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Strong Solvent and pH Dependence in the Photolysis of Diphenylmethanimine

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Synopsis. Benzophenone imine photolysis shows a strong product solvent and pH dependence: Diphenylmethane is by far the dominating outcome in methanol.

Although a relatively large amount of work has been done on *N*-substituted imines of the general type R′-CH=NR″, the rarity itself of known imines of the type RCH=NH has prevented a wide study of their photochemical behavior. Previous works, nevertheless, have reported the photolytic outcome of diphenylmethanimine (**1**) in isopropyl alcohol.[1)]

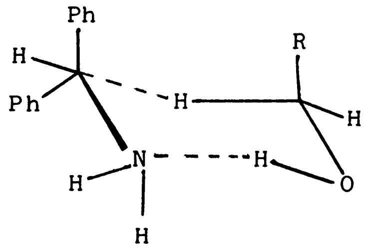
Experimental

Diphenylmethanimine (**1**) was prepared according to a described procedure.[2)] The hydrochloride of **1** (**2**) was obtained by precipitating **1** from an ether solution with dry gaseous hydrogen chloride: The IR spectrum ruled out the presence of ketonic impurities. All other chemicals were obtained from commercial sources and conveniently purified before use.

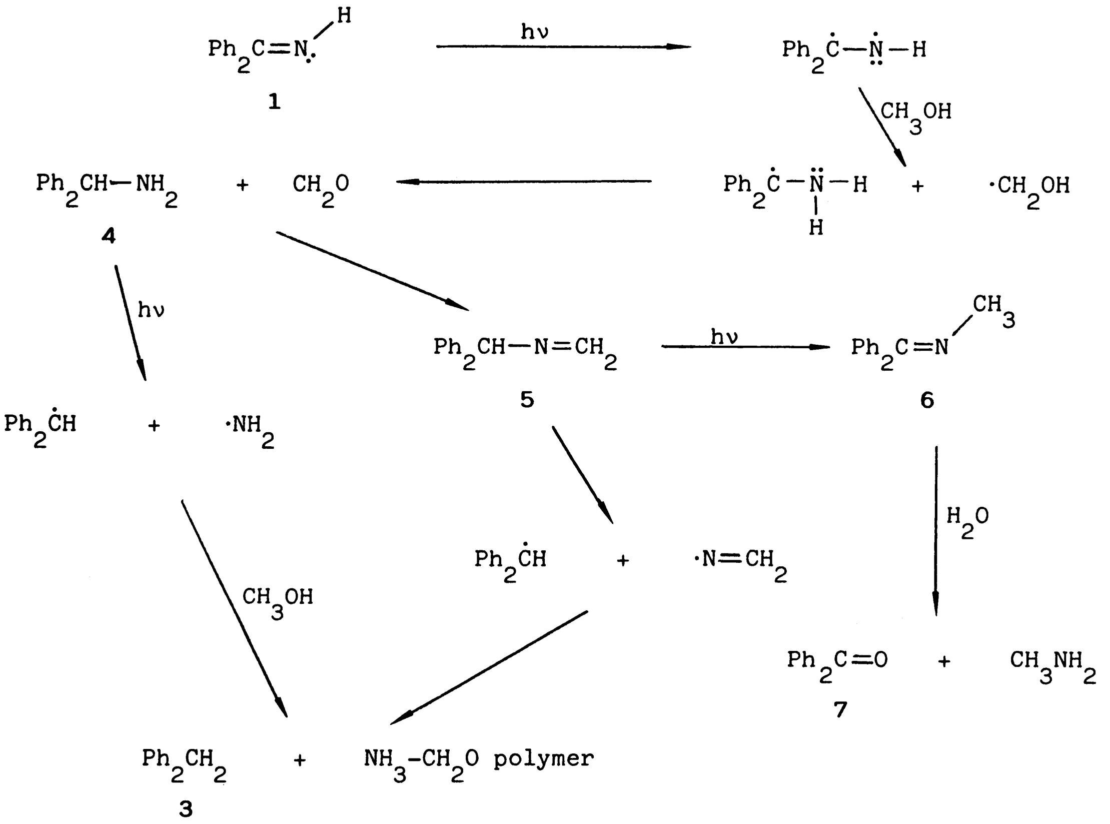
The yields of diphenylmethane (**3**) were determined by GC with a Carlo Erba HRGC Fractovap 4160 gas chromatograph equipped with an FID using a fused silica capillary column (FFAP, 25 m) by the internal standard (naphtalene) method using a calibration factor. The GC peak for **3** was found homogeneous under the whole area by capillary GC-MS analysis (Finnigan 1020 quadrupole mass spectrometer equipped with gas chromatograph and automatic data retrieval). IR spectrum (recorded with a JASCO DS-702G spectrometer) and ^{1}H NMR spectrum (recorded with a Bruker WP 80 SY spectrometer) of separated **3** were in agreement with those of a pure specimen.

Results and Discussion

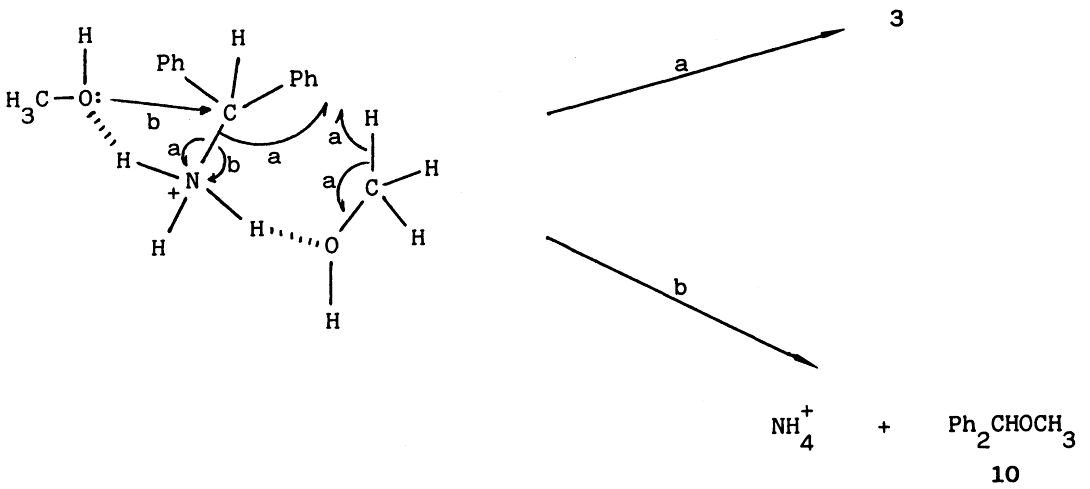
We have irradiated **1** with a Hanovia High Pressure lamp (350 W, 48 h) in methanol solution: The outcome was dramatically different, the sole product retaining the benzhydrylidene moiety being diphenylmethane (**3**), separated in 91.6% yield (GC yield:



8a R=H; **8b** R=CH_3



Scheme 1.



95%). This result indicates a strong solvent effect on product outcome. Since the donor property of hydrogen atoms is considered superior for isopropyl alcohol and the initial abstracting center should be the electronically excited imine's nitrogen atom interacting with the alcohol's tertiary hydrogen, this solvent dependence might be ascribed either to longer reaction times or to a true solvent effect. In fact, shorter reaction times did not change significantly the fate of **1**, only depressing the actual amount transformed.[3] This is an indication that any necessary intermediate in presence of methanol rapidly goes on to **3**. The obvious intermediacy of the reduction product benzhydrylamine[1] (**4**) requires the closer association of the solvent reactive molecule perhaps due to the limited steric hindrance, which allows the prompt capture of the separate fragments before recombination in the solvent cage, as in Scheme 1.

Amine **4** in methanol did photolyze[1b] to hydrocarbon **3**. This ruled out the occurrence of the possible intermediate **5**, as the obligatory passage to **3**: **4** would rather photolyze to isomeric **6**, a minor product eventually reacting with water to yield benzophenone (**7**) also present in traces. The action of light on **4** in methanol can actually be visualized as the interaction of hydrogen bonded tight adduct **8a**. 1,3-Interaction between one of the methyl groups of isopropyl alcohol would make the complex (or transition state) less tight allowing recombination or simply not favoring complete dissociation. In keeping with this rationale, photolysis of **1** in ethanol yielded a good amount (48%, 8 h) of **3**, but photolysis in xylene did not at all. In diethyl ether, capable of a similar but weaker association, adduct **8** again showed poor donor properties toward any eventual (but undetected) **4** (16% **3**, 24 h). Triethylamine, in keeping with this rationale, gave an yield of **3** (20%, 12 h), intermediate between ether and ethanol. When the hydrochloride of **1**, namely **2**, was used in the photolysis in methanol the reactivity pattern as resulting from product composition was deeply affected. The production of **3** was strongly depressed (0.56%, 4 h) and the retention of nitrogen in the molecular structure was favored. Alongside amine **4** (64%), monomethylation products of both the imine **1** and the amine **4** at the nitrogen center were present. They were probably generated by reaction with formed formaldehyde, followed by subsequent reduction induced by some photochemical process. Amine **4** as well as any nitrogen containing species is expected to be largely protonated under the photolysis conditions. Excitation of methanol solvated benzhydrylammonium cation has an additional neutral breakdown alternative, where one charged particle is generated, i.e., the diphenylmethyl cation (**9**) which is immediately captured by a molecule of methanol to eventually produce the observed ether **10**.

The role of apparently dimeric products as well as their precise identification are presently under study in our laboratory.

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References

1) a) E. S. Huyser, R. H. S. Wang, and W. T. Short, *J. Org. Chem.*, **33**, 4323 (1968); b) N. Toshima, H. Hirai, and S. Makishima, *Kogyo Kagaku Zasshi*, **72**, 184 (1969); c) H. Hirai and N. Toshima, *J. Fac. Eng. Univ. Tokyo*, **A-8**, 56 (1970).

2) P. L. Pikard and T. L. Tolbert, *J. Org. Chem.*, **26**, 4886 (1961).

3) It was reported[1b] that **1** gives 53% conversion of **1**: Less than 0.5% diphenylmethane (**3**) was produced. At the same time our conversion was about the same, but by far the largest product was **3**.