

79. *Alkylation of the Aromatic Nucleus. Part X.<sup>1</sup> Cyclohexylation of the Monoalkylbenzenes, and the Course of Thermal Alkylation.*

By J. BLACKWELL and W. J. HICKINBOTTOM.

The thermal decomposition of cyclohexyl toluene-*p*-sulphonate in toluene, and in ethyl-, isopropyl-, cyclohexyl-, and *t*-butyl-benzene has been studied. From each, a mixture of *o*-, *m*-, and *p*-alkylcyclohexylbenzene is formed and the isomer distribution has been estimated in each product.

The proportion of *meta*-isomer increases from 16% with toluene to 32% with *t*-butylbenzene; this proportion of *meta*-substitution is greater than would be expected from the normal experience of electrophilic substitution. An hypothesis is advanced to account for this and for the occurrence of *meta*-substitution in other alkylations.

In previous papers in this series it is reported that the introduction of the cyclopentyl,<sup>1</sup> cyclohexyl,<sup>2</sup> cycloheptyl,<sup>1</sup> and methylcyclohexyl<sup>3</sup> groups into toluene gives a much higher proportion of *meta*-substitution than would normally be expected in an electrophilic substitution. It seemed desirable to examine how this proportion of *meta*-substitution would be influenced if the methyl group of toluene were replaced by ethyl, isopropyl, or *t*-butyl, since it is known that in such a series the relatively small proportion of *meta*-substitution in the nitration of toluene increases progressively as the bulk of the alkyl group increases up to *t*-butyl.<sup>4</sup> Similar observations have been made for chloromethylation<sup>5</sup> and acylation.<sup>6</sup> In the cyclohexylation of toluene by thermal decomposition of cyclohexyl esters of sulphonic acids, *meta*-substitution accounts for about 17% of the product and it might be expected that the amount of *meta*-substitution in *t*-butylbenzene should constitute a substantial proportion of the product. The observed isomer distributions for cyclohexylation are shown in Table 1.

Estimations of the isomer distribution are based on gas-liquid chromatography, with a reproducibility better than 1% except for the cyclohexylation of toluene, where the resolution was not sufficient to afford a clear separation of the *ortho*- and *meta*-isomer. It gave *o*- and *m*-cyclohexyltoluene, 46%; *p*-cyclohexyltoluene, 54%. More satisfactory

<sup>1</sup> Part IX, Davies and Hickinbottom, *J.*, 1963, 373.

<sup>2</sup> Hickinbottom and Rogers, *J.*, 1957, 4124.

<sup>3</sup> Blackwell and Hickinbottom, *J.*, 1963, 366.

<sup>4</sup> Knowles, Norman, and Radda, *J.*, 1960, 4885.

<sup>5</sup> Freeman, *J. Org. Chem.*, 1961, **26**, 212.

<sup>6</sup> Brown and Marino, *J. Amer. Chem. Soc.*, 1959, **81**, 5611.

analysis was obtained from the infrared spectrum by using the following bands: *ortho* 13.35 and 13.85  $\mu$ ; *meta* 12.85 and 14.3  $\mu$ ; *para* 12.34  $\mu$ .

TABLE 1.

	Isomer distribution (%)		
	<i>ortho</i>	<i>meta</i>	<i>para</i>
Toluene *	30	17	53
Ethylbenzene †	18	20	62
Isopropylbenzene	4	29	67
t-Butylbenzene ‡	0	32	68
Cyclohexylbenzene	6	26	68
Fluorobenzene	35	0	65
Chlorobenzene	—	0	—

\* Reaction of cyclohexene and toluene-*p*-sulphonic acid in toluene gave *ortho* 30, *meta* 17, *para* 53%. † Sample and reference compounds were kindly supplied by R. Williamson, Esq., B.Sc. ‡ Corrected for the dismutation of t-butylbenzene.

It is clear from Table 1 that the alkylbenzenes give a much greater proportion of *meta*-isomer than would be expected from the normal experience of electrophilic substitution. This is also observed with cyclopentylation<sup>1</sup> and cycloheptylation<sup>1</sup> where the percentage of *meta*-substitution is of the order of 20% and 15%, respectively. With methylcyclohexylation,<sup>3</sup> the *meta*-substitution is about 30%. With phenanthrene,<sup>7</sup> fluorene, and acenaphthene<sup>8</sup> it has also been observed that thermal alkylation gives an isomer distribution which differs from that for nitration or halogenation and approaches a random substitution (Table 2). Although the experimental evidence is not complete for naphthalene, there are observations to support the view that random substitution occurs here also.

It has been established that these alkyl derivatives do not suffer dismutation or rearrangement when they are heated with toluene-*p*-sulphonic acid under the conditions of the alkylations described in this series; t-butylbenzene is an exception, although the effect is relatively small (about 5%). It may then be assumed that the proportions of isomers

TABLE 2.

	Substituting group	Proportion of isomers (%)
Naphthalene	Cyclohexyl	$\alpha$ - 60; $\beta$ - 40
	NO <sub>2</sub>	$\alpha$ - ~95
Fluorene	s-Butyl	1-, 7; 2-, 45; 3-, 25; 4-, 23
	NO <sub>2</sub>	2-, 63; 3-, 3; 4-, 29
Acenaphthene	s-Butyl	3-, 28; 4-, 39; 5-, 33
	NO <sub>2</sub>	5-, >55, with some 3-isomer
Phenanthrene	Cyclohexyl	1-, 15; 2-, 18; 3-, 27; 4-, 0; 9-, 35
	NO <sub>2</sub>	1-, 26; 2-, 7; 3-, 22; 4-, 6; 9-, 36

given in Table 1 and in Parts IV and VI—IX represent the reactivity of these positions towards alkylation.

It might be supposed that this approximation to random substitution indicates a free-radical mechanism for the alkylation. The evidence, however, is wholly and convincingly against this. Alkylation of the aromatic nucleus by thermal decomposition of alkyl sulphonates is proton-catalysed. The kinetic measurements of Ogata *et al.*<sup>9</sup> and of Nenitzescu *et al.*<sup>10</sup> on the rate of thermal decomposition of benzyl esters in organic solvents establish that the reaction is autocatalytic; it is accelerated by the addition of a free sulphonic acid, prevented by the addition of bases, and retarded by ether which acts as a

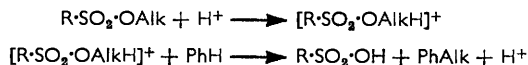
<sup>7</sup> Hickinbottom and Rule, *J.*, 1959, 2517.

<sup>8</sup> Cairns and Hickinbottom, *J.*, 1962, (a) 1867; (b) 870; (c) Dewar and Urch, *J.*, 1958, 3079; (d) Dewar and Warford, *J.*, 1956, 3570; (e) Jarasca, Batzis, and Kroeger, *J. Org. Chem.*, 1960, **25**, 1571; (f) Morgan, *J. Soc. Chem. Ind.*, 1930, **49**, 413.

<sup>9</sup> Ogata, Yonetani, and Oda, *Bull. Inst. Phys. Chem. Res.*, Tokyo, 1943, **22**, 583.

<sup>10</sup> (a) Nenitzescu, Auram, and Sliam, *Bull. Soc. chim. France*, 1955, 1266; (b) Nenitzescu, Ioan, and Teodorescu, *Chem. Ber.*, 1957, **90**, 585.

weak base. The observations suggest that the following scheme can adequately represent the course of the alkylation in general terms:



It is characteristic of this alkylation that it can only be applied successfully to aromatic systems which are not deactivated; no reaction occurs with nitrobenzene, esters of aromatic acids, aromatic ketones, and aldehydes, or nitriles. Even with chloro- or bromobenzene alkylation by saturated alkyl groups is slow, and only poor yields are obtained; fluorobenzene is an exception.

The polar character of the reaction is also supported by observations on the decomposition of esters of the general form  $\text{X}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{O}\cdot\text{C}_6\text{H}_4\text{Y}$  in aromatic solvents ( $\text{X}$  and  $\text{Y} = \text{Alk}, \text{NO}_2, \text{Cl}$ , etc.). The stability of such esters can be predicted from a knowledge of the nature of  $\text{X}$  and  $\text{Y}$  on the assumption that the reaction is polar.

A further argument against free-radical substitution is that at no time during this work, involving many hundreds of alkylations, has there been any qualitative evidence of a free-radical reaction.

Further, it must be emphasised that this approximately random substitution is observed only when saturated alkyl and cycloalkyl groups are introduced into monoalkylbenzenes. Benzyl and substituted benzyl groups follow the usual pattern of electrophilic substitution.

It has been known for some time that in Friedel-Crafts alkylation a considerable amount of *meta*-substitution occurs, and that, under suitable conditions, this may account for most of the product. Some of this *meta*-substitution is known to be due to the isomerising effect of the Friedel-Crafts catalyst on the *ortho*- and *para*-isomers but it is by no means easy to estimate how much *meta*-compound is derived from primary substitution. Allen and Yats<sup>11</sup> carried out a large number of alkylations of toluene under different conditions and obtained a wide range of values for the proportion of *meta*-product: between 11% and 21% for methylation; between 18% and 74% for ethylation; and between 16% and 70% for isopropylation. From these values they calculated what the isomer distribution was before isomerisation. The values thus obtained were 14% of *meta*-product for methylation; 18% for ethylation; and 21% for isopropylation. The last value agrees with that obtained by the thermal decomposition of isopropyl sulphonic ester in toluene.

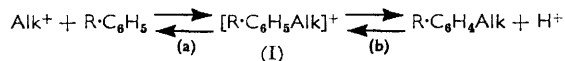
Brown *et al.*,<sup>12</sup> by using conditions designed to restrict isomerisation, have similarly concluded that *meta*-alkylation occurs as a primary reaction although it is clear that no accurate estimate can be made. They suggested that *meta*-alkylation is due to the high reactivity of the substituting alkyl group and is accompanied by a low selectivity—conditions which they consider to favour random rather than directed substitution. It is clear from a wider survey of this problem that Brown's explanation is not satisfactory. In the alkylations brought about by the thermal decomposition of alkyl esters of sulphonic acids at least two factors are of importance: (a) the substituting group and (b) the group already present in the aromatic nucleus. In amplification of the second condition, *meta*-alkylation is characteristic of the alkylbenzenes and does not occur to an appreciable extent with other substituted benzenes having other *ortho*- and *para*-directing groups. Thus phenols, phenol ethers, and fluorobenzene undergo no appreciable amount of *meta*-alkylation although the substituting alkyl groups, on Brown's classification, are extremely reactive and non-selective (Table I, Part VIII). The influence of the directing group is also shown in the progressive increase in the proportion of *meta*-isomer in nitration,<sup>4</sup> chloromethylation,<sup>5</sup> acylation,<sup>6</sup> and cycloalkylation of the monoalkylbenzenes as the alkyl

<sup>11</sup> Allen and Yats, *J. Amer. Chem. Soc.*, 1961, **83**, 2799.

<sup>12</sup> Brown and Smoot, *J. Amer. Chem. Soc.*, 1956, **78**, 6255.

group passes from methyl through ethyl and isopropyl to *t*-butyl, although it is not possible to separate the steric from other effects sharply.

Although there is good reason for assuming that some alkylations proceed by a molecular displacement,<sup>1</sup> it is probable that the carbonium ion  $\text{Alk}^+$  is the active substituting agent in all reactions involving saturated alkyl or cycloalkyl groups. A satisfactory picture of the course of the alkylation is obtained by assuming that substitution is a two-stage process<sup>13,14</sup> represented by the following scheme. The intermediate ion (I) will consist of three species resulting from addition at the *ortho*-, *meta*-, and *para*-positions. An enhanced proportion of *meta*-substitution in the final product will occur if the 1,3-addition compound loses a proton more readily than the 1,2- or 1,4-addition compound.



It is not yet possible to obtain direct proof of this hypothesis, but indirect support is afforded by observations on the relative stability of *o*-, *m*-, and *p*-dialkylbenzenes towards dealkylation under the influence of aluminium halides and halogen hydrides, that is, conditions which favour the reversibility of reactions (b) and (a). Further, the increasing formation of *m*-dialkylbenzenes in the Friedel-Crafts reaction as the reaction proceeds is readily understandable on this hypothesis.

One of the deductions from this hypothesis is that this approximately random substitution can occur with suitable substituting agents if the directing group exerts only an inductive effect. Any mesomeric effect would influence the intermediate ion (I) during the reaction to favour *ortho*- and *para*-substitution.

#### EXPERIMENTAL

*Cyclohexylation of the Alkylbenzenes.*—The cyclohexylations were carried out with cyclohexyl toluene-*p*-sulphonate in an excess of the alkylbenzene. The product was isolated in the same way as in previous alkylations.

*Toluene.* Repetition of the work of Hickinbottom and Rogers<sup>2</sup> gave a mixture of cyclohexyltoluenes (65%), b. p. 126—130°/21 mm.,  $n_D^{20}$  1.5244 (Hickinbottom and Rogers report b. p. 126—129°/20 mm.,  $n_D^{20}$  1.5246).

For comparison cycloalkylation was brought about by heating together, under reflux, toluene (2.1 moles), cyclohexene (0.2 mole), and anhydrous toluene-*p*-sulphonic acid (0.2 mole) for 5 hr. The product (72%), b. p. 134—137°/26 m.m.,  $n_D^{20}$  1.5238, was a mixture of cyclohexyltoluenes (Found: C, 89.5; H, 10.3. Calc. for  $\text{C}_{13}\text{H}_{18}$ : C, 89.6; H, 10.4%).

*Isopropylbenzene.* From 0.15 mole of ester the following fractions were obtained: (i) cyclohexylisopropylbenzenes (66%), b. p. 140—149°/18 mm.,  $n_D^{20}$  1.5185 (Found: C, 89.0; H, 11.1. Calc. for  $\text{C}_{15}\text{H}_{22}$ : C, 89.0; H, 11.0%); (ii) dicyclohexylisopropylbenzenes (5%), b. p. 142—144°/0.3 mm.,  $n_D^{20}$  1.5335 (Found: C, 88.4; H, 11.3. Calc. for  $\text{C}_{21}\text{H}_{32}$ : C, 88.6; H, 11.4%).

*t*-Butylbenzene. The ester (0.20 mole) gave 30 g. of product, b. p. 65—98°/0.2 mm.,  $n_D^{20}$  1.5133, which, from its gas-liquid chromatogram, was a mixture of five components. Distillation separated it into two main fractions: (i) b. p. 104—116°/16 mm.,  $n_D^{20}$  1.5008 (Found: C, 88.5; H, 11.7. Calc. for  $\text{C}_{14}\text{H}_{22}$ : C, 88.3; H, 11.7%); and (ii) b. p. 149—156°/16 mm.,  $n_D^{20}$  1.5169 (Found: C, 88.8; H, 11.2. Calc. for  $\text{C}_{16}\text{H}_{24}$ : C, 88.8; H, 11.2%). Fraction (i) is a mixture of *m*- and *p*-di-*t*-butylbenzene. The *para*-isomer was deposited on cooling as white rods, m. p. 80°, from methanol (Found: C, 88.4; H, 11.7%) [mononitro-derivative, m. p. 86—87°; dinitro-derivative, m. p. 192—193° (Found: C, 60.2; H, 7.0; N, 10.2. Calc. for  $\text{C}_{14}\text{H}_{20}\text{N}_2\text{O}_4$ : C, 60.0; H, 7.2; N, 10.0%)] (lit., mononitro-,<sup>15</sup> m. p. 87—88°; dinitro-,<sup>16</sup> m. p. 193—195°; Legge<sup>17</sup> gives for *p*-di-*t*-butylbenzene, m. p. 77.7—78.4°). From the liquid portion

<sup>13</sup> Ingold, "Structure and Mechanism in Organic Chemistry," G. Bell & Sons, London, 1953, pp. 280, 281, 301.

<sup>14</sup> Hughes, Ingold, and Reed, *J.*, 1950, 2412, 2426.

<sup>15</sup> Carpenter, Easter, and Wood, *J. Org. Chem.*, 1951, 16, 586.

<sup>16</sup> Carpenter and Easter, *J. Org. Chem.*, 1954, 19, 77.

<sup>17</sup> Legge, *J. Amer. Chem. Soc.*, 1947, 69, 2079.

of fraction (i), still containing some 6% of the *para*-isomer, were obtained by nitration 1,3-di-*t*-butyl-4-nitrobenzene, m. p. 52°, and 1,3-di-*t*-butyl-4,6-dinitrobenzene, m. p. 164—165° (Found: C, 59.9; H, 7.3; N, 10.2. Calc. for  $C_{14}H_{20}N_2O_4$ : C, 60.0; H, 7.2; N, 10.0%) (lit.,<sup>18</sup> m. p. 52—53° for mononitro-compound; m. p. 164—165° for dinitro-compound). Fraction (ii) is a mixture of *m*- and *p*-*t*-butylcyclohexylbenzene.

**Cyclohexylbenzene.** From 0.15 mole of ester a mixture of dicyclohexylbenzenes was obtained, b. p. 112—147°/0.5 mm. (66% yield) (Found: C, 89.4; H, 10.6. Calc. for  $C_{18}H_{26}$ : C, 89.2; H, 10.8%), which solidified on cooling. From it di-*p*-cyclohexylbenzene, m. p. 101—102° (lit.,<sup>18</sup> m. p. 101—102°), was isolated by crystallisation from light petroleum, (b. p. 40—60°). By oxidation with boiling 25% nitric acid, terephthalic acid was obtained (dimethyl ester, m. p. and mixed m. p. 140°).

**Fluorobenzene.** The ester (0.15 mole) and fluorobenzene (1.15 mole), heated together for 14 hr., gave an oil (63%), b. p. 105—108°/13 mm.,  $n_D^{20}$  1.5064 (Found: C, 81.1; H, 8.9; F, 10.4. Calc. for  $C_{12}H_{15}F$ : C, 80.9; H, 8.5; F, 10.7%).

**Chlorobenzene.** The product obtained when chlorobenzene (2.2 moles) and cyclohexyl toluene-*p*-sulphonate (0.25 mole) were heated together for 10 hr. was a mixture (16%), b. p. 124—138°/14 mm.,  $n_D^{20}$  1.5168, containing, not only *o*- and *p*-chlorocyclohexylbenzene, but hydrocarbons derived from cyclohexene (cf. Hickinbottom and Rogers<sup>19</sup>) (Found: C, 77.8; H, 9.8; Cl, 12.4.  $C_{12}H_{15}Cl$  requires C, 73.9; H, 7.8; Cl, 18.3%). By further distillation, the alkylation products were concentrated into the range b. p. 137—140°/16 mm.,  $n_D^{20}$  1.5379 (Cl, 16.7%).

**Reaction of *t*-Butylbenzene with Toluene-*p*-sulphonic Acid.**—Anhydrous toluene-*p*-sulphonic acid (0.10 mole) and *t*-butylbenzene (1.0 mole) were heated together at 125° for 5 hr. After removal of the acid and distillation to remove unchanged *t*-butylbenzene, the following fractions were obtained: (i) b. p. 104—106°/13 mm.,  $n_D^{20}$  1.4872 (2.2 g.); (ii) b. p. 106—109°/13 mm.,  $n_D^{20}$  1.4881 (1.0 g., semisolid); (iii) b. p. 109—113°/13 mm., m. p. 78—79° (3.1 g.). Fraction (i) was mostly *m*-di-*t*-butylbenzene (dinitro-derivative, m. p. and mixed m. p. 163—164°). Fraction (iii) was *p*-di-*t*-butylbenzene, m. p. and mixed m. p. 80° (from methanol). Fraction (ii) was a mixture of *m*- and *p*-di-*t*-butylbenzene.

**Preparation of Reference Compounds.**—The general method of preparation was by reaction of cyclohexanone with the Grignard reagent from the appropriate alkyl- or cycloalkyl-bromobenzene. The alcohol thus formed was dehydrated by boiling it with 15% aqueous oxalic acid

TABLE 3.

	B. p./mm.	$n_D^{20}$	Found (%)		Formula	Required (%)	
			C	H		C	H
<i>(Isopropylphenyl)cyclohexenes</i>							
<i>ortho</i>	147—149°/18	1.5329	89.6	10.2	$C_{15}H_{20}$	90.0	10.0
<i>meta</i>	159—163°/17	1.5426	89.8	9.9	"	"	"
<i>para</i>	170—173°/27	1.5436	89.6	10.2	"	"	"
<i>(Isopropylphenyl)cyclohexanes</i>							
<i>ortho</i>	138—139°/16	1.5194	88.8	10.9	$C_{15}H_{22}$	89.0	11.0
<i>meta</i>	146—148°/16	1.5181	88.7	11.2	"	"	"
<i>para</i>	157—159°/27	1.5186	89.0	11.0	"	"	"

for several hours, and the resulting olefin was hydrogenated at about 3 atm. in ethanol over palladium-charcoal. It was more satisfactory to hydrogenate *ortho*-substituted olefins at 50°. The products are recorded in Tables 3—6 and the following list.

*m-t*-Butylphenylcyclohexanol, b. p. 108—113°/0.2 mm.,  $n_D^{20}$  1.5345 (Found: C, 82.1; H, 10.6.  $C_{16}H_{24}O$  requires C, 82.7; H, 10.4%).

*m-t*-Butylphenylcyclohexene, b. p. 93—96°/21 mm.,  $n_D^{20}$  1.5268 (Found: C, 89.8; H, 10.3.  $C_{16}H_{22}$  requires C, 89.6; H, 10.4%).

*m-t*-Butylphenylcyclohexane, b. p. 159—160°/21 mm.,  $n_D^{20}$  1.5148 (Found: C, 89.0; H, 11.1.  $C_{16}H_{24}$  requires C, 88.8; H, 11.2%) [*dinitro-derivative*, slightly yellow needles m. p. 106—107° (Found: C, 62.6; H, 7.3; N, 7.3.  $C_{16}H_{22}N_2O_4$  requires C, 62.7; H, 7.2; N, 9.15%)].

<sup>18</sup> Corson and Ipatieff, *Org. Synth.*, Coll. Vol. II, 1943, 151.

<sup>19</sup> Hickinbottom and Rogers, *J.*, 1957, 4131.

TABLE 4.

	B. p./mm.	$n_D^{20}$	Found (%)		Formula	Required (%)	
			C	H		C	H
<i>(Cyclohexylphenyl)cyclohexanols</i>							
<i>ortho</i>	136—140°/0.3 *	1.5450	84.0	10.2	C <sub>18</sub> H <sub>26</sub> O	83.7	10.15
<i>meta</i>	150—155°/0.3	1.5350	84.2	10.4	„	„	„
* M. p. 70—71°.							
<i>(Cyclohexylphenyl)cyclohexenes</i>							
<i>ortho</i>	118—123°/0.3	1.5472	90.0	10.2	C <sub>18</sub> H <sub>24</sub>	89.9	10.1
<i>meta</i>	140—144°/0.3	1.5490	89.7	10.1	„	„	„
<i>(Cyclohexylphenyl)cyclohexanes</i>							
<i>ortho</i> *	109—111°/0.2	1.5350	89.1	10.7	C <sub>18</sub> H <sub>26</sub>	89.2	10.8
<i>meta</i> * †	141—142°/0.5	1.5356	89.0	10.9	„	„	„

\* Prepared by hydrogenation in ethyl acetate. † *Dinitro-derivatives*, m. p. 141—142° (Found: C, 64.8; H, 7.4; N, 8.6. C<sub>18</sub>H<sub>24</sub>N<sub>4</sub>O<sub>2</sub> requires C, 65.0; H, 7.3; N, 8.4%).

TABLE 5.

	B. p./mm.	M. p.	Found (%)		Formula	Required (%)	
			C	H		C	H
<i>(Fluorophenyl)cyclohexanols</i>							
<i>meta</i>	106—108/0.8	60°	74.2	7.8	C <sub>12</sub> H <sub>15</sub> FO	74.2	7.8
<i>para</i>	—	76—77	74.2	8.1	„	„	„
<i>Fluorophenylcyclohexenes</i>							
<i>meta</i>	135—138°/24	$n_D^{20}$ 1.5411	81.4	7.4	C <sub>12</sub> H <sub>13</sub> F	81.8	7.45
<i>para</i>	135—137/23 *	—	82.0	7.6	„	„	„
<i>Fluorophenylcyclohexanes</i>							
<i>ortho</i> †	108—109°/14	1.5109	81.1	8.4	C <sub>12</sub> H <sub>15</sub> F	80.85	8.5
<i>meta</i>	122—124/23	1.5070	81.0	8.4	„	„	„
<i>para</i>	122—123/23	1.5053	80.8	8.7	„	„	„

\* M. p. 29°. † Prepared by the diazoreaction from *o*-cyclohexylaniline; *mononitro-derivative*, m. p. 65° (Found: C, 64.7; H, 6.5; N, 6.3. C<sub>12</sub>H<sub>14</sub>FNO<sub>2</sub> requires C, 64.6; H, 6.3; N, 6.3%). Found, F 10.4% (Reqd., F 10.7%).

TABLE 6.

	B. p./mm.	$n_D^{20}$	Found (%)			Formula	Required (%)		
			C	H	Cl		C	H	Cl
<i>(Chlorophenyl)cyclohexenes</i>									
<i>ortho</i> *	137—141°/16	1.5528	—	—	—	—	—	—	—
<i>meta</i>	163—166°/28	1.5438	74.5	6.8	18.1	C <sub>12</sub> H <sub>13</sub> Cl	74.8	6.8	18.4
<i>para</i>	151—152°/11 (m. p. 69—70°)	—	75.0	6.6	18.1	„	„	„	„
<i>(Chlorophenyl)cyclohexanes</i>									
<i>ortho</i> †	126—128°/16	1.5436	—	—	—	—	—	—	—
<i>meta</i>	153—155°/28	1.5432	73.8	7.9	18.0	C <sub>12</sub> H <sub>15</sub> Cl	74.0	7.8	18.2
<i>para</i> ‡	144—146°/15	1.5442	—	—	—	—	—	—	—

\* Parham, Wheeler, and Wright (*J. Amer. Chem. Soc.*, 1960, **82**, 139) give b. p. 77°/0.7 mm.  $n_D^{25}$  1.5582. † McGuire and Dull (*ibid.*, 1947, **69**, 1469) give b. p. 118—120° (3 mm.,  $n_D^{24}$  1.5429). ‡ Mayes and Turner (*J.*, 1929, 503) give b. p. 140°/15 mm.,  $n_D^{20}$  1.5386.

*p-t-Butylphenylcyclohexanol*, m. p. 68°, b. p. 113—115°/0.2 mm. (Found: C, 83.0; H, 10.2%). The alcohol is not easily dehydrated by boiling aqueous oxalic acid. Hydrogenolysis (palladium-charcoal in acetic acid containing a trace of perchloric acid) gave *p-t-butylphenylcyclohexane*, b. p. 158—159°/16 mm.,  $n_D^{20}$  1.5168 (Found: C, 88.6; H, 11.3%).