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ON CARBENE ALKENE COMPLEXES

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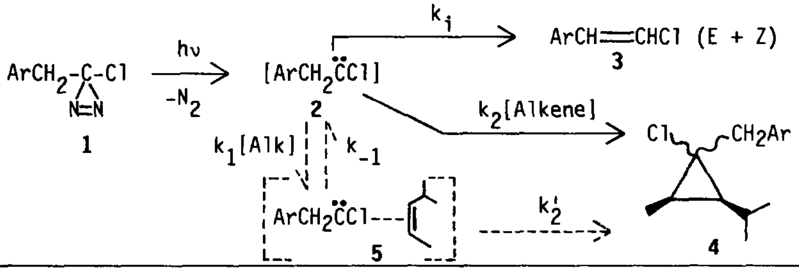
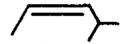
Summary: It is shown that a recent claim for the intermediacy of a carbene alkene complex is unsubstantiated. An alternative mechanism is proposed.

One of the most important recent developments in carbene chemistry is the idea that carbenes may **reversibly** form intermediates (e.g. nitrile ylids,[1,2] alcohol ylids[2,3]) on their way to products. Of paramount interest[4] is the possible formation of carbene alkene complexes, first suggested by Moss and Turro[5] to explain their observations on phenylchlorocarbene. Since theoretical support[6] for such complexes is questionable, it is important to obtain more experimental evidence for these species. In that regard, a recent paper[7] on the competitive hydride shift vs. olefin cycloaddition chemistry of a series of chlorobenzylcarbenes purports to provide kinetic evidence for carbene alkene complexes. As we show herein, such is not the case at all.

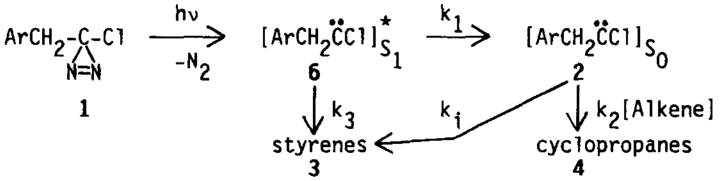
Scheme I



The reaction reported is reproduced in Scheme I (solid arrows). Based on this scheme, one would expect that **4**/**3** = (k_2/k_i)[]. However, the expected linear relationship between product ratio and alkene concentration was not observed. This led the authors to consider a more elaborate mechanism, involving a carbene alkene complex (dotted lines in Scheme I), wherefrom they derived the following kinetic relationship:

$$\frac{3}{4} = \frac{k_i}{k_2'} + \frac{k_i}{k_1 k_2'[1/(k_{-1} + k_2')]} \cdot \frac{1}{[\text{Alkene}]} \qquad (1)$$

Scheme II



Although plots of **3/4** vs. 1/[] were linear, it is readily seen that eqn. (1) is **incorrect** for the carbene alkene complex mechanism of Scheme I; only the second term of eqn. (1)

applies (and thus plots of **4**/**3** vs. [] should be linear). Indeed, for eqn. (1) to be appropriate, two parallel routes to **3** must be operative. A reasonable mechanism of this type is shown in Scheme II.

$$\frac{\mathbf{3}}{\mathbf{4}} = \frac{k_3}{k_1} + \frac{k_i\,(k_1 + k_3)}{k_1 k_2} \cdot \frac{1}{[\text{Olefin}]} \qquad (2)$$

Equation (2) is readily derived from Scheme II (steady-state assumption for **6** and **2**). Although any mechanism wherein both **1** and **2** are precursors of **3**[8] will satisfy the kinetic observations, the notion that an excited carbene state (**6**) is involved is paralleled by other recent suggestions[9] of excited state carbene formation in photoreactions. From the published data[7] and eqn. (2), one may derive k_3/k_1 (intercept) and k_i/k_2 (slope/[1 + intercept]). The k_i/k_2 values yield a good Hammett relationship using σ^+ ($\rho = -0.70 \pm 0.04$, rmsd = 0.037). As already noted,[7] the intercept values (k_3/k_1) do not obey a Hammett relationship; rather a parabolic curve is obtained. Perhaps the internal conversion of **6** to **2** is facilitated by the vibrational state structure of the heavier aryl groups (k_3/k_1 is at a minimum for Ar=Ph); steric factors may also be involved.

One final caution is necessary. The curvature seen in the **4**/**3** vs. [] plots could be (partially) due to the increase in solvent polarity as more alkene is added to the cyclohexane solvent.[10] However, the variation in the curvature observed as a function of the aryl group makes this seem less likely. In any event, **no evidence for a carbene alkene complex** can be obtained from the Tomioka study.[7,11]

References and Notes

1. (a) Kende, A. S.; Hebeisen, P.; Sanfilippo, P. J.; Toder, B. H. J. Am. Chem. Soc. **1982**, 104, 4244; (b) Barcus, R. L.; Wright, B. B.; Platz, M. S.; Scaiano, J. C. Tetrahedron Lett. **1983**, 24, 3955; (c) Janulis, E. P.; Wilson, S. R.; Arduengo, III, A. J. Ibid. **1984**, 25, 405.
2. (a) Warner, P.; Chu, I.-S. J. Am. Chem. Soc., submitted; (b) Ibid., unpublished.
3. (a) Kirmse, W.; Loosen, K.; Sluma, H.-D. J. Am. Chem. Soc. **1981**, 103, 5935; (b) Grasse, P. B.; Brauer, B.-E.; Zupancic, J. J.; Kaufmann, K. J.; Schuster, G. B. Ibid. **1983**, 105, 6833.
4. Platz, M. S. Tetrahedron Lett. **1983**, 24, 4763.
5. (a) Turro, N. J.; Butcher, J. A., Jr.; Moss, R. A.; Guo, W.; Munjal, R.; Fedorynski, M. J. Am. Chem. Soc. **1982**, 104, 1754; (b) Ibid. **1980**, 102, 7576; (c) Moss, R. A.; Perez, L. A.; Turro, N. J.; Gould, I. R.; Hacker, N. P. Tetrahedron Lett. **1983**, 24, 685.
6. Houk, K. N., private communication.
7. Tomioka, H.; Hayashi, N.; Izawa, Y.; Liu, M. T. H. J. Am. Chem. Soc. **1984**, 106, 454.
8. Any scheme in which a second intermediate (or **1**) gives cyclopropanes (**4**) in a parallel reaction to their formation from **2** will not fit the observed kinetics.
9. (a) Gallucci, R. R.; Jones, M., Jr. J. Am. Chem. Soc. **1976**, 98, 7704; (b) Chang, K.-T.; Schechter, H. Ibid. **1979**, 101, 5082; (c) Kraska, A. R.; Chang, K.-T.; Chang, S.-J.; Moseley, C. G.; Schechter, H. Tetrahedron Lett. **1982**, 23, 1627.
10. For such a misleading solvent effect, see Jones, W. M.; Walbrick, J. M. J. Org. Chem. **1969**, 34, 2217.
11. However, we emphasize that nothing in the Tomioka study[7] or this work precludes reversible carbene alkene complex formation.

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