The $-\Delta\Delta\nu$(1–2) correlations reported here represent the first linear free energy relationships involving N–H acids and the pK_{HB} scale.[8]

(8) Note Added in Proof. The pK_{HB} scale has very recently been applied to hydrogen-bonded complex formation with 5-fluoroindole; J. Mitsky, L. Joris, and R. W. Taft, *ibid.*, **94**, 3442 (1972).

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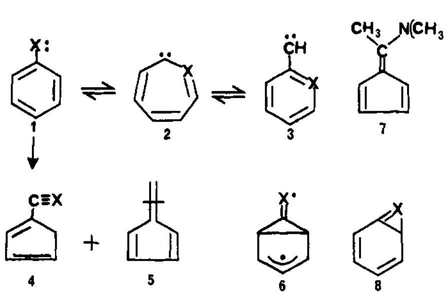
On the Mechanism of the Ring Contraction of Phenylcarbene to Fulvenallene. A Carbon-13 Labeling Study

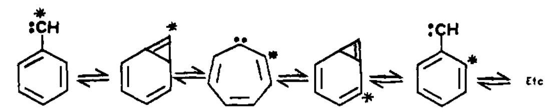
Sir:

Two facts have emerged from recent studies on the properties of arylcarbenes generated in the gas phase. Firstly, phenylcarbene (**1a**) undergoes ring contraction[1a,2] yielding fulvenallene (**5**) and ethynylcyclopentadiene (**4a**) at temperatures $\geqslant$600°. The mechanism for the ring contraction is thought to involve bond formation between C_2 and C_6 giving a prefulvene type intermediate[3] **6a**. Secondly, phenylcarbene rapidly interconverts[1a,1c,2] with cycloheptatrienylidene (**2a**) at temperatures $\leqslant$600° by way of the bicyclic intermediate **8a**. The cycloheptatrienylidene (**2a**) may revert to phenylcarbene in two ways giving **1a** or **3a**, thereby permitting a series of degenerate rearrangements, which will eventually result in a uniform distribution of the label X over all positions of phenylcarbene except C_1. This process is outlined in Scheme I and is valid only for the case in which hydrogen shifts are absent. This scheme was proposed by Jones and coworkers[7] and has been used to account for the isomerization of *m*- and *p*-tolylcarbenes to *o*-tolylcarbene and methylphenylcarbene. This has been subsequently verified by Hedaya[8,9] using ^{13}C labeling studies.



a, X = CH
b, X = N

Scheme I



Direct[10] gas-phase generation of cycloheptatrienylidene under conditions which bring about ring contraction in phenylcarbene does not, however, result in formation of fulvenallene. This led Hedaya[1] and Wentrup[2] to the conclusion that the ring contraction route and the ring expansion route are two separate, competing pathways. We were surprised therefore to learn that under the conditions in which phenylcarbene yields fulvenallene, *p*-tolylcarbene did not yield methylfulvenallenes but instead gave products resulting from the intramolecular trapping of *o*-tolylcarbene and methylphenylcarbene. Evidently the rearrangement of *p*-tolylcarbene *via* Scheme I must be proceeding at a greater rate than that of ring contraction to methylfulvenallenes. If the methyl group has no profound effect on the relative rates of ring contraction and ring expansion it follows that, in the case of phenylcarbene, we are forced to conclude that a similar series of degenerate rearrangements (Scheme I) involving ring expansion should precede ring contraction, *i.e.*, these are not separate competing pathways. This conclusion is at variance with that reached by Hedaya[1] and Wentrup[2] and therefore we decided to test this by an appropriate labeling experiment.

The dry sodium salt of benzaldehyde tosylhydrazone[11] labeled at the aldehydic carbon[12] with 92% excess ^{13}C was heated at 90° and the phenyldiazomethane led directly into the furnace[13] at 770° and 0.05 mm. The crude mixture of fulvenallene and its isomer **4a** was converted to 6-dimethylamino-6-methylfulvene (**7**) with ethanolic dimethylamine at −30° and the product[14] was examined by 22.63-MHz ^{13}C nmr.[16]

The pulsed Fourier transform spectrum (^{1}H broad-band decoupling) of the enamine **7** (Figure 1) shows that enrichment at every carbon atom of fulvenallene has occurred. Tentative assignments of the signals[16] are: a, C_7 (methyl); b, NCH_3 (natural abundance);[17] c and e–g, C_1, C_2, C_3, and C_4 (tertiary ring carbons); d, C_5 (quaternary ring carbon); and h, C_6 (quaternary carbon).[18] It is evident from the spectrum that both

(1) (a) P. O. Schissel, M. E. Kent, D. J. McAdoo, and E. Hedaya, *J. Amer. Chem. Soc.*, **92**, 2147 (1970); (b) J. A. Myers, R. C. Joines, and W. M. Jones, *ibid.*, **92**, 4740 (1970); (c) this pathway has been postulated in order to rationalize certain arylcarbene rearrangements occurring in the solution phase: G. G. Vander Stouw, *Diss. Abstr.*, **25** (12), 6974 (1965) (*Chem. Abstr.*, **63**, 13126b (1965)), under the direction of H. Shechter.

(2) C. Wentrup and K. Wilczek, *Helv. Chim. Acta*, **53**, 1459 (1970).

(3) For the related ring contraction of phenylnitrene (**1b**) to cyanocyclopentadiene (**4b**) see ref 4–6.

(4) W. D. Crow and C. Wentrup, *Tetrahedron Lett.*, 4379 (1967).

(5) E. Hedaya, M. E. Kent, D. W. McNeil, F. P. Lossing, and T. McAllister, *ibid.*, 3415 (1968).

(6) W. D. Crow and C. Wentrup, *ibid.*, 5569 (1968).

(7) W. J. Baron, M. Jones, Jr., and P. P. Gasper, *J. Amer. Chem. Soc.*, **92**, 4739 (1970).

(8) E. Hedaya and M. E. Kent, *ibid.*, **93**, 3283 (1971).

(9) For the related interconversion between phenylnitrene (**1b**) and 2-, 3-, and 4-pyridylcarbenes see (a) W. D. Crow and C. Wentrup, *Tetrahedron Lett.*, 6149 (1968); (b) W. D. Crow, M. N. Paddon-Row, and D. S. Sutherland, *ibid.*, in press.

(10) *I.e.* from the tosylhydrazone salt of tropone.

(11) G. M. Kaufman, J. A. Smith, G. G. Vander Stouw, and H. Shechter, *J. Amer. Chem. Soc.*, **87**, 935 (1965).

(12) The labeled benzaldehyde was obtained from Merck Sharp and Dohme, Canada Ltd., and the position of the label was verified by mass spectrometry.

(13) W. D. Crow and R. K. Solly, *Aust. J. Chem.*, **19**, 2119 (1966).

(14) The properties of compound **7** were in agreement with those reported[15] for 6-dimethylamino-6-methylfulvene. The overall yield of **7** based on the tosylhydrazone salt was 14%.

(15) A. P. Downing, W. D. Ollis, and I. O. Sutherland, *J. Chem. Soc. B*, 111 (1969), and ref 11 therein.

(16) The solvent was $CDCl_3$, the signal of which occurred at 68.3 ppm. The chemical shifts of the resonances relative to $CDCl_3$ are: (a) +57.2; (b) +33.3; (c) −38.5; (d) −39.2; (e) −40.6; (f) −42.2; (g) −43.2; (h) −80.2.

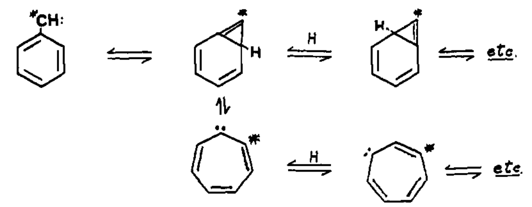
(17) This signal is considerably enhanced by the nuclear Overhauser effect and is yet less intense than those of the quaternary carbon atoms C_5 (d) and C_6 (h) (the signals of which cannot be significantly enhanced by this effect). It is evident, therefore, that enrichment of C_5 and C_6 has occurred.

(18) Assignments were made on the basis of chemical-shift data[19]

quaternary carbon atoms, C_5 and C_6, have the same degree of enrichment. Continual sweep scanning (1200 scans) without ^1H decoupling[20] and CAT output gave the following integration for the peak areas a:c–g:h = 1:5:1. This result demonstrates the *uniform* distribution of the ^{13}C label over *every* carbon atom of fulvenallene.[21] The enrichment of carbon atom C_6 of fulvenallene (which is formally derived from C_1 of phenylcarbene) is possible only *via* a hydrogen-shift mechanism *prior* to the formation of the prefulvene type intermediate[22] **6**.

The most likely mechanism which accounts for our labeling results involves the degenerate rearrangement of phenylcarbene *via* the bicyclic intermediate **8a** and the ring-expanded cycloheptatrienylidene (Scheme I) with concomitant hydrogen shifts (Scheme II). The occurrence of hydrogen shifts prior to ring contraction[23] of phenylcarbene has been observed for the closely related ring contraction of phenylnitrene to cyanocyclopentadiene.[24]

Scheme II



Our results are clearly consistent with the postulate that, prior to ring contraction, there is established a "preequilibrium" in which phenylcarbene rapidly interconverts with the bicyclic intermediate **8a** and with cycloheptatrienylidene.[25] We conclude that the formation of a pool of rapidly interconverting intermediates *via* the ring expansion route is a *basic* property of gas-phase generated arylcarbenes (and nitrenes[24]). Dimerization,[1,2] intramolecular trapping,[7] and ring contraction[1–3] are the major pathways leading from this pool. The absence of fulvenallene as a product from the direct generation of cyclophetatrienylidene[1,2,26] is surprising. However, we make the point that cycloheptatrienylidene may have been generated in a different electronic state[28] from that formed *via* phenylcarbene. Until data concerning the electronic states of these reacting species are available, we advocate caution in correlating results obtained for different generators.

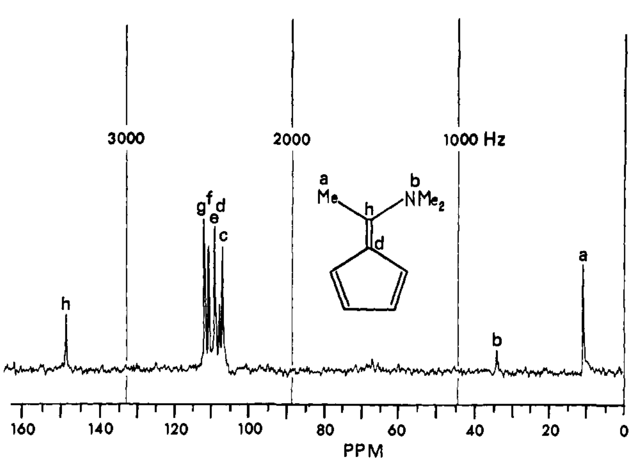


Figure 1. 22.63-MHz pulsed Fourier transform ^{13}C nmr spectrum (^1H broad-band decoupling) of 6-dimethylamino-6-methylfulvene (**7**) in deuteriochloroform.

Acknowledgments. This work is part of a project supported by the Australian Research Grants Committee, whose financial support is gratefully acknowledged. We thank H. B. Selby Pty. Ltd., Melbourne, for the use of their Bruker nmr spectrometer and Mr. Hans Hollenweger for determining the ^{13}C nmr spectra.

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and "off-resonance" partial decoupling: a, quartet; c, e, f, and g, doublets; d and h, singlets.

[19] E. Breitmaier, C. Jung, and W. Voelter, *Angew. Chem.*, **83**, 659 (1971); *Angew. Chem., Int. Ed. Engl.*, 10, 673 (1971).

[20] Thereby eliminating nuclear Overhauser effects.

[21] The complexity of the proton nmr spectrum in the olefinic region prevented an additional confirmation of the distribution of label obtained from the ^{13}C nmr spectrum. However, we were able to examine the ^{13}C satellites of the *C*-methyl group a. The percentage of label at this position was computed to be 16 ± 1%, a result consistent with complete scrambling of the label over all carbon atom sites.

[22] It is possible to envisage a process by which ^{13}C may "leak" into the 6 position of ethynylcyclopentadiene (**4a**) *via* scission of the C_5–C_6 bond, hydrogen migration in the acetylenic radical, and subsequent recombination of the radicals. Achievement of uniformly distributed label in the product by this mechanism would be very coincidental however.

[23] It is noteworthy that hydrogen shifts were not detected during the isomerization of *p*-tolylcarbene to *o*-tolylcarbene and methylphenylcarbene.[8] This observation suggests that the rate of hydrogen shifts may be much slower than the rate of carbene migration according to Scheme I, but that both processes are much faster than the rate of ring contraction.

[24] W. D. Crow and M. N. Paddon-Row, *Tetrahedron Lett.*, in press.

[25] We realize that our results do not demand the intermediacy of cycloheptatrienylidene as they may be accounted for in terms of a series of vinylcyclopropene rearrangements in the bicyclic intermediate **8a** with concomitant hydrogen shifts. This type of rearrangement has been discussed in ref 1b and 7. However, the evidence (although by no means unequivocal) for the phenylcarbene–cycloheptatrienylidene[2] and the diphenylcarbene–phenylcycloheptatrienylidene[1b] interconversions at lower temperatures argues for the intermediacy of cycloheptatrienylidene under our conditions of pyrolysis.

[26] A referee has pointed out the possibility that cycloheptatrienylidene actually may not have been exposed to the conditions assumed by the authors.[1a,2] This point becomes significant when it is realized that, unlike phenyldiazomethane, diazocycloheptatriene cannot be distilled from its tosylhydrazone sodium salt.[27]

[27] W. M. Jones, private communication.

[28] For example, calculations[29] have revealed that the difference in energy between the first two electronic states (singlet and triplet) of cycloheptatrienylidene may be small.

[29] R. Gleiter and R. Hoffmann, *J. Amer. Chem. Soc.*, 90, 5457 (1968).

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The Oxymercuration of Bicyclo[2.2.2]octene. Evidence for a Solvated Mercurinium Ion

Sir:

Hydroxymercuration of bicyclo[2.2.2]octene (**1**), which is symmetrical about the double bond, produces both cis and trans hydroxymercurials.[1a] However, acetoxymercuration of **1** with mercuric acetate in acetic acid solvent has been reported to afford only the *cis*-2-acetoxymercurial **3**.[1a] A mechanism involving a single mercurinium ion intermediate leading to both cis and trans products was invoked by Traylor.[1a] The failure to observe any alteration in the trans oxymercuration products with the hydroxymercuration of **1**

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[1] (a) T. G. Traylor, *J. Amer. Chem. Soc.*, **86**, 244 (1964); (b) T. T. Tidwell and T. G. Traylor, *J. Org. Chem.*, **33**, 2614 (1968); (c) T. G. Traylor, *Accounts Chem. Res.*, **2**, 152 (1969).