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# Thermal and photolytic decomposition of N-benzhydrylidene azidobenzhydrylamine

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The thermal and photolytic decomposition of *N*-benzhydrylidene azidobenzhydrylamine (2) in aromatic solvents gave *N*-phenyl-*N'*-benzhydrylidene benzamidine (5); no benzophenone azine could be isolated. Photolysis in methanol gave no 5 but instead benzophenone dimethylketal and ammonium azide were obtained. Attempts to trap the presumed nitrene intermediate with cyclohexene gave only 5. Thermal decomposition in decalin gave *N*-benzhydryl benzophenone imine (9). The possible mechanisms of these transformations are presented.

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The formation of *N*-benzhydrylidene azidobenzhydrylamine (2) from the reaction of lithio benzophenone imine and tosyl azide has been reported recently (1). This result involves the dimerization of the lithium salt followed by the *diazo transfer* reaction (2) to the resulting dianion (1) to give 2.

The assignment of structure 2 was based on its elemental analysis, its molecular weight, and its reactions (1). We would like to report now its photolytic and thermal decompositions, the results of which confirm further the assigned structure.

Triarylmethyl azides, upon the loss of nitrogen, undergo the Stieglitz rearrangement (3) to give the corresponding imines, possibly via a discrete nitrene intermediate (3) or through a concerted displacement (3, 4). Two products 5 and 6 could arise from the rearrangement of 2. However, when a solution of 2 in benzene was irradiated with a 200 W high-pressure mercury lamp in a quartz apparatus, the only product isolated in 83% yield was a canary yellow solid, m.p. 138– 140°. Its identity as N-phenyl-N'-benzhydrylidene benzamidine (5) was proved by its elemental analysis, its infrared (i.r.) spectrum, and by comparison with an authentic sample prepared from N-phenyl benzimidoyl chloride and benzophenone imine.

The addition of benzophenone had no effect on the nature or the yield of the products. No evidence for the formation of benzophenone azine



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(6) could be obtained. The absence of the product resulting from nitrogen migration (hetero rearrangement (5)) recalls the similar behavior of the so-called "rigid" azides (6). An attempt to trap the presumed nitrene intermediate was made by carrying out the photolysis in cyclohexene as solvent. However, **5** was the only product isolated in 79% yield. None of the anticipated bicyclic aziridine could be detected.

When methanol was used as a solvent, the photo-induced decomposition of 2 followed a completely different course. No 5 was formed; instead, benzophenone dimethylketal (7) and ammonium azide were formed. Both compounds were identified by the comparison of their i.r. spectra with those of authentic samples. The reaction of 2 with methanol, under identical conditions (time and temperature), in the absence of light gave 7 but in much lower yield; no ammo-

nium azide could be detected. Thus, the effect of light on the course of the reaction is unquestionable although it is difficult at this time to decide in which step it is involved. The absence of ammonium azide in the control run indicates that the light-induced decomposition of hydrazoic acid is the source of ammonium azide (7). The irradiation of benzophenone imine with methanol did not give any appreciable amount of the ketal. A solution of 5 in methanol heated to  $40-45^{\circ}$  for 6 h did not give any benzophenone dimethylketal (7). Irradiation of this solution under the same conditions failed to give any 7. Irradiation of benzophenone imine (10) in methanol also failed to produce any 7, even in the presence of hydrazoic acid; ammonium azide, traces of benzophenone, and unreacted benzophenone imine were obtained. The formation of 7 and ammonium azide may be summarized as shown in the following equations:



The thermal decomposition of 2 in naphthalene at 190° was not as clean as the photolysis. A black tarry mass was obtained after removal of the naphthalene and only 5 could be isolated in 23%yield; none of the azine (6) could be detected. The pyrolysis of 2 in benzophenone azine (6) at  $190^{\circ}$ gave a tarry residue from which 5 and 6 were obtained by chromatography on alumina. The tarry product of the pyrolysis of 2 in 5 did not yield any benzophenone azine. In decalin, the thermal decomposition at 190° followed a different path and from the black tarry pyrolyzate, a 20% yield of a solid was obtained. It was identified as *N*-benzhydryl benzophenone imine (9) by comparison with an authentic sample. The formation of 9 may be viewed as arising via the formation of the azo compound 8 or less likely via the homolytic cleavage of the  $C-N_3$  bond of 2 (8). Although the rearrangement product (5) is stable thermally up to  $200^\circ$ , the reaction of 5 with

2 at 200° gave a black mass. This may account for the absence of 5 in the thermolysis in decalin and its low yield from the thermolysis in naphthalene.

The fact that no benzophenone azine (6) was detected from the products of the decomposition of 2 is reminiscent of the failure of N.N-dialkylcarbonyl azides and of azidoformates to undergo Curtius-type rearrangement (9). In all these cases, the migrating groups are anchored by hetero atoms such as nitrogen or oxygen. The transition state for the migration of a phenyl group to an electron-deficient center such as a carbonium ion has been described (10). A similar picture can be used to rationalize the migration of the phenyl group in the rearrangement of 2 to give 5. However, a major difference becomes apparent when the transition state for the migration of -N=CPh<sub>2</sub> is visualized. The presence of a nonbonded pair of electrons on the nitrogen may result in the electrostatic repulsion with the non-

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bonded electrons of the migration terminus. This could slow down the rearrangement and would explain the absence of benzophenone azine.<sup>2</sup>

## Experimental

All melting points are uncorrected. Infrared (i.r.) spectra were obtained on a Perkin-Elmer Infracord. The photolyses were carried out under nitrogen in a quartz apparatus similar to that described by De Boer et al. (11). A Hanovia 200 W high-pressure mercury lamp was used as the light source.

## Photolysis of 2 in Benzene

A solution of 2.0 g (5 mmoles) of 2 in 175 ml of benzene was photolyzed for 6 h. The maximum temperature during the photolysis was 40-45°. Removal of the solvent left a crude oil which crystallized. Recrystallization from cyclohexane gave 1.5 g (83%) of a fine yellow powder, m.p. 138-140°. Its i.r. spectrum exhibited aromatic absorptions at normal positions and a cluster of four closely spaced bands at 1645, 1610, 1585, and 1570 cm<sup>-1</sup>. It was identical to the spectrum of an authentic sample of 5 (see below) and the mixture m.p. was not depressed.

Anal. Calcd. for  $C_{26}H_{20}N_2$ : C, 86.66; H, 5.55; N, 7.76. Found: C, 86.76; H, 5.64; N, 7.55.

### N-Phenyl-N'-benzhydrylidene Benzamidine (5)

A mixture of 2.1 g (10 mmoles) of benzimidoyl chloride, 1.8 g (10 mmoles) of benzophenone imine, and 5 ml of dry pyridine was heated on a steam-bath for 2h. The reaction mixture was poured into 100 ml of ice water and the organic layer was extracted with two 30 ml portions of ether. The dried ether extract was evaporated to dryness and 3.0 g of crude yellow solid were obtained. One recrystallization from cyclohexane gave 2.4 g (66%) of a yellow powder, m.p. 138-140°. It was identical in all respects with the product obtained from the photolysis of 2 in benzene.

### Photolysis of 2 in Cyclohexene

A solution of 3.0 g (7.7 mmoles) of 2 in 175 ml of cyclohexene was photolyzed for 6 h at 40-45°. Work-up of the photolyzate as previously described gave 2.2 g (79%) of 5, m.p. 137-138°. All attempts to detect the presence of the bicyclic aziridine failed.

Photolysis of 2 in Methanol

A solution of 2.0 g (5 mmoles) of 2 in 200 ml of methanol was photolyzed for 6 h. After removal of the solvent, the residue was extracted with 100 ml of ether. Evaporation of the ether gave 2.0 g (mixture of 7 and 10) of an oil. Crystallization from methanol gave 0.5 g (45% based on eq. [1] of 7, m.p. 105.5-106°. Its i.r. spectrum was superimposable on that of an authentic sample of benzophenone dimethylketal. The ether insoluble fraction (0.2 g) was identified as ammonium azide by comparison of its i.r. spectrum with that of an authentic sample.

When 2 was kept for 6 h in methanol, only 40% of 7 was isolated and no ammonium azide was obtained. The irradiation of benzophenone imine in methanol for 6 h did not give 7 in any appreciable amounts.

# Thermal Decompositions of 2

(a) In Decalin

A solution of 1.0 g (2.5 mmoles) of 2 in 20 ml of decalin was heated at 190° for 2 h. Removal of the solvent in vacuo left a black tar which was chromatographed on Fisher A-540 alumina. Elution with benzene gave 0.17 g (20%) of benzhydryl benzophenone imine (9), identical with an authentic sample (12).

(b) In Naphthalene

A mixture of 1.0 g (2.5 mmoles) of 2 in 3 g of naphthalene was heated at 190° for 2 h. The naphthalene was sublimed and the tarry residue was chromatographed as above. Elution with 1:3 *n*-hexane – benzene gave 0.2 g (23%) of 5, m.p. 136–137°.

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<sup>&</sup>lt;sup>2</sup>The arguments presented here would hold equally well (with minor differences) for a transition state involving the azide (concerted displacement) instead of a nitrene.

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