113°, and thereby established the presence of methylamine.

Pyridine.—Pyridine was not isolated from the pyrolysis products of nicotine over quartz at temperatures of 600° or lower. Pyridine was obtained, however, when nicotine was pyrolyzed at 700° in the presence of quartz or at 500° over activated alumina. The picric acid derivative melted at 168.5 to 170°.

β-Picoline.—Only 1.4 g. of the product distilled at 100 to 135°. Although this fraction appeared to have no definite boiling point, it was shown to be principally β-picoline by its picric acid derivative, which melted at 148.0 to 149.0°. The 4.1 g. distilling at 135.0 to 155.0° was shown to be β-picoline by the same procedure.

β-Ethylpyridine.—The 7.0-g. fraction distilling at 155 to 180° was probably a mixture of β-ethylpyridine and β-vinylpyridine. Repeated recrystallization of the picric acid derivative of this fraction did not yield a pure picrate. Redistillation of the fraction gave a distillate which again yielded an inseparable mixture of picrates, while the residue in the distillation flask yielded a picrate melting at 141 to 143°. The latter compound was identical with β-vinylpyridine picrate.

In Experiment 8, however, the fraction distilling at 155 to 180° yielded a picrate which melted at 128.0 to 129.5°. Since this is the reported melting point of β-ethylpyridine picrate, a synthetic sample of β-ethylpyridine was prepared by the following procedure:

A solution of 7.6 g. of β-acetylpyridine hydrochloride[13] dissolved in 30 ml. of water was added to a solution of 5.6 g. of semicarbazide hydrochloride and 8.0 g. of sodium acetate in 30 ml. of water. After being warmed on the steam-bath for twenty minutes and then cooled in an ice-bath, the semicarbazone acetate salt precipitated. The yield of product after drying *in vacuo* was 13.1 g.

The semicarbazone acetate salt was reduced to β-ethylpyridine by the general method of Wolff and Kishner. Thirteen grams of the semicarbazone acetate salt was mixed with 15.6 g. of sodium ethylate in a distillation flask, which was then heated in an oil-bath. As the oil-bath temperature was gradually increased to 180°, a few grams of liquid distilled which had the smell of alcohol and formed no picrate. The 2.8 g. of liquid distillate obtained at a bath temperature of 180 to 220° formed a picrate melting at 128.5 to 130.0° (cor.) after two crystallizations from water. Stoehr[14] reported 128.0 to 130.0° as the melting point of β-ethylpyridine picrate. The melting point was not depressed when this picrate was mixed with the suspected β-ethylpyridine picrate from the nicotine pyrolysis.

β-Vinylpyridine.—About 0.7 g. of the pyrolysis product distilled at 57.0 to 66.0° (2.7 mm.). The picric acid derivative melted at 142.0 to 144.0°, which is in agreement with the reported melting point of β-vinylpyridine picrate. An authentic sample of β-vinylpyridine was prepared by the dehydration of 3-(α-hydroxyethyl)-pyridine with phosphorus pentoxide.[15] The picrate of the synthetic material melted at 142.0 to 144.0°, and was identical with the picric acid derivative of the pyrolysis product.

Nicotine.—A total of 97.4 g. of unchanged nicotine was recovered from the reaction mixture. The major portion distilled at 104 to 109° (4.9 mm.). The limited number of experiments herein reported indicated that the highest yields of myosmine were obtained under experimental conditions which did not completely destroy the nicotine.

Unidentified Fraction and Residue.—The 4.1-g. fraction distilling at 152.0 to 165.0° (2.8 mm.) was not soluble in water or distillable with steam. No crystalline derivatives were obtained with methyl iodide or picric acid.

The 46.0 g. of distillation residue solidified to an amorphous mass on cooling. No nicotinic acid was isolated from the oxidation products when this residual, resinous material was oxidized with alkaline permanganate. This negative result may indicate that the pyridine nucleus of the nicotine molecule was partially destroyed in the pyrolysis but no conclusive evidence was obtained to confirm this assumption.

Summary

1. Ammonia, methylamine, hydrogen cyanide, pyridine, β-picoline, β-ethylpyridine, β-vinylpyridine, and 3,2′-nicotyrine have been obtained in small quantities from the pyrolysis products of nicotine.

2. Myosmine, a comparatively rare alkaloid, has been obtained in fair yields by the pyrolysis of nicotine over quartz at 570°.

3. A new synthesis of β-ethylpyridine is described.

PHILADELPHIA, PA. RECEIVED FEBRUARY 7, 1944

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[13] Strong and McElvain, THIS JOURNAL, 55, 816 (1933).

[14] Stoehr, *J. prakt. Chem.*, [2] 45, 38 (1892).

[15] Iddles, Lang and Gregg, THIS JOURNAL, 59, 1945 (1937).

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

The Dissociation of Hexaarylethanes. XVI.[1] Alkyl and Halogen Derivatives

BY C. S. MARVEL, H. W. JOHNSTON, J. W. MEIER, T. W. MASTIN, JOHN WHITSON AND CHESTER M. HIMEL

Earlier papers in this series[2] have shown that in general unsymmetrically substituted hexaarylethanes are less dissociated than are closely related symmetrically substituted ethanes. Thus, di-*p*-*t*-butylphenyltetraphenylethane is dissociated to the extent of 7.5 ± 1% and tetra-*p*-*t*-butylphenyldiphenylethane to the extent of 8.5 ± 1% under the same conditions where hexa-*p*-*t*-butylphenylethane is dissociated to the extent of 20–25%.[2] Likewise di-*p*-tolyl-tetra-*p*-*t*-butylphenylethane and di-*p*-*t*-butylphenyl-tetra-*p*-tolylethane show equal degrees of dissociation of 5 ± 1%. We were accordingly very much surprised to find in the present work that a variety of alkyl substituted hexaarylethanes with mixed *m*- and *p*-substitution showed in general a higher degree of dissociation than many related hexa-*p*-alkylphenylethanes. We have no theory to account for the unexpected values which are reported here, for the work was stopped before a sufficiently large variety of compounds could be studied to make generalization significant.

The *p*-*t*-butyl group seems to have a very marked effect in promoting dissociation in the

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(1) For the fifteenth communication in this series, see THIS JOURNAL, 66, 415 (1944).

(2) Marvel, Kaplan and Himel, THIS JOURNAL, 63, 1892 (1941); Marvel and Himel, *ibid.*, 64, 2227 (1942).

TABLE I

DISSOCIATION OF SUBSTITUTED HEXAARYLETHANES

Ethane	% in Benzene	Molarity	$-\chi_{\text{sol.}} \times 10^6$	α, % (observed)	α, % 0.1 *M* (calcd.)
Tetra-*m*-cyclohexylphenyl-di-*p*-cyclohexylphenyl	11	0.1	0.6000	39	39
Tetra-*p*-cyclohexylphenyl-di-*m*-cyclohexylphenyl	5.6	.05	.6757	21	16
Di-*p*-*t*-butylphenyltetra-*m*-cyclohexylphenyl	5.3	.05	.6616	27	20
Di-*m*-tolyltetra-*p*-*t*-butylphenyl	8.4	.1	.5908	42	42
	8.4	.1	.6160	33	33
	8.4	.1	.5891	42	42
Di-*o*-tolyltetra-*p*-*t*-butylphenyl	4.25	.05	.6003	76	65
	3.85	.046	.6045	80.4	68
Di-*m*-bromophenyltetra-*p*-*t*-butylphenyl	11.6	.1	.5869	40	40
	11.4	.1	.5841	38	38
Di-*o*-bromophenyltetra-*p*-*t*-butylphenyl	5.8	.05	.5618	97	94
	5.8	.05	.5566	100	
Diphenyltetra-*p*-fluorophenyl	3.2	.05	.6948	7.2	5.3
	3.2	.05	.6903	10.2	7.6
Hexa-*p*-fluorophenyl	3.4	.05	.7111	5.2	3.8
Tetraphenyldi-*m*-fluorophenyl	5.9	.1	.6885	5.8	5.8
	4.4	.073	.6952	5	4
Diphenyltetra-*m*-fluorophenyl	6.4	.1	.6856	5.5	5.5
	6.3	.1	.6902	3.9	3.9
Tetra-*p*-tolyldi-*m*-tolyl	6.5	.1	.7011	2.1	2.1

hexaarylethanes of this type. For example, di-*o*-tolyl-tetraphenylethane shows a dissociation of 25 ± 1%[2] whereas introduction of four *p*-*t*-butyl groups in its four unsubstituted benzene rings raises the dissociation of the ethane to 65–68%. Likewise di-*o*-bromophenyltetraphenylethane shows a dissociation of 17 ± 1%[3] whereas di-*o*-bromophenyltetra-*p*-*t*-butylphenylethane shows a value of 94%.

The hexaarylethanes substituted with cyclohexyl groups in the *m*- and *p*-position were prepared in the hope that one would be identical with the hexacyclohexylphenylethane described earlier[4] as the pure *para* isomer but later shown[5] to be a mixture of mixed *m*- and *p*-derivatives. This hope was not realized. It should be noted, however, that the magnetic susceptibility measurements reported on tetra-*p*-cyclohexylphenyl-di-*m*-cyclohexylphenylethane may be low, as this ethane has a tendency to crystallize from a 0.05 *M* solution. However, a more dilute solution gave unsatisfactory readings. All of the ethanes having *p*-cyclohexylphenyl groups were very unstable and in a few hours decomposed in solution as shown by magnetic susceptibility measurements. The *p*-*t*-butylphenyl substituted ethanes were stable in benzene solution over a period of twenty-four hours.

Since it is doubtful when work on this general problem can again be taken up in this Laboratory, we are recording in this paper some fluorine substituted hexaphenylethanes whose dissociations have been checked by the magnetic susceptibility methods. We are also recording a variety of intermediates which have been prepared in anticipation of further study of related ethanes.

The fluoro substituted ethanes showed marked decomposition when their solutions stood for twenty-four hours.

The values for the dissociation of the ethanes (α) recorded in Table I were obtained by the magnetic susceptibility method.[6]

Experimental

***p*-*t*-Butylbenzoic Acid.**—This compound was prepared by the general method illustrated in "Organic Syntheses"[7] for the conversion of *t*-butyl chloride to *t*-butylacetic acid. Thirty-four and seven-tenths grams of magnesium turnings, covered with 100 cc. of dry ether, and 304 g. of *p*-*t*-butylbromobenzene in 300 cc. of dry ether were used for making the Grignard reagent. The crude *p*-*t*-butylbenzoic acid was twice recrystallized from ethanol and water to yield 198 g. (78%) of a product which melted at 164°. Kelbe and Pfeiffer[8] have reported a melting point of 164°.

Ethyl *p*-*t*-Butylbenzoate.—A procedure similar to that used in the preparation of ethyl *m*-methoxybenzoate[9] was followed with the exception that calcium carbide was used to fill the extraction shell. One hundred and twenty-four grams of *p*-*t*-butylbenzoic acid, 1000 cc. of absolute ethanol, 200 cc. of dry benzene and 4 cc. of concentrated sulfuric acid were used as reactants. The reaction mixture was refluxed for seventy-two hours and was then worked up as described in the previous preparation. The yield was 108 g. (75%) of product; b. p. 120–120.5° (4 mm.).

Anal. Calcd. for $C_{13}H_{18}O_2$: C, 75.72; H, 8.74. Found: C, 75.62; H, 8.63.

Cyclohexylbenzene.—Cyclohexylbenzene was prepared according to the procedure given in "Organic Syntheses."[10] The product boiled at 237–238° (740 mm.).

***p*-Bromocyclohexylbenzene.**—The bromination of cyclohexylbenzene was carried out according to directions given

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[3] Marvel, Dietz and Himel, *J. Org. Chem.*, **7**, 392 (1942).

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

[5] Marvel and Himel, *ibid.*, **62**, 1550 (1940).

[6] Mueller, Mueller-Rodloff and Bunge, *Ann.*, **520**, 235 (1935); Roy and Marvel, THIS JOURNAL, **59**, 2622 (1937).

[7] Gilman and Kirby, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., second edition, 1941, p. 361.

[8] Kelbe and Pfeiffer, *Ber.*, **19**, 1723 (1886).

[9] Marvel, Whitson and Johnston, THIS JOURNAL, **66**, 415 (1944).

[10] Corson and Ipatieff, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 151.

by Marvel and Himel.[9] The yield of bromo compound was 85% of the theoretical amount; b. p. 135–137° (6 mm.).

***p*-Aminocyclohexylbenzene.**—This compound was prepared by reduction of *p*-nitrocyclohexylbenzene over Raney nickel in 85% yield; m. p. 53–54°.

***p*-Cyclohexylacetanilide.**—Four hundred and seventy-eight grams of *p*-aminocyclohexylbenzene was dissolved in 400 cc. of glacial acetic acid. One gram of zinc dust was added and the solution refluxed for seven hours. Connected to the reaction flask was an air condenser made of an 18-mm. Pyrex tube 120 cm. long. The flame was adjusted so that the condensing vapors of acetic acid remained about 15 cm. from the top of the condenser. By this means, most of the water formed in the acylation was lost through the air condenser thus forcing the reaction forward. This technique is described by Fieser[11] for the preparation of acetanilide.

The hot acetic acid solution was poured into 7 liters of cold water. The precipitated product was filtered off, washed with water and recrystallized from 50% ethyl alcohol. The yield of *p*-cyclohexylacetanilide was 507 g. (86%); m. p. 129–130°. Ipatieff and Schmerling reported a melting point of 130–131°.[12]

2-Bromo-4-cyclohexylacetanilide.—Six hundred and thirty-two grams of *p*-cyclohexylacetanilide was dissolved in 1800 cc. of glacial acetic acid and 3 g. of powdered iron was added to the solution. The reaction vessel was a 3-liter, three-necked flask equipped with a gas trap, dropping funnel and stirrer. The stirrer was started and 480 g. of bromine was added dropwise to the reaction mixture. The temperature was kept between 30 and 40° by means of a cold bath. When about one-third of the bromine had been added, a solid began to precipitate. Stirring was continued for five hours after all the bromine had been added; then the reaction mixture was poured into 12 l. of vigorously stirred cold water. The precipitate was filtered off, washed with water and partially dried. The crude material was recrystallized twice from 70% ethanol. The yield was 580 g. (71.5%) of a product melting at 122–123°.

Hydrolysis of 2-Bromo-4-cyclohexylacetanilide.—Five hundred and eighty grams of 2-bromo-4-cyclohexylacetanilide was dissolved in a mixture of 1600 cc. of 95% ethanol and 1000 cc. of concentrated hydrochloric acid. The solution was boiled for two or three minutes before the hydrochloride started crystallizing out. At this point a cold water-bath was used to prevent the alcohol from going out the top of the condenser. After this initial vigorous reaction had subsided, the solution was refluxed for two hours. The mixture was cooled and the product separated on a Büchner funnel, washed once with cold 95% ethanol and allowed to dry. The yield of 2-bromo-4-cyclohexylaniline hydrochloride was 564 g. (98%); m. p. 207° with decomposition.

***m*-Bromocyclohexylbenzene.**—In a 5-liter flask equipped with a dropping funnel, stirrer and thermometer were placed 363 g. of 2-bromo-4-cyclohexylaniline hydrochloride, 1800 cc. of glacial acetic acid, 1200 cc. of water, and 400 cc. of concentrated hydrochloric acid. The stirrer was started and the mixture cooled to 0–5° in an ice-bath. From the dropping funnel was added slowly 92 g. of sodium nitrite dissolved in 500 cc. water. The temperature was kept between 0 and 5° throughout the addition of sodium nitrite solution. The clear diazonium solution (0°) was poured into 2200 cc. of cold (0°) 30% hypophosphorous acid and the total solution allowed to stand in an icebox at 5° for three days. The flask was removed and allowed to stand at room temperature for an additional day. The red-colored oil which separated was removed by use of a separatory funnel, dissolved in ether, washed with water, 5% sodium hydroxide solution and again with water. The ether solution was dried over calcium chloride, the ether removed and the product distilled. The yield of *m*-bromocyclohexylbenzene was 236 g. (79%); b. p. 122–123° (4 mm.); $n^{20}D$ 1.5602.

Anal. Calcd. for $C_{12}H_{15}Br$: C, 60.25; H, 6.29. Found: C, 60.58; H, 6.43.

***p*-Bromo-*t*-butylbenzenes.**—In a 3-liter, three-necked flask equipped with a mechanical stirrer, dropping funnel and reflux condenser leading to a trap for absorption of hydrogen bromide, were placed 375 g. of *t*-butylbenzene[13] and 5 g. of iron powder. The mixture was stirred and cooled by an ice-bath to 0–5°. From the dropping funnel was added, over a period of one to two hours, 500 g. of bromine. Stirring was continued for two hours after all the bromine had been added. The reaction mixture was allowed to stand overnight and then washed with 5% sodium sulfite solution, twice with 5% sodium carbonate solution, twice with water and dried over calcium chloride. The product was distilled from a modified Claisen flask and collected at 80–81° (2 mm.). The yield of *p*-bromo-*t*-butylbenzene was 444 g. (75%). This method of preparation is faster than that described in a previous paper of this series.[14]

***p*-Amino-*t*-butylbenzene.**—This compound was prepared by reduction of *p*-nitro-*t*-butylbenzene over Raney nickel catalyst in a manner similar to that used for the preparation of *p*-aminocyclohexylbenzene. The yield was 298 g. (73%) of product from 488 g. of *p*-nitro-*t*-butylbenzene. The boiling point was 90–93° (3 mm.).

***m*-Bromo-*t*-butylbenzene.**—This compound was synthesized in a manner similar to that used for *m*-bromocyclohexylbenzene. The product boiled at 222–223° (740 mm.); $n^{20}D$ 1.5279.

Anal. Calcd. for $C_{10}H_{13}Br$: Br, 37.56. Found: Br, 38.51.

Ethyl *p*-Cyclohexylbenzoate.—A procedure similar to that used in the preparation of ethyl *m*-methoxybenzoate[9] was followed. From 204 g. of *p*-cyclohexylbenzoic acid, 800 cc. of absolute ethanol, and 5 cc. of concentrated sulfuric acid there was obtained 214 g. (92%) of product; m. p. 58–60°.

***m*-Cyclohexylbenzoic Acid.**—This compound was prepared in a manner similar to that for the preparation of *p*-*t*-butylbenzoic acid. From 24.3 g. of magnesium, and 240 g. of *m*-bromocyclohexylbenzene there was obtained 159 g. (68%) of product; m. p. 120–121°.

Anal. Calcd. for $C_{13}H_{16}O_2$: C, 76.50; H, 7.85. Found: C, 77.05; H, 8.18.

Esterification of *m*-Cyclohexylbenzoic Acid.—The esterification was carried out exactly as the esterification of the *para* isomer.[9] The yield of ester from a one mole run was 204 g. (88%); b. p. 137–139° (3 mm.); $n^{20}D$ 1.5239.

Anal. Calcd. for $C_{15}H_{20}O_2$: C, 77.59; H, 8.62. Found: C, 77.65; H, 8.77.

Ethyl *m*-Toluate.—Seventy-five grams of *m*-toluic acid (m. p. 107–109°) was esterified with 600 cc. of absolute ethanol, 150 cc. of dry benzene and 3 cc. of concentrated sulfuric acid.[9] Five grams of *m*-toluic acid was recovered, and on this basis the yield was 55 g. (64%) of product which boiled at 117° (15 mm.).

Another preparation was made using 200 g. of *m*-toluic acid. The extractor was in this case filled with calcium carbide. The yield was 218 g. (90%) of a product which boiled at 95–97° (15 mm.).

Ethyl *o*-Toluate.—A procedure similar to that for the preparation of ethyl *m*-toluate was used. From 175 g. of *o*-toluic acid, 1200 cc. of absolute ethanol and 4 cc. of concentrated sulfuric acid there was obtained 155 g. (75.5%) of ester; b. p. 88–92° (5 mm.).

Ethyl *o*-Bromobenzoate.—From 165 g. of *o*-bromobenzoic acid, 110 cc. of absolute ethanol, and 6 cc. of concentrated sulfuric acid there was obtained 150 g. (82%) of ester which distilled at 117° (17 mm.).

Ethyl *m*-Bromobenzoate.—In a manner similar to that used for the above esters, 100 g. of *m*-bromobenzoic acid was esterified, using 1000 cc. of absolute ethanol and 3 cc.

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(11) Fieser, "Experiments in Organic Chemistry," D. C. Heath Co., New York, N. Y., 1935, p. 163.

(12) Ipatieff and Schmerling, THIS JOURNAL, **59**, 1056 (1937).

(13) Huston, Fox and Binder, *J. Org. Chem.*, **3**, 251 (1938).

(14) Marvel, Mueller, Himel and Kaplan, THIS JOURNAL, **61**, 2771 (1939).

TABLE II

TRIARYLCHLOROMETHANES

Chloromethane	Solvent	M. p., °C.	Active chlorine analyses, %	
			Calcd.	Found
Phenyldi-*p*-chlorophenyl-	Low-boiling petroleum ether	50–51	10.22	10.11
Di-*m*-cyclohexylphenyl-*p*-cyclohexylphenyl	Ethyl acetate and low boiling petroleum ether	151–152	6.77	7.07
Di-*p*-cyclohexylphenyl-*m*-cyclohexylphenyl		172–173	6.77	6.65
Di-*m*-cyclohexylphenyl-*p*-*t*-butylphenyl	Ethyl acetate and low boiling petroleum ether	133–134	7.11	6.78
Di-*m*-*t*-butylphenyl-*p*-cyclohexylphenyl		127–129	7.53	7.26
o-Tolyldi-*p*-*t*-butylphenyl	Mixed petroleum ether	171–172	8.77	8.79
m-Tolyldi-*p*-*t*-butylphenyl	Ethyl acetate	132–133	8.77	8.52
o-Bromophenyldi-*p*-*t*-butylphenyl	Petroleum ether	135–136	7.56	7.77
m-Bromophenyldi-*p*-*t*-butylphenyl	Mixed petroleum ether	144–145	7.56	7.27
Diphenyl-*m*-fluorophenyl	Low boiling petroleum ether	84–84.5	11.94	12.12
Phenyldi-*m*-fluorophenyl	Low boiling petroleum ether	72.5–73	11.28	11.57
Tri-*m*-fluorophenyl	Ethyl acetate[a]	92–93	10.66	10.92
Phenyldi-*m*-chlorophenyl	Mixed petroleum ether	57–59	10.21	10.10
Tri-*m*-chlorophenyl	High boiling petroleum ether	90–92	9.32	9.57
m-Tolyldi-*p*-tolyl	Ethyl acetate[b]	67–69	11.05	10.92

[a] The chloromethane was best prepared by refluxing the carbinol in dry ethyl acetate for two hours with a large excess acetyl chloride. [b] It was found that the usual refluxing with acetyl chloride and benzene resulted in low yields of chloromethane. A less vigorous treatment consisted of treating the carbinol with a large excess of acetyl chloride for forty-five minutes at room temperature. The excess acetyl chloride was removed under vacuum and the resultant oil recrystallized from dry ethyl acetate containing a trace of acetyl chloride.

of sulfuric acid. The yield was 98 g. (88%); b. p. 115° (7 mm.).

Ethyl *m*-Chlorobenzoate.—From 20 g. of *m*-chlorobenzoic acid, 140 cc. of absolute ethanol and 1 cc. of concentrated sulfuric acid there was obtained in the usual manner 19 g. (81%) of product; b. p. 85–86° (5 mm.).

Phenyl-di-*p*-chlorophenylcarbinol.—The carbinol was prepared in good yield from 17 g. of magnesium, 128 g. of *p*-bromochlorobenzene and 50 g. of ethyl benzoate. The carbinol melted at 87–88° after recrystallization from high petroleum ether. Gomberg and Cone[15] reported a melting point of 87°.

***p*-*t*-Butylphenyl-di-*m*-tolylcarbinol.**—The crude carbinol was prepared from 35 g. of magnesium, 246.3 g. of *m*-bromotoluene and 108 g. of ethyl *p*-*t*-butylbenzoate. It could not be caused to crystallize even though distilled (b. p. 175° (1 mm.)). It was converted into the ethyl ether by treatment of the oily residue with an excess of hot absolute ethanol and a few cc. of concentrated sulfuric acid for two hours. When the solution was cooled, crystallization occurred. After recrystallization from absolute ethanol the yield was 180 g. (67%); m. p. 79–80°.

Anal. Calcd. for $C_{27}H_{32}O$: C, 87.05; H, 8.66. Found: C, 87.06; H, 8.76.

Di-*m*-cyclohexylphenyl-*p*-cyclohexylphenylcarbinol.—From 135 g. of ethyl-*p*-cyclohexylbenzoate, 239 g. of *m*-bromocyclohexylbenzene and 24 g. of magnesium turnings 128 g. (49%) of product was recovered; m. p. 139°, recrystallized from a mixture of dry ethyl acetate and low boiling petroleum ether.

Anal. Calcd. for $C_{37}H_{48}O$: C, 87.87; H, 8.97. Found: C, 87.64; H, 9.01.

Di-*p*-cyclohexylphenyl-*m*-cyclohexylphenylcarbinol.—The same procedure that was used in the preparation of di-*m*-cyclohexylphenyl-*p*-cyclohexylphenylcarbinol was followed. From 24 g. of magnesium, 135 g. of ethyl *m*-cyclohexylbenzoate and 239 g. of *p*-bromocyclohexylbenzene there was obtained an oil which could not be caused to crystallize. A crystalline chloromethane was obtained from this product as described later.

Di-*m*-cyclohexylphenyl-*p*-*t*-butylphenylcarbinol.—From 239 g. of *m*-bromocyclohexylbenzene, 24 g. of magnesium and 103 g. of ethyl *p*-*t*-butylbenzoate an oil was obtained which was converted into a crystalline chloromethane as described later.

Di-*m*-*t*-butylphenyl-*p*-cyclohexylphenylcarbinol.—From 213 g. of *m*-bromo-*t*-butylbenzene, 24 g. of magnesium and 135 g. of ethyl *p*-cyclohexylbenzoate there was obtained an oil which was converted into a crystalline chloromethane as described later.

***o*-Tolyl-di-*p*-*t*-butylphenylcarbinol.**—From 82 g. of ethyl-*o*-toluate, 213 g. of *p*-bromo-*t*-butylbenzene, and 24 g. of magnesium there was recovered 70 g. (32%) of crude crystals. Recrystallization from petroleum ether yielded a product which melted at 129.5–130°.

Anal. Calcd. for $C_{28}H_{34}O$: C, 87.07; H, 8.80. Found: C, 87.23; H, 8.99.

***m*-Tolyl-di-*p*-*t*-butylphenylcarbinol.**—From 213 g. of *p*-bromo-*t*-butylbenzene, 24 g. of magnesium and 74 g. of ethyl *m*-toluate an oil was obtained which was converted into a crystalline chloromethane as described later.

***o*-Bromophenyl-di-*p*-*t*-butylphenylcarbinol.**—From 70 g. of ethyl-*o*-bromobenzoate, 130 g. of *p*-bromo-*t*-butylbenzene, and 14.6 g. of magnesium there was recovered 60 g. (43%) of crude carbinol; m. p. 136.5–137° after recrystallization from high boiling petroleum ether.

Anal. Calcd. for $C_{27}H_{31}OBr$: C, 71.84; H, 6.87. Found: C, 72.01; H, 6.95.

***m*-Bromophenyl-di-*p*-*t*-butylphenylcarbinol.**—From 90 g. of *p*-bromo-*t*-butylbenzene, 9.9 g. of magnesium and 47 g. of ethyl *m*-bromobenzoate there was obtained an oil which could not be caused to crystallize. A crystalline chloromethane was obtained from this product as described later.

Phenyl-di-*p*-fluorophenylcarbinol.—The crude carbinol has been prepared by Bacon and Gardner.[16] A white crystalline product melting at 100° was obtained after several recrystallizations from petroleum ether.

Anal. Calcd. for $C_{19}H_{14}OF_2$: C, 77.03; H, 4.73. Found: C, 77.03; H, 4.76.

Tri-*p*-fluorophenylcarbinol.—Bacon and Gardner[16] obtained the crystalline carbinol but did not report the melting point or analysis. We have recrystallized the carbinol from low petroleum ether; m. p. 94°.

Anal. Calcd. for $C_{19}H_{13}OF_3$: C, 72.61; H, 4.14. Found: C, 72.63; H, 4.25.

Diphenyl-*m*-fluorophenylcarbinol.—From 82 g. of benzophenone, 80 g. of *m*-fluorobromobenzene, and 10.9 g. of magnesium there was obtained 100 g. (80%) of the crude

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[15] Gomberg and Cone, *Ber.*, **39**, 1461 (1906).

[16] Bacon and Gardner, *J. Org. Chem.*, **3**, 283 (1938).

TABLE III

PEROXIDES

Radical	Formula	M. p., °C.	Analyses, % Calcd. C	Calcd. H	Found C	Found H
Di-*m*-cyclohexylphenyl-*p*-cyclohexylphenylmethyl	$C_{74}H_{90}O_2$	169-170	87.8	8.97	87.47	9.16
Di-*p*-cyclohexylphenyl-*m*-cyclohexylphenylmethyl	No peroxide isolated					
p-*t*-Butylphenyl-di-*m*-cyclohexylphenylmethyl	$C_{70}H_{82}O_2$	163-164.5	87.99	8.66	88.11	9.27
o-Tolyldi-*p*-*t*-butylphenylmethyl	$C_{56}H_{66}O_2$	159-161	87.23	8.62	87.41	8.46
m-Tolyldi-*p*-*t*-butylphenylmethyl	$C_{56}H_{66}O_2$	185-186	87.23	8.62	87.24	8.54
o-Bromophenyldi-*p*-*t*-butylphenylmethyl	No peroxide isolated					
m-Bromophenyldi-*p*-*t*-butylphenylmethyl	No peroxide isolated					
Phenyldi-*p*-fluorophenylmethyl	No peroxide isolated					
Tri-*p*-fluorophenylmethyl	No peroxide isolated					
Diphenyl-*m*-fluorophenylmethyl	$C_{38}H_{28}O_2F_2$	173-174	82.29	5.10	82.44	5.32
Phenyldi-*m*-fluorophenylmethyl	$C_{38}H_{26}O_2F_4$	169-170	77.27	4.43	77.24	4.54
Di-*p*-tolyl-*m*-tolylmethyl	No peroxide isolated					

carbinol, which, after recrystallization from high boiling petroleum ether, melted at 117°.

Anal. Calcd. for $C_{19}H_{15}OF$: C, 82.01; H, 5.40. Found: C, 81.96; H, 5.48.

Phenyl-di-*m*-fluorophenylcarbinol.—From 25.7 g. of ethyl benzoate, 60 g. of *m*-fluorobromobenzene, and 8.25 g. of magnesium, 35 g. (70%) of crude carbinol was obtained; m. p. 114–114.5°, recrystallized from high boiling petroleum ether.

Anal. Calcd. for $C_{19}H_{14}OF_2$: C, 77.03; H, 4.73. Found: C, 77.19; H, 4.85.

Tri-*m*-fluorophenylcarbinol.—From 20.8 g. of ethyl carbonate, 100 g. of *m*-fluorobromobenzene, and 13.7 g. of magnesium 40 g. (80%) of crude carbinol was isolated; m. p. 118.5–119° after recrystallization from high boiling petroleum ether.

Anal. Calcd. for $C_{19}H_{13}OF_3$: C, 72.61; H, 4.14. Found: C, 72.76; H, 4.13.

Phenyl-di-*m*-chlorophenylcarbinol.—From 125 g. of *m*-chlorobromobenzene, 15.6 g. of magnesium and 47 g. of ethyl benzoate a concentrated oil was obtained which failed to crystallize. A crystalline chloromethane was obtained from this product as described later.

Tri-*m*-chlorophenylcarbinol.—From 39.5 g. of *m*-bromochlorobenzene, 5 g. of magnesium, and 19 g. of ethyl *m*-chlorobenzoate a concentrated oil was obtained which was converted into a crystalline chloromethane as described later.

***m*-Tolyldi-*p*-tolylcarbinol.**—From 67 g. of ethyl *m*-toluate, 150 g. of *p*-bromotoluene, and 21 g. of magnesium, 78 g. (62%) of crude carbinol was obtained; m. p. 95–96° after recrystallization from petroleum ether.

Anal. Calcd. for $C_{22}H_{22}O$: C, 87.44; H, 7.28. Found: C, 87.44; H, 7.42.

Triarylchloromethanes.—The chloromethanes were prepared by treating the carbinols in dry benzene with excess acetyl chloride.[17] They are described in Table II.

Preparation of Peroxides.—After the magnetic susceptibility measurements had been completed the benzene solutions of the ethanes were exposed to air and then worked up for peroxides. The yields of pure crystalline peroxide usually ran about 40–60% of the theoretical. The peroxides were crystallized from benzene by the addition of five to six volumes of absolute alcohol and slow evaporation of the resultant solution at room temperature. Recrystallization was accomplished by redissolving the crystals in hot dry benzene and addition of absolute alcohol in large excess to the hot solution after which the solvent was permitted to evaporate at room temperature.

The new peroxides are listed in Table III.

Summary

Twelve new substituted hexaarylethanes containing different alkyl groups and various halogen atoms have been prepared and their dissociations measured by the magnetic susceptibility method. Some related derivatives have been characterized and the methods of preparation are reported.

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[17] Gomberg, *Chem. Rev.*, 1, 91 (1924).