from 4-bromo-2-phenylphenol, which had been obtained by the bromination of 2-phenylphenol; m. p. 138–139.5°. Ethanol, ethanol-water (1:1), and ligroin were found to serve as suitable solvents for recrystallization.

*Anal.*[6] Calcd. for $C_{14}H_{11}O_3Br$: Br, 26.06; neut. equiv., 307. Found: Br, 26.1; neut. equiv., 305.

The two samples were shown to be the same compound; mixtures of them melted without depression at 138–139°.

**4,6-Dibromo-2-phenylphenyl Acetate.**—(a) The residue (3 g.) after the distillation of 4-bromo-2-phenylphenyl acetate solidified on cooling and was crystallized from ligroin. Light yellow needles resulted, m. p. 73–74°.

(b) Ten grams of 2-phenylphenyl acetate was dissolved in 20 ml. of glacial acetic acid and treated in exactly the same manner as in the monobromination of this ester except that more bromine (18.8 g. or approximately 2.5 molecular proportions) was added. The heating and stirring were continued for eleven hours. The product was recovered in the same manner as the monobromo compound, and, after crystallization from ligroin, an 80% yield (14 g.) of fine, colorless needles resulted; m. p. 73–74°.

*Anal.* Calcd. for $C_{14}H_{10}O_2Br_2$: Br, 43.24. Found: Br, 43.3.

(c) This compound was prepared also by the following procedure. Five grams of 4,6-dibromo-2-phenylphenol was refluxed gently for three hours with 10 ml. of acetic anhydride to which had been added 1 g. of anhydrous sodium acetate. The ester was recovered in the usual way, and a nearly quantitative yield (5.6 g.) of a viscous yellow oil was obtained. This was crystallized from ligroin (boiling range 70 to 90°), and colorless needles resulted; m. p. 73–74°.

The three samples which were obtained by the methods described above were shown to be the same compound; mixtures of them melted without depression at 73–74°.

**Hydrolysis of 4,6-Dibromo-2-phenylphenyl Acetate.**—Four grams of the dibromo ester, which had been prepared by method (b), was refluxed for sixty hours in a solution containing 22 g. of sodium hydroxide and 50 ml. each of ethanol and water. Two and five-tenths grams (70% yield) of the phenolic component was obtained, and, after recrystallization from ligroin (boiling range 70 to 90°), light yellow needles were obtained; m. p. 59–60°.

That this was 4,6-dibromo-2-phenylphenol was demonstrated by mixing equal amounts of this sample and 4,6-dibromo-2-phenylphenol, which had been prepared by the method of Auwers and Wittig; the mixture melted without depression at 58–60°.

**4,6-Dibromo-2-phenylphenoxyacetic Acid.**—4,6-Dibromo-2-phenylphenol, which had been prepared by the method of Auwers and Wittig, was treated with chloroacetic acid as in the preparation of 4-bromo-2-phenylphenoxyacetic acid. The procedure was carried out a number of times, but in each case the yield was very low; *e. g.*, 0.4 g. (8.5% yield) of the aryloxyacetic acid was obtained from 4 g. of the phenol. (The major portion of the phenol was recovered.) From ligroin the compound was obtained as long, colorless needles; m. p. 123–124°.

*Anal.* Calcd. for $C_{14}H_{10}O_3Br_2$: Br, 41.5; neut. equiv. 386. Found: Br, 41.6; neut. equiv., 394.

## Summary

The bromination of 2-phenylphenyl acetate, as is the case with the 4-isomer, proceeds in a manner which is strictly analogous to that of the corresponding phenol. The first bromine atom enters the molecule in the position para with respect to the acetyloxy group, and the second bromine goes to the available ortho position.

4,6-Dibromo-2-phenylphenoxyacetic acid has been prepared, but the yield is very poor.

PULLMAN, WASHINGTON RECEIVED APRIL 21, 1941

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[6] In ref. 3b carbon and hydrogen analyses were reported.

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

# Alkyl Substituted Hexaarylethanes. XI.[1] Symmetry and Steric Effects as Factors in Dissociation

BY C. S. MARVEL, JULIUS F. KAPLAN AND CHESTER M. HIMEL

In previous communications from this Laboratory it has been shown[2] that the introduction of two *para*-alkyl groups into a hexaarylethane (I) gives an ethane which is dissociated to the extent of 5 to 10% at 0.1 molar concentration; whereas, if six alkyl groups are introduced in similar positions (III) the effect upon the dissociation is more marked and the free radical exists to the extent of 17 to 27% at 0.08 molar concentration. Where R is cyclohexyl,[1] the disubstituted ethane dissociates to the extent of 9% at 0.1 molar solution and the hexasubstituted to the extent of 50 ± 7% in 0.01 molar solution. Strangely enough the tetrasubstituted ethane (II, R = cyclohexyl) is no more dissociated than is the disubstituted ethane at the same concentration. This surprising result led us to prepare a number of di- and tetraalkyl substituted ethanes with the alkyl groups in the ortho-, meta- and para-positions. Magnetic susceptibility measurements

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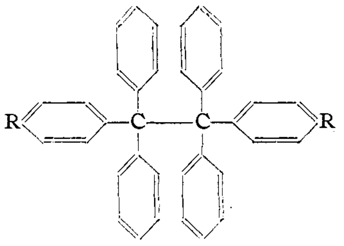
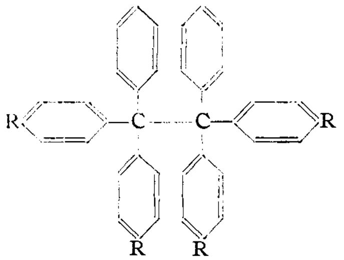
[1] For the tenth communication see THIS JOURNAL, **62**, 1550 (1940).

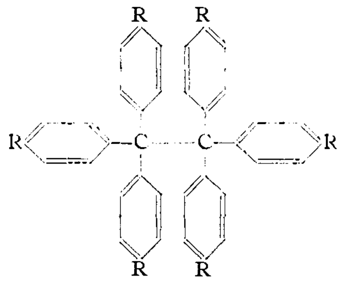
[2] Marvel, Mueller, Himel and Kaplan, *ibid.*, **61**, 2771 (1939).



I



II



III

were used to determine the degree of dissociation of the ethane.[3] The results of these studies are summarized in Table I.

TABLE I

DISSOCIATION OF DI- AND TETRAALKYLHEXAARYLETHANES AT 0.1 *M* AND 25°

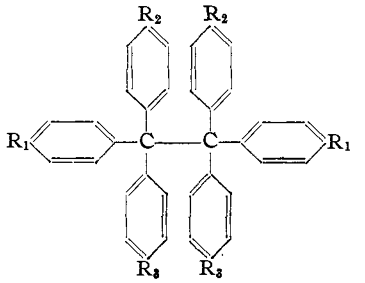
| Alkyl group and position | Dissociation of: Disubstituted ethane, % | Tetrasubstituted ethane, % | Hexasubstituted ethane, % |
|---|---|---|---|
| *p*-$CH_3$ | 5 ± 1[2] | 5.5 ± 1 | 16 ± 2[4] |
| *m*-$CH_3$ | 6.5 ± 1 | 7.0 ± 1 | 40 ± 2[2] |
| *o*-$CH_3$ | 25 ± 1[2] | 82.0 ± 2 | ... |
| *o*-$C_2H_5$ | 33.0 ± 2 | ... | ... |
| *p*-*n*-$C_3H_7$ | 6.5 ± 1 | ... | 21 ± 2[2] |
| *p*-*i*-$C_3H_7$ | 8–10 ± 1[2] | 8.0 ± 1 | 26 ± 2[2] |
| *p*-*n*-$C_4H_9$ | ... | ... | 20 ± 2 |
| *p*-*i*-$C_4H_9$ | 7.5 ± 1 | ... | 27 ± 2[2] |
| *p*-*s*-$C_4H_9$ | 7.5 ± 1 | 8.5 ± 1 | 33 ± 2[2] |
| *p*-*t*-$C_4H_9$ | 7.5 ± 1 | 8.5 ± 1 | 43 ± 4 (0.0125 *M*) |
| *p*-*t*-$C_5H_{11}$ | 7.5 ± 1 | 9.0 ± 1 | 40 ± 2 (0.05 *M*) |
| *m*-*n*-$C_5H_{11}$ | 9.0 ± 1 | ... | ... |

Results now available show several very interesting facts. Alkyl groups in the ortho-positions have a very marked effect on dissociation. The 33% dissociation of di-*o*-ethylphenyltetraphenyl ethane and the 82% dissociation of tetra-*o*-tolyldiphenylethane show that the ortho-effect or steric factor is certainly an extremely important one in producing dissociation. With the alkyl groups in the para-positions, there is little difference between the degree of the dissociation of the di- and tetrasubstituted ethanes, as evidenced by the 5% dissociation of di-*p*-tolyltetraphenylethane[2] and the 5.5% dissociation of tetra-*p*-tolyldiphenylethane. The hexasubstituted ethanes, on the other hand, are dissociated to a much greater extent in every case. This seems to indicate that symmetry of the ethanes is a factor in dissociation.

If symmetry is an important factor in dissociation, hexa-*p*-alkylphenylethanes having unlike alkyl substituents might be expected to show a degree of dissociation much below that of symmetrical hexasubstituted ethanes. In order to test this last point a number of ethanes having unlike alkyl groups in various *para*-positions have been prepared and their dissociations measured. The results are listed in Table II.

TABLE II

DISSOCIATION OF HEXAARYLETHANE OF THE TYPE



| $R_1$ | $R_2$ | $R_3$ | Dissociation of ethane at 0.1 *M* and 25°, % |
|---|---|---|---|
| H | $CH_3$ | $C_2H_5$ | 6.0 ± 1 |
| H | $CH_3$ | *t*-$C_4H_9$ | 6.5 ± 1 |
| $CH_3$ | $CH_3$ | *t*-$C_4H_9$ | 5.0 ± 1 |
| $CH_3$ | *t*-$C_4H_9$ | *t*-$C_4H_9$ | 5.0 ± 1 |
| $CH_3$ | $C_2H_5$ | *i*-$C_3H_7$ | 10.0 ± 1 |

It will be noted that unlike alkyl groups have much less effect in promoting dissociation than do like groups in the para-position. The low degrees of dissociation of tetra-*p*-tolyl-di-*p*-*t*-butylphenylethane and di-*p*-tolyltetra-*p*-*t*-butylphenylethane were confirmed by repeated check runs. The para-hexasubstituted ethane with two methyl, two ethyl and two isopropyl groups showed a degree of dissociation (10%) which approaches that of the hexa-*p*-ethyl compound (17%).[2]

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(3) Müller, Müller-Rodloff and Bunge, *Ann.*, **520**, 235 (1935); Roy and Marvel, THIS JOURNAL, **59**, 2622 (1937).

(4) Marvel, Rieger and Mueller, *ibid.*, **61**, 2769 (1939).

The degree of dissociation of di-*o*-tolyltetraphenylethane has been measured by Bowden and Clark[5] using the cryoscopic method in benzene at 1 to 3.7% (0.017 to 0.063 *M*) concentrations. These authors report the degree of dissociation to be 22.7 to 16.3% under these conditions. In view of these results we have reëxamined the degree of dissociation of this ethane by the magnetic susceptibility method. The value reported[2] previously was 25 ± 1% (0.1 *M*) and our check value is 24 ± 1% at the same concentration. We have been unable to raise the melting point of the peroxide of this ethane above 149–150° whereas the English workers report[5] it to be 164°.

Bowden and Thomas[6] have reported that the di-*m*-tolyltetraphenylethane is dissociated to the extent of 18.6 to 24.6% in 2.8 to 3.3% (0.048 to 0.056 *M*) solution in benzene. These values are much higher than the values which we have obtained by magnetic susceptibility measurements on this ethane in 0.1 *M* solution. The intermediates which we have used in this case agreed in properties with those reported.[6]

The great difference in the effect of two and four methyl groups in ortho-positions compared to the rather minor differences produced by these groups in the para-positions shows that steric factors are far more important than symmetry factors in determining the degree of dissociation of hexaarylethanes.

It is important to mention again that all of the *p*-alkyl substituted ethanes in this series which have hydrogen on the carbon attached to the benzene ring gradually disproportionate on standing. This disproportionation is shown by a change in the magnetic susceptibility although there is little or no change in the color of the solutions when this disappearance of free radical occurs. Thus, care must be taken in interpreting degrees of dissociation measured by either colorimetric or molecular weight methods on compounds of this type.

## Experimental

***o*-Bromoethylbenzene.**—The crude *o*-bromostyrene, prepared from 60 g. of *o*-bromophenylmethylcarbinol,[7] was dissolved in excess thiophene-free benzene and reduced by means of hydrogen and a platinum oxide catalyst.[8] By distillation of the solution, 23 g. of the bromo compound was obtained; b. p. 86–88° at 18 mm.

***m*-Bromo-*n*-amylbenzene** (by D. G. Botteron[9]).—*m*-Bromophenyl-*n*-butylcarbinol was prepared from 14.6 g. of magnesium turnings, 82 g. of *n*-butyl bromide and 92.5 g. of *m*-bromobenzaldehyde by the usual Grignard procedure. The crude carbinol was dehydrated by heating it with freshly fused and pulverized potassium bisulfate at 185° for about four hours.[10] The product was then distilled and 71 g. of *m*-bromophenylpentenylbenzene boiling at 142–145° under 20 mm. pressure was obtained. This product was reduced in alcohol with hydrogen and platinum oxide catalyst.[8] The *m*-bromo-*n*-amylbenzene boiled at 127–131° at 16 mm., $n^{20}_{D}$ 1.5284. The yield was 66 g. (58%).

*Anal.*[11] Calcd. for $C_{11}H_{15}Br$: Br, 35.19. Found: Br, 35.17.

***p*-Bromo-*t*-amylbenzene.**—*t*-Amylbenzene was prepared from benzene, *t*-amyl alcohol and aluminum chloride[12] and brominated in the presence of iron to give the *p*-bromo compound. From 222 g. of *t*-amylbenzene, 6 g. of powdered iron and 246 g. of bromine there was obtained 234 g. (70%) of product boiling at 123–125° at 20 mm., $n^{20}_{D}$ 1.5321. Gledistsch[13] has prepared this product from bromobenzene and 1-chloro-3-methylbutane in the presence of aluminum chloride.

***p*-Tolyl *p*-Ethylphenyl Ketone.**—This ketone was prepared by the usual Friedel and Crafts procedure from 400 cc. of ethylbenzene, 155 g. of *p*-toluoyl chloride and 140 g. of anhydrous aluminum chloride. The yield was 185 g. (83%) of a high-boiling liquid; b. p. 196–198° at 5 mm.; $n^{20}_{D}$ 1.5755; $d^{20}_{20}$ 1.039.

*Anal.* Calcd. for $C_{16}H_{16}O$: C, 85.67; H, 7.20. Found: C, 86.76; H, 7.94.

Two cubic centimeters of this ketone gave 2.6 g. of crude 2,4-dinitrophenylhydrazone, m. p. 155–167°. Repeated recrystallizations of this derivative from ethanol gave a derivative, m. p. 166–167°.

*Anal.* Calcd. for $C_{22}H_{20}N_4O_4$: C, 65.32; H, 4.99. Found: C, 65.29; H, 5.17.

**Preparation of Triarylcarbinols.**—The triarylcarbinols were prepared from the appropriate Grignard reagents and carbonyl compounds by the usual procedures. In three cases, namely, di-*m*-tolylphenylcarbinol, *o*-tolyldiphenylcarbinol and di-*o*-tolylphenylcarbinol, the forced conditions of Bachmann and Kloetzel[14] were used. The crude carbinols after steam distillation were usually obtained as viscous liquids and only when these liquids crystallized readily was any attempt made to purify the carbinol. In one case, namely, di-*o*-tolylphenylcarbinol, steam distillation caused extensive decomposition. The viscous liquids served well as sources for pure triarylchloromethanes.

**Triarylchloromethanes.**—The chloromethanes were prepared from either the crude or crystalline carbinol by treatment with acetyl chloride.[15] The carbinol was dissolved

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[5] Bowden and Clark, *J. Chem. Soc.*, 883 (1940).

[6] Bowden and Thomas, *ibid.*, 1242 (1940).

[7] Marvel and Moon, This Journal, **62**, 45 (1940).

[8] Adams, Vorhees and Shriner, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1929, p. 452.

[9] D. G. Botteron, M. S. Thesis, University of Illinois, 1937.

[10] Brown and Marvel, This Journal, **59**, 1176 (1937).

[11] The analyses reported in this paper are microanalyses by Mr. L. G. Fauble and Miss Mary Kreger.

[12] Huston, Fox and Binder, *J. Org. Chem.*, **3**, 251 (1938).

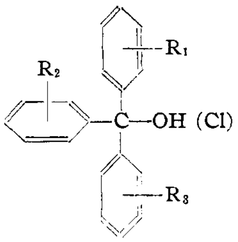
[13] Gledistsch, *Bull. soc. chim.*, (3) **35**, 1096 (1906).

[14] Bachmann and Kloetzel, *J. Org. Chem.*, **2**, 356 (1937).

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

TABLE III

TRIARYLCARBINOLS AND TRIARYLCHLOROMETHANES



| No. | $R_1$ | Carbinol $R_2$ | $R_3$ | Halogen compound used to make RMgX | G. | Carbonyl compound | Grams | Yield of chloromethane, g. | M. p., °C. | Chlorine analyses, % Calcd. | Found |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | H | *p*-$CH_3$ | *p*-$CH_3$ | *p*-$BrC_6H_4CH_3$ | 129 | Ethyl benzoate | 52 | 19 | 108–109 | 11.60 | 11.74 |
| 2 | H | *m*-$CH_3$ | *m*-$CH_3$ | *m*-$BrC_6H_4CH_3$ | 171 | Ethyl benzoate | $68^a$ | 9 | 59–61 | 11.60 | $11.86^f$ |
| 3 | H | *o*-$CH_3$ | *o*-$CH_3$ | *o*-$BrC_6H_4CH_3$ | 342 | Ethyl benzoate | $120^b$ | 9 | 92–94 | 11.60 | $11.43^f$ |
| 4 | H | H | *o*-$C_2H_5$ | *o*-$BrC_6H_4C_2H_5$ | 42 | Benzophenone | $40^c$ | 17 | 87–88 | 11.60 | $11.45^g$ |
| 5 | H | H | *p*-*n*-$C_3H_7$ | *p*-$BrC_6H_4C_3H_7$-*n* | 100 | Benzophenone | 75 | 24 | 90–91 | 11.07 | 10.90 |
| 6 | H | *p*-*i*-$C_3H_7$ | *p*-*i*-$C_3H_7$ | *p*-$BrC_6H_4C_3H_7$-*i* | 100 | Ethyl benzoate | 35 | 21 | 120–121 | 9.82 | 9.78 |
| 7 | H | H | *p*-*i*-$C_4H_9$ | *p*-$BrC_6H_4C_4H_9$-*i* | 107 | Benzophenone | 88 | 26 | 79–80 | 10.61 | 10.82 |
| 8 | H | H | *p*-*s*-$C_4H_9$ | *p*-$BrC_6H_4C_4H_9$-*s* | 107 | Benzophenone | 85 | 22 | 84–85 | 10.61 | 10.84 |
| 9 | H | *p*-*s*-$C_4H_9$ | *p*-*s*-$C_4H_9$ | *p*-$BrC_6H_4C_4H_9$-*s* | 107 | Ethyl benzoate | 35 | 21 | 94–95 | 9.08 | 9.05 |
| 10 | H | *p*-*t*-$C_4H_9$ | *p*-*t*-$C_4H_9$ | *p*-$BrC_6H_4C_4H_9$-*t* | 70 | Ethyl benzoate | 21.5 | 14 | 162–163 | 9.08 | 9.07 |
| 11 | *p*-*t*-$C_4H_9$ | *p*-*t*-$C_4H_9$ | *p*-*t*-$C_4H_9$ | *p*-$BrC_6H_4C_4H_9$-*t* | 75 | Ethyl carbonate | $10.5^d$ | 13 | 259–260 | 7.94 | $7.69^h$ |
| 12 | H | H | *p*-*t*-$C_5H_{11}$ | *p*-$BrC_3H_4C_5H_{11}$-*t* | 57 | Benzophenone | 40 | 11 | 90–91 | 10.17 | 10.42 |
| 13 | H | *p*-*t*-$C_6H_{11}$ | *p*-*t*-$C_5H_{11}$ | *p*-$BrC_6H_4C_6H_{11}$-*t* | 76 | Ethyl benzoate | 22.5 | 9 | 98–99 | 8.47 | 8.18 |
| 14 | *p*-*t*-$C_5H_{11}$ | *p*-*t*-$C_5H_{11}$ | *p*-*t*-$C_5H_{11}$ | *p*-$BrC_6H_4C_5H_{11}$-*t* | 90 | Ethyl carbonate | 13 | 7 | 160–161 | 7.27 | 7.46 |
| 15 | H | H | *m*-*n*-$C_5H_{11}$ | *m*-$BrC_6H_4C_5H_{11}$-*n* | 66 | Benzophenone | 47 | 13 | 54–55 | 10.13 | 10.38 |
| 16 | H | *p*-$CH_3$ | *p*-$C_2H_5$ | *p*-$BrC_6H_4C_2H_5$ | 40 | *p*-Tolyl phenyl ketone | 39 | 8 | 107–108 | 11.08 | 11.22 |
| 17 | H | *p*-$CH_3$ | *p*-*t*-$C_4H_9$ | *p*-$BrC_6H_4C_4H_9$-*t* | 71 | *p*-Tolyl phenyl ketone | 60 | 17 | 120–121 | 10.17 | 9.94 |
| 18 | *p*-$CH_3$ | *p*-$CH_3$ | *p*-*t*-$C_4H_9$ | *p*-$BrC_6H_4C_4H_9$-*i* | 71 | Di-*p*-tolyl ketone | 65 | 30 | 147–148 | 9.79 | 9.79 |
| 19 | *p*-$CH_3$ | *p*-*t*-$C_4H_9$ | *p*-*t*-$C_4H_9$ | *p*-$BrC_6H_4C_4H_9$-*t* | 106.5 | Ethyl *p*-toluate | $37.1^e$ | 9 | 192–193 | 8.76 | $8.54^i$ |
| 20 | *p*-$CH_3$ | *p*-$C_2H_5$ | *p*-*i*-$C_3H_7$ | *p*-$BrC_6H_4C_3H_7$-*i* | 100 | *p*-Tolyl *p*-ethylphenyl ketone | 63 | 15 | 104–105 | 9.82 | $9.48^j$ |

[a] Made under "forced conditions."[14] The yield of carbinol was 105 g., m. p. 81–82° after recrystallization from mixed high and low boiling petroleum ether. *Anal.* Calcd. for $C_{21}H_{20}O$: C, 87.50; H, 6.96. Found: C, 87.58; H, 7.25. [b] Made under "forced conditions."[14] The yield of carbinol was 87 g., m. p. 81–82° after recrystallization from high boiling petroleum ether. *Anal.* Calcd. for $C_{21}H_{20}O$: C, 87.50; H, 6.96. Found: C, 87.44; H, 7.18. [c] Yield 32 g., m. p. 77–77.5° after recrystallization from high boiling petroleum ether. *Anal.* Calcd. for $C_{21}H_{20}O$: C, 87.50; H, 6.96. Found: C, 87.50; H, 7.14. [d] Yield 34 g., m. p. 212–213° after crystallization from high boiling petroleum ether. *Anal.* Calcd. for $C_{31}H_{40}O$: C, 86.92; H, 9.34. Found: C, 86.91; H, 9.28. [e] Yield 24 g., m. p. 141–142° after crystallization from mixed high and low boiling petroleum ether. *Anal.* Calcd. for $C_{28}H_{34}O$: C, 86.99; H, 8.87. Found: C, 87.24; H, 9.01. [f] Twenty grams of crystalline carbinol was used in this preparation. [g] Thirty-two grams of crystalline carbinol was treated with hydrogen chloride and calcium chloride. [h] Nineteen grams of crystalline carbinol was used in this experiment. [i] The yield is not significant as this compound was made from the residues left after the crystalline carbinol had been isolated. [j] This chloride was extremely sensitive to moisture.

in acetyl chloride and warmed until the vigorous reaction subsided. On cooling the crystalline chloromethane was usually obtained. In a few cases it was necessary to remove excess acetyl chloride under reduced pressure before crystallization took place. In one case hydrogen chloride and calcium chloride[16] were used to convert a carbinol to the chloride. When the crude carbinol was used as a starting material for the preparation of the chloromethane, the amount used was that obtained in the experiment reported in Table III. The chloromethanes were readily hydrolyzed by moisture and the usual precautions were observed to avoid decomposition of the products in moist air. All of the chlorides, except the di-*m*-tolyl derivative, were recrystallized from dry ethyl acetate. The di-*m*-tolyl derivative was recrystallized from low-boiling petroleum ether. All the chlorides were crystallized to constant melting point and the emphasis of each experiment was on obtaining a pure compound rather than maximum yield.

The results are summarized in Table III.

**Preparation and Measurement of the Degree of Dissociation of the Hexaarylethanes.**—The hexaarylethanes were prepared from the chlorides and molecular silver in benzene solution in the apparatus previously described[2,3] for magnetic susceptibility measurements. Most of the dissociation measurements were made on 0.1 *M* solutions but in a few cases the low solubility of the ethane necessitated the use of more dilute solutions. These, of course, show a higher dissociation. The ethane from tri-*p*-*n*-butylphenylchloromethane was examined at different periods after preparation and the per cent. dissociation at zero time was calculated as reported earlier for related compounds.[2] All of the radicals having hydrogens on carbons attached to the ring *para* to the central methyl carbon showed a marked tendency to undergo disproportionation. The

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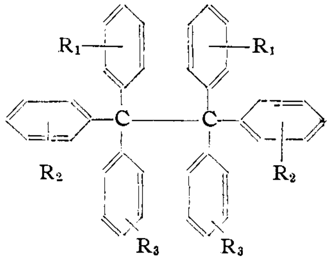
[16] Tousley and Gomberg, THIS JOURNAL, **26**, 1516 (1904).

TABLE IV

DISSOCIATION OF HEXAARYLETHANES; TRIARYLMETHYL PEROXIDES



| No. | R₁ | R₂ | R₃ | % Ethane in benzene | Molarity | $\chi_{sol.} \times 10^6$ | α, % | Peroxides M. p., °C. | Formula | Analyses, % Calcd. C | Calcd. H | Found C | Found H |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | H | *p*-$CH_3$ | *p*-$CH_3$ | 6.16 | 0.1 | 0.6910 | 5.5 ± 1 | 139–140 | $C_{42}H_{38}O_2$ | 87.81 | 6.62 | 87.63 | 6.77 |
| 2 | H | H | *m*-$CH_3$ | 5.84 | .1 | .6881 | 6.5 ± 1[a] | 154–155[6] | $C_{40}H_{34}O_2$ | 87.91 | 6.22 | 88.10 | 6.38 |
| 3 | H | *m*-$CH_3$ | *m*-$CH_3$ | 6.14 | .1 | .6871 | 7.0 ± 1 | 152–153 | $C_{42}H_{38}O_2$ | 87.81 | 6.62 | 88.15 | 6.81 |
| 4 | H | *o*-$CH_3$ | *o*-$CH_3$ | 6.14 | .1 | .4756 | 82.0 ±2 | No peroxide isolated | | | | | |
| 5 | H | H | *o*-$C_2H_5$ | 6.13 | .1 | .6150 | 33.0 ± 1 | 140–141 | $C_{42}H_{38}O_2$ | 87.81 | 6.62 | 87.99 | 6.88 |
| 6 | H | H | *p*-*n*-$C_3H_7$ | 6.48 | .1 | .6880 | 6.5 ± 1 | 135–136 | $C_{44}H_{42}O_2$ | 87.70 | 6.97 | 87.59 | 7.14 |
| 7 | H | *p*-*i*-$C_3H_7$ | *p*-*i*-$C_3H_7$ | 7.48 | .1 | .6860 | 8.0 ± 1 | 140–141 | $C_{50}H_{54}O_2$ | 87.46 | 7.80 | 87.32 | 8.00 |
| 8 | *p*-*n*-$C_4H_9$ | *p*-*n*-$C_4H_9$ | *p*-*n*-$C_4H_9$ | 7.60 | .08 | .6640 | 20.0 ± 2[b] | Previously reported[b] | | | | | |
| 9 | H | H | *p*-*i*-$C_4H_9$ | 6.83 | .1 | .6871 | 7.5 ± 1 | 121–122 | $C_{46}H_{46}O_2$ | 87.62 | 7.30 | 87.90 | 7.57 |
| 10 | H | H | *p*-*s*-$C_4H_9$ | 6.83 | .1 | .6869 | 7.5 ± 1 | 135–136 | $C_{45}H_{46}O_2$ | 87.62 | 7.30 | 87.97 | 7.49 |
| 11 | H | *p*-*s*-$C_4H_9$ | *p*-*s*-$C_4H_9$ | 7.77 | .1 | .6861 | 8.5 ± 1 | 130–131 | $C_{54}H_{62}O_2$ | 87.33 | 8.36 | 87.28 | 8.48 |
| 12 | H | H | *p*-*t*-$C_4H_9$ | 6.89 | .1 | .6869 | 7.5 ± 1[c] | Reported previously[2] | | | | | |
| 13 | H | *p*-*t*-$C_4H_9$ | *p*-*t*-$C_4H_9$ | 8.06 | .1 | .6853 | 8.5 ± 1 | 177–178 | $C_{54}H_{62}O_2$ | 87.33 | 8.36 | 87.27 | 8.58 |
| 14 | *p*-*t*-$C_4H_9$ | *p*-*t*-$C_4H_9$ | *p*-*t*-$C_4H_9$ | 1.16 | .0125 | .6948 | 43.0 ± 4 | 160–161 | $C_{62}H_{78}O_2$ | 87.11 | 9.13 | 86.76 | 9.34 |
| 15 | H | H | *p*-*t*-$C_5H_{11}$ | 7.10 | .1 | .6850 | 8.0 ± 1 | 147–148 | $C_{48}H_{50}O_2$ | 87.54 | 7.59 | 87.56 | 8.01 |
| 16 | H | *p*-*t*-$C_5H_{11}$ | *p*-*t*-$C_5H_{11}$ | 8.60 | .1 | .6840 | 9.0 ± 1 | 151–152 | $C_{58}H_{70}O_2$ | 86.89 | 8.99 | 87.31 | 8.59 |
| 17 | *p*-*t*-$C_5H_{11}$ | *p*-*t*-$C_5H_{11}$ | *p*-*t*-$C_5H_{11}$ | 5.10 | .05 | .6545 | 40.0 ± 1 | 162–163 | $C_{68}H_{90}O_2$ | 87.20 | 9.58 | 87.70 | 9.73 |
| 18 | H | H | *m*-*n*-$C_5H_{11}$ | 7.10 | .1 | .6831 | 9.0 ± 1 | 102–103 | $C_{48}H_{50}O_2$ | 87.54 | 7.59 | 87.91 | 7.83 |
| 19 | H | *p*-$CH_3$ | *p*-$C_2H_5$ | 6.48 | .1 | .6905 | 6.0 ± 1 | 93–94 | $C_{44}H_{42}O_2$ | 87.70 | 6.97 | 87.89 | 7.03 |
| 20 | H | *p*-$CH_3$ | *p*-*t*-$C_4H_9$ | 7.12 | .1 | .6900 | 6.5 ± 1 | 143–144 | $C_{48}H_{50}O_2$ | 87.54 | 7.59 | 87.40 | 7.66 |
| 21 | *p*-$CH_3$ | *p*-$CH_3$ | *p*-*t*-$C_4H_9$ | 7.40 | .1 | .6942 | 5.0 ± 1 | 174–175 | $C_{50}H_{54}O_2$ | 87.46 | 7.80 | 87.87 | 7.92 |
| 22 | *p*-$CH_3$ | *p*-*t*-$C_4H_9$ | *p*-*t*-$C_4H_9$ | 8.40 | .1 | .6966 | 5.0 ± 1 | 175–176 | $C_{56}H_{66}O_2$ | 87.22 | 8.63 | 87.13 | 7.92 |
| 23 | *p*-$CH_3$ | *p*-$C_2H_5$ | *p*-*i*-$C_3H_7$ | 7.45 | .1 | .6802 | 10.0 ± 1[d] | No peroxide isolated | | | | | |

[a] This ethane has been described by Bowden and Thomas.[6] [b] The intermediates were prepared as described by Copenhaver, Roy and Marvel, THIS JOURNAL, **57**, 1311 (1935). [c] This ethane was previously examined and reported[2] as 8–9% dissociated. [d] This value is based on one measurement and is therefore less certain than the others reported in this table.

tertiary-*p*-alkyl derivatives and all of the *m*-substituted radicals were apparently stable in the dark. The *o*-tolyl derivatives showed slight decomposition after three days at room temperature. No attempt was made to isolate the hydrocarbons although hexa-*p*-*t*-butylphenylethane did crystallize readily from the more concentrated solutions. The experimental results are summarized in Table IV.

**Characterization of the Hexaarylethanes as 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 yield of pure crystalline peroxide was observed in each case and usually ran about 50–60% of the theoretical. These figures are based on a peroxide crystallized from benzene by the addition of five to six volumes of absolute alcohol. Di-*o*-tolylphenylmethyl did not readily yield a crystalline peroxide but seemd to undergo some secondary oxidation. As a second derivative in this case, the ethyl ether of the carbinol was characterized. No peroxide was obtained from the di-*p*-tolyl-di-*p*-ethylphenyl-di-*p*-*i*-propylphenylethane due to the small amounts of the ethane available for study. The results are collected in Table IV.

**Phenyl-di-*o*-tolylcarbinol Ethyl Ether.**—The ether was obtained by dissolving a little of the carbinol in ethyl alcohol and adding a drop of sulfuric acid. The ether crystallized from the solution, m. p. 99.5–100°. The ether was also obtained by dissolving the corresponding chloromethane in hot ethyl alcohol.

*Anal.* Calcd. for $C_{23}H_{24}O$: C, 87.34; H, 7.59. Found: C, 87.20; H, 7.45.

## Summary

1. Various mono-, di- and trialkyl substituted triarylcarbinols have been prepared and converted to the corresponding chloromethanes, hexaarylethanes and triarylmethyl peroxides.

2. Magnetic susceptibility measurements have been made on the ethanes and from these measurements the per cent. dissociations of the ethanes have been calculated.

3. The results show that (a) ortho-alkyl substitution greatly increases the degree of dissociation of a hexaarylethane, (b) meta-alkyl groups are more effective in promoting dissociation than para-alkyl groups, (c) next to the ortho-effect, symmetry of the ethane seems to be the most important factor in promoting dissociation.

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