Pressure-dependent Formation of Bicyclo[3,2,0]hepta-1,4,6-triene, Fulvenallene, and Ethynylcyclopentadiene in the Pyrolysis of 1,2-Diethynylcyclopropane

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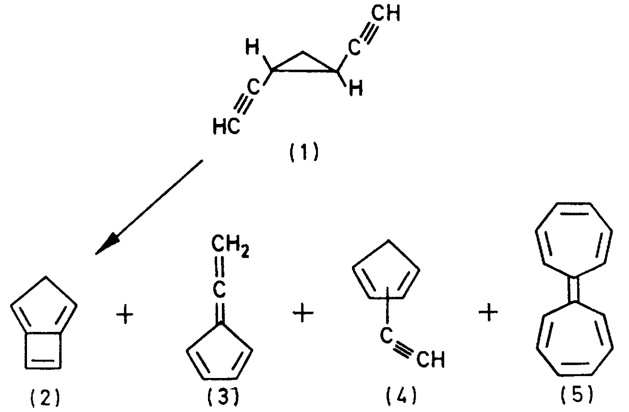
Summary Thermolysis of *trans*-1,2-diethynylcyclopropane at pressures near 100 Torr produces only bicyclo[3,2,0]-hepta-1,4,6-triene; as the pressure is lowered, however, fulvenallene and ethynylcyclopentadiene became major components of the primary product distribution, indicating that the bicycloheptatriene is generated in a vibrationally excited form which, in time, can rearrange to the additional products observed at low pressure.

We report a study of the thermolysis of *trans*-1,2-diethynylcyclopropane (**1**) and its isomer, bicyclo[3,2,0]hepta-1,4,6-triene (**2**). Our observations provide an interesting and rare example of product control by pressure variation of a unimolecular rearrangement process,[1] an unusual rearrangement of (**2**) to fulvenallene[2] (**3**), and two ethynylcyclopentadienes[2] (**4**), and additional information concerning the nature of the C_7H_6 energy surface.[3,4]

The cyclopropane (**1**) was pyrolysed in (a) a low-pressure vacuum-transfer flow apparatus, (b) a 200 ml static reactor, or (c) the flash vacuum pyrolysis (f.v.p.) system described earlier.[4] Formation of (**2**)—(**5**) was observed in relative amounts which depended markedly on the reaction conditions (Tables 1 and 2).



The data in Table 1 show a strong pressure effect on the product distribution where (**3**) and (**4**) increased at the expense of (**2**) as the pressure was lowered. In the flow system, the effective pressure must be higher when a larger quantity of material is transferred through the

Table 1. *Vacuum flow and static pyrolyses of* trans-1,2-*diethynylcyclopropane under varying conditions*

Reactor	Sample pyrolysed[d,f]	P_i(Torr)[g]	T(°C)	Products (%) (2)	(3)	(4)	(5)
Flow[a]	1 µl (1), 10 µl hexane	0·02	460	64·5	24·5	11·0	0[c]
Flow[a]	1 µl (1), 200 µl hexane	0·02	460	86·0	10·2	3·8	0
Flow[a]	60 µl (1), 2 ml hexane	0·02	460	84·0	11·0	4·0	1[h]
Flow[b]	1 µl (1), 200 µl hexane	0·02	460	88·7	8·3	3·0	0
Static[e]	pure (1)	0·10	247	70·5	19·9	9·6	0
Static	pure (1)	100	247	100	—	—	—

[a] Pyrolysis carried out by vacuum transfer through a hot tube (hot zone volume *ca.* 20 ml, contact time *ca.* 0·5 s) from a room temperature trap to one held at 77 K. [b] Pyrolysis carried out under same conditions as (a), but the tube was packed with quartz tubes (surface-to-volume increased by factor of 4·5). [c] Less than 0·1% detectable. [d] All flow pyrolyses run with > 90% conversion of (**1**) into products. [e] 25% conversion of (**1**) into products. [f] All pyrolyses were carried out under conditions where products are thermally stable. [g] Initial system pressure before vacuum transfer of sample through hot tube. [h] Heptafulvalene (**5**) is reproducibly formed in low yield when (**1**) is pyrolysed at relatively high partial pressures.

Table 2. *Flash vacuum pyrolysis of* trans-1,2-*diethynylcyclopropane and bicyclo*[3,2,0]*hept*-1,4,6-*triene*

Isomer	Oven	$\bar{p}$(torr)[b]	T(°C)	Products (%)[c] (1)	(2)	(3)	(4)
(1)	5 in, unpacked	0·07	500	90	≤0·1	7·5	2·5
(1)	5 in, unpacked	0·10	900	—	—	42	58
(1)	5 in, packed[a]	0·25	500	1·5	50	31	16·5
(2)	5 in, unpacked	0·07	600	—	100	—	—
(2)	5 in, unpacked	0·10	900	—	—	65	35

[a] Oven packed with quartz fibres. [b] Average oven pressure; pressure at which reaction is taking place is considerably lower. [c] Product distribution determined by g.l.c. Efficiencies were ≥ 90%.

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pyrolysis tube. The absence of surface effects was demonstrated by showing that the product distribution remained unchanged when the flow system was packed with quartz tubes. These data imply the initial conversion of (**1**) into vibrationally excited (**2**) which can rearrange to (**3**) and (**4**), in competition with collisional deactivation, at sufficiently low pressures.[6]‡ We estimate[5] that the reaction (**1**) → (**2**) is $\geqslant 38$ kcal mol^{-1} exothermic and since the activation energy for this reaction is 43·0 kcal mol^{-1}, the triene (**2**) must be formed at least 80 kcal mol^{-1} above its ground vibrational state. This is certainly sufficient chemical activation[6] to produce rearrangement of (**2**) into (**3**) and (**4**).

The f.v.p. system (*cf.* Table 2) is characterized by shorter contact times (about 100 gas–wall collisions) and lower effective pressures compared to the flow system (a). Here the pressure was increased by packing the pyrolysis tube with quartz fibre; this also decreased the flow rate and increased the number of gas–surface collisions. The consequence of increasing the effective pressure in this way led to a dramatic change in the relative amounts of (**2**); at 500 °C the yield of (**2**) could be varied from $\leqslant 0{\cdot}1$ to 50 % (Table 2). This is undoubtedly the same type of pressure effect observed in the experiments shown in Table 1, although further experiments will be required to reconcile other features of the data in Tables 1 and 2.

Furthermore, labelling experiments are being carried out to define the mechanism of conversion of (**2**) into (**3**) and (**4**), as well as the source of heptafulvene (**5**). At present, we believe that the latter may not be formed *via* cycloheptatrienylidene,[1a,b] but rather through fragmentation of a dimer generated from a reactive bicycloheptatriene isomer[7] of (2).

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‡ For some other examples of molecules which undergo further reaction when produced in "chemically activated" (vibrationally excited) states in exothermic reactions, see ref. 5.

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