The electron resonance spectra of I and II in their ionized forms are similar to that of bis(2,2,6,6-tetramethylpiperidin-4-ol) glutarate (IV) at 23° (Figure 1). In the un-ionized forms the widths of the second and fourth lines have decreased and the spectra resemble that of IV at 46°. The observation of five equally spaced spectral lines shows that the spin exchange, $\bar{J}$, is much greater than the nitrogen coupling constant, a, and so $\bar{J}$ cannot be determined from the spectrum. However, the heights and hence widths of the lines are said to be a measure of the spin exchange. It is clearly impossible to make such an interpretation without examining the factors which determine the line widths.

Except at low temperatures the dominant relaxation mechanism for flexible biradicals is modulation of J *via* the intramolecular motion.[2] When $\bar{J} \gg a$ the electron resonance spectra exhibit line-width alternation as shown in Figure 1. The width of the second and fourth lines is given by

$$T_2^{-1} = a^2 j(\bar{J})/(2\bar{J})^2$$

where $j(\bar{J})$ is the spectral density

$$j(\bar{J}) = {}^1/_2 \int_{-\infty}^{\infty} (J(0) - \bar{J})(J(t) - \bar{J}) \cos \bar{J}t \, \mathrm{d}t$$

The observation of an increase in the line width can therefore result from a decrease in $\bar{J}$ or an increase in the spectral density, $j(\bar{J})$, or both. As long as $\bar{J} \gg a$ it is impossible to distinguish between these alternatives. Since a change in the nature of the ionizable groups in I and II could affect both $\bar{J}$ and $j(\bar{J})$ it is not possible, as Ferruti, *et al.*,[1] have done, to ascribe the line-width differences to variations in $\bar{J}$ alone.

The spectrum of III at pH 2.6 resembles that of IV at 23° and an increase in pH to 10.8 results in a three-line spectrum similar to IV at −22°. The observation of three lines is consistent with a small value of $\bar{J}$ (in fact $\bar{J} \ll a$) and would suggest a dramatic change in the spin exchange. However, any value of $\bar{J}$ in the presence of extreme line broadening would also produce a three-line spectrum. Indeed, in the case of the glutarate, IV, the spectral changes shown in Figure 1 result predominantly from an increase in the line widths. The variation in the spectra of III observed by Ferruti, *et al.*, might be caused by a reduction in $\bar{J}$, but on the basis of their results an increase in $j(\bar{J})$ cannot be ignored. It is possible to distinguish between these two alternatives by measuring the intensities of the lines for solutions of known concentration.[3] The interpretation of biradical spectra measured in spin-labeled studies of nerve membranes suffers from similar errors.[4]

In conclusion we emphasize that caution must be exercised in the interpretation of the electron resonance spectra of flexible biradicals when the number of spectral lines may often be obscured by extreme line broadening.

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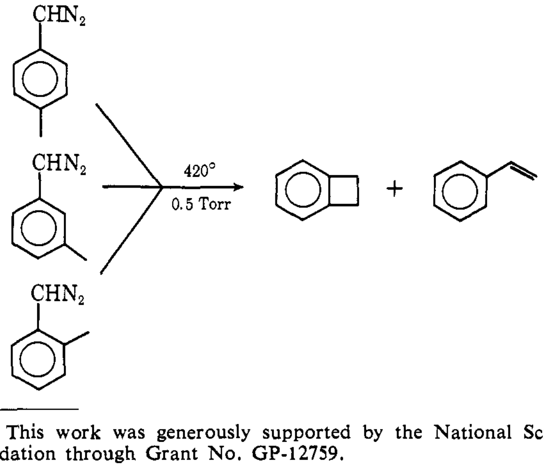
Interconversion of *o*-, *m*-, and *p*-Tolylcarbene[1]

Sir:

The rearrangement of phenylcarbene to cycloheptatrienylidene has recently been reported.[2] We describe here reactions which demonstrate the interconversion of substituted phenylcarbenes and their further rearrangement to methylphenylcarbene, and which suggest that the ring expansion of phenylcarbene to cycloheptatrienylidene is reversible.

The interconversion of substituted phenylcarbenes was demonstrated by constructing molecules incorporating a carbene trap at a remote position. The carbene can only react with the internal trap if rearrangements occur. The internal trap chosen was a methyl group and it was anticipated that should interconversion of the tolylcarbenes occur, products from *o*-tolylcarbene would be isolated no matter which of the three isomers was used as starting material. It was expected that *o*-tolylcarbene would be trapped as benzocyclobutene and that further rearrangement to methylphenylcarbene would be signaled by the appearance of styrene. The carbenes were generated in the gas phase by evaporating the corresponding diazo compound at 0.5 Torr through a 420° furnace into a trap cooled in a Dry Ice–acetone slurry. There can be little doubt that the initial species produced under these conditions is the unrearranged carbene.[3] Remarkably, it was found that generation of either *m*- or *p*-tolylcarbene under these conditions led to benzocyclobutene and styrene in the ratio 0.8.[4] The yield



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[1] This work was generously supported by the National Science Foundation through Grant No. GP-12759.

[2] R. C. Joines, A. B. Turner, and W. M. Jones, *J. Amer. Chem. Soc.*, **90**, 7754 (1969).

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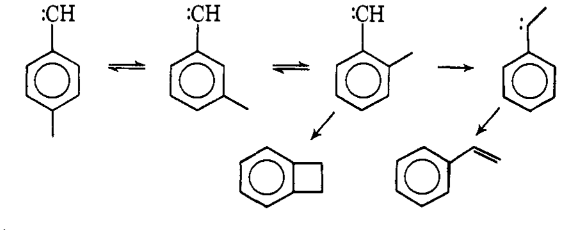
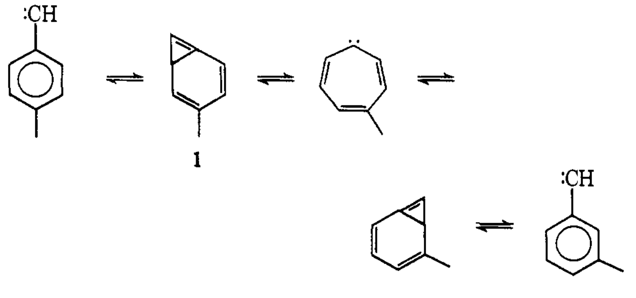
[4] The yield was measured for the *para* case, but the *meta* is very similar. A number of trivial sources of the products have been eliminated. Thus the aldehydes from which the diazo compounds were made survive the reaction conditions unchanged and benzocyclobutene is not converted to styrene under the reaction conditions. Styrene is not isomerized in the flowing system at 350–600°.[5]

of hydrocarbons was >20%. Under the same conditions, *o*-tolyldiazomethane gives the same two products, but the ratio has changed. Benzocyclobutene is now favored by a factor of 2.8.[6] Thus *o*-tolylcarbene is converted to methylphenylcarbene and very probably the *meta* and *para* species as well. Methylphenylcarbene does not rearrange to the tolyl species as only styrene is found in the pyrolysis of methylphenyldiazomethane.

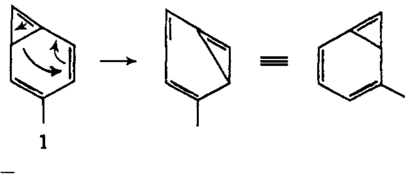


Several mechanisms can be postulated for these changes, but it is not yet possible to distinguish between them. To us the most likely seems to be an equilibration process which requires that the known[2] conversion of phenylcarbene to cycloheptatrienylidene be reversible.[7] As shown in the figure, the cycloheptatrienylidene formed from *p*-tolylcarbene can revert to a phenylcarbene in two ways, one of which moves the methyl group to the *meta* position. A second set of rearrange-

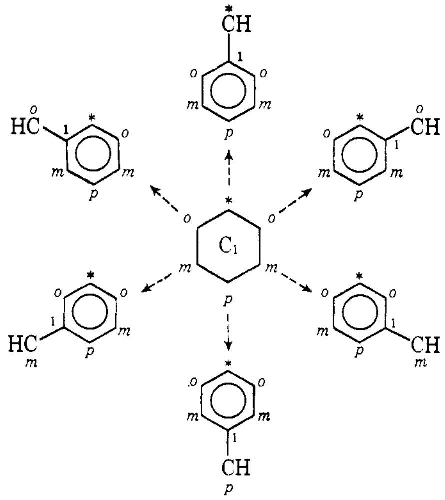


ments serves to move the methyl group to the *ortho* position where it is trapped as benzocyclobutene, and a third series generates methylphenylcarbene, which inevitably yields styrene.

While other mechanisms involving thermal rearrangements of compounds intermediate in the phenylcarbene to cycloheptatrienylidene conversion (*i.e.*, **1**) are possible, we are somewhat reluctant to speculate upon them in the absence of data indicating their existence. One particularly attractive example which involves the rearrangement of compound **1** seems worth mentioning, however.



The general structural consequences of either the equilibration or thermal rearrangement mechanism are demonstrated graphically by the following device: the unique carbon "1" to which the carbene is attached is placed at the center of a hexagon made up of the *ortho*, *meta*, *para*, and divalent (*) carbons. Any carbene formed by displacing a hexagon carbon with carbon "1" can be formed by either the equilibration mechanism or by rearrangements of compound **1**. However carbon "1" cannot wander from its unique position, and the order of the carbons about the hexagon cannot be changed. It remains to be seen if this limited degeneracy is altered (as it very well may be!) by hydrogen shifts in cycloheptatrienylidenes.



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[5] L. O. Schwab, unpublished results.

[6] A possible explanation for the change in ratio involves either a direct insertion reaction of the diazo compound or formation of the carbene in a geometry especially favorable for insertion.

[7] Such a reversal has been postulated.[8] Further, W. M. Jones has informed us that 2-methylcycloheptatrienylidene does form some styrene.[9]

[8] P. Ashkenazi, S. Lupan, A. Scharz, and M. Cais, *Tetrahedron Lett.*, 817 (1969).

[9] W. M. Jones, J. A. Meyers, and R. C. Joines, private communication with permission to cite.

Multiple Carbene Rearrangements In the Diphenylmethylene Series

Sir:

We have recently reported the gas-phase thermal rearrangement of phenylcarbenes to cycloheptatrienylidenes,[1,2] reorganizations which constitute evidence for carbene stabilization occurring by rearrangement to lower energy carbenes.[3]

At this time we wish to report observations which lead us to the conclusion that, under similar pyrolytic conditions, diaryl carbenes also expand to give arylcycloheptatrienylidenes and, further, that arylcycloheptatrienylidenes ring contract to give biphenylcarbenes (Scheme I).

In a typical experiment, diphenyldiazomethane (deposited on acid-washed Chromosorb P) was introduced slowly into the pyrolysis column at 350–375° (1–3

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[1] R. C. Joines, A. B. Turner, and W. M. Jones, *J. Amer. Chem. Soc.*, **91**, 7754 (1969).

[2] P. Schissel, M. E. Kent, D. C. McAdoo, and E. Hedayo, *ibid.*, **92**, 2149 (1970).

[3] For examples of other reactions that may involve comparable rearrangements, see ref 1.