## REACTION OF AZIDOBENZENE WITH CARBONYL COMPOUNDS\*

#### (UDC 542.91 + 541.124)

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It has been considered until recently (see e. g. the review [2]) that azides do not react with carbonyl compounds. This view was based on the work of Schönberg and Urban [3], who were unable to isolate any reaction products when a mixture of azidobenzene and benzophenone was heated at temperature of 115 to 170°.

We undertook a new investigation of the reactions of azidobenzene with aldehydes and ketones, which we regarded as possibly providing methods for the synthesis of the oxaziridine system  $\bigvee_{O}^{N-N-}$ . Ways of forming the related oxadiaziridine system  $\bigvee_{O}^{N-N-}$  are also being studied in our laboratory [4,5]. We carried out the thermal de-

composition of azidobenzene in boiling benzaldehyde and cyclohexanone: we added a dilute solution of azidobenzene in the carbonyl compound slowly to a large excess of the latter. In both cases, instead of the expected oxaziridines or nitrones (which could be formed as a result of the thermal isomerization of the oxaziridines [6, 7]), the reaction products were the corresponding azomethines—N-benzylideneaniline (yield 75%) and N-cyclohexylideneaniline (yield 70%).

It has now been established [8-11] that the first stage in the thermal decomposition of azides in various media is the elimination of a molecule of nitrogen and formation of an azen RN $\cdot$ , known also as the nitren or imen radical (see the review [12]). As regards the further conversion of phenylazen in aldehydes or ketones into Schiff bases, two different mechanisms for this can be suggested. The first envisages the addition of the azen radical at the C=Obond

with formation of oxaziridines  $\begin{array}{c} RR'C - NC_{\theta}H_5 \\ O \end{array}$ . Such a mechanism has many analogies: a similar scheme-

the addition of phenylazen at the C=S bond—has been proposed to explain the reaction of azidobenzene with thiones [3] and carbon disulfide [13]; later it was shown that as a result of the addition of arylazen [11] and acylazen [14,

15] radicals to the C=C bond aziridines > C - C < are formed. Finally, we recently proved the possibility of the re-

action of an arylazen radical with the -N=0 group [5]. On the other hand it is known [16] that carbones, which are analogs of the second se

of azens, add to the carbonyl group with formation of oxiranes > C - CH<sub>2</sub> O

with carbonyl compounds oxaziridines are indeed formed, then as they have powerful oxidizing properties [6, 17] they may, particularly at hightemperatures, oxidize carbonyl compounds, being reduced themselves to azomethines, which were, in fact, isolated. The other possible variant of the conversion of oxaziridines into Schiff bases—the ther-

<sup>\*</sup>This article is published in accordance with a resolution of the Conference of Chief Editors of Journals of the Academy of Sciences of the USSR of July 12, 1962, as a dissertation paper by L. A. Neiman. For preliminary communication see [1].

mal isomerization of oxaziridines to nitrones >  $C = N(O) C_6H_5$  [6, 7] with subsequent cleavage to azomethines [18]we rejected, for after being boiled for more than 2.5 h in benzaldehyde N, $\alpha$ -diphenylnitrone  $C_6H_5CH = N(O) C_6H_5$  was recovered unchanged in more than 80% yield.

However, our reaction, leading to the formation of azomethines, may proceed by a second mechanism, which is different in principle. It is known [10, 11] that the azen radical is capable of abstracting hydrogen, both from another such radical, and from a molecule of the medium. The resulting aniline can then react in the usual way with aldehydes and ketones with formation of Schiff's bases. In the first place [1] we did not consider this mechanism at all, for according to the literature [19, 20] the reaction between aniline and cyclohexanone goes only to a small extent, and even in presence of catalysts the yield of N-cyclohexylideaniline does not exceed 50%. However, control experiments showed that under the conditions that we used (high temperature, very large excess of cyclohexanone) N-cyclohexylideneaniline is formed in about 70% yield. Moreover, it was found that aniline, though obtained in only low yield, is the only product in the thermal decomposition of azidobenzene in benzophenone( the reaction was carried out under the same conditions as the decomposition.

Though these experiments support the second of the mechanisms examined for the formation of azomethines, it should be noted that, in view of the steric factors operating, the mechanism of the reaction of the azen radical with benzophenone may differ substantially from the mechanism of the reaction of phenylazen with benzaldehyde or cyclohexanone. Moreover, even in the thermal decomposition of azidobenzene in decalin [10], i. e., under conditions most favorable for the abstraction of hydrogen, aniline is formed in a yield of only 40%. This yield is not in good accord with the high yields of azomethines which we obtained in the case of benzaldehyde and cyclohexanone. Hence, the available experimental data do not permit us to make a final choice between the two mechanisms discussed above for the formation of azomethines. It is interesting that as a by-product of azidobenzene we isolated the trimer of the latter, which has been obtained previously only in very small amounts by the irradiation of benzaldehyde is analogous to the already known [22] catalytic action of arylazen radicals on the polymerization of acrylonitrile.

We were unable to conduct the reaction of azidobenzene with aldehydes and ketones under the conditions for the photolysis of azides. In the ultraviolet irradiation of solutions of azidobenzene in cyclohexanone or in a mixture of hexane and cyclohexanone (at 20° and 80°) the resulting decomposition of azidobenzene quickly came to a stop because of the clouding and darkening of the solutions. However, in the photolysis of azidobenzene in boiling methanol in presence of benzaldehyde we obtained azobenzene (the product of the combination of two phenylazen radicals) and also benzaldehyde dimethyl acetal, which is formed in the irradiation of benzaldehyde in methanol even in absence of azidobenzene.

## EXPERIMENTAL

Thermal Decomposition of Azidobenzene in Benzaldehyde. In an atmosphere of nitrogen, a solution of 5 g of azidobenzene in 100 ml of benzaldehyde was added dropwise in the course of 2.5 h to 300 ml of boiling benzaldehyde. The mixture was boiled further for 30 min and then left for 12 h at 20°. Benzaldehyde was driven off at 15 mm, 100 ml of ether was added to the residue, and the crystalline precipitate of the trimer was filtered off and washed with ether; yield 2.5 g; m. p. 245-246° (from glacial acetic acid) (cf. [21]). The filtrate was washed with saturated sodium carbonate solution and then water, and it was dried over anhydrous sodium sulfate. Ether was driven off, and the residue was distilled at 1 mm; at 128-132° N-benzylideneaniline came over; yield 5.7 g (75%). After two crystallizations from 70% alcohol it had m. p.  $50-51^{\circ}$  (cf. [23]).

Thermal Decomposition of Azidobenzene in Cyclohexanone. A solution of azidobenzene in 100 ml of cyclohexanone was added dropwise in the course of 4 h to 300 ml of boiling cyclohexanone. During this time 910 ml (97%) of nitrogen was liberated. The mixture was kept for 12 h at 20°, cyclohexanone was vacuum-distilled off, and the residue was distilled at 1 mm; at 105-109 N-cyclohexylideneaniline came over; yield 5.07 g (70%); after redistillation, b. p. 93-94° (50  $\mu$ ); n<sup>20</sup><sub>D</sub> 1.5248.Its picrate melted with decomposition at 174-175° (from a mixture of alcohol and ether). Found: N 14.00%. C<sub>18</sub>H<sub>18</sub>O<sub>7</sub>N<sub>4</sub>. Calculated: N 13.92%. The methiodide had m. p. 159-160°. Found; I 39.92%. C<sub>13</sub>H<sub>18</sub>NI. Calculated I 40.3%.

Thermal Decomposition of Azidobenzene in Benzophenone. A solution of 5 g of azidobenzene in 10 g of benzophenone was added dropwise with stirring to 300 ml of benzophenone at 180°. The reaction mixture rapidly went dark-colored. When the addition was complete, the mixture was heated further for 15 min and then left for 12 h at 20°. It was then distilled at 1 mm. From Fraction I (volume 70 ml), after dissolution in 120 ml of dry ether and the passage of dry HCl, we precipitated aniline hydrochloride (yield 1.0 g; about 20%). In another experiment the presence of aniline in Fraction I was proved by its isolation in the form of diphenylthiourea.

Photolysis of Azidobenzene in Presence of Benzaldehyde. A boiling solution of 5 g of azidobenzene and 50 ml of benzaldehyde in 350 ml of methanol was exposed to ultraviolet radiation (PRK-4 lamp at a distance of 10 cm from the walls of the flask). The liberation of nitrogen began, but slowed down as the solution darkened. After a 10 hir-radiation of the boiling solution 770-790 ml of nitrogen (82-85%) was liberated altogether. Methanol and benzaldehyde were driven off in a vacuum, and the residue (20-25 ml) was distilled at 1 mm. At 39-45° benzaldehyde dimethyl acetal came over [yield 13.7 g; b. p. 192-194°(cf. [24]);  $n_D^{17.5}$  1.51531]; at 130-133° azobenzene came over; yield 3.4 g (90%).

<u>N-Cyclohexylideneaniline</u>. A solution of 4 g of freshly distilled aniline in 100 ml of cyclohexanone was added in the course of 2 h to 285 ml of freshly distilled cyclohexanone at the boil (reflux condenser). The mixture was boiled further for 1 h and then left for 12 h. Cyclohexanone was vacuum-distilled off, and the residue was distilled. We obtained 5.15 g (about 70%) of N-cyclohexylideneaniline, b. p. 145-148° (16 mm) (cf. [19]). Picrate, m. p. 174-175° (decomp.).

# SUMMARY

In the decomposition of azidobenzene in benzaldehyde and in cyclohexanone the corresponding Schiff bases are formed.

Two possible mechanisms for this reaction are discussed.

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