

tetrachloride solution. In the first the reaction was interrupted after six hours and, in the second, after twelve and a half hours. Both gave acidic fractions boiling from 90–180° (1 mm.), but no pure product was isolated. The boiling point changed continuously. The ozonization was not complete in either case. The acidic fraction amounted to 2.1 g. boiling below 100° (1 mm.) and 3.2 g. boiling from 100–180° (1 mm.) with some residue, when the ozonization was carried out for twelve and a half hours. The acid fraction gave no 2,4-dinitrophenylhydrazone.

Preparation of Δ^{11} -Dodecahydro-9-phenanthrene.—This ketone was prepared by the formic acid cyclization of dicyclohexenylacetylene.^{4a} The ketone was fractionated to give a fraction boiling at 135–136° (2 mm.) with the refractive index n_D^{20} 1.5296. The refractive index of the sample did not vary during distillation.

Hydrogenation of Δ^{11} -Dodecahydro-9-phenanthrene to Tetradecahydro-9-phenanthrol.—A solution of 22.2 g. of the ketone in 120 ml. of ethyl alcohol was hydrogenated at 185° under a pressure of 100–200 atmospheres of hydrogen using Raney nickel¹⁰ as the catalyst. Four hours were required for complete reduction to the saturated alcohol. The product from the hydrogenation was filtered and the solvent distilled. The residue was fractionally distilled through a modified Widmer column. The portion boiling at 136–138° (2 mm.) solidified to a waxy solid on standing for a few hours. The product did not give a sharp melting point and it has not been possible to purify it by recrystallization. The wide melting range indicates that the tetradecahydro-9-phenanthrol is a mixture of *cis-trans* isomers.

Anal. Calcd. for $C_{14}H_{24}O$: C, 80.77; H, 11.54. Found: C, 80.87; H, 11.38.

Δ^{11} -Dodecahydrophenanthrene.—The reduction of Δ^{11} -dodecahydro-9-phenanthrene to the corresponding un-

saturated hydrocarbon was carried out by the method of Clemmensen¹⁵ in the manner previously described.^{4a}

Dehydrogenation of Δ^{11} -Dodecahydrophenanthrene.—Four and two-tenths grams of Δ^{11} -dodecahydrophenanthrene was passed repeatedly over platinum-charcoal catalyst⁸ until the material was solid. The dehydrogenation product was removed from the apparatus with acetone and filtered. On recrystallization of the solid, after evaporation of the acetone, phenanthrene separated. The non-crystalline portion which remained in the solvent was recovered and again dehydrogenated and the product recrystallized. The phenanthrene amounted to 2.3 g. and melted at 97–98°. No other dehydrogenation product was isolated.

Anal. Calcd. for $C_{14}H_{10}$: C, 94.38; H, 5.62. Found: C, 94.20; H, 5.90.

Summary

1. Evidence has been presented to show that the cyclization of di- Δ^{11} -cyclohexenylacetylene yields Δ^{11} -dodecahydro-9-phenanthrene and not a spiran derivative.

2. Further evidence to support the view that cyclization of dienes produces ring systems with the *trans*-configuration has been described.

3. Clemmensen reduction of *trans*-3-methyl-4-propyl-1,2,4a,5,6,7,8,8a-octahydro-1-naphthalenone has been found to cause a partial rearrangement of the carbon skeleton to a seven-five fused ring system which yields azulene derivatives on dehydrogenation.

URBANA, ILLINOIS

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

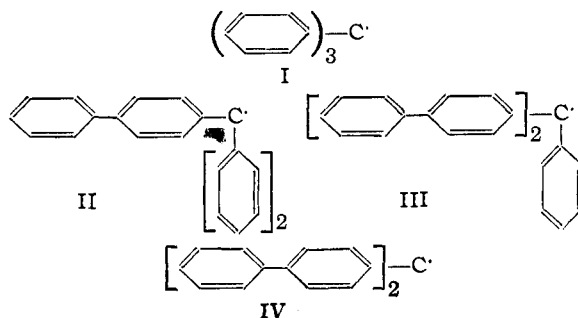
Effect of Substitution on the Dissociation of Hexaarylethanes. VII.¹ Meta and Para Phenyl Groups

By C. S. MARVEL, MAX B. MUELLER AND EMANUEL GINSBERG

A comparison of the degree of dissociation of hexaarylethanes which have phenyl groups substituted for hydrogen atoms in the meta and para positions with respect to their attachment to the ethane carbon atoms is of considerable interest in testing the resonance theory of dissociation of hexaarylethanes.²

It has been pointed out previously² that in triphenylmethyl (I) the odd electron can resonate among ten positions, in diphenyl-*p*-biphenyl-

methyl (II), among thirteen positions, in di-*p*-biphenylmethyl (III), among sixteen positions and in tri-*p*-biphenylmethyl (IV) among nineteen positions.

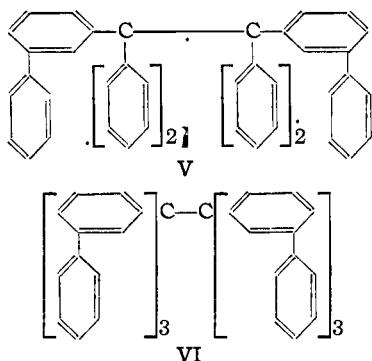


(1) For the sixth communication in this series see THIS JOURNAL, 61, 77 (1939).

(2) Pauling and Wheland, *J. Chem. Phys.*, 1, 362 (1933); 2, 482 (1934); Wheland, *ibid.*, 2, 474 (1934); Hückel, *Trans. Faraday Soc.*, 30, 40 (1934); see also Gilman, "Organic Chemistry," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1938, p. 1850.

Accurate measurements³ have shown that hexaphenylethane and hexa-*p*-biphenylethane dissociate to the extent of 2-3% and 100%, respectively, in one-tenth molar benzene solutions of the ethane at 20°. Hence, the introduction of the para phenyl group has the effect predicted on the resonance theory of increasing markedly the dissociation of the hexaarylethane.

The introduction of a phenyl group into a meta position of triphenylmethyl would not be expected to increase the number of resonance forms. Hence if this factor is the most important one in determining dissociation it would be expected that such ethanes as tetraphenyl-di-*m*-biphenylethane (V) and hexa-*m*-biphenylethane (VI) would exhibit approximately the same degree of dissociation as hexaphenylethane.



Recently it was reported from this Laboratory that hexa-*m*-biphenylethane (VI) was dissociated to the extent of about 60% in a 2.5% solution in benzene at 25°. We have now prepared the tetraphenyl-di-*m*-biphenylethane (V) and find by measurement of its magnetic susceptibility that it is dissociated to the extent of 11-12% in a 3.6% solution of the ethane in benzene at 25°. A determination of the magnetic susceptibility of the corresponding *p*-biphenyl derivative (II) has also been made under the same conditions. This hydrocarbon exists to the extent of 13-14% as the free radical in a 3.6% solution. As would be expected, the dissociation in 7% solution is only 10%.

It is very significant that the degree of dissociation of the mono-*m*-phenyl and mono-*p*-phenyl derivatives of triphenylmethyl should fall so close together and that hexa-*m*-biphenylethane should be dissociated to the extent of 60% which approaches the complete dissociation shown by

(3) (a) Ziegler and Ewald, *Ann.*, **473**, 163 (1929); (b) Roy and Marvel, *This Journal*, **59**, 2622 (1937); (c) Müller, *et al.*, *Ann.*, **520**, 235 (1935); **521**, 89 (1935).

the corresponding para isomer. In view of these values it is evident that the number of resonance forms of the free radical must play a rather minor part in determining the degree of dissociation of these hexaarylethanes.

Another interesting fact has been observed in this study of the meta and para phenyl substituted hexaphenylethanes. Whereas Schlenk, Weikel and Herzenstein⁴ have shown that progressive substitutions of pairs of *p*-phenyl groups in hexaphenylethane produces a shift in the color of the solution from the characteristic yellow of this hydrocarbon to orange-red, red and violet, the substitution of two phenyl groups in the meta position gives only a yellow-orange color and six phenyl groups in the meta position give only an orange-red color although the dissociations of the two series of ethanes seem to be of the same general order. It is thus evident that the depth of color of a free radical solution is not a reliable index of the degree of dissociation. The color of the free radical solution is partly a characteristic of the groups present and their positions and not of the degree of dissociation alone.

Experimental

Diphenyl-*m*-biphenylcarbinol.—The Grignard reagent was prepared from 30 g. of *m*-bromobiphenyl and 3.4 g. of magnesium in 200 cc. of dry ether. The reaction was started by addition of a little ethylmagnesium bromide. To this Grignard reagent was added, with stirring, 25 g. of benzophenone dissolved in 100 cc. of dry ether during about three hours. The solution was then refluxed and stirred another hour. The reaction mixture was treated with a solution of ammonium chloride and cracked ice and then steam distilled. The solid residue was dissolved in an excess (400 cc.) of petroleum ether (b. p. 90-110°) and dried with calcium chloride. The yellow solution was filtered from the calcium chloride and concentrated. The light yellow solid which separated on cooling was recrystallized from hot petroleum ether. The yield was 32 g. (80%) of white crystals melting at 104-105°.

Anal. Calcd. for C₂₆H₂₀O: C, 89.24; H, 6.00. Found: C, 89.24; H, 6.05.

Diphenyl-*m*-biphenylcarbinol Ethyl Ether.—To a solution of 5 g. of the carbinol in 150 cc. of dry ether was added 5 g. of calcium chloride and then dry hydrogen chloride was passed into the mixture until it was saturated. The solution was filtered from the calcium chloride and was concentrated under reduced pressure to a brown viscous sirup. This residue was washed with petroleum ether (b. p. 30-60°) to remove much of the tarry impurity and then dissolved in 100 cc. of hot absolute ethanol. On concentration and cooling 5 g. (94%) of white prismatic needles melting at 78-79° was obtained.

(4) Schlenk, Weikel and Herzenstein, *Ann.*, **372**, 1 (1910); *Ber.*, **43**, 1753 (1910).

TABLE I

Ethane	t_c , °C.	% Ethane	$-x \times 10^4$ Soln.	$-x \times 10^4$ Ethane	$-x \times 10^4$ mol.	$-x\alpha$ $\times 10^4$	$x_p \times 10^4$	α in %	$K = 4\alpha^2/(1-\alpha)$
Di- <i>p</i> -biphenyl-	26	3.63	0.688 ± 0.001	0.006 ± 0.001	103 ± 18	423	320 ± 18	12.8 ± 0.7	3.76×10^{-3}
tetraphenyl-	26	3.63	.686 ± .001	.004 ± .001	70 ± 18	423	353 ± 18	14.1 ± .7	4.63×10^{-3}
	28	7.24	.676 ± .002	.019 ± .002	167 ± 18	423	256 ± 18	10.3 ± .7	4.73×10^{-3}
Di- <i>m</i> -biphenyl-	27	3.63	.690 ± .001	.008 ± .001	140 ± 18	423	283 ± 18	11.4 ± .7	2.93×10^{-3}
tetraphenyl-	26	3.61	.689 ± .001	.007 ± .001	124 ± 18	423	299 ± 18	12.0 ± .7	3.31×10^{-3}

Anal. Calcd. for $C_{27}H_{24}O$: C, 88.97; H, 6.63. Found: C, 88.96; H, 6.55.

Diphenyl - *m* - biphenylchloromethane.—Twenty-five grams of the pure carbinol (or ethyl ether) was dissolved in 100 cc. of hydrogen chloride-free acetyl chloride and the solution refluxed for two hours in an all-glass apparatus. After standing a few hours the dark brown solution was filtered through a sintered glass funnel to remove any tarry material. The filtrate was concentrated and cooled to 0°. The crystals which separated in the course of twenty-four hours were collected and recrystallized from acetyl chloride. The yield was 21 g. (80%) of white crystals melting at 86–87°.

Anal. Calcd. for $C_{26}H_{19}Cl$: Cl, 10.00. Found: Cl, 9.95.

Diphenyl-*m*-biphenylmethyl Peroxide.—A solution of 0.786 g. of diphenyl-*m*-biphenylchloromethane in 25 cc. of dry, thiophene-free benzene was shaken with 3 g. of molecular silver for ten hours in the evacuated measuring apparatus already described. After determining the magnetic susceptibility of the solution, it was transferred as completely as possible to an open beaker. The color disappeared completely within ten minutes. The colorless solution was evaporated to dryness. The slightly colored crystalline residue was recrystallized by dissolving it in 10 cc. of dry benzene followed by the addition of 20 cc. of absolute ethanol. The white crystalline material which separated over a period of twenty-four hours was collected, dried, and weighed: yield, 0.489 g. (66%); m. p. 164–165°.

Anal. Calcd. for $C_{50}H_{38}O_2$: C, 89.55; H, 5.67. Found: C, 89.63; H, 6.01.

***p*-Biphenyl Derivatives.**—These compounds were prepared by the methods of Schlenk.^{4,5}

	Found m. p., °C.	Reported ^{4,5} m. p., °C.
<i>p</i> -Biphenyldiphenylchloromethane	146.5–147	147.5
<i>p</i> -Biphenyldiphenylmethyl peroxide	179–180	180
Di- <i>p</i> -biphenylphenylcarbinol	150–151	151
Di- <i>p</i> -biphenylphenylchloromethane	131–132	131.5

Magnetic Susceptibility Measurements.—The general procedure used for the determination of the dissociation of hexaarylethane has been described previously.^{3b} The results for di-*p*-biphenyltetraphenylethane and di-*m*-biphenyltetraphenylethane are summarized in the table.

Summary

1. Di-*m*-biphenyltetraphenylethane has been prepared in benzene solution.
2. Magnetic susceptibility measurements show that in a 3.6% benzene solution, di-*m*-biphenyltetraphenylethane is 11–12% dissociated while di-*p*-biphenyltetraphenylethane is 13–14% dissociated.
3. It is suggested that the number of resonance forms of the free radical plays a rather minor part in determining the degree of dissociation of an hexaphenylethane.

(5) Schlenk, *Ann.*, **368**, 295 (1909).

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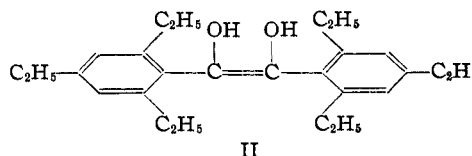
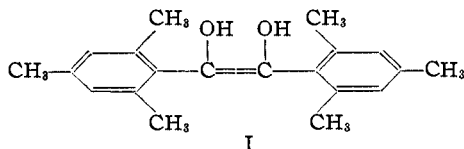
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1,2-Diarylacetylene Glycols. II. An Enediol from Hexaethylbenzil

BY REYNOLD C. FUSON, JOSEPH CORSE AND C. H. MCKEEVER¹

The remarkable stability of the enediol, 1,2-dimesitylacetylene glycol (I),² is even more pronounced in its ethyl analog 1,2-di-(2,4,6-triethylphenyl)-acetylene glycol (II).



The latter, for example, is much more stable in air; it can be exposed to the atmosphere for hours without appreciable change. The methyl compound, on the other hand, is so readily oxidized that it is extremely difficult to purify.

(1) Röhlm and Haas Research Assistant.

(2) Fuson and Corse, *THIS JOURNAL*, **61**, 975 (1939).