

PREPARATIVE FLASH VACUUM THERMOLYSIS <sup>1</sup>.  
A CONVENIENT PREPARATION OF FULVENALLENE FROM PHTHALIDE

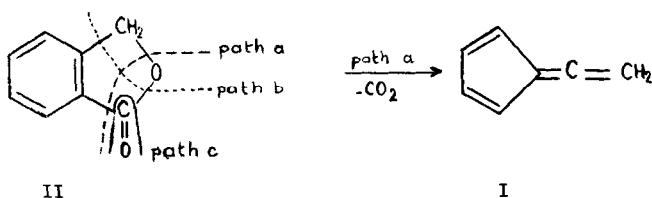
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Fulvenallene (I) has recently been obtained as a product in flash vacuum thermolysis reactions of phenylcarbene<sup>2</sup>, indane-1,2-dione<sup>3</sup>, trans-1,2-diethynylcyclopropane<sup>4</sup>, homophthalic anhydride<sup>5</sup>, indazole<sup>6</sup> and benzocyclobutenone<sup>7</sup> at temperatures between 600 and 900°C. From a preparative point of view these reactions suffer from incomplete conversion of the starting materials and the formation of reactive byproducts such as ethynylcyclopentadiene.

We now report that fulvenallene may be prepared in convenient quantities by flash vacuum thermolysis of phthalide (II). When II is passed at pressures below 0.1 mmHg through an unpacked 10 inch long quartz tube of 0.8 inch in diameter at 700-750°, carbon dioxide is expelled and a bright yellow liquid containing I and benzene (up to 40%) is obtained. The main thermal fragmentation (path a) does not parallel our observation that phthalide undergoes primary degradation in the mass-spectrometer exclusively according to path b, although the formation of benzene might originate from the latter



breakdown. Sequential loss of carbon monoxide leads to benzyne, which ultimately yields benzene, possibly by reaction with the formaldehyde fragment as a hydrogen source <sup>8</sup>. Above

750° benzaldehyde appears as a third thermal product from phthalide <sup>9</sup>. This implies primary degradation via path c with loss of carbon monoxide.

Under our reaction conditions <sup>10</sup> about 5% of phthalide is converted per pass. To obtain appreciable amounts of I the starting material was continuously passed through the hot zone of a recycle apparatus. The separate pieces of this apparatus are connected by balljoints as indicated. 25 g of phthalide (mp. 73°) is placed in flask A (50 ml) and evaporated through the quartz tube B at a rate of 15-20g.h.<sup>-1</sup>. Unreacted phthalide is returned to the flask by means of the condenser C, kept at 75°, while the volatile products fulvenallene (I) and benzene escape to the cold trap D. <sup>11</sup> The fulvenallene content (60-70%) of the thermolysate (3 g. in 6-8 h) is determined from the nmr spectrum, which shows two singlets for I at  $\delta 6.26$  (ring H) and  $\delta 5.13$  (CH<sub>2</sub>) together with a singlet at  $\delta 7.24$  due to the presence of benzene.

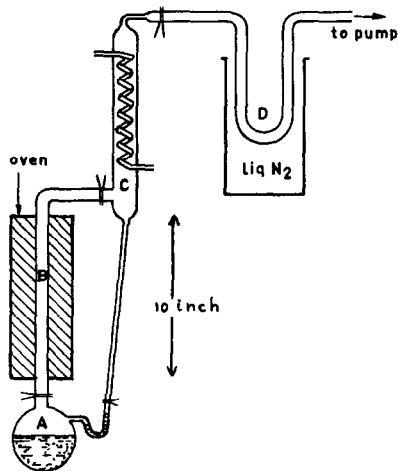
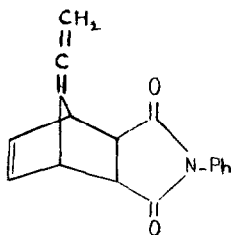


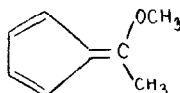
Figure. Thermolysis apparatus

Fulvenallene is a bright yellow liquid with an awful olefinic smell. The thermolysate was directly used to study some reactions of I. At room temperature in contact with air it decomposes to a brittle intractable material. When warmed on a steam bath, exothermic decomposition to a carbonaceous residu occurs suddenly.

With N-phenylmaleimide in ether at room temperature, the previously described <sup>3</sup> Diels-Alder adduct III, mp. 168-169° was obtained as a stable derivative of I. The addition of methanol to I was found to occur rapidly in the presence of a trace of sodium methoxide and furnished 6-methoxy-6-methyl-



III

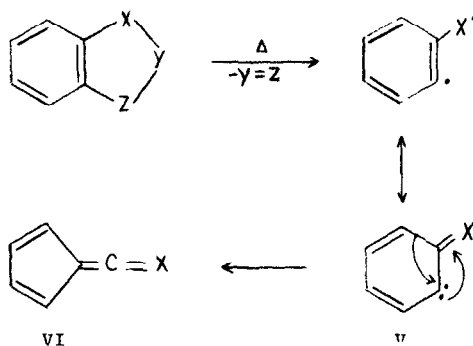


IV

fulvene (IV) in 90% yield. The nmr spectrum of IV shows a multiplet around  $\delta 6.24$  (ring H) and singlets at  $\delta 3.73$  (OCH<sub>3</sub>) and  $\delta 2.12$  (CH<sub>3</sub>). The addition of alcohols to

fulvenallene may become an attractive method for the preparation of 6-alkoxy-6-methyl-fulvenes.

The ring contraction into fulvenallene obviously proceeds through a 1,3-diradical via the carbene species V, ( $X=CH_2$  <sup>12</sup>) and must be considered as an example of a quite general process <sup>15</sup>, represented by the following scheme:



The ultimate reaction is a Wolff-type rearrangement of the cyclohexadienylidene V, invariably leading to the 6-cumulated fulvene system VI, ( $X=O$ : fulvene-6-one <sup>16,17</sup>;  $X=NH$ : 6-iminofulvene, which rearranges into cyanocyclopentadiene <sup>6,18</sup>;  $X=CH_2$ : fulvenallene). In the case of phenylcarbene and phenylnitrene an equilibration via a hydrogen-shift mechanism <sup>19</sup> to the cyclohexadienylidene V can be assumed prior to the ring-contraction <sup>15</sup>.

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9. C.Wentrup, University of Lausanne, Switzerland informed us that he has obtained similar results with phthalide.
10. When the temperature was raised, carbonisation begins and the yield of I decreases while benzaldehyde gradually becomes the main product; at lower temperatures the conversion declines and the relative amount of benzene increases.
11. Homophthalic anhydride <sup>5</sup> or benzocyclobutenone <sup>7</sup> might serve as well as precursors for I in this apparatus.
12. Both this type of intermediate and phenylcarbene <sup>2</sup> show ringcontraction to I around 700°. In contrast, o-, m and p-tolylcarbene give benzocyclobutene and styrene <sup>13</sup>, while 4- and 6-methylphthalide yield methylfulvenallenes <sup>14</sup>.
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