Tetrahedron Letters No. 7, pp. 33-36, 1960. Pergamon Press Ltd. Printed in Great Britain.

INDOLE RING FORMATION FROM
β,β-DIPHENYLETHYLENEAZOBENZENE

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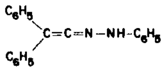
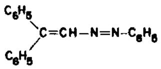
(Received 15 February 1960; in revised form 15 March 1960)

SOME years ago, Zerner and Goldhammer reported[1] that the red dehydration product (A) of diphenylglycolaldehyde phenylhydrazone, which they considered to be I, was a precursor of a new dimer of diphenylketene. In the course of reinvestigation of the reactions of A (in which we failed to detect any diphenylketene dimer) we have found that A should be reformulated as II, and that in acid it undergoes isomerization to III. The change II ⟶ III represents an



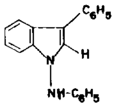
$(C_6H_5)_2C{=}C{=}N{-}NH{-}C_6H_5$

I



$(C_6H_5)_2C{=}CH{-}N{=}N{-}C_6H_5$

II



III

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[1] E. Zerner and H. Goldhammer, Monatsh. 54, 485 (1929).

unusual method of forming an indole derivative which, in a later step, can undergo reductive cleavage of the N-N linkage.

Compound A, m.p. 72°, (Anal. Calcd. for $C_{20}H_{16}N_2$: C, 84.48; H, 5.67; N, 9.85. Found: C, 84.37; H, 5.71; N, 10.12) was prepared according to the method of Zerner by the dehydration of diphenylglycolaldehyde phenylhydrazone[2] (IV) in dilute sulfuric acid. IV, prepared from the reaction of ethyl diazoacetate with excess phenylmagnesium bromide, was identical with the material, m.p. 130°, derivable from (a) the condensation of diphenylglycolaldehyde with phenylhydrazine, or (b) the addition of phenylmagnesium bromide to phenylglyoxal phenylhydrazone.

Structure I for A was ruled out on the following grounds: (i) Related ketenimines undergo rapid hydration to amides under the conditions leading to the formation of A.[3] (ii) The infrared spectrum of A lacks both the 3 μ (NH) and the 5 μ ($>C=C=N-$) absorption bands expected of I.[3] The conjugated (ethyleneazobenzene) structure (II), on the other hand, fits the spectroscopic as well as the chemical[4] evidence. In particular, there is close correspondence between the ultraviolet absorption spectrum of A and the spectrum of the related ethyleneazobenzene formed by air oxidation of

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[2] E. Zerner, ibid. 34, 1609 (1913).

[3] C. L. Stevens and J. C. French, J. Am. Chem. Soc., 75, 657 (1953).

[4] Among other reactions, the reduction of A to diphenylacetaldehyde phenylhydrazone by zinc in ethanolic KOH.

9-formylfluorene phenylhydrazone.[5]

On warming a solution of II in acetic acid in the presence of a trace of sulfuric acid, a gradual conversion takes place to a colorless isomer, B, m.p. 140°, which shows NH absorption in the infrared (Anal. Found: C, 84.48; H, 5.46; N, 9.86; Mol. wt., 242). The key to the structure of B was provided by its ultraviolet absorption spectrum. As shown in Fig. 1, the spectrum of B is strikingly similar to the spectrum obtained by adding the molar extinction coefficients of aniline and 3-phenylindole. This suggests that B is N-anilino-3-phenylindole(III). In confirmation of this assignment, it was found that when B is heated in ethylene glycol, it undergoes cleavage to 3-phenylindole.

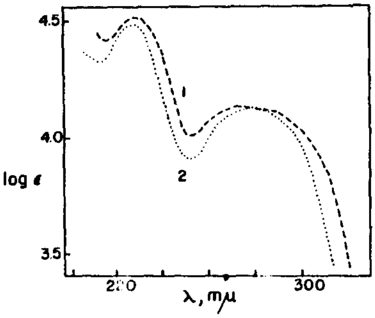

FIG. 1. Ultraviolet absorption spectra in ethanol Curve 1 (----), Compound B (III); Curve 2 (••••) obtained by adding the extinction coefficients of the aniline and 3-phenylindole spectra.

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[5] W. Wislicenus and K. Russ, Ber. 43, 2719 (1910).

The conversion of II to III may be pictured as shown: Cyclization of the protonated species IIa takes place through the transition state IIb, and leads to the product, III.