

last three are due to  $\text{Bu}_4\text{N}^+$  with the expected integration ratios for the two high-field lines. We expected the chemical shift of the aromatic protons to appear at higher field than pyrene because the molecule is doubly negatively charged; instead, 7.8 ppm is precisely the chemical shift of the low field set of hydrogens in pyrene.

After several abortive trials to obtain characterizable products from attempted oxidations of **3a** to **2** or **1**, we decided to examine the solution electrochemistry of **3**. Cyclic voltammetry of **3a** in acetonitrile (0.1 M *n*-butylammonium perchlorate as supporting electrolyte and platinum bead as working electrode) revealed a one-electron reversible reduction (with peak-to-peak separation of 60 mV at a scan rate of 50–500  $\text{mV s}^{-1}$ ) at  $-1.55$  V vs.  $\text{Ag}/0.01$  M  $\text{AgNO}_3$ . No oxidation wave was observed in the range from  $-0.88$  to  $+1.8$  V. However, electrolysis at voltages more negative than  $-0.6$  V produced a species which exhibited two irreversible oxidation waves at  $+0.16$  and  $+0.56$  V.<sup>15</sup> The reversible reduction at  $-1.55$  V could be assigned to the couple 3–4 on the basis of ESR experiments.

Electrolysis of **3a** in  $\text{CH}_3\text{CN}$  at  $-1.35$  V vs. SCE in an ESR cavity generated a relatively stable radical trianion (**4**) ( $g = 2.0033$ ,  $t_{1/2}$  ca. 2 min.,  $a_{\text{H}} = a_{\text{N}} = 2.53$  G) with a 13-line spectrum.<sup>15</sup> From the analysis of the normalized intensities we deduced that the radical had four equivalent hydrogens and four equivalent nitrogens (calcd, 262:232:160:84:32:8:1; found, 262:235:164:82:33:8:1). There is practically no coupling to the nitrile nitrogens.

It is interesting to note that the most stable species among 1–5 are **3** and **4** and not **2** or **1**. This, of course, does not mean that the radical anion derived from **B** will also be unstable.

Current studies on the solid state structure of **3a** and the metathesis products of it with radical cations will be reported in a separate publication.

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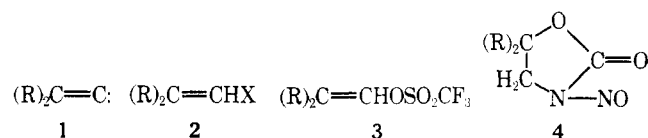
Received January 7, 1977

### Alkylidene Carbene Generation from Tosylazoalkenes and Silylvinyl Triflates<sup>1,2</sup>

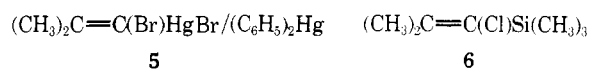
**Summary:** Thermal decomposition of tosylazoalkenes,  $\text{R}_2\text{C}=\text{CHN}=\text{NTs}$ , at 25 °C gave unsaturated carbene derived

products in 25–40% yield; similarly fluoride ion initiated decomposition of silylvinyl triflates  $\text{R}_2\text{C}=\text{C}(\text{OTf})\text{Si}(\text{CH}_3)_3$  in cyclohexene or ethyl vinyl ether gave quantitative yields of carbene adducts in 1–2 h at  $-20$  or  $0$  °C; these two methods represent the mildest known conditions for alkylidene carbene generation to date.

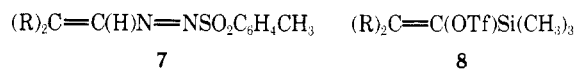
**Sir:** There has been considerable interest and work lately in alkylidene, **1**, and other unsaturated carbenes.<sup>3</sup> Such carbenes have primarily been generated by  $\alpha$  elimination from primary vinyl halides,<sup>4</sup> **2**, or vinyl triflates,<sup>5</sup> **3**, and base-promoted decomposition of *N*-nitrosooxazolidones, **4**, or related com-



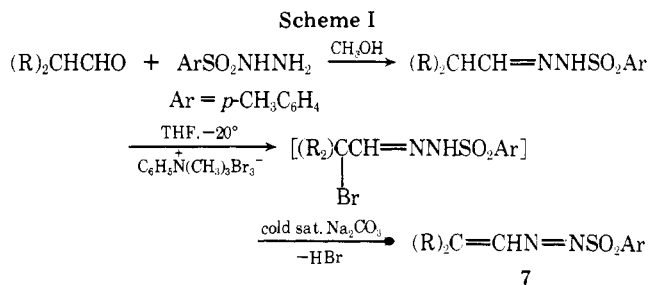
pounds.<sup>6</sup> However, all of these techniques require strong bases such as  $\text{RLi}$ , *t*-BuOK or  $\text{ROLi}$ , preventing the possible interaction of **1** with base-sensitive substrates and thereby limiting the potential synthetic uses of these carbenes. Until recently, with the exception of two photochemical processes,<sup>7,8</sup> both in very low yield, and the nitrite deamination of certain unique vinyl amines,<sup>9</sup> there was no known technique for the generation of **1** in the absence of strong base analogous to the diverse nonbasic generation of saturated carbenes.<sup>10</sup> In early 1976 Seyferth and Dagani<sup>11</sup> reported the thermal generation of **1** from organomercurial **5** at 150 °C and Cunico and Han<sup>12</sup>



reported the formation of **1** via the fluoride promoted decomposition at 25 °C of  $\alpha$ -chlorovinylsilane (**6**), thus providing the first useful generations of **1** under relatively mild and neutral conditions in good yields. Therefore, in this communication we wish to report two additional means of alkylidene carbene **1** generation under even milder conditions involving tosylazoethylenes **7** and silylvinyl triflates **8** as progenitors, in the latter case in quantitative yields.

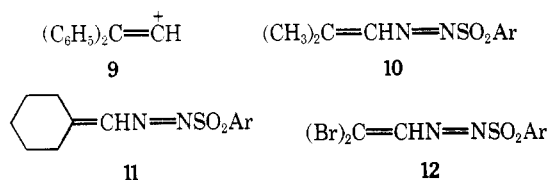


Tosylazoethylenes, **7**, are known<sup>13</sup> and can be readily prepared in good yields according to the procedure of Rosini and coworkers<sup>13</sup> as shown in Scheme I. In fact, Rosini and Cacchi<sup>14</sup>

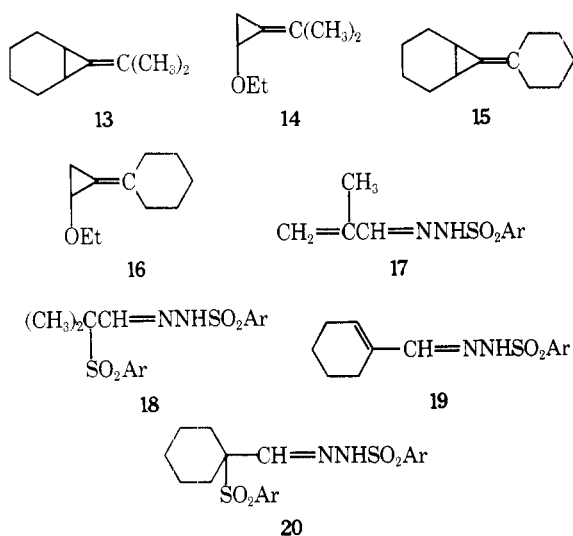


have shown that the tosylazoethylene derived from diphenylacetaldehyde (**7**,  $\text{R} = \text{C}_6\text{H}_5$ ) decomposes in chloroform at 25 °C to give >85% diphenylacetylene via either the carbene **1** ( $\text{R} = \text{C}_6\text{H}_5$ ) or vinyl cation **9**. Since ion **9** would be a primary vinyl cation,<sup>15</sup> and hence energetically extremely unlikely,<sup>15</sup> their decomposition most likely involved carbene **1**. Such diaryl carbenes (**1**,  $\text{R} = \text{C}_6\text{H}_5$ ) however, cannot be successfully trapped<sup>3,5</sup> intermolecularly and are known<sup>3,5</sup> to intramolecularly rearrange to the acetylene. Therefore we prepared

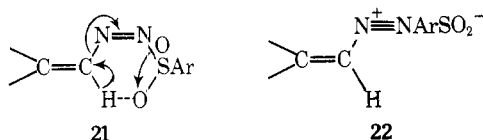
tosylazoalkenes<sup>16</sup> 10, 11, and 12 and investigated their decomposition in various olefins as both solvents and possible carbene traps.



Indeed in both pure cyclohexene and pure ethyl vinyl ether compounds 10 and 11 readily decompose at 25 °C in 8–24 h or at 0 °C in 2–4 days giving, besides N<sub>2</sub> and some CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>H, 25–40% adducts 13 and 14 and 15 and 16, respectively, as well as two other products each, 17 and 18 and



19 and 20 from 10 and 11, respectively.<sup>19</sup> Adducts 13–16 are the products of unsaturated carbenes 1 or carbenoids,<sup>20</sup> and hence represent a simple, mild and presumably general method of thermal dialkyl unsaturated carbene, 1, generation, albeit in only moderate yields. At the moment we do not know the exact mechanism for the formation of 1 from tosylazoethylenes, but there are at least two reasonable alternatives: one involving a concerted rearrangement via a six-membered cyclic transition state 21, the other a possible diazonium ion pair,<sup>14</sup> 22. Tosylhydrazones 17 and 19 arise via known<sup>21</sup> re-

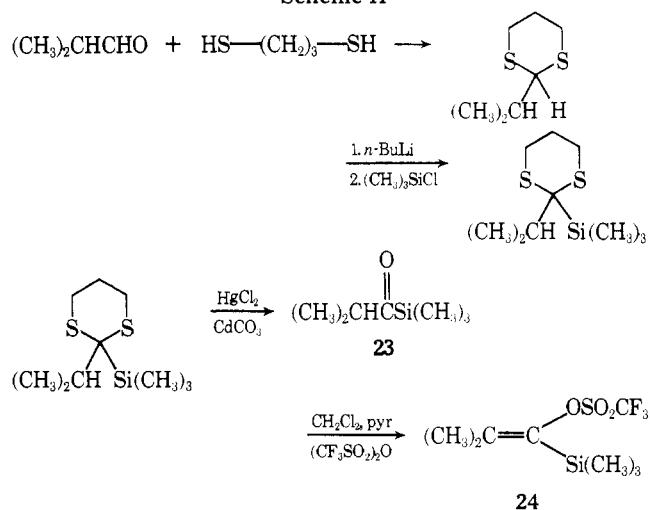


arrangement of tosylazoalkenes, as do compounds 18 and 20 by the known<sup>22</sup> addition of sulfinic acid to the unreacted<sup>23</sup> starting azoalkenes 10 and 11. Interestingly, for reasons presently unknown, tosylazoalkene 12 does not give any carbene derived products<sup>24</sup> upon thermolysis in cyclohexene. We have also carried out preliminary experiments in the photolysis<sup>25</sup> of 10, 11, and 12, but to date no (<1%) carbene derived products have been observed.

Silylvinyl triflate 24<sup>18</sup> can be prepared in reasonable yield from isobutyraldehyde via<sup>26</sup> the  $\alpha$ -silyl ketone 23 that can be obtained by procedures similar to those of Brook<sup>27</sup> and Corey<sup>28</sup> shown in Scheme II.

Silylvinyl triflate 24 gives quantitative yields<sup>19</sup> of adducts 13 and 14 in cyclohexene and ethyl vinyl ether, respectively, in the presence of unencumbered fluoride ion. Reaction may be carried out with KF and crown ethers<sup>29</sup> or with anhydrous R<sub>4</sub>N<sup>+</sup>F<sup>-30</sup> at –20 or 0 °C in 1–2 h or via KF and phase transfer

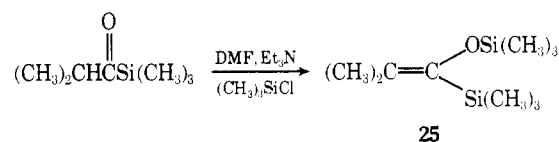
Scheme II



procedures<sup>31</sup> using Aliquat 336 as the transfer agent. These reactions are extremely clean and simple and probably represent the most convenient and mildest alkyldiene carbene 1 generation to date.

The mechanism of the reaction is similar to that observed by Cunico and Han<sup>12</sup> in the case of precursor 6 and involves nucleophilic attack by F<sup>-</sup> on the silicon<sup>32</sup> and displacement of the triflate leaving group. However, unlike the decomposition of 6 where significant amounts of (CH<sub>3</sub>)<sub>2</sub>C=CHCl were observed,<sup>12</sup> we did not see any (CH<sub>3</sub>)<sub>2</sub>C=CHOTf, strongly suggesting a stepwise process in the decomposition of 6 and a concerted process in the decomposition of 24. This hypothesis is in accord with the superior leaving ability of triflate compared to halides.<sup>15</sup>

Silyl ketone 23 may also be converted to silylsiloxyethylene 25<sup>18</sup> which in turn decomposes to give carbene, 1, derived products but at temperatures much too high to be useful.<sup>33</sup>



In summary, we have shown that tosylazoalkenes 7 as well as silylvinyl triflates 8 give carbene derived products under mild neutral conditions: in the case of 7 via thermolysis at room temperature in the absence of any base or nucleophile albeit in only moderate yields; in the case of 8 quantitatively at 0 °C in 1–2 h in the presence of F<sup>-</sup>. The exact nature<sup>20</sup> of such thermally and nucleophilically generated alkyldiene carbenes 1 or carbenoids as well as the potential synthetic uses of these techniques are under active investigation.

**Acknowledgment.** This investigation was supported by Public Health Service Research Grant 1-RD-CA16903-02 from the National Cancer Institute. We are grateful to Dr. J. McCloskey for mass spectrometric determinations.

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 (24) Neither adduct nor BrC≡CBr were observed.  
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Received March 8, 1977

### A Linear Relation between Nuclear Magnetic Resonance Chemical Shifts of Tetra-*tert*-butyldehydro[*n*]annulenes and Resonance Energies per $\pi$ Electron

**Summary:** A linear correlation has been found between the Hückel resonance energies per  $\pi$  electron of  $4N$  and  $4N + 2$  systems and the differences between chemical shifts of the inner and outer protons in tetra-*tert*-butyldehydro[*n*]annulenes.

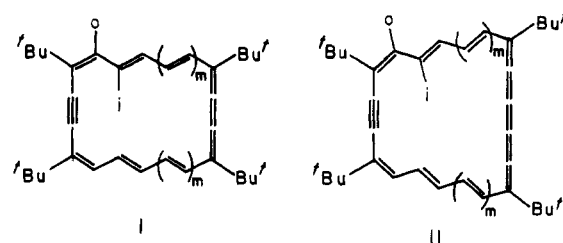
**Sir:** The question of the aromaticity of the annulenes has been of interest for several decades, and in recent years there has been considerable progress in the synthesis of these compounds. Sondheimer among others has prepared many of the parent systems as well as dehydroannulenes.<sup>1</sup> Vogel,<sup>2</sup> Boekelheide,<sup>3</sup> and Sondheimer<sup>4</sup> have also prepared successfully a number of bridged annulenes. In most cases the two criteria reported for the aromaticity of these annulenes were their observed NMR chemical shifts and stabilities. However, fair

Table I. Chemical Shifts, Their Differences, and REPE of Dehydro[*n*]annulenes

[ <i>n</i> ]	$\tau_o$	$\tau_i$	$\tau_o - \tau_i$	REPE
14	0.68	14.44	-13.76	0.0161
16	5.92	-7.17	13.09	-0.0111
18	0.62	13.42	-12.80	0.0118
20	5.48 <sup>a</sup>	-3.78 <sup>a</sup>	9.26	-0.0052
22	1.28	10.83 <sup>a</sup>	-9.55	0.0096
24	5.00	-1.79 <sup>a</sup>	6.79	-0.0020
26	2.07	8.05	-5.98	0.0084
30	2.50 <sup>a</sup>	6.50 <sup>a</sup>	-4.00	0.0076

<sup>a</sup> Center of band.

agreement has been reached that there is not necessarily any basis for a relationship between NMR chemical shifts and aromatic character or resonance stabilization.<sup>5</sup> On the other hand, in recent papers one of the present authors (M.N.) has determined that there is a decrease in the difference in chemical shifts of the inner and outer protons of both dehydro[ $4N + 2$ ]- (I)<sup>6</sup> and  $-[4N]$ annulenes (II)<sup>7</sup> as the ring size is



increased from 14 to 30 carbons. He suggested that this might be an indication of the decreasing aromaticity and antiaromaticity within this series in possible agreement with theoretical predictions.<sup>8</sup>

In order to test this hypothesis quantitatively we decided to examine these chemical shift differences in both the  $4N$  and  $4N + 2$  dehydroannulenes and to compare them with the calculated resonance energies per  $\pi$  electron (REPE) of Hess and Schaad.<sup>8e</sup> The calculated REPEs of the annulenes indicate there should be strong alternation between aromatic and antiaromatic character in the smaller annulenes with this alternation becoming less intense as the annulenes increase in size.<sup>9</sup> The two series of annulenes I and II are a particularly good set of compounds for making this comparison as they are all similar in structure and relatively planar. Furthermore, chemical shift data are available for a number of compounds in both series ( $4N + 2$  and  $4N$ ) which represent the [*n*]annulenes where *n* is 14,<sup>10</sup> 16,<sup>11</sup> 18,<sup>12</sup> 20,<sup>13</sup> 22,<sup>14</sup> 24,<sup>7</sup> 26,<sup>15</sup> and 30.<sup>16</sup>

Since the overall environment of a proton affects its chemical shift we chose to take the difference ( $\tau_o - \tau_i$ ) as the difference between the outer proton *o* in I and II and the inner proton *i* on the adjacent carbon. In most cases the assignments of protons *o* and *i* had been made. However, in several compounds the inner and outer proton absorption bands were not well enough resolved to make individual assignments. In these cases the center of the inner or outer proton absorption bands was used. Where this was done the proton patterns were narrow and any error introduced by this would be quite small relative to  $\tau_o - \tau_i$ .

In Table I are listed the chemical shifts of the inner and outer protons *o* and *i*, their differences, and REPE of the corresponding annulenes. A plot of  $\tau_o - \tau_i$  vs. REPE (Figure 1) shows a definite linear correlation between these two quantities. This is the first example of a correlation between NMR chemical shifts and calculated resonance energies and