

for the gift of most of the alcohols from which the bromides were prepared.

### Summary

1. The 1,*n*-alkyl-cyclopentanols have been characterized as a series, through the preparation and study of four new members, together with a more complete and uniform study of six previously prepared members.

2. Some of the data thus obtained have been plotted, and compared with similar curves representing other relevant series. The unusual form of the density curves has been discussed.

3. Esters of *p*-nitrobenzoic acid have been

prepared from five of these alcohols, and esters of 3,5-dinitrobenzoic acid have been prepared from all ten, and the melting points of these esters have been determined.

4. Seven *p*-(1,*n*-alkyl-cyclopentyl)-phenols have been prepared by condensation of these alcohols with phenol, and characterized. Their bacteriostatic strengths have been determined. Four of them were found to be effective toward *Staph. aureus*.

5. Three 2,6-dibromo-4-(1,*n*-alkyl-cyclopentyl)-phenols have been prepared, and their melting points determined.

BATON ROUGE, LA.

RECEIVED AUGUST 2, 1943

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

## The Coupling of $\alpha,\beta$ -Unsaturated Compounds with Diazonium Salts<sup>1</sup>

BY C. F. KOELSCH AND VIRGIL BOEKELHEIDE

In a previous paper<sup>2</sup> it was shown that the reaction between acrylonitrile and diazonium chlorides in buffered solutions and in the presence of cupric chloride led to the formation of  $\alpha$ -chloro-hydrocinnamionitriles. Since Meerwein, Buchner and van Emster<sup>3</sup> had considered that in similar reactions the aryl group always became attached to the  $\alpha$ -carbon of  $\beta$ -substituted  $\alpha,\beta$ -unsaturated compounds, it was believed that an explanation of the anomalous results with acrylonitrile might involve steric hindrance. This belief is now shown to be without foundation, for the behavior of acrylonitrile is not anomalous. Also some of the structures advanced by the earlier investigators are now shown to be incorrect, and a new reaction mechanism is proposed.

The experimental results of the present investigation will first be summarized.

(a) Methyl crotonate and 2,4-dichlorobenzene-diazonium chloride yielded methyl  $\alpha$ -chloro- $\beta$ -(2,4-dichlorophenyl)-butyrate.<sup>4</sup> Similarly ethyl crotonate and benzene- (and *p*-chlorobenzene-) diazonium chloride yielded ethyl  $\alpha$ -chloro- $\beta$ -phenyl- (and *p*-chlorophenyl-) butyrate.

(b) Crotonic acid and *p*-nitrobenzenediazonium chloride gave  $\alpha$ -chloro- $\beta$ -(*p*-nitrophenyl)-butyric acid.<sup>5</sup>

(c) Methyl cinnamate and *p*-chlorobenzene-diazonium chloride yielded methyl  $\beta$ -chloro- $\alpha$ -(*p*-chlorophenyl)-hydrocinnamate.<sup>6</sup>

(1) From the Ph. D. Thesis of Virgil Boekelheide, September, 1943.

(2) Koelsch, *THIS JOURNAL*, **65**, 57 (1943).

(3) Meerwein, Buchner and van Emster, *J. prakt. Chem.*, **152**, 237 (1939).

(4) Meerwein, Buchner and van Emster believed that this compound was methyl  $\beta$ -chloro- $\alpha$ -(2,4-dichlorophenyl)-butyrate.

(5) Meerwein, Buchner and van Emster reported that this compound was  $\beta$ -chloro- $\alpha$ -(*p*-nitrophenyl)-butyric acid.

(6) The structure of this product was reported correctly by Meerwein, Buchner and van Emster.

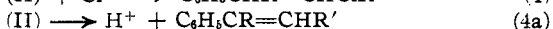
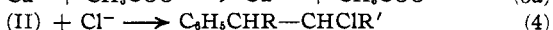
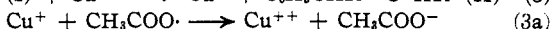
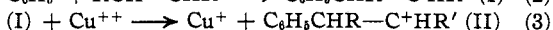
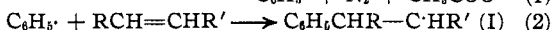
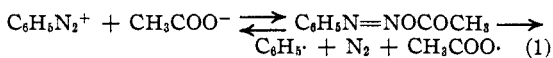
(d) Cinnamalacetic acid and benzenediazonium chloride gave 1,4-diphenylbutadiene.

(e) Methyl cinnamalacetate and benzene- (and *p*-chlorobenzene-) diazonium chloride gave methyl  $\alpha$ -phenyl- (and *p*-chlorophenyl)-cinnamalacetate.

(f) Sorbic acid and benzenediazonium chloride gave 1-phenylpentadiene-1,3.

It is clearly seen that the volume occupied by the group on the  $\beta$ -carbon atom of the unsaturated compound is not a factor in determining the point of entry of the aryl group. A methyl group occupies at least as large a portion of the space in the immediate vicinity of the  $\beta$ -carbon atom as does a vinyl group, yet crotonic acid and its derivatives undergo  $\beta$ -coupling, whereas  $\alpha$ -coupling takes place with the vinyl compounds listed in paragraphs d, e and f.

The following mechanism appears to account for the products obtained.



Equation 1 shows the function of the buffer; the diazonium salt cannot, but the homopolar diazoacetate can decompose easily into a free phenyl radical.<sup>7</sup> Equation 2 represents the "electron pairing"<sup>8</sup> attack of the free radical on the unsaturated compound. The structure of I is determined by considerations analogous to those advanced by Mayo and Walling<sup>9</sup> to account for the orientations observed in Kharasch's peroxide

(7) Hey, *Ann. Rep. Chem. Soc.*, **37**, 280 (1940).

(8) Remick, "Electronic Interpretations of Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1943, p. 259.

(9) Mayo and Walling, *Chem. Rev.*, **27**, 351 (1940).

directed addition of hydrogen bromide to olefins; coupling takes place to yield the more stable of the two possible products. If R is saturated and R' contains C=O (or C $\equiv$ N), the free radical I will be stabilized by resonance of the odd electron into R'. But if R is phenyl or vinyl, then the more stable free radical (I) will be the one with the odd electron on the carbon attached to R,<sup>10</sup> since the resonance in the more symmetrical system  $\overset{\curvearrowright}{\text{C}}=\overset{\curvearrowright}{\text{C}}-\overset{\curvearrowright}{\text{C}}$  will be greater than the resonance  $\overset{\curvearrowright}{\text{C}}-\overset{\curvearrowright}{\text{C}}=\overset{\curvearrowright}{\text{O}}$ .

Equations 3 and 3a show the function of the cupric salt, while equations 4 and 4a indicate how two characteristic products of the reaction are formed. It is of some interest that if in II R is COOH and  $\alpha$ -coupling has taken place (e. g., cinnamic acid, cinnamalacetic acid and sorbic acid), then decarboxylation of II follows, as would be predicted; whereas if in II R' is COOH and  $\beta$ -coupling has taken place (e. g., crotonic acid), then the ion II retains the carboxyl group and acquires an anion (Cl<sup>-</sup>), again as would be predicted.

The foregoing equations do not show all of the processes involved in the reaction. For example, the rate of nitrogen evolution from a reaction mixture is highly dependent on the particular unsaturated compound used, and this must indicate that a complex is formed between the unsaturated compound and a nitrogen-containing reactant. However, the structure of this complex cannot now be determined. Furthermore, the yields of pure products are always low; the by-products are non-volatile tarry substances.

### Experimental

Orienting experiments were made in the following way. A mixture of 0.1 mole of an aromatic amine with 10 ml. of water and 20 ml. of hydrochloric acid was warmed until homogeneous and then cooled in ice. Ten grams of ice was added, and then a concentrated solution of 7 g. of sodium nitrite was dropped in. The resulting solution was filtered and added dropwise and with stirring to a mixture (at 0°) of 0.1 mole of the unsaturated compound in 75 ml. of acetone with 0.1 mole of sodium acetate and 3 g. of cupric chloride in a minimum amount of water. The reaction mixture was warmed to a temperature (3 to 30°) at which gas was evolved evenly and not too rapidly, and stirring was continued until approximately the theoretical amount of nitrogen had been collected (two to six hours). The gases evolved were passed through sulfuric acid, then through a weighed Ascarite tube, and finally collected over water. When the reaction was complete, two liquid phases were present, a green aqueous layer containing mainly inorganic salts, and a brown oily layer which contained most of the product.

**Ethyl Crotonate and *p*-Chlorobenzenediazonium Chloride.**—An experiment was carried out using 1 mole of each of the reactants in 500 ml. of acetone, etc. The reaction required five hours at 20°. The product (108 g., 41%), isolated by ether extraction and distillation, was a pale red

oil, b. p. 100–150° at 6 mm. A second distillation through a short column gave 88 g. (34%) of ethyl  $\alpha$ -chloro- $\beta$ -(*p*-chlorophenyl)-butyrate, a pale yellow oil, b. p. 125–140° at 2–3 mm.

*Anal.* Calcd. for C<sub>13</sub>H<sub>14</sub>Cl<sub>2</sub>O<sub>2</sub>: C, 55.2; H, 5.4; Cl, 27.2. Found: C, 55.3; H, 5.1; Cl, 27.7.

When 6.8 g. of this ester was allowed to stand for twelve hours with 12 g. of potassium hydroxide in 75 ml. of methanol, it furnished 3.2 g. (62%) of *p*-chloro- $\beta$ -methylcinnamic acid, colorless crystals from ligroin, m. p. 134° (reported,<sup>11</sup> 133.5°). The acid formed a liquid-crystalline melt that became clear at 138.5°. For comparison the acid was synthesized from 30 g. of *p*-chloroacetophenone, through ethyl *p*-chloro- $\beta$ -hydroxy- $\beta$ -methylhydrocinnamate<sup>12</sup> (yield, 52%; b. p. 160–162° at 11 mm.), which was dehydrated with formic acid<sup>11</sup> to ethyl *p*-chloro- $\beta$ -methylcinnamate (yield, 93%); the latter ester was hydrolyzed with 10% sodium hydroxide, giving the desired acid in 93% yield; it melted at 134° to a turbid liquid that became clear at 138.5°, and a mixture with the acid from the coupling showed the same behavior. Furthermore, each product was partly rearranged to a stereoisomer, m. p. 92–99° (reported<sup>11</sup> 94°) when it was warmed in concd. sulfuric acid for a few minutes.

That the coupling reaction yielded no ethyl  $\beta$ -chloro- $\alpha$ -(*p*-chlorophenyl)-butyrate was shown in the following way. Forty-one grams of once-distilled material from another experiment was boiled for ten minutes with 200 g. of diethylaniline, giving 33 g. of crude unsaturated ester. This was saponified, and 22.5 g. of the resulting crude acid was dissolved in 250 ml. of 5% sodium hydroxide and shaken with hydrogen at 40 lb. in the presence of Raney nickel. Gas absorption stopped after twenty-four hours, and titration then showed the presence of 0.14 mole of chloride ion (calcd. 0.11 mole). There was isolated 12.8 g. of an oily acid, b. p. 126–128° at 3 mm., neut. equiv., 164 (calcd. for phenylbutyric acid 164). Twelve grams of this acid in 40 ml. of benzene was treated with 18 g. of phosphorus pentachloride and then with 10 g. of aluminum chloride. This reaction yielded 4.4 g. (40%) of 3-methylindanone, b. p. 128–131° at 16 mm. (identified through its oxime and by comparison with an authentic sample), and 2 g. of a neutral substance, b. p. 144–148° at 16 mm. The higher boiling fraction was not ethyldeoxybenzoin, for it gave no solid oxime under conditions which were found to yield this oxime, m. p. 127–129°, when an authentic sample of the ketone was used.

**Ethyl Crotonate and Benzenediazonium Chloride.**—A one-mole experiment required three and one-half hours at 20–35° for completion of the nitrogen evolution. There was obtained 26.5 g. (11.5%) of once-distilled product, b. p. 110–150° at 11 mm., and this furnished 17 g. (7.5%) of a refracted ester, b. p. 100–104° at 4 mm. Analysis indicated that the expected ethyl  $\alpha$ -chloro- $\beta$ -phenylbutyrate lost some hydrogen chloride on distillation.

*Anal.* Calcd. for C<sub>12</sub>H<sub>16</sub>ClO<sub>2</sub>: C, 63.6; H, 6.6. Found: C, 65.1; H, 6.7.

When 3.8 g. of the chloro ester was allowed to stand for twelve hours with 4.5 g. of potassium hydroxide in 30 ml. of methanol, it gave 1.75 g. (65%) of  $\beta$ -methylcinnamic acid, which melted at 97–98° (reported<sup>13</sup> 97–98°) after it had been made sterically homogeneous by boiling it for three hours with excess 5% sodium hydroxide. The acid was identified by comparison with an authentic sample synthesized<sup>11,12</sup> from acetophenone.

**Methyl Crotonate and 2,4-Dichlorobenzenediazonium Chloride.**—A solution of 20.3 g. (0.13 mole) of 2,4-dichloroaniline in 100 g. of hydrochloric acid was diazotized and then partly neutralized by adding 26.2 g. (0.65 mole) of sodium hydroxide in 100 ml. of water at –5°. The solution was mixed with 12.5 g. of methyl crotonate in 200 ml. of acetone, then with 23.3 g. of sodium chloroacetate in 50 ml. of water, and finally with 5.3 g. of cupric

(11) v. Braun and Heider, *Ber.*, **49**, 1272 (1916).

(12) Rupe, *Ann.*, **369**, 322 (1909).

(13) Schroeter and Wulfig, *Ber.*, **40**, 1593 (1907).

(10) It is to be noted that the present results indicate that the normal mode of addition of hydrogen bromide to cinnamic acid may be reversed by peroxides. It has been stated (ref. 9, p. 363) that this reversal cannot be achieved, but actually a conclusive experimental test of the matter has not been made (cf. Michael, *J. Org. Chem.*, **4**, 128 (1939)).

chloride in 10 ml. of water. Nitrogen was evolved rapidly at 5°, and the reaction was complete after two and one-half hours. There was obtained 7 g. (20%) of methyl  $\alpha$ -chloro- $\beta$ -(2,4-dichlorophenyl)-butyrate,<sup>4</sup> b. p. 155–170° at 3 mm. (reported<sup>3</sup> 130–140° at 0.1 mm.).

Treatment of 5 g. of the ester with potassium hydroxide in methanol yielded 2,4-dichloro- $\beta$ -methylcinnamic acid, which formed colorless crystals (1.2 g., 30%) from ligroin, m. p. 126–127°.

*Anal.* Calcd. for C<sub>10</sub>H<sub>8</sub>Cl<sub>2</sub>O<sub>2</sub>: C, 52.0; H, 3.5. Found: C, 52.5; H, 3.6.

When 0.62 g. of the unsaturated acid was dissolved in a solution of 0.4 g. of sodium hydroxide in 30 ml. of water and shaken with Raney nickel under hydrogen at atmospheric pressure, it absorbed 230 ml. of the gas (calcd. 210 ml.) in ninety minutes. The resulting  $\beta$ -phenylbutyric acid was identified by comparison with an authentic sample, and by conversion into its amide (yield 50%), which melted at 105–106° (mixed m. p.) in agreement with the reported figure.<sup>14</sup>

**Crotonic Acid and *p*-Nitrobenzenediazonium Chloride.**—

A diazonium salt solution prepared from 69 g. of *p*-nitroaniline, 138 g. of hydrochloric acid, and 35 g. of sodium nitrite was stirred into a mixture containing 43 g. of crotonic acid, 600 ml. of acetone, 100 g. of sodium chloroacetate, 20 g. of cupric chloride, and 100 ml. of water. Gas was evolved rapidly at 0°, and after one hour the reaction was complete. Extraction of the mixture with ether and of the ether with aqueous sodium bicarbonate furnished 16 g. of a nearly black oily acidic material, which could not be distilled, and from which no crystalline material could be obtained.<sup>15</sup> Fifteen grams of the oil was boiled for four hours with 40 ml. of methanol containing 5 g. of hydrogen chloride. There was obtained 11.3 g. of methyl  $\alpha$ -chloro- $\beta$ -(*p*-nitrophenyl)-butyrate, a pale red oil that distilled at 175–180° at 3 mm. with some loss of hydrogen chloride.

*Anal.* Calcd. for C<sub>11</sub>H<sub>12</sub>ClNO<sub>4</sub>: C, 51.3; H, 4.7. Found: C, 53.5; H, 4.7.

When 10.7 g. of the ester was boiled for fifteen minutes with 60 g. of diethylaniline, it was dehalogenated, giving 7.2 g. (76%) of methyl  $\beta$ -methyl-*p*-nitrocinnamate, b. p. 156–160° at 3 mm., m. p. 120–121° (reported<sup>13</sup> 121–122°). Saponification of this product with 5% sodium hydroxide gave  $\beta$ -methyl-*p*-nitrocinnamic acid in 52% yield, m. p. 167–168° (reported<sup>13</sup> 168–169°). The melting points of the cinnamic ester and of the acid were unchanged when the substances were mixed with the corresponding compounds synthesized by the methods of Schroeter and Wulfig.<sup>13</sup>

**Methyl Cinnamate and *p*-Chlorobenzenediazonium Chloride.**—A solution prepared from 25.6 g. (0.2 mole) of *p*-chloroaniline, 54 g. of hydrochloric acid and 14 g. of sodium nitrite was stirred slowly into a mixture of 32.4 g. of methyl cinnamate, 150 ml. of acetone, 26 g. of pyridine, 20 g. of acetic acid, 6 g. of cupric chloride, and 100 ml. of water. Gas evolution began at 30° and ended after two hours. The volatile constituents were removed by distillation from a steam-bath, and the remaining oil was extracted with 500 ml. of benzene. From this extract there was obtained 12.8 g. of pure methyl  $\beta$ -chloro- $\alpha$ -(*p*-chlorophenyl)-hydrocinnamate,<sup>6</sup> colorless crystals from methanol, m. p. 121–122° (reported<sup>3</sup> 124–124.5°).

When 2.2 g. of the ester was allowed to stand for twelve hours at room temperature with 3.5 g. of potassium hydroxide in 30 ml. of methanol, it yielded 1.65 g. (86%) of  $\alpha$ -(*p*-chlorophenyl)-cinnamic acid, m. p. 180–181°. And when a solution of 0.75 g. of this acid in 35 ml. of 1% aqueous sodium hydroxide was shaken with hydrogen under atmospheric pressure and in the presence of Raney nickel, it yielded 0.52 g. (84%) of  $\alpha$ -phenylhydrocinnamic acid, m. p. 95–96° alone or mixed with a sample prepared by reducing  $\alpha$ -phenylcinnamic acid.

<sup>14</sup> Kohler and Reimer, *Am. Chem. J.*, **33**, 353 (1905).

<sup>15</sup> Meerwein, Buchner and van Emster reported that this procedure gave 3.5 g. of an acid C<sub>10</sub>H<sub>8</sub>NO<sub>4</sub>, m. p. 173.5–174.5°

**Cinnamalacetic Acid and Benzenediazonium Chloride.**—

A mixture of 0.1 mole of each of the reactants (but containing 0.2 mole of sodium acetate and 160 ml. of acetone) evolved gas at 10°. The reaction was complete after five hours, and 1.4 g. of carbon dioxide was collected. Only 0.9 g. of acidic product was obtained, and this was unchanged cinnamalacetic acid. Crystallization of the neutral products from benzene-ligroin gave 5.7 g. (28%) of 1,4-diphenylbutadiene, m. p. 149–150° alone or mixed with a sample synthesized by the method of Thiele and Schlessner.<sup>16</sup>

**Methyl Cinnamalacetate<sup>17</sup> and Benzenediazonium Chloride.**—A mixture of one mole of each of the reactants prepared in the usual way, but containing 0.17 mole of pyridine acetate in place of sodium acetate, began to evolve nitrogen at 15°, and the reaction was complete after five hours. Distillation of the products gave 4 g. of unchanged methyl cinnamalacetate and 5 g. (19%) of the expected coupling product, a pale red oil, b. p. 180–190° at 2 mm. Since some decomposition had accompanied its distillation, the substance was treated directly with 10% potassium hydroxide in methanol. No chloride ion was formed, but there was obtained 2.5 g. (10%) of pure  $\alpha$ -phenylcinnamalacetic acid, faintly yellow crystals from benzene-ligroin, m. p. 186–187° alone or mixed with a sample prepared by the method of Thiele.<sup>16</sup>

**Methyl Cinnamalacetate and *p*-Chlorobenzenediazonium Chloride.**—A mixture containing 0.17 mole of each of the reactants, 0.16 mole of sodium acetate, 5 g. of cupric chloride, and the necessary solvents began to evolve gas at 15°, and the reaction was complete after two hours. There was obtained 53 g. of a dark oily product from which no pure substance could be isolated directly. Eighteen grams of this oil was allowed to stand with 15 g. of potassium hydroxide in 120 ml. of methanol, and the potassium salt which had separated after thirty minutes was removed. This salt yielded 4.4 g. of cinnamalacetic acid. The solution was allowed to stand for twelve hours and then acidified. The resulting sticky acid was dissolved in 50 ml. of hot concd. aqueous sodium carbonate. The sodium salt which separated when the solution was cooled was washed with ether, then dissolved in water and decomposed, giving 1.7 g. of  $\alpha$ -(*p*-chlorophenyl)-cinnamalacetic acid, faintly yellow needles from acetic acid, m. p. 233–234°.

*Anal.* Calcd. for C<sub>17</sub>H<sub>14</sub>ClO<sub>2</sub>: C, 71.8; H, 4.6. Found: C, 72.0; H, 5.0.

**Sorbic Acid and Benzenediazonium Chloride.**—A solution prepared from 0.125 mole of aniline, 0.375 mole of hydrochloric acid, and 0.125 mole of sodium nitrite was added to a mixture containing 0.1 mole of sorbic acid,<sup>18</sup> 0.2 mole of sodium acetate, 5 g. of cupric chloride, and 160 ml. of acetone. Nitrogen was evolved at 0°, and the reaction was complete after two and one-half hours. Steam distillation gave 3.8 g. (26%) of 1-phenylpentadiene-1,3, b. p. 118–124° at 24 mm.;  $n_D^{20}$  1.6002;  $n_D^{25}$  1.6025 (reported<sup>19</sup> b. p. 116° at 16 mm.;  $n_D^{18}$  1.6111). A sample of the hydrocarbon obtained in 57% yield by the method of Klages<sup>20</sup> boiled at 118–120° at 24 mm. and had a refractive index ( $n_D^{20}$ ) of 1.6010. Both samples of the hydrocarbon yielded an adduct with maleic anhydride, m. p. 157–158° (reported<sup>21</sup> 157–158°), alone or mixed.

## Summary

It is suggested that aryl radicals arising from the decomposition of diazo acetates attack the C–C double bond of an  $\alpha,\beta$ -unsaturated compound in such a way that the new radical formed will have

(16) Thiele and Schlessner, *Ann.*, **306**, 198 (1899).

(17) Hinrichsen and Triepel, *ibid.*, **336**, 198 (1904).

(18) Doebner, *Ber.*, **35**, 2137 (1902).

(19) Klages, *ibid.*, **40**, 1769 (1907).

(20) Ref. 19, of Muskau and Herman, *This Journal*, **53**, 252 (1931).

(21) Döls and Albre, *Ber.*, **62**, 2086 (1929).

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 cor-

rections 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.<sup>1</sup> 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<sup>2</sup> 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.<sup>3</sup> 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	$\alpha$ at 0.1 <i>M</i> , %	Reported dis- sociation, %	Ref.
Tetraphenyldi- <i>o</i> -anisyl	3.8 ± 1	26	2a
Tetraphenyldi- <i>m</i> -anisyl	2.6 ± 1		
Tetraphenyldi- <i>p</i> -anisyl	4.4 ± 1	24	2b
Diphenyltetra- <i>o</i> -anisyl	7.3 ± 1	40	2d
Hexa- <i>o</i> -anisyl	42 ± 5	100	2d
Hexa- <i>m</i> -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

(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) Bowen, *J. Chem. Soc.*, 33 (1939).

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

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.<sup>4</sup> 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<sup>5</sup> 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.<sup>6</sup> 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.

(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).