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MECHANISM OF THE THERMAL CONVERSION OF TETRACYCLO[3.3.0.0^{2,4}.0^{3,6}]OCT-7-ENE INTO DIHYDROPENTALENES

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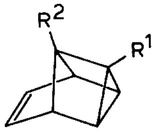
Abstract—One of a number of possible mechanisms has been established for the title reaction.

Compounds with formula $(CH)_n$ have generated much interest.[1] Their interconversions can be considered as archetypal since reaction paths are determined solely by the way in which a certain number of CH groups is interconnected. As such they have evolved into important test substrates for the rules of molecular orbital theory and the methods of thermochemical analysis. In this paper we give a full account of our work on the thermal rearrangement of tetracyclo[3.3.0.0^{2,4}.0^{3,6}]oct - 7 - ene (**1a**, TCO) whose synthesis was reported by us in 1977 and which has remained the youngest valence isomer of the $(CH)_8$ family, since then.[2]



1

a: $R^1 = R^2 = H$
b: $R^1 = D$; $R^2 = H$
c: $R^1 = H$; $R^2 = CH_3$
d: $R^1 = CH_3$; $R^2 = H$
e: $R^1 = R^2 = CH_3$

RESULTS

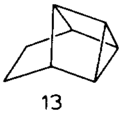
Products. Although among known $(CH)_8$ valence isomers **1a** is second in strain only to cubane, and although its double bond may be considered a "weak spot" apt to induce thermal rearrangement, it proved stable in benzene solution for several hours at 130°. At higher temperatures these solutions afforded mainly polymer. Therefore we turned to thermolysis in a flow system (carrier gas: N_2; 2 Torr; reaction time: 1-2 sec).[4] After thermolysis at temperatures of 200° and above a reactive mixture was found in the cold trap, which rapidly polymerized and showed isomerization upon glc. Comparison of the ^1H NMR spectrum of the crude product mixture with the one reported[5] for the dihydropentalene (DHP) **2** showed that **2** was very likely to constitute the major component, whereas possible products like semibullvalene **3** (SBV) and cyclooctatetraene **4** (COT) were absent within the limits of detection of the NMR technique. When the thermolysis mixture was hydrogenated catalytically *cis*-bicyclo[3.3.0]octane **5** was obtained as the only product in 40% yield. The identity of **5** was confirmed by comparison of its spectral data with those of an authentic sample.

Additional insight into the nature of the products was obtained by reacting them in the cold trap with hexafluorobut-2-yne (HFB), a powerful dienophile.[6] After preparative glc four products were found in 75–85% yield. Mass spectrometry showed the presence of a C_8H_8, two mono-adducts, C_8H_8-HFB, and a di-adduct, C_8H_8-$(HFB)_2$. The C_8H_8 was identified as the fulvene **6** by comparison of its spectral data with those of an authentic sample.[7] The structures of the HFB-adducts were derived from their ^1H NMR and UV spectra as being **7**, **8** and **9**. In the case of **9** distinction between **9a** and **9b** could not be achieved by spectral analysis; however, models reveal that more steric hindrance is incurred in the transition state of the second Diels-Alder reaction leading to **9b**. We therefore prefer to assign structure **9a** to the di-adduct.

Adducts **7**, **8** and **9** are derived from the dihydropentalenes **10**, **11** and **2**, respectively, by Diels–Alder reaction with HFB. In some experiments the formation of small quantities of **12**, the Diels-Alder adduct of **6** with HFB, was also observed. Under similar conditions authentic **2** reacted with HFB to give **9** as the only product. The cyclopentadiene moieties present in **2**, **6**, **10** and **11** account for the polymerization and isomerization (by rapid 1,5 hydrogen shifts)[8] observed when no HFB is present in the cold trap. At temperatures of 590° and above the thermolysis of **1a** also afforded aromatic products (benzene, toluene and styrene). A diagram showing the temperature dependence of the composition of the product mixture is given in Fig. 1.

Thermolysis of the major product **2** followed by HFB-trapping yielded the same mixture of **6**, **7**, **8** and **9** as obtained from **1a**. At higher temperatures (≥600°) pyrolysis of **2** also gave rise to the formation of the aromatic products found in the reaction of **1a**. The formation of **6** and, at higher temperatures, of aromatic products from **2** has precedence.[9]

In order to study the influence of the double bond in **1a** tetracyclo[3.3.0.0^{2,4}.0^{3,6}]octane **13** was subjected to flow



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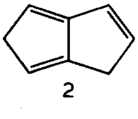

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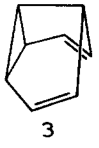

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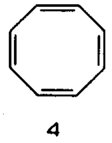

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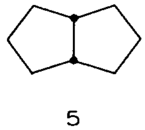

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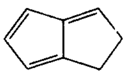

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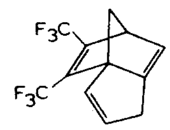

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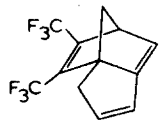

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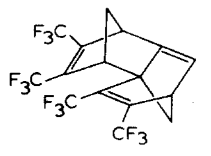
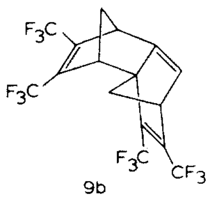
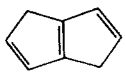


9a



9b



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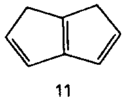

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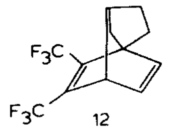

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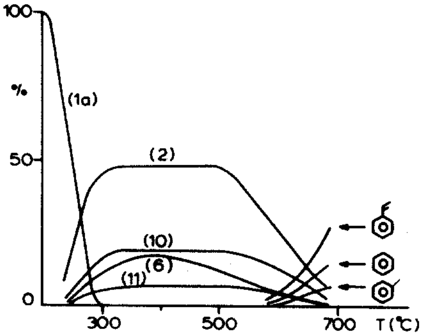


Fig. 1. Composition (%) of the mixtures obtained from the thermolysis of **1a** at various temperatures.

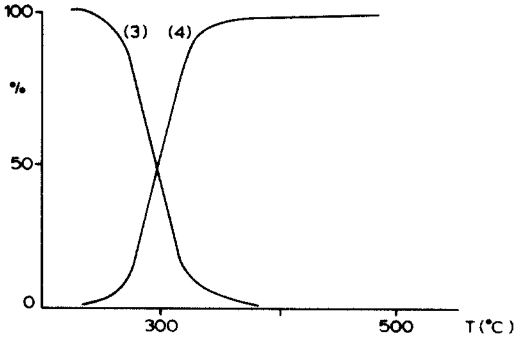
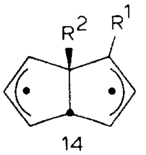


Fig. 2. Composition (%) of the mixtures obtained from the thermolysis of **3** at various temperatures.

pyrolysis. This compound turned out to be rather stable, and was converted into products only above 400° giving a low yield (*ca.* 45%) of ten products: benzene, toluene, *cis* - bicyclo[3.3.0]octa - 2,6 - diene, *cis* - bicyclo[3.3.0]octa - 2,7 - diene, ethylbenzene, styrene, 1 - vinylcyclohexa - 1,3 - diene and three unidentified compounds with compositions C_6H_6, C_6H_8 and C_8H_{10}, respectively, C_6H_6 most likely being fulvene. Identifications were achieved by comparison of spectral data and glc retention times with those of authentic samples. Vinylcyclohexadiene constituted the major product between 490 and 540° (10–15%), whereas the aromatic compounds dominated above these temperatures. For details see experimental section.

Thermolyses of semibullvalene and cyclooctatetraene. In view of a possible role of the *cis* - bicyclo[3.3.0]octa - 2,6 - diene - 4,8 - diyl **14a** in the rearrangement of **1a** to **2**, **6**, **10** and **11** (*vide infra*), and as this diradical had been postulated as an intermediate in the thermal conversions of tricyclo[3.3.0.0^{2,6}]octa - 3,7 diene to SBV (**3**),[10] of SBV (**3**) to COT (**4**),[11] and of COT (**4**) to, *inter alia*, **2**,[12] the flow thermolysis of **3** and **4** was studied under our conditions.



14

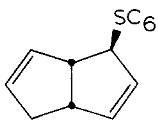
a: $R^1 = R^2 = H$
b: $R^1 = H$; $R^2 = CH_3$
c: $R^1 = CH_3$; $R^2 = H$

SBV (**3**), prepared by lithium p,p'di-*t*-butylbiphenyl reduction[13] of 2(4)-chloro-SBV,[14] showed the exclusive formation of COT (**4**) in the temperature range studied (200–500°) in accordance with the literature (Fig. 2). Note that **3** is recovered for *ca.* 85% at 270°, at which temperature **1a** is converted into DHP's (*ca.* 80%).

As shown in Fig. 2, COT (**4**) is stable in our flow system up to *ca.* 490°. At higher temperatures normal work-up afforded **2** and **6** in addition to the expected aromatic products. The formation of **6** from **4** or **2** and the origin of the aromatic products is being discussed in Ref. 9. When the reaction was carried out under the HFB trapping conditions the ratio in which **6**, **7**, **8** and **9** were obtained indicated that the same mixture of DHP's as arising from **1a** had been formed.

In order to study the possible role of chemical activation the thermolyses of **1a**, **3** and **4** were also studied in the liquid phase. Samples of **1a**, **3** and **4**, respectively, dissolved in benzene (0.1 M) were rapidly heated in sealed ampoules to 270° and the concentration of the respective hydrocarbons monitored as a function of time. At times after which **3** and **4** were recovered almost quantitatively **1a** was decomposed to an extent of more than 50% with no monomeric products detectable (in particular no **3** and **4** were found). In order to eliminate the possibility that all **3** and/or **4**, after being formed from **1a**, had been consumed by polymerization, a mixture of **1a** and **3** was heated in benzene. Under conditions where **1a** was consumed for 58%, 68% of a *ca.* 9:1 mixture of **3** and **4** was recovered, showing that polymerization had occurred but only to a minor extent. A worst case analysis based on these observations indicates that the formation of **3** and/or **4** from **1a** constitutes only a minor process (< 10%) but probably is absent at all during solution thermolysis of **1a**, where chemical activation is very unlikely to influence product formation.[15]

Attempts to trap the postulated diradical **14a** in the solution thermolysis of **3** to **4** with elemental sulphur[16] or benzenethiol[17] failed as reaction with sulphur led to intractable tar and benzenethiol added to **3** yielding at least three products, the main product being **15**.[18]



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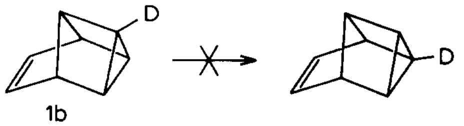
Labelling experiments. Other information with regard to the mechanism of formation of **2**, **6**, **10** and **11** from **1a** was hoped to be gained from labelling studies. The rapid 1,5 hydrogen shifts in the products exclude deuterium as a tracer of the fates of hydrogen atoms on rearrangement and also render equal various sets of carbon atoms in the DHP's. However, it was found that TCO-4-*d* (**1b**)[19] recovered after thermolysis at 270° had not undergone scrambling of deuterium (e.g. from position 4 to positions 2 and 3, see eqn 1).

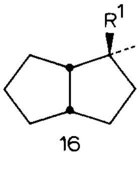


(1)

1b

Since the specific introduction of two or more ^{13}C labels in **1a** is an impossible synthetic task yet, we settled on methyl substitution. The syntheses of 5-methyl-TCO (**1c**), 4-methyl-TCO (**1d**) and 4,5-dimethyl-TCO (**1e**) are described elsewhere.[19] As HFB trapping of the thermolysis products of these compounds might give rise to host of adducts, the thermolysis mixtures of **1c** and **1d** were catalytically hydrogenated at temperatures below − 5° directly after formation.

Thermolysis of **1c** at 310° and subsequent hydrogenation of the products afforded only a very low yield of monomeric products (14%) in addition to a nonvolatile residue accounting for 60% of the starting material. The monomeric products consisted of 7,7-dimethylnorbornane (3%), known to be the hydrogenation product of **1c**,[19] *endo* - 2 - methyl - *cis* - bicyclo[3.3.0]octane (**16a**, 8%), *exo* - 2 - methyl - *cis* - bicyclo[3.3.0]octane (**16b**, < 1%), and *endo* - 3 - methyl - *cis* - bicyclo[3.3.0]octane (**17**, 3%). *Exo* - 3 - methyl - *cis* - bicyclo[3.3.0]octane and 1 - methyl - *cis* - bicyclo[3.3.0]octane **18** were not detected. The identities of **16a**, **16b** and **17** were established by comparison of their spectral data with those of authentic samples.



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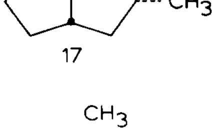
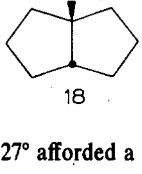


17

a: $R^1 = H; R^2 = CH_3$
b: $R^1 = CH_3; R^2 = H$



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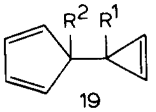
Analogous reaction of **1d** at 327° afforded a high yield (71%) of the same products, **16a** (58%), **16b** (5%) and **17** (8%) with no other products detectable. The relative yields of **16a** + **16b** and **17** are shown in Table 1.

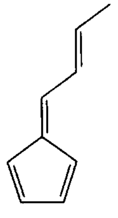


19

a: $R^1 = R^2 = H$
b: $R^1 = H; R^2 = CH_3$
c: $R^1 = CH_3; R^2 = H$
d: $R^1 = R^2 = CH_3$

The thermolysis of **1e** was aimed at the eventual isolation of a dihydrocalicene (i.e. **19d**) if such species were intermediates in the thermolyses of TCO's. However, direct glc work-up and NMR analysis of the thermolysis (310°) mixture of **1e** afforded 16% starting material and 65% of a mixture of at least ten components, none of which showed c_s symmetry as required for **19d**. These products are probably all dimethyl-DHP's and were not investigated further.

Any mechanism for the thermolysis of **1c** and **1d** has to account for the methyl shifts observed. Sigmatropic shifts of alkyl groups are known to occur in cyclopentadienes,[8] whereas in our dihydropentalene cases also an electrocyclic ring opening-ring closure mechanism as outlined in Ref. 20 may be operative. In order to check on these possibilities 6-(*trans*-propenyl)fulvene **20** was synthesized.[21] This compound is known to give 2-methyl-DHP's upon thermolysis.[20] We subjected **20** to flow thermolysis at various temperatures and hydrogenated the thermolysis mixtures for analysis. At all temperatures studied a moderate yield of methyl - *cis* - bicyclo[3.3.0]octanes was obtained, consisting of **16a**, **16b** and **17** as the only components. The results are given in Table 1. It is clear from Table 1 that methyl shifts in 2-methyl-DHP's require temperatures that lie above the ones used for the thermolyses of **1c**, **1d** and **1e**. The methyl migrations observed in the latter therefore have to occur *prior* to the formation of the 2-methyl-DHP's.



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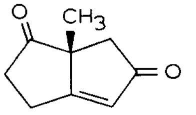

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Table 1. Yields of 2-methyl and 3 - methyl - *cis* - bicyclo[3.3.0]octanes **16a,b** and **17** as obtained from different starting materials[a]

Starting material	T (°C)	Yields of methylbicyclooctanes		
		absolute	relative	
		total	16a+16b	17
1c	310	11	75	25
1d	327	71	89	11
20	310	44	100	--
20	342	47	98	2
20	380	47	89	11
20	415	a	71	29
20	460	58	72	28

[a] Not determined.

Information on the stability of the two possible 1-methyl-DHP's was sought. However, efforts to synthesize such trienes from the dienone **21** *via* the bistosylhydrazone and subsequent Bamford–Stevens reaction have so far not been successful.[22]

DISCUSSION

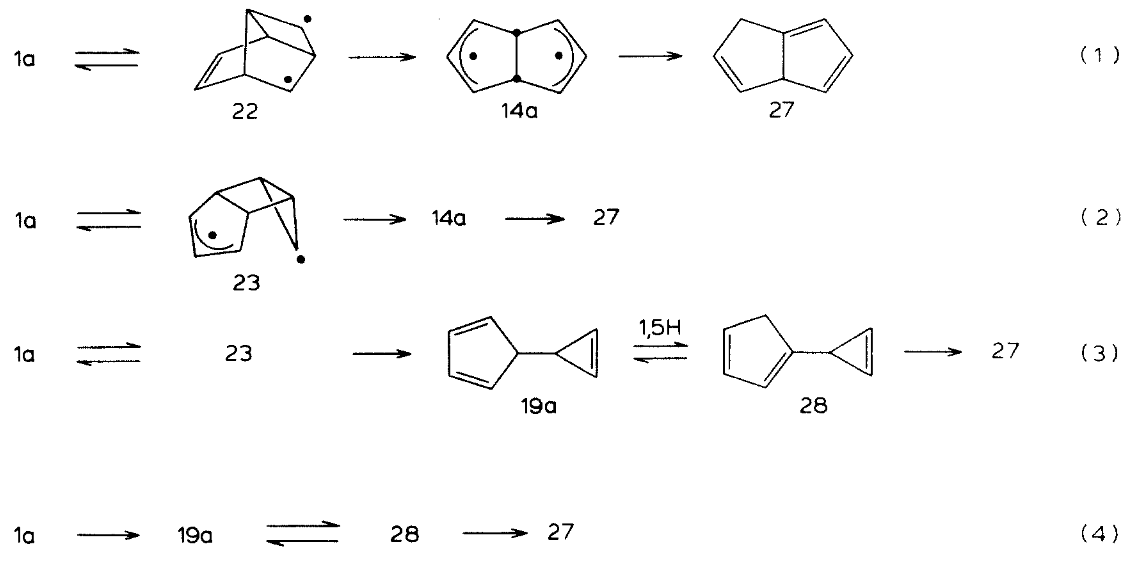
Between 250° and *ca.* 550° the flow thermolysis of TCO **1a** yields a mixture of isomeric DHP's. This behaviour has to be contrasted with results obtained in the thermolyses of various substituted TCO's,[23] which all led to the formation of substituted COT's *via* bicyclo[4.2.0]octa - 2,4,7 - trienes and 7,8-diaza-TCO,[24] which gave benzene. The presence of radical stabilizing substituents in the former cases and the tendency to liberate molecular nitrogen in the latter undoubtedly explain this dichotomy. As the formation of aromatic products (at $T > ca.$ 550°) can be ascribed to further reaction of **2** (*vide supra*),[5,9] our primary concern will be the mechanism of the formation of DHP's from **1a**.

The main property one expects to determine the reactivity of TCO (**1a**) is its large amount of strain. Due to release of part of this strain carbon–carbon bond homolyses are expected to be facilitated in TCO's. Four mechanisms, which, in a reasonable way,[25] explain the formation of DHP's and which are also compatible with the experimental fact that **1a** reacts faster than **13**, are summarized in Scheme 1.[26] Mechanisms 1–3 involve the diradicals **22** and **23** as respective first intermediates, whereas mechanism 4 is a reverse Diels–Alder reaction of **1a** yielding dihydrocalicene **19a** in a single step. In mechanism 3 **19a** is formed by fragmentation of **23**; **19a** is expected to undergo rapid 1,5 hydrogen shifts forming *inter alia* **28** which can yield DHP **27** by a bond reorganization (1,3 carbon shift) analogous to that of the vinylcyclopropane-cyclopentene rearrangement. In mechanisms 1 and 2 *cis* - bicyclo[3.3.0]octa - 2,6 - diene - 4,8 - diyl **14a** is formed from **22** and **23** by double β-fission and disrotatory cyclopropyl radical opening,[29] respectively. A 1,2 hydrogen shift converts **14a** into DHP **27**. Intermediacy of **14a** in formation of DHP's has been proposed before.[9,12] Rate determining formation of **14a** (mechanism 1) and more favourable preequilibria involving **23** could explain the higher reactivity of **1a**. The corresponding dihydro intermediates derived from **13** lack stabilization by allylic resonance. Mechanism 4 can operate only for **1a**.

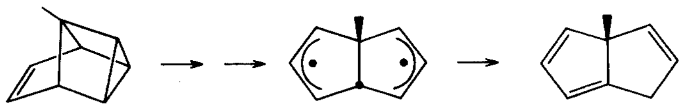
In the first steps of mechanisms 1–3, respectively, **1a** and diradicals **22** and **23** are assumed to be in equilibrium[30] since, in general, (re)closure of a (small) ring is the easiest reaction of 1,3 and 1,4-diradicals.[31] Therefore, our observation that on thermolysis (270°) of TCO-4-d (**1b**) no scrambling of label has taken place in recovered starting material (eqn 1) excludes mechanisms 2 and 3 since intermediacy of (symmetrical) **23** should have led at least to partial scrambling of deuterium from position 4 to positions 2 and 3. Also mechanism 1 becomes at least suspect on this basis since the ring closure of **14a** to SBV—expected in analogy with the behaviour of other 1,3-diradicals[31]—does not occur under the conditions employed by us. β-fission of **14a** (commonly observed in systems able to produce 1,4-diradicals;[31] **14a** is both a 1,3 and a 1,4-diradical) to COT **4** also is not observed. This contrasts with several reports invoking species **14** as intermediates in reactions leading to SBV's[10] or COT's.[11] Could the highly strained **1a** have generated **14a** in a chemically activated state[32] enabling it to cross the high barrier of 1,2 hydrogen shift to **27**[33,34] (thereby, in effect, bypassing the formation of any SBV and/or COT)? The answer to this question must be *no*. Thermolysis of diluted solutions of **1a** in benzene does not yield SBV or COT, which were both shown to survive (to a sufficient degree) the reaction conditions employed. Since collisional deactivation of excited molecules is much faster than even the more readily occurring rearrangements[36] this result effectively excludes **14a** as an intermediate in the thermolysis of **1a**.

The results with methyl-TCO's likewise do not support intermediates of type **14**. According to mechanisms 1 and 2 **1c** would yield **14b**, which by 1,2 hydrogen shift should give **29** (eqn 2).

However, as shown in Table 1, only 2-methyl and 3 - methyl - *cis* - bicyclo[3.3.0]octanes **16a,b** and **17** are obtained on catalytic hydrogenation of the thermolysis



Scheme 1. Possible mechanisms for the thermal rearrangement of **1a** into DHP's



(2)

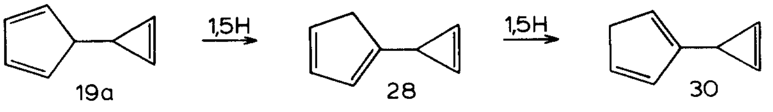
mixtures of **1c**. Whereas the absence of **29** (and **18**) is only suggestive of the non-occurrence of **14b** (the thermal stability of **29** still being unknown) the finding of hydrogenation product **17** (together with **16a,b**) from thermolysis mixtures of **1d** cannot be ascribed in a straightforward manner to the intermediacy of **14c** or the 2-methyl-DHP's derived thereof by 1,2 hydrogen shift: we have demonstrated that 2-methyl-DHP's (generated from **20**) under our flow pyrolysis conditions (320°) *do not* isomerize to precursors of **17** to a significant degree.

Mechanism 1 could account for the results obtained in this work only if the assumption of the intermediacy of **14a** in the conversions tricyclo[3.3.0.0^{2,6}]octa - 3,7 - diene→SBV[10] and SBV→COT[11] were incorrect, if diradicals of type **14** would behave differently from other 1,3 and 1,4-diradicals, and if chemical activation or some other as yet unidentified phenomenon would determine a substantial part of the pathway leading from **14b** and **14c** to the products.

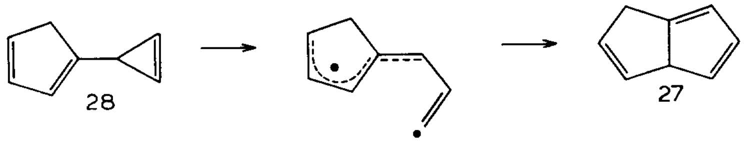
At this point, mechanisms 1,2 and 3 being excluded, we are left with mechanism 4. Reverse Diels–Alder reactions as implied in mechanism 4 are well documented for norbornenes and norbornadienes.[37] **19a** formed from **1a** in this way is expected to undergo very fast 1,5 hydrogen shifts within its cyclopentadiene moiety,[8] leading to 1 - (3 - cyclopropenyl) - cyclopentadiene (**28**) and from there to 2 - (3 - cyclopropenyl) - cyclopentadiene **30** (eqn 3). These derivatives of 3-vinylcyclopropene can transform into DHP's by a bond shift analogous to that of the vinylcyclopropane→cyclopentene rearrangement, the vinylcyclopropene rearrangement being presumed to be more rapid due to the larger amount of strain being relieved[38] (see eqn 4 and Scheme 2, path A). Finally, thermal equilibration by 1,5 hydrogen shifts converts **27** and **31** into the mixture of **2**, **10** and **11**.

The origin of **6** is unclear. It may have been produced from DHP's by wall catalyzed 1,3 H shift (a process observed upon glc of **2**, see Experimental). However, another source of **6** may be opening of **30** according to path B in Scheme 2. **32** may then close to **33**, which might yield **6** by 1,2 hydrogen migration.[34]

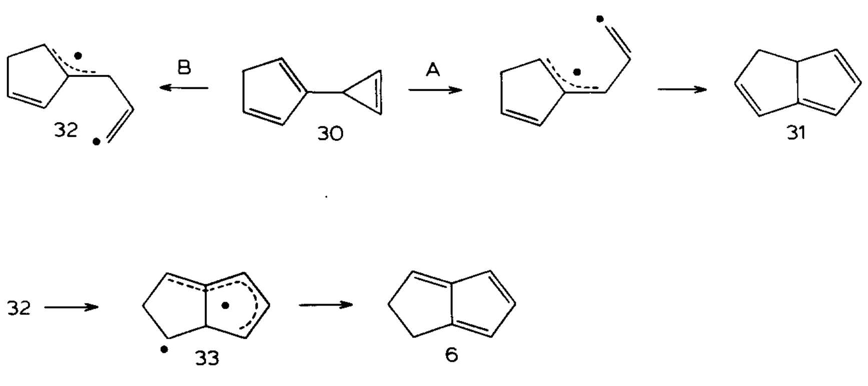
Corresponding sequences leading to 2-methyl-DHP **34**



(3)



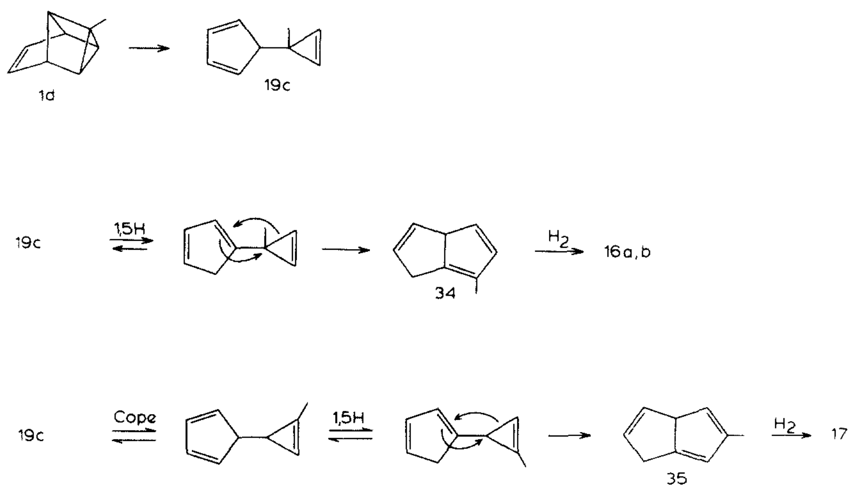
(4)



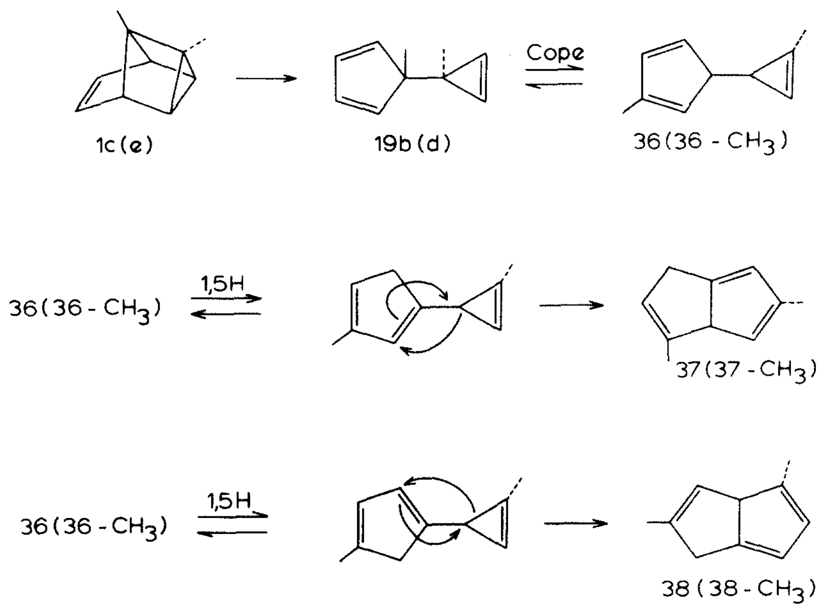
Scheme 2. Reaction paths of **30**. Possible mode of formation of **6**.

(and from there to **16a** and **16b** by hydrogenation) can be written for **1d** (Scheme 3). In the cases of **1c** and **1e** the dihydrocalicenes initially formed (**19b** and **19d**) are unable to rearrange into a 3-vinylcyclopropene derivative by 1,5 hydrogen shift. It is assumed that the first rearrangement of **19b** and **19d** is Cope rearrangement, which moves the methyl group out of the 5-position of the respective cyclopentadiene moieties, thereby enabling subsequent 1,5 hydrogen shift of **36** to form the 3-vinylcyclopropene precursors of **37** and **38** (Scheme 4).

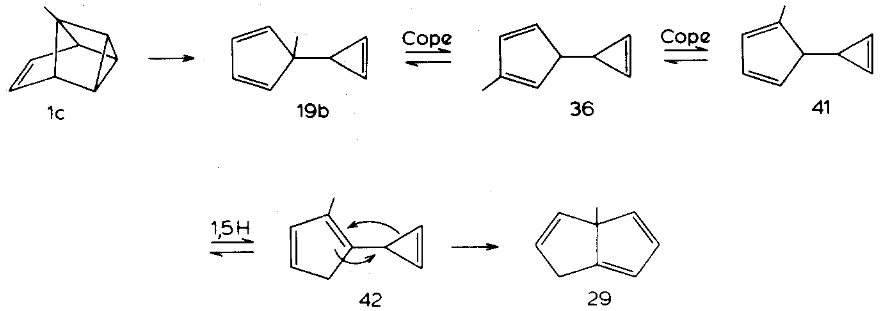
Competition between 1,5 hydrogen shift and Cope rearrangement of the dihydrocalicene **19c** formed from **1d** is assumed to explain the formation of 3-methyl-DHP's that lead to **17** on hydrogenation (see Scheme 3). Cope rearrangements involving cyclopropenes have been observed before[40] and recently Padwa and Blacklock have found that Cope rearrangements of 3-allylcyclopropenes are stepwise processes proceeding through intermediate bicyclo[3.1.0]hexyl diradicals.[30] In the cases of the dihydrocalicenes **19b,c,d** *non-concerted* rearrangement would have to occur through diradicals of types **39** and **40** ($\mathrm{R}^1 = \mathrm{CH}_3$, $\mathrm{R}^2 = \mathrm{H}$; $\mathrm{R}^1 = \mathrm{H}$, $\mathrm{R}^2 = \mathrm{CH}_3$; $\mathrm{R}^1 = \mathrm{R}^2 =$



Scheme 3. Shortest paths from **1d** to **16a, b** and **17**.

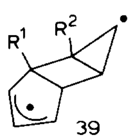


Scheme 4. Shortest paths from **1c** (.... = −H) and **1e** (.... = $-\mathrm{CH}_3$) to the corresponding DHP's.

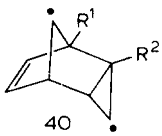


(5)

CH_3). These diradicals are considered unlikely since in the thermolysis of **1b** the related *boat* diradicals (**23**-2-*d* and **24**-3-*d*) can be excluded and no reason can be seen which would account for the formation of chair diradicals (e.g. **39** and **40**) in pronounced preference over corresponding boat diradicals (e.g. **23** and **24**).[41] As shown in eqn (5), Cope rearrangement of **36** could lead to 1-methyl-DHP's (e.g. **29**) whose hydrogenation product **18** was not found. The absence of **29** may reflect the longer route that has to be traversed (in competition with more favourable 1,5 H shifts of **36** and **41**) to generate this carbon skeleton as well as a slower vinylcyclopropene → cyclopentadiene rearrangement of the sterically more encumbered precursor **42**.



39



40

CONCLUSION

The flow pyrolysis of tetracyclo[3.3.0.$0^{2,4}$.$0^{3,6}$]oct - 7 - ene (**1a**) has been subjected to mechanistic scrutiny. On the basis of the different reactivities of **1a** and **13** and of the absence of label scrambling in recovered deuterated starting material **1b** certain diradical mechanisms were discounted. Diradicals of type **14** invoked in several $(CH)_8$ transformations[9–12] could be excluded by chemical reasoning and because they cannot explain the formation of all products in the flow pyrolyses of 4-methyl and 5-methyl-TCO, respectively. The migrations of methyl groups are best explained by the intermediacy of dihydrocalicenes, which are presumed to undergo Cope rearrangements and series of 1,5 hydrogen shifts, the latter yielding dihydrocalicenes of the 3-vinylcyclopropene type. These should lead to DHP's by fast bond reorganizations. With various diradicals excluded, formation of dihydrocalicenes from TCO's is ascribed to a concerted reverse Diels–Alder reaction. Operation of this mechanism even in the present case where diradicals could be formed rather easily (due to considerable strain relief) testifies to the important role of aromaticity in lowering energies of transition states.[42]

EXPERIMENTAL

General and analytical procedures. IR spectra were recorded as 10% solutions in CCl_4 on a Perkin–Elmer 580B spectrophotometer. Only strong and medium absorptions are given (cm^{-1}) with a precision of 5 cm^{-1}. Mass spectra were obtained from a Finnigan 4000 mass spectrometer (70 eV) or a Varian Mat CH_5-DF mass spectrometer (70 eV); for GC/MS a Varian Aerograph 1740 was coupled to the mass spectrometer in the latter case. Peak heights of fragments are given in brackets relative to the base peak (100%). Gaschromatographic analyses were performed on a Varian 90-P or 920 or on an Intersmat GC 120 or GC 16. H_2 was used as carrier gas. Columns (stainless steel) used: A: 15% SE30 on Chromosorb WAW-DMCS, 60–80 mesh (0.4 × 180 cm); B: 3.8% SE30 on Chromosorb WAW-DMCS, 60–80 mesh (0.4 × 150 cm); C: 10% Carbowax 20M on Chromosorb W-HP, 80–100 mesh (0.4 × 150 cm); D: 10% SE30 on Chromosorb PAW, 80–100 mesh (0.2 × 150 cm); E: 15% Apiezon M on Chromosorb WAW-DMCS, 60–80 mesh (0.5 × 150 cm); F: 20% SE30 on Chromosorb WAW-DMCS, 60–80 mesh (0.5 × 150 cm). Chromatograms were integrated with a Pye Unicam DP 101. Routinely glc analyses were performed by subjecting the samples first to glc on a non-polar column, collecting the peak(s) and then resubjecting any individual peak to glc on a polar column. NMR spectra were recorded on a Bruker WH-90 (90 MHz) spectrometer in $CDCl_3$ with $CHCl_3$ as internal standard; chemical shifts (δ_{tms}) are given in ppm with a precision of 0.01 ppm; coupling constants have an accuracy of 0.3 Hz. The ^1H NMR spectra of new compounds were checked by double resonance experiments: the results of these experiments were in accordance with the proposed structures. Abbreviations used: b = broad, s = singulet, d = doublet, m = multiplet, rrv = relative retention volume, ltp = linear temperature programme. All compounds are colourless liquids unless stated otherwise. Solvents were distilled shortly before use. *n*-Pentane was washed twice with concentrated H_2SO_4, twice with brine, dried over $CaCl_2$, distilled from $LiAlH_4$ and stored over Na wire. THF was dried by distillation from $LiAlH_4$ and stored over Na wire and benzene was dried by distillation, discarding the first distillate, and stored over molecular sieves. The flow thermolysis apparatus used is described elsewhere.[43] Temperatures given (°C) were measured with a Ni–CrNi thermocouple and have an accuracy of 5°. The pyrolyses were conveniently carried out with 0.03–1.00 mmol of starting material dissolved in 50–400 μl dry *n*-pentane.

Starting materials. Compounds **1a** through **1e**[19] and **20**[21] were prepared according to published procedures.

Semibullvalene **3**. To 13.6 ml of a magnetically stirred 0.15 M radical anion solution, prepared according to Ref. 13, 143 mg (1.0 mmol), 2(4)-chloro-SBV[14] was added with a syringe at −78°. After 1 min the mixture was quenched with 1 ml H_2O and subsequently diluted with 45 ml *n*-pentane. After extraction with ten portions of 20 ml H_2O the organic layer was washed with brine and dried over $MgSO_4$. The mixture was carefully concentrated through a 20 cm vacuum jacketed Vigreux column. The residue was connected to a trap maintained at −196° and volatile products were collected there under vacuum (*ca.* 1 torr). The contents of the cold trap were subjected to preparative glc (A, 60°) affording 5 mg (0.04 mmol, 4%) of a *ca.* 2:1 mixture of *cis* - bicyclo[3.3.0]octa - 2,6 - diene and *cis* - bicyclo[3.3.0]octa - 2,7 - diene (rrv: 0.81) and 45 mg (0.4 mmol, 40%) **3** (rrv: 1.00). The ratio **3**/C_8H_{10}-products varied in each experiment. **3** prepared in this way was identical in all respects with a sample obtained by a published procedure.[44]

Flow thermolysis of **1a** *with HFB trapping. Ca.* 25 ml (*ca.* 1.1 mmol) gaseous HFB was condensed in the cold trap maintained at − 196°. By syringe 18.5 mg (0.18 mmol) **1a** dissolved in *ca.* 50 μl dry *n*-pentane was placed in the sublimation vessel, kept at − 196°. Vacuum was applied to the thermolysis apparatus (*ca.* 2 torr) and the quartz tube was heated to 370°. After 1.5 h the temperature showed no more variation and the carrier gas (N_2) flow was adjusted to 4.0 ml/min. *Via* rates of known reactions the contact time was determined to be 1–2 sec under these conditions.[45] Subsequently, the solution of **1a** was slowly sublimed through the hot tube by raising the temperature of the sublimation vessel. After the sublimation was complete the gas flow was checked again and then pumping was stopped and the system allowed to come to atmospheric pressure by admitting N_2. The contents of the cold trap were flushed to the bottom of the trap, now maintained at − 78°, with *ca.* 1 ml dry *n*-pentane. The mixture was allowed to warm to room temperature within *ca* 2 h and then subjected to preparative glc (B, 83°) affording 3.0 mg (0.03 mmol, 16%) **6** (yellow liquid; rrv: 0.26), 7.6 mg (0.03 mmol, 16%) **7** (rrv: 0.39), 1.5 mg (0.01 mmol, 3%) **8** (rrv: 0.44) and 31.9 mg (0.07 mmol, 42%) **9** (rrv: 1.00). **7** and **8** were separated more conveniently on column C (98°): **7** (rrv: 0.81) and **8** (rrv: 1.00). The identity of **6** was confirmed by comparison of its spectral data with those of an authentic sample.[7] The ^1H NMR and UV spectra of **7**, **8** and **9** have been reported.[4]. The identities of **7** [IR: 1339, 1291, 1279, 1261, 1240, 1172, 1143, 1132, 977; MS (*m*/*e*): 266(45), 197(100), 177(57), 128(42)], **8** [IR: 1340, 1301, 1285, 1271, 1241, 1170, 1148, 1128, 1112, 976; MS (*m*/*e*): 266(60), 197(100), 177(70), 128(51)] and **9**[IR: 1356, 1340, 1290, 1276, 1190, 1179, 1160, 1148; MS (*m*/*e*): 428(57), 409(19), 359(100), 339(28), 319(32), 290(26)] were derived from their spectral data. Sometimes the presence of some **12** (B, rrv: *ca* 0.40; C, rrv: 0, 72; ^1H NMR: 2.15–2.73(m, 4H), 4.38(m, 2H), 6.97(d, 1.8 Hz, 2H); IR: 1732, 1338, 1303, 1280, 1160, 1148, 719; MS (*m*/*e*): 266) was observed; **12** had to be separated from **7** by repeated glc treatment on column C. The aromatic products obtained after thermolyses at higher temperatures also were separated on column B: benzene (rrv; 0.05), toluene (rrv: 0.08) and styrene (rrv: 0.17). The identities of these products were confirmed by comparison of their spectral data with those of authentic samples. A diagram of product composition vs temperature is shown in Fig. 1.

Flow thermolysis of **1a** *and subsequent reduction of the products.* A flow thermolysis of 6.0 mg (0.07 mmol) **1a** dissolved in *ca.* 200 μl dry *n*-pentane at 370° was carried out as described above. The contents of the cold trap were dissolved in *ca.* 500 μl EtOH 96% and added by syringe to a pre-hydrogenated mixture of a spatula tip PtO_2 in 1500 μl EtOH (96%) at room temperature. The rapid H_2 uptake ceased after 5 min and the mixture was diluted with 5 ml *n*-pentane, filtered, extracted 4 times with 5 ml H_2O, washed once with brine and dried ($MgSO_4$). After careful concentration through a 20 cm vacuum jacketed vigreux column the crude residue was subjected to preparative glc (E, 88°) to afford 2.6 mg (0.02 mmol, 41%) of a single product, **5**. The identity of **5** was established by comparison of its spectral data with those of an authentic sample.

Flow thermolysis of **2** *with HFB trapping.* The flow thermolysis of **2**, obtained in the flow thermolysis of **4** (*vide infra*) was carried out as described in the case of **1a**. The **2** used contained some 30% **6** resulting from glc isolation (*vide infra*). After pyrolysis at 370° a mixture consisting of 34% **6**, 10% **12**, 13% **7**, 4% **8** and 34% **9** was found. After pyrolysis at 645° a mixture consisting of 10% benzene, 18% styrene, 7% **6**, 8% **12**, 7% **7**, 3% **8** and 15% **9** was found. For glc conditions and rrv's, see the thermolysis of **1a**.

Flow thermolysis of **13**. The thermolyses of **13** were carried out at various temperatures as in the case of **1a**, no HFB being condensed in the cold trap before thermolysis. *n*-Decane was used as internal standard. Analysis of the reaction mixtures on column D (60°) afforded unknown $C_6H_6 + C_6H_8$ (yellow liquid; rrv: 0.12), benzene (rrv: 0.14), toluene (rrv: 0.33), an unseparated mixture of **13** + *cis* - bicyclo[3.3.0]octa - 2,6 - diene + *cis* - bicyclo[3.3.0]octa - 2,7 - diene + ethylbenzene + unidentified C_8H_{10} (rrv: *ca.* 0.67), styrene (rrv: 0.90) and 1 - vinylcyclohexa - 1,3 - diene (rrv: 1.00). The broad peak with rrv of *ca.* 0.67 was analyzed on column C (68°) yielding **13** (rrv: 1.00), *cis* - bicyclo[3.3.0]octa - 2,6 - diene + *cis* - bicyclo[3.3.0]octa - 2,7 - diene (rrv: 1.24), ethylbenzene (rrv: 1.89) and unidentified C_8H_{10} (rrv: 2.42). The identities of the products were established by comparison of their spectral data and glc retention times with those of authentic samples. The yellow mixture of the unknown C_6H_6 and C_6H_8 reacted with excess HFB (*n*-pentane, − 45°, then warming to room temperature) to afford two mono-adducts: C_6H_6-HFB. Ms(*m*/*e*): 240(100), 173(60), 171(94), 151(83) and C_6H_8-HFB, Ms (*m*/*e*): 242(35), 229(28), 202(63), 173(100), 133(69) according to mass spectrometry. The yields of the products at various temperatures are given in Table 2.

Flow thermolysis of SBV **3**. The flow pyrolysis of **3** was carried out as described for **13** with mesitylene as internal standard. Glc analysis (A, 80°) showed the presence of a single

Table 2. Yields of products obtained in the thermolyses of **13**

	Temp. (°C)						
Compound	420	460	473	500	530	560	597
13	96	75	28	23	5	6	-
unknown C_6H_6 + C_6H_8	a	a	4	5	4	2	4
benzene	a	a	7	7	9	14	22
toluene	a	a	b	b	b	3	3
cis-bicyclo[3.3.0]octa-2,6-diene	a	a	2	1	2	1	1
cis-bicyclo[3.3.0]octa-2,7-diene	a	a	3	2	3	2	2
ethylbenzene	a	a	b	b	2	3	9
unknown C_8H_{10}	a	a	3	5	4	1	0
styrene	a	a	b	b	2	5	6
1-vinylcyclohexa-1,3-diene	a	a	4	11	14	4	1
Total			51	54	45	41	48

[a] Not determined; [b] Trace.

peak at all temperatures studied. The **3**/**4** ratio was determined by integration of the ^{1}H NMR spectrum. The absolute yield **3** + **4** was over 90% at all temperatures studied. Figure 2 shows the product variation with temperature.

Flow thermolysis of COT **4**. *A. Without HFB trapping*: The flow thermolyses of **4** were carried out as described in the case of **13**. Glc analysis (E, 98°) showed the presence of five peaks: benzene (rrv: 0.20), **4**, (rrv: 1.00), styrene (rrv: 1.16), **2** (rrv: 1.60) and **6** (rrv: 2.04). The identity of the products was established by comparison of their spectral data with those of authentic samples. **2** was shown to rearrange to **6** to an extent of *ca.* 30% under these glc conditions. *B. With HFB trapping*: The flow thermolysis of **4** was carried out as described in the corresponding case of **1a**. Preparative glc (B, 82°) afforded benzene, **4** and styrene in addition to **6**, **7**, **8** and **9** in a ratio which was also found during the thermolyses of **1a**. The finding of **6** under these conditions (**2**, **10** and **11** removed by reaction with HFB) proves that **6** constitutes a primary reaction product and not an artifact formed from other DHP's during glc work-up.

Solution thermolysis of **1a**, **3** *and* **4**. Ampoules (inner sizes: 2 × *ca.* 120 mm) were cleaned by rinsing with 4N NH_4OH and subsequently dried overnight at 150°. Under nitrogen the ampoules were charged with *ca.* 120 μl of *ca.* 0.1 M solutions of **1a**, **3** or **4**, respectively, in dry benzene with *n*-undecane as internal standard, degassed and sealed under vacuum. These samples were heated by placing the ampoules in holes of a massive aluminum bloc kept at 270° by external heating. Dummies showed the temperature in the ampoules to reach 270° after *ca* 85 sec. The thermolyses were stopped by dropping the ampoules into a beaker with melting ice. The reaction mixtures were analyzed by glc (C, 61°). The detection limit could be set at 0.5%. 71 sec after being placed into the aluminum bloc **1a** was recovered for 48% with no other products detectable (in particular no **3** and/or **4** were found). Similarly, **3** gave a 97% recovery of a 96:4 mixture of **3** and **4** after 82 sec. **4** was shown to be stable for at least 555 sec under these conditions. After 71 sec a mixture of **1a** and **3** gave a recovery of 42% **1a** in addition to 68% of a 87:13 mixture of **3** and **4**; some **2** also was found. If the assumption is made that two molecules of **1a** are consumed (by Diels-Alder reaction) for every molecule of **2** formed, then the 42% recovery of **1a** could indicate that *ca.* 20% of **1a** had actually undergone thermal rearrangement to DHP's (e.g. **2**). If, in addition to DHP's **3** had been formed from **1a** its amount having survived the reaction conditions must have been less than 0.5%. Assuming formation of maximally 0.7% **3** a maximum contribution of 3.5% to the total rate of thermal rearrangement (20%) of **1a** could be ascribed to the formation of **3**. However, the actual contribution is probably much lower.

Attempted trapping of **14a** *with benzenethiol.* On preparation of a sample for solution thermolysis *ca.* 4 mg **3**, containing *ca.* 4% **4** as a result of its mode of synthesis,[44] was dissolved in 150 μl freshly distilled benzenethiol. After *ca.* 5 min the mixture was analyzed by glc showing the complete disappearance of **3**. Glc under appropriate conditions (F, 180°) showed the presence of two new peaks in a 9:2 ratio (rrv: 1.00 and 1.32). The major peak was collected and appeared to be *ca.* 85% pure by ^{1}H NMR. The identity of the main component **15** [(^{1}H NMR: 1.98–2.27(md, 17.0 Hz, 1H), 2.34–2.74(m, 1H), 3.19–3.53(m, 2H), 4.05(bs, 1H), 5.64(m, 4H), 7.17–7.54(m, 5H); IR: 3055, 2915, 2850, 1583, 1480, 1438, 1062, 692; MS (*m*/*e*): 214(2), 105(100), 104(23), 79(32), 77(42)], was derived from its spectral data. No attempt was made to identify other products.

Flow thermolysis of **1c** *and subsequent reduction of the products.* The flow thermolysis of 10.1 mg (0.09 mmol) **1c** in *ca.* 100 μl dry *n*-pentane was carried out as described in the case of **13** at 310.° After finishing pumping and reestablishing atmospheric pressure the cold trap was warmed to *ca.* −35° and the contents were flushed to the bottom of the trap with 1500 μl EtOH 96%. In the mean time, a spatula tip PtO_2 in 1500 μl EtOH 96% was pre-hydrogenated for 10 min at −10°. The contents of the cold trap then were added to the reduction mixture with the aid of a syringe. The mixture was stirred vigorously for 45 min after which the temperature was −6°. The colourless reaction mixture was allowed to warm to room temperature, diluted with 30 ml *n*-pentane, filtered and extracted 4 times with 25 ml H_2O, once with 10 ml brine and dried ($MgSO_4$). After careful concentration through a 20 cm vacuum jacketed vigreux column the residue was connected to a trap maintained at −196° and the volatile products were collected there under vacuum (*ca.* 1 torr). The non-volatile residue (6.1 mg, 60%) easily dissolved in *n*-pentane and was shown by GCMS not to contain any significant compounds. The contents of the cold trap were subjected to glc (D, 60°, ltp: 2°/min) affording three peaks: 0.4 mg (white solid, 0.003 mmol, 3%) 7,7-dimethylnorbornane (rrv: 1.00), 0.3 mg (0.002 mmol, 3%) **16b** + **17** (rrv: 1.17) and 0.8 mg (0.006 mmol, 8%) **16a** (rrv: 1.40). The mixture of **16b** and **17** could not be separated on a variety of columns, including a 50 m OV 225 capillary column. The mixture of **16b** and **17** was therefore analyzed in this case and in the thermolyses of **1d** and **20** by comparing its spectra (^{1}H NMR, IR and MS) with those of mixtures of different compositions of **16b** and **17**, prepared by independent routes. The ratio **16b**/**17** was derived from the heights of the methyl doublets in the ^{1}H NMR spectrum. 7,7-Dimethyl-norbornane was established to be the main hydrogenation product of **1c** under comparable conditions.[19] The identity of **16a** was established by comparison of its spectral data with those of an authentic sample. The relative yields of **16a** + **16b** and **17** are given in Table 1.

Flow thermolysis of **1d** *and subsequent reduction of the products.* The flow thermolysis at 327° and subsequent reduction of the products of 10.2 mg (0.09 mmol) **1d** was carried out exactly as described in the case of **1c** affording 1.4 mg (0.01 mmol, 13%) **16b** + **17** and 6.2 mg (0.05 mmol, 58%) **16a**. The relative yields of **16a** + **16b** and **17** are given in Table 1.

Flow thermolysis of **1e**. The flow thermolysis of 8.2 mg (0.06 mmol) **1e** at 310° was carried out as described in the case of **13**. The yellow product mixture was analyzed by glc (B, 70°, ltp; 4°/min). Besides 1.3 mg (16%) starting material 4.6 mg (65%) of a mixture of at least ten compounds was found. ^{1}H NMR analysis of all peaks showed the absence of any compound with c_s symmetry and/or signals in the cyclopropene region (*ca.* 7 ppm). No attempt was made to identify these compounds.

Flow thermolyses of **20** *and subsequent reduction of the products.* The thermolyses of **20** were carried out as described in the case of **1c**. The hydrogenation of the products was carried out at room temperature; the other conditions were the same as in the case of **1c**. The absolute and relative yields at various temperatures are given in Table 1.

Acknowledgement—We thank Prof. Dr. K. Hafner for sending us spectra of **6**. Part of this work has been carried out with financial aid from the Netherlands Organization for the Advancement of Pure Research (Z.W.O) via the Netherlands Foundation for Chemical Research (S.O.N.).

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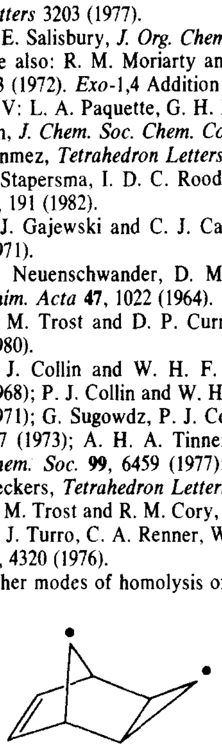
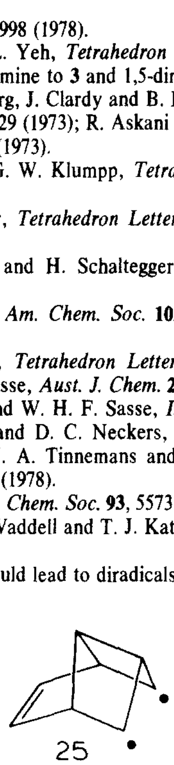
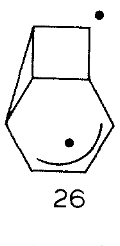
[25] Other modes of homolysis of **1a** could lead to diradicals **24**–**26**.



24



25



26

In the present case diradical **24** is excluded since it cannot explain the substantial reactivity difference between **1a** and **13**. Pathways invoking the intermediacy of **25** and **26** are not considered, since the most reasonable reactions of these species lead to SBV (**3**) and COT (**4**), respectively. Under our conditions **3** and **4** do *not* transform into DHP's.

[26] Similar mechanisms can be written for the thermal decomposition of **13** (compare Scheme 1 and Ref. 25). Diradicals **22-H$_2$**, **23-H$_2$** and **24-H$_2$** could lead to **14-H$_2$** and **19-H$_2$**. **19-H$_2$** could transform into **14-H$_2$** *via* its vinylcarbene tautomer;[27] **14-H$_2$** can also be formed from **25-H$_2$** via double β-fission and the intermediacy of dihydrosemibullvalene (SBV-H$_2$).[28] **14-H$_2$** can yield *cis* - bicyclo[3.3.0]octa - 2,6 - diene, *cis* - bicyclo[3.3.0]octa - 2,7 - diene, and cyclooctatriene - 1,3,5, the latter being known to lead to 1 - vinylcyclohexa - 1,3 - diene under reaction conditions which are comparable with those employed by us.[28] **26-H$_2$** is recognized as another possible source of cyclooctatriene-1,3,5.

[27] *Cf* A. Padwa, T. J. Blacklock. R. Loza and R. Polniaszek, *J. Org. Chem.* **45**, 2181 (1980).

[28] W. R. Roth and B. Peltzer, *Liebigs Ann.* **685**, 56 (1965).

[29] *Cf* the related ring opening of 2-bicyclo[1.1.0]butyl: P. J. Krusic, J. P. Jesson and J. K. Kochi, *J. Am. Chem. Soc.* **91**, 4566 (1969).

[30] An example most pertinent to the present mechanisms 2 and 3 has been discussed by Padwa: A. Padwa and T. J. Blacklock, *J. Am. Chem. Soc.* **102**, 2797 (1980). In their schemes boat diradicals comparable with **24** undergo ring closure to tricyclohexane and ring inversion to the corresponding chair diradical much faster than fragmentation.

[31] Examples of ring closure: Ref. 10; M. P. Schneider, *Angew. Chem., Int. Ed. Engl.* **14**, 707 (1975); M. P. Schneider and B. Csacsko, *J. Chem. Soc. Chem. Comm.* 330 (1977); R. J. Crawford and A. Mishra, *J. Am. Chem. Soc.* **88**, 3963 (1966); W. Adam, N. Carballeira and O. De Lucchi, *Ibid.* **103**, 6406 (1981); Ref. 43. Examples of β-fission: Ref. 11; J. A. Berson, P. B. Dervan, R. Malherbe and J. A. Jenkins, *J. Am. Chem. Soc.* **98**, 5937 (1976); W. R. Roth, M. Biermann, G. Erker and K. Jelich, *Chem. Ber.* **113**, 586 (1980); W. Grimme and H.-J. Rother, *Angew. Chem., Int. Ed. Engl.* **12**, 505 (1973).

[32] For examples of the effect of chemical activation on reaction pathways, see: R. G. Bergman, *Free Radicals* (Edited by J. K. Kochi), Vol. I, p. 219. Wiley, New York (1973).

[33] The conversion of COT to **2** at temperatures above 480° probably occurs through 1,2 hydrogen shift of **14a**.[12] The activation energy of this conversion was found to be 45.7 kcal/mole.[9,34] Normally (e.g. in the examples of Ref. 31) 1,2 hydrogen shifts in mesomeric 1,3 and 1,4-diradicals either are not observed at all or constitute only minor processes [*cf* also W. von E. Doering and W. R. Roth, *Tetrahedron* **19**, 715 (1963)].

[34] From the difference in heat of formation of COT [71 kcal/mol (J. D. Cox and G. Pilcher, *Thermochemistry of Organic and Organometallic Compounds*. Academic Press, New York (1970)] and **14a** (91 kcal/mol, estimated from the calculated[35] heat of formation of *cis* - bicyclo[3.3.0]octa - 2,6 - diene, the C–H bond dissociation energy and the allylic resonance energy; see also Ref. 9) the energy of activation for 1,2 hydrogen shift of **14a** is $\approx$26 kcal/mol. The energy of activation of 1,2 hydrogen shift of 1-pentene-3,5-diyl to give pentadiene-1,4 is 7.6 kcal/mol higher than the energy of activation of the ring closure to give cyclopentene [C. A. Willington, *J. Phys. Chem.* **66**, 1671 (1962)]. In trimethylene the barrier of 1,2 hydrogen shift is *ca.* 1 kcal/mol higher than that of ring closure [Ref. 35, p. 87; see also the product ratios of Crawford (Ref. 31)].

[35] S. W. Benson, *Thermochemical Kinetics*. Wiley, New York (1968).

[36] *Cf* the behaviour of 2,3 - bismethylenecyclohexa - 1,4 - diyl described by Roth (Ref. 31). In this case even fragmentation and ring closure are suppresssed (in favour of dimerization) by working in the liquid phase. This may be caused by the orthogonality of the two π-systems in the diradical and the σ-bonds to be cleaved or to be closed, respectively. The same degree of orthogonality is not present in **14a** and SBV is formed from tricyclo[3.3.0.0^{2,6}]octa - 3,7 - diene (presumably through **14a**) even at 25° in DMSO.[10]

[37] H. Kwart and K. King, *Chem. Rev.* **68**, 415 (1968); J. C. Ripoll, A. Rouessac and F. Rouessac, *Tetrahedron* **34**, 19 (1978); J. Sauer and R. Sustmann, *Angew. Chem. Int. Ed. Engl.* **19**, 779 (1980).

[38] Whereas the photochemical 3-vinylcyclopropene → cyclopentadiene rearrangement is well documented [*cf* Ref. 31 and A.

Padwa, *Acc. Chem. Res.* **12**, 310 (1979)] only scant mention is made in the literature of the corresponding thermal process.[39]

[39a] R. Breslow, *Molecular Rearrangements* (Edited by P. de Mayo), Vol. I, p. 236. Interscience, New York (1963); [b] see also the formation of a DHP-derivative on reaction of 1 - ethoxy - 2,3 - di - *t* - butylcyclopropenium ion with 1,2,3,4 - tetrachlorocyclopentadienide: I. Murata, K. Nakasuji and H. Kume, *Chem. Letters* 561 (1973).

[40a] See Ref. 30; [b] W. H. de Wolf, I. J. Landheer and F. Bickelhaupt, *Tetrahedron Letters* 2813 (1974), 175, 349 (1975); [c] R. Weiss and H. Kolbl, *J. Am. Chem. Soc.*, **97**, 3222, 3224 (1975); [d] J. H. Davis, K. J. Shea and R. G. Bergman, *Angew. Chem., Int. Ed. Engl.* **15**, 232 (1976); [e] J. H. Davis, K. J. Shea and R. G. Bergman, *J. Am. Chem. Soc.* **99**, 1499 (1977).

[41] A possible reason for the non-occurrence of diradicals in the Cope rearrangement of dihydrocalicenes **19** may be the strain increase caused by their tricyclo[3.3.0.0^{2,4}]oct - 6 - ene and norbornene skeletons, respectively.

[42] M. J. S. Dewar, *Angew. Chem., Int. Ed. Engl.* **10**, 761 (1971).

[43] J. Japenga, G. W. Klumpp and M. Kool, *Recl. Trav. Chim. Pays-Bas* **97**, 7 (1978).

[44] N. J. Turro, J.-M. Liu, H. E. Zimmerman and R. E. Factor, *J. Org. Chem.* **45**, 3511 (1980).

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