Table II

Milligrams of Phosphorus from the Phospholipins of 1 g. of Material

Subs.	Darso	Red kafir	White kafir	White milo	Feterita
Grav. method	31	42	33	36	26
Micro-col. method	30	40	32	36	27

In conclusion, I take pleasure in thanking Dr. C. T. Dowell, Dr. V. G. Heller, and Mr. W. D. Gallup for their suggestions and coöperation, during this investigation.

Summary

A quick and accurate method for the estimation of the relative amounts of phospholipins in various seeds is described. Results obtained by this method check very satisfactorily with those obtained by the usual gravimetric method, which requires a hundred times the amount of material. The phospholipin content of a number of seeds has been determined. A few results are given here in order to show the accuracy of the method, and other results will be published in due time.

Stillwater, Oklahoma

[Contribution from the Chemical Laboratory of Iowa State College]

BETA-XENYLHYDROXYLAMINE AND ITS REARRANGEMENT

By Henry Gilman and James E. Kirby[1]

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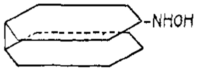
Introduction

The reactions of a number of diphenyl derivatives have been interpreted on the basis that the two phenyl groups have at times a bi-planar and not a co-planar configuration.[2] If this is the case with β-xenylhydroxylamine, then one of its bi-planar formulas can be represented as follows.



Aryl hydroxylamines undergo ready rearrangement, particularly under the influence of mineral acids, to give aminophenols, the hydroxyl group rearranging to the *para* and, to a less extent, to the *ortho* position. Be-

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[1] This paper is an abstract of a part of a thesis presented by James E. Kirby in partial fulfilment of the requirements for the degree of Master of Science in Chemistry at Iowa State College.

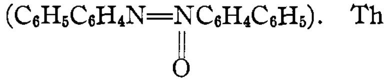
[2] Kaufler, *Ann.*, **351**, 151 (1907); *Ber.*, **40**, 3250 (1907). Cain, Coulthard, and Micklethwait, *J. Chem. Soc.*, **101**, 2298 (1912). Cain and Micklethwait, *ibid.*, **105**, 1437 (1914). Turner, *ibid.*, **107**, 1495 (1915). Kenner and Stubbings, *ibid.*, **119**, 593 (1921). Christie and Kenner, *ibid.*, **121**, 614 (1922). Adams, Bullock and Wilson, This Journal, **45**, 521 (1923). Raiford and Clark, *ibid.*, **48**, 485 (1926).

cause of the proximity of the *p'* or 4' position in the above bi-planar formula for β-xenylhydroxylamine, there is the possibility that on rearrangement the hydroxyl group might go to the *para* position of the second phenyl group to give the known 4-amino-4'-hydroxydiphenyl (4-$NH_2C_6H_4$.-C_6H_4OH-4').

It has been shown that a rearrangement of this type does not take place. This agrees with related work reported recently by Raiford and Clark.[3] They obtained the acetyl-benzoyl derivatives of 4-amino-4'-hydroxydiphenyl in isomeric forms that showed no tendency to rearrange. This behavior opposes the theory that Positions 4 and 4' in diphenyl derivatives are fixed relatively as suggested by the Kaufler-Cain bi-planar formula.

Rearrangements of the kind shown by arylhydroxylamines can be better studied by other classes of compounds. For example, the allyl ethers of phenols and the bromo- and chloro-anilines undergo smooth rearrangements to the *para* and, to a smaller extent, to the *ortho* positions. Studies now in progress on the allyl ether of *p*-hydroxydiphenyl and on *p*-bromo-aminodiphenyl (*p*-$BrNHC_6H_4.C_6H_5$) show that the allyl group and the bromine rearrange almost exclusively to the *ortho* position to the hydroxyl and amino groups, respectively. These are hardly unexpected results inasmuch as it is well known that when the *para* position is blocked (and a phenyl group blocks the *para* position in diphenyl derivatives) the group that rearranges enters the *ortho* position. Obviously a more satisfactory test for the bi-planar formula in rearrangements of this type is to be found in compounds where the two *ortho* positions are blocked. Then, if any rearrangement takes place, and if the *ortho* substituents are of the kind that do not submit to displacement, the group that rearranges should go to the second phenyl group inasmuch as *meta* rearrangement rarely occurs and then only to a very limited extent.

Experimental Part

The β-xenylhydroxylamine was prepared in the customary manner by reducing *p*-nitrodiphenyl by means of zinc dust in a neutral alcoholic solution. The hydroxylamine was precipitated by pouring into water. At first it was virtually impossible to obtain the hydroxylamine by filtration. It is unusually sensitive[4] to oxidation and is readily and almost completely converted to *p,p'*-azoxybisbiphenyl  $(C_6H_5C_6H_4N{=}\underset{\underset{O}{\|}}{N}C_6H_4C_6H_5)$. The dilute alcoholic solution prior to filtration showed the usual reactions for

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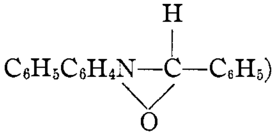
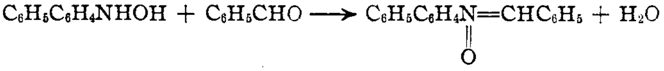
[3] Raiford and Clark, Ref. 2, p. 483.

[4] Diphenylhydroxylamine ($(C_6H_5)_2NOH$) has been prepared from the Grignard reagent by Wieland and Roseeu [*Ber.*, **45**, 494 (1912); **48**, 1117 (1915)]. It, too, is unusually unstable. 4,4'-Di-β-hydroxylaminodiphenyl ($HONHC_6H_4.C_6H_4NHOH$) has been prepared by Fischer and Hepp [*Ber.*, **20**, 2471 (1887)] by a diazo-coupling reaction.

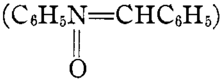
an arylhydroxylamine. In particular, it underwent ready condensation with benzaldehyde to give the corresponding α-phenyl-N-xenylnitrone (or N-α-epoxy-N-xenylbenzylamine, $C_6H_5C_6H_4\underset{\diagdown O \diagup}{N{-}\overset{\overset{H}{|}}{C}}{-}C_6H_5$) as follows.





$$C_6H_5C_6H_4NHOH + C_6H_5CHO \longrightarrow C_6H_5C_6H_4\underset{\overset{\|}{O}}{N}{=}CHC_6H_5 + H_2O$$

This nitrone was prepared also according to the suggestive work of Gattermann[5] who reduced nitrobenzene electrolytically in the presence of benzaldehyde in order to arrest reduction at the hydroxylamine stage by having it combine *in situ* with benzaldehyde to form the corresponding nitrone. The α-phenyl-N-phenylnitrone ($C_6H_5\underset{\overset{\|}{O}}{N}{=}CHC_6H_5$) was prepared previously by Bamberger[6] from β-phenylhydroxylamine and benzaldehyde. These nitrones undergo ready hydrolysis by mineral acids to the corresponding hydroxylamine and aldehyde, and the rearrangement reactions of β-hydroxylamines can be carried out by means of them.[5,6]



The β-xenylhydroxylamine was finally prepared in a pure condition by pouring the reduction mixture of *p*-nitrodiphenyl first into some acetic acid and then into water. The dil. acetic acid was found to render the hydroxylamine less sensitive to oxidation. When so prepared it could be filtered and dried and was comparatively quite stable.

Reduction of *p*-Nitrodiphenyl.—In all experiments 5 g. of *p*-nitrodiphenyl was added to 250 cc. of 95% alcohol, 30 cc. water, 3 g. of ammonium chloride and 5 g. of zinc dust. The mixture was cooled by running water until no heat of reaction was evident, and stirring was then continued at room temperature for 30 minutes. On filtering the mixture into an equal volume of water, an almost white precipitate formed at once. When filtered it was found to have undergone, in a very short time, conversion to the *p,p'*-azoxybisbiphenyl, melting[7] at 207.5°. The identity of the azoxy compound was confirmed by analysis and by a mixed-melting-point determination of the same compound prepared according to the method of Zimmermann.[7]

Anal. Calcd. for $C_{24}H_{20}ON_2$: N, 8. Found: 8.32.

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[5] Gattermann, *Ber.*, **29**, 3040 (1896).

[6] Bamberger, *Ber.*, **27**, 1548 (1894), etc. A paper with new observations and corrections from his earlier extensive publications has appeared recently [*Ber.*, **57B**, 2082 (1924)].

[7] The temperatures recorded in this paper are uncorrected. The azoxy compound was crystallized from glacial acetic acid, in which it is sparingly soluble. It melts several degrees higher than the temperature given by Zimmermann, [*Ber.*, **13**, 1960 (1880)].

Preparation of α-Phenyl-N-xenylnitrone.—The nitrone was prepared in three ways: first, benzaldehyde was added to the precipitated hydroxylamine prior to filtration and in the absence of acetic acid; second, the reduction of *p*-nitrodiphenyl was carried out in the presence of benzaldehyde; third, the benzaldehyde was condensed with the hydroxylamine after filtration of the dil. acetic acid solution. It is obtained pure as a yellow compound melting at 174–175° when recrystallized from alcohol.

Anal. Calcd. for $C_{19}H_{15}ON$: C, 83.5; H, 5.5; N, 5.1. Found: C, 83.1; H, 5.5; N, 5.5.

The nitrone is readily hydrolyzed to benzaldehyde by means of dil. hydrochloric and sulfuric acids. When hydrolyzed with dil. mineral acids in a current of steam to remove benzaldehyde, and then treated with slightly stronger mineral acids in order to effect the hydroxylamine rearrangement, no 4-amino-4′-hydroxydiphenyl was obtained. Under these conditions *p*-aminophenol is formed from the corresponding α-phenyl-N-phenylnitrone.[5,6]

Preparation of β-Xenylhydroxylamine.—The reduction mixture of *p*-nitrodiphenyl, alcohol, water, ammonium chloride and zinc dust was filtered into 15 cc. of glacial acetic acid. This solution, not entirely clear, was filtered into a volume of water equal to that of the reduction mixture and acetic acid. A pale yellow precipitate of the β-xenylhydroxylamine formed. It melts with preliminary softening and decomposition at 158° and is readily soluble in ether, acetone, alcohol and glacial acetic acid, and somewhat less soluble in benzene.

Anal. Calcd. for $C_{12}H_{11}ON$: N, 7.57. Found: 7.59, 7.84.

Like the hydroxylamine that is precipitated by water containing no acetic acid it gives the characteristic tests of hydroxylamine with Fehling's solution and ammoniacal silver nitrate, and forms the α-phenyl-N-xenylnitrone with benzaldehyde.

The authors wish to acknowledge help from Professor W. H. Perkin and Mr. L. C. Heckert.

Summary

β-Xenylhydroxylamine has been prepared by the reduction of *p*-nitrodiphenyl. It does not rearrange to 4-amino-4′-hydroxydiphenyl.

AMES, IOWA

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

OPTICALLY ACTIVE DYES. III. PHYSICAL PROPERTIES, DYEING REACTIONS AND MECHANISM OF DYEING

BY WALLACE R. BRODE[1] WITH ROGER ADAMS

RECEIVED MAY 24, 1926 PUBLISHED AUGUST 5, 1926

In the previous papers[2] of this series a method was described for the preparation of optically active dyes and the physical properties of the basic dyes of this type were studied as to their suitability for use in the experiments on the absorption of dyes by fibers. This paper describes the re-

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[1] This communication is an abstract of a portion of a thesis submitted by Wallace R. Brode in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[2] (a) Ingersoll with Adams, THIS JOURNAL, 44, 2930 (1922). (b) Brode with Adams, *ibid.*, 46, 2032 (1924).