the more stable structure. This suggestion is used to explain the products obtained in several new examples of the coupling reaction, and has led to corrections in the structures of some of the compounds prepared in the same way by earlier workers.

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

The Dissociation of Hexaarylethanes.[1] XV. Methoxyl Substituents

BY C. S. MARVEL, JOHN WHITSON AND H. W. JOHNSTON

Substitution of methoxyl groups for hydrogen atoms in the aryl rings of a hexaphenylethane has been reported[2] to lead to compounds which dissociate to a much greater extent than does the parent hydrocarbon. In all of these reports the degrees of dissociation were determined by cryoscopic molecular weight methods. In this paper we are reporting figures on the degrees of dissociation of certain methoxyl substituted hexaarylethanes determined by the magnetic susceptibility method.[3] Our values are much lower than those previously reported. All of the methoxyl substituted hexaarylethanes were found to be relatively unstable, and the change in magnetic susceptibility with the age of the solution showed that these radicals decompose quickly. The molecular weight determinations undoubtedly show too high values for the radical because of the presence of disproportionation products in the aged solution of the ethanes.

The ethanes which have been prepared and whose dissociations have been measured by the magnetic susceptibility method are listed in Table I. The dissociations reported are on benzene solutions and are calculated for 0.1 *M* solutions from the actual data measured at other concentrations.

TABLE I

DISSOCIATIONS OF VARIOUS METHOXYL SUBSTITUTED HEXAPHENYLETHANES

Ethane	α at 0.1 *M*, %	Reported dissociation, %	Ref.
Tetraphenyldi-*o*-anisyl	3.8 ± 1	26	2a
Tetraphenyldi-*m*-anisyl	2.6 ± 1		
Tetraphenyldi-*p*-anisyl	4.4 ± 1	24	2b
Diphenyltetra-*o*-anisyl	7.3 ± 1	40	2d
Hexa-*o*-anisyl	42 ± 5	100	2d
Hexa-*m*-anisyl	8.5 ± 1.5		

The ethanes with ortho- and para-methoxyl groups used in our work were made from triarylchloromethanes described by the earlier workers and the physical properties checked those reported and the analyses indicated the chlorides were pure. In general we used new reactions to produce our intermediates and brief descriptions of our processes are given. The *m*-methoxyl substituted ethanes are new but the carbinols have been described.[4] We have also used different methods for the preparation of these compounds but have found the properties to be identical with those previously reported.

The degrees of dissociation for these ethanes which we have determined by the magnetic susceptibility method are much nearer those which would be expected by comparison with other substituted ethanes studied in this Laboratory than were the older values. It has been rather generally observed that an ortho substituent has the most marked effect on dissociation and hexa-*o*-anisylethane is highly dissociated. The very low value for the dissociation of tetraphenyl-di-*o*-anisylethane is surprising yet the relative interference value of the methoxyl group as measured by the ease of racemization of ortho-substituted diphenyls[5] indicates that it has much less steric effect than a methyl group.

Experimental

Ethyl *m*-Methoxybenzoate.—One hundred grams of *m*-methoxybenzoic acid (m. p. 106°), 600 cc. of absolute ethyl alcohol, 150 cc. of thiophene-free benzene especially dried by distillation and 3 cc. of concentrated sulfuric acid were placed in a 1-liter round-bottomed flask. A 200-cc. Soxhlet extractor filled with anhydrous potassium carbonate was inserted between the flask and a reflux condenser whose top was connected to a calcium chloride tube. The contents of the flask were refluxed for twenty-four hours. After this the reaction mixture was filtered and the product was then distilled until all solvents boiling below 82° were removed. The residue, which contained the ester, was washed with 10% sodium hydroxide. The mixture formed an emulsion which was extracted with benzene. The benzene extract was washed with water and distilled from a modified Claisen flask. The yield was 75 g. (60%) of product which boiled at 130–135° (15 mm.).

Preparation of Triarylcarbinols.—The triarylcarbinols were prepared from the appropriate Grignard reagents and carbonyl compounds by the usual procedures using the forced conditions of Bachmann and Kloetzel.[6] The crude carbinols were obtained as viscous liquids and in some cases steam distillation was employed to purify the product of the reaction. In cases where the viscous oil could not be caused to crystallize it was converted directly into the corresponding chloromethane. All of these carbinols have been prepared previously but by more complex methods.

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[1] For the fourteenth communication in this series, see THIS JOURNAL, **64**, 2227 (1942).

[2] (a) Gomberg and Nishida, *ibid.*, **45**, 190 (1923); (b) Gomberg and Buchler, *ibid.*, **45**, 207 (1923); (c) Gomberg and Forester, *ibid.*, **47**, 2373 (1925); (d) Lund, *ibid.*, **49**, 1346 (1927); (e) Bowden, *J. Chem. Soc.*, 33 (1939).

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

[4] (a) Baeyer, *Ann.*, **354**, 152 (1907); (b) Baeyer and Villiger, *Ber.*, **35**, 3013 (1902).

[5] Adams and Yuan, *Chem. Rev.*, **12**, 261 (1933).

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

***o*-Anisyldiphenylcarbinol.**—From 26 g. of magnesium, 172.5 g. of bromobenzene, and 45 g. of methyl *o*-methoxybenzoate there was obtained 53 g. (68%) of product; m. p. 128–129° recrystallized from absolute alcohol. Baeyer reported a melting point of 128–129°.[4a]

This compound was also prepared from the reaction of 8 g. of magnesium with 63 g. of *o*-bromoanisole, and the subsequent addition of 61 g. of benzophenone; the yield was 92 g. (95%).

Phenyldi-*o*-anisylcarbinol.—From 25.7 g. of magnesium, 200 g. of *o*-bromoanisole and 75 g. of ethyl benzoate there was obtained 105 g. (66%) of product; m. p. 115–116°, recrystallized from a mixture of ligroin and ethyl acetate. Baeyer reported a melting point of 115°.[4a]

Tri-*o*-anisylcarbinol.—From 40.5 g. of magnesium, 323 g. of *o*-bromoanisole, and 59 g. of diethyl carbonate there was recovered 157.5 g. (90%) of product. The carbinol was highly insoluble in organic solvents; glacial acetic acid was the most suitable solvent for recrystallization; m. p. 181°. Baeyer and Villiger reported the melting point as 181°.[4b]

***m*-Anisyldiphenylcarbinol.**—From 28 g. of magnesium, 185 g. of bromobenzene and 72 g. of ethyl *m*-methoxybenzoate there was obtained 110 g. (95%) of product which melted at 88° after recrystallization from a mixture of ligroin and ethyl acetate. Baeyer reported a melting point of 88°.[4a]

Tri-*m*-anisylcarbinol.—From 25.7 g. of magnesium, 200 g. of *m*-bromoanisole and 39.3 g. of diethyl carbonate there was obtained 57.5 g. (56%) of product having a melting point of 119° after recrystallization from benzene followed by a second recrystallization from absolute ethanol. Baeyer and Villiger reported a melting point of 119.5°.[4b]

***p*-Anisyldiphenylcarbinol.**—From 15 g. of magnesium, 118 g. of *p*-bromoanisole and 91 g. of benzophenone there was obtained 101 g. (70%) of product. The carbinol was difficult to crystallize. Crystallization was induced by dissolving the oily product in ether and adding low-boiling petroleum ether to the point of turbidity. After several recrystallizations the carbinol had a melting point of 60°. Baeyer and Villiger have reported a melting point of 58–61°[4b] and later also reported a melting point of 84°.[7] Kauffmann and Pannwitz obtained a melting point of 84°[8] and Gomberg and Buchler reported 82°.[9] The compound can evidently exist in two crystalline modifications.

Triarylchloromethanes.—The chloromethanes were prepared from the pure crystalline carbinols. The carbinol was dissolved in dry benzene, excess acetyl chloride[10] was added, and the solution refluxed for several hours. The excess acetyl chloride was removed under reduced pressure and the crude chloromethane crystallized out on standing at 5°. The chloromethanes were hydrolyzed readily by moisture and the usual precautions were observed to avoid decomposition of the products in moist air. All of the crude chloromethanes were recrystallized to constant melting point and the emphasis of each experiment was on obtaining a pure compound rather than maximum yield. The new chloromethanes are listed in Table II and the appropriate solvent used for recrystallization of the crude product is indicated.

TABLE II

METHOXYSUBSTITUTED TRIPHENYLCHLOROMETHANES

Chloromethanes	M. p. found, °C.	M. p. reported, °C.	Ref.
o-Anisyldiphenyl	125–126	126	4a
Di-*o*-anisylphenyl	95– 96	95	2e
Tri-*o*-anisyl	170–173	170–175 (dec.)	2d
p-Anisyldiphenyl	122–123	124 122	9 2b
m-Anisyldiphenyl	89– 90[a]		
Tri-*m*-anisyl	123–124[b]		

[a] Recrystallized from ethyl acetate. *Anal.* Calcd. for $C_{20}H_{17}OCl$: Cl, 11.48. Found: Cl, 11.50. [b] Recrystallized from ethyl acetate. *Anal.* Calcd. for $C_{22}H_{21}O_3Cl$: Cl, 9.61. Found: Cl, 9.49.

Magnetic Susceptibility Measurements.—The hexaarylethanes were prepared in the apparatus previously described,[3,11] for magnetic susceptibility measurements. Dissociation measurements were made on 0.1 *M* benzene solutions except in certain experiments in which the ethane was found to be insoluble in 0.1 *M* benzene. More dilute solutions were used and the dissociation values were calculated back to 0.1 *M* by use of the mass law.[12] Measurements were made over varying periods of time to check stability of the ethanes. Ethanes carrying methoxy groups were found to undergo slow decomposition on standing twenty-four hours. A decomposition of 40% was estimated for diphenyl-tetra-*o*-anisylethane over a twenty-four hour period. It was interesting to note that solutions of tri-*o*-anisylchloromethane when cooled to −70° during the preparation of the ethane solidified to a purple ice. The original colorless benzene solution was obtained upon warming to room temperature. Other chloromethanes of this series did not show this phenomenon. The chloromethane and the corresponding ethane were insoluble in 0.1 *M* benzene solution and heat was necessary to dissolve the chloromethane in benzene to make up a 0.05 *M* solution.

The experimental data are summarized in Table III.

TABLE III

EXPERIMENTAL DATA ON MAGNETIC SUSCEPTIBILITY

Ethane	% in benzene	Molarity	$-\chi$ Sol. 10^6	α% (observed)
Tetraphenyldi-*o*-anisyl	6.199	0.1	0.6938	3.8
	3.118	.05	.6988	5.32
Tetraphenyldi-*m*-anisyl	6.18	.1	.7001	2.1
	6.14	.1	.6959	3.1
Tetraphenyldi-*p*-anisyl	6.20	.1	.6900	5.2
	3.06	.05	.6982	5.8
	6.21	.1	.6944	3.8
Diphenyltetra-*o*-anisyl	6.9	.1	.6842	6.8
	7.0	.1	.6806	8.0
	6.9	.1	.6835	7.0
Hexa-*o*-anisyl	1.9	.025	.6638	60
	3.75	.05	.6332	52
Hexa-*m*-anisyl	3.8	.05	.6920	9.4
	7.5	.1	.6750	10

Peroxides.—Exposure of the fresh solutions from the magnetic susceptibility measurement to air produced the peroxides except in the case of diphenyltetra-*o*-anisylethane. In this case we isolated a product which melted at 114–116°, whereas the diphenyl-di-*o*-anisylcarbinol melts at 115° and a mixed melting point was found to be 113–115°. Bowden has reported[2e] the peroxide as melting at 110°. It is possible that our chloromethane hydrolyzed for some reason and that our dissociation value on this ethane is too low.

The *m*-anisyl derivatives gave new peroxides which were isolated and purified in the standard manner.

Diphenyl-*m*-anisylmethyl peroxide, m. p. 156–157°. *Anal.* Calcd. for $C_{40}H_{34}O_4$: C, 83.04; H, 5.91. Found: C, 83.02; H, 6.20.

Tri-*m*-anisylmethyl peroxide, m. p. 155–156°. *Anal.* Calcd. for $C_{44}H_{42}O_8$: C, 75.64; H, 6.07. Found: C, 75.55; H, 6.35.

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(7) Baeyer and Villiger, *Ber.*, **36**, 2774 (1913).

(8) Kauffmann and Pannwitz, *ibid.*, **45**, 766 (1912).

(9) Gomberg and Buchler, THIS JOURNAL, **45**, 207 (1923).

(10) Gomberg, *Chem. Rev.*, **1**, 91 (1924).

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

(12) (a) Preckel and Selwood, *ibid.*, **63**, 3397 (1941); (b) Marvel, Shackleton, Himel and Whitson, *ibid.*, **64**, 1824 (1942).

Summary

Redetermination of the degrees of dissociation of methoxyl substituted hexaarylethanes by the magnetic susceptibility method has shown that the values in the literature determined by cryoscopic molecular weight values are too high due to the instability of these ethanes. The new values show that the *o*-methoxyl group is much less effective than the *o*-methyl group in causing dissociation. In the *m*- and *p*-positions the methoxyl groups are also somewhat less effective than methyl groups but the difference is less marked.

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[CONTRIBUTION NO. 35 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TENNESSEE]

The Action of Formaldehyde on *m*-Hydroxybenzoic Acid. I

BY C. A. BUEHLER, TROY A. POWERS[1] AND JULIAN G. MICHELS[2]

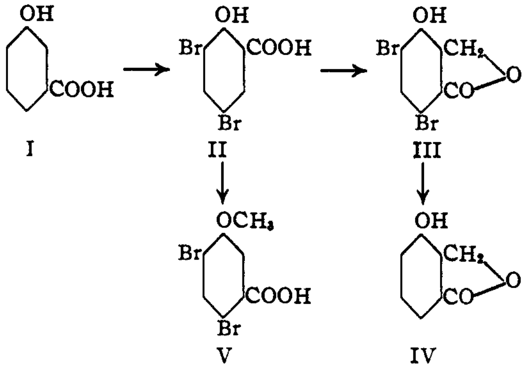
This study is one of a series[3] dealing with the action of formaldehyde on substituted phenols in hydrochloric acid solution. At room temperature *m*-hydroxybenzoic acid produces chiefly two compounds melting at 175 and 254°. The latter is the subject of this investigation. This compound, of formula $C_8H_6O_3$, contains a hydroxyl group since it gives unsaponifiable methoxy and ethoxy derivatives, and an acetyl derivative. In addition, the presence of a phthalide ring is indicated by the fluorescence which develops with resorcinol and sulfuric acid.

Of the possible structures, 4-hydroxy- or 6-hydroxyphthalide, for the condensation product, the latter is ruled out since the melting points of our product and of its methoxy and ethoxy derivatives do not agree with those of the known 6-hydroxyphthalide and its known methoxy and ethoxy derivatives. Indirectly, then, the structure of our compound corresponds to that of 4-hydroxyphthalide.

Direct methods for proving the structure were:

1. Oxidation of the methoxy derivative with dilute potassium permanganate produced the known 3-methoxyphthalic acid, which in turn with methyl alcohol and hydrogen chloride gave the known dimethyl 3-methoxyphthalate.

2. It was found possible to synthesize 4-hydroxyphthalide by blocking the reactive positions (those *o*- or *p*- to the hydroxyl) with the exception of 2-, then introducing the phthalide ring and finally removing the blocking groups. This synthesis was accomplished by brominating *m*-hydrobenzoic acid, I, in glacial acetic acid solution to give 4,6-dibromo-3-hydroxybenzoic acid, II. Although the structure of this acid was arrived at by analogy by Coppadoro,[4] we confirmed its structure by conversion into the known 4,6-dibromo-3-methoxybenzoic acid, V. On treatment of II with methylal, hydrochloric and sulfuric acids, 4-hydroxy-5,7-dibromophthalide, III, was obtained. The latter could not be debrominated with sodium and ethyl or amyl alcohols, or with zinc and alcoholic potassium hydroxide, but on hydrogenation under pressure with Raney nickel at a temperature of 150–200°, it gave 4-hydroxyphthalide, IV, identical with the original condensation product.



It is interesting to note that the orientation in this condensation is similar to that which occurred at low temperatures in the case of *m*-nitrophenol,[5] in that the entering group takes the position ortho to the two substituents.

Experimental

I. Preparation of 4-Hydroxyphthalide.—*m*-Hydroxybenzoic acid, m. p. 200–201°, 25 g., was dissolved in 500 cc. of 40% U. S. P. formaldehyde, and 500 cc. of concentrated hydrochloric acid and 25 cc. of concentrated sulfuric acid were added. The solution was stirred at 30–40° in a three-necked, round-bottomed flask, equipped with a mercury-sealed stirrer, a thermometer, and a glass tube with an opening of about 1 mm. in diameter leading to the bottom of the flask for introducing dry hydrogen chloride. Any excess of hydrogen chloride was removed through an exhaust tube, in the side arm of the flask opposite to the one containing the inlet, attached to an aspirator pump. After the introduction of hydrogen chloride gas for two hours, followed by cooling in the refrigerator, the precipitate which had formed was filtered off and crystallized once from water to give 6 to 8 g. of white crystals, m. p. 254°. Dilution of the filtrate with water to twice its volume and then standing overnight in the refrigerator gave more crystals, which when crystallized twice from water weighed 6 to 8 g. and melted at 175°.

The first crystals produced a fluorescence when heated with resorcinol and sulfuric acid, but there was no color

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[3] For the previous publication, see *J. Org. Chem.*, **6**, 902 (1941).

[4] Coppadoro, *Gazz. chim. ital.*, **32**, II, 332–339 (1902).

[5] Buehler, Deebel and Evans, *J. Org. Chem.*, **6**, 216 (1941).