

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

The Dissociation of Hexaarylethanes. XII.¹ The Effect of Naphthyl and Biphenyl Groups

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Work by Bachmann and Kloetzel² has indicated that the very high dissociations reported in the older literature for triarylmethyls containing *p*-biphenyl, α -naphthyl and β -naphthyl groups are in error. This communication confirms their results and extends them to a larger number of derivatives. The dissociations were measured by the magnetic susceptibility method previously described.³

To be comparable degrees of dissociation should be measured at the same concentration. This is not always possible because of solubility difficulties. It is possible, however, to calculate all the dissociations at 0.1 molar concentration by applying the mass law. That this calculation is justified for toluene solution has been shown recently by Preckel and Selwood.⁴ We have extended this to benzene solutions and determined the degree of dissociation of di- α -naphthyltetraphenylethane at 25° at different concentrations. The results of these experiments are given in Table I.

TABLE I
DISSOCIATION OF DI- α -NAPHTHYLTETRAPHENYLETHANE AT 25° IN BENZENE SOLUTION

Ethane	Molarity	$-\chi$ Sol. $\times 10^3$	α , %	α at 0.1 M calcd. from mass law, %
7.0	0.107	0.6315	25 \pm 2	26 \pm 2
6.63	.1	.6296	27 \pm 2	27 \pm 2
3.34	.05	.6550	36 \pm 2	27 \pm 2
1.67	.025	.6755	45 \pm 4	26 \pm 3
0.839	.0125	.6852	66 \pm 7	29 \pm 5

The aryl substituted ethanes which have been studied are reported in Table II.

TABLE II

Ethane	M	Concn. ethane, %	$-\chi$ Sol. $\times 10^3$	α Measured, %	α calcd. at 0.1 M, %
Tetra- <i>p</i> -biphenyldiphenyl-	0.1	8.9	0.6539	18 \pm 2	18 \pm 2
Hexa- <i>p</i> -biphenyl-	.0125	1.34	.6874	56 \pm 10	26 \pm 5
Di- β -naphthyltetraphenyl-	.1	6.16	.6887	6 \pm 2	6 \pm 2
Tetra- β -naphthyl-diphenyl-	.1	7.85	.6668	13 \pm 2	13 \pm 2
Hexa- β -naphthyl-	.0062	0.56	.6928	80 \pm 15	21 \pm 10
	.0125	1.113	.6869	53 \pm 10	24 \pm 5
Di- α -naphthyl-di- <i>p</i> -biphenyldiphenyl-	.1	8.3	.5512	54 \pm 2	54 \pm 2

(1) For the eleventh communication in this series see *THIS JOURNAL*, **63**, 1892 (1941).

(2) Bachmann and Kloetzel, *J. Org. Chem.*, **2**, 362 (1937).

(3) Müller, *et al.*, *Ann.*, **520**, 235 (1935); **521**, 89 (1935); Roy and Marvel, *THIS JOURNAL*, **59**, 2622 (1937).

(4) Preckel and Selwood, *ibid.*, **63**, 3397 (1941).

Discussion of Results

All except one of the ethanes have been studied previously, and our methods of preparation and the properties of the intermediates in general checked those reported. The new ethane, diphenyltetra- β -naphthylethane, was prepared by standard procedures and characterized as the peroxide. Bachmann and Kloetzel measured the molecular weight in freezing benzene and calculated the dissociation of di-*p*-biphenyltetraphenylethane as 16% at 0.032 *M*, of hexa-*p*-biphenylethane as 76% at 0.0086 *M*, of di- α -naphthyltetraphenylethane as 28-31% at 0.04 *M*, and of di- β -naphthyltetraphenylethane as 6-9% at 0.04 *M*. If these values are calculated to 0.1 *M* by means of the mass law they become 9, 36, 20 and 5%, respectively. These values are in fair agreement with the values determined by the magnetic susceptibility method.

It should be noted that Müller, Müller-Rodloff and Bunge,⁵ have shown that tri-*p*-biphenylmethyl is 100% free radical in the solid state. Apparently the free radical is less soluble than the ethane and in the solid state only the one phase exists, whereas in solution the radical and ethane are in equilibrium.

The dissociations of the series of β -naphthyl derivatives show that there is a steady increase in dissociation as the number of β -naphthyl groups increases, but the degree of dissociation of the hexa-substituted compound is less than that reported by Tschitschibabin and Korjagin.⁶ The marked difference in the dissociation of the di- β -

naphthyl derivatives (6 \pm 2%) and of the di- α -naphthyl derivative (26 \pm 2%) indicates again

(5) Müller, Müller-Rodloff and Bunge, *Ann.*, **520**, 231 (1935).

(6) Tschitschibabin and Korjagin, *J. prakt. Chem.*, **88**, 505 (1913).

the importance of the steric factor. This was also pointed out by Preckel and Selwood.⁴

Another point which should be emphasized is that there is a difference in the di- and tetra-substituted β -naphthyl derivatives (6 and 13%), whereas in the alkyl substituted compounds in this general series these differences between di- and tetra-substituted compounds were not found.¹ However, the hexa-substituted derivatives in the alkyl and aryl series all seem to fall in about the same range (25-35%). From the data of Gomberg and Schoepfle⁷ it seems likely that our 0.1 *M* solutions of di- α -naphthyltetraphenylethane were supersaturated.

All of the aryl-substituted ethanes except tetra-*p*-biphenyldiphenylethane were relatively stable as indicated by the constant value for their magnetic susceptibilities over twenty-four hour periods. Tetra-*p*-biphenyldiphenylethane solutions deposited heavy white crystalline precipitates in twenty-four hours. Hexa- β -naphthylethane showed a decrease in color and a change in magnetic susceptibility on exposure to diffused daylight over a period of one week.

(7) Gomberg and Schoepfle, *THIS JOURNAL*, **39**, 1652 (1917).

The following new compounds were characterized:

Phenyldi- β -naphthylmethylperoxide, m. p. 168-169°.

Anal. Calcd. for $C_{34}H_{38}O_2$: C, 90.25; H, 5.30. Found: C, 90.12; H, 5.84.

Phenyldi-*p*-biphenylmethylperoxide, m. p. 151-152°.

Anal. Calcd. for $C_{12}H_{16}O_2$: C, 90.51; H, 5.59. Found: C, 90.54; H, 5.94.

Phenyldi- β -naphthylmethylchloride, m. p. 159-160°.

Anal. Calcd. for $C_{27}H_{17}Cl$: Cl, 9.42. Found: Cl, 8.92.

Summary

The degrees of dissociation of several hexaphenylethanes combining α -naphthyl, β -naphthyl and *p*-biphenyl radicals have been examined by the magnetic susceptibility method. The dissociations observed are lower than reported in the older literature. The difference in the effect of an α - and a β -naphthyl group on the degree of dissociation is very marked.

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[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

The Preparation of Orthoesters

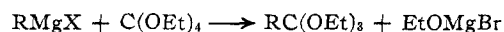
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The work in this Laboratory to date indicates that the only general method that is available for the preparation of ketene acetals of the type $RCH=C(OEt)_2$ involves the elimination of the elements of ethyl hypohalite from an α -halogenated orthoester by the action of metallic sodium.¹ Consequently, the preparation and study of these higher ketene acetals are dependent upon the availability of the corresponding orthoesters as starting materials. The present paper is a summary of a large number of experiments which had as their objective practical and reliable procedures for the preparation of the esters of orthoacetic acid, certain of its derivatives and higher homologs.

Two methods of preparation of orthoesters that would seem to be of general applicability have been reported in the literature. One of these is

(1) Walters and McElvain, *THIS JOURNAL*, **62**, 1482 (1940).

the Tschitschibabin procedure² which involves the reaction of a Grignard reagent with ethyl orthocarbonate



This procedure is analogous to the widely used Tschitschibabin method for the preparation of acetals by the reaction of a Grignard reagent with ethyl orthoformate, $HC(OEt)_3$. While the latter reaction is a very useful preparational method, all of the experience in this Laboratory points to the conclusion that the reaction between a Grignard reagent and orthocarbonic ester is not a satisfactory method of preparation of orthoesters. Instead of the desired orthoester the reaction products are practically wholly a mixture of the ketal $R_2C(OEt)_2$ and the ether R_3COEt and all attempts to alter this result have been consistently unsuccessful.³

(2) Tschitschibabin, *Ber.*, **38**, 563 (1905).

(3) McBane, M.S. Thesis, University of Wisconsin, 1941.