

CARBENE-CARBENE REARRANGEMENTS IN THE ACENAPHTHYLCARBENE-PHENALENYLIDENE SYSTEM

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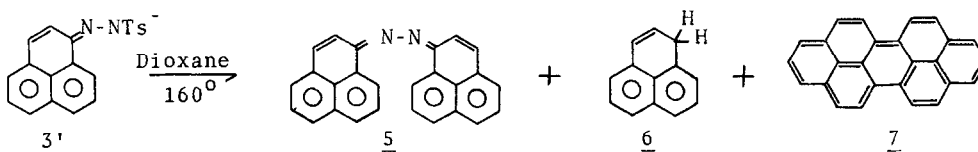
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As a part of a continuing investigation of the interconversion of aryl-carbenes and aromatic carbenes, we have studied phenalenylidene (1) and acenaphthylcarbene (2). Originally the results of this work left much to be desired due to the abnormal properties of phenalenylidene (1) and the small yield of carbene products detected; however, the recent report of carbene 1 and its reactions<sup>1</sup> prompts a report of our results.

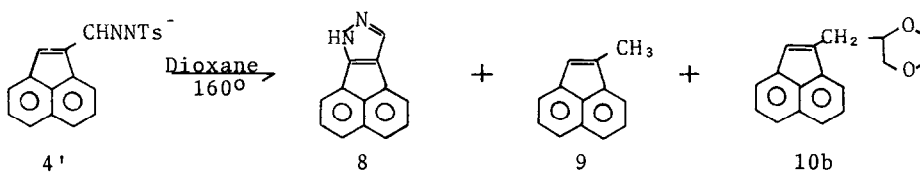
Phenalen-1-one tosylhydrazone<sup>2</sup> (3) was prepared from commercial phenalen-1-one (Aldrich) by the standard method<sup>3</sup> and had properties identical to those reported previously.<sup>1,4</sup> Acenaphthylene-1-carboxaldehyde<sup>2</sup> was synthesized from acenaphthylene by the Vilsmeier-Hack reaction.<sup>5</sup> In our hands this aldehyde was obtained in 24% yield as a solid (mp 55.5-57°) which formed a semicarbazone with mp 241-243° (lit.<sup>5</sup> 240°) and was oxidized to 1,8-naphthalic anhydride in the reported manner.<sup>5</sup> Acenaphthylene-1-carboxaldehyde tosylhydrazone<sup>2</sup> (4) was obtained in the standard way.<sup>3</sup> Tosylhydrazones 3 and 4 were converted to sodium salts 3' and 4' with sodium hydride employing a method similar to that described previously.<sup>3</sup>

Thermolysis of phenalen-1-one tosylhydrazone sodium salt (3') in diglyme or dioxane (sealed tube) at 160° produced phenalen-1-one azine (5) (ir, uv,<sup>4</sup> tlc identical to authentic material) as reported by others;<sup>1,4</sup> however, 5 was

not completely stable to these reaction conditions and its yield was irreproducible. Phenalene<sup>1</sup> (6) (6.9%; uv, nmr,<sup>6</sup> gc, tlc identical to authentic material<sup>7</sup>) was also isolated along with a small quantity of previously undetected peropyrene<sup>8</sup> (Dibenzo[*cd,lm*]perylene, 7) (0.7%; uv-vis,<sup>10</sup> gc, tlc identical with authentic material<sup>11</sup>). Thermolysis of acenaphthylene-1-carbox-

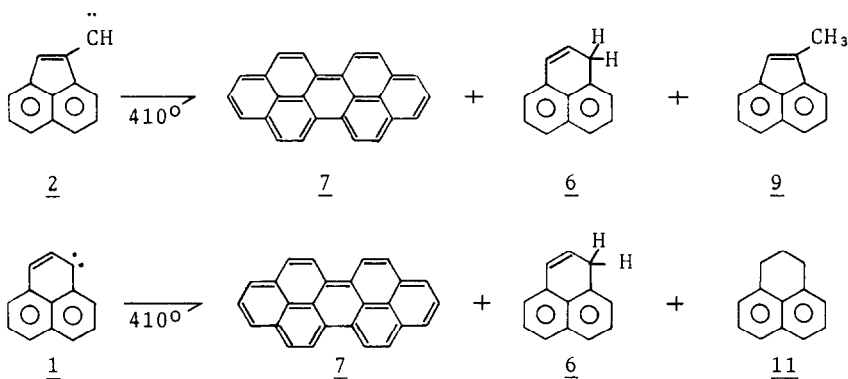


aldehyde tosylhydrazone sodium salt (4') under conditions similar to those employed for generation of phenalenylidene (1) gave about 50% nitrogen evolution and 7*H*-acenaphtho[1,2-*c*]pyrazole (8) (mp 238-241<sup>o</sup>, lit.<sup>12</sup> 239<sup>o</sup>) as the major product. 1-Methylacenaphthylene (9) (7%, identical with authentic material<sup>13</sup> by uv and mass spec.) and compounds tentatively identified (nmr, ir, mass spec.) as diglyme or dioxane insertion products of acenaphthylcarbene (10a, 10a', and 10a''; or 10b) (~3%) were also isolated. No trace of any common product could be detected by gas chromatography of the two reaction mixtures.



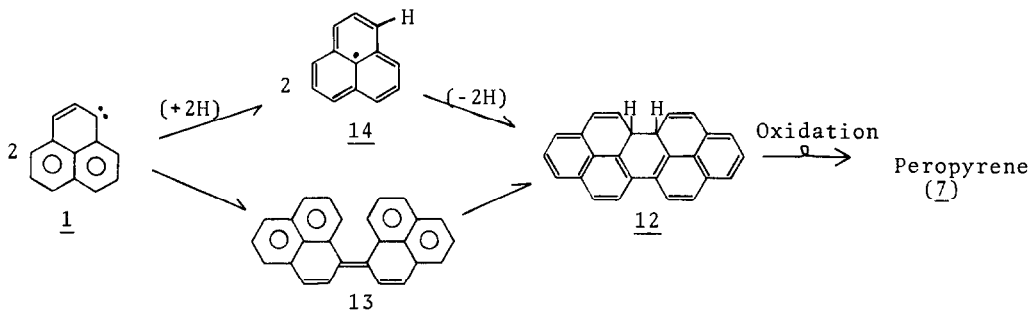
Hot tube pyrolysis of 4' under the conditions employed for isomerization of phenylcarbene to cycloheptatrienylidene<sup>3</sup> successfully effected rearrangement of the arylcarbene 2 to phenalenylidene (1) as evidenced by detection of peropyrene (7) and phenalene (6) in product mixtures. In fact, 6 and 7 were the major volatile products from hot tube pyrolysis of acenaphthylene-1-carboxaldehyde tosylhydrazone sodium salt (4') at 410<sup>o</sup> (5.3% 7<sup>8</sup>, 3.2% 6, 1.8% 9 detected). No acenaphthylcarbene products such as 9 were obtained from hot tube pyrolysis of 3' (limit of detection 0.01% by gc). Hot tube thermolysis of phenalen-1-one tosylhydrazone sodium salt (3') at 410<sup>o</sup> gave peropyrene (7) and phenalene (6) as major volatile products along

with a trace of 2,3-dihydrophenalene (11) identified by preparative gas chromatography followed by uv<sup>7</sup> and mass spec. (3.8% 7<sup>8</sup>, 0.5% 6, 0.05% 11 detected). Isolation of 2,3-dihydrophenalene (11) indicates a strongly reductive environ-

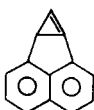


ment in the pyrolysis tube which may possibly be due to the transient presence of dihydroperopyrene (12) (a logical precursor of peropyrene). In addition, gas chromatography of both pyrolysis product mixtures showed products from sodium *p*-toluenesulfinate at various stages of reduction (e.g., thiocresol and tolyl disulfide).

The origin of peropyrene (7) (or its precursor 12) is not clear at this time. It could reasonably originate from either the carbene dimer<sup>3</sup> 13 or the known<sup>14</sup> disproportionation of the phenalenyl radical 14 (a logical precursor of phenalene 6). In either event, it is apparent that acenaphthylcarbene (2)



undergoes carbene-carbene rearrangement to phenalenylidene (1). This carbene-carbene rearrangement is unique in that it is the first example requiring expansion of a five-membered ring. The cyclopropene intermediate or transition state 15 -- implicated by the structure of the rearranged carbene which requires migration of C-2 -- is the most highly strained bicyclic structure yet postulated in arylcarbene-aromatic carbene isomerizations.

15

## References

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