Tetrahedron Vol. 41, No. 8, pp. 1427 to 1428, 1985
Printed in Great Britain.

0040-4020/85 $3.00 + .00
Pergamon Press Ltd.

THE BEGINNINGS OF MODERN CARBENE CHEMISTRY TRIPLETS AND SINGLETS

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(*Received in USA* 18 *April* 1984)

There are clear and *valid* indications of carbene (and nitrene) intermediates sprinkled through the early literature, none of which ignited the modern activity in the carbene field. Some of the more prominent names associated with this earlier work were Buchner and Curtius (1885),[1] Staudinger and Kupfer (1912),[2] Rice and Glasebrook (1934)[3] and Meerwein *et al.* (1942).[4] Modern carbene chemistry had an unusual genesis, since it is a relatively rare occurence for a mechanism study to open-up a 'new' field. Mechanism studies mainly sharpen our understanding of fields already discovered.

The work of Hine (1950),[5] a kinetic study of the unusual features of alkaline hydrolysis of chloroform, started the modern development. Hine proposed that hydrolysis proceeds by a two step α-elimination, involving a new intermediate, CCl_2. Doering and Hoffman (1954)[6] suggested that as a consequence of the Hine postulate one should be able to devise a non-aqueous system useful in synthesis. Employing base and a haloform they were able to generate CCl_2 and CBr_2 under conditions which made addition to alkenes the major pathway, making 1,1-dihalocyclopropanes in good yields. With this demonstration of important consequences in the synthesis of cyclopropanes, interest in the field was fully ignited.

Our contribution followed, providing an organizing principle in the form of a postulate: carbenes might be found in triplet and singlet states. These two varieties of carbene should be recognizable through their chemical properties, a consequence of the requirement for spin conservation, Skell and co-workers (1956),[7–9] an extension of the Wigner–Witmer correlation rules.

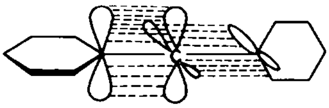
The triplet, it was proposed, could engage a reactant partner only with an orbital having one-electron occupancy. Thus, the triplet would have the selectivity characteristic of radicals, and also addition to a double bond would be a two-step process. Spin conservation requires that addition of a triplet carbene to an alkene must produce a triplet state 1,3-diradical intermediate. The intermediate might live long enough to lose the stereochemical integrity of the alkene (*E* or *Z*) in proceeding to the cyclopropane, thus resulting in a non-stereospecific addition.

On the other hand, the singlet should have no spin conservation restrictions to using the two electrons of the carbene to make simultaneously two bonds to the alkene. Thus, double bond addition should be stereospecific, a notion also applicable to insertion reactions. The selectivity of the singlets, it was further postulated, would be non-radical in nature and therefore similar to carbonium ions (empty orbital) or carbanions (filled orbital).

The value of these concepts was soon demonstrated with CBr_2 (Skell and Garner, 1956)[8,9] and CCl_2 (Doering and co-workers, 1956, 1958).[10,11] These dihalocarbenes add stereospecifically to alkenes, and with selectivities characteristic of two-electron deficient species. We attributed these observations to ground state singlet behavior of these carbenes.

Methylene, CH_2 was shown to add to alkenes stereospecifically, Skell and Woodworth (1956),[7] and insert into alkanes with unprecedented indiscrimination, Doering *et al.* (1956).[12] To put an instructive perspective on the methylene field, it should be noted that during the preceding three decades low pressure gas phase studies of methylene (from ketene) and alkenes had *not* been found to produce cyclopropanes. Our success in producing cyclopropanes in the liquid phase and gas phase experiments (at one atmosphere pressure of 2-butenes) resulted in an immediate modification of hitherto unsuccessful experimental designs. Ethylene–ketene experiments at one atmosphere pressure then produced cyclopropane in good yields, Frey and Kistiakowsky (1957).[13] Cyclopropanes had not been recognized in the earlier low pressure studies because they were formed with sufficient vibrational excitation, and with no means for disposal of this excess energy, resulted exclusively in isomerization and decomposition of the primary products.

The quest for a triplet state species was influenced by the notion that a carbene with a degenerate pair of non-bonding orbitals would be more stable in the triplet state, a consequence of applying Hund's rule and the Pauli exclusion principle. The first recognized triplet, diphenylmethylene, was examined for this reason and found to be radical-like in its selectivities, and non-stereospecific in olefin additions, Etter *et al.* (1959).[14] While the same reasoning led directly to propargylene, Skell and Klebe (1960),[15] H—C—C≡C—H, with a linear triplet structure and cyanomethylene, Bernheim *et al.* (1964, 1965),[16,17] the hypothesis which had led to diphenylmethylene proved incorrect when it was later found to be a bent molecule, ESR, Murray *et al.*,[18] Brandon *et al.* (1962).[19]† The first recognition of a spectrum for a carbene, CH_2, Herzberg and Shoosmith (1959),[20] Herzberg (1961),[21] also resulted in a similar erroneous conclusion, that the triplet was linear. Thus, even incorrect concepts can lead one to significant areas of research.



The recognition of a bent geometry for triplet methylene followed the discovery of methylene in inert-

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† Dimesitylmethylene, Zimmerman and Paskovich[27] has a linear structure in the triplet state, Griller and Nazran.[28]

gas matrices, Bernheim *et al.* (1970),[23] analysis of isotopically substituted methylenes, Bernheim *et al.* (1971),[24] Wasserman *et al.* (1970),[25] and reinterpretation of the original optical spectra, Herzberg and Johns (1971).[26]

From the reaction-chemistry view, an exciting aspect of the report from the National Research Council Laboratories was the observation that dilution with helium increased the triplet yield at the expense of the singlet, Herzberg and Johns (1966).[22] This type of experiment would prove fruitful in succeeding years for both gas phase and liquid phase experimentation. By increasing the lifetime of the carbene with inert diluents, decay to a lower state is favored.

The spectroscopic detection of CH_2 was the harbinger of an extraordinarily fruitful development in this field. Ultimately, spectroscopy provided detailed structural information, and provided analytical methods that have served to unravel kinetic details which formerly were only the subject of speculation. Nonetheless, it is worth noting that prior to the time of this landmark achievement the field of *carbene chemistry* had already managed to achieve an early maturity through the efforts of numerous investigators.

The contributions of these new methods were made with two distinct qualities, and in two distinct time periods. The early period, starting in approximately 1960, related to the detection of radicals by various spectroscopic methods and revealed the fine structural details which were of primary interest to physicists and theoreticians. The development of some of these methods as fast analytical tools, coming to substantial strength by approximately 1975, made possible examination of kinetics, leading to improvements in understanding the mechanisms of carbene reactions. This latter development was important to the chemists concerned with reaction dynamics. From the more recent efforts precise information is becoming accessible: interconversion rates of triplet and singlet states and *absolute* rates of reactions of singlets and triplets with various substrates. Earlier treatments of singlet–triplet interconversion rates were only rough conjectures. The early rationales were based on competitive rate data which were far more easily obtained than absolute rates, but the latter proved nonetheless to be only slightly less incisive. This is not a surprising outcome, for in most instances the absolute rates are compared with one another, and thus are used in the form of relative rates.

The current recognition of the importance of $\Delta S^{\dagger}$ in rationalizing rates of carbene reactions leads me to mention a study of CCl_2 reactivity which went largely unnoticed for more than a decade, Skell and Cholod (1969).[29] The study recognized, somewhat to our dismay at the time, that the discrimination between electron-poor and electron-rich alkenes by CCl_2 was more a consequence of $\Delta S^{\dagger}$ than $\Delta H^{\dagger}$, as had been assumed until then. It was pointed out that this might also prove to be true for other fast, low activation energy reactions.

The success of the triplet–singlet concept in carbene chemistry *may* also have influenced modern photochemistry. While separation into singlet and triplet behavior is a major organizing feature of photochemistry today, in the pre-1960 period it was not of recognizable importance.

Thus, today both triplet and singlet behaviors have been observed. It can now be stated that all of the accumulated results are consistent in detail with the spin-conservation-based hypotheses, although often with more advanced titles (State Selection Rules, etc.).

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