Electron Transfer in Competition with Loss of Nitrogen in Photochemical Reactions of Aryldiazomethane with Diethylamine

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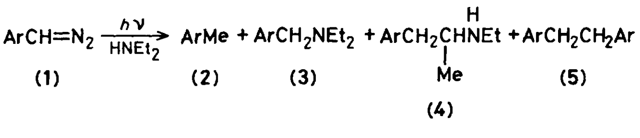
The photolysis of aryldiazomethanes was studied as a function of aryl substituents and the *p*-nitro group was found to exert a special effect on product distribution.

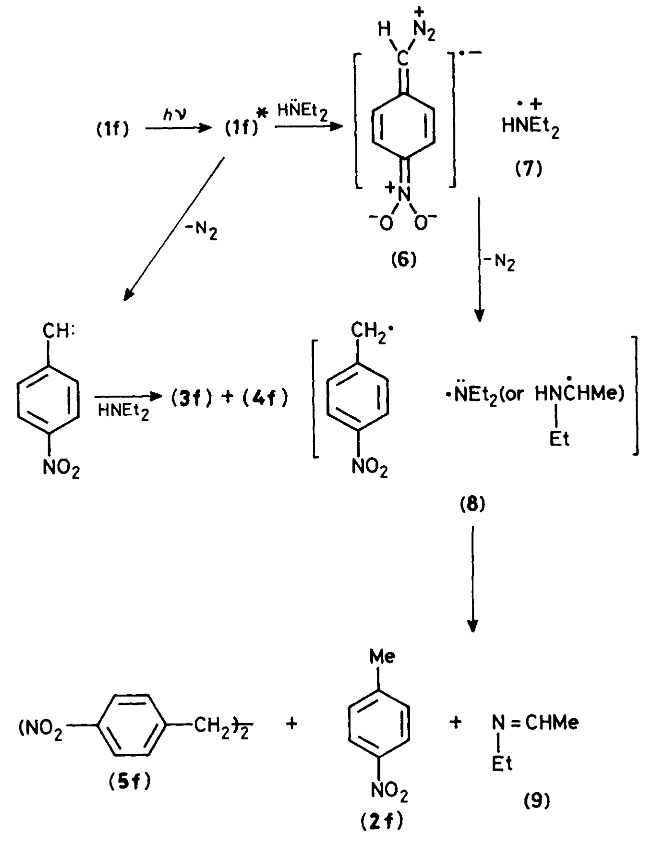
In view of the many cases in which formal carbenic products have been obtained in the photolysis of diazo compounds, the intermediacy of free carbenes in these experiments has been widely accepted.[1] Conceivably, however, excited precursor molecules may act as carbenoid species, mimicking free carbene in their reactions. In fact, a recent product analysis[2] as well as spectroscopic[3] studies revealed that carbene-mimicking reactions of excited diazo compounds are involved in the photochemical processes of several α-diazocarbonyl compounds. In this communication, we report that irradiation of some aryldiazo compounds in amine solution afforded the product presumably arising *via* electron transfer from amine to the diazo compound in its excited state.

Irradiation of phenyldiazomethane (**1a**) in a degassed diethylamine solution resulted in the formation of benzyldiethylamine (**3a**) as the main product along with amine (**4a**), toluene (**2a**), and bibenzyl (**5a**) in the yields indicated in Table 1. These products are apparently formed from photolytically generated phenylcarbene which is known to undergo insertion into the N–H bond as well as C–H bonds in its singlet state.[4,5] Support is lent to the above assignments by the finding that irradiation of *trans*-diphenyloxirane, a well known precursor for phenylcarbene,[6] in diethylamine also gave essentially the same product mixtures.

Similar irradiation of the amine solution of other aryldiazomethanes (**1b**—**e**) listed in Table 1, except the *p*-nitro derivative (**1f**), also afforded products (**2**)—(**5**) in essentially similar distributions. Photolysis of *p*-nitrophenyldiazomethane (**1f**), however, resulted in a completely different product distribution; the double-hydrogen abstraction product (**2**) was dramatically increased at the expense of the insertion products (**3**) and (**4**).



$$\underset{(1)}{\mathrm{ArCH{=}N_2}} \xrightarrow[\mathrm{HNEt_2}]{h\nu} \underset{(2)}{\mathrm{ArMe}} + \underset{(3)}{\mathrm{ArCH_2NEt_2}} + \underset{(4)}{\mathrm{ArCH_2}\underset{\mathrm{Me}}{\underset{|}{\mathrm{C}}}\mathrm{H}\overset{\mathrm{H}}{\mathrm{N}}\mathrm{Et}} + \underset{(5)}{\mathrm{ArCH_2CH_2Ar}}$$



Scheme 1

What is the origin of the marked effect of the p-nitro group on product distribution? It is generally accepted[1,4,5] that the N–H insertion is a characteristic reaction for the singlet carbene, while the C–H insertion is not only derived from the singlet state *via* a one-step mechanism but also formed from the triplet state *via* abstraction of a hydrogen atom followed by coupling of the radical pair. Toluene and bibenzyl are most probably formed from the radical pair. The observed substituent effects can then be explained in terms of the effect on the singlet–triplet equilibrium since efficiencies of arylcarbene intersystem crossing can be influenced by substituents. Closs and Moss[7] estimated involvement of the triplet state to be not more than 5% based on the degree of loss of stereospecificity in the addition of substituted phenylcarbenes to alkenes. This means that intersystem crossing processes are relatively insensitive to the nature of the aryl substituents. More recently we[8] have examined the effect of aryl substituents on arylcarbene reactivity in competition reactions between addition to the double bond of alkenes and insertion into C–H bonds of alkanes and found that the product ratios changed linearly as the ring substituents are changed from electron-donating to -withdrawing groups. Thus, the relative rate constants correlate well with the Hammett equation.

These facts suggest that the drastic change in the product distribution caused by the p-nitro group can be interpreted as indicating that an intermediate other than free carbene may be involved in the photolysis of p-nitrophenyldiazomethane in diethylamine. One possibility is that **(2f)** may not be derived from p-nitrophenylcarbene but is most probably formed through the interaction of excited p-nitrophenyldiazomethane with diethylamine as outlined in Scheme 1. Thus, **(1f)** is excited to its singlet state, which dissociates partly to give nitrogen and singlet carbene. The singlet carbene subsequently undergoes insertion into N–H and C–H bonds of diethylamine. Most of the excited singlet **(1f)***, however, undergoes electron transfer from diethylamine to give the radical anion **(6)** before it loses nitrogen. This seems quite reasonable since the p-nitro group can stabilize the anion radical by delocalizing either the electron pair or odd electron developing as a result of electron transfer. The radical anion **(6)** then undergoes proton transfer from the diethylammonium ion radical **(7)** and loss of nitrogen presumably occurs simultaneously to form the radical pair **(8)**, which then undergoes disproportionation to give **(2)** and imine **(9)**.

Table 1. Photolysis of substituted phenyldiazomethanes in diethylamine.

		Relative yield (%)[a]			
	X in $XC_6H_4CH{=}N_2$	**(2)**	**(3)**	**(4)**	**(5)**
a;	H	1	60.4	35.5	3.1
b;	m-Br	1	63.6	30.3	2.1
c;	m-CN	2.0	62.0	31.5	4.5
d;	p-CN	4.0	58.9	33.8	3.3
e;	m-NO_2	5.2	58.4	32.8	2.6
f;	p-NO_2	73.6	14.1	2.8	9.5

[a] Total product yields were 60—70%. Other minor products detected were stilbenes and aldazine.

It is important to note here that diazoalkane anion radicals have usually been generated electrochemically and that the reduction products such as **(2)** are often formed as main products in the presence of a proton donor by a mechanism similar to that in Scheme 1.[9] Thus, the present finding indicates that the diazoalkane anion radicals can be generated even by direct irradiation of diazoalkane in suitable cases, in competition with loss of nitrogen to form carbene.

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