

Flash Vacuum Pyrolysis of 5-Diazodibenzo[*ad*]cycloheptene. Some Insights into Aromatic Carbene- Arylcarbene Rearrangement

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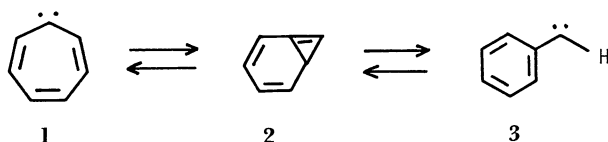
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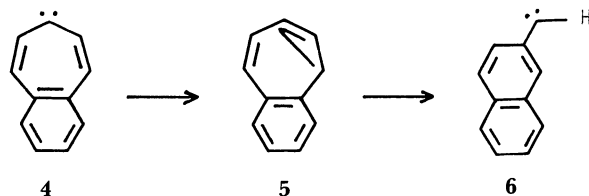
Synopsis. Flash vacuum pyrolysis of the title diazo compound gives 4*H*-cyclopenta[*def*]phenanthrene, which is interpreted as indicating that dibenzo[*ad*]cycloheptatrienylidene (**13**) undergoes the carbene-carbene rearrangement to generate 4-phenanthrylcarbene. The reactivities of **13** are compared with those of other benzoannulated cycloheptatrienylidenes and discussed in terms of the effect of the benzo ring to the activation energy for the rearrangement.

Interconversion of aromatic carbenes (e.g., cycloheptatrienylidene, **1**) and arylcarbenes (e.g., phenylcarbene, **3**) had been attracting continued attention since its discovery not only from the synthetic viewpoint but also from the standpoint of mechanism.^{1,2)} The rearrangement has permitted the straightforward synthesis of many useful organic compounds which are otherwise not readily obtained, and the mechanism of rearrangement still continues to plague organic chemists.

Although phenylcarbene and cycloheptatrienylidene rapidly interconvert in the gas phase at moderate to high temperatures, this is not a typical reaction of these carbenes in solution. The mechanism involves initial closure of a singlet carbene onto the π system of the aromatic ring to give a cyclopropene intermediate

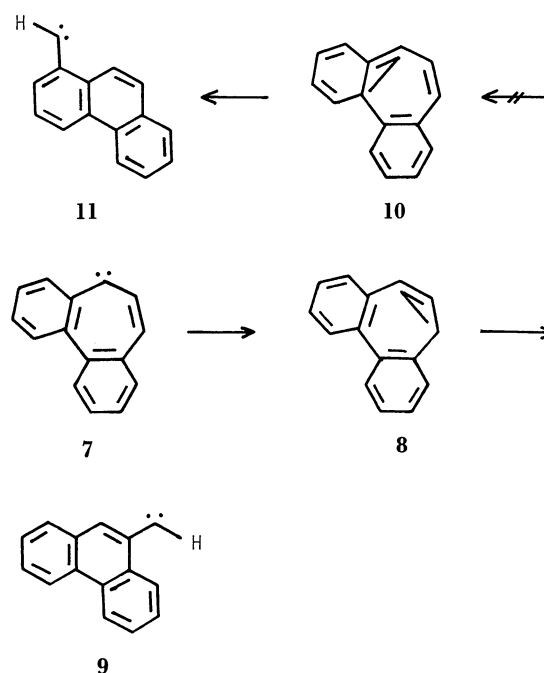


(**2**) that then opens to the new carbene (**3**). It is apparent that the interconversion of aromatic and arylcarbenes should be favored by perturbations that reduce the activation energy for the rearrangement presumably by accelerating closure to **2**. This is supported by the findings³⁾ that 7*H*-benzocyclohepten-



7-ylidene (**4**) gives the products expected from the rearranged carbene (**6**) even in solution at -30°C , suggesting that the benzannulation reduces the loss of aromaticity when the ring closes to the nonaromatic tricyclo[5.4.0.0^{4,6}]undeca-2,4,7(1),8,10-pentane **5**. More interestingly, dibenzo[*ac*]cyclohepten-5-ylidene (**7**) also

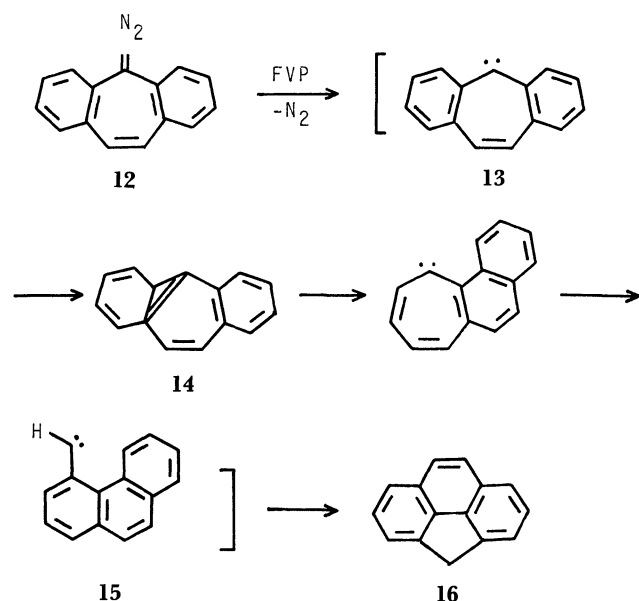
rearranges in solution but only products from 9-phenanthrylcarbene (**9**) are formed and no trace of those expected from 1-phenanthrylcarbene (**11**) are



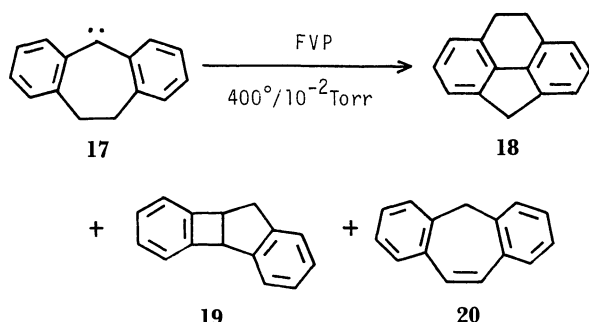
detected.⁴⁾ This is reasonably understood as indicating that the ring closure onto the 2, 3 π system forming **10** and then **11** will result in the destruction of aromaticity of one of the benzocyclic systems. In order to ascertain the mechanism of the rearrangement, we examined the reactivities of dibenzo[*ad*]cyclohepten-5-ylidene (**13**), whose rearrangement will be forced to cause the loss of aromaticity of either of the benzene rings and therefore is expected to be highly unfavorable.

Results and Discussion

Flash vacuum pyrolysis ($450^\circ\text{C}/10^{-5}$ Torr, 1 Torr = 133.322 Pa) of 5-diazodibenzo[*ad*]cycloheptene (**12**) produced 4*H*-cyclopenta[*def*]phenanthrene (**16**) as a main volatile product in 17% yield along with dibenzo[*ad*]cyclohepten-5-one and dibenzo[*ad*]cycloheptene. The formation of **16** is interpreted as indicating that 4-phenanthrylcarbene (**15**) must be generated presumably by the rearrangement of the carbene (**13**) through tetracyclo intermediate (**14**), since it has been reported⁵⁾ that 9-phenanthrylcarbene (**9**) generated by FVP ($590^\circ\text{C}/0.1$ Torr) also produces **16**



via **15** generated through the repeated carbene rearrangements. The reaction is very similar to that of 10,11-dihydrodibenzo[*ad*]cyclohepten-5-ylidene (**17**), a dihydro analogue of **13**. Thus **17** generated in the gas phase produces 8,9-dihydro-4*H*-cyclopenta[*def*]phenanthrene (**18**) along with two $C_{15}H_{12}$ hydrocarbons (**19**, **20**).⁵⁾ The formation of **18** is explicable in terms of the



rearrangement forming 1-(9,10-dihydrophenanthryl)carbene, while **19** and **20** can be formed by the transannular insertion reaction in **17**. Apparently, transannular interaction is not feasible in **13** due to the increased strain.

The reactions of **13** in fluid solution or in rigid matrix have been investigated^{6,7)} to show that it is trapped by trapping reagents before it undergoes the rearrangement. For example, photolysis of **12** in the presence of alkenes at room temperature results in the formation of spirocyclopropanes by the addition of **13** to the alkenes.^{6a)} This is in a marked contrast with that observed⁴⁾ for the isomeric dibenzocycloheptenylienes (i.e., **7**) which undergoes the rearrangement leading to arylcarbenes (i.e., **9**) in solution even at -60°C . The contrasting difference in the behavior between these two isomeric dibenzannulated aromatic carbenes (i.e., **7** and **13**) can be ascribed to the difference in the activation energy for the rearrangement as advanced above.

The present results coupled with those reported by

Table 1. Effect of Benzannulation on Carbene-Carbene Rearrangement

Carbenes	Temp/ $^\circ\text{C}^a$	Conditions	Ref.
1	300	Δ at 10^{-4} Torr	This work
4	-30	$h\nu$ in PhH	3)
7	-60	$h\nu$ in THF	4)
13	250	Δ at 10^{-4} Torr	This work

a) The lowest temperature required for rearrangement.

the others suggest that, although the rearrangement of dibenzo[*ad*]cycloheptenyliene is not observed at low temperature obviously due to the introduction of benzo ring in an improper position, it does undergo the rearrangement at much higher temperature in spite of the destruction of aromaticity of one of the benzocyclic systems during the rearrangement. It is very interesting then to know to what extent the rearrangement will be disfavored by these two benzocyclic groups. The simplest way to estimate this is to determine roughly the lowest temperature at which the rearrangement products form. Thus, we decomposed **12** at various temperatures from 450 to 150°C at 50°C intervals in the gas phase and estimated the lowest temperature required for the rearrangement to be 250°C . For comparison purposes, similar experiments were done with cycloheptatrienyliene (**1**) which produces stilbenes and heptafulvalene, the former being formed as a result of cycloheptatrienyliene-phenylcarbene rearrangement. Stilbenes were not detected when the pyrolysis was carried out at $<250^\circ\text{C}$.

In Table 1, we summarize the lowest temperature required for carbene-carbene rearrangement for a series of isomeric mono-(**4**) and dibenzocycloheptenyliene (**7**, and **13**) as well as the parent carbene (**1**). The results suggest that, although the rearrangement in **13** is highly unfavorable compared to that in **4** and **7**, it is not unduly disfavored compared with that of **1**. Presumably, carbenes generated in the gas phase are forced to undergo multiple rearrangements if possible until they are quenched by a proximate reactive center leading to stable final products. It is very interesting to note here in this connection that tolylmethylenes generated photolytically in the vapor phase produce benzocyclobutene and styrene as a result of rearrangement even at 30°C .⁸⁾

Experimental

Instrumentation. The IR spectra were determined with a JASCO A-100 spectrometer, while the ^1H NMR spectra were measured on a JEOL JNM-MH-100 and JNM-GX-400 spectrometer with Me_4Si as the internal reference. The mass spectra were recorded on a Shimadzu QP-1000 mass spectrometer. The GC analyses were performed on a Yanagimoto instrument, Model G-80. The GC column A was prepared from 5% SE-30 on Diasolid L (5.0 mm $\times$ 2.0 m); column B consisted of 5% PEG-20M on Diasolid L (5.5 mm $\times$ 1.0 m).

Materials. The diazo compound (**12**) was prepared according to the methods described.⁶⁾

Flash Vacuum Pyrolysis. The apparatus used for the FVP consisted of a quartz tube (30 mm i.d. $\times$ 35 cm long)

maintained at the desired temperature by resistance wire. The tube was fitted with a loose plug of quartz wool 10 cm below the top of the heated zone. At the top of the tube, provision was made for the introduction of solid reactants via a solid addition tube. The lower end of the tube was fitted with consecutive U-tubes which were immersed in liquid nitrogen. The pyrolysis tube was bent near the bottom such that the pyrolysis zone was angled about 35° from the vertical.

The carbene precursor was introduced into the hot tube either by subliming at 10^{-4} Torr or by adding the precursor coated on inert support such as powdered quartz. Solvent-assisted sublimation recently advanced by Fowler⁹ was also used especially for non-volatile precursors. Products were collected in the U-tubes at -196°C and analysed by MS and NMR.

FVP of 12. In a typical experiment, 50 mg of **12** was dissolved in pentane, quartz powder (ca. 1 ml) was added and the pentane was removed under reduced pressure leaving the diazoalkene coated on the support. The sample was continuously added from the top of the tube at an operating pressure of 10^{-5} Torr. The volatile products were collected in a trap cooled with liquid nitrogen and chromatographed on the preparative TLC over Merck Kieselgel 60 PF₂₅₄ eluting with pet. ether to give a white solid (mp 114–115°C), with NMR and MS spectra identical with those of an authentic sample¹⁰ of 4*H*-cyclopenta[*def*]phenanthrene (**16**).

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