Tetrahedron Letters Vol. 21, pp 3553 - 3556
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0040-4039/80/0908-3553$02.00/0

THE DISAPPEARANCE OF ARYL CARBENES IN A REACTIVE MATRIX

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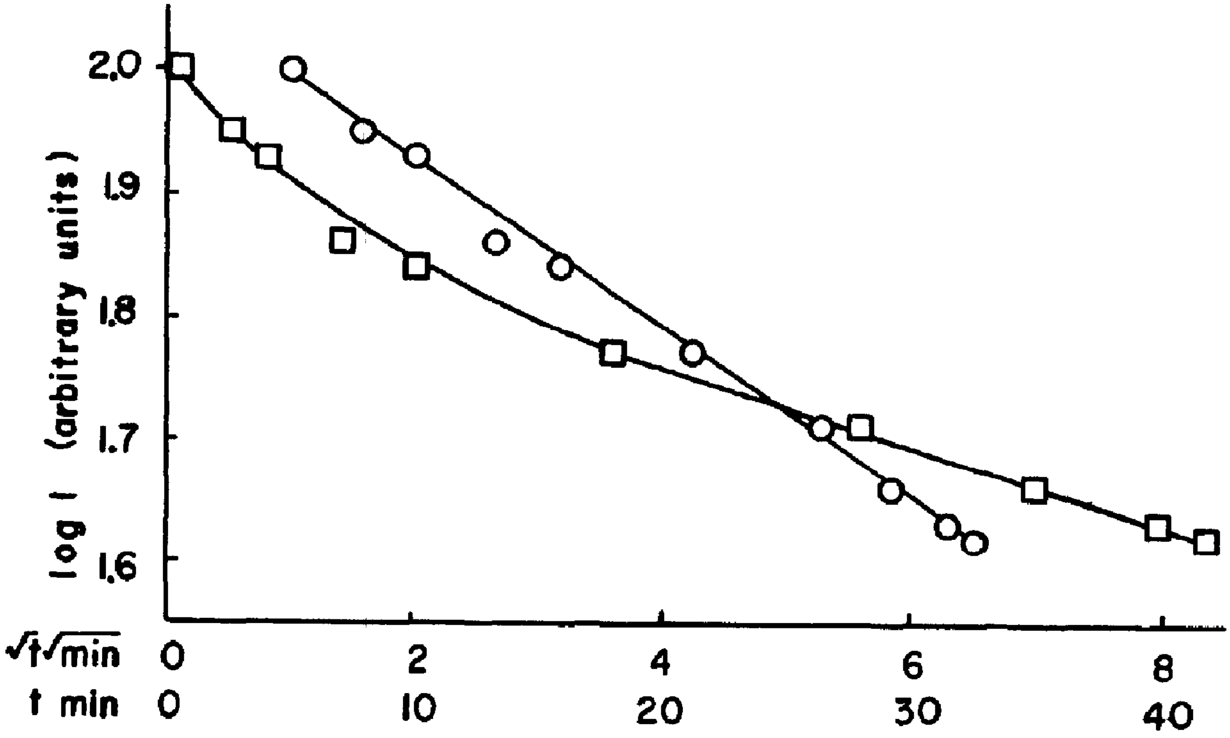
ABSTRACT: The disappearance of diphenylmethylene, fluorenylidene and phenylmethylene in isobutylene and fluorolube was monitored by esr spectroscopy at temperatures between 77°K and 171°K.

The two groups of Moss[1-4] and Tomioka[5-7] have reported dramatic changes in the reactivity of aryl carbenes at low temperatures. Moss and coworkers have found that at 77°K substantial yields of products are formed via hydrogen atom abstraction and radical recombination in the reactions of diphenylmethylene, fluorenylidene and phenylmethylene with various butene isomers.[1] Cyclopropanation is the dominant process with terminal olefins at higher temperatures. Tomiok has found that the selectivity of insertion by phenylmethylene and diphenylmethylene into oxyge hydrogen and various carbon-hydrogen bonds is significantly altered by decreasing the temperature from 273°K to 77°K, and the selectivity depends on the nature of the matrix and on the ca bene precursor.[5-7] Various suggestions have been made concerning the role of the matrix, but i seems agreed that the reactions of triplet carbenes are emphasized at the lower temperatures.[1-

Since triplet aryl carbenes are easily detected in frozen solutions by esr spectroscopy,[8] we decided to look directly at the fate of diphenylmethylene, fluorenylidene and phenylmethylene in a reactive matrix of isobutylene to see whether kinetic studies that could clarify the mechanisms of low-temperature carbene reactions might be feasible.

Degassed solutions 4 to 15% by volume of diphenyldiazomethane, diazofluorene and phenyldiazomethane in isobutylene were prepared in sealed quartz and Pyrex tubes and irradiated _in situ_ in the microwave cavity of a Varian E-3 epr spectrometer. The samples were maintained at constant temperature at 77°K in liquid nitrogen using a transparent quartz Dewar and in a cold nitrogen gas stream for experiments at higher temperatures. An Eimac 150 w xenon lamp was use to decompose the carbene precursors. The carbenes were also generated photochemically in an inert medium, employing similar solutions in HO-125 fluorolube (Hooker Chemical Corporation).

Only ten seconds of irradiation time was required to obtain the characteristic triplet esr signals for all three carbenes. The decrease with time of the carbene concentrations was monitored by periodic scanning of the esr spectrum and measurement of the change in signal intensity. A logarithmic plot of signal intensity versus time for diphenylmethylene at 113°K is given in the figure. For quantitative purposes the following peaks in the esr spectra were employed: diphenylmethylene 4565 Gauss (literature 4588 G)[8], fluorenylidene 5475 G (lit. 5493 G)[9] and phenylmethylene 5800 G (lit. 5830 G)[9].



Decay of the 4565 G signal intensity in the esr spectrum of ϕ_2C: in isobutylene at 113°K. Log I plotted against t (□) and √t (○).

At 77°K diphenylmethylene and fluorenylidene both react very slowly in isobutylene. The decrease in the signal intensity after one hour was 8% for diphenylmethylene and 11% for fluorenylidene. There was no detectable decay of the esr signal for any of the three carbenes in fluorolube after an hour at 77°K. In isobutylene however, phenylmethylene disappeared much more rapidly than diphenylmethylene and fluorenylidene, the esr signal intensity for phenylmethylene decreasing by 69% in an hour at 77°K.

These results were reproduced in a series of experiments, and for diphenylmethylene the precursor concentration was varied over a two-fold range and the irradiation time increased by tenfold without changing the rate of decay of the esr signal intensity. This suggests that the carbenes are disappearing by pseudo-first-order processes. For all three carbenes the initial signal intensity in isobutylene is about half that found in fluorolube, so it is possible that some of the carbene molecules react rapidly in isobutylene and are therefore not detected. A substantial fraction of the carbenes formed is being observed, however.

Experiments were also carried out at higher temperatures. In isobutylene at 113°K the esr signal for diphenylmethylene and fluorenylidene decreased to half the initial values in 30 min., but phenylmethylene could not be detected. At 122°K, only 11° below the melting point of pure isobutylene, 15 min. was required for the diphenylmethylene signal to drop to half its initial value. Even higher temperatures were practical in fluorolube. At 133°K the diphenylmethylene signal intensity decreased by 16% in 32 min., and for fluorenylidene a 20% decrease in 30 min. was observed. Phenylmethylene could not be detected even in fluorolube at this temperature. Th esr spectrum of diphenylmethylene was easily observable at 171°K in fluorolube, and decayed to 44% of its initial value in 15 min.

When kinetic plots were constructed it was found that the logarithm of the signal intensity is a linear function of $t^{1/2}$ or $t^{1/3}$, as has also been found by Platz.[10] A linear $t^{1/2}$ plot and a curved first-order plot are displayed in the Figure. Second-order plots are also curved. Thi deviation from simple first-order kinetics has been attributed to the effects of different matri sites offering various degrees of freedom for reaction.[11]

The data reported here indicate that phenylmethylene is more reactive at low temperatures than diphenylmethylene and fluorenylidene. These latter species disappear quite slowly at 77°K in isobutylene. Therefore care must be exercised in product studies employing matrix photolysis to allow sufficient time before the matrix is thawed for carbene reactions to be complete. Othe wise products are likely to be formed during the thawing process.

The experiments in fluorolube cover nearly a hudred degree temperature range. In this medium the tumbling time for diphenylmethylene and fluorenylidene is sufficiently slow to permit detection of the carbene triplet esr signal over a wide temperature domain.[12] Thus viscous media doped with reactive substrates may permit the kinetics of aryl carbene triplet state reactions to be studied at temperatures sufficiently high so that the mechanisms of their "normal" reactions can be clarified using esr techniques to detect the triplet carbenes.

Acknowledgment: This research has been supported by National Science Foundation Grant No. CHE75-20163. We are grateful to Professor Matthew S. Platz for communicating his results on similar systems prior to publication. We thank Professor Sam Weissman for the practical and theoretical advice that made it possible for us to carry out these experiments. Professor T.-S. Tom Lin and Mr. Daniel J. Graham also were very helpful, and we appreciate the discussions with Professors Robert A. Moss and Maitland Jones, Jr.

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(Received in USA 19 May 1980)