CHEMISTRY LETTERS, pp. 293-296, 1980.

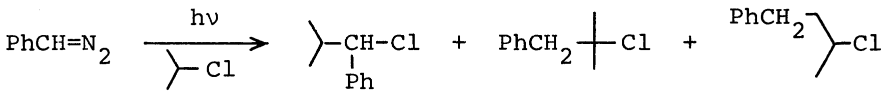
TEMPERATURE AND MATRIX EFFECTS ON MULTIPLICITY-SPECIFICITY AND C-H INSERTION SELECTIVITY IN REACTION OF PHENYLCARBENE

Hideo TOMIOKA,* Shinji SUZUKI, and Yasuji IZAWA
Chemistry Department of Industry and Resources, Faculty of Engineering,
Mie University, Tsu, Mie 514

Photochemical studies of phenyldiazomethane in 2-chloropropane as a function of temperature reveal that C-Cl insertion of singlet phenylcarbene is dominant at lower temperature as long as the solvent is liquid, but primary C-H insertion becomes near-exclusive in a rigid matrix, suggesting that two kinds of matrix effect are operating.

In recent years interest has increased in the low temperature photolysis of aryldiazo compounds in reactive organic matrices, *i.e.*, olefins,[1] alcohols,[2] and ethers,[3] since arylcarbene generated in rigid matrices at -196 °C gives mainly the products apparently arising from the triplet carbene. Thus, the generation of phenylcarbene in alcohols led mainly to formation of the alkylbenzyl ether (OH insertion), a characteristic product of singlet carbene, at 0 °C, but resulted in the dramatic increase in the C-H "insertion" at -196 °C, which were attributable to abstraction-recombination (*a*-*r*) reactions of triplet carbene.[2] There is, however, some ambiguity as to the reason why the triplet contribution is enhanced at -196 °C. It has been suggested[1b] that the restricted mobility enforced by the solid matrix may have effect on reactant orientation in the transition state. Thus "singlet reactions" may be geometrically more demanding than "triplet reactions" because, in the former, two bonds form simultaneously through the triangle transition state, whereas, in the latter reactions, these bonds form sequentially. Hence, matrix favors reaction from the triplet which is expected to react in a geometrically less-demanding mode. The reactions of PhCH: with alkyl chloride are, then, of special interest in this connection since, unlike other system thus far reported, not only the C-H insertion of triplet carbene, but also the C-Cl insertion of singlet carbene is shown[4] to take place stepwisely (via *a*-*r* mechanisms), and there may be little difference in geometrical requirement between the reactions of singlet and triplet carbenes. We have investigated the product distributions in the reactions of PhCH: with 2-chloropropane as a function of temperature and found that two kinds of matrix effects as well as temperature effect are operating in this special system.

Irradiation[5] of an 8.4mM solution of $PhCHN_2$ (1) in 2-chloropropane at 15 °C gave[6] two insertion products into the solvent, C-Cl insertion product (2, 24.1%) and tertiary C-H insertion product (3, 6.5%). In contrast, irradiation[5] of 1 in frozen 2-chloropropane matrix at -196 °C resulted[6] in dramatic change in the product distributions; primary C-H insertion product (4), which was not detected in the room temperature photolytic run, appeared as a main product (36.2%) along with lesser amount of the tertiary C-H insertion product (3, 10.5%) and the C-Cl insertion product was completely diminished. Other minor products detected in each run were toluene, bibenzyl, benzyl chloride, stilbenes, and aldazine. These by-products were apparently arising from the reactions effectively competing with the relatively sluggish insertion reaction. A more detailed study on the temperature dependence gave the results shown in Figure. The product distributions



1 2 3 4

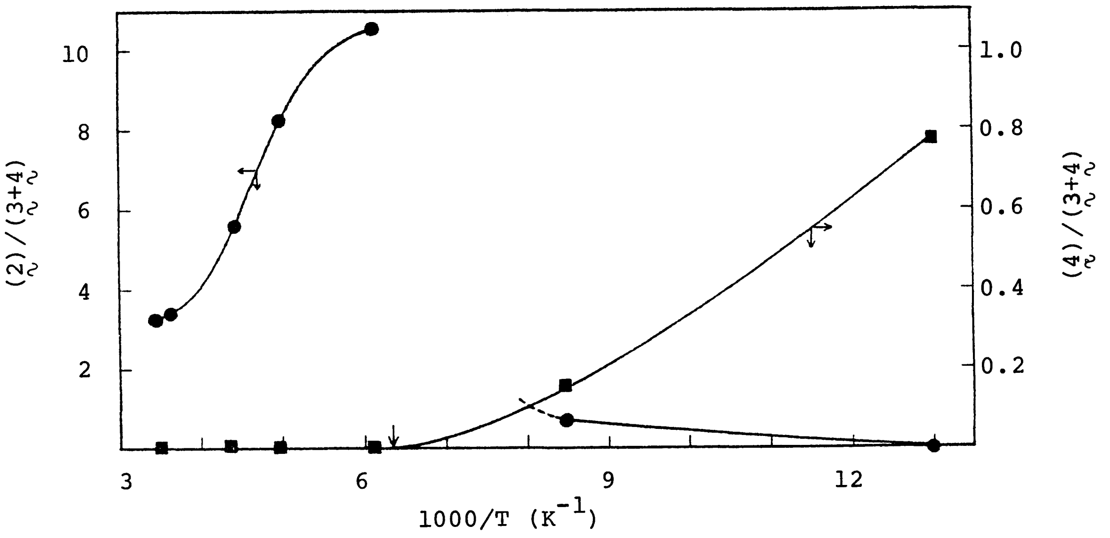


Fig. Temperature and Matrix effects on C-Cl/C-H (-●-) and C-H (-■-) insertion selectivities.

were found to be highly sensitive to the reaction temperature as well as the reaction phase. A similar but less dramatic temperature dependency of the product distributions was also observed in the reaction of PhCH: with chloroethane. Thus, as temperature decreases in liquid phase, **2** continues to increase as long as the solvent is liquid, but its formation is remarkably suppressed once matrix is formed. Such a sharp discontinuity (maximum) in the graph of apparent "singlet/triplet product ratio" (**2**/(**3**+**4**)) vs T^{-1} in the region of a liquid-solid phase transition has not been observed in other reaction systems; the singlet/triplet product ratios have been shown to change rather monotonously with decrease in temperature including liquid and solid runs in the reactions of PhCH: with olefins[1c,d] and alcohols,[2] indicating[1d] that the enchancement of the triplet contribution at lower temperature can be explained simply as a temperature effect without recourse to a matrix effect in these reaction systems. Increase in C-Cl insertion with decrease in temperature in the liquid phase clearly indicates that this process should have lower activation energy than the C-H insertion, as is evident from the difference in bond energy ($D_{C-Cl} < D_{C-H}$). Dramatic decrease in the formation of **2** in solid phase, in spite of the energetic advantage, is ascribable not to a simple temperature effect at all, but totally to a matrix effect, *i.e.*, a change in environment. Origin of the matrix effect is uncertain at present. But the interpretation of these results which we favor is that the stabilization of ionic intermediate, *e.g.*, the halonium ylide,[7] by solvation becomes less important in the solid phase and hence C-Cl insertion comes to be effectively suppressed. This kind of matrix effect would be prominent only on the singlet reaction involving electrophilic attack on lone-pair electrons of the hetero-atom.

Dominant formation of the primary C-H insertion product (**4**) in the lower temperature matrix suggests that a second kind of matrix effect previously proposed,[8] *i.e.*, topochemical factors, is also operative in this case. It is important to note here that the insertion selectivity into C-H bonds of 2-chloropropane, *i.e.*, tertiary: primary ratio on a "per bond" basis, (1.7) in -196 °C photolytic run is much lower than that (4.1) observed[8a] in isobutane matrix in spite of the fact that the tertiary C-H bond of the chloride is weaker[9] than that of isobutane. This might suggest that the tertiary C-H bond in 2-chloropropane is more effectively blocked by chlorine atom and hence steric hindrance as regards the accessibility of the tertiary C-H bond becomes more severe in rigid matrix.

In conclusion, it should be pointed out that the selectivities of carbene insertion reactions can be improved by simply controlling the reaction phase and temperature.

Acknowledgement

Support of this work by a Grant-in-Aid for Scientific Research from the Ministry of Education and the Asahi Glass Foundation is gratefully acknowledged.

References and Notes

1) (a) R. A. Moss and U.-H. Dolling, J. Am. Chem. Soc., **93**, 954 (1971); (b) R. A. Moss and M. A. Joyce, ibid., **99**, 1262 (1977); (c) R. A. Moss and J. K. Huselton, ibid., **100**, 1314 (1978); (d) R. A. Moss and M. A. Joyce, ibid., **100**, 4475 (1978).

2) (a) H. Tomioka, T. Inagaki, and Y. Izawa, J. Chem. Soc., Perkin Trans. 1, 130 (1979); (b) H. Tomioka and Y. Izawa, J. Am. Chem. Soc., **99**, 6128 (1977).

3) H. Tomioka, M. Itoh, S. Yamakawa, and Y. Izawa, J. Chem. Soc., Perkin Trans. 2, in press.

4) See for example, H. D. Roth, Acc. Chem. Res., **10**, 85 (1977).

5) The degassed Pyrex tubes containing chloropropane solutions of diazo compound were suspended in a transparent Pyrex Dewar flask filled with coolant and irradiated with a Halos 300-W high-pressure mercury lamp untill all of the diazo compound was destroyed.

6) All products were identified by gas-chromatographic (2.5 m × 5 mm 5% OV-17 column) comparison with authentic samples. Yields were based on **1** used. Total yields of the insertion products were 30-50% over the temperature range studied. Control experiments ruled out the interconversion of the products during the irradiation.

7) See for example, W. Kirmse, "Carbene Chemistry", 2nd ed., Academic Press, New York, N. Y., 1971, p 442.

8) (a) H. Tomioka, J. Am. Chem. Soc., **101**, 256 (1979); (b) H. Tomioka, G. W. Griffin, and K. Nishiyama, ibid., **101**, 6009 (1979).

9) H. Sakurai and K. Tokumaru, Ed., "Chemistry of Free Radicals", Nanko-do, Kyoto, 1967, p 23.

(Received November 19, 1979)