



since substituted vinyl residues having one substituent on each of the carbon atoms rarely polymerize easily. The color of the solution obtained by treating tri-*p*-ethylphenylchloromethane with silver was qualitatively the same as the color of the solution obtained by treating the same chloride with pyridine in the manner used by Schlenk and Meyer<sup>3</sup> to obtain quinoid derivatives related to VIII. The fact that the color does not change to an appreciable extent as the radical changes into a mixture of triarylmethane and the quinoid derivative is evidence in favor of Gomberg's well-known idea that the quinoid ring structure of the radical is the form which contributes the color to the solution.<sup>4</sup>

In addition to the *p*-ethyl derivative, the *p*-*n*-propyl, *p*-isopropyl, *p*-isobutyl and *p*-*s*-butyl derivatives also have been reexamined.<sup>5</sup> In each case the solution of the hydrocarbon first obtained showed a high free radical content and this disappeared on standing. The rate of disproportionation of the various free radicals was determined by following the change in magnetic susceptibility. The order of increasing stability of the various free radicals agreed exactly with the previously reported order of increasing dissociation. The results are plotted in Fig. 1.

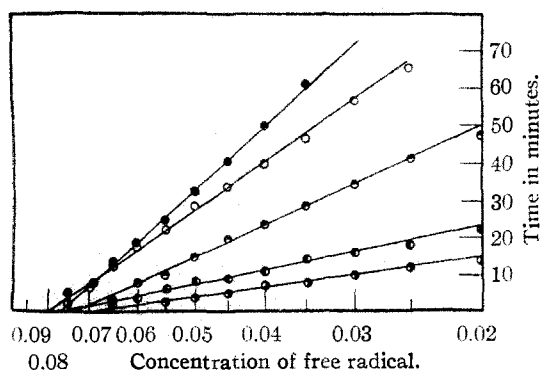


Fig. 1.—Rate of decomposition of  $(R\text{---}\langle\text{C}_6\text{H}_4\rangle)_3\text{C}\cdot$ :  
 ●, R = Et; ○, R = *n*-Pr; ○, R = *i*-Pr; ○, R = *s*-Bu; ●, R = *i*-Bu.

By use of the data on the rate of disproportionation it was possible to calculate the dissociation of the various ethanes at zero time and thus to obtain fairly accurate estimates of the effects of the various para-alkyl groups on the degree of dissociation. These effects were much more marked

(3) Schlenk and Meyer, *Ber.*, **52**, 9 (1919).

(4) Gomberg, *ibid.*, **40**, 1847 (1907).

(5) The *p*-*n*-butyl derivative will be reported in a later communication.

than had been anticipated and it is obvious that the size and shape of a para-alkyl group is an important factor in the amount of radical formation in the hexa-*p*-alkylphenylethane series. Table I contains a summary of the new results.

TABLE I  
 DISSOCIATION OF HEXA-*p*-ALKYLPHENYLETHANES

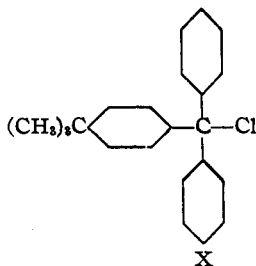
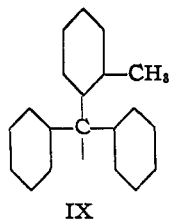
Alkyl group	Degree of dissociation, %
Ethyl	17 ± 2
<i>n</i> -Propyl	21 ± 2
Isopropyl	26 ± 2
<i>s</i> -Butyl	33 ± 2
Isobutyl	27 ± 2

Certain other observations also contribute evidence to support the above view of the disproportionation of these *p*-alkylphenylethanes. Hexa-*m*-tolylethane<sup>6</sup> was prepared in benzene solution and it was stable more or less indefinitely. The magnetic susceptibility of its solutions did not change over a twenty-four hour period. This stability was expected as meta-quinone structures cannot form. The meta-methyl group was even more effective than the para-methyl group in producing dissociation since hexa-*m*-tolylethane existed to the extent of at least 40% as the free radical. No other crystalline tri-*m*-alkylphenylchloromethane has been obtained, so the effect of other meta-alkyl groups cannot yet be reported.

It might be predicted that an ortho-methyl group also would contribute to the instability of the radical since ortho-quinoid molecules form rather easily. It has not been possible to prepare tri-*o*-tolylchloromethane due apparently to steric factors but *o*-tolylidiphenylchloromethane with silver gave a stable ethane which was dissociated to the extent of 25%. This result showed the very marked effect of introducing more steric hindrance around the central carbon atom of the free radical since one ortho-methyl group was more effective in producing dissociation than were three para-methyl groups. These steric factors must also explain the stability of the ortho-methyl derivative. If it is assumed that a free radical must collide with the methyl group of another radical before a hydrogen atom can be removed it is rather easy to see why the ortho-methyl compound (IX) does not undergo the disproportionation reaction characteristic of the para-series.

*p*-*t*-Butylphenyldiphenylchloromethane (X) has been prepared and converted to the correspond-

(6) Brown and Marvel, *THIS JOURNAL*, **59**, 1175 (1937).



ing ethane. Since there are no hydrogen atoms on the alkyl carbon attached to the ring, this compound did not undergo the disproportionation observed with the other *p*-alkyl derivatives. For comparison the mono-*p*-methyl and *p*-isopropyl derivatives were prepared. Both of these radicals showed the disproportionation reaction but both decomposed more slowly than did the corresponding tri-*p*-alkylphenylmethyl radicals. This increased stability was expected as the chance of the radical colliding with an active hydrogen atom is much less in the monosubstituted series than in the trisubstituted series. In Table II are recorded the degrees of dissociation of these dialkylphenyltetraphenylethanes.

TABLE II

DEGREE OF DISSOCIATION OF SOME DIALKYLPHENYLTETRA-PHENYLETHANES

Alkyl group	Degree of dissociation, %
<i>p</i> -Methyl	5 ± 1.0
<i>o</i> -Methyl	25 ± 1.0
<i>p</i> -Isopropyl	8-10 ± 1.0
<i>p</i> - <i>t</i> -Butyl	8-9 ± 1.0

Thus all the *p*-alkylphenylmethyl radicals which can lose hydrogen from the  $\alpha$ -carbon of the para-alkyl group undergo rather rapid disproportionation. When there is no possibility of quinoid structure formation by loss of hydrogen, the radicals are relatively stable as is triphenylmethyl. Alkyl groups in the para-position have a marked effect on increasing the dissociation of hexaphenylethane and the larger groups are more effective than the smaller ones. A meta-methyl group is more effective than a para-methyl group in promoting dissociation. An ortho-methyl group is very effective in this regard. These effects of ortho- and meta-substituents must be due in part to steric factors.

### Experimental

**Preparation of *p*-*t*-Butylbromobenzene.**—This compound was prepared by Schramm<sup>7</sup> by the bromination of

(7) Schramm, *Monatsh.*, **9**, 848 (1888).

*t*-butylbenzene; however, no specific directions for the preparation were given. The following procedure has been found to give satisfactory results. A solution of 80 g. (0.5 mole) of bromine in 67 g. (0.5 mole) of *t*-butylbenzene<sup>8</sup> in a 500-cc. round-bottomed flask connected to a reflux condenser by a ground-glass joint was exposed to sunlight for four days. The initial reaction was rather vigorous and it was necessary to cool the flask in ice for the first four or five hours. When the evolution of hydrogen bromide ceased (four days), the reaction mixture was washed with 10% sodium bisulfite solution, water, 10% sodium carbonate solution and water. The organic layer was separated, dried and distilled through a fourteen-inch (35-cm.) modified Widmer column. A small low boiling fraction consisting chiefly of unreacted *t*-butylbenzene was obtained, but the bulk of the distillate was collected at 230°. The yield was 64 g. which is 60% of the theoretical.

**Preparation of *p*-Isopropylphenyldiphenylcarbinol.**—The Grignard reagent was prepared from 100 g. of *p*-bromoisopropylbenzene and 12 g. of magnesium in about 200 cc. of anhydrous ether. After the addition of the bromide the mixture was stirred and refluxed for two hours. Then 88 g. of benzophenone in 100 cc. of dry benzene was added and the mixture was stirred and refluxed for an additional three hours. The reaction mixture was decomposed by pouring it into dilute sulfuric acid containing some cracked ice. The organic layer was separated and the ether and benzene removed by distillation. The residue was distilled with steam until no trace of organic material was detectable in the distillate. The carbinol was obtained as a clear glass. No attempt was made to purify it. Instead the impure product was used directly in the preparation of the chloromethane.

**Preparation of *p*-*t*-Butylphenyldiphenylcarbinol.**—This carbinol was prepared from *p*-*t*-butylbromobenzene by the same procedure used for *p*-isopropylphenyldiphenylcarbinol. Again the impure carbinol was used directly in the preparation of the corresponding chloromethane.

**Preparation of Triarylchloromethanes.**—The procedures used in the preparation of most of the chloromethanes reported in this communication were those reported by Marvel, Copenhaver and Roy.<sup>2a</sup> It was discovered, however, that chloromethanes which melted above 130° were prepared more easily by dissolving the corresponding impure carbinol in acetyl chloride.<sup>9</sup> The crystalline chloromethane was obtained by concentrating and cooling the solution. The chloromethanes were purified as before by recrystallization from ethyl acetate. The following compounds were prepared in this way: tri-*p*-ethylphenylchloromethane, tri-*p*-isopropylphenylchloromethane, tri-*p*-*s*-butylphenylchloromethane and tri-*p*-isobutylphenylchloromethane.

**Analysis of *p*-isopropylphenyldiphenylchloromethane,** m. p. 90-91°. Calcd. for C<sub>22</sub>H<sub>21</sub>Cl: C, 82.37; H, 6.55. Found: C, 83.41; H, 7.06. **Analysis of *p*-*t*-butylphenyldiphenylchloromethane,** m. p. 133-134°. Calcd. for C<sub>23</sub>H<sub>23</sub>Cl: C, 82.53; H, 6.88. Found: C, 82.53; H, 7.02.

The melting points of the previously known triarylchloromethanes are listed in Table IIA.

(8) Huston, Fox and Binder, *J. Org. Chem.*, **8**, 251 (1938).

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

TABLE IIA

Chloromethane	M. p., °C.	
	Found	Reported
<i>p</i> -Tolyldiphenylchloromethane	99	99 <sup>10</sup>
<i>o</i> -Tolyldiphenylchloromethane	135	136-137 <sup>10</sup>
Tri- <i>m</i> -tolylchloromethane	83-84	84-85 <sup>5</sup>
Tri- <i>p</i> -ethylphenylchloromethane	156-157	157-158 <sup>2a</sup>
Tri- <i>p-n</i> -propylphenylchloromethane	89-90	90 <sup>2a</sup>
Tri- <i>p</i> -isopropylphenylchloromethane	166-167	167-168 <sup>2a</sup>
Tri- <i>p</i> -isobutylphenylchloromethane	134-135	135-136 <sup>2a</sup>
Tri- <i>p-s</i> -butylphenylchloromethane	130-131	132 <sup>2a</sup>

**Preparation of Peroxides.**—Five-thousandths of a mole of the appropriate triarylchloromethane was shaken with three grams of molecular silver for fifteen minutes in the apparatus described previously.<sup>2b</sup> The solution was filtered from the silver-silver chloride, removed from the apparatus and exposed to the air until it was entirely decolorized. The solvent was removed and the residue was purified by several recrystallizations from a mixture of benzene and absolute ethanol.

**Analysis of *o*-tolyldiphenylmethyl peroxide, m. p. 148-149°.** Calcd. for C<sub>16</sub>H<sub>14</sub>O<sub>2</sub>: C, 87.91; H, 6.23. Found: C, 87.63; H, 6.26. **Analysis of *p*-isopropylphenyldiphenylmethyl peroxide, m. p. 139-140°.** Calcd. for C<sub>14</sub>H<sub>12</sub>O<sub>2</sub>: C, 87.71; H, 6.98. Found: C, 87.59; H, 7.33. **Analysis of *p*-*t*-butylphenyldiphenylmethyl peroxide, m. p. 156-157°.** Calcd. for C<sub>16</sub>H<sub>16</sub>O<sub>2</sub>: C, 87.62; H, 7.30. Found: C, 88.07; H, 7.67.

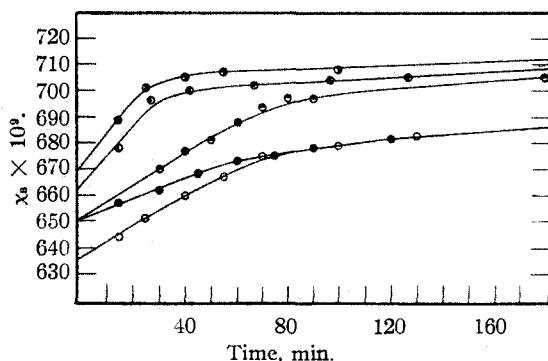


Fig. 2.—The change of magnetic susceptibility ( $\chi_a$ ) of solutions of  $(R-\text{C}_6\text{H}_4)_3\text{C}-\text{C}(\text{C}_6\text{H}_4\text{R})_3$ , with time:  $\circ$ , R = Et;  $\bullet$ , R = *n*-Pr;  $\circ$ , R = *i*-Pr;  $\circ$ , R = *s*-Bu;  $\bullet$ , R = *i*-Bu.

**Preparation of Hexaarylethanes.**—Because of the instability of the hexa-*p*-alkylphenylethanes reported in this communication it was necessary to determine the time required for the completion of the reaction between molecular silver and triarylchloromethanes. This was done by measuring the amount of oxygen absorbed by a sample of the chloromethane when it was shaken with molecular silver in the presence of oxygen.<sup>11</sup> The results are tabulated in Table III.

(10) Bistrzycki and Gyr, *Ber.*, **37**, 661, 1250 (1904).

(11) Bachman and Kloetzel, *J. Org. Chem.*, **2**, 358 (1937).

TABLE III

Triarylchloromethane	Time, min.	% oxygen absorbed
<i>p</i> -Tolyldiphenylchloromethane	4	83
	15	84
<i>o</i> -Tolyldiphenylchloromethane	7	90
<i>p</i> -Isopropylphenyldiphenylchloromethane	10	83
	30	96
Tri- <i>p</i> -ethylphenylchloromethane	10	80
	15	83
Tri- <i>p-n</i> -propylphenylchloromethane	10	80
	15	82
Tri- <i>p</i> -isopropylphenylchloromethane	8	90
	23	93
Tri- <i>p</i> -isobutylphenylchloromethane	15	80
Tri- <i>p-s</i> -butylphenylchloromethane	3	83
	20	90

**The Dissociation of Hexaarylethanes.**—The degree of dissociation of the hexaarylethanes studied was measured by the magnetic susceptibility method<sup>12</sup> in the apparatus described previously.<sup>2b</sup> In the case of the hexa-*p*-alkylphenylethanes which decompose rapidly, 0.02 molar solutions of the chloromethanes were shaken with molecular silver for fifteen minutes, filtered and the magnetic susceptibility of the solutions determined immediately. Determinations were then made on the same sample at ten or fifteen minute intervals until the sample showed a constant magnetic susceptibility. By extrapolation from these values the magnetic susceptibility at zero time (*i. e.*, before any decomposition took place) was calculated. These extrapolations are shown in Fig. 2.

In order to calculate the degree of dissociation from these data, it is necessary to know the concentration of the ethane. Since oxygen absorption experiments under similar conditions have shown that the chloromethane is converted to the ethane to the extent of at least 80% in every case, the ethane solution was assumed to be 0.08  $\pm$  0.01 molar. This comparatively large possible variation in concentration, however, causes a maximum uncertainty of only  $\pm$  2% in the degree of dissociation.

In the case of the more stable ethanes, the chloromethanes were shaken with molecular silver until parallel oxygen absorption experiments indicated that the reaction was complete. The experimental data for all of the ethanes reported are collected in Table IV.

**Rate of Decomposition of Hexa-*p*-alkylphenylethanes.**—From the values of  $\alpha$  listed in Table IV

(12) Müller, *et al.*, *Ann.*, **520**, 235 (1935); **521**, 89 (1935); see also ref. 2b.

TABLE IV

Ethane	T°	% ethane	$\frac{-x_s}{\times 10^4}$	$\alpha$
Di- <i>p</i> -tolyltetraphenylethane	28	4.74	0.695	0.063 $\pm$ 0.02
Di- <i>o</i> -tolyltetraphenylethane	30	5.85	.632	.287 $\pm$ .02
Di- <i>p</i> -isopropylphenyltetraphenylethane	28	6.77	.680	.083 $\pm$ .02
Di- <i>p</i> - <i>t</i> -butylphenyltetraphenylethane	29	6.09	.688	.078 $\pm$ .02
Hexa- <i>m</i> -tolylethane	28	6.47	.594	.400 $\pm$ .02
Hexa- <i>p</i> -ethylphenylethane	29	6.06	.670	.167 $\pm$ .03
Hexa- <i>p</i> - <i>n</i> -propylphenylethane	29	6.81	.662	.209 $\pm$ .03
Hexa- <i>p</i> -isopropylphenylethane	28	6.85	.660	.260 $\pm$ .03
Hexa- <i>p</i> -isobutylphenylethane	29	7.65	.650	.269 $\pm$ .03
Hexa- <i>p</i> - <i>s</i> -butylphenylethane	29	7.66	.635	.330 $\pm$ .03

it is possible to calculate the equilibrium constant for the dissociation of any ethane from the equation

$$K = \frac{\alpha^2 w_0}{1 - \alpha}$$

where  $w_0$  = initial concentration of the ethane.

Then from the equation

$$x_p = \frac{1233}{w_1} \sqrt{K^2 + 4Kw_1} - K$$

where  $w_1$  = the concentration of the ethane, it is possible to calculate the paramagnetic susceptibility due to the free radical for any value of  $w_1$ , and from the equation

$$x_s = \frac{X_d}{M} w_3 + 0.708 w_2 - \frac{\rho}{M} w_1$$

where  $w_2$  = the weight fraction of the solvent, the corresponding measured susceptibility of the solution. Using the values of  $x_s$  obtained in this way,

the amount of undecomposed ethane present at any given time may be obtained from Fig. 2. When the logarithms of the concentrations so obtained are plotted against time (see Fig. 1) a series of straight lines are obtained indicating that the decomposition is apparently a first order reaction.

### Summary

1. Hexa-*p*-alkylphenylethanes in which the alkyl group has a hydrogen atom on the carbon atom attached to the ring have been found to dissociate to free radicals which undergo disproportionation.

2. The degree of dissociation of ethanes in this series has been found to be much higher (17–33%) than was previously thought (2–6%).

3. Ortho- and meta-methyl substituents in hexaphenylethanes have a greater effect on the degree of dissociation than do para-methyl substituents and the ortho- and meta- derivatives give relatively stable radicals.

4. A few di-*p*-alkylphenyltetraphenylethanes have been described. They are more highly dissociated than hexaphenylethane and disproportionate less rapidly than the corresponding hexa-alkyl derivatives. In this series the *t*-butyl derivative did not undergo disproportionation.

URBANA, ILLINOIS

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## The Alleged *cis-trans* Isomerism of alpha- and beta-*p*-Azophenol

BY W. M. LAUER, H. P. KLUG AND S. A. HARRISON<sup>1</sup>

The existence of isomeric forms of *p*-azophenol was reported in 1906 by Willstätter and Benz.<sup>2</sup> One form, designated  $\alpha$ , was obtained by coupling *p*-hydroxybenzenediazonium chloride with phenol or preferably by the fusion of *p*-nitrophenol with potassium hydroxide, while the second form, designated  $\beta$ , resulted from the reduction of benzoquinoneazine with phenylhydrazine.<sup>3</sup> An analysis of the evidence at their disposal led these investigators to the view that *cis-trans* isomerism was the most likely basis upon which to account

for the existence of isomers in this case. This interpretation also was favored by Hantzsch,<sup>4</sup> who studied the absorption spectra of  $\alpha$ - and  $\beta$ -azophenol and their sodium salts. Several years later, Robertson<sup>5</sup> also concluded that this was a case of *cis-trans* isomerism on the basis of a difference in behavior of the two forms, which he observed on bromination and nitration. Thus, he reported that nitration of  $\alpha$ -azophenol gave a tetranitro derivative (m. p. 230°), whereas dinitroazophenol (m. p. 240°) was obtained from  $\beta$ -azophenol, and that bromination produced different tetrabromo derivatives (m. p. 250–252°, m. p.

(1) Abstract of Ph.D. Thesis, 1939.

(2) Willstätter and Benz, *Ber.*, **39**, 3492 (1906).

(3) Two additional forms were described in a later publication [Willstätter and Benz, *ibid.*, **40**, 1578 (1907)], which lists the properties of all of the alleged isomers.

(4) Hantzsch, *ibid.*, **43**, 2512 (1910); see also Tuck, *J. Chem. Soc.*, **95**, 1816 (1909).

(5) Robertson, *ibid.*, **103**, 1472 (1913).