

was dissolved in absolute ethanol and reprecipitated with dry ether; m. p. 145–146°.

Anal. Calcd. for $C_{10}H_{18}N_2Cl_2$: N, 11.81. Found: N, 11.68, 11.63.

N,N'-Dibenzoyl-4-phenyl-1,3-butanediamine.—When 0.8 g. of the above diamine sulfate was mixed with 12 cc. of 15% sodium hydroxide solution, an oil appeared on the surface of the alkali. Addition of 1.35 g. of benzoyl chloride and shaking precipitated 1.1 g. of the colorless benzoyl derivative which was recrystallized from ethanol; m. p. 174–175°.

Anal. Calcd. for $C_{24}H_{24}O_2N_2$: N, 7.52. Found: N, 7.58, 7.62.

Summary

1. 5-Benzyl- and 6-benzyluracil have been reduced catalytically to the corresponding hydro-

uracils, and to the corresponding 2-ketohexahydro-pyrimidines.

2. The benzene ring in the benzyl group occupying the 5-position was attacked, one of the products of reduction of 5-benzyluracil being 2-keto-5-hexahydrobenzylhexahydro-pyrimidine. No hydrogenation was observed of the benzene ring in the isomeric 6-benzyluracil.

3. The structures of the reduction products of 6-benzyluracil were established by hydrolysis of 6-benzylhydrouracil to β -benzalpropionic acid, and of 2-keto-6-benzylhexahydro-pyrimidine to 4-phenyl-1,3-butanediamine.

NEW HAVEN, CONN.

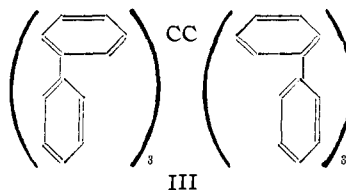
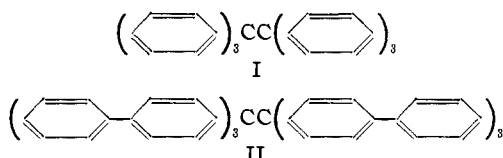
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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Effect of Substitution on the Dissociation of Hexaarylethanes. VI. Hexa-*m*-biphenylethane¹

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

The effect of substituting phenyl groups for the para-hydrogen atoms in hexaphenylethane (I) has been studied by Schlenk and his students.² Whereas hexaphenylethane is dissociated to the extent of only 2.5%, tetraphenyldibiphenylethane exists to the extent of 15% as a free radical, the corresponding tetrabiphenyl derivative is 80% free radical and the hexa-*p*-biphenyl derivative (II) is completely dissociated. The increased possibility for resonance in the *p*-biphenyl derivative has been cited as one reason for this marked increase in dissociation.³ On this basis the *m*-biphenyl group would not be expected to have a much greater effect than an unsubstituted phenyl group. Hence it seemed of interest to prepare hexa-*m*-biphenylethane (III) and to determine the degree of dissociation by the magnetic susceptibility method.⁴



m-Bromobiphenyl was prepared from *m*-bromoaniline and benzene according to the general method devised by Gomberg and Bachmann⁵ for the preparation of substituted biphenyls. Conversion of the *m*-bromobiphenyl to the Grignard reagent and addition of this to ethyl carbonate gave tri-*m*-biphenylcarbinol. The chloride and ethane (III) were obtained by the usual procedures.⁶ The ethane was not isolated but the solution was exposed to the air and the peroxide thus produced was characterized.

A light red, 0.025 molar solution of hexa-*m*-biphenylethane in benzene was prepared by shaking the chloromethane in benzene with silver for ten hours and then filtering the solution. Experiments showed that a 0.1 molar solution such as was used in the earlier work⁶ could not be prepared because of low solubility of the ethane. Also it was found in these preliminary experiments that shaking the solutions used in the preparation of the ethane for more than ten hours caused a

(1) For the fifth communication in this series see *THIS JOURNAL*, **59**, 2622 (1937).

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

(3) Pauling and Wheland, *J. Chem. Phys.*, **1**, 362 (1933).

(4) Müller, *et al.*, *Ann.*, **520**, 235 (1935); **521**, 89 (1935); see also ref. 1.

(5) Gomberg and Bachmann, *THIS JOURNAL*, **46**, 2339 (1924).

(6) Copenhaver, Roy and Marvel, *ibid.*, **57**, 1311 (1935).

decrease in the apparent dissociation which was probably due to rearrangement of the ethane. Magnetic susceptibility determinations showed that the ethane was dissociated to the extent of 59–60%.

Experimental

***m*-Bromobiphenyl.**—The procedure described by Gomberg and Bachmann⁷ for *p*-bromobiphenyl was adapted to this preparation. The runs were twice the size of those reported for the *p*-isomer. After the coupling reaction was completed, the benzene layer was washed with sodium carbonate solution, with water and then four to six times with 100-cc. portions of concentrated sulfuric acid until the reddish color of the benzene layer had almost completely disappeared. The benzene was then removed and the *m*-bromobiphenyl distilled with superheated steam as described for the *p*-isomer. The oily product was separated, dried and distilled under reduced pressure. The yield was 17 g. (16%) of a light yellow oil boiling at 169–173° at 17 mm.; n_D^{20} 1.6411; d_4^{20} 1.410.

Anal. Calcd. for $C_{12}H_{10}Br$: Br, 34.32. Found: Br, 34.42.

Tri-*m*-biphenylcarbinol.—The Grignard reagent was prepared from 20 g. of *m*-bromobiphenyl and 2.2 g. of magnesium in about 120 cc. of dry ether. The reaction was started by addition of a little iodine and activated magnesium.⁸ To this Grignard reagent was added, with stirring, 3 cc. of ethyl carbonate in 25 cc. of dry ether during about three hours. The solution was then refluxed and stirred for another three hours. The reaction mixture was treated with a solution of ammonium chloride and cracked ice and steam distilled. The solid residue was collected on a filter and dried. The yield was 12 g. of a powdery product which melted over a wide range and which was not further purified.

Tri-*m*-biphenylchloromethane.—To ten grams of the crude carbinol in 200 cc. of dry ether was added 10 g. of calcium chloride and then dry hydrogen chloride was passed into this mixture. The solution turned brown and

(7) Gomberg and Bachmann, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1932, p. 109.

(8) Gilman and Kirby, *Rec. trav. chim.*, **54**, 577 (1935).

a precipitate separated. The solid was collected on a filter and recrystallized from hot benzene. The yield was 4.6 g. (44%) of white crystals melting at 200–201°.

Anal. Calcd. for $C_{27}H_{27}Cl$: Cl, 7.00. Found: Cl, 6.89, 7.15.

Tri-*m*-biphenylmethyl Peroxide.—A solution of 1.2 g. of hexa-*m*-biphenylethane, prepared by shaking 1.3 g. of tri-*m*-biphenylchloromethane in 25 cc. of dry benzene with 4 g. of molecular silver in a sealed tube for twenty-four hours, was exposed to the air. The color disappeared rapidly. The supersaturated solution of the peroxide was allowed to stand for twenty-four hours. At the end of that time the precipitated peroxide (about 0.5 g.) was collected on a filter. The compound was recrystallized by dissolving it in 50 cc. of dry benzene and adding 150 cc. of absolute alcohol. After several recrystallizations the compound melted at 179.5–180°.

Anal. Calcd. for $C_{74}H_{56}O_2$: C, 91.17; H, 5.52. Found: C, 91.20; H, 5.67.

Magnetic Susceptibility Measurements.—The general procedure used for the determination of the dissociation of hexaarylethanes has been described previously.¹ The dissociation of hexa-*m*-biphenylethane was determined for two samples of the material. The results are summarized in the table.

<i>t</i> , °C.	25	25
Ethane, %	2.53	2.53
$-x \times 10^6$ soln.	0.667 ± 0.001^a	0.666 ± 0.001^a
$-x \times 10^6$ ethane	-0.023	-0.024
$-x_{mol} \times 10^6$ ethane	-857	-895
$-x_d \times 10^6$ ethane	620	620
$x^{\beta} \times 10^6$	1477	1515
α , %	59.1 ± 1.5	60.6 ± 1.5

^a This value is calculated from the average of 48 cathetometer readings.

Summary

Hexa-*m*-biphenylethane has been prepared. Magnetic susceptibility measurements show that it is dissociated to the extent of 59–60% in an approximately 2.5% benzene solution at 25°.

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