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# CONFORMATIONS OF DIRADICALS

Raymond A. Firestone

Merck Sharp & Dohme Research Laboratories, P.O. Box 2000, Rahway, NJ 07065

The diradical intermediates in 1,3-dipolar cycloadditions can be formed in several different conformations. Since rotations of even single bonds are not fast relative to many other molecular events, interconversion among the various conformations of a diradical may be slower than their subsequent individual transformations. Consequently, a diradical of given connectivity may give rise to different products from each of its kinetically distinguishable conformations.

The diradical from benzonitrile oxide and phenylacetylene can be formed at any dihedral angle of the reactants, idealized here in the two extreme forms cyclo and extended. Other than revert to reactants, they can only cyclize to isoxazole (cyclo) or transfer hydrogen intramolecularly, forming an oxime (extended). The ratio of isoxazole to oxime depends in large part on the ratio of cyclo to extended diradicals initially formed. This in turn is influenced by the electrostatic charges, induced by radical stabilization, at the two radical sites that are to unite in the cyclo form. Like charges favor a greater proportion of extended diradicals and hence oxime, while unlike charges favor cyclo, leading to isoxazole. A large body of data is interpreted on this basis. The fact that most 1,3-dipoles are more reactive with electron-poor than electron-rich olefins, and the phenomenon of "inverse electron demand" in Diels-Alder reactions, can also be understood in the same way.

A recent criticism of the diradical mechanism was based on the observation that 1-p-nitrobenzylideneamino-1,2-diphenyl cyclopropane pyrolyzes at 70° to a diradical that partly recyclizes to the cyclopropane and partly cyclizes to a pyrroline, but does not cleave to benzonitrile p-nitrobenzylide and styrene. The latter two compounds, however, which apparently ought to combine to the same diradical, give at 20° only the pyrroline (the normal 1,3-cycloadduct) and none of the cyclopropane (the 1,1-cycloadduct). The conclusion was that cycloaddition cannot involve the diradical since it gives, in part, products different from those arising from the bona fide diradical made from the cyclopropane.

The argument, however, is not valid because the two diradicals formed respectively by cycloaddition and by pyrolysis, although they have the same connectivity, differ both in conformation and in bonding. The difference goes beyond that between cyclo and extended, involving in addition two types of bonding arrangement not hitherto recognized. Interconversion among them occurs via rotations requirin uncoupling and coupling of adjacent pi-orbitals, which are anticipate to have significant barriers. Thus the cycloaddition and pyrolysis manifolds are kept largely separated despite the superficial similarity of their respective diradical intermediates. Therefore I conclude that both cycloaddition and pyrolysis reactions proceed through diradical intermediates.