

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	$.686 \pm .001$	$.004 \pm .001$	70 ± 18	423	353 ± 18	$14.1 \pm .7$	4.63×10^{-3}
	28	7.24	$.676 \pm .002$	$.019 \pm .002$	167 ± 18	423	256 ± 18	$10.3 \pm .7$	4.73×10^{-3}
Di- <i>m</i> -biphenyl-	27	3.63	$.690 \pm .001$	$.008 \pm .001$	140 ± 18	423	283 ± 18	$11.4 \pm .7$	2.93×10^{-3}
tetraphenyl-	26	3.61	$.689 \pm .001$	$.007 \pm .001$	124 ± 18	423	299 ± 18	$12.0 \pm .7$	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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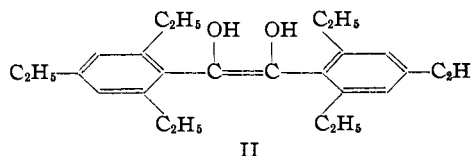
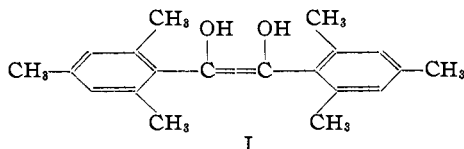
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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

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

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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) Röhm and Haas Research Assistant.

(2) Fuson and Corse, *This Journal*, **61**, 975 (1939).

from the mixture by washing with low-boiling petroleum ether. The enediol could be recrystallized by dissolving it in a small amount of ether, evaporating this solution to a small volume and adding low-boiling petroleum ether. There was obtained 8 g. of the enediol, m. p. 148–152° (with decomposition) in an open capillary and 154–155° in a nitrogen-filled capillary.

Anal. Calcd. for $C_{26}H_{36}O_2$: C, 82.05; H, 9.53. Found: C, 81.71; H, 9.79.

The low-boiling petroleum ether solution was allowed to stand at room temperature. After several hours the 2,4,6,2',4',6'-hexaethylbenzil started to crystallize; yield, 5 g. From the potassium bicarbonate washings there was obtained 1.5 g. of triethylbenzoic acid.

The enediol did not dissolve in cold 40% aqueous sodium hydroxide solution. It reduced Tollens' reagent as well as ferric chloride and cupric acetate at 0°, and gave a positive test with 2,6-dichlorobenzeneoneindophenol. Oxidation converts it to the benzil.

The glycol was prepared also by hydrogenation of the benzil on methyl alcohol according to the procedure of Thompson⁴ for the methyl analog.

The enediol was recrystallized from ether-petroleum ether mixture. The melting point in an open capillary was 149–151°, with decomposition. In a nitrogen-filled capillary the melting point was 154–155.5°. The melting point of a mixture of this product with the sample prepared from the acid chloride showed no depression.

In later experiments it was found more convenient to use low-boiling petroleum ether as the solvent in the reduction. The enediol precipitated as it was formed. The reaction mixture was filtered and the enediol dissolved in a small amount of ether. This solution was filtered to remove the catalyst and the enediol reprecipitated by evaporating most of the ether and adding low-boiling petroleum ether.

Diacetate (Low-Melting).—When the benzil was hydrogenated in acetic anhydride according to the method of Thompson⁴ a diacetate was formed. It crystallized from methyl alcohol in glistening white columns melting at 133.5–134°.

Anal. Calcd. for $C_{30}H_{40}O_4$: C, 77.55; H, 8.68. Found: C, 77.49; H, 8.21.

Diacetate (High-Melting).—One-half gram of the enediol was washed with low-boiling petroleum ether, then added to 3 cc. of acetic anhydride, and the solution refluxed gently for three hours. The light brown reaction mixture was poured into water and heated on the steam cone for a few minutes to decompose the excess acetic anhydride. It was extracted with ether, the ether extracts washed with three portions of a 10% solution of potassium carbonate, then with water. The ether was removed and the solid recrystallized from ethyl alcohol. There was obtained 0.2 g. of white needles which melted at 188–190°, and a very small amount of light yellow oil.

Anal. Calcd. for $C_{30}H_{40}O_4$: C, 77.55; H, 8.68. Found: C, 77.64; H, 8.83.

Dibenzoates.—A mixture of 1.8 g. of the enediol, 30 cc. of pyridine and 5 cc. of benzoyl chloride was refluxed gently for three and one-half hours. The reaction mixture, now red, was allowed to stand at room temperature for three hours, then poured into 100 cc. of water. It was extracted with 70 cc. of benzene, the benzene extract washed three times with a 10% solution of potassium bicarbonate, then acidified with dilute hydrochloric acid, washed several times with large portions of very dilute hydrochloric acid, and finally washed with water. The benzene was removed by an air blast. The white solid which remained was partially soluble in alcohol. It was recrystallized from a benzene-absolute alcohol mixture, m. p. 235–236°.

Anal. Calcd. for $C_{40}H_{44}O_4$: C, 81.6; H, 7.53. Found: C, 81.82; H, 7.82.

The filtrate was evaporated to dryness. There remained 0.8 g. of a compound which crystallized readily from 95% alcohol, m. p. 124–124.5°.

Anal. Calcd. for $C_{40}H_{44}O_4$: C, 81.6; H, 7.53. Found: C, 81.35; H, 7.40.

2,4,6,2',4',6'-Hexaethylbenzoin.—To 40 cc. of methyl alcohol saturated with dry hydrogen chloride was added 1.8 g. of the enediol. The solution was refluxed for two and one-half hours. The reaction vessel was stoppered tightly and allowed to stand overnight at room temperature. The reaction mixture was then poured into water and extracted with ether; the ether extracts were washed and dried over calcium chloride. After the ether had been removed, there remained 1.6 g. of a light yellow mixture of compounds. By washing this mixture with small portions of low-boiling petroleum ether the yellow color was removed. From these washings a small amount of 2,4,6,2',4',6'-hexaethylbenzil was obtained. The benzoin was recrystallized from low-boiling petroleum ether, m. p. 64–65.5°.

Anal. Calcd. for $C_{26}H_{36}O_2$: C, 82.05; H, 9.53. Found: C, 82.37; H, 9.23.

The benzoin did not reduce Tollens' reagent or copper acetate. It gave a negative test with 2,6-dichlorobenzeneoneindophenol. Oxidation with chromic anhydride, however, converted it to the benzil.

Summary

A new enediol, 1,2-di-(2,4,6-triethylphenyl)-acetylene glycol (II), has been synthesized and characterized.

It yields two diacetates and two dibenzoates, and can be caused to rearrange to the corresponding benzoin.

It is readily oxidized, but is not soluble in aqueous alkali.

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