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FACILE THERMAL CYCLIZATION OF 6-VINYLFULVENE TO DIHYDROPENTALENE

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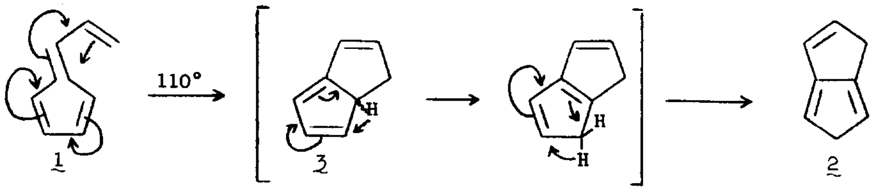
Current interest in cycloadditions to fulvenes[1] and homofulvenes[2] where these are used as 6 electron components, prompts us to report the intramolecular analogue of the above cycloadditions, namely the thermally induced cyclization of 6-vinylfulvene, 1.[3,4]

Vapor phase pyrolysis of 10mg of 1 in a carefully neutralized 250ml Pyrex tube at 110° for eight hours gave a light yellow liquid in good yield whose nmr spectrum (HR 220) was that of the dihydropentalene, 2, which was first prepared by Katz.[5a,b] Other, less intense, resonance lines were present but have not yet been characterized. Pyrolysis of 10mg of 1 in a 50ml tube at 105° for four hours also gave 2, albeit in poor yield as evidenced by the large quantity of clear, non-volatile material on the walls of the pyrolysis tube. The most reasonable pathway for formation of 2 is via cyclization of 1 to the dihydropentalene, 3, which then undergoes the facile 1,5-hydrogen shifts characteristic of cyclopentadienes[6] to 2 which now appears to be one of the more stable of the dihydropentalenes.



Since the transition state for conversion of 1 to 3 is "pentalenoid," the stereochemistry of the cyclization should provide evidence on whether pentalene is aromatic, non-aromatic, or anti-aromatic.[7] Pentalene is a non-alternant hydrocarbon, and therefore molecular orbital theory, even sophisticated approximations, may not be able to make correct predictions with regard to its stability. The cyclization above can also be construed to be that of a 1,3,5,7-octatetraene which would be expected to proceed via conrotatory motions.[8] However, the non-alternant arrangement of interacting p-orbitals in the transition state for cyclization of 1 also renders this approximation suspect.

Unfortunately, an attempt to obtain experimental data on the stereochemistry of the cyclization failed, but did provide insight into the ease with which dihydropentalenes are interconverted. Thus, 6-(trans-1-propenyl)fulvene, 4,[9] was heated at 65° for 30 hours (20mg in a 5 l bulb). The pmr spectrum of the reaction mixture indicated the presence of roughly 37% of starting material and a very complicated mixture of products. In an effort to isolate products, flow pyrolyses of 4 were conducted in the injector block of a gas chromatograph using a 1/4" x 8" di-n-butyltetrachlorophthalate (DBTCP) column for separation. In this way four major components, 5-8, isomeric with 4 (M/e = 118) were obtained. The distribution of products as a function of percent conversion and their nmr spectra are given in Table 1.

TABLE 1

Distribution of Products[a] from Flow Pyrolysis[b] of 4

Injector Temp.	%5	%6	%7	%4	%8
137	--	--	--	100	--
180	--	--	--	100	--
213	3.1	1.5	2.1	93.3	--
250	3.2	10.0	8.4	63.0	15.5
340	4.8	32.7	23.7	4.3	35.0
400	4.1	31.0	23.2	trace	42.0

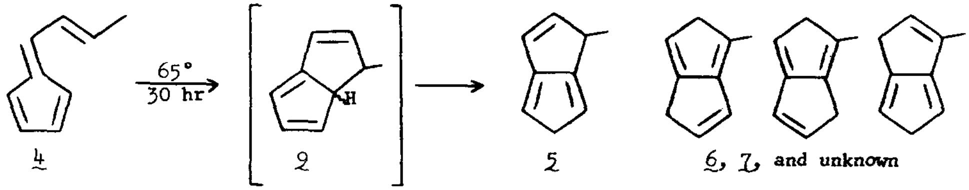
5	6	7	8
δ1.20, 3H(d,J=7Hz)	δ1.89, 3H(q,J=2Hz)	δ2.0, 3H(S)	δ2.18, 3H(S)
δ3.23, 3H(S)[d]	δ2.94, 2H(m)[e]	δ2.98, 2H(s)[e]	δ2.61, 2H(m)[g]
δ5.69, 1H(S)[d]	δ3.21, 2H(s)[d]	δ3.10, 2H(s)[d]	δ2.95, 2H(m)[g]
δ5.79, 1H(S)[d]	δ5.65, 1H(s)[d]	δ5.60, 1H(s)[d]	δ5.70, 1H(s)[d]
δ6.26, 2H(m)[f]	δ5.76, 1H(s)[d]	δ6.22, 1H(m)[f]	δ5.99, 1H(d,J=5Hz)
	δ5.97, 1H(m)[e]	δ6.29, 1H(m)[f]	δ6.60, 1H(d,J=5Hz)

(a) Listed in order of retention times on a 1/4" x 8" DBTCP column
(b) The helium flow rate was 150 ml/min and the sample size was 3μl in each run.
(c) Spectra were run in carbon tetrachloride with TMS reference at 220 MHZ. Chemical shifts are in ppm downfield from TMS.
(d) Width at half-height ($W_{h/2}$) = 4.5Hz
(e) $W_{h/2}$ = 7Hz
(f) $W_{h/2}$ = 10Hz
(g) $W_{h/2}$ = 12Hz

The nmr spectrum of the pyrolysate from the static reaction at 63% conversion revealed the presence of 5-8 with the addition of extra peaks. Thus, the relative amounts of 4, 5, 6, 7, and 8 were 37%, trace, 33%, 15%, trace respectively, plus 15% of an unknown with an allylic methyl group.

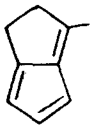
That 5 could not be detected in the relatively low conversion static reaction is reasonable in that it was but a minor production in the flow pyrolysis (Table 1). However, the absence of 8 in the 63% conversion static reaction suggests that this material is formed catalytically in the vpc system, and the presence of extra peaks in the static reaction suggests that these components either had exceedingly long retention times or were destroyed on the vpc column.

Necessary to isolate for purposes of determining the stereochemistry of the cyclization was the dihydropentalene, 9. However, the pmr spectra of 5-8 were not consistent with this structure. Indeed, 5, 6, and 7 and the unknown in the static pyrolysis appear to be dihydropentalenes with the Katz arrangement of pi bonds.[5a]



4 9 5 6, 7, and unknown

The compound 8 remains an enigma. It may be the remaining dihydropentalene discussed above, but the broad allylic methylene group resonance lines are suggestive of vicinal coupling and it emerged from the chromatograph as a brilliant yellow liquid. Thus, we suggest that it is a dihydropentalene with the fulvene arrangement of double bonds, and the low field methyl further suggests the following structure although others are not excluded.



8

As indicated above, 8 is produced only in the gc. pyrolysis and it is worthwhile mentioning that it cannot be formed from 9 by 1,5-hydrogen shifts. Only a symmetry forbidden, suprafacial 1,3- or 1,7-hydrogen shift,[8] or a catalyzed (acid, base, metal) reaction would allow production of 8 from 9.

Efforts are continuing to determine the stereochemistry of the cyclization.

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