# Novel pericyclic reactions in π-perimeter chemistry

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Abstract – A [5,5]sigmatropic rearrangement never previously ob-
served with a carbon skeleton was discovered during attempts to de-
velop a new and versatile access to 3,8-disubstituted heptalenes as
building blocks for the still unknown parent heptalenophanes. Di-
methyl 5,5a,10,10a-tetrahydroheptalene-3,8-dicarboxylate (8),
easily synthesized from cis-bicyclo[3.3.0]octane-3,7-dione (4), re-
arranges even below 0°C to the isomeric 1,6-dicarboxylate 9, which
can be transformed into 1,6-dimethylheptalene. Measurement of the
kinetic and thermodynamic parameters of the rearrangement of deri-
vatives of 8, together with studies on the influence of substitu-
ents and semiempirical AM1 calculations, gave information on the
mechanism of the pericyclic reaction.

INTRODUCTION

Three-dimensional structures with chiral heptalene moieties, as represented by the
still unknown heptalenophanes, are of considerable interest for several reasons.
First of all, the view has long been held that [2$_n$]cyclophanes, constructed of decks
possessing 4n π-electrons, will differ intrinsically in chemical properties from
their structural counterparts in which both decks have (4n+2) π-electrons (ref. 1).
The ability to alter the cavity size reversibly by means of redox reactions is parti-
cularly fascinating (ref. 2). Furthermore, unusual opportunities for metal complexa-
tion should also be offered by these systems, with potential for the construction of
new organic conductors or catalysts for asymmetric syntheses. For these and many
other reasons the parent heptalenophanes constitute attractive synthetic targets. It
seems especially intriguing to synthesize heptalenophanes from optically acti deri-
vatives of the axial chiral heptalene, e.g. by connecting the two enantiomers ε hep-
talene by two ethano bridges, which should result in a meso-compound. Since they are
unknown, we have sought to develop methods for their synthesis. One promising route
to [2.2](3,8)-heptalenophane (1) comprises the bimolecular coupling of appropriate
precursors. Retrosynthetic considerations indicate that heptalenes 2 or 3 which are

| R	CH$_2$Hal	CO$_2$Me
	2	**3**
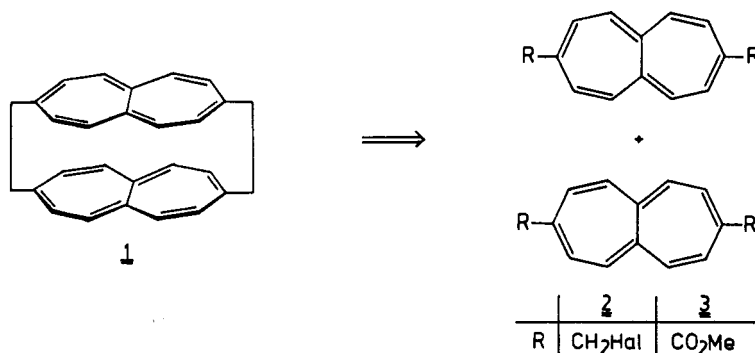
substituted in 3- and 8-positions by functional groups should be suitable starting
materials for the desired heptalenophane 1. Additionally, dimethyl 3,8-heptalene di-
carboxylate (3) could also be a precursor for derivatives such as 2. The diester 3
was already synthesized by Vogel et al. (ref. 3) as a thermally stable compound by a
multistep reaction sequence, but with an overall yield of less than 3%. It was there-
fore desirable to develop a new strategy for a more versatile and rational synthesis
of heptalenes substituted in 3- and 8-positions. Following this goal, we have been
able to design a new, surprisingly simple and high-yielding reaction sequence to
several derivatives of 5,5a,10,10a-tetrahydroheptalene. However, contrary to our ex-
pectations, all attempts to convert these into the required 3,8-disubstituted hepta-
lenes 2 or 3 furnished the regioisomeric heptalenes substituted in the 1- and 6-posi-
tions. This finding led to the discovery of a sigmatropic rearrangement never pre-
viously observed with a carbon skeleton and allowed for the first time a detailed
study of this reaction.

SYNTHESIS AND REARRANGEMENT OF 5,5a,10,10a-TETRAHYDROHEPTALENE DERIVATIVES

For the synthesis of 5,5a,10,10a-tetrahydroheptalenes, the commercially available
cis-bicyclo[3.3.0]octane-3,7-dione (4) (ref. 4) is converted into the 3,7-dipyrroli-
dino-cis-bicyclo[3.3.0]octa-2,6-diene (5b) by reaction with pyrrolidine. Fortunately,
from the two expected regioisomers 5a and b only the latter with C2-symmetry is
formed in nearly quantitative yields (ref. 5). As already reported for monocyclic
enamines (ref. 6), the bicyclic bis-enamine 5b reacts with methyl propiolate by a
two-fold formal [2+2]-cycloaddition to yield the bis-cyclobutene derivative 6, which
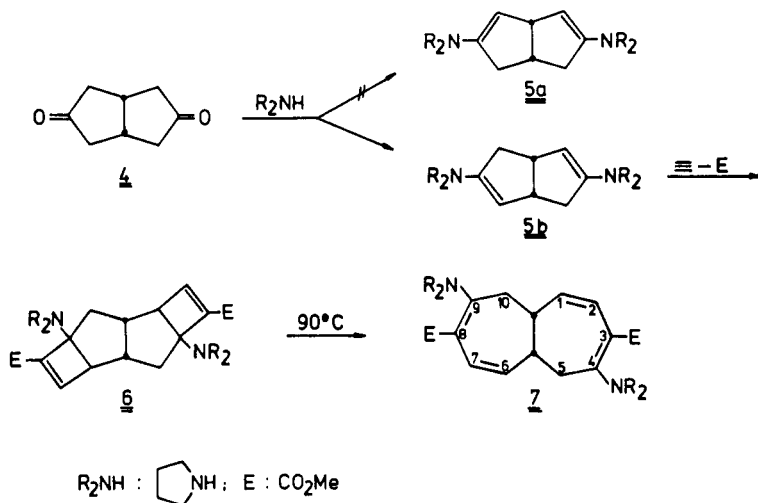
smoothly undergoes electrocyclic ring-openings of the 4-membered rings at elevated
temperatures yielding the dimethyl 4,9-dipyrrolidino-5,5a,10,10a-tetrahydroheptalene-
3,8-dicarboxylate (7) in an overall yield of 66%. The reductive elimination of the
two amino groups with borane should lead – as described for other monocyclic systems
with a vinyloguous urethane moiety (ref. 7) – to the dimethyl 5,5a,10,10a-tetrahydro-
heptalene-3,8-dicarboxylate (8a) which should be easily dehydrogenated to 3. In fact,
reduction by the borane-dimethyl sulfide complex takes place even below·0°C, but in-
stead of the expected diester 8a, only the regioisomeric dimethyl 5,5a,10,10a-
tetrahydroheptalene-1,6-dicarboxylate (9a) can be isolated with 60% yield. This re-
sult led to the conclusion that the bis-enaminoester 7 was reduced to the desired
3,8-diester 8a, which immediately isomerizes to the regioisomer 9a. In order to prove
this assumption, the bis-enaminoester 7 was reacted with the trideuterioborane-
tetrahydrofuran complex (ref. 8) to replace the amino groups by deuterium. Again in
this case, 3,8-diester 8b deuteriated in 4- and 9-position, which is presumably first
formed, could not be isolated. Instead the 1,6-diester 9b deuteriated in the two
bridgehead positions is obtained as the only product. However, in contrast to these

7 → 8 a : R = H ; b : R = D → 9 a : R = H ; b : R = D
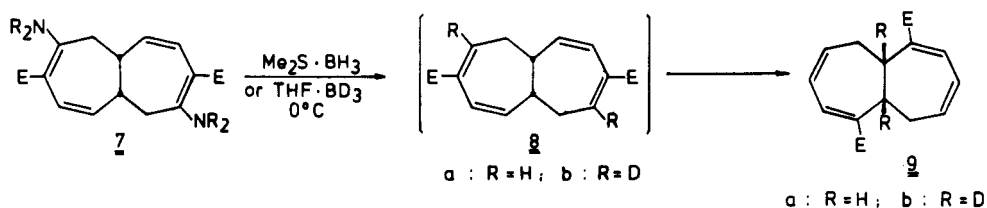
results the bis-enaminoester **7** reacts with methyllithium at -10°C to yield not the rearranged product **11** with the two methyl groups in the bridgehead positions, but exclusively the dimethyl 4,9-dimethyl-5,5a,10,10a-tetrahydroheptalene-3,8-dicarboxylate (**10**), which even at elevated temperatures shows no tendency to rearrange into the 1,6-diester **11**.

7 → 10 → 11
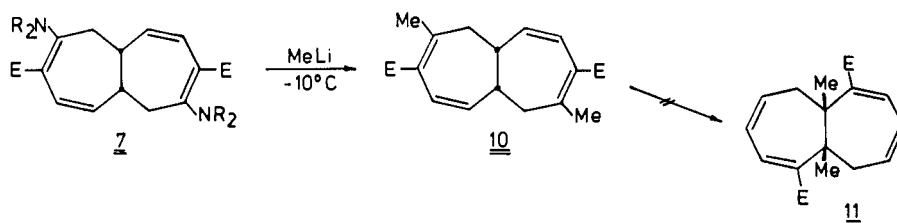
In order to learn more about the mechanistic pathway of the formation of the 1,6-diesters **9a** and **9b** by reduction of the bis-enaminoester **7**, this rearrangement reaction was studied in some more detail.

Inspections of models indicate that the 5,5a,10,10a-tetrahydroheptalene system can exist in two preferred conformations, one of which consists of an open-shaped structure, the other one of a more cage-like geometry (Fig. 1 a and b). An X-ray analysis of the bis-enaminoester **7** shows that this derivative occurs – at least in the crystal – exclusively as the open-shaped structure, presumably due to the two bulky pyrrolidino groups in the 4- and 9-position. The replacement of these substituents by hydrogen or deuterium in the dimethyl 5,5a,10,10a-tetrahydroheptalene-3,8-dicarboxylates **8a** and **b** removes the steric congestion in positions 4 and 9, so that an equilibrium between the open-shaped conformation and the cage-like conformation of the molecule can be expected. In the case of the latter the distance between the positions 4 and 9 should be around 3Å, close enough for a bonding interaction between these terminal centers of the two diene moieties of **8a** and **b**. A 10π-sigmatropic rearrangement, presumably an allowed [5a,5a]process, with a transition state like **12**, can then occur. In the case of replacement of the two pyrrolidino groups of **7** by methyl groups, to give **10**, the cage-like conformation will be sterically disfavoured, so that the rearrangement can not take place.

a : R = H ; b : R = D
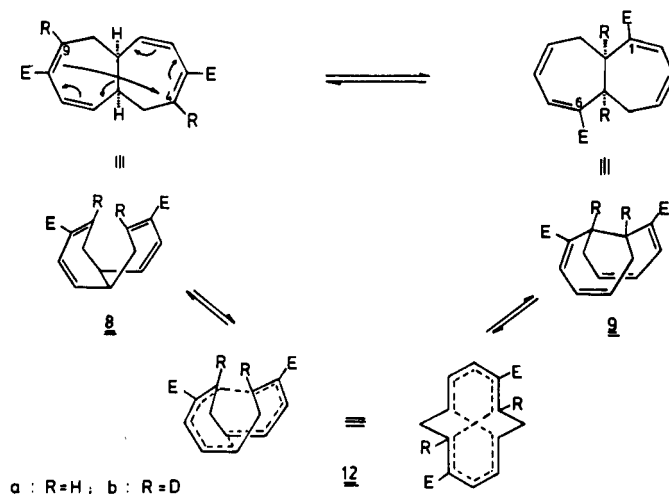
The rearrangement of the 5,5a,10,10a-tetrahydroheptalenes **8a** and **b** represents the first proved example for a [5,5]sigmatropic process of a hydrocarbon derivative (ref. 9). Contrary to the well known [3,3]sigmatropic processes of 1,5-dienes (ref.10), only a few [5,5]sigmatropic rearrangements are so far known, in all of which hetero-atoms are involved. To these belongs the transformation of (2E)-penta-2,4-dienyl phenyl ether at 186°C into 4-[(2E)-penta-2,4-dienyl]phenol studied by Fráter and Schmid in detail (ref. 11). An analogous rearrangement of 2-[(2E)-penta-2,4-dienyl-oxy]pyridine N-oxides was recently reported by Ollis et al. (ref. 12). Shine et al. obtained evidence for a concerted [5,5]sigmatropic process of the benzidine rear-rangement (ref. 13) and Wender et al. reported on a transformation of the potassium salt of 1,2-(E,E)-di(1-buta-1,3-dienyl)cyclohexanol into cyclotetradeca-3,5,7-trien-1-one by an oxy-Cope and enolate-Cope as well as an oxy-[5,5]sigmatropic process (ref. 14).

Although it is suggested that [5,5]sigmatropic rearrangements proceed via 10-membered transition states, only few experimental data for the kinetics of these reactions were previously available. Therefore, we determined the kinetic and thermodynamic parameters of the pericyclic reaction of derivatives of the 5,5a,10,10a-tetrahydro-heptalene system.

First, it was established by examination of the reversibility of the rearrangement of the 3,8-diester **8a** into the 1,6-diester **9a** that the latter does not rearrange at tem-peratures up to 100°C into the regioisomer **8a**. At about 140°C, however, a slow rear-

a : R = H; b : R = D
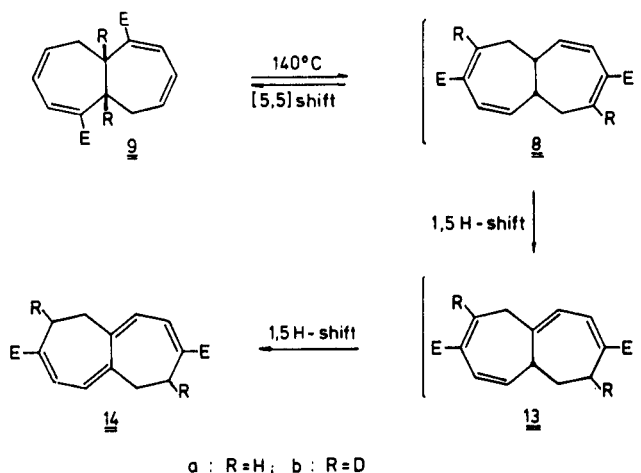
rangement can be observed by following the reaction by ^{1}H-NMR spectroscopy. Unfortu-nately, however, the 3,8-diester **8a**, which is formed under these conditions, could not be detected with certainty, as it evidently reacts immediately by two 1,5H-shifts – probably via **13a** – to the thermodynamically more stable dimethyl 1,2,6,7-tetra-hydroheptalene-3,8-dicarboxylate (**14a**) with a conjugated octatetraene moiety, which can be isolated as stable yellow crystals (ref. 15). A convincing proof for this rearrangement and the subsequent 1,5H-shifts is the formation of the dideuteriated bicyclic tetraene **14b** by thermolysis of the 1,6-diester **9b** deuteriated in the bridge-head positions.

After obtaining these results it was of special interest to learn more about the in-fluence of substituents on the 10π-electron rearrangement of the 5,5a,10,10a-tetrahy-droheptalene system. From extensive studies of the Cope rearrangement, it is well known that the rate of the reaction is significantly enhanced by electron-attracting substituents in positions 2 and 5 of the 1,5-hexadiene system (ref. 10). A similar effect should be expected for the [5,5]sigmatropic rearrangements. In the case of the 5,5a,10,10a-tetrahydroheptalene system, a replacement of the ester groups in 1,6- or 3,8-position by less electron-withdrawing or even electron-donating substituents should decrease the rate or even inhibit the isomerization of the bicyclic system.

In order to investigate the postulated influence of substituents on the rearrangement of the tetrahydroheptalene system, the 1,6-diester **9a** was reduced with diisobutylalu-minium hydride to the 1,6-bis(hydroxymethyl)-5,5a,10,10a-tetrahydroheptalene (**15**)

a : R=H ; b : R=OMe
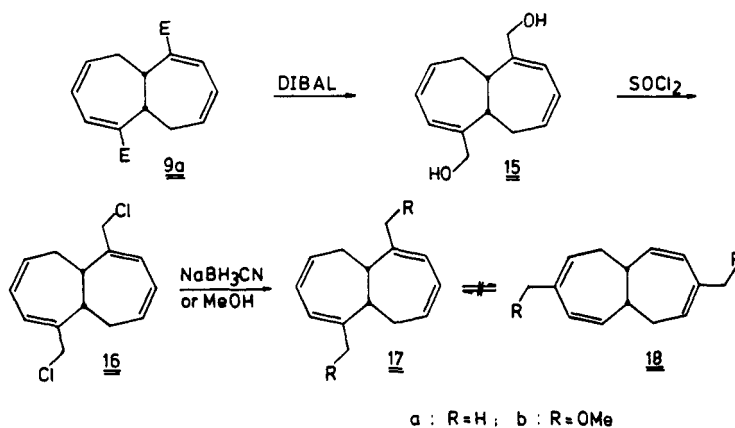
(ref. 16), and this was transformed via the corresponding bis(chloromethyl) derivative 16 into the 1,6-dimethyl- (17a) and also into the 1,6-bis(methoxymethyl)tetrahydroheptalene (17b). As expected, all attempts to rearrange these compounds, in which the two diene systems are not activated by electron-withdrawing groups, into the corresponding 3,8-disubstituted tetrahydroheptalenes 18a,b failed. Even at temperatures above 140°C no products indicating a rearrangement could be observed.

These results prompted attempts to convert the ester groups of dimethyl 5,5a,10,10a-tetrahydroheptalene-1,6-dicarboxylate (9a) into slightly less electron-attracting substituents in order to reduce the rate of the [5,5]sigmatropic rearrangement, but only to a lesser extent. Therefore, the corresponding 1,6-bis-dimethylamide 21a was


a : R=H; b : R=D
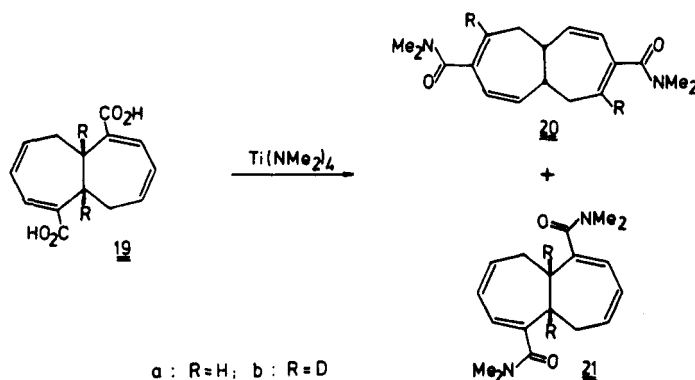
prepared by reaction of the 1,6-dicarboxylic acid 19a with tetrakis(dimethylamino)-titanium (ref. 17). To our surprise, however, this reaction even at 25°C yields not only the expected 1,6-bis-amide 21a but also the 3,8-bis-amide 20a in a ratio of about 5:1, which can be separated by column chromatography and isolated as pure crystalline compounds. Both regioisomers rearrange slowly in solution to the equilibrium mixture already at room temperature. The isomerization of the 3,8-bis-amide 20a into the 1,6-bis-amide 21a reaches an equilibrium ratio of 1:3 at room temperature within 27 days and of 1:4 at 80°C within 20h. The same results were obtained with the deuteriated bis-amides 20b and 21b, synthesized from the 1,6-dicarboxylic acid 19b deuteriated in the bridgehead positions. Obviously the less electron-accepting amide group - compared to the ester group - decreases the rate of the [5,5]sigmatropic rearrangement considerably.

For a determination of the thermodynamic and kinetic parameters of the new [5,5]sigmatropic rearrangement, we followed the dynamic process of the 3,8-bis-amide 20a into the 1,6-bis-amide 21a in p-xylene-d_{10} using ^{1}H-NMR spectroscopy in the temperature range 70 - 100°C. Measurement of the equilibrium constants yields the difference of the heats of formation for the two isomers 20a and 21a of ΔH_o = 2 kcal/mol and the difference of the entropy of ΔS_o = 4 eu. For the [5,5]sigmatropic rearrangement from the 3,8-bis-amide 20a to the more stable 1,6-bis-amide 21a $\Delta H^{\neq}_{25°C}$ was measured to be 21 kcal/mol and $\Delta S^{\neq}_{25°C}$ to be -13 eu. These values give for the inverse rearrangement 21a → 20a the $\Delta H^{\neq}_{25°C}$ of 23 kcal/mol and $\Delta S^{\neq}_{25°C}$ of -9 eu.
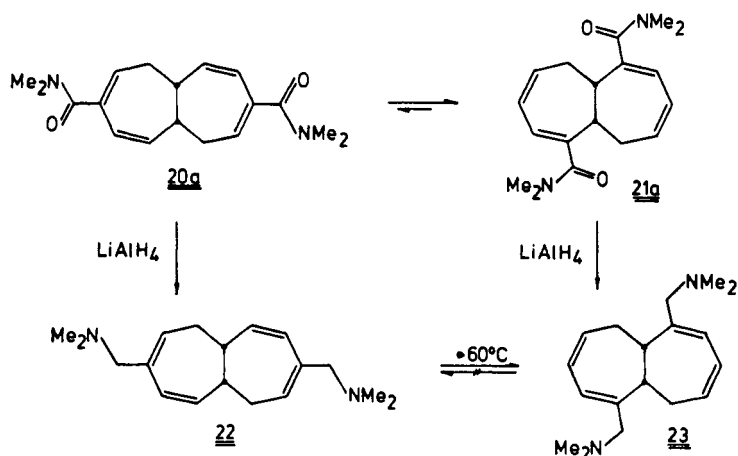
Both the regioisomeric bis-amides **20a** and **21a** can easily be reduced with LiALH$_4$ to
the corresponding 3,8- and 1,6-bis(dimethylaminomethyl)-5,5a,10,10a-tetrahydrohepta-
lenes (**22**) and (**23**). Just as in the case of the 1,6-dimethyl- or 1,6-bis(methoxy-
methyl)tetrahydroheptalenes **17a** and **17b**, no rearrangement of the 1,6-bis(dimethyl-
aminomethyl) derivative **23** could be observed at temperatures up to 100°C, while
decomposition occured at elevated temperatures. By contrast, the less stable 3,8-bis-
(dimethylaminomethyl)-5,5a,10,10a-tetrahydroheptalene (**22**) undergoes a [5,5]sigmatro-
pic rearrangement to **23** between 60°C and 110°C with increasing rates. This shows once
more a considerable influence of substituents on this [5,5]-sigmatropic rearrange-
ment. While the 3,8-bis(dimethylaminomethyl) derivative **22** only rearranges at
temperatures above 60°C, the corresponding 3,8-diesters **8** undergo this reaction
already below 0°C with a high rate. Furthermore, the significantly negative activa-
tion entropy of the new [5,5]sigmatropic rearrangement indicates a concerted 10π-
electron process.

In view of these results, it is rather surprising that the tetramethyl 5,5a,10,10a-
tetrahydroheptalene-2,3,7,8-tetracarboxylate (**25**) does not undergo any rearrangement.
For synthesis of **25**, also the cis-bicyclo[3.3.0]octane-3,7-dione (**4**) proved to be a
valuable starting material. The bis-enamine **5b** reacts smoothly with dimethyl acety-
lenedicarboxylate (ref. 18) to give the tetramethyl 4,9-dipyrrolidino-5,5a,10,10a-
tetrahydroheptalene-2,3,7,8-tetracarboxylate (**24**). Reduction with the borane-dimethyl
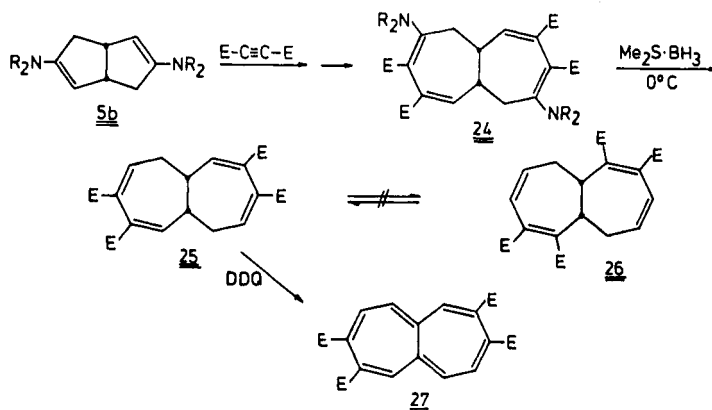
sulfide complex furnishes the corresponding tetrahydroheptalene-2,3,7,8-tetraester **25**
in good yield, which does not show any tendency to rearrange into the 1,2,6,7-tetra-
ester **26** even at temperatures up to 100°C. Obviously, the two additional ester groups
in 2- and 7-position inhibit a [5,5]sigmatropic process. Inspections of models indi-
cate that the two additional ester groups should not impede the formation of a cage-
like conformation, which seems to be a prerequisite for the [5,5]sigmatropic rear-
rangement. On the other hand, the tetrahydroheptalene tetraester **25** can easily be
dehydrogenated with DDQ to the thermally stable yellow crystalline tetramethyl hepta-
lene-2,3,7,8-tetracarboxylate (**27**), a promising building block for syntheses of
heptalenophanes like **1** as well as of linear annelated heptalenoheptalenes (ref. 15).

AM1 CALCULATIONS

To obtain further information on the mechanism of the [5,5]rearrangement of 5,5a,10,10a-tetrahydroheptalenes and its relation to the Cope rearrangement, a series of semiempirical AM1 calculations (ref. 19) with the program MOPAC (ref. 20) was performed using the procedures described by Dewar and Jie (ref. 10a) in their AM1 study of the Cope rearrangement in order to compare both reactions. Heats of formation for 2,5-disubstituted 1,5-hexadienes 28, the transition states (TS) and the stable intermediates (SI) (Table 1) are either taken from Dewar's work (28a,b; ref. 10a) or calculated using the option quoted there. All geometries calculated by the RHF procedure are fully optimized, transition states are located by calculation of

28,29	a	b	c	d
R	H	Ph	Me	CN
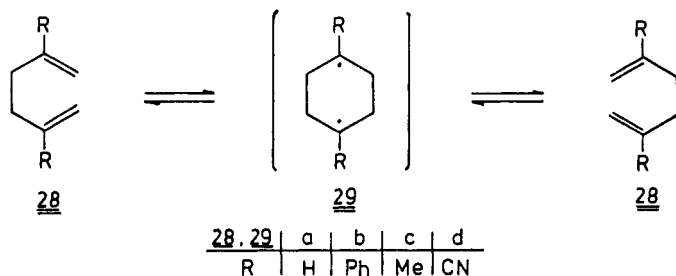
reaction paths and refined by minimizing the norm of the gradients and characterized by calculating force constants. The HE-CI values are from single point 3x3 CI(AM1-HE-CI) calculations (ref. 21) with the optimized RHF geometries. According to Dewar and Jie the AM1 calculations support the Doering biradicaloid mechanism with the species 29 as an intermediate or transition state (ref. 22). The effects of substituents in 28b to 28d are in agreement with this model. The decrease of the heats of activation calculated for the Cope rearrangement for these compounds correspond to the radical and alkene stabilizing effects of these substituents.

AM1 calculations of the [5,5]rearrangement of a series of 5,5a,10,10a-tetra-hydroheptalenes using the options described above yielded the heats of formation collected in Table 2 and the geometries of the most stable open-shaped

Table 1: Calculated heats of formation for the Cope rearrangement (kcal/mol)

		$\Delta H_f(ED)^{a)}$	$\Delta H_f(SI)^{b)}$	$\Delta H_f(TS)^{c)}$	$\Delta\Delta H_f^{d)}$
28a[e)]	RHF	18.6		55.6	37.1
	HE-CI			33.4	
28b[e)]	RHF	72.6	100.3	101.6	29.0
	HE-CI		85.8	93.9	
28c	RHF	4.6	37.4	37.5	32.9
	HE-CI		13.5	14.0	
28d	RHF	81.4	111.8	112.4	31.0
	HE-CI		90.8	96.8	

a) Heats of formation calculated for the 1,5-hexadienes
b) Heats of formation calculated for the stable intermediates
c) Heats of formation calculated for the transition states
d) Calculated heats of activation
e) Values from ref. 10a

Table 2: Calculated heats of formation for the [5,5] rearrangement of tetrahydroheptalenes (kcal/mol)

		$\Delta H_f(ED)$	$\Delta H_f(TS)$	$\Delta H_f(SI)$	$\Delta H_f(TS)$	$\Delta H_f(ED)$		$\Delta\Delta H_f \rightarrow$	$\Delta\Delta H_f \leftarrow$
30a	RHF	50.7	97.7	97.6				47.0	
	HE-CI		71.4	69.0					
30b	RHF	38.4	84.1	84.1				45.7	
	HE-CI		57.7	55.6					
30c	RHF	115.1	161.3	161.3				46.2	
	HE-CI		134.9	133.2					
18a[a)]	RHF	38.1	80.2	79.9	81.1	36.1	17a	43.0	45.0
	HE-CI		57.0	51.9	58.6				
30dA[b)]	RHF	114.9	155.1	155.0	156.6	114.3	30dB	41.7	42.3
	HE-CI		134.1	129.3	137.5				
8[c)]	RHF	-110.7	-72.8	-73.2	-71.7	-114.0	9	39.1	42.3
	HE-CI		-94.2	-98.7	-91.1				

a) Values describing the rearrangement 18a ⇌ 17a
b) Values describing the rearrangement 30dA ⇌ 30dB
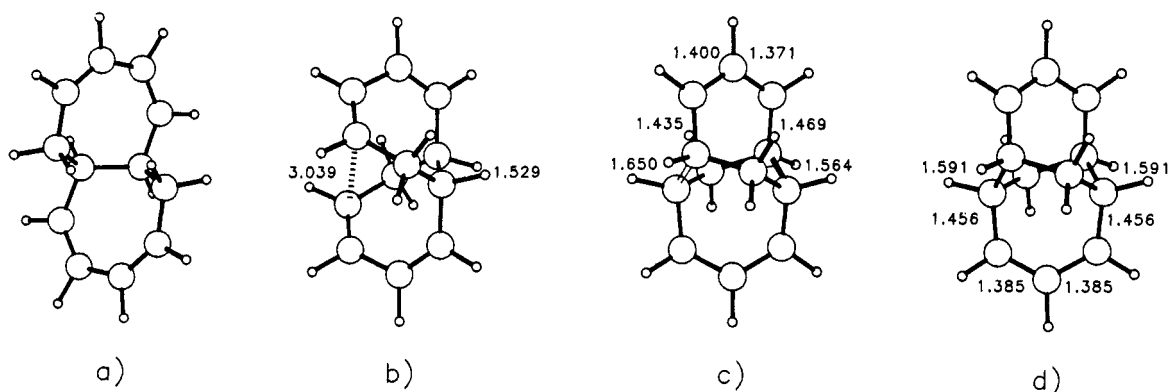c) Values describing the rearrangement 8 ⇌ 9

Fig. 1: PLUTO plots with selected bond lengths (Å) of the most stable conformation of
30a (a), the cage-like conformation (b), the transition state (c) and the
stable intermediate (d)

conformation (ED) (a), of the cage-like conformation (b) from which the rear-
rangement starts (ΔH_f 60,7 kcal/mol), of the transition state (TS) (c), and
of the intermediate (SI) (d) of **30a**, as shown in Figure 1. According to these
results the [5,5]rearrangement of **30A** = **30B** can be described in the same way
as the Cope rearrangement as biradicaloid mechanism with an intermediate or
transition-state **31**, a bridged bisallylhomologues of **29**. The larger gap between
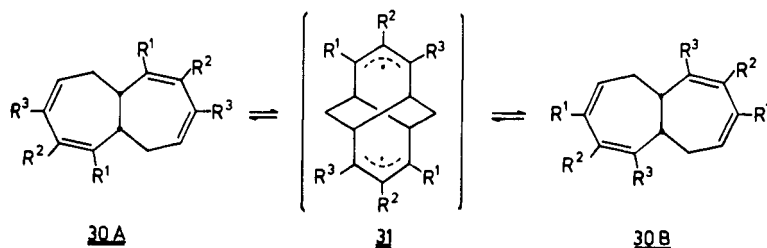
30. 31	a	b	c	d
R^1	H	H	H	H
R^2	H	Me	CN	H
R^3	H	H	H	CN

RHF and HE-CI values (**31a** (TS) 26,3 kcal/mol vs. **29a** (TS) 22,2 kcal/mol) indicates
that the radical character of **31** should be greater than the one of **29**. This should
also lead to an increased overestimation of the heat of activation by the RHF proce-
dure. According to Dewar, the heat of activation can be estimated to be the more
negative of the values calculated by RHF and that calculated by HE-CI plus 20 kcal/
mol; therefore the RHF heats of activation may be estimated 6 to 10 kcal/mol too
high. The calculated lengths of the bonds formed and broken during the reaction (see
Fig. 1) are even shorter than those calculated for **29a** (approx. 1.65Å) (ref. 10a) and
are also evidence for a more pronounced biradical character of **31a**.

The calculated substituent effects on the [5,5]rearrangement agree well with the pro-
posed mechanism. The structure of **31** with two allylradical-like moieties indicates
that substituents R^2 should not influence the rearrangement except by steric effects.
Indeed the heats of activation for **30b** (45.7 kcal/mol) and **30c** (46.2 kcal/mol) do not
differ significantly from that of **30a**.

On the other hand substituents R^1 and R^3 should show effects similar to those ob-
served in the Cope reaction. The rearrangement in these cases is no longer degene-
rate, as R^3 is converted to R^1 and vice versa. In the examples studied **18a** → **17a**,
30dA → **30dB** and **8** → **9** the 5,5a,10,10a-tetrahydroheptalenes with the substituents in
1,6-position are calculated to be the more stable. In this series the RHF heats of

activation for **18a** → **17a** (43.0 kcal/mol, **30dA** → **30dB** (41.7 kcal/mol) and **8** → **9** (39.1 kcal/mol) decrease as expected, but the effects are very small compared to the experimental results of studies of the rearrangement of **8** to **9**, the dimethylamides **20a** and **21a** and the 3,8- and 1,6-dimethylaminomethyl derivatives **22** → **23**. The unexpected observation that the tetraester **25** does not rearrange to **26** may be due to the higher stability of **25** compared to **26**. This is supported by RHF calculations of these compounds that predict **25** to be 1.4 kcal/mol more stable than **26** (ref. 23)

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