An Experimental Approach to the C_8H_{10} Hypersurface. Kinetic and Thermochemical Investigations on a Formally Forbidden Ground-state [2σ + 2π] Cycloaddition[1)]

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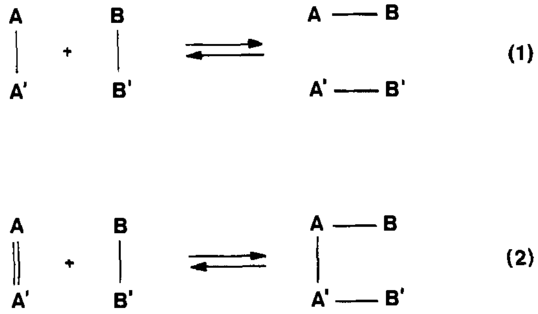
The C_8H_{10} hydrocarbons **1**, **3**, **4**, and **6** have been thermolyzed in a static system and the Arrhenius parameters have been obtained. Calorimetric measurements have been carried out to determine the heats of formation. From these data an experimental energy hypersurface is constructed which shows the following remarkable features: 1) The ground-state energy of *endo*-**1** is higher than that of *exo*-**4** by 8 kcal mol^{-1}. 2) The predominant reaction pathway of *endo*-**1** is the formally forbidden [2σ + 2π] cycloaddition to **3**, the mechanism of which is discussed. 3) Although the activation energies of the routes **4** → **6** and **4** → **3** are the same, the reaction yielding **6** is faster due to a sizeably higher *A* factor. 4) The tetracycle **3** chooses the microscopic reverse pathway, i.e. its thermolysis proceeds via *exo*-**4** to give the diene **6**.

Ein experimenteller Zugang zur C_8H_{10}-Energiehyperfläche. Kinetische und thermochemische Untersuchungen über eine formal verbotene [2σ + 2π]-Grundzustands-Cycloaddition[1)]

Die C_8H_{10}-Kohlenwasserstoffe **1**, **3**, **4** und **6** wurden im statischen System thermolysiert, und die Arrhenius-Parameter wurden gemessen. Die Bildungswärmen wurden kalorimetrisch bestimmt. Aus diesen Daten läßt sich eine experimentelle Energiehyperfläche konstruieren, die folgende Merkmale aufweist: 1) Die Grundzustandsenergie von *endo*-**1** ist um 8 kcal mol^{-1} höher als die von *exo*-**4**. 2) Der wichtigste Reaktionsweg ausgehend von *endo*-**1** ist die formal verbotene [2σ + 2π]-Cycloaddition zu **3**, deren Mechanismus diskutiert wird. 3) Obwohl die Aktivierungsenergien der Wege **4** → **6** und **4** → **3** gleich sind, verläuft die Reaktion zu **6** aufgrund des größeren *A*-Faktors rascher. 4) Der Tetracyclus **3** thermolysiert gemäß dem Prinzip der mikroskopischen Reversibilität über *exo*-**4** zu dem Dien **6**.

Thermally "forbidden" [2 + 2] reactions have aroused great interest both from a theoretical and preparative point of view. One category of the four-centre reactions comprises those of the [2σ + 2σ] type (Scheme 1, (1)), another contains the [2π + 2σ] reactions (Scheme 1, (2)).

Scheme 1



Whereas examples, which formally belong to type (1), have been cited[2)], more important reactions are to be found within category (2). The transition state for hydroboration, e.g. by-passes the forbiddenness by using two atomic orbitals of the boron atom (sp^2 and p) thus avoiding a cyclic arrangement of four interacting AOs[3)]. The conflict with forbiddenness in the four-centre concerted elimination of hydrogen chloride from ethyl chloride is also only apparent. The chlorine atom destroys the pericyclic nature of the transition state by bringing two atomic orbitals into play[4)]. Finally, the concerted symmetry-forbidden 1,2-elimination of molecular hydrogen from the ethane radical cation and other molecules has been inferred from the measured kinetic energy release[5)].

The first example of a thermally forbidden [2π + 2σ] cycloaddition of a cyclopropane σ bond to a π_{cc} double bond was reported in 1968[6)] (Scheme 2, (1)). Since then several further reactions of this type have been described[7–22)]. As regards the intermolecular variant there are not only reported examples[23,24)] but some cycloadditions point to the fact that forbiddenness is avoided by selecting the $[2\pi_s + 2\sigma_a]$ pathway[25)]. The mechanism of reaction (1) (Scheme 2) has been explained as taking place via an intermediate trimethylene diradical[6b)] (Scheme 2, (2)). As Hoffmann showed[26)], this diradical is capable of adding to the double bond in a concerted manner owing to the antisymmetric nature of its occupied frontier orbital. It was assumed that the conformation of the cyclopropanonorbornene as well as of the diradical plays a decisive role in that

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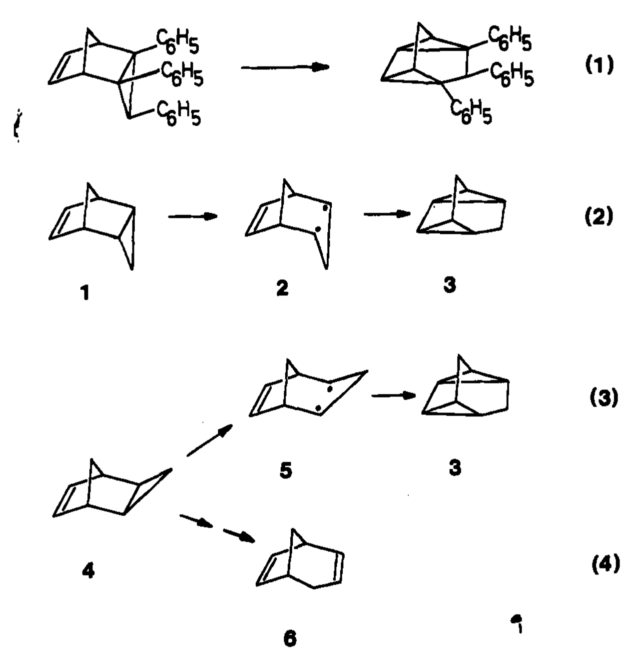
cycloaddition[6b,c]. Both the *exo*-tricyclic olefin **4** and the *exo*-diradical **5** have a greater overlap between the π orbital and the *Walsh* orbitals of the cyclopropane or the ring opened diradical, resp., than the respective *endo*-isomer **1**[6b,27]. Thus, considering a least-motion pathway for this intramolecular cycloaddition one would anticipate a greater tendency and higher reactivity for the *exo*-isomer **4** (Scheme 2, (3)). Interestingly, however, Kinnel and Freeman[19] observed that the rate of formation of **3** for the *endo*-isomer **1** is approximately 45 times the rate for the *exo*-isomer **4**. In addition, they found that the *exo*-compound **4** rearranges faster to the diene **6** than to the tetracycle **3**. Since the authors did not report either ground state energies or activation parameters (they confined themselves to only one temperature), they have not been able to account for the surprising rate differences of the processes (2), (3), and (4) (Scheme 2). In particular, the following questions arise and are waiting for a solution:

a) Is the higher reactivity of the *endo*-isomer **1** associated with a stronger forbiddenness of this [2π + 2σ] cycloaddition in the *exo*-compound **4** (because of greater four-electron overlap)?
b) If either isomer reacts via a diradical, could the higher rate observed for **1** be explained by a higher ground-state energy on account of possible torsional or other strain?
c) Why is the rearrangement of *exo*-isomer **4** to the diene **6** faster than the intramolecular cycloaddition to **3**? Since both processes stand to gain by the presupposed overlap between *Walsh* and π orbitals, is this a question of allowedness versus forbiddenness?

We report here on kinetic and thermochemical experiments which have been carried out in order to solve these problems.

Scheme 2



Results

Kinetic Studies

The hydrocarbons **1**, **3**, **4**, and **6** have been thermolyzed in a static system similar to that described earlier[28]. Details are given in the experimental part.

A) *endo-Tricyclo[3.2.1.0*^{2,4}*]oct-6-en* (**1**)

Good linear plots of ln (100/100 − *x*) against time were obtained, for conversions (*x*) of up to 65%, for five temperatures in the range 553 – 593 K. The rate constants obtained together with their standard deviations are shown in Table 1. These constants were independent of pressure in the range of 1 – 10 Torr. A further set of runs in the packed vessel at 290.3 °C (563.5 K) gave $k = 1.96 \pm 0.10 \times 10^{-4}$ s^{-1}, a value in sufficiently close agreement with the unpacked vessel figure to remove any suspicion of a heterogenous process. The presence of propene (inhibition of possible radical chains) did not alter the rate constants. An Arrhenius plot of the constants in Table 1 gave ($\Theta = RT \ln 10$)

$$\log k/s^{-1} = (14.16 \pm 0.07) - (46.00 \pm 0.19 \text{ kcal mol}^{-1})/\Theta$$

where the error limits correspond to one standard deviation.

The product distribution at one selected temperature turns out to be independent of the time (Table 2).

Scheme 3

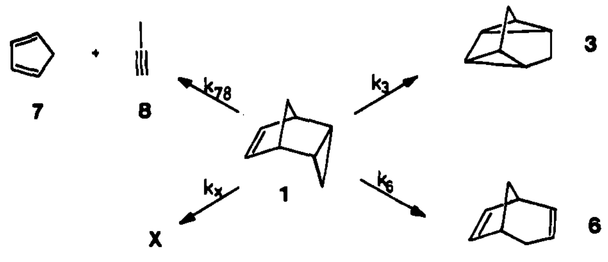


Table 1. Rate constants of the thermolyses of **1**, **3**, **4** and **6** as a function of temperature

1		**4**		**3**		**6**	
T[K] (°C)	10^4 k /s^{-1}	T[K] (°C)	10^4 k /s^{-1}	T[K] (°C)	10^4 k /s^{-1}	T[K] (°C)	10^4 k/s^{-1}
553.4(280.2)	0.993±0.028	573.8(300.6)	0.645±0.011	643.4(370.2)	0.548±0.010	613.3(340.2)	0.683±0.032
563.5(290.3)	2.075±0.053	583.2(310.0)	1.327±0.016	653.7(380.5)	1.163±0.046	623.3(350.1)	1.333±0.045
573.8(300.6)	4.613±0.115	593.2(320.0)	2.563±0.026	663.8(390.6)	2.265±0.034	633.3(360.2)	2.449± .078
583.2(310.6)	8.567±0.291	603.3(330.2)	5.480±0.024	673.5(400.6)	4.295±0.052	643.4(370.2)	4.689±0.196
593.1(320.0)	16.344±0.499	613.3(340.2)	10.839±0.079	683.8(410.7)	8.382±0.155	653.7(380.5)	9.042±0.324

Table 2. Product distribution for the thermolysis of **1**, individual Arrhenius parameters and rate constants (Scheme 3). X means an unidentified by-product

T K	553.4	563.5	593.1	E_a (kcal mol^{-1})	log(A/s^{-1})
°C	280.2	290.3	320.0		
% 3	94.15	93.47	92.02	45.64±0.21	13.99±0.08
% 6	2.81	2.95	3.31	48.67±0.10	13.67±0.04
% (7 + 8)	1.92	2.31	2.95	52.72±1.05	15.11±0.40
% X	1.12	1.27	1.73	53.09±0.03	15.01±0.01
$k_3 \cdot 10^4$ /s^{-1}	0.935	1.94	15.04		
$k_6 \cdot 10^5$ /s^{-1}	0.279	0.612	5.41		
$k_{78} \cdot 10^5$ /s^{-1}	0.191	0.479	4.822		
$k_x \cdot 10^5$ /s^{-1}	0.111	0.264	2.828		

In Table 2 the dependence of the distribution on temperature is also shown. The four primary processes are depicted in Scheme 3.

It is worth adding that <0.5% of **4** is formed from **1**, i.e. *endo*→*exo*-isomerization is negligible.

B) *exo-Tricyclo[3.2.1.0^{2,4}]oct-6-en* (**4**)

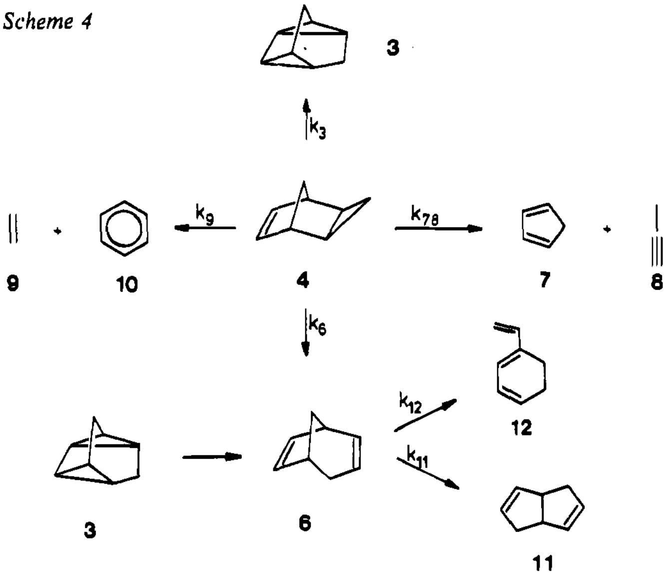
Good linear plots of ln (100/100−x) against time were obtained for conversions (x) of up to 80% in the temperature range 573−673 K. The rate constants are shown in Table 1. These constants were independent of pressure in the range of 2−7 Torr. Packed vessel runs at 310.0°C gave k = 1.366 ± 0.038 × 10^{-4} s^{-1}, i.e. a negligible effect. No indication for radical chains could be obtained by means of added propene. An Arrhenius plot of the rate constants in Table 1 gave (Θ = RT ln 10)

$$\log k/\mathrm{s}^{-1} = (14.75 \pm 0.23) - 49.73 \pm 0.62\ \mathrm{kcal\ mol^{-1}})/\Theta$$

The product percentage distribution against time at one temperature reveals that there are four primary processes and one secondary reaction (Scheme 4). The individual rate constants are given in Table 3.

It is worth noting that <0.5% of **1** is formed from **4**, i.e. *exo*→*endo*-isomerization is negligible.

Scheme 4



C) *Tetracyclo[3.3.0.0^{2,8}.0^{4,6}]octane* (**3**)

Good linear plots of ln (100/100−x) against time were obtained for conversions (x) of up to 70% in the temperature range 643−683 K. The rate constants are listed in Table 1. The rate equation is of first order. No indications for heterogeneous catalysis or radical chains could be obtained. The pressure dependence of the rate constants is negligible. The temperature dependence obeys the following equation (Θ = RT ln 10).

$$\log k/\mathrm{s}^{-1} = (15.69 \pm 0.13) - (58.72 \pm 0.39\ \mathrm{kcal\ mol^{-1}})/\Theta$$

The product distribution against time shows that there is only one important primary process: the formation of the diene **6**. Other secondary products derived from **6** are tetrahydropentalene **11**, vinylcyclohexadiene **12**, ethylene (**9**), benzene (**10**), and styrene. Minor quantities of cyclopentadiene (**7**) and propyne (**8**) are also observed, while the *endo*-**1** and *exo*-**4** tricyclooctenes were not present (above 0.5%). Scheme 4 presents the most important pathways.

Table 3. Product distribution for the thermolysis of **4**, individual Arrhenius parameters and rate constants (Scheme 4). **11** and **12** are formed in a secondary reaction from **6**. They are added to **6**

T K	573.8	583.2	593.2	603.3	613.2	E_a (kcal mol^{-1})	log(A/s^{-1})
°C	300.6	310.0	320.0	330.2	340.2		
% 3	16.64	16.33	16.83	16.16	16.00	49.10±0.23	13.73±0.09
% (6+11+12)	82.40	82.68	82.32	82.90	83.01	49.86±0.68	14.72±0.25
% (7+8)	0.30	0.26	0.16	0.19	0.23		
% (9+10)	0.67	0.74	0.69	0.74	0.76		
$k_3 \cdot 10^5$ /s^{-1}	1.074	2.168	4.314	8.856	17.34		
$k_6 \cdot 10^4$ /s^{-1}	0.532	1.097	2.110	4.543	8.998		
$k_3 \cdot 10^6$ /s^{-1}	0.194	0.345	0.410	1.041	2.493		
$k_4 \cdot 10^6$ /s^{-1}	0.130	0.982	1.769	4.055	8.238		

D) *Bicylco[3.2.1]octa-2,6-diene* (**6**)

Since the thermal behaviour of this diene is of minor importance in our context, and since the pyrolysis in a flow-system of **6** and some alkyl derivatives has been explored by Klumpp et al.[29], we confine ourselves to describe some aspects which are novel as well as useful to an understanding of the product spectrum of **3** and **4**. As main products in the thermal rearrangement of **6**[29] vinylcyclohexadiene **12** and tetrahydropentalene **11** have already been identified (Scheme 4).

In a static system, as used here, they are formed as well. Both hydrocarbons arise in primary processes as is shown by the dependence of product distribution on time. In addition minor products cyclopentadiene (**7**), propyne (**8**), ethylene (**9**) and benzene (**10**) are also formed. Good linear plots of ln (100/100 − x) against time were obtained in the temperature range 613 − 654 K for conversions (x) of up to 70%. The rate constants are listed in Table 1. An Arrhenius plot of these constants gave ($\Theta = RT \ln 10$)

$$\log k/\mathrm{s}^{-1} = (13.93 \pm 0.21) - (50.78 \pm 0.60\ \mathrm{kcal\ mol}^{-1})/\Theta$$

Packed vessel runs in a deactivated system (with hexamethyldisilazane) show a negligible effect. There is no pressure dependence of the rate constants in the range 1 − 7 Torr. Added nitrogen (up to 40 Torr) does not change k. No indication for radical chains was obtained by added propene. The product distribution and individual rate constants are shown in Table 4.

Calorimetric Studies

The results of combustion are presented in standard form. Gas-phase values have been obtained by use of reasonable estimates of vaporization enthalpies (e.g. xylenes). The results are collected in Tables 5 − 8.

Table 4. Product distribution for the thermolysis of 6, individual Arrhenius parameters and rate constants (Scheme 4). All minor subsequent products derived from 12 are added to 12: according to the time independence of 11 they do not originate from 11

T K °C	613.3 340.2	623.3 350.1	643.4 370.2	653.7 380.5	E_a (kcal mol^{-1})	log(A/s^{-1})
% **11**	31.00	33.17	36.78	39.17	55.30 ± 0.55	15.03 ± 0.19
% (**12** + ...)	69.00	66.83	63.22	60.83	48.36 ± 0.32	12.90 ± 0.11
$k_{11} \cdot 10^4$ / s^{-1}	0.212	0.442	1.724	3.542		
$k_{12} \cdot 10^4$ / s^{-1}	0.471	0.891	2.964	5.500		

Table 5. Summary of five calorimetric experiments at 298.15 K for *endo*-isomer **1**. Symbols as in ref.[30], except that internal energy is represented by u

m' (compound) / g	0.074891	0.054019	0.050120	0.042596	0.061277
m'' (polyester) / g [a]	0.014183	0.012766	0.012642	0.012732	0.012673
m''' (fuse) / g	0.000540	0.000476	0.000498	0.000574	0.000457
Δt_c / K [b]	2.75553	2.03470	1.90269	1.65209	2.27607
ε(calor)($-\Delta t_c$) / cal [c]	883.04	652.04	609.74	529.43	729.39
ε(cont)($-\Delta t_c$) / cal [d]	1.81	1.30	1.20	1.04	1.45
Δu (correction to standard states) / cal [e]	0.46	0.33	0.31	0.27	0.37
$-$ (m''Δu_c°/M) (polyester) / cal	77.72	69.95	69.28	69.77	69.45
$-$ (m'''Δu_c°/M) (fuse) / cal	2.19	1.93	2.02	2.33	1.85
Δu_c° /M (compound) / cal g^{-1}	−10737.2	−10751.2	−10753.7	−10746.2	−10751.4
ΔH_c° (compound) / kcal mol^{-1}	−1141.34	−1142.83	−1143.09	−1142.20	−1142.85
ΔH_f° (compound) / kcal mol^{-1}	47.36	48.85	49.11	48.32	48.86
ΔH_f° (mean) / kcal mol^{-1}	48.50 ± 0.31				
ΔH_f° (l) (mean) / kcal mol^{-1}	49.05 ± 0.31				
ΔH_f° (g) / kcal mol^{-1} [g]	59.0 ± 1.0				

[a] Corrected to relative humidity of 0%, see ref.[31]. − [b] $\Delta t_c = t_f - t_i + \Delta t_{corr.}$ − [c] ε(calor) = 320.461 ± 0.045 cal K^{-1}. − [d] ε(cont)($-\Delta t_c$) = ε^i(cont.)(t_i − 298.15) + ε^f(cont.)(298.15 − t_f + Δt_{corr}). − [e] Sum of items 81 − 85, 87 − 90, 93 and 94 in ref.[30]. − [f] ΔH_m (heat of fusion) = 0.55 kcal mol^{-1}. − [g] ΔH_v (heat of vaporization) ≈ 10 kcal mol^{-1} (estimated).

Table 6. Summary of five calorimetric experiments at 298.15 K for *exo*-isomer **4**. a) to g) as in Table 5, except for c) ε(calor) = 320.29 ± 0.053 cal K^{-1}

m' (compound) / g	0.052853	0.054576	0.050392	0.046479	0.036869
m'' (polyester) / g a)	0.013228	0.011734	0.011564	0.012891	0.011118
m''' (fuse) / g	0.000421	0.000488	0.000462	0.000519	0.000521
Δt_c / K b)	1.99176	2.02314	1.88000	1.77291	1.42369
ε(calor) $(-\Delta t_c)$ / cal c)	637.94	647.99	602.15	567.84	455.99
ε(cont) $(-\Delta t_c)$ / cal d)	1.26	1.29	1.19	1.12	0.90
Δu (correction to standard states) / cal e)	0.32	0.32	0.30	0.28	0.23
$-(m''\Delta u_c^\circ/M)$ (polyester) / cal	72.13	63.98	63.06	70.29	60.62
$-(m'''\Delta u_c^\circ/M)$ (fuse) / cal	1.71	1.98	1.87	2.10	2.11
$\Delta u_c^\circ/M$ (compound) / cal g^{-1}	−10684.1	−10675.5	−10671.3	−10669.9	−10674.7
ΔH_c° (compound) / kcal mol^{-1}	−1135.71	−1134.81	−1134.35	−1134.20	−1134.71
ΔH_f° (compound) / kcal mol^{-1}	41.72	40.82	40.37	40.22	40.73
ΔH_f° (l) (mean) / kcal mol^{-1}	40.77 ± 0.33				
ΔH_f° (g) / kcal mol^{-1} g)	51.0 ± 1.0				

Table 7. Summary of five calorimetric experiments at 298.15 K for tetracycle **3**. a) to g) as in Table 5

m' (compound) / g	0.051694	0.057052	0.054909	0.0562903	0.054746
m'' (polyester) / g a)	0.012552	0.012219	0.012818	0.010030	0.012186
m''' (fuse) / g	0.000481	0.000511	0.000463	0.000539	0.000538
Δt_c / K b)	1.92911	2.10388	2.04085	2.03844	2.02344
ε(calor)$(-\Delta t_c)$ / cal c)	618.20	674.21	654.01	653.24	648.43
ε (cont)$(-\Delta t_c)$ / cal d)	1.22	1.33	1.30	1.29	1.29
Δ u (correction to standard states) / cal e)	0.31	0.34	0.33	0.32	0.32
$-(m''\Delta u_c^\circ/M)$(polyester) / cal	68.78	66.96	70.24	54.96	66.77
$-(m'''\Delta u_c^\circ/M)$(fuse) / cal	1.95	2.07	1.88	2.18	2.18
$\Delta u_c^\circ/M$ (compound) / cal g^{-1}	-10601.4	-10605.4	-10608.6	-10600.1	-10595.9
ΔH_c° (compound) / kcal mol^{-1}	-1126.93	-1127.35	-1127.69	-1126.79	-1126.35
ΔH_f° (compound) / kcal mol^{-1}	32.94	33.37	33.71	33.81	32.36
ΔH_f° (l) (mean) / kcal mol^{-1}	33.04 ± 0.23				
ΔH_f° (g) / kcal mol^{-1} g)	43.0 ± 1.0				

Table 8. Summary of four calorimetric experiments at 298.15 K for the bicyclic diene **6**. a) to g) as in Table 5, except for c) ε(calor) = 320.29 ± 0.053 cal K^{-1}

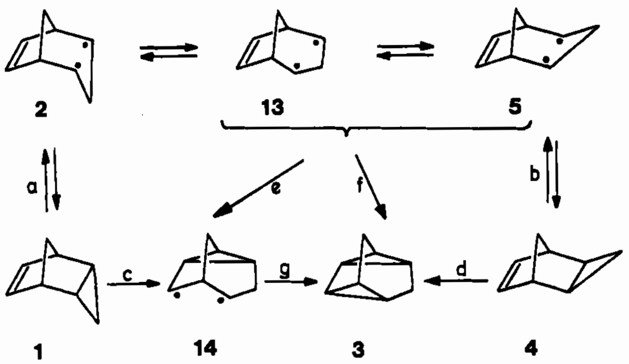
m' (compound) / g	0.042701	0.050910	0.047535	0.029091
m'' (polyester) / g a)	0.010808	0.010810	0.012409	0.012318
m''' (fuse) / g	0.000610	0.000497	0.000476	0.000586
Δt_c / K b)	1.59901	1.86490	1.78618	1.17543
ε(calor)$(-\Delta t_c)$ / cal c)	512.15	597.31	572.10	376.48
ε(cont)$(-\Delta t_c)$ / cal d)	1.03	1.02	1.15	0.74
Δu (correction to standard states) / cal e)	0.25	0.30	0.29	0.19
$-(m''\Delta u_c^\circ/M)$(polyester) / cal	58.93	58.95	67.66	67.17
$-(m'''\Delta u_c^\circ/M)$ (fuse) / cal	2.47	2.01	1.93	2.37
$\Delta u_c^\circ/$ M (compound) / cal g^{-1}	-10565.4	-10546.0	-10581.8	-10557.6
ΔH_c° (compound) / kcal mol^{-1}	-1123.10	-1121.05	-1124.85	-1122.28
ΔH_f° (compound) / kcal mol^{-1}	29.12	27.06	30.87	28.29
ΔH_f° (l) (mean) / kcal mol^{-1}	28.8 ± 0.8			
ΔH_f° (g) / kcal mol^{-1} g)	38.0 ± 1.5			

Discussion

Intramolecular Cycloaddition

The unimolecular reaction of the *endo*-isomer **1** to the tetracycle **3** may follow one of the pathways depicted in Scheme 5.

Scheme 5



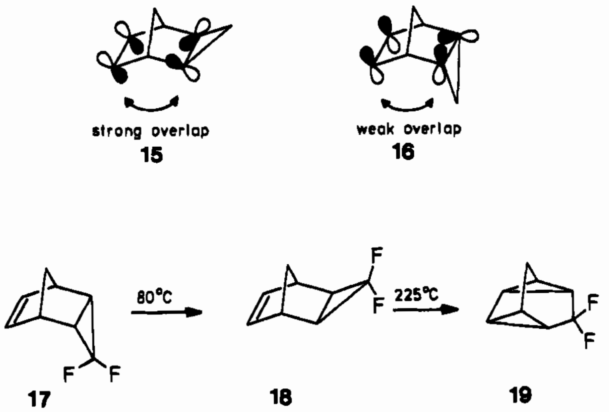
Route a and b, resp., represent the ring opening to a conformationally flexible diradical species (**2**, **13**, **5**) which may lead to the tetracyclooctane **3** in a nonconcerted (e, g) or concerted way (f). The cycloaddition – no matter which way it will choose – is associated with either the planar (**13**) or the *exo* (**5**) conformation by obvious reasons of overlap between the odd atomic orbitals and the π orbital. On the other hand, **1** and **4** may select other trajectories on the route to the thermodynamically favoured sink of the tetracycle **3**. Reaction pathway c, e.g., can be classified as tanycyclophile attack of the double bond, a term coined by Gassman and reminiscent of the underside addition of olefins to bicyclo[1.1.0]butane[23]. This route necessarily discharges into that channel leading from **5**/**13** to **3** via **14** (e,g). The *exo*-isomer **4** may possibly cycloadd directly to **3** (d). This would be the symmetry-forbidden [2σ + 2π] cycloaddition.

We will now present some arguments that support – in our opinion – the diradical mechanism (a and b) and disprove or at least argue against routes c and d.

In the first place both the forbidden attack d and the two-step underside addition c, g are strongly affected by a strong overlap between the cyclopropane bent bond and the π bond. In particular the stronger the overlap the more forbidden will reaction d be. Allowedness only comes into play by admixture of an antisymmetric component of the cyclopropane σ bond but in the ring-closed three-membered ring of **4** this doubly excited configuration is energetically too far away to play any important role.

This stronger overlap in the *exo*-isomer **4** compared with **1** has indeed been proved experimentally. A photoelectron spectroscopic study of **1** and **4** disclosed without any doubt that the *exo*-positioned cyclopropane ring in **4** homoconjugatively interacts with the π orbital whereas in the *endo*-isomer **1** no such interaction can be detected[27,32] (see **15** and **16**).

Scheme 6



If such overlap is absent in the *endo*-compound **1** we anticipate that the tanycyclophilic attack of the double bond will be highly disfavoured. A nice experiment confirming this hypothesis has been carried out by Jefford et al.[9]. The difluoro derivative **17** rearranges smoothly to the *exo*-isomer **18** at 80°C before cyclizing to the tetracycle **19** at 225°C. This means that the tanycyclophilic attack requires much more activation energy (because of bad overlap) than the cleavage of the cyclopropane bond with reclosure to the more stable *exo*-isomer (Scheme 6).

What is then the reason for the absence of *exo*-isomer **4** in the rearrengement of *endo*-isomer **1** in contrast to the *endo*-derivative **17**? If **4** had been formed it should have been detected since the half-life of **4** is sufficient under the thermolysis conditions for **1**. The answer is straightforward if the diradical mechanism a and b (Scheme 5) is accepted. In the ring-opened difluoro derivative **17** the two electrons of the singlet diradical occupy the symmetric combination φ_s (with respect to the mirror plane). The hyperconjugative influence of the C–F bonds does not suffice to raise this symmetric level and render the antisymmetric combination φ_a occupied. In the diradical **13**, however, the antisymmetric combination φ_a lies below the symmetric one and therefore is occupied[6b,c]. Thus, the cycloaddition of the 1,3-diradical **13** to the π bond is symmetry-allowed, the addition of the diradicaloid species derived from **17** is not. On the other hand, ring-closure to the epimeric *exo*-isomer requires an occupied symmetric level φ_s as can be found in the difluoro compound. This simple view of these diradicals may be refined by inclusion of configuration interaction. The wavefunction of **5** is then given approximately by[6c]

$$\psi = 1/\sqrt{2}\,(\,|\cdots\varphi_a\,\bar{\varphi}_a| - |\cdots\varphi_s\,\bar{\varphi}_s|\,)$$

This mixing imparts to diradical **5** properties of both the antisymmetric and the symmetric level.

We are now in a position to answer two of the above mentioned questions (a and b): The higher reactivity of the *endo*-isomer **1** is not associated with a stronger forbiddenness in **4** but has to be accounted for by a higher ground-state energy of the *endo*-isomer **1**.

The observed difference in ΔH_f° amounts to $\Delta\Delta H_f^\circ = 33.4$ kJ mol^{-1} (8 kcal mol^{-1}), the *exo*-compound being the more stable isomer (Tables 5 and 6). It has to be noted that $\Delta H_f^\circ(4) = 213.2$ kJ mol^{-1} (51.0 kcal mol^{-1}) equals the value derived from the strainless Benson increments[33] plus the strain energies of cyclopropane[34] and norbornene[35]:

$$\Delta H_f^\circ(4)_{calc.} = 0.56 + 27.6 + 22.4 = 50.5\,\mathrm{kcal\,mol^{-1}}$$
$$(211.3\,\mathrm{kJ\,mol^{-1}})$$

We infer from this result that the *exo*-isomer **4** does not possess any "extra" strain whatsoever. This assumption is supported by the MM2[36] calculated heat of formation for **4** (Table 9).

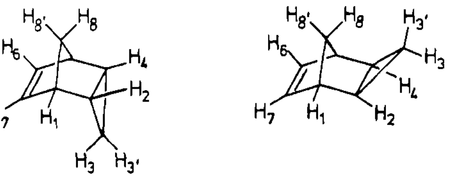
Table 9. Calculated (MM2[36]) and observed (Tables 5−8) heats of formation (gas, 25°C) and strain energies in kJ mol^{-1} (kcal mol^{-1})

	ΔH_f° (strainless)	ΔH_f° (MM2)	ΔH (strain)	ΔH_f° (obs)
1	-11.16 (-2.67)	222.50 (53.23)	233.66 (55.90)	246.6 (59.0)
3	-97.93 (-23.43) -97.93 (-23.43)	254.22 (60.82) 159.8 (38.23)[a]	352.16 (84.25) 257.69 (61.65)	179.7 (43.0)
4	-11.16 (-2.67)	217.02 (51.92)	228.18 (54.59)	213.2 (51.0)
6	74.98 (17.94)	141.74 (33.91)	66.75 (15.97)	158.8 (38.0)

[a] Modified MM2 version for use on cyclopropane derivatives[37].

Inspection of molecular models of **1** and **4** reveals a remarkable feature. In the *endo*-isomer **1** the torsional situation along the C1−C2 (or C5−C4) bond is virtually eclipsed (1H−C1−C2−2H, C7−C1−C2−C3, C8−C1−C2−C4) when taking into account the bent-bond character of the banana bonds. In the *exo*-isomer **4**, however, a staggered arrangement of the respective bonds prevails (Scheme 7).

Scheme 7



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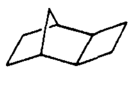

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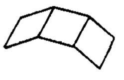

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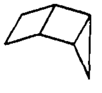
23



24

25

The non-bonding interaction 3H′-8H in **4** is of minor importance (0.89 kcal mol^{-1}). The amount of the corresponding interaction 3H-π in the *endo*-compound **1** is unknown but very probably not negligible. Altogether it is clear that **1** suffers more from torsional ground-state strain than **4**. Force-field MM2 calculations agree with this prediction (Table 9) but underestimate the $\Delta\Delta H_f^\circ$ difference which is obtained by the calorimetric studies (Table 9). We are unable at present to account for this but it has to be pointed out that there are difficulties with cyclopropane rings in MM2 calculations (see below). A similar difference in ΔH_f° to that found for the pair **1**/**4** has been calculated by v. R. Schleyer et al.[38] for the *endo-exo* pair **20**/**21**: 20.1 kJ mol^{-1} (4.8 kcal mol^{-1}). We recently determined $\Delta\Delta H_f^\circ$ = 24.2 kJ mol^{-1} (5.8 kcal mol^{-1}) for **22**/**23**[39]. Roth et al.[40] succeeded in obtaining ground-state energies for **24**/**25**, and the difference $\Delta\Delta H_f^\circ$ = 35.5 kJ mol^{-1} (8.5 kcal mol^{-1}) is in excellent harmony with our calorimetric difference for **1**/**4**.

The transition state for pathway **1**→→**3** is located at an energy higher by 5 kcal mol^{-1} than that for the rearrangement of **4**→→**3**. Although smaller this difference corresponds to the ground-state energy difference. It can therefore be concluded that the transition state structures are not near the flattened diradical **13** but are best represented by **2** and **5**, respectively. These *endo*- or *exo*-conformations then ensure that the transition states retain part of the strain energy difference of the molecular ground-states.

It has been argued that the absence of the more stable *exo*-isomer in the thermolysis of **1** is completely in conformity with the diradical pathway, but there is still a possibility that **1** could be an intermediate in the rearrangement of **4**. From a steady state analysis we can show that at most ca. 20% of the total reaction may choose this channel:

For $\mathbf{4} \xrightarrow{k_u} \mathbf{1} \xrightarrow{k_v} \mathbf{3}$,

at steady state $[\mathbf{1}]/[\mathbf{4}] = k_u/k_v$ and (from Tables 2 and 3)

$$(k_u/\mathrm{s^{-1}}) = 10^{(13.73-(49.10\,\mathrm{kcal\,mol^{-1}})/RT\,\ln 10)}$$
$$(k_v/\mathrm{s^{-1}}) = 10^{(13.99-(45.64\,\mathrm{kcal\,mol^{-1}})/RT\,\ln 10)}$$

we obtain

$$[\mathbf{1}]/[\mathbf{4}] = 10^{(-0.26-(3.46\,\mathrm{kcal\,mol^{-1}})/RT\,\ln 10)}$$

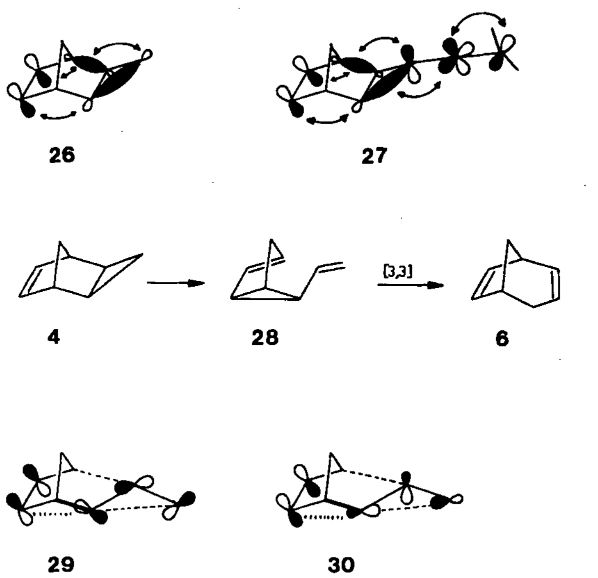
and at 593.1 K : $[\mathbf{1}]/[\mathbf{4}] = 0.030$.

Thus 3% **1** should have been detected according to such a mechanism. From the limit of detection (≤0.5%) therefore only a minor portion (≤20%) of **4** may react in this way.

Formation of Diene 6

The formation of diene **6** from **1** and **4** displays some remarkable differences. Whereas in the case of **4** the rearrangement to diene **6** constitutes a predominant part of the total reaction, it is of minor importance in the thermal reorganization of **1**. Secondly, diene **6** is formed from **4** with the same activation energy as tetracyclooctane **3**, but with a considerable higher reaction rate. This, of course, has to be traced back to the higher frequency factor observed for diene formation ($10^{14.7}$ vs. $10^{13.7}$). It is clear that this result has implications for the mechanism. Kinnel and Freeman[19] strongly advocate a concerted $[2\pi_s + 2\sigma_a + 2\sigma_a]$ pathway (**26**), based on the experimental deuterium distribution in the product. This proposal is supported by the finding that the alkenylidene derivative **27**[16)] rearranges even faster than **4** showing that the cleavage of both the norbornane and the outer cyclopropane σ bond is sizeably enhanced by the two orthogonal allenic double bonds (Scheme 8).

Scheme 8



The *A* factor of $10^{14.7}$ s^{-1}, measured for the isomerization of **4** to **6**, not only completely concurs with this concerted mechanism, but may be looked on as a final proof. Since in going from **4** to **28** there is a gain in a) one degree of freedom of internal rotation (around a single bond), b) a low frequency torsion (about the incipient vinyl double bond) and c) low frequency bending vibrations, an increase of the activation entropy ($\Delta S^{+} = 5.4$ e.u.) can reasonably be expected. In contrast to this, there is no obvious structural loosening during the $[2\pi + 2\sigma]$ cycloaddition **4**→**3**, and the *A* factor is therefore normal at $10^{13.7}$ s^{-1}.

A second aspect of this unusual $[2\pi_s + 2\sigma_s + 2\sigma_s]$ reorganization deserves attention. Whereas the simple orbital diagram **26** is sufficient to point out allowedness and stereochemistry, it does not reveal the connection with the canonical symmetry-adapted orbitals which are responsible for interactions seen in the photoelectron or electron transmission spectra of these molecules[32)]. These are outlined in **29** and **30**. An antisymmetric stretching motion brings about increasing overlap between C-7 and C-2, thereby allowing charge transfer from the occupied π level into the two low-lying orbitals of the three-membered ring with simultaneous weakening of the C2−C3 cyclopropane σ bond. It is also interesting to note that under the influence of that antisymmetric bond stretch the mixing of low-lying antisymmetric excited states with the ground-state becomes possible and leads to a reduction of the activation energy for that process (second order Jahn-Teller effect[41)]).

The formation of diene **6** from the *endo*-isomer **1** takes a different reaction pathway. Ring-opening to the diradical **13** (estimated heat of formation 94 kcal mol^{-1} according to Benson increments) is followed by a 1,2-H shift. From the measured activation energy $E_a = 48.6$ kcal mol^{-1} and the estimated ΔH_f° (**13**) ≈ 94 kcal mol^{-1} we conclude that the activation energy of the 1,2-H migration in the diradical **13** is about 14 kcal mol^{-1}.

Formation of Diene 6 from 3

A priori, the possibilities for this diene formation are: a) cycloreversion to diradical **13** followed by 1,2-H shift, b) cycloreversion to *endo*-isomer **1** followed by ring-opening to **13** and 1,2-H migration, and c) cycloreversion to *exo*-isomer **4** followed by the reaction sequence discussed in Scheme 9. It is relatively easy to differentiate between these alternatives. Since it was shown in the preceding section that the 1,2-H migration crosses a saddle-point located at 59 + 48.6 = 107.6 kcal mol^{-1}, the activated complex involved in the thermolysis of **3** (43 + 58.7 = 101.7 kcal mol^{-1}) cannot be identical with that species. Thus, routes a) and b) can safely be excluded. Proposal c), however, is nicely reconciled with the saddle-point energies for $\mathbf{3}^{+}$ (101.7 kcal mol^{-1}) and $\mathbf{4}^{+}$ (100.8 kcal mol^{-1}). The microscopic reverse pathway thus proceeds via the *exo*-isomer **4**, completely in accordance with our view that it is the *exo*-geometry which leads to a least-motion $[2\pi + 2\sigma]$ cycloaddition. Using the steady-state approximation for the sequence

$$3 \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} 4 \xrightarrow{k_b} 6$$

we obtain

$$[4]/[3] = k(3)_{obs}/k_b$$

At 663.8 K this ratio is (Tables 1 and 4)

$$[4]/[3] = 0.011$$

and therefore only very small quantities of **4** are to be expected (i.e. at the detection limit).

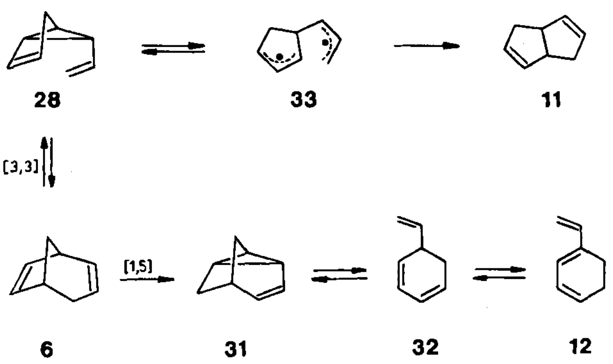
The heat of formation of **3** is 43 kcal mol^{-1}. The calculated value (MM2) amounts to 60 kcal mol^{-1}. Applying the modified parameters suggested by Ivanov[37)], a far better result is obtained: 38 kcal mol^{-1}. Even better values are calculated using the force-field developed by Lindner[42)]: 43 kcal mol^{-1}.

Thermolysis of Diene 6

Two primary processes are open to the thermal reorganization of **6**: the formation of tetrahydropentalene **11** and vinylcyclohexadiene **12**. Klumpp et al. suggested a reversible Cope-rearrangement as pathway for the formation of **11** and a 1,5-H shift as first step on the route to **12**[29)]. Roth et al. showed that **31** equilibrates with **12** and **32** above 250°C[43)].

Recalling the discussion of the *A* factor in the rearrangement of **4**, a value of ca. 10^{15} is expected for **6**→**28**. On the other hand, the direct fission to diradical **33** cannot be dismissed. The activation energy is in agreement with a bond cleavage facilitated by twice the allylic resonance energy and the release of the strain of bicyclo[3.2.1]octadiene **6**.

Scheme 9



The low activation energy $E_a = 48.3$ kcal mol^{-1} for the rearrangement to vinylcyclohexadiene **12** is not compatible with a CC bond fission to a diradical. Both the A factor and the activation energy are, however, in conformity with a mechanism consisting of a primary 1,5-H homodienyl shift with subsequent cleavage of the tricycle **31** to a vinyl-substituted cyclohexadiene.

The heat of formation of **6** is in very good agreement with the value derived from the heat of hydrogenation, 37 kcal mol^{-1}[44]. Force-field calculations (MM2) afford a slightly lower value.

Retro-Diels-Alder Reaction

The fragmentation of **1** into cyclopentadiene (**7**) and propyne (**8**) (Table 2) has an activation energy higher than the corresponding cycloreversion of *endo*-5-methylnorbornene (44.4 kcal mol^{-1}[45]) but of the same order of magnitude as the cleavage of norbornadiene into cyclopentadiene and acetylene[46]. Cyclopropene, the initial product, is not stable under the reaction conditions but rearranges to propyne with an activation energy $E_a = 37.31$ kcal mol^{-1}[47].

The determination of the Arrhenius parameters was not possible in the case of the *exo*-isomer **4** on account of too small product quantities.

Potential Energy Hypersurface for C_8H_{10} Hydrocarbons

Figure 1 presents the determined hypersurface and summarizes the energetics of ground and transition states as worked out in this and other studies. The diradical heat of formation is calculated by the methods of thermochemical kinetics[33] and is found to lie satisfactorily 6–10 kcal mol^{-1} below those of the transition states. Other heats of formation were either taken from the literature or estimated.

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Experimental

Kinetic Studies: Experiments were carried out in a conventional high vacuum static pyrolysis system[28] with greaseless Teflon-glass stopcocks and salt bath thermostat (47% $NaNO_2$, 53% KNO_3), whose temperature was controlled to ± 0.05°C. The handling line and product sample transfer bulbs were all heated to ca. 70°C to minimize handling losses by adsorption. Most runs were carried out in a cylindrical reaction vessel of volume ca. 100 ml and surface-to-volume ratio of 0.7 cm^{-1}; to test for surface activity a packed vessel of surface-to-volume ratio of 13.3 cm^{-1} was used. Both vessels were conditioned prior to use by three exposures to hexamethyldisilazane. Initial pressures of 2–4 Torr (266.64–533.28 Pa) were employed.

Product analyses were carried out by GLC (Perkin-Elmer F22, FID) using a 50 m capillary column of silicon oil MS550 operated at 80°C with a carrier gas (N_2) pressure of 1.03 bar (103 kPa). Under these conditions retention times (in min) for observed products were as follows:

a) Products of **1** (column temp. 80°C): propyne (**8**) 15.8, cyclopentadiene (**7**) 17.5, bicyclooctadiene **6** 34.8, *endo*-isomer **1** 36.9, unknown product X 41.6, tetracyclooctane **3** 47.0. b) Products of **4** (column temp. 70°C): propyne (**8**) and ethylene (**9**) 15.1, cyclopentadiene (**7**) 17.5, benzene (**10**) 22.1, bicyclooctadiene **6** 40.1, *exo*-isomer **4** 41.1, tetrahydropentalene **11** 42.0, tetracyclooctane **3** 56.4, vinylcyclohexadiene **12** 58.0.

Combustion Calorimetry: Experimental procedures involving the aneroid isoperibolic calorimeter have been described previously[48]. The temperature was measured by a quartz thermometer (Hewlett-Packard HP 2804 A). A desk top computer (Hewlett-Packard HP 9815 A) was used to start the ignition (u_{ign} 0.36 cal) automatically and perform all calculations to process the calorimetric data[30]. A set of 6–8 calibration runs with benzoic acid (National Bureau of Standards sample 39 i) was interspersed within the series of runs. The steel bomb (internal volume 0.0445 dm^3) equipped with a pla-

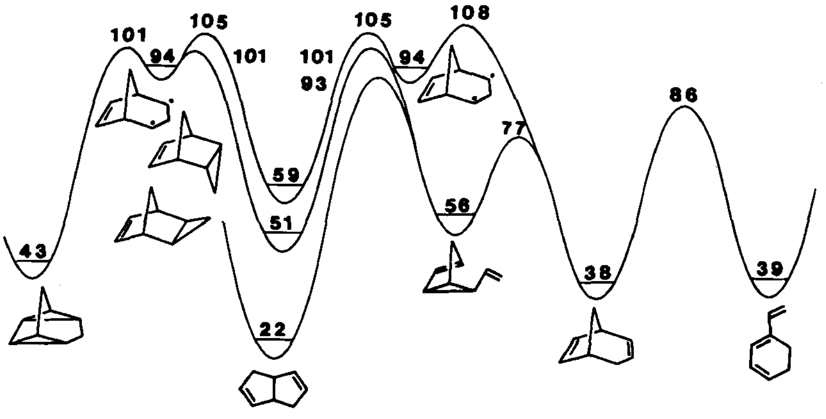

Fig. 1. Energy hypersurface for a selection of C_8H_{10} hydrocarbons. Energies in kcal mol^{-1}

tinum crucible (2.19 g) was flushed and charged to 30.0 atm (25°C) with ultrahigh-purity O_2. After this procedure the bomb contained m^i (H_2O) 0.23 g. The volatile compounds were sealed in small terephthalic acid polyester (Mylar; du Pont) bags by soldering iron[48], to avoid touching the film. Since the film is slightly hygroscopic its weight was corrected[31] via $m_{dry} = m\,[1 - 4.6_2 \times 10^{-6}\,x$ (relative humidity in %)].

All data reported are based on the 1976 IUPAC atomic weights[49] and fundamental constants[50]. For use in reducing weights in air to in vacuo, in correcting the energy of the actual bomb process to the isothermal bomb process, and in correcting to standard states[30] the following values were used (estimated values in parentheses).

Polyester film ($C_{10}H_8O_4$), ϱ 1.38 g cm^{-3}, c_p 0.315 cal g^{-1} K^{-1}, $(\delta V/\delta T)_p$ 10^{-7} K^{-1}, $\Delta u_c^\circ = -5479.7$ cal g^{-1}.

Fuse ($C_{1.0}H_{1.774}O_{0.887}$), ϱ 1.5 g cm^{-3}, c_p 0.4 cal g^{-1} K^{-1}, $(\delta V/\delta T)_p$ 10^{-6} K^{-1}, $\Delta u_c^\circ = -4050$ cal g^{-1}[31].

1 (C_8H_{10}), ϱ 0.88 g cm^{-3}, c_p 0.32 cal g^{-1} K^{-1}, $(\delta V/\delta T)_p$ 10^{-6} K^{-1}
3 (C_8H_{10}), ϱ 0.86 g cm^{-3}, c_p 0.32 cal g^{-1} K^{-1}, $(\delta V/\delta T)_p$ 10^{-6} K^{-1}
4 (C_8H_{10}), ϱ 0.95 g cm^{-3}, c_p 0.32 cal g^{-1} K^{-1}, $(\delta V/\delta T)_p$ 10^{-6} K^{-1}
6 (C_8H_{10}), ϱ 0.92 g cm^{-3}, c_p 0.38 cal g^{-1} K^{-1}, $(\delta V/\delta T)_p$ 10^{-6} K^{-1}

Materials: Compounds were prepared according to literature procedures[51].

CAS Registry Numbers

1: 3635-94-7 / **3**: 765-72-0 / **4**: 3635-95-8 / **6**: 4096-95-1

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