

**Figure 1.** Values of  $J_{FF}$  (circles, left-hand ordinate) for compounds 1–4 and  $J_{HF}$  (squares, right-hand ordinate) for H-5, H-12, and H-11 in compounds 7–9, respectively, plotted against  $n$ , where  $n$  is the number of bonds along the shortest pathway through the molecular framework that connects the two fluorines in 1–4 or that connects the fluorine and the carbon bearing the coupled hydrogen in 7–9. The number of connecting bonds  $n$  is used here merely as an index of structural type in these polynuclear systems; coupling through these bonds is considered negligible in magnitude for all cases except 1 and 7, in which small through-bond contributions to the observed coupling cannot be ruled out.

directly, since those interactions presumably would be optimized in 7 just as the FF interactions are evidently optimized in 2, but rather are those between F and the carbon to which the H is attached.<sup>16</sup> Thus, we conclude that the large value of  $J_{HF}$  for the benzo[*c*]phenanthrene 8 results from an especially favorable spatial relationship between F-1 and C-12 in 8, analogous to the especially favorable spatial relationship between F-4 and F-5 that gives rise to the large value of  $J_{FF}$  in the phenanthrene 2.

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- Except as noted, values of  $J_{FF}$  and  $J_{HF}$  were determined from <sup>19</sup>F spectra at 56.4 MHz and <sup>1</sup>H spectra at 60 MHz in C<sub>6</sub>D<sub>6</sub> solution.
- Full synthetic details for all new compounds will be reported later.
- Nomenclature: 1, 4,5-difluoro-1-methylnaphthene; 2, 4,5-difluoro-1-methylphenanthrene; 3, 1,12-difluoro-4-methylbenzo[*c*]phenanthrene; 4, 10,11-difluoro-1-methyldibenzo[*c,g*]phenanthrene; 5, 9,12-difluoro-1-methyldibenzo[*c,g*]phenanthrene; 6, 7,8-difluoro-1-methylbenzo[*ghi*]perylene.
- Values of 167–170 Hz have been reported previously for  $J_{FF}$  in several 1,8-disubstituted-4,5-difluorophenanthrenes by K. L. Servis and K.-N. Fang, *J. Am. Chem. Soc.*, **90**, 6712 (1968).
- The 5-methyl isomer of 3 has a  $J_{FF}$  value of 45.3 Hz.
- The <sup>19</sup>F spectra of 4 and 6 were measured in DMF at 94.1 MHz; the <sup>1</sup>H spectrum of 8 was measured in C<sub>6</sub>D<sub>6</sub> at 100 MHz. We are grateful to Professor David R. Dalton of Temple University for obtaining these spectra.
- The signal for H-5 in the <sup>1</sup>H spectrum of 7 was simplified to a 2.6-Hz doublet (also 2.6 Hz in CCl<sub>4</sub>) by decoupling all the other hydrogens.
- Measured in CCl<sub>4</sub> solution.
- Values of  $J_{HF}$  up to 16 Hz have been reported for the NH hydrogens in some 2-fluorobenzamide derivatives in which the nuclear spin information is thought to be transmitted through intramolecular HF hydrogen bonds.<sup>51</sup>
- This concept has been suggested previously on the basis of HF coupling studies involving aliphatic hydrogens.<sup>5n,u,cc</sup> See also ref 5ee.
- (a) This work is taken in part from the Ph.D. Thesis of W.M.R., Bryn Mawr College, 1974; (b) National Science Foundation Trainee, 1969–1970, and U.S. Steel Foundation Fellow, 1970–1972.

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## Flash Pyrolysis of $\alpha$ -(*p*-Tolylsulfonyl)phenyldiazomethane. Carbene Formation by Loss of Sulfur Dioxide<sup>1</sup>

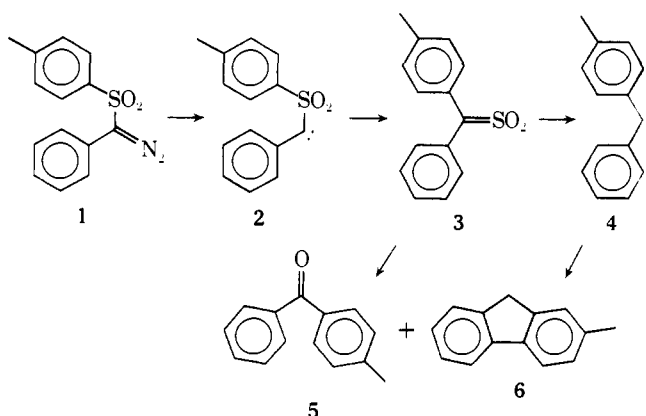
Sir:

This communication is prompted by our discovery of the apparent expulsion of sulfur dioxide from a sulfene. Such extrusion reactions were postulated over 60 years ago,<sup>2</sup> but no example has withstood close attention. As remarked in a recent cogent review,<sup>3</sup> loss of sulfur dioxide from a sulfene is "conspicuously absent", and all earlier attempts to use external addition reactions to trap the carbene so formed have failed.<sup>2,4-6</sup> The Wolff-like rearrangement of sulfonyl carbenes to give sulfenes is known<sup>7</sup> and our interest in carbene chemistry and the use of gas-phase reactions of carbenes<sup>8</sup> in synthesis led us to examine the flash pyrolysis of  $\alpha$ -(*p*-tolylsulfonyl)phenyldiazomethane (1).<sup>9</sup>

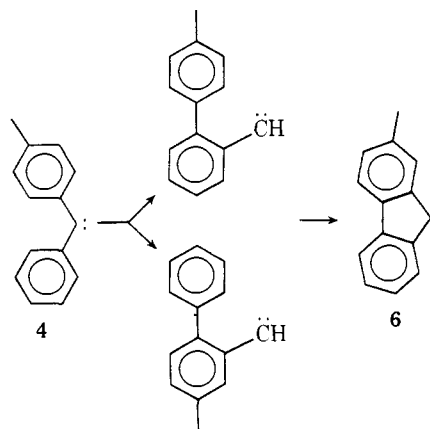
It was our thought that a carbene might be trapped more successfully by an internal reaction rather than an external addition, and we further hoped that the two benzene rings would render the fragmentation substantially less endothermic than the 55–60 kcal/mol estimated for the cleavage of

sulfene itself.<sup>4</sup> Our choice for a target intermediate was *p*-tolylphenylcarbene (4) (Scheme I) and thus the diazo compound 1 was indicated as the starting material.

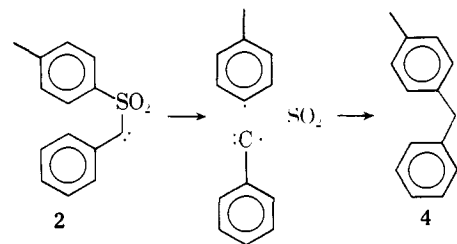
Scheme I



At 350–600° *p*-tolyl phenyl ketone (5, 13–15%) and 2-methylfluorene (6, 3–5%) appeared as the only two nonvolatile monomeric compounds of the pyrolysis of 1.<sup>10</sup> Substantial amounts of polymer and a gas (ca. 10%) were recovered as well. Infrared analysis of the gas showed it to consist mainly of sulfur dioxide. These results are quite consistent with loss of nitrogen from 1 to give *p*-tolylsulfonylphenylcarbene 2 followed by rearrangement to the sulfene 3. Sulfenes are known to lose sulfur monoxide to give the residual carbonyl compound,<sup>3,11</sup> and this appears to be the major observable route followed by 3. The presence of 2-methylfluorene reveals that *p*-tolylphenylcarbene must have been present as well. Fluorenes are the ultimate products of gas-phase rearrangements of diphenylcarbenes, and the methyl group serves as a further label, ensuring that the "migration" to the 2-position required by the carbene-to-carbene process does take place.<sup>12,13</sup>



An alternative mechanism involves fragmentation of 2 to an aryl radical and a carbyne. Were these two reactive species to recombine, *p*-tolylphenylcarbene would result. However, the gas phase should not be conducive to facile recombination, and we would expect to find other products if such a fragmentation were taking place. We are not certain what to expect of phenylcarbyne, but we are unable to detect the product of dimerization, tolan. The aryl radical should appear as toluene and bitolyl, and we can find neither. We could detect substantially less than 1% of these three compounds. In other gas-phase carbene reactions proceeding through aryl radicals, biaryls are found in 10–20% yield.<sup>14</sup>



Data bearing on the lifetime of the sulfene, possibilities of trapping with external agents, and the effect of substituents on the ease of cleavage of the carbon-to-sulfur double bond await further experiments.

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## Stereochemistry of Ketone Insertion and Enol Salt Formation at Alkyl Carbon-Aluminum Bonds<sup>1</sup>

Sir:

Much attention has been given to the reactions of ketones with aluminum alkyls, with the hope of finding new, selective alkylations and reductions and of unraveling the intricate reaction mechanisms involved. By changing the structure of the reactants or the experimental conditions, varying amounts of alkylation,<sup>2</sup> reduction,<sup>3</sup> enol salt formation,<sup>2b,3b</sup> and free radical-induced conjugate alkylation<sup>4</sup> can be observed. Indeed, even the simple insertion of a ketone into the carbon-aluminum bond has been shown to proceed via two competing pathways, each having a different rate law and a distinctive stereoselectivity.<sup>5-7</sup> In donor solvents or in