[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Hexa-*p*-alkylphenylethanes. X.[1] *p*-Cyclohexyl Derivatives of Hexaphenylethane

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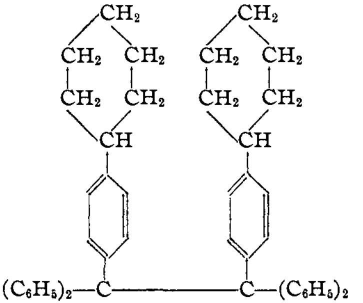
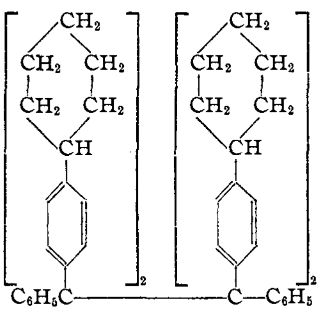
In connection with the study of the effect of alkyl groups on the dissociation of substituted hexaphenylethanes, di- (I), tetra- (II) and hexa- (III) -*p*-cyclohexylphenylethanes have been prepared and their dissociation measured by the magnetic susceptibility method.[2]



I



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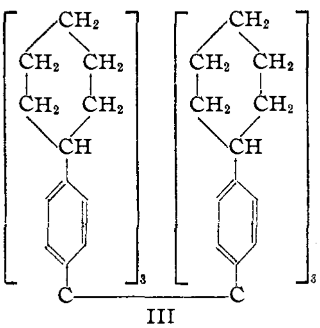
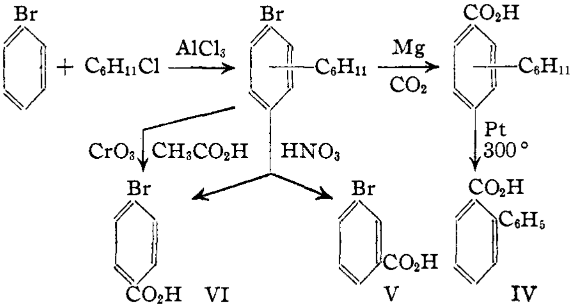


III

Zugrăvescu and Zugrăvescu[3] already have reported the preparation of di-*p*-cyclohexylphenyltetraphenylethane (I), and Brown and Marvel[4] have described a hexacyclohexylphenylethane which was believed to be the *para*-isomer (III). However, that product was prepared from a bromocyclohexylbenzene obtained by the action of cyclohexyl chloride on bromobenzene in the presence of aluminum chloride[5] and has been shown to be a mixture of isomers.

The bromocyclohexylbenzene obtained from the Friedel–Crafts reaction[4,5] has a fairly constant boiling point and its refractive index is very close to that of the product prepared by diazotization of *p*-aminocyclohexylbenzene and replacement of the diazonium group with bromine.[5] The product of the Friedel–Crafts reaction, however, contains the ortho-, meta- and para-isomers. The presence of the ortho-isomer has been demonstrated by carbonation of the Grignard reagent from the bromocyclohexylbenzene to give a mixture of acids which on dehydrogenation gave *o*-phenylbenzoic acid (IV). Meta- and para-isomers have been shown to be present by oxidation with nitric acid to yield a mixture of bromobenzoic acids from which pure *m*-bromobenzoic acid (V) and pure *p*-bromobenzoic acid (VI) have been separated. The presence of the para-isomer also has been established by the oxidation of the bromocyclohexylbenzene in acetic acid solution by chromic acid to give pure *p*-bromobenzoic acid.



Bodroux and Thomassin[6] have described the bromination of cyclohexylbenzene to give *p*-bromocyclohexylbenzene. This reaction takes place readily and apparently yields the pure para-isomer since oxidation has given only *p*-bromobenzoic acid and conversion to the Grignard reagent followed by carbonation has produced *p*-cyclohexylbenzoic acid (VII) in yields of 80% of

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[1] For the ninth communication in this series see THIS JOURNAL, **61**, 2771 (1939).

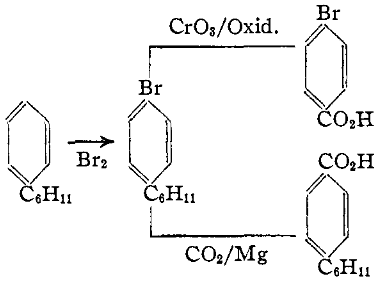
[2] (a) E. Müller and Müller-Rodloff, *Ann.* **520**, 235 (1935); (b) Roy and Marvel, THIS JOURNAL, **59**, 2622 (1937).

[3] Zugrăvescu and Zugrăvescu, *Bul. Soc. Chim. Romania*, **19A**, 85 (1937); *C. A.*, **33**, 4228 (1939).

[4] Brown and Marvel, THIS JOURNAL, **59**, 1175 (1937).

[5] Mayes and Turner, *J. Chem. Soc.*, 503 (1929).

[6] Bodroux and Thomassin, *Compt. rend.*, **205**, 991 (1937); *Bull. soc. chim.*, [5] **6**, 1411 (1939).



VII

the theoretical amount. As a further check on the purity of the *p*-bromocyclohexylbenzene obtained by this process, a sample has been made from *p*-aminocyclohexylbenzene and one of the carbinols described below has been made from each sample of the bromo compound. No difference in the properties of the carbinols thus obtained has been detected.

The three triarylcarbinols corresponding to the desired ethanes (I, II and III) have been prepared by treating the Grignard reagent from *p*-bromocyclohexylbenzene with benzophenone, ethyl benzoate and diethyl carbonate, respectively. All three carbinols thus prepared were obtained in crystalline form. The tri-*p*-cyclohexylphenylcarbinol melted at 180–181°, or twelve degrees higher than has been reported by Neunhoeffer.[7] It seems probable that Neunhoeffer may have had some ethyl ether of the carbinol mixed with the carbinol. We found that unless unusual care was taken to use alcohol-free ether in handling the carbinol, some ether formed and a low-melting product resulted. Our mono-*p*-cyclohexylphenyldiphenylchloromethane melted at 126–127°. Zugrăvescu and Zugrăvescu[8] report the melting point to be 123°. Our sample of the corresponding hexaarylethane peroxide melted at 158–159° whereas it has been reported[8] to melt at 164°.

The tri-*p*-cyclohexylphenylcarbinol, the corresponding chloromethane and peroxide obtained in this work did not have properties which agreed with those previously reported by Brown and Marvel.[4] It seems obvious that the products reported earlier as para-isomers are really mixtures of unknown composition.

The ethanes (I, II and III) were prepared from the carbinols by the usual procedures. The ethanes were not isolated but were characterized by conversion to the corresponding peroxides. Magnetic susceptibility measurements on benzene solutions of the ethanes showed that di-*p*-cyclohexylphenyltetraphenylethane (I) was dissociated to the extent of 9 ± 1% at 0.1 molar concentration and 25°. Its solution was an orange-yellow. This ethane, like other mono-*p*-alkylphenylethanes, decomposed very slowly. The tetra-*p*-cyclohexylphenyldiphenylethane gave a cherry-red solution and was dissociated to the extent of 10 ± 1% at 0.1 molar concentration and 25°. This ethane decomposed extensively in thirty-six hours. Hexa-*p*-cyclohexylphenylethane was quite insoluble and very unstable so that magnetic susceptibiliy measurements were not very satisfactory. The freshly prepared solutions had a Burgundy-red color and measurements at 0.01 molar and 25° indicated a dissociation of 50 ± 7%. Assuming that the mass law holds, this would indicate a dissociation of about 22% at 0.08 molar concentration. This value is very close to those found for other hexa-*p*-alkylphenylethanes.[1] The most remarkable fact concerning these dissociation measurements is that the disubstituted ethane is dissociated to almost the same extent as the tetra-substituted compound.

Experimental

***p*-Bromocyclohexylbenzene.—(a) Bromination of Cyclohexylbenzene.**—The method described by Bodroux and Thomassin[6] was used with the modification that iron was added as a bromination catalyst and the reaction mixture was stirred. The yield of bromo compound was 85%; b. p. 106–108° (1.5 mm.); n^{20}_{D} 1.5588; d^{25}_{4} 1.275.

(b) **From *p*-Aminocyclohexylbenzene.**—*p*-Nitrocyclohexylbenzene was prepared according to the method of Neunhoeffer[8] and reduced over Raney nickel to give a 97% yield of the amine. The amine hydrobromide was suspended in 40% hydrobromic acid and diazotized at 5°. The insoluble diazonium salt was decomposed with copper bronze powder. The material which separated from solution was a mixture of the phenol and the bromo compound. The phenol was removed with some difficulty by extraction with 10% potassium hydroxide solution. The yield of bromo compound was about 35%; b. p. 110° (1.5–2 mm.); n^{20}_{D} 1.5594; d^{25}_{4} 1.265.

(c) **From Bromobenzene, Cyclohexyl Chloride and Aluminum Chloride.**—This procedure previously described[4,5] gave a product of b. p. 93–95° (1 mm.); n^{20}_{D} 1.5605; d^{20}_{4} 1.300.

The ether solution of the Grignard reagent from 24 g. of this bromo compound was poured on solid carbon dioxide and the organic acids thus formed were isolated. The yield was 14.2 g. (70%) of product melting at 103–106°. A 0.3-g. sample of this acid was dehydrogenated by heating with a platinum on charcoal catalyst[9] at 300° for two hours. This treatment gave 0.02 g. of *o*-phenylbenzoic acid, m. p. 113°. This acid when mixed with an

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(7) Neunhoeffer, *Ann.*, **526**, 61 (1936).

(8) Neunhoeffer, *J. prakt. Chem.*, **241**, 95 (1932).

(9) Linstead, Millidge, Thomas and Walpole, *J. Chem. Soc.*, 1146 (1937).

authentic specimen of *o*-phenylbenzoic acid (m. p. 114°) did not depress its melting point.

Oxidation of 9.5 g. of this bromocyclohexylbenzene in 100 cc. of boiling 50% acetic acid with 20 g. of chromic acid for twenty-four hours gave 0.3–0.5 g. of *p*-bromobenzoic acid, m. p. 252°.

By refluxing 2 g. of the bromo compound with 150 cc. of dilute nitric acid (sp. gr. 1.04) for four days, then adding 10 cc. of concentrated nitric acid (sp. gr. 1.42) and continuing the heating for three more days, some oxidation was obtained. The yield of acidic products was 0.6 g. The portion least soluble in hot water melted at 252° and was considered to be *p*-bromobenzoic acid. *m*-Bromobenzoic acid, m. p. 152–154°, was obtained from the remainder. This material did not depress the melting point of an authentic specimen of *m*-bromobenzoic acid whereas a mixture of it with *o*-bromobenzoic acid melted at 137–142°.

p-Cyclohexyl Derivatives of Triphenylcarbinol.—The Grignard reagent of *p*-bromocyclohexylbenzene (prepared by method (a)) was obtained in ether solution using a little ethylmagnesium bromide as a catalyst to start the reaction. Most of the ether was distilled from the reaction mixture and replaced by dry benzene. Then about 70% of the calculated amount of benzophenone, ethyl benzoate or diethyl carbonate, depending on the carbinol desired, was added. The reactions were carried out and the products isolated in the usual manner. The carbinols crystallized readily. Alcohol-free ether was used to avoid formation of some ether of the carbinol. Unless this precaution was taken the carbinols melted low.

From 86 g. of *p*-bromocyclohexylbenzene, 75 g. (65%) of *p*-cyclohexylphenyldiphenylcarbinol was obtained. The product was purified by recrystallization from petroleum ether (b. p. 90–100°) and then melted at 95–96°.

Anal.[10] Calcd. for $C_{25}H_{26}O$: C, 87.72; H, 7.60. Found: C, 87.55; H, 7.62.

From 239 g. of bromo compound, 65 g. (30%) of phenyldicyclohexylphenylcarbinol was obtained. This product first separated as an oil. A sample dissolved in low-boiling petroleum ether and held at the temperature of solid carbon dioxide for three days deposited a few crystals. When these were added to the main oil it crystallized completely. Recrystallization from petroleum ether (b. p. 90–100°) gave a product melting at 102–103°.

Anal. Calcd. for $C_{31}H_{36}O$: C, 87.73; H, 8.49. Found: C, 88.26; H, 8.66.

From 358 g. of the bromo compound, 80 g. (35%) of tri-*p*-cyclohexylphenylcarbinol was obtained. The first crop of crystals amounted to 65 g. The residual oil was distilled with steam and then washed with low-boiling petroleum ether to give an additional 15 g. of crystals. This second lot of crystals was recrystallized from reagent acetone. The first crop of crystals weighing 3–4 g. was *p,p'*-dicyclohexylbiphenyl.[7] The second crop of crystals was added to the 65 g. of crude product first obtained and all of this carbinol recrystallized from acetone. The pure carbinol thus obtained melted at 180–181°.

Anal. Calcd. for $C_{37}H_{46}O$: C, 87.75; H, 9.09. Found: C, 87.71; H, 9.18.

From the acetone mother liquors 2–3 g. of *p,p'*-dicyclohexylbenzophenone, m. p. 136°,[7] was isolated.

A 3.58-g. sample of *p*-bromocyclohexylbenzene prepared by method (b) was converted to the Grignard reagent and treated with diethyl carbonate. The product was isolated as above. The carbinol thus prepared also melted at 180–181° and a mixture of this sample with a sample of carbinol prepared from *p*-bromocyclohexylbenzene obtained by method (a) also melted at 180–181°.

p-Cyclohexyl Derivatives of Triphenylchloromethane.—The carbinols were dissolved in dry benzene and acetyl chloride and heated for several hours at reflux temperature. The solutions were concentrated and cooled and then an excess of petroleum ether (b. p. 30–60°) was added. The chlorides thus precipitated were recrystallized from absolute ethyl acetate.

p-Cyclohexylphenyldiphenylchloromethane, m. p. 125–126°.

Anal. Calcd. for $C_{25}H_{25}Cl$: Cl, 9.83. Found: Cl, 9.70, 10.19.

Phenyldi-*p*-cyclohexylphenylchloromethane, m. p. 155–156°.

Anal. Calcd. for $C_{31}H_{35}Cl$: Cl, 8.01. Found: Cl, 7.95.

Tri-*p*-cyclohexylphenylchloromethane, m. p. 169–170°.

Anal. Calcd. for $C_{37}H_{45}Cl$: Cl, 6.76. Found: Cl, 6.73.

p-Cyclohexyl Derivatives of Triphenylmethyl Peroxide.—Solutions of the cyclohexylphenylethanes for use in the magnetic susceptibility measurements were prepared by treating solutions of the chloromethanes in benzene with silver and filtering the solutions. After the measurements were made the solutions were exposed to the air and evaporated to dryness. The solid residue thus obtained was dissolved in hot benzene, filtered and diluted with six to ten volumes of absolute alcohol. The peroxides crystallized from this mixture.

p-Cyclohexylphenyldiphenylmethyl peroxide, m. p. 158–159°, was obtained in 65–75% yields.

Anal. Calcd. for $C_{50}H_{50}O_2$: C, 87.98; H, 7.33. Found: C, 88.57; H, 7.47.

Phenyldi-*p*-cyclohexylphenylmethyl peroxide, m. p. 120–121°, was obtained in 55–60% yields.

Anal. Calcd. for $C_{62}H_{70}O_2$: C, 87.94; H, 8.27. Found: C, 88.47; H, 8.39.

Tri-*p*-cyclohexylphenylmethyl peroxide, m. p. 178–179°, was obtained by shaking a benzene solution of the chloromethane with silver in the air and recrystallizing as outlined above. The ethane decomposed so rapidly that by the time the magnetic susceptibility measurements were completed there were too many products in solution to give a peroxide which could be purified.

Anal. Calcd. for $C_{74}H_{90}O_2$: C, 87.92; H, 8.91. Found: C, 87.66; H, 9.26.

p-Cyclohexyl Derivatives of Triphenylcarbinol Ethyl Ether.—The respective carbinols were dissolved in ethyl alcohol, a drop of concentrated hydrochloric acid added, and the solutions boiled for a few minutes. On cooling the ethers crystallized.

p-Cyclohexylphenyldiphenylmethylcarbinol ethyl ether, m. p. 106–107°.

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(10) The analyses reported in this paper are microanalyses and were done by Messrs. L. G. Fauble and W. H. Taylor.

Anal. Calcd. for $C_{27}H_{30}O$: C, 87.57; H, 8.10. Found: C, 87.66; H, 8.14.

Phenyldi-*p*-cyclohexylphenylmethylcarbinol ethyl ether, m. p. 152–153°.

Anal. Calcd. for $C_{33}H_{40}O$: C, 87.61; H, 8.85. Found: C, 88.12; H, 8.94.

Tri-*p*-cyclohexylphenylmethylcarbinol ethyl ether, m. p. 189–190°.

Anal. Calcd. for $C_{39}H_{50}O$: C, 87.64; H, 9.36. Found: C, 87.97; H, 9.40.

Magnetic Susceptibility Measurements.—The magnetic susceptibility measurements were made as previously described.[2] Some difficulty was encountered due to the insolubility of the ethanes and for that reason it is necessary to report some of the details of the preparation of the ethane solutions which were used.

When a 0.2 molar solution of *p*-cyclohexylphenyldiphenylchloromethane (1.802 g. of chloride in 25 cc. of benzene) was shaken with silver, a heavy precipitate formed. This was obviously the ethane since on opening the tube to the air a 60–70% yield of peroxide was obtained and the orange-yellow color of the solution did not fade until the precipitate had completely disappeared. Similar results followed the first attempts to prepare 0.05 molar solutions of the ethane. It was then discovered that traces of undissolved chloromethane in the apparatus seemed to cause the rapid crystallization of ethane. A supersaturated solution of the ethane which could be used in the magnetic susceptibility measurements was obtained by putting 0.08 to 0.1 mole of the chloromethane in the apparatus with benzene, evacuating and sealing the outfit and then gently boiling the benzene until the vapor had condensed over the walls to remove stray crystals. After cooling, the silver was added and the mixture was shaken and filtered. Ethane began to crystallize from the solution in about three to six hours but the measurements could be completed before that happened. The values for dissociation of the ethane obtained on these supersaturated solutions checked well with those calculated from measurements made with a 0.025 molar solution of the ethane. After each measurement the apparatus was opened to the air and the peroxide which formed was isolated. The yields were usually about 70%, showing that the ethane had not undergone complete disproportionation.

No difficulties were encountered in preparing the solutions of the tetra-*p*-cyclohexyldiphenylethane. Measurements were made on both 0.1 and 0,05 molar benzene solutions. These solutions were cherry-red. Magnetic susceptibility measurements showed that this ethane had undergone extensive decomposition after thirty-six hours.

The ethane from tri-*p*-cyclohexylphenylchloromethane was very insoluble. By dissolving 0.305 g. of the chloride in 25 cc. of benzene, shaking with silver for fifteen minutes and filtering, a clear Burgundy-red solution of ethane was obtained. The magnetic susceptibility measurements were made at intervals until no free radical remained in solution. The values for $\chi_{\text{sol.}}$ obtained in these measurements were plotted and extrapolated to zero time[1] and this value used to calculate the degree of dissociation. The errors involved in this measurement may be large as no information is available as to the amount of ethane or radical held by the silver. Since the measured dissociation is 50% the exact concentration of ethane or radical is more important than it is in measurements of solutions which contain less radical. The calculations here are based on the assumption that the ethane in solution is 80% of the theoretical amount at zero time. The uncertainty in the value of 50% for the dissociation is thus about ±7%. The table gives the data on magnetic susceptibility.

MAGNETIC SUSCEPTIBILITY AND DEGREE OF DISSOCIATION OF *p*-CYCLOHEXYL DERIVATIVES OF HEXAPHENYLETHANE

Hexaphenylethane	t, °C.	% Ethane in benzene	$-\chi \times 10^6$ solution	α %	Molarity	$K \times 10^3$	α at 0.1 M %
Di-*p*-cyclohexyl (I)	27	3.0	0.6924	13.5	0.04	3.36	8.5
	26	3.0	.6931	13.0	.04	3.08	8.0
	26	3.7	.6908	12.0	.05	3.23	8.5
	28	1.84	.6938	19.5	.025	4.40	10.0
Tetra-*p*-cyclohexyl (II)	27	8.4	.6838	9.5	.1	4.0	9.5
	27	8.4	.6853	9.0	.1	3.76	9.0
	28	4.5	.6871	15.0	.05	5.28	11.0
	28	4.5	.6864	15.5	.05	5.68	11.0
Hexa-*p*-cyclohexyl (III)	26	1.1	.6938	50	.01		

Summary

The dissociation of di-*p*-cyclohexylphenyltetraphenylethane, tetra-*p*-cyclohexylphenyldiphenylethane and hexa-*p*-cyclohexylphenylethane into free radicals has been measured by the magnetic susceptibility method, The dissociation in benzene at 26–28° is 9 ± 1% in 0.1 M solution, 10 ± 1% in 0.1 M solution and 50 ± 7% in 0.01 M solution, respectively.

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