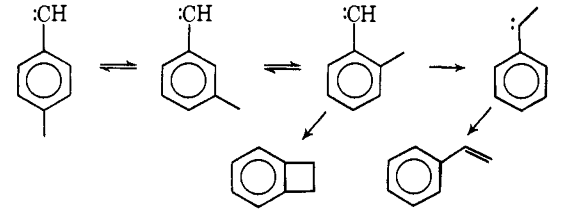
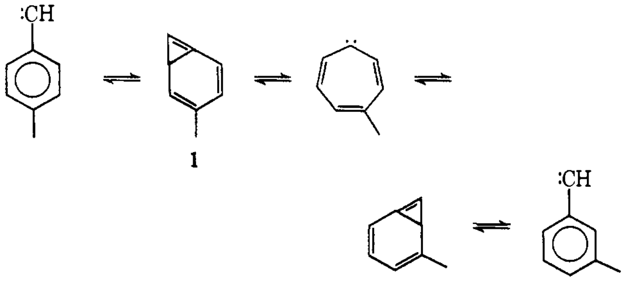
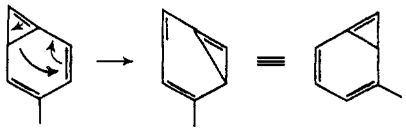
of hydrocarbons was >20%. Under the same conditions, *o*-tolyldiazomethane gives the same two products, but the ratio has changed. Benzocyclobutene is now favored by a factor of 2.8.[6] Thus *o*-tolylcarbene is converted to methylphenylcarbene and very probably the *meta* and *para* species as well. 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 rearrangements 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.



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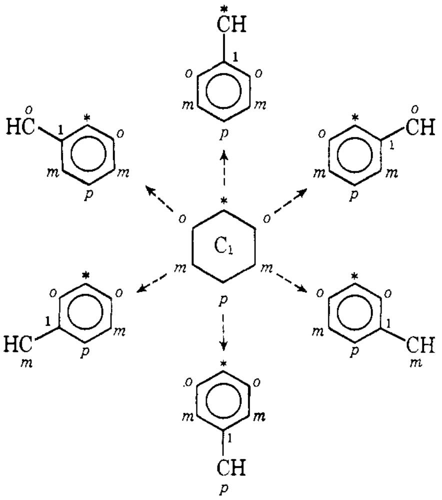
The general structural consequences of either the equilibration or thermal rearrangement mechanism are demonstrated graphically by the following device: the unique carbon "1" to which the carbene is attached is placed at the center of a hexagon made up of the *ortho*, *meta*, *para*, and divalent (*) 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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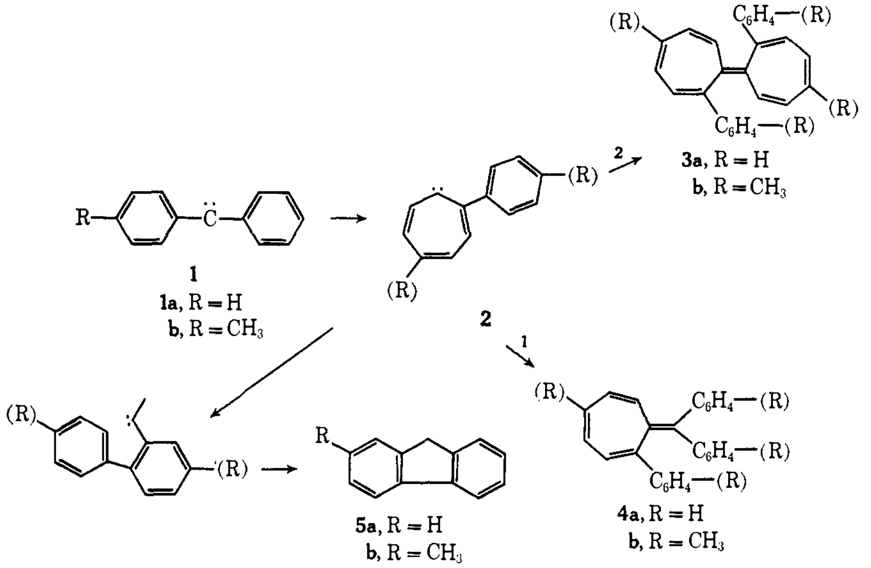
(1) R. C. Joines, A. B. Turner, and W. M. Jones, *J. Amer. Chem. Soc.*, **91**, 7754 (1969).

(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.

Scheme I



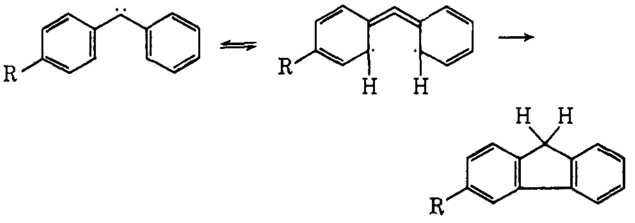
mm) with a nitrogen flow of approximately 0.1 l./min (external flow).[1] The pyrolysate was immediately quenched in a receiver cooled with liquid nitrogen. Chromatography of the volatiles on basic alumina afforded fluorene (**5a**) in 25–30% yield (mp 110–112°, ir and nmr identical with authentic material), a red viscous liquid (30–35%), and, in addition, the expected benzophenone azine and tetraphenylethylene. Composite yield of all products was 90–95%.

Careful chromatography of the red, pentane-soluble liquid revealed the presence of two components in a ratio of about 3:1, triphenylheptafulvene (**4a**) and diphenylheptafulvalene (**3a**). Nmr analysis of **4a** (distilled as a red liquid at 110–120° (0.06 mm)) revealed aromatic phenyl resonances at τ 2.6–3.2 (15 protons) and cycloheptatriene vinyl proton resonances at τ 3.5–4.1 (5 protons).[4] The ultraviolet spectrum displayed λ_{max} (EtOH) 320 (ϵ 8670), 238 mμ (ϵ 22,000). The mass spectral data showed a molecular ion at 332 (base peak) and other mass peaks at *m/e* 255, 254, 253, 252, 178, 167, and 165. Chemical degradation employing conventional ozonization techniques yielded benzophenone. In addition, hydrogenation produced a substance having a molecular weight of 338 (saturation of three of the four double bonds) and an nmr spectrum consistent with the corresponding diphenylmethylenephenylcycloheptane (a satisfactory analysis was obtained).

The diphenylheptafulvalene (**3a**) was confirmed by an unambiguous synthesis from 2-phenyltropone tosylhydrazone sodium salt. The product obtained from thermal decomposition of the salt at 100° in diglyme was identical with the diphenylheptafulvalene obtained from the diphenylcarbene[5] rearrangement: nmr, aromatic phenyl resonance at τ 2.5–3.2 (10 protons), cycloheptatriene vinyl protons at τ 3.5–4.4 (10 protons); ultraviolet, λ_{max} (EtOH) 319 (ϵ 13,540) and 245 mμ (ϵ 17,080); mass spectrum, 332, 255, 254, 253, 252, 241, 239, 178 (base peak), 165; mp 137–142°; satisfactory analysis.

Fluorene is not an unknown product from reactions that may involve diphenylcarbene. As early as 1913, Staudinger observed fluorene from the gas-phase pyrolysis of diphenylketene (700°).[8] Benzhydrylamine, benzhydryl bromide (900°),[9] and diphenyldiazomethane[10] all give fluorene during high-temperature pyrolyses. In all of these cases, the mechanism has been presumed to involve hydrogen migrations. For example, Harrison and Lossing suggested the mechanism given in Scheme II. To distinguish between the hydrogen migration mechanism (Scheme II) and the one involving multiple carbenes (Scheme I) *p*-methyldiphenyldiazomethane was pyrolyzed. As depicted in Scheme II, the hydrogen migration mechanism predicts only 3-methylfluorene (mp 88°)[11] while the multiple carbene scheme predicts only 2-methylfluorene (**5b**) (mp 104°)[12] regardless of which ring expands and contracts. In fact, after isolation of the fluorene product from the reaction, it showed a melting point of 100–102° (purified, mp 104°) and had nmr and ir spectra identical with authentic 2-methylfluorene. Independent synthesis of 3-methylfluorene and glpc

Scheme II



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[4] For substantiating nmr and uv spectral data of several heptafulvenes see H. J. Dauben, Jr., and R. B. Medz, Abstracts, 145th National Meeting of the American Chemical Society, New York, N. Y., Sept 1963, p 7S; and T. Nozoe, T. Mukai, A. Sato, and I. Osaka, *Bull. Chem. Soc. Jap.*, **34**, 1384 (1961).

[5] Dimerization of cycloheptatrienylidenes, effected from thermal decomposition of tropone and 2-benzyltropone tosylhydrazone sodium salts in diglyme, has been reported to yield heptafulvalene[6] and dibenzylheptafulvalene,[7] respectively.

[6] W. M. Jones and C. L. Ennis, *J. Amer. Chem. Soc.*, **91**, 6391 (1969).

[7] T. Mukai, H. Tsuruta, T. Nakazawa, K. Isobe, and K. Kurabayashi, *Sci. Rep. Res. Inst. Tohoku Univ., Ser. A*, **51**, 113 (1968).

[8] H. Staudinger and R. Endle, *Ber.*, **46**, 1437 (1913).

[9] H. D. Harrison and F. P. Lossing, *J. Amer. Chem. Soc.*, **82**, 1052 (1960).

[10] F. O. Rice and J. D. Michaelsen, *J. Phys. Chem.*, 66, 1535 (1962).

[11] A. Sieglitz and J. Schatzkes, *Ber.*, **54**, 2070 (1921).

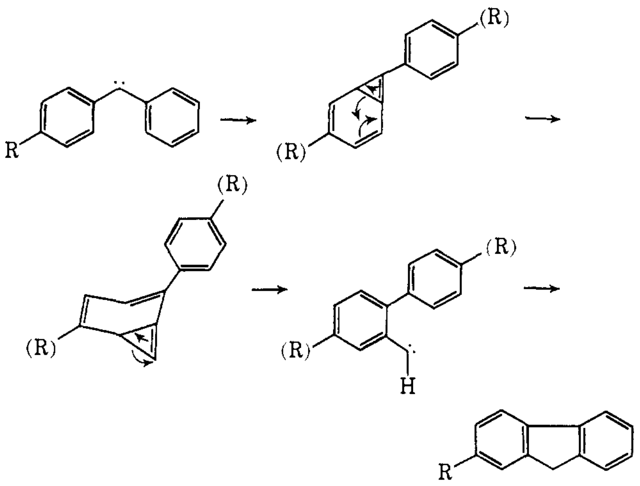
[12] O. Kruber, *ibid.*, **65**, 1382 (1932).

analysis of the crude reaction product showed no detectable quantity (<1%) of the 3 isomer. Thus, apparently all of the fluorene arises by the ring expansion–contraction mechanism![13]

In the suggested mechanism, ring contraction of phenylcycloheptatrienylidene was particularly surprising since cycloheptatrienylidene generated in solution does not show typical carbene properties.[6] Furthermore, Hedaya[15] has found that the sodium salt of tropone tosylhydrazone, when pyrolyzed at 900°, gives no fulvenallene, a product that would be expected[2] if cycloheptatrienylidene contracted to phenylcarbene. In contrast, 2-methylcycloheptatrienylidene generated in these laboratories at 350° gives 10–15% styrene—thus requiring contraction—and Cais[16] and his group have found that reaction of phenyltropylium fluoroborate with diisopropylamine gave products that may have arisen from ring contraction of complexed cycloheptatrienylidene.

It was, therefore, imperative that the proposed intermediate phenylcycloheptatrienylidene be generated under our pyrolysis conditions. Moreover, it became even more important when it was realized that a vinylcyclopropene → vinylcyclopropene rearrangement, as shown in Scheme III, could be envisaged which would by-pass the expanded carbene while retaining the requirements for the exclusive formation of 2-methylfluorene (**5b**).

Scheme III



The sodium salt of 2-phenyltropone tosylhydrazone was synthesized and subjected to reaction conditions. In addition to the above mentioned diphenylheptafulvalene, fluorene was formed in 10–15% yield.

The formation of fluorene from phenylcycloheptatrienylidene thus requires the intermediacy of phenylcycloheptatrienylidene (but not as the sole source of fluorene) in these pyrolyses. Its intermediacy is further supported by the structures of the other two products mentioned before, triphenylheptafulvene and diphenylheptafulvalene.

Other multiple carbene rearrangements are presently under intensive investigation.

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[13] In like manner, pyrolysis of *p*-methoxydiphenyldiazomethane gave 2-methoxyfluorene (mp 108°, lit. 109°).[14] Moreover, preliminary results indicate that pyrolysis of *p*-phenylphenyldiazomethane gives fluorene. This observation suggests a series of ring expansions and contractions involving several intermediate carbenes. Both M. Jones, Jr., of Princeton University and E. Hedaya of Union Carbide have advised us of similar multiple carbene rearrangements of *p*- and *m*-tolylcarbenes yielding benzocyclobutene and styrene.

[14] G. W. Gray, J. B. Hartley, and A. Ibbotson, *J. Chem. Soc.*, 2686 (1955).

[15] Private communication from E. Hedaya.

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

[17] National Science Foundation Trainee, 1965–1969.

Effect of Ion-Pair Solvation on the Paramagnetic Solvent Shift of Aromatic Radical Anion Solutions. Spin Density on Solvating Molecules

Sir:

Theory predicts that the solvent protons of a solution of paramagnetic species undergo an upfield nmr shift due to the paramagnetic bulk susceptibility. The magnitude of this shift for cylindrical sample tubes is, according to Langevin, given by

$$\delta_s\,(\text{ppm}) = -\frac{2}{3}\pi 10^3 \frac{N\beta_e{}^2}{kT}c$$

N being Avogadro's number, β_e the Bohr magneton, and c the concentration in mol/l.[1]

The expression has often been utilized to determine the concentration of paramagnetic species from the observed solvent shift, and as long as no scalar interactions with the solvent molecules exist, the procedure appears to be reliable.[2] However, recent reports indicate that the molar solvent shift of ethereal solutions of certain radical anion salts is considerably smaller than the theoretically predicted value.[3] Apparently the solvent protons are also subjected to a downfield shift, due to specific ion pair solvation, which brings them in close proximity to the unpaired electron.

We were able to confirm this hypothesis and clearly demonstrate the downfield shift by investigating the nmr spectra of complexes of triphenylenesodium with glyme-5 (tetraethylene glycol dimethyl ether). Solutions of triphenylene in THF, stirred on a sodium mirror, are quantitatively converted to the radical anion salt $\text{Tp}\cdot^-,\text{Na}^+$. Addition of glyme-5 to this salt in a 1:1 ratio (excess glyme-5 must be avoided) yields the glyme-separated ion pair $\text{Tp}\cdot^-,\text{G5},\text{Na}^+$. Optical and esr data show that between concentrations of 0.1 and 1 M essentially all of the glyme-5 is bound to $\text{Tp}\cdot^-,\text{Na}^+$, the complexation constant at 25° being higher than $10^4\ M^{-1}$. The proton nmr spectra were recorded on a Varian DP60 spectrometer.

The observed solvent shifts δ_s of THF solutions of $\text{Tp}\cdot^-,\text{Na}^+$ and $\text{Tp}\cdot^-,\text{G5},\text{Na}^+$ (relative to a THF solution of the nonreduced hydrocarbon) are plotted in Figure 1 *vs.* the radical anion concentration. While

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[1] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw Hill, New York, N. Y., 1959, p 20.

[2] E. de Boer and C. MacLean, *J. Chem. Phys.*, 44, 1334 (1966); E. de Boer and H. v. Willigen, *Prog. Nucl. Magn. Resonance Spectrosc.*, 2, 157 (1967); A. Calder, A. R. Forrester, J. W. Emsley, G. R. Luckhurst, and R. A. Storey, *Mol. Phys.*, **18**, 481 (1970).

[3] G. W. Canters, Ph.D. Thesis, University of Nijmegen, The Netherlands, 1969; R. E. Jesse, Ph.D. Thesis, University of Amsterdam, The Netherlands, 1966.