

## Absence of the '*p*-Nitro Effect' in the Photochemical Reactions of 3-Chloro-3-aryldiazirines in the Presence of Amines

Hideo Tomioka,\* Fusao Haya, and Kunihiko Suzuki

Department of Industrial Chemistry, Faculty of Engineering, Mie University, Tsu, Mie 514, Japan

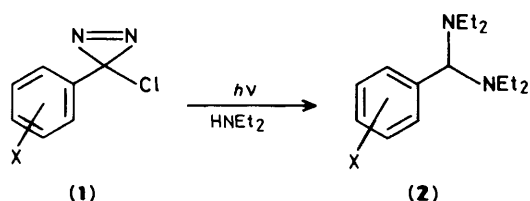
Photochemical generation of arylchlorocarbenes from 3-chloro-3-aryldiazirines in the presence of diethylamine afforded *N,N,N',N'*-tetraethylbenzylidenediamines regardless of the nature of the aryl substituent.

Photolysis of diazo compounds is believed to generate free carbenes, and has been conveniently employed for carbene generation.<sup>1</sup> Conceivably, however, excited diazo compounds may act as carbenoid species, mimicking free carbenes in their reactions. Indeed, a recent product analysis<sup>2</sup> and spectroscopic studies<sup>3</sup> have revealed that carbene-mimicking reactions of excited diazo compounds are involved in the photochemical processes of several  $\alpha$ -diazocarbonyl compounds. More recently we have noted<sup>4</sup> that electron transfer reactions compete with the carbenic reactions. Thus, irradiation of phenyldiazomethane in diethylamine afforded primarily the N-H insertion product, whereas similar irradiation of *p*-nitrophenyldiazomethane resulted in the formation of *p*-nitrotoluene almost exclusively. The results were explained as indicating that the excited *p*-nitrophenyldiazomethane participates in electron transfer from diethylamine. Similar electron transfer reactions have subsequently been found<sup>5</sup> to occur generally in the photolysis of most aryldiazo compounds bearing a *p*-nitro substituent, in the presence of an amine. Schuster has reported<sup>6</sup> that electron transfer is also involved in

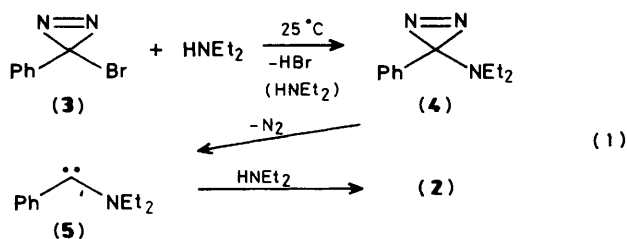
the photochemistry of *p*-nitrophenyl azide, a possible precursor of a nitrogen analogue of a carbene, in the presence of amines. These observations that electron transfer is often involved in the photochemical generation of divalent species, with extrusion of a nitrogen molecule, prompted us to investigate the photochemical pathways of diazirines, which are also important precursors<sup>7</sup> of divalent carbon, in the presence of amines.

Irradiation of a solution of 3-chloro-3-phenyldiazirine (**1a**) in degassed benzene in the presence of a 5 molar excess of diethylamine at 0°C resulted in a white precipitate of diethylamine hydrochloride. Evaporation of the filtered reaction mixture afforded *N,N,N',N'*-tetraethylbenzylidenediamine (**2a**), which was purified by short-path distillation.

The mechanism of this reaction is interesting in connection with Moss's observation<sup>8</sup> that 3-bromo-3-phenyldiazirine (**3**) reacts with diethylamine in the dark to give (**2**). The latter reaction was explained in terms of initial amine/bromide exchange affording the unstable 3-amino-3-phenyldiazirine (**4**), followed by spontaneous loss of nitrogen and liberation of



X: a, H; b, 4-MeO; c, 4-Me; d, 4-Cl; e, 3-NO<sub>2</sub>; f, 4-NO<sub>2</sub>



the amino(phenyl)carbene (5) [reaction (1)]. Not surprisingly, however, compound (1) does not undergo thermal reaction with the amine at 25°C in 24 h; the poor chloride leaving group inhibits amine/halide exchange. It is probable then that irradiation results in the generation of free chloro(phenyl)carbene (6), which reacts with N-H bonds of the amine to afford the  $\alpha$ -chlorobenzylamine (7). The  $\alpha$ -chloro amine (7) easily undergoes attack by a second diethylamine to give (2) and the amine hydrochloride [reaction (2)].

In order to establish whether electron transfer from the amine is involved in the diazirine route to carbene under irradiation, a series of 3-chloro-3-aryldiazirines (1a-f) bearing various aryl substituents, including *p*-nitro, were irradiated in diethylamine. The results are summarized in Table 1. The *p*-nitro group showed no appreciable effect on product distribution; no trace of benzyl chloride, expected to be formed in the electron transfer reaction, was detected. This is in marked contrast to the photochemical reactions of many aryldiazo compounds<sup>4,5</sup> as well as aryl azides<sup>6</sup> in the presence of amines, where dramatic '*p*-nitro effects' were observed, and clearly indicates that electron transfer is not involved in the photochemical reaction of diazirine generating carbene.

The exact reason for the observed difference in photochemical behaviour between diazo compounds and diazirine is not clear at present. It is important, however, to note that, while diazo compounds are highly sensitive to acid, 3-chloro-diazirines are known<sup>7</sup> to be resistant to strong acid; they are decomposed only by 80% sulphuric acid! The crucial step of the electron transfer process in the photochemical reaction of *p*-nitrophenyldiazo compounds with amines is presumed<sup>4,5</sup> to be the protonation of the diazonium anion radical by the amine cation radical, with simultaneous loss of nitrogen. A reasonable explanation might be, then, that even if a single electron is transferred to the excited diazirine from the amine, the resulting diazirinium cation radical does not effectively undergo protonation, presumably owing to the lack of a driving force for elimination of nitrogen.

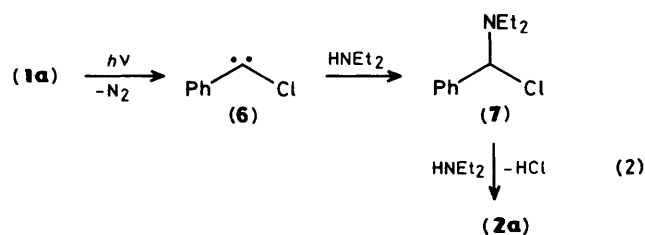


Table 1. Photolysis of 3-chloro-3-aryldiazirine (1) in the presence of diethylamine.

| X in (1)            | Yield (%) <sup>a</sup> of (2) |
|---------------------|-------------------------------|
| a H                 | 76.1                          |
| b 4-MeO             | 67.6                          |
| c 4-Me              | 65.2                          |
| d 4-Cl              | 65.5                          |
| e 3-NO <sub>2</sub> | 65.0                          |
| f 4-NO <sub>2</sub> | 64.9                          |

<sup>a</sup> Determined by g.l.c.; a small amount (<2–3%) of benzaldehyde was also detected.

On the other hand, Schuster<sup>6</sup> has demonstrated that, in the photochemical reaction of aryl azides in the presence of an amine, electron transfer from the amine involves the triplet *p*-nitrophenylnitrene, not the excited nitrene precursor. Although we have no experimental data which clearly identify the intermediate involved in electron transfer, the observed difference might be due to a difference in the ground state multiplicity between arylcarbenes and chlorocarbenes. It is well known<sup>9</sup> that most arylcarbenes have a triplet ground state whereas arylchlorocarbenes have a singlet ground state.

Received, 6th April 1988; Com. 8/01356J

## References

- For reviews, see W. Kirmse, 'Carbene Chemistry,' 2nd edn., Academic Press, New York, 1971; 'Carbenes,' eds. R. A. Moss and M. Jones, Jr., vols. I and II, Wiley, New York, 1973 and 1975.
- H. Tomioka, H. Okuno, and Y. Izawa, *J. Org. Chem.*, 1980, **45**, 5278; H. Tomioka, M. Kondo, and Y. Izawa, *ibid.*, 1981, **46**, 1090; H. Tomioka, H. Okuno, S. Kondo, and Y. Izawa, *J. Am. Chem. Soc.*, 1980, **102**, 7123.
- H. D. Roth and M. L. Manion, *J. Am. Chem. Soc.*, 1976, **98**, 3392; H. D. Roth, *Acc. Chem. Res.*, 1977, **10**, 85.
- H. Tomioka, K. Tabayashi, and Y. Izawa, *J. Chem. Soc., Chem. Commun.*, 1985, 906.
- H. Tomioka, K. Tabayashi, and K. Suzuki, unpublished results.
- T.-Y. Liang and G. B. Schuster, *J. Am. Chem. Soc.*, 1986, **108**, 546; *Tetrahedron Lett.*, 1986, **27**, 3325; *J. Am. Chem. Soc.*, 1987, **109**, 7803.
- M. T. H. Liu, *Chem. Soc. Rev.*, 1982, **11**, 127.
- R. A. Moss, D. P. Cox, and H. Tomioka, *Tetrahedron Lett.*, 1984, **25**, 1023.
- A. M. Trozzolo and E. Wasserman in 'Carbene Chemistry,' eds. M. Jones and R. A. Moss, Wiley, New York, 1974, vol. II, p. 185.