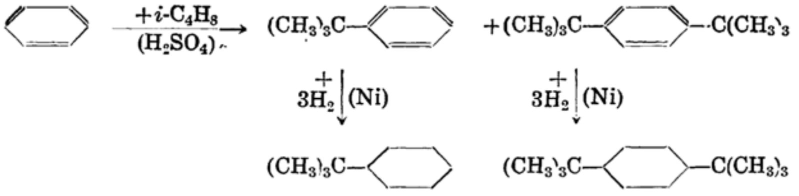
(1) T. Suwa, *Report of the Imperial Fuel Research Inst. Japan*, **30**(1935), 49, etc.

(2) W. G. Lovell, J. M. Campbell, and T. A. Boyd, *Ind. Eng. Chem.*, **25**(1933), 1107; F. H. Garner, E. B. Evans, C. H. Sprake, and W. E. S. Broom, *Proc. World Petrol. Congress*, **2**(1933), 170.



1, 4-Di-*tert*-butyl cylohexane, though the octane number of which has not been known, has been expected to have high octane number because of the existence of two *tert*-butyl radicals on the cyclohexane ring. It is found to have high octane number as expected and may be used as a constituent of safety fuels.

The Alkylation of Benzene with Isobutylene. Among various catalysts for the alkylation of benzene with isobutylene, such as, $AlCl_3$, BF_3, anhydrous $FeCl_3$, HF, P_2O_5(3), concentrated sulfuric acid etc., concentrated sulfuric acid has been used in the present investigation. According to V. N. Ipatieff, B. B. Corson and H. Pines,(4) 90–96% sulfuric acid alkylates benzene with isobutylene, 80% acid only polymerises isobutylene without alkylation, and 70% acid only hydrates isobutylene into *tert*-butyl alcohol. In the present investigation some of the above results have been reconfirmed, and the effect of the change of the amount of isobutylene against benzene has also been investigated. Isobutylene used was not satisfactorily pure, containing probably propylene and *n*-butylene, which caused the formation of a considerable amount of byproducts and the purification of *tert*-butyl benzene was difficult.

The Effect of the Concentration of Sulfuric Acid. The results are summerised in Table 1. The reactions were carried out at about 15°C. In a series of experiments, Expt. DF 11, DF 7, DF 15, DF 14, the concentration of the aqueous solutions of sulfuric acid was varied, and the results of V. N. Ipatieff, B. B. Corson and H. Pines(5) were reconfirmed. With 91 or 96% acid, benzene was rapidly alkylated with isobutylene to form *tert*-butyl and *p*-di-*tert*-butyl-benzene (DF 11, DF 7, DF 8). The fractions of the reaction products do not decolorise or only faintly decolorise Br_2-CCl_4 solution, showing that the polymerisation takes place little or only slightly. With 86% acid (DF 15), the alkylation and polymerisation simultaneously take place, and the *tert*-butyl benzene fraction and the *p*-di-*tert*-butyl benzene fraction contain triisobutylene (b.p. 170–176°C (uncorr.)(6)) and tetraisobutylene (b.p. 224–241°C (uncorr.)(6)), respectively, each fraction decolorising strongly Br_2-CCl_4 solution. With 82% sulfuric acid, a little alkylation takes place, giving no crystal of *p*-di-*tert*-butyl benzene, while polymerisation of isobutylene takes place mainly to form diisobutylene and triisobutylene, each distilling in the

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(3) B. W. Malishew, *J. Amer. Chem. Soc.*, **57** (1935), 883.

(4) V. N. Ipatieff, B. B. Corson and H. Pines, *J. Amer. Chem. Soc.*, **58** (1936), 919.

(5) V. N. Ipatieff, B. B. Corson and H. Pines, *J. Amer. Chem. Soc.*, **58** (1936), 919.

(6) Cf. M. Katuno, *J. Soc. Chem. Ind. Japan*, **45** (1942), 102B.

Table 1. Alkylation of Benzene with Isobutylene.

Exptl. No.	Sulfuric Acid			Benzene		Absorbtion of Isobutylene			
	Conc. (%)	Amount (g.)	(mol. of H_2SO_4)	(g.)	(mol.)	Temp. (°C)	Time(2) (hrs.)	Amount absorbed (g.)	Amount absorbed (mol.)
DF11	96	100	1	117	1.5	14–16	$^{40}/_{60}+1$	$57._{7}$	1.03
DF 7	91	105	1	117	1.5	13–17	$1^{5}/_{60}+1$	$56._{1}$	1.00
DF15	86	111	1	78	1.0	11–16	$1^{5}/_{60}+1$	$61._{2}$	1.09
DF14	82	118	1	78	1.0	12–16	1.0+1	$58._{5}$	1.04
DF 8	91	105	1	117	1.5	15–17	$^{40}/_{60}+1$	$33._{8}$	0.60_{2}
DF 9′	91	105	1	117	1.5	13–17	$2^{5}/_{60}+1$	$109._{9}$	1.96
DF10	91	105	1	117	1.5	12–18	$2^{35}/_{60}+1$	119	2.12
DF12	91	70	$^{2}/_{3}$	78	1.0	13–17	$1^{40}/_{60}+1$	$118._{8}$	2.12
DF13	91	70	$^{2}/_{3}$	78	1.0	12–17	$2^{20}/_{60}+1$	$176._{0}$	3.14
DF16	91	105	1	78	1.0	11–16	$5^{10}/_{60}+1$	$300._{3}$	5.36

Exptl. no.	Benzene recovered		Crude *tert*-Butyl-benzene Fraction				
			Yield		Theoretical Yield		Decolorisation(1) of Br_2-CCl_4 soln.
	(g.)	(%)	(g.)	(mol.)	against benzene (%)	against i-C_4H_8 (%)	
DF11	37	$31._{6}$	45	0.33_{5}	$22._{3}$	$32._{5}$	—
DF 7	61	$52._{1}$	36	0.26_{8}	$17._{9}$	$26._{8}$	—
DF15	44	$56._{4}$	29	0.21_{6}	$21._{6}$	$19._{8}$	+++
DF14	99	$126._{9}$	38	0.27_{6}	$27._{6}$	$26._{5}$	+++
DF 8	81	$69._{2}$	22	0.16_{4}	$10._{9}$	$27._{3}$	—
DF 9′	27	$23._{1}$	33	0.24_{6}	$16._{4}$	$12._{5}$	—
DF10	27	$23._{1}$	37	0.27_{5}	$18._{3}$	$13._{0}$	—
DF12	11	$14._{1}$	9	0.06_{7}	$6._{7}$	$3._{2}$	—
DF13	0	0	7	0.05_{2}	$5._{2}$	$1._{7}$	—
DF16	6	$7._{7}$	8	0.06_{0}	$6._{0}$	$1._{1}$	++

Exptl. no.	Crude *p*-Di-*tert*-butyl-benzene Fraction						
	Yield		Theoretical Yield		Mother Liquor(3)		
					Yield		Decolorisation(1) of Br_2-CCl_4 soln
	(g.)	(mol.)	against benzene (%)	against i-C_4H_8 (%)	(g.)	(%)	
DF11	67	0.35_{2}	$23._{4}$	$69._{4}$	$27._{4}$	$40._{9}$	—
DF 7	69	0.36_{2}	$24._{1}$	$72._{4}$	$24._{8}$	$35._{9}$	—
DF15	$57._{8}$	0.30_{4}	$30._{4}$	$55._{7}$	$17._{1}$	$29._{6}$	++
DF14	$9._{5}$	0.05_{0}	$5._{0}$	$9._{6}$	$9._{5}$	100	++
DF 8	41	0.21_{5}	$14._{3}$	$71._{4}$	$13._{4}$	$32._{7}$	—
DF 9′	149	0.78_{3}	$52._{2}$	$79._{9}$	$6._{5}$	$37._{9}$	+/4
DF10	$157._{6}$	0.82_{8}	$55._{2}$	$78._{1}$	$66._{3}$	$42._{1}$	+/4
DF12	177	0.93_{0}	$93._{0}$	$87._{8}$	$80._{8}$	$45._{6}$	+/4
DF13	218	1.14_{2}	$114._{2}$	$72._{6}$	$140._{3}$	$64._{4}$	+
DF16	$340._{6}$	1.79_{1}	$179._{1}$	$66._{8}$	$249._{4}$	$73._{2}$	+++

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(1) Strengths of decolorisation are represented qualitatively by the signs +++, ++, +, +/2, +/4, —.

(2) Stirred for another 1 hour without introduction of isobutylene after absorbtion.

(3) Separated by repeating decantation, and is saturated with *p*-di-*tert*.-butyl-benzene at the room temperature of about 25–7°C.

benezene and *tert*-butyl-benzene fraction, respectively. The marked formation of diisobutylene is due to the lower concentration of the sulfuric acid employed.(7) Above results show that the alkylation reaction takes place predominantly with 91–96% sulfuric acid, as already reported by Ippatieff and his co-laborators.(8)

The Change of the Amount of Isobutylene against Benzene. Using 91% sulfuric acid as catalyst, alkylation of benzene was attempted with various amount of isobutylene against benzene (Expt. DF 8, DF 11, DF 9, DF 10, DF 12, DF 13, DF 16). In all cases a considerable amount of *p*-di-*tert*-butyl benzene fraction was formed.

Even when the amount of absorption of isobutylene is decreased to 1.0 mol. or 0.6 mol. against 1.5 mol. of benzene (DF 11, DF 8), the formation of *tert*-butyl benzene is not satisfactory, the theoretical yields against benzene being 24% and 11%, respectively, and a considerable amount of *p*-di-*tert*-butyl benzene fraction was formed, although a considerable amount of benzene was recovered unchanged. It seems to be difficult to obtain *tert*-butyl benzene fraction as the main product by the present method of alkylation.

The increase of the amount of isobutylene against benzene to $i\text{-}C_4H_8:C_6H_6 \fallingdotseq 2:1.5$, 2.1:1.5 and 2.1:1.0 (in mole ratio) (DF 9, DF 10, and DF 12) increases the formation of *p*-di-*tert*-butyl benzene fraction with decrease of *tert*-butyl benzene fraction. The theoretical yield of *p*-di-*tert*-butyl benzene fraction amounts to about 93% against benzene and 88% against isobutylene (DF 12). The increase of the absorption of isobutylene against benzene to the mole ratios of 3.1:1.0 and 5.4:1.0 (DF 13 and DF 16), causes the *p*-di-*tert*-butyl benzene fraction to contain a large amount of oily substances, which showes olefinic reaction to decolorise Br_2-CCl_4 solution, and the amount of olefin increases with increasing amount of the absorption of isobutylene (DF 16). This olefinic high-boiling substace is probably formed by the polymerisation of isobutylene by 91% sulfuric acid after complete alkylation of benzene, and has relatively high boiling point due to the high concentration of sulfuric acid.(9)

Experimental Apparatus and Procedure of Alkylation.

Absorption of Isobutylene. The experimental apparatus was almost the same as that employed in the polymerisation of isobutylene(10). Definite amounts of aqueous solution of sulphuric acid and benzene were weighed into a 500 c.c. three necked flask, equipped with a thermometer, a mercury-sealed stirrer, isobutylene inlet and outlet tubes. Isobutylene was introduced into the flask, under vigorous mechanical stirring of the liquid, from a gas holder, passing through a gas meter, a regulating cock and two calcium chloride towers. The reaction is exothermic, and the temperature of

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(7) V. N. Ipatieff and H. Pines, *J. Org. Chem.*, **1**(1936), 464; M. Katuno, *J. Soc. Chem. Ind.*, **45**(1942), 102B.

(8) V. N. Ipatieff, B. B. Corson and H. Pines, *J. Amer. Chem. Soc.*, **58**(1936), 919.

(9) V. N. Ipatieff and H. Pines, *J. Org. Chem.*, **1**(1936), 464; M. Katuno, *J. Soc. Chem. Ind.*, **45**(1942), 102B.

(10) M. Katuno, *J. Soc. Chem. Ind. Japan*, **45**(1942), 102B.

the liquid was regulated at about 15°C, by raising and lowering the ice-water bath and by regulating the speed of isobutylene. Crystals of *p*-di-*tert*-butyl-benzene separated in the course of the reaction. After absorption of a define amount of isobutylene, the liquid was stirred vigorously for more than one hour, without the introduction of isobutylene.

Separation of the Products. The amount of isobutylene absorbed was known by the increase of the weight of the flask. The brown sulfuric acid layer was pipetted out, and the product was shaken or stirred with 50–100 c.c. of 77% sulfuric acid in order to remove di-*sec*-alkyl sulfate, which is expected to be formed from the secondary olefins contained in the isobutylene gas as impurities. After removing the acid layer, a weighed amount of benzene, later to be reduced from the amount of benzene recovered, was added, with slight warming if necessary in order to dissolve the *p*-di-*tert*-butyl benzene. The mixture was then washed with 20–30% sulfuric acid, water, and strong sodium hydroxide solution.

The product was then distilled through a 20 cm. Widmer column, to draw a distillation curve against the weight of the distillate, by collecting the distillate in a vessel placed on a rough balance(11). The distillation was stopped when the temperature reached about 210–220°C. The fractionation of benzene and *tert*-butyl benzene was sharp, while that of *tert*-butyl benzene and *p*-di-*tert*-butyl benzene was less sharp. The yields of three fractions, namely, benzene, *tert*-butyl benzene and the *p*-di-*tert*-butyl benzene fractions, were known by the cross of the distillation curve with the middle temperature of boiling points(12) (boiling points of benzene, *tert*-butyl-benzene and *p*-di-*tert*-butyl-benzene are 80.1°, 168.2° and 236.5°C., respectively). The residue crystallised after cooling, accompanied by a considerable amount of mother liquor, which has probably been derived from secondary olefins contained as impurities. The mother liquor was separated from the crystal by repeating three times the melting, slow cooling to 25–7°C., in order to allow the crystal to grow large, and decantation. The results are shown in Table 1. The theoretical yields against benzene and isobutylene were calculated from the yields of *tert*-butyl-benzene and di-*tert*-butyl-benzene fractions. When the fractions are considered to contain a considerable amount of the polymerised products of isobutylene, the figures in Table 1 are brackettted.

Preparation of a large Quantities of *tert*-Butyl- and *p*-Di-*tert*-Butyl-benzene. A relatively large quantities of *tert*-butyl- and *p*-di-*tert*-butyl-benzene were prepared by repeating experiments, the conditions of which are approximate to those of Expt. DF9 and DF10.

Namely, about 180 l. of isobutylene gas was added in about 4–6 hrs. into a vigorously stirred mixture of 250 g. of 91% sulfuric acid and 350 g. (4.49 mol.) of recrystallised benzene in a 1 l. three-necked flask, at the temperature of about 10–20°C. After the absorption, the mixture was stirred for one hour at the same temperature without introduction of isobutylene, and the amount of isobutylene absorbed was known from the increase of the weight of the flask. The acid layer was syphoned off, and the oily layer was stirred vigorously with 200 c.c. of 40% sulfuric acid for one hour with subsequent washing with water and NaOH solution, and then was fractionated through a 20 cm. Widmer column into fraction A boiling up to 100°C., fraction B boiling from 100°C. to 220°C. and fraction C or the residue, which separates the crystal of *p*-di-*tert*-butyl-benzene after cooling.

The crystal was filtered (Crystal R_I; Mother Liquor F_I), and the mother liquor was cooled with ice and again filtered from the crystal (Crystal R_2; Mother Liquor F_2). The yields of the fraction B, the crystal R_1+R_2 and the mother liquor F_2 were 140–220 g., 200–290 g. and 170–220 g., respectively, in most cases. About 6.5 kg. of the crystal was obtained by repeating the above-mentioned process, some of which being shown in Table 2.

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(11) Cf. M. Katuno, *J. Soc. Chem. Ind. Japan*, **45** (1942), 103B; **41** (1938), 76B.

(12) S. Young, "Distillation Principles and Processes," 170, (1922).

Purification of the Products. A. *tert-Butyl-benzene.* The fractions containing *tert*-butyl-benzene were repeatedly fractionated through a 20 cm. Widmer column. The complete purification of *tert*-butyl-benzene by fractional distillation seems to be difficult, due to the existence of lower and higher boiling byproducts, which are probably isopropyl-benzene (b.p. 152–3°C.; 152.5–3.0°C.) and *sec*-butyl-benzene (b.p. 173–4°C.; 173.2–174.2°C.) derived from propylene and *n*-butylene contained in the isobutylene gas as impurities. The fractionated *tert*-butyl-benzene boiling at 165–168.5C. (uncorr.) is a colourless liquid with pleasant odour, having the following constants. d_4^{20} 0.8585; n_D^{20} 1.4894; $MR_D=45.150$ (obsd.); 44.78 (calcd. for $C_{10}H_{16}\overline{|}_3$). Found: C, 89.25, 89.06; H, 10.60, 10.81. Calculated for $C_{10}H_{16}$; C, 89.49; H, 10.51%.

B. *p-Di-tert-butyl-benzene.* The crude crystal R_1+R_2 was recrystallised twice from anhydrous ethanol (m.p. 74.0–75.0°C.), and then once from benzol (m.p. 75.5–76.5°C.). Some of the crystals were further purified by distillation through a 20 cm. Widmer column (b.p. 233.5–235°C. (uncorr.)). The product is colourless crystal, which grows in large prisms when cooled slowly. Found: C, 88.33, 87.93; H, 11.76, 11.57. Calculated for $C_{14}H_{22}$: C, 88.35; H, 11.65%.

C. *High-boiling oily Substance* CF_2R: The mother liquor of the crystal R_1+R_2 was washed twice with NaOH solution and then with water, and was fractionated using a 20 cm. Widmer column. A small amount of benzene was added in order to remove a small amount of water. The majority of the oil (about 82–3%) distilled between 220–250°C. (uncorr.). The fraction boiling between 220–250°C. was cooled with ice to remove the crystal of *p*-di-*tert*-butyl-benzene by subsequent rapid filtration, and the filtrate is named as CF_2R. It is an almost colourless liquid, and relatively viscous. It does not decolorise the Br_2–CCl_4 solution, and dissolves completely in 100% sulfuric acid, suggesting that it is an aromatic hydrocarbone, probably composed of hydrocarbons having isopropyl or *sec*-butyl- radical as well as *tert*-butyl radical on the benzene nucleus, d_4^{20} 0.8586, n_D^{20} 1.4896. Found: C, 88.29, 88.19; H, 11.63, 11.85. Calculated for $C_{14}H_{22}$: C, 88.35; H, 11.65; for $C_{16}H_{26}$: C, 88.00; H, 12.00; for $S_{12}H_{18}$: C, 88.82; H, 11.18%.

Experimental Materials. *Isobutylene.* Commercial crude isobutanol was refractionated 2–4 times through a 1 m. Hempel column with 2.0 cm. internal diameter (used for experiments in Table 1; d_4^{20} 0.8035; n_D^{20} 1.3956), or through a 1 m. Widmer column (used for experiments in Table 2; d_4^{20} 0.8030; n_D^{20} 1.3956), and the fraction boiling at 106.0–107.5°C. (uncorr.) was collected. The complete removal of *n*-propanol (b.p. 97.2°C., d_4^{20} 0.8036, n_D^{20} 1.3854) seems to be difficult.

Table 2. Alkylation of Benzene with Isobutylene.

Exptl. no.	Absorbtion of Isobutylene (Benzene 350 g. (4.49 mol.) and 91% sulfuric acid 250 g.)				Fractionation of the Products			Crude Crystall	Mother Liquor
	Temp.	Time	Amount absorbed		Fraction A (−100°C)	Fraction B (100–220°C)	Fraction C (220°C–)	(R_1+R_2)	(F_2)
	(°C)	(hrs)	(g.)	(mol.)	(g.)	(g.)	(g.)	(g.)	(g.)
DFG 2	12–20	$5^{50}/_{60}$	342	6.10	80	183	380	203	180
DFG 3	14–22	6.0	354	6.31	80	161	442	239	191
DFG20	16–22	$3^{45}/_{60}$	392	6.99	—	149	457	279	175
DFG22	13–20	$5^{25}/_{60}$	391	6.97	—	135	486	278	196
DFG23	14–19	4.5	394	7.02	68	210	431	249	175
DFG24	12–20	$5^{20}/_{60}$	405	7.22	78	198	438	239	195
DFG26	11–20	4.5	431	7.68	—	142	504	286	208
DFG28	16–20	$4^{35}/_{60}$	406	7.23	74	216	412	221	182
DFG29	14–20	6.0	400	7.13	61	189	461	244	208
DFG30	13–21	$5^{35}/_{60}$	406	7.23	75	177	460	241	212

The isobutanol fractionated was then dehydrated catalytically over activated alumina at about 370–380°C., using the apparatus described before(13), and the isobutylene gas formed was stored in a gas holder of about 1 $m.^3$ content. The analysis of the gas, obtained from the isobutanol, fractionated with 1 m. Hempel column, by the modified Matuszack method by H. Shingu and N. Mutuda(14) showed that gas contained about 75% (by vol.) of isobutylene, the remainder being mainly secondary olefines, probably propylene and *n*-butylene.

Benzene. Commercial pure product was further purified by twice crystallisation by cooling with ice water. Mp. 4.5–5.5°C., n_D^{20} 1.5018.

Sulfuric Acid. Commercial pure product containing 96% of H_2SO_4 (by titration) was used.

Hydrogenation of *tert*-Butyl Benzene and *p*-Di-*tert*-butyl Benzene into corresponding Cyclohexane Hydrocarbons.

A few literatures(15) are found on the hydrogenation of *tert*-butyl benzene into *tert*-butyl cyclohexane, generally using Pt catalyst. *p*-Di-*tert*-butyl benzene has also been hydrogenated into 1,4-di-*tert*-butyl cyclohexane by H. Koch and H. Steinbrink(16) using Ni-Mn-Al-kieselguhr catalyst.

In the present investigation, *tert*-butyl-benzene and *p*-di-*tert*-butyl-benzene have been hydrogenated using Ni-kieselguhr catalyst at 160–180°C., and the corresponding cyclohexane hydrocarbons, namely, *tert*-butyl-cyclohexane and 1,4-di-*tert*-butyl-cyclohexane, have been obtained in satisfactory yields. The hydrogenation of *p*-di-*tert*-butyl benzene has been carried out in the presence of cyclohexane, because this hydrocarbon is a crystal with the melting point of 76°C. The results are summerised in Table 3.

The *tert*-butyl-cyclohexane obtained from *tert*-butyl-benzene, which was prepared in the previous report, could not be completely purified by fractional distillation owing to the presence of nearly boiling impurities, probably isopropylcyclohexane (b.p. 154.5°C.) and *sec*-butyl-cyclohexane (b.p. 178.5–9.5°C.). The fraction boiling at 167.0–170.2°C. (uncorr.) has been collected as *tert*-butyl-cyclohexane after repeated redistillation.

1,4-Di-*tert*-butyl-cyclohexane, obtained by the hydrogenation of *p*-di-*tert*-butyl-benzene, is composed of cis and trans isomers of 1,4-di-*tert*-butyl-cyclohexane, crystallising partially at room temperature. It melts completely into transparent liquid at 31°C. and crystallises almost completely into soft crystal by cooling. H. Koch and H. Steinbrink(17) obtained the trans isomer in pure state (M.p. 95°C.), however, the separation of the two isomers has not been attempted in the present investigation. The other properties are described later.

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(13) M. Katuno, *J. Soc. Chem. Ind. Japan,* **42** (1939), 424B; **44** (1941), 276B.

(14) H. Shingu and N. Mutuda, *J. Soc. Chem. Ind. Japan,* **44** (1941), 242B; M. P. Matuozak, *Ind. Eng. Chem., Anal. Ed.,* **10** (1938), 354.

(15) O. Halse, *J. prakt. Chem.,* (2), **92** (1915), 40; F. K. Signaigo and P. L. Cramer, *J. Amer. Chem. Soc.,* **55** (1933), 3326; J. W. Baker and L. G. Groves, *J. Chem. Soc.,* **1939**, 1148.

(16) H. Koch and H. Steinbrink, *Brennstoff-Chem.,* **19** (1938), 277.

(17) H. Koch and H. Steinbrink, *Brennstoff-Chem.,* **19** (1938), 277.

Tabel 3. Hydrogenation of the *tert*-Butyl-benzene and *p*-Di-*tert*-butyl-benzene.

Exptl. No.	Mono- or *p*-Di-*tert*-butyl-benzene		Cyclo-hexane	1:1-Ni-kieselguhr Catalyst		Hydrogenation					Mono- or 1,4-Di-*tert*-butyl-cyclohexan			Remarks
				$NiCO_3$-kieselguhr	Ni	Temp.(3)	Time(3)	Initial Pressure (Room Temp.)	Pressure Drop	Absorption of H_2	Yield		Theor. yield	
	(g.)	(mol.)	(g.)	(g.)	(g.)	(about °C.)	(hrs.)	(atm.) (°C.)	(atm.) (0°C.)	(mol.)	(g.)	(mol.)	(%)	
	tert-butyl-benzene										*tert*-butyl-cyclohexane			
Q101	67	0.50	—	4.0	1.3_2	160 (155–160)	$2^{30}/_{60}$	97(32)	$62._8$	1.5_4(2.1)	$65._6$	0.46_8	$93._6$	
Q102	134	1.00	—	8.0	2.6_5	120 (114–125) 160 (157–161)	1.0 $^{15}/_{60}$ (intermed.) $2^{15}/_{60}$	90(31)	$151._4$	3.3_8(2.2)	$123._7$	0.88_3	$88._3$	A small amount of loss
QG2(1)	1206	9.0	—	80	26.5	180 (178–187)	$3^{45}/_{60}$	98(19)	$186._5$	$30._8$(2.3)	1207	8.62	$95._9$	
	p-Di-*tert*-butyl-benzene										1,4-Di-*tert*-butyl-cyclohexan			
Q6	95	0.50	30	5.0	1.6_6	160 (157–160)	$3^{15}/_{60}$	97(30)	$75._4$	1.6_8(2.2)	$95._0$	0.48_3	$96._6$	
Q2	95	0.50	30	5.0	1.6_6	180 (176–183)	$1^{50}/_{60}$	98(27)	$74._3$	1.6_6(2.2)	$92._4$	0.46_9	$93._8$	
Q8	95	0.50	30	5.0	1.6_6	180 (175–181)	$1^{45}/_{60}$	101(20)	$71._1$	1.5_8(2.2)	$93._0$	0.47_3	$94._6$	
Q10	95	0.50	30	5.0	1.6_6	180 (177–179)	$1^{10}/_{60}$	100(17)	$71._4$	1.5_9(2.2)	$97._0$	0.49_3	$98._6$	
Q4	57	0.30	30	3.0	0.9_9	180 (175–180)	$1^{40}/_{60}$	95(22)	$39._2$	0.96(2.1)	$55._1$	0.28_0	$93._4$	
Q3	57	0.30	30	3.0	0.9_9	180 (174–182)	$1^{5}/_{60}$	96(28)	$39._1$	0.96(2.1)	$54._6$	0.27_8	$92._4$	
				+ 2.0 g Na_2CO_3										
QG1(1)	942	4.96	100	50	16.5	180 (178–185) 190 (185–194)	$2^{40}/_{60}$ $2^{10}/_{60}$	93(28)	$96._1$	15.9(2.3)	906	4.62	$93._2$	
QG3(1)	1070	5.63	80	60	19.9	180 (177–182)	$4^{35}/_{60}$	84(21)	$119._1$	19.7(2.3)	1063	5.42	$96._4$	

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(1) 5 l rotating autoclave was used. (2) Calculated assuming the space in the autoclave to be (2.1) 0.55 l, (2.2) 0.50 l and (2.3) 3.7 l, respectively. (3) Hydrogenation takes place to a considerable extent before reaching the reaction temperature.

Experimental Details.

Experimental Details. *1:1-Ni-Kieselguhr Catalyst.* $NiCO_3$ was precipitated on kieselguhr in the ratio Ni: kieselguhr ≒ 1:1 (by weight) (18). It was reduced with hydrogen stream at about 450°C. for one hour before use. In the case of the hydrogenation of *p*-di-*tert*-butyl-benzene, the reduced catalyst was added into cyclohexane taken in an autoclave, with subsequent addition of the crystal of the hydrocarbon.

Hydrogenations. A horizontal shaking autoclave of about 660 c.c. content and a horizontal rotating autoclave of about 5 l. content were used. The initial pressure of hydrogen was about 84–101 atm. at room temperature. Hydrogen was absorbed rapidly at the reaction temperature of about 160–180°C. Hydrogen was charged when the pressure dropped below 50 atm. The hydrogenation was continued till the pressure became constant after complete hydrogenation, and then the autoclave was allowed to cool.

The reaction product was pipetted out and filtered from the catalyst. The filtrate was weighed as the yield of the crude *tert*-butyl-cyclohexane in the case of the hydrogenation of *tert*-butyl-benzene, although the fractionation showed it not to be completely pure. In the case of the hydrogenation of *p*-di-*tert*-butyl-benzene, cyclohexane was distilled off from the filtrate, using a 20 cm. Widmer column, till the temperature rised rapidly to 180–190°C., after cyclohexane distilled constantly at its boiling point. The yield of the residue was regarded as the yield of the crude 1,4-di-*tert*-butyl-cyclohexane, which is colourless and almost pure as far as pure *p*-di-*tert*-butyl-benzene is used, and crystallises partly by cooling to the room temperature.

In order to prepare a relatively large amount of *tert*-butyl and 1,4-di-*tert*-butyl cyclohexane for measuring octane number, a relatively large amounts of *tert*-butyl and *p*-di-*tert*-butyl benzene were hydrogenated using the horizontal rotating autoclave with about 5 l. content (Expt. QG 1, QG 2, QG 3 in Table 3).

Tert-butyl Cyclohexane. The crude *tert*-butyl-cyclohexane was purified by repeated fractionation through a 20 cm. Widmer column and the fraction boiling at 167.0–170.2°C. (uncorr.) was collected. However, the complete purification seems to be difficult owing to the presence of lower and higher nearly boiling impurities, probably isopropyl cyclohexane (b.p. 154.5°C.) and *sec*-butyl-cyclohexane (b.p. 178.5–9.5°C.). The *tert*-butyl-cyclohexane thus obtained is a colourless liquid and has the following constants: b.p. 167.0–170.2°C. (uncorr.); d_4^{20} 0.8084; n_D^{20} 1.4454; MR_D 46.21_4 (observed) (calcd. for $C_{10}H_{20}$ 46.18). Found: C, 85.61; 85.34; H, 14.32; 14.18. Calculated for $C_{10}H_{20}$: C, 85.63; H, 14.37%.

1,4-Di-tert-bytul Cyclohexane. The crude 1,4-di-*tert*-butyl cyclohexane is almost pure, as far as pure *p*-di-*tert*-butyl benzene is used. It melts completely into transparent liquid at 30–31°C. Some of the sample was redistiled using a 20 cm. Widmer column, and the main fraction boiling at 238.0–242.0°C. (uncorr.) was collected as pure substance. It is a mixture of cis and trans isomers, partly crystallising at room temperature. It melts completely into transparent liquid at 31.3°C., and crystallises almost completely by cooling. The crystal is soft, resembling that of paraffins. d_4^{35} 0.8225; n_D^{35} 1.4519; MR_D 64.39 (observed); 64.65 (calculated for $C_{14}H_{28}$). Found: C, 85.44; 85.45; H, 14.19; 14.46. Calculated for $C_{14}H_{28}$: C, 85.63; H, 14.37%.

The Octane Number, Flash Point and other Properties of 1,4-Di-*tert*-butyl Cyclohexane, *tert*-Butyl Cyclohexane etc.

The blending octane number of 1,4-di-*tert*-butyl cyclohexane, measured by the CER motor method, has shown high values as predicted, and is shown in Table 4.

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(18) M. Katuno, *J. Soc. Chem. Ind. Japan,* **46** (1943), No. 2.

Table. 4. Blending octane number of 1,4-di-*tert*-butyl cyclohexane.

Mixture with base Gasoline, having Octane Number of 49.6		
Content of 1,4-di-*tert*-butyl cyclohexane (vol. %)	Octane number of the mixture	Blending Octane number
20	62.1	112.1
20*	62.2*	112.6*
50	77.0	104.4
80	88.8	98.6

* A sample purified by redistillation.

It has a flash point of 80.5°C., measured by the Pensky-Martens apparatus. The lead susceptibility may be also satisfactory, because the hydrocarbon is naphthenic, though not measured in the present investigation.

This hydrocarbon is partially crystallised at room temperature, but it is highly soluble in hydrocarbones to form homogeneous liquid, and has considerable solubility even at low temperature. The results of a rough experiments of the cooling of the solution of the hydrocarbon (about 75, 50 and 25% by wt.) with *n*-heptane, isoctane, methylcyclohexane and toluene, as the representatives of paraffinic, naphthenic and aromatic hydrocarbons, are shown in Table 5.

Table. 5. Deep Cooling of the Solution of 1,4-Di-*tert*-butylcyclohexane with Hydrocarbons.

Hydrocarbone	Content of 1,4-di-*tert*-butyl cyclohexane (% by Wt.)	Results of Deep Cooling
n-Heptane	0	liq. at −70°C.
	25	liq. at −55°C., partially crystd. at −68°C.
	50	liq. at −20°C., partially crystd. at −30°C.
	75	liq. at + 2°C., considerably crystd. at −15°C.
Isooctane	0	liq. at −70°C.
	25	liq. at −60°C.
	50	liq. at −18°C., liq. for the most part at −26°C.
	75	liq. at + 6°C., considerably crystd. at −10°C.
Methylcyclohexane ..	0	liq. at −70°C.
	25	liq. at −70°C.
	50	liq. at −23°C.
	75	liq. at − 0°C., crystd. in small amount at −10°C.
Toluene	0	liq. at −70°C.
	25	liq. at −50°C., crystd. at −70°C.
	50	liq. at −10°C., liq. for the most part at −30°C.
	75	liq. at − 1°C.

The above results show that 1,4-di-*tert*-butyl cyclohexane may be used as a constituent of safety fuels.

The *tert*-butyl cyclohexane obtained had the octane number of 83, measured by the CFR motor method without blending with base gasoline, which is lower than the known value of 99(19). Although the known value 99 is not yet reliable, it is to be expected that the octane number of

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(19) W. G. Lovell, J. M. Campbell and T. A. Boyd, *Ind. Eng. Chem.*, **25** (1933), 1107; F. H. Garner, E. B. Evans, C. H. Sprake, and W. E. S. Broom, *Proc. World Petrol. Congress*, **11** (1933), 170; cf. K. Yamazaki, *J. Fuel. Soc. Japan*, **20** (1941), 487.

tert-butyl cyclohexane obtained in the present investigation may be somewhat lower than the true octane number of pure *tert*-butyl cyclohexane, owing to the presence of a small amount of isopropyl cyclohexane and *sec*-butyl cyclohexane, which have lower octane number of 55 and 45(19), respectively. *tert*-Butyl-cyclohexane has the flash point of 40.2°C., and it may also be used for the safety fuel.

The high boiling aromatic oil CF_2R, obtained by the purification of the mother liquor of the crystall of *p*-di-*tert*-butyl benzene, having constants, b.p. 220–250°C. (uncor.), d_4^{20} 0.8586, n_D^{20} 1.4894, showed the octane number of 95, by the CFR motor method without blending with base gasoline and the flash point of 88.5°C., by the Pensky-Martens apparatus. This substance may also be used as an aromatic safety fuel.

Summary.

1. Benzene has been alkylated with isobutylene using sulfuric acid of various concentrations, and some of the results of V. N. Ipatieff, B. B. Corson and H. Pines have been reconfirmed. The alkylation takes place predominantly with 91–96% sulfuric acid.

2. Using 91% sulfuric acid as catalyst, benzene has been alkylated with varied amount of isobutylene against benzene. The increase of the yield of *tert*-butyl benzene caused by the decrease of the amount of isobutylene against benzene is not remarkable, forming a considerable amount of *p*-di-*tert*-butyl benzene fraction. By the increase of the amount of isobutylene against benzene, the yield of *p*-di-*tert*-butyl benzene fraction increases to the main reaction product, with the decrease of *tert*-butyl benzene fraction. The reaction of excess isobutylene with benzene causes the mere polymerisation of isobutylene with 91% sulfuric acid to yield high-boiling olefinic polymer after complete alkylation of benzene.

3. *tert*-Butyl benzene and *p*-di-*tert*-butyl benzene have been readily hydrogenated into *tert*-butyl cyclohexane and 1,4-di-*tert*-butyl cyclohexane, respectively, using nickel-kieselguhr catalyst. 1,4-Di-*tert*-butyl cyclohexane is a mixture of cis and trans isomers, and is partially crystallised at room temperature and melts completely at 31°C.

4. Octane numbers of 1,4-di-*tert*-butyl cyclohexane, *tert*-butyl cyclohexane and the high boiling aromatic hydrocarbon CF_2R have been measured. 1,4-Di-*tert*-butyl cyclohexane has high octane numbers as predicted, the 20% blending octane number amounting to 113. It has the flash point of 80.5°C., and is highly soluble in hydrocarbones, and therefore may be used as a constituent of safety fuels.

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