TABLE I											
Ethane	°Ċ.	% Ethane	$-x \times 10^{6}$ Soln.	$-x \times 10^{6}$ Ethane	$-x \times 10^{6}$ mol.	$-\chi_{lpha} \times 10^6$	$\chi_ ho imes 10^8$	αin %	$K = 4\alpha^2 c / (1 - \alpha)$		
Di-p-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	$14.1 \pm .7$	4.63×10^{-3}		
	28	7.24	$.676 \pm .002$	$.019 \pm .002$	167 ± 18	423	$256 \neq 18$	$10.3 \pm .7$	4.73×10^{-3}		
Di-m-biphenyl-	27	3.63	.690 = .001	.008 ± .001	140 = 18	423	283 ± 18	$11.4 \pm .7$	2.93×10^{-3}		
tetraphenyl-	26	3.61	.689 ± .001	$.007 \pm .001$	124 = 18	423	299 = 18	$12.0 \pm .7$	3.31×10^{-3}		

Anal. Calcd. for C₂₇H₂₄O: 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 $C_{25}H_{19}Cl$: 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 C₅₀H₂₈O₂: 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 ^{4,6} m. p., °C.
<i>p</i> -Biphenyldiphenylchloromethane	146.5 - 147	147.5
p-Biphenyldiphenylmethyl per-		
oxide	179 - 180	180
Di-p-biphenylphenylcarbinol	150 - 151	151
${\it Di-p-biphenylphenylchloromethane}$	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).

URBANA, ILLINOIS

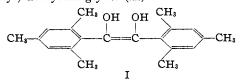
RECEIVED MAY 27, 1939

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

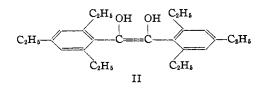
1,2-Diarylacetylene Glycols. II. An Enediol from Hexaethylbenzil

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

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



⁽¹⁾ Röhm and Haas Research Assistant.



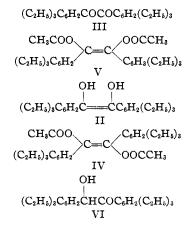
The latter, for example, is much more stable in air; it can be exposed to the atmosphere for hours without appreciable change. The methyl compound, on the other hand, is so readily oxidized that it is extremely difficult to purify.

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

Considerable practical advantage is gained, therefore, by working with the ethyl compound.

The new enediol (II) was made by the action of the binary mixture, Mg + MgI₂,³ on 2,4,6triethylbenzoyl chloride and by the method of Thompson⁴—catalytic hydrogenation of the corresponding benzil (III). Both synthetic products melted at 154–155.5° and a mixed melting point showed no lowering.

The action of acetic anhydride gave a diacetate (IV), melting at $189-190^{\circ}$ —probably the *trans* form. A second diacetate (V) forms when the benzil is hydrogenated in acetic anhydride solution. This isomer—assigned the *cis* configuration—melts at $133.5-134^{\circ}$.



A mixture of two dibenzoates was formed by the action of benzoyl chloride in pyridine. These melt at 124.5° and $235-236^{\circ}$ and presumably possess, respectively, the *cis* and *trans* configurations; treatment with alcoholic potassium hydroxide converts them to the benzil (III).

Like the methyl analog the new glycol (II) can be caused to rearrange slowly to the corresponding benzoin (VI) by heating in a methanol solution containing hydrogen chloride. The benzoin is stable in air and shows no tendency to revert spontaneously to the glycol. In this respect the new enediol and the benzoin appear to differ from ordinary keto-enol pairs; these compounds are not readily interconvertible.

Another property which distinguishes this enediol from ordinary enols is its neutral character. This behavior suggests that vinyl alcohols in general may prove to be neutral substances and that they take on an acidic character only when conjugated with a negative group such as the carbonyl group. This point of view is supported by the observation that in reductone⁵ and ascorbic acid⁶ the β -hydroxyl group is acidic while the α -hydroxyl group is neutral. The enediol shows infrared absorption maxima at 2.78 and 2.83 μ which may be interpreted to indicate the presence of two hydroxyl groups. Maxima in this region are normally indicative of acidic hydroxyl groups. The double peak observed here is similar to those of compounds in which two hydroxyl groups are held by the same atom. The benzoin, on the other hand, shows a single absorption maximum at 2.85 μ —presumably due to one hydroxyl group.

The authors are indebted to Professors A. M. Buswell and W. H. Rodebush and to Mr. J. R. Downing for the determination and interpretation of the infrared absorption data.

Experimental

2,4,6-Triethylbenzoyl Chloride.—Consistently high yields of this acid chloride were obtained by the thionyl chloride method. This procedure is preferable to that using phosphorus pentachloride⁷ since the latter occasionally gave low yields. To 30 g. of 2,4,6-triethylbenzoic acid which had been dried for twelve hours at 60° over phosphorus pentoxide was added, all at once, 21 cc. of thionyl chloride. The reaction started immediately. The mixture was allowed to stand for four hours at room temperature. The excess thionyl chloride was removed under diminished pressure and the acid chloride distilled *in vacuo*. There was obtained 27.5 g. (85% of the theoretical amount) of 2,4,6-triethylbenzoyl chloride, b. p. 108–110° (2 mm.).

1,2-Di-(2,4,6-triethylphenyl)-acetylene Glycol.—A binary mixture of magnesium and magnesium iodide was prepared from 9 g. of magnesium and 46 g. of iodine according to the method of Gomberg and Bachmann.³ A stream of dry nitrogen was passed through the vessel throughout the period of reaction.

A solution of 32.6 g. of 2,4,6-triethylbenzoyl chloride in 30 cc. of dry ether was added dropwise to the binary mixture. The reaction mixture was stirred for twenty-four hours before nearly all the magnesium had gone into solution. The solution was decanted into a separatory funnel which contained 200 g. of eracked ice and 16 cc. of glacial acetic acid. The ether-benzene layer was separated and washed *rapidly* with three portions of a 10% solution of potassium bicarbonate, once with water, twice with a 5% solution of sodium thiosulfate and twice more with water. The benzene and ether were removed as rapidly as possible under diminished pressure, using a nitrogenfilled capillary tube. The residue was a mixture of white and yellow crystals. The yellow benzil was separated

(7) Fuson and Corse, THIS JOURNAL, 60, 2063 (1938).

⁽³⁾ Gomberg and Bachmann, THIS JOURNAL, 49, 236) 1927).

⁽⁴⁾ Thompson, *ibid.*, **61**, 1281 (1939).

⁽⁵⁾ Euler and Martins, Svensk. Kem. Tidskr., **45**, 73 (1933); Norrish and Griffiths, J. Chem. Soc., 2837 (1928).

⁽⁶⁾ Reichstein, Grüssner and Oppenauer, Helv. Chim. Acta, 17, 510 (1934).

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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. $148-152^{\circ}$ (with decomposition) in an open capillary and $154-155^{\circ}$ in a nitrogen-filled capillary.

Anal. Calcd. for C₂₆H₃₆O₂: 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 $149-151^{\circ}$, with decomposition. In a nitrogen-filled capillary the melting point was $154-155.5^{\circ}$. 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 $133.5-134^{\circ}$.

Anal. Calcd. for C₈₀H₄₀O₄: 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 C₈₀H₄₀O₄: 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. $235-236^{\circ}$.

Anal. Calcd. for C₄₀H₄₄O₄: 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. $124-124.5^{\circ}$.

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. $64-65.5^{\circ}$.

Anal. Calcd. for C₂₈H₃₆O₂: 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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RECEIVED MAY 31, 1939