

PHOTOSOLVOLYSIS OF A CARBON-CARBON BOND. THE PHOTOLYSIS OF N,N-DIMETHYL-
2,2-DIPHENYLETHYLAMINE IN METHANOL.¹

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SUMMARY: The title compound is photolyzed in methanol to give good yields (ca. 50%) of diphenylmethane indicating that the C-C bond undergoes a formal heterolytic cleavage from the excited state as predicted from the measured redox potentials of the two ions.

The photosolvolysis of organic molecules is a well documented reaction which involves the formal heterolysis of a bond between a carbon atom and a heteroatom such as halogen, oxygen or sulfur.²⁻⁵ In many of these reactions a significant fraction of the products is derived from homolysis of the C-X bond even though the homolytic cleavage may be as much as 20-30 kcal mol⁻¹ less energetically favorable. Much work has been devoted to understanding the factors which influence the competition between the homolytic and heterolytic processes.³⁻⁴ Recently a semi-quantitative scale of leaving group abilities (photofugacities) for these reactions has been proposed.^{3a}

Heterolytic photocleavage of a C-C bond is much less common and, to our knowledge, the only examples reported in the literature have been in aqueous solutions and were extremely pH dependent.^{5a} We now report results from the photolysis of N,N-dimethyl-2,2-diphenylethylamine (1)⁶ which, in methanol, leads to the formation of significant amounts of diphenylmethane (ca. 50%). These results are consistent with a mechanism in which the C-C bond undergoes a formal heterolysis.

The overall thermochemistry for homolysis versus heterolysis of a C-C bond can be calculated if the oxidation and reduction potentials of the radicals are known. The free energy difference between the radical pair and the ion pair is simply the difference between the oxidation potential of the donor ($E_{ox}(\text{donor})$) and the reduction potential of the acceptor ($E_{red}(\text{acceptor})$) eq. 1) where F is the Faraday (23.06 kcal mol⁻¹ eV⁻¹).

$$\Delta G(\text{ion pair} - \text{radical pair}) = F(E_{ox}(\text{donor}) - E_{red}(\text{acceptor})) \quad (1)$$

Recently, we have reported the measurement of the oxidation and reduction potentials of several carbon centered free radicals.⁷ The requirement for the energetically favorable heterolysis would be a system in which the oxidation potential of one radical was actually more negative than the reduction potential of the other. While this is almost always the case for a bond between a carbon atom and a heteroatom, it is seldom the case for C-C bonds. We have chosen to study the photochemical behaviour of 1, taking advantage of the fact that the N,N-dimethylaminomethyl radical is an excellent reducing agent ($E_{ox} = -1.03$ V vs SCE in

acetonitrile^{6b}) and that the diphenylmethyl radical is quite readily reduced ($E_{red} = -1.14$ V vs SCE^{6a,b}). In this case the ion pair and the radical pair will have approximately the same energy.

The products obtained from the photolysis of $\underline{1}$ in methanol and in cyclohexane are given in Table 1. In methanol, the major product was the solvolysis product, diphenylmethane ($\underline{2}$). Other products which were identified were 1,1,2,2-tetraphenylethane ($\underline{3}$), as well as a rearrangement product, 4-(N,N-dimethylamino)diphenylmethane ($\underline{4}$) and 1-(N,N-dimethylamino)-2,2-diphenylethene ($\underline{5}$).⁸ In cyclohexane, the major product was $\underline{3}$ as expected from the homolytic fragmentation of $\underline{1}$ in this nonpolar solvent. Prolonged irradiation of this mixture led ultimately to the destruction of $\underline{3}$ since this compound is also photolabile.⁹ The formation of $\underline{4}$ was expected from the photo-Fries type rearrangement of $\underline{1}$ after the fission of the C-C bond. No evidence for the formation of the ortho-derivative was found. The presence of $\underline{5}$ is likely the result of a small amount of hydrogen atom abstraction from $\underline{1}$ by one of the free radical intermediates.

Table 1. Products from the photolysis of $\underline{1}$.^{a,b}

solvent	conversion (%)	$\underline{2}$ (%)	$\underline{3}$ (%)	$\underline{4}$ (%)	$\underline{5}$ (%)
methanol	65	45	4	9	2
cyclohexane	62	4	36	8	2

^aPhotolysis of $\underline{1}$ (1.0×10^{-2} M) at 254 nm.

^bIsolated yields after preparative layer chromatography (9:1 chloroform:methanol)

The proof that $\underline{2}$ was formed by a heterolytic fragmentation was straight forward. Irradiation of $\underline{1}$ in methanol-OD led exclusively to the monodeuterated derivative of $\underline{2}$ as shown by mass spectrometry. Irradiation of 1,1,3,3-tetraphenyl-2-propanone in methanol-OD gave only $\underline{3}$ as product proving that the diphenylmethyl radical was not an intermediate in the formation of $\underline{2}$. It was tempting to determine the relative rates of heterolytic and homolytic cleavage reactions from the ratio of $\underline{2}$: $\underline{3}$. For a system under thermodynamic control this ratio can be calculated from eq. 1. While this approach has been used successfully by Pincock and his coworkers in their studies of photocleavage reactions³ and by Arnold and his coworkers¹⁰ for the cleavage of radical cations, it is difficult in this case to apply such a treatment since the material balances were not high (ca. 50-60%).

Further insight into the mechanism of the photosolvolysis of $\underline{1}$ could be obtained from fluorescence quenching studies. In acetonitrile, $\underline{1}$, fluoresces with a maximum at 405 nm (excitation maximum at 270 nm). In methanol no emission was observed. However, at concentrations less than 0.8 M, methanol was unable to efficiently quench the fluorescence in acetonitrile. At higher concentrations the fluorescence could be quenched but the resulting Stern-Volmer plot was curved (Figure 1) indicative of a non-diffusional quenching process. Results from the dynamic quenching fell on the same curve (Figure 1).¹¹ Analysis of the

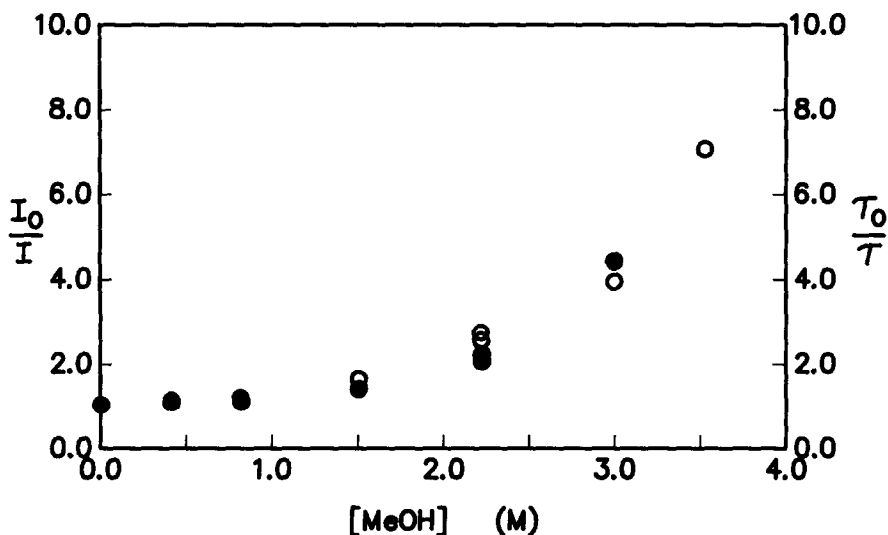
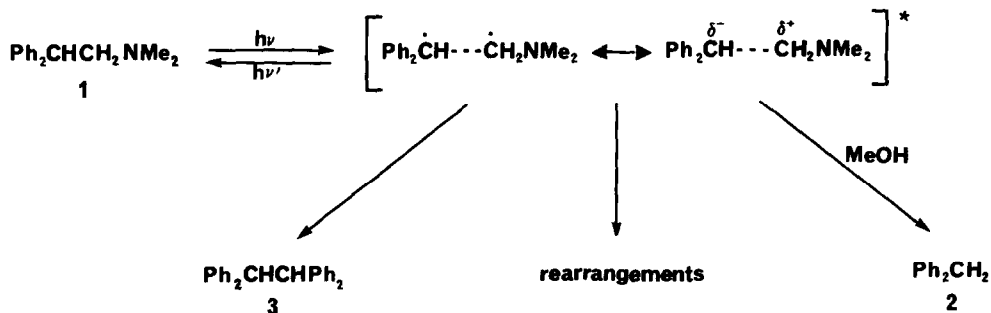


Figure 1. Stern-Volmer plot for the quenching of (1)* by methanol. The closed circles are from the steady state quenching. The open circles are from the dynamic quenching.

initial slope of the Stern-Volmer plot gave an upper limit for the reaction of methanol with the excited singlet of $\underline{1}$ of only $4 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$.

It was also found that the emission maximum was solvent polarity dependent; in cyclohexane, diethylether and chloroform the emission maxima were at 320 nm, 355 nm and 360 nm respectively. Analysis of these data using the Lippert equation¹² gave an estimate of the dipole moment of the excited state of $\underline{1}$ of ca. 20 D. The results of the product and emission studies, therefore, are consistent with a mechanism in which the highly polarized electronically excited amine can react with solvent in competition with radical or ion pair collapse to give back the starting material and rearrangement products (Scheme 1).



Scheme 1

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