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STRAINED CYCLOALKENYNES

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Abstract—Presently known strained cycloalkynes with one, two or three additional *cis*- or *trans*-configurated double bonds are summarized in Table 3. The main topics of this article are the geometrical ring strain, the preparation or *in situ* generation of these compounds by fragmentation of the corresponding 1,2,3-selenadiazoles, and the thermal isomerization processes performed at room temperature or in flash pyrolysis experiments at 440–640°.

Strained molecules have always been of special interest in chemistry because of their enhanced reactivity and their unusual physical and spectroscopical properties. About 30 years ago, Blomquist and co-workers succeeded in the syntheses of the first strained cycloalkynes: cyclononyne[1] and cyclooctyne.[2] Since that time a lot of stimulating work has been done in this field and a series of new highly strained cycloalkynes has been investigated.[3]

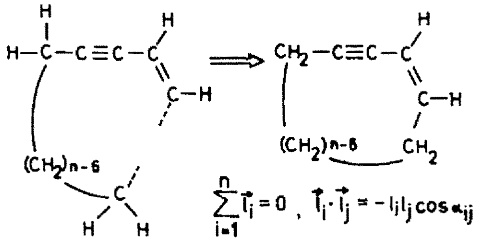
Our own efforts are mainly directed towards cyclic alkynes with additional *Z*- or *E*-configurated double bonds. Although there are some naturally occurring macrocyclic enynes,[4,5] the literature about strained, as well as about unstrained cycloalkenynes, is rather limited. A survey of strained systems, including this paper, is given in Table 3.

Ring strain

An undistorted triple bond requires four linearly arranged carbon atoms. Obviously, this condition can only be fulfilled in cyclic systems if the ring size is large enough.

Otherwise, strain is introduced into the molecule: bond lengths, bond angles, torsional angles, Van der Waal's interactions, etc. are influenced. The strain energy is manifested in the difference of these parameters in comparison to standard values. Of course, the strain is distributed over the whole molecule in such a manner that the strain energy is minimized. We may have a single energy—lowest, non-chiral conformation on the energy hypersurface of the ground state or two enantiomeric conformations, but there are also examples in which at least two energetically similar diastereomeric conformations participate in the ground state.[6]

The force constant for the angle bending at the triple bond is relatively low, so that a significant part of the deformation is always localized in these angles.[7] How much strain can be "delivered" from the triple bond depends on the other ring members. Olefinic double bonds are fairly rigid in comparison to the more flexible $CH_2—CH_2$ link and therefore generally cause an increase in the strain. Furthermore, the configuration of the double bonds plays an important role. Normally the *E*-configuration is much more unfavourable than the Z-configuration, but there are exceptions. In order to comprehend the ring strain more in detail let us take for example a (*Z*)-1-cycloalken-3-yne. A chain of *n* carbon atoms, built up in a way that all bond lengths *l* and all bond angles α correspond to standard values, is to be closed to a ring system.



$$\sum_{i=1}^{n} \vec{l}_i = 0\ ,\ \vec{l}_i \cdot \vec{l}_j = -l_i l_j \cos \alpha_{ij}$$

Applying the standard values $|\mathbf{l}_i| = l_i$ for the bond lengths and α_{ij} for the angles between neighbouring bonds *i* and *j*, the crucial question is whether or not the vector addition has at least one solution equal to zero. This is a simple mathematical criterion for what we call *geometrical strain*. All non-covalent interactions are neglected in this model.

The strain energy E_g of a certain conformation can be defined as the sum of deformation energies which are caused by changes of the bond lengths Δl_i, the bond angles $\Delta\alpha_{ij}$ and by torsions of the double and triple bond

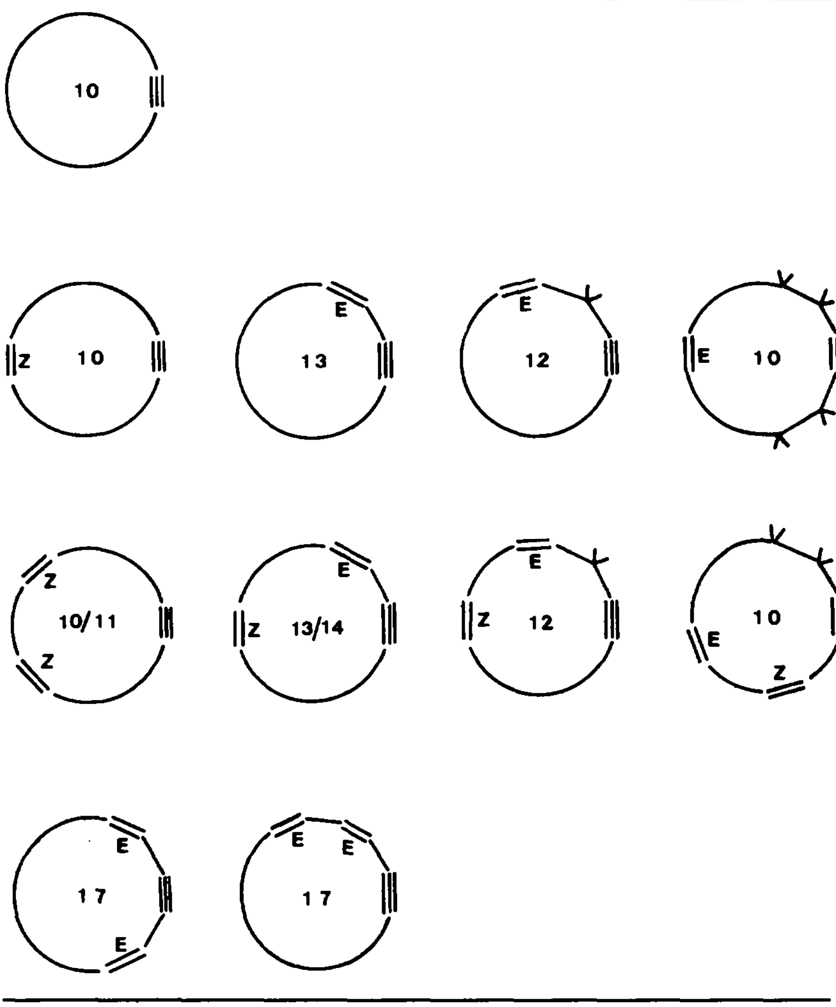
$$E_g = f(\Delta l_i, \Delta\alpha_{ij}, \theta_i).$$

Additional consideration of all interactions of atoms or groups not directly bonded to each other leads to the total sum of steric energy, as a function of the increments of the bond lengths and bond angles, of all torsion angles and all Van der Waal's interactions

$$E_{st} = f(\Delta l'_i, \Delta\alpha'_{ij}, \theta'_i, r_i).$$

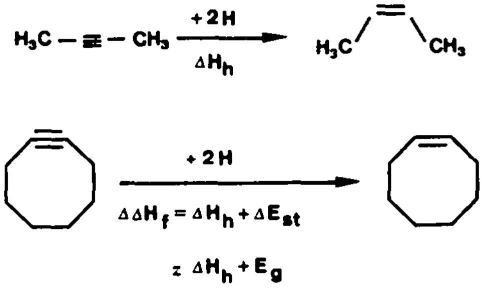
A lot of different algorithms have been used in force field theory, furnishing different values for the ring strain.[8] E_g is always a part of E_{st} and is the most important part. Molecules like cyclooctane or (*Z*)-cyclooctene also possess steric energy. Geometrical strain is confined in the 8-membered ring series to, e.g. (*E*)-cyclooctene and to cyclooctyne, that means to systems which are strained in a sense organic chemists use in view of the chemical behaviour. A survey of the different cycloalkenyne types and their individual limit for $E_g = 0$ is given in Table 1. The parent compounds, the cycloalkynes, have $E_g = 0$ for $n = 10, 11, \ldots$; i.e. cyclononyne and the lower homologues possess geometrical strain. The limit 10 is not changed by the

Table 1. Geometrical strain in cycloalkynes, cycloalkenynes and cycloalkadienynes: the numbers indicate the lowest ring size *n* for which $E_g = 0$ is valid



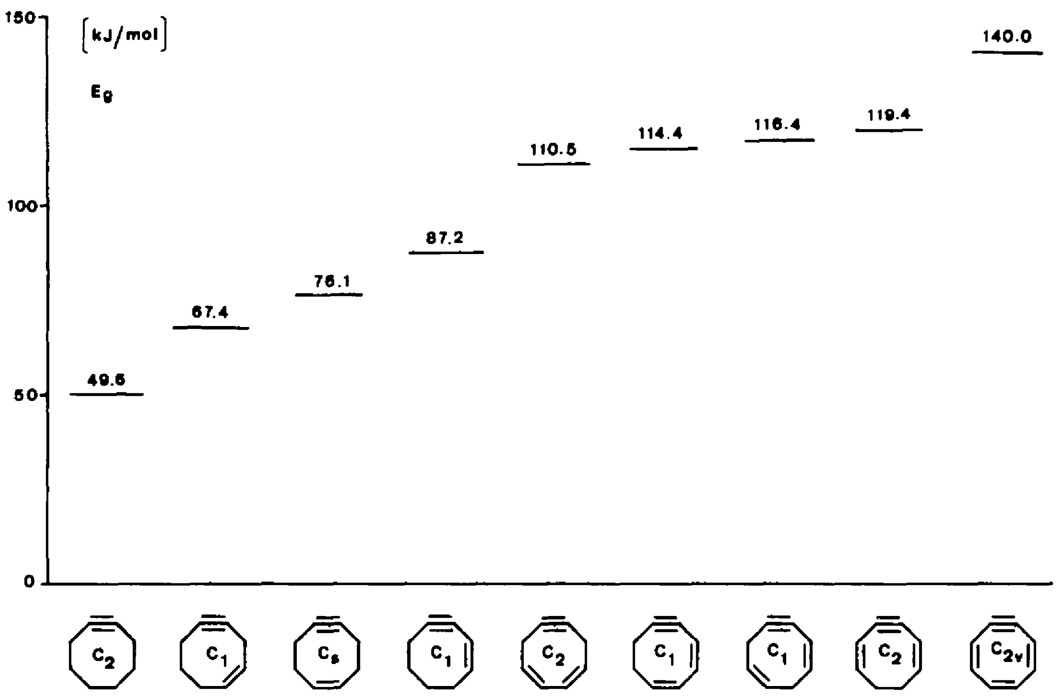
introduction of a *Z*-configurated double bond in any position in the ring. However, an *E*-configurated double bond raises the limit for $E_g = 0$ to $n = 13$ in the conjugated system and to $n = 12$ in the homoconjugated system. The introduction of two *Z*-configurated double bonds is, depending on their position, free of strain in a 10- or 11-membered dienyne ring. The limit is changed again if one of them has an *E*-configuration. Two *E*-configurated double bonds neighbouring a triple bond (either one on both sides or both on one side) lead to the limit $n = 17$. Table 1 reveals that macrocyclic ring systems can also be considerably strained if certain building blocks are present.

A quantitative evaluation of E_g is possible on the basis of the enthalpies of formation. The hydrogenation of 2-butyne to (*Z*)-2-butene is combined with an enthalpy of hydrogenation ΔH_h. The difference of the enthalpies of formation of cyclooctyne and (*Z*)-cyclooctene is larger than this ΔH_h. The excess is due to the difference of steric energies. Since all interactions of atoms not directly bonded to each other are very similar in both 8-membered rings, ΔE_{st} is a good approximation for the geometrical strain of cyclooctyne.



Applying semiempirical quantum mechanics—originally MINDO/2,[9] later on MNDO,[10] we have calculated the ΔH_f-values of cyclooctyne, the three isomeric (*Z*)-cyclooctenynes,[11] the four isomeric (*Z*,*Z*)-cyclooctadienynes[12] and finally of cyclooctatrienyne (1,2-didehydrocyclooctatetraene). All geometries have been fully optimized. The point group of the lowest energy conformation is indicated in each formula of Table 2. As mentioned above, the E_g-values are estimated by comparison with the calculated ΔH_f-values of the corresponding cycloolefins ((*Z*)-cyclooctene, . . . , 1,3,5,7-cyclooctatetraene). The E_g-values increase gradually on the introduction of one,

Table 2. Geometrical strain energies E_g in the 8-membered ring series

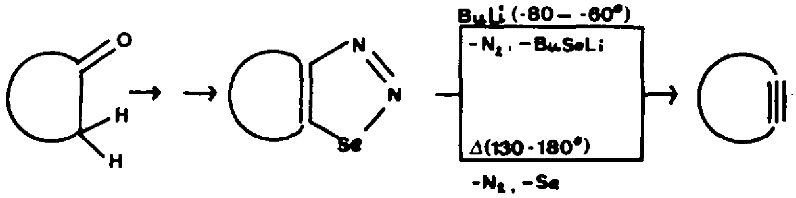


two or three double bonds. The effect is very strong. In cyclooctyne we have an E_g-value of about 50 kJ mol^{-1}; on the other end of the diagram the value is almost three times higher! Experimental thermochemical data for cycloalkynes are rare;[3,13] nevertheless, for cyclooctyne the experimentally determined E_g of 54 kJ mol^{-1} agrees satisfactorily.

Generation

Until now, mainly three methods have been applied for the generation of the known strained cycloalkenynes (Table 3). The common feature is that the triple bond is always introduced in the final step, either by dehydrohalogenation (**3**,[14] **4**,[15-17] **12**,[18-24] **13**,[25] **14**,[26,27] **15**,[28] **16**,[28] **17**,[29] **18**)[29,30] or by oxidation of 1,2-dihydrazones and 1-amino-1,2,3-triazoles (**7**,[31] **11**,[32,33] **12**)[34] or by fragmentation of 1,2,3-selenadiazoles (**1**, **2**, **5**–**10**, **20**, **21**).

We have especially elaborated the selenadiazole method. An α-methylene ketone is transformed by way of the semicarbazone to the corresponding 1,2,3-selenadiazole, which is cleaved by the action of strong bases like n- or t-BuLi or by thermolysis.



The BuLi method works very well for cyclooctyne and cycloalkynes with similar ring strain.[35] Nevertheless, it is often necessary to quench the reaction immediately in order to avoid contact of BuLi still present and the generated cycloalkyne. In the case of extremely highly strained systems the corresponding 1,2,3-selenadiazoles have to be cleaved by a bulk pyrolysis on Cu powder or by a flash pyrolysis in the gas phase. Table 4 reviews these processes.

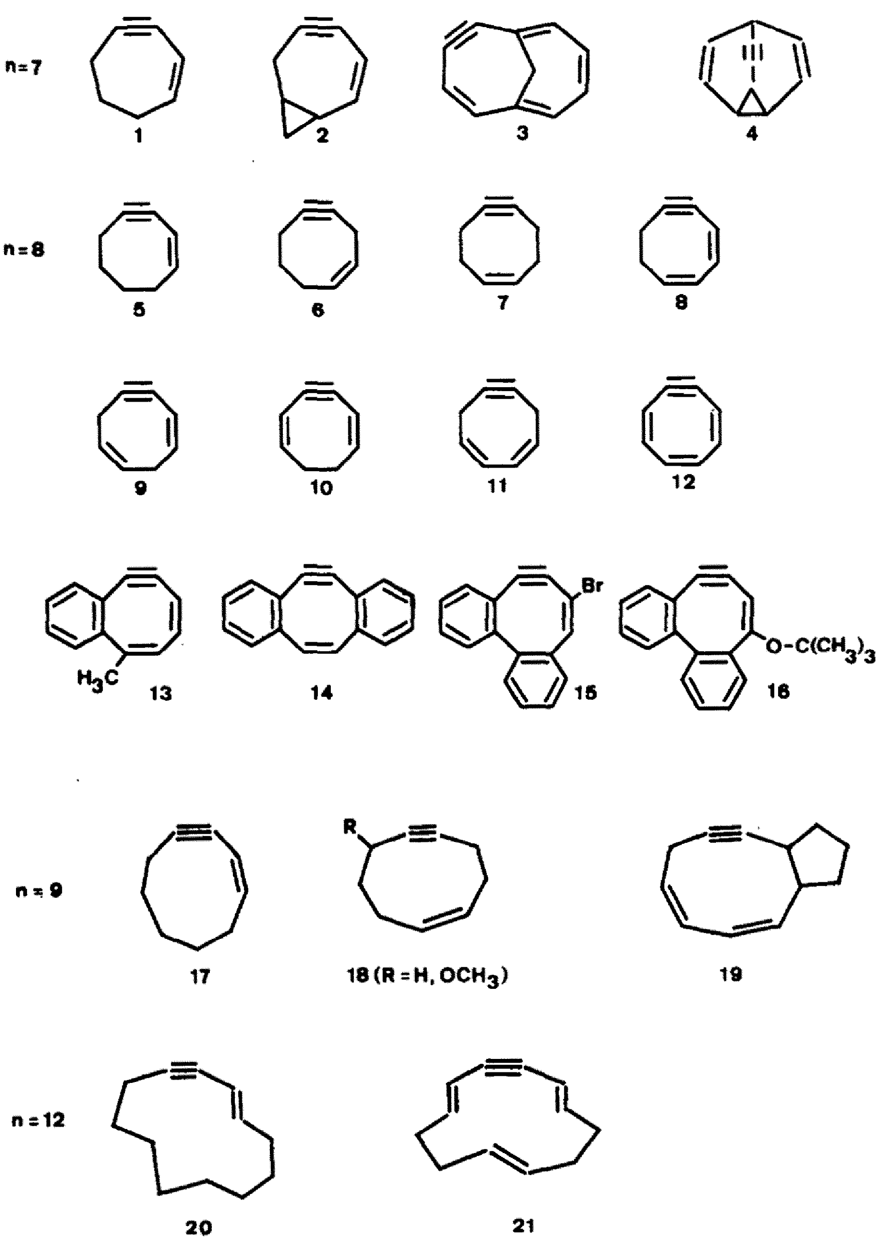
There is no direct relation between E_g or E_{st} and the half-life; nevertheless, the more strained a cycloalkyne is, the less likely is its isolation.

The half-life of strained cycloalkynes is often reduced by isomerization reactions and/or by di- and oligomerizations. Of the compounds in Table 3, the monoenynes **5**–**7**, **14**, **17**, **18** and **20** and the dienynes **10**, **11** and **19** can be isolated at room temperature in a pure state. The 7-membered ring systems **1**–**4**, the 8-ring systems **8**, **9**, **12**, **13**, **15**, **16**, and also the 12-membered ring **21** are too short-lived for this purpose; they can only be handled in solution.

In contrast to the symmetrical cyclooctadienynes **10** and **11**[32,33,36] the unsymmetrical species **8** and **9**[37-39] cannot be isolated in a pure state; they show fast isomerization reactions. The dienyne **8** is completely transformed into benzocyclobutene and **9** mainly into styrene and a small amount of benzocyclobutene (78 : 22). Note, however, the energies of the geometrical strain are approximately the same for all four cyclooctadienynes **8**–**11** (Table 2).

(*E*)-1-Cyclododecen-3-yne **20**, the first known

Table 3. Strained cycloalkenynes, cycloalkadienynes and cycloalkatrienynes



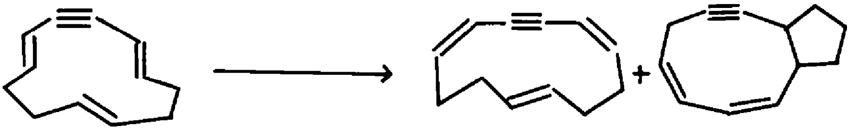
strained *trans*-cycloalkenyne,[40] can be isolated in the pure state. The half-life at room temperature is 6 h. Its geometrical strain is totally lost on rotation about the C=C bond to the *Z*-isomer. This process with an activation barrier $\Delta G^{\ddagger}_{20} = 23$ kcal mol^{-1} is very unusual for an olefinic double bond.

As a consequence of the building block of a triple bond with two adjacent *trans*-configurated double

Table 4. Generation of cycloalkenynes by fragmentation of the corresponding 1,2,3-selenadiazoles (isolated yields (%) with the BuLi method or in the bulk thermolysis and yields of the trapping reaction with tetraphenylcyclopentadienone)

	Compound									
Method	1	2	5	6	7	8	9	10	20	21
BuLi			19	50	42			trace	38	
Δ(Cu)			10	14	12		trace	10		
Δ(trapping)	12	14	58	54	60	29	64	40		40

bonds, system **21** is extremely strained.† Its isolation in the pure state is prevented by isomerization to **22**. However, the rotation about two C=C bonds demands obviously higher activation energy, so that an additional process can compete, namely the formation of the bicyclic enyne **19**.‡

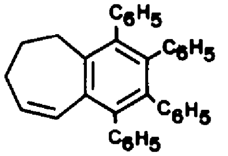


21 **22** **19**

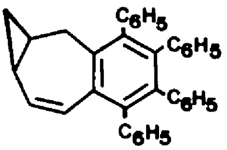
The (*Z,Z,E*)-configuration of 1,5,9-cyclododecatrien-3-yne **22** is established by the vicinal coupling constants of the olefinic protons. The structure elucidation of bicyclo[7.3.0]dodeca-2,4-dien-7-yne **19** is based on the ^{1}H- and ^{13}C-NMR data, which have been assigned by homo- and heteronuclear double resonance and INDOR experiments. The constitution of **19** is somewhat surprising because **19** itself is a strained system. The carbon skeleton of a 9- and a 5-membered ring with an incorporated triple bond reminds one of the chromophor of neocarzinostatin, a recently elucidated polypeptide antibiotic.[5]

The isomerization processes of **8**, **9**, and **21** and the oligomerization of **1** and **2** can be suppressed if the thermal fragmentation of the corresponding 1,2,3-selenadiazoles is carried out in the presence of a scavenger like tetraphenylcyclopentadienone.

Diels–Alder reactions with inverse electron request lead to the cycloadducts of the *in situ* generated cycloalkynes and tetracyclone, which lose carbon monoxide by aromatization. The yields of the adducts are listed in Table 4. Adduct **26** (44%) is only formed in the reaction of the isolated alkyne **19**.



23



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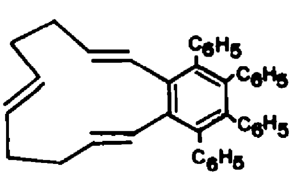

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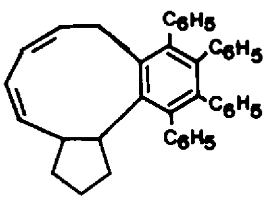

26

Strained cycloalkynes possess a higher lying HOMO, the in-plane π-orbital of the triple bond, and a significantly lower lying LUMO. In terms of frontier orbital theory these facts often serve as an explanation for enhanced reactivity. Tetracyclone is an electron-poor diene. Therefore, the LUMO (diene)–HOMO (dienophile) interaction is most important.§ In contrast to the strained systems **21** and **19**, the unstrained isomer **22** does not react with tetracyclone!

Thermolysis

By their nature, the isomerizations mentioned above are thermolytic, albeit of modest activation energy. To study processes of higher activation energies, we have performed many *flash pyrolyses* of strained cycloalkenynes. 1-Cycloocten-3-yne **5**, thermolyzed in a molecular distillation at 440° and 3×10^{-2} Torr in a quartz vessel filled with quartz chips yielded the isomers **27**–**31** in the ratio 54:12:14:6:14.

Raising the temperature to 600° favours **29** and lowering the temperature reduces the formation of **28**–**31** in favour of **27**.‖ At 300° no reaction occurs at all. There is a single primary process, namely the transformation of the triple bond into two double bonds leading to 1,3,5-cyclooctatriene **27**. A control experiment of the thermolysis of **27** under our conditions, as well as the earlier investigation of Doering and Roth[41] under somewhat modified conditions, shows that all other products can be rationalized in terms of consecutive reactions.

The isomer **32** and the valence tautomer **33** are in equilibrium with the primary product **27**, but normally they play a minor role. The formation of benzene by cleavage of **33** becomes more efficient (> 5%) only at temperatures above 550°. A conrotatory electrocyclic

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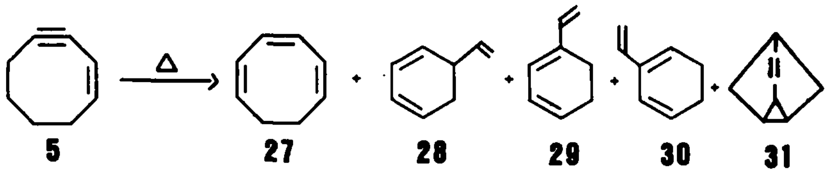
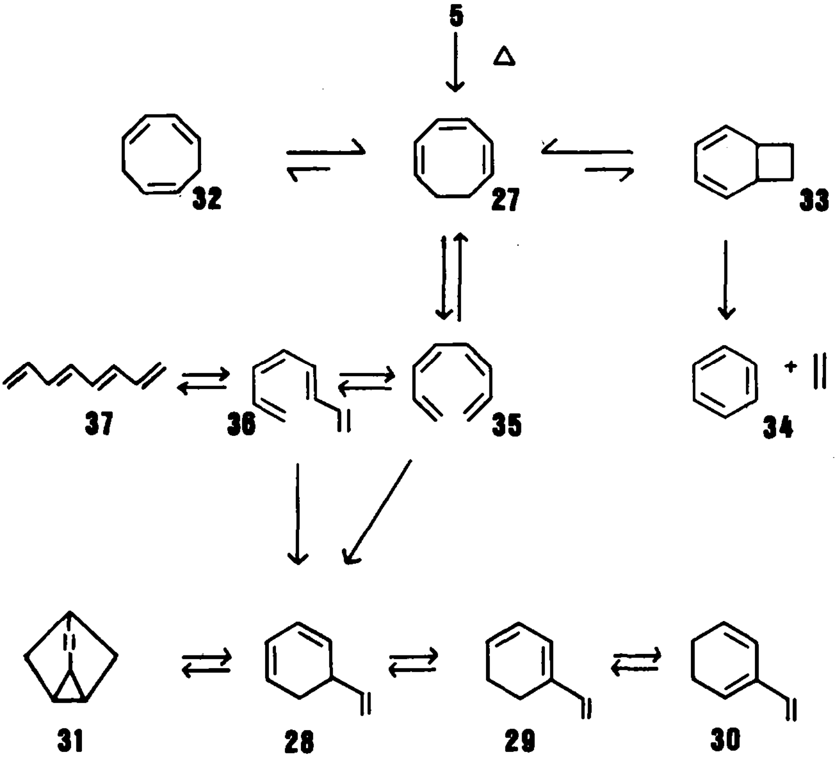
† This building block stretches the ring such that the link $—C_8—C_9{\equiv}C_{10}—C_{11}—$ on the opposite ring side would be the most suitable one. Simple model studies demonstrate that a saturated chain $—C_8—C_9—C_{10}—C_{11}—$ or a *trans*-configurated olefinic link $—C_8—C_9\overset{E}{=}C_{10}—C_{11}—$ effect a somewhat higher strain—but less than a *cis*-configurated double bond $—C_8—C_9\overset{Z}{=}C_{10}—C_{11}—$ would introduce. This is a good example that whether an additional double bond causes more strain in the *E*- or in the *Z*-configuration depends on the respective geometry of the cyclic alkyne.

‡ Additionally 1,5,9-cyclododecatriene (12%, (*EEE*):(*ZEE*) = 7:3) is formed.

§ By reason of the orbital coefficients the in-plane π-orbital of the triple bond serves here as HOMO in conjugated enynes, too. In this case the regarded HOMO lying in the reaction plane is not the absolute highest occupied molecular orbital!

‖ In the middle of this temperature range an additional C_8H_{10} isomer of unknown structure can be observed.





ring opening of **27** leads to 1,3,5,7-octatetraene with three possible configurations: **35** (*Z,Z*), **36** (*E,Z*) and **37** (*E,E*).[41] A disrotatory ring closure [π_s^6] furnishes 5-ethenyl-1,3-cyclohexadiene **28**. In reversible 1,5-H shifts 1-ethenyl-1,3-cyclohexadiene **29** and 2-ethenyl-1,3-cyclohexadiene **30** are formed.† Another reversible reaction path, an intramolecular [$\pi_s^2+\pi_s^4$] cycloaddition yields tricyclo[3.2.1.0^{2,7}]oct-3-ene. High temperatures and an increased number of collisions in the hot zone favour **29** in the so-called thermodynamic control.‡

The thermal isomerizations on the C_8H_8 energy hypersurface are of similar or even higher complexity. Therefore, only *primary* processes starting with the energetically high-lying cyclooctadienynes **8–11** and with the bicyclic alkyne **2** shall be regarded. Principally, three reaction routes can be observed:

(a) maintenance of the 8-membered ring and transformation of the triple bond into two double bonds;

(b) ring contraction to styrene, the absolute minimum on the C_8H_8 energy hypersurface;

(c) transannular C—C bond formation leading to bicyclic systems.

All three routes are exothermic. The ring strain is completely lost—or at least to a great extent. Table 5 gives a survey of these thermolyses.

Control experiments revealed that under the conditions applied here cyclooctatetraene **32** and benzocyclobutene **35** are not transformed into styrene **34**. The most interesting process is the formation of 1,2-dihydropentalene **36**. In the bulk pyrolysis on Cu powder, mentioned earlier, styrene is the main product and no trace of **36** can be detected. Obviously, the flash pyrolysis conditions (520°, 3×10^{-1} Torr) turn the reaction in another direction.

CONCLUDING REMARKS

Closely related to the cycloalkenynes discussed here are benzocycloalkenynes,[3] cyclopropanocycloalkynes,[42] cycloalkadiynes,[3,5] arynes,[36,42] didehydrotropones[44] and heteroarynes.[48] The *unusual molecular structures* and the *exceptional reactivity* are common characteristic features of these classes of compounds. The reactive centre is the bent triple bond.

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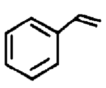
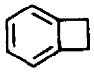
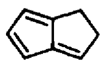
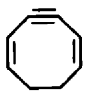
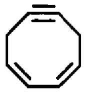
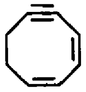
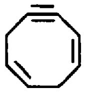
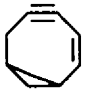
† In contrast to the thermolysis of **27**[41] a third ethenylcyclohexadiene **30** was detected and no styrene. We assume that this result is due to the different reaction conditions and not to the different starting compound.

‡ The lowest energy minimum of the C_8H_{10} hypersurface, namely ethylbenzene, is not formed, because too many bonds would have to be rearranged!

Table 5. Isomerization reactions by flash thermolysis in the series of C_8H_8 cycloalkynes, yields (%) on route a–c

	a	b	c	
	 **38**	 **39**	 **40**	 **41**
 **10**	49	51	-	-
 **11**	-	100	-	-
 **8**	-	91	9	-
 **9**	-	37	3	60
 **2**	-	88	12	-

With very few exceptions,[32] this is also true for the addition[46,47] or cycloaddition[32,37,46,48] reactions of strained cyclic enynes.

EXPERIMENTAL

IR spectra were recorded with a Perkin–Elmer spectrometer 221 or 281b. ^{1}H- and ^{13}C-NMR measurements were carried out using the Bruker spectrometers AM 400 and WH 90. MS spectra were taken on a MAT 711 A operating at 70 eV. GLC analyses were performed on a Carlo Erba apparatus F 2150 (Carbowax/Apiezon M (2 m), and SE 52 (20 m), peak integration: Hewlett–Packard 3385 A). For the GC-MS analysis the spectrometer MAT 112 S was used. Preparative GC separations were obtained with the chromatograph A PG 402 Hupe (SE 30, ϕ 18 mm). The m.ps are uncorrected.

General procedure for the generation of cycloalkynes by fragmentation of the corresponding 1,2,3-*selenadiazoles*

(a) *Butyllithium method.* 5 mmol n- or t-BuLi (15% soln in pentane or hexane) is added at −70° under N_2 and vigorous stirring to 5 mmol selenadiazole dissolved in 25 ml anhyd THF. Immediately at the end of the N_2 evolution 3 ml MeOH and 3 ml water are added and the stirring continued for 5–10 min at 0–5°. The mixture is poured onto ice and extracted three times with 50 ml pentane. The cycloalkenynes are purified by chromatography on silica gel eluted with n-pentane. The evaporation of the solvent has to be done carefully at −20° in order to avoid losses of highly volatile cycloalkenynes (for yields see Table 4).

(b) *Bulk pyrolysis.* Cu powder (5 g) is added to 5 mmol of selenadiazole dissolved in 5 ml ether. The solvent is slowly removed in a rotating flask, in order to get a uniform distribution of the selenadiazole on the surface of the Cu powder. The flask is connected to a trap, cooled to −196°, purged carefully with N_2, evacuated to 20 Torr and then immersed in a bath at 180°. As soon as the reaction starts (20–30 s), the pressure is lowered to 1 Torr. The isolated cycloalkenynes or the isomerization products are purified by column chromatography (silica gel/n-pentane, compare method a). The yields are listed in Table 4. Compounds **22** (3%) and **19** (3%) are obtained in this sequence after a fraction of 1,5,9-cyclododecatriene (12%, (*ZEE*):(*EEE*) = 3:7).

(c) *Pyrolysis in the presence of tetraphenylcyclopentadienone.* Selenadiazole (1 mmol) and 5 mmol tetracyclone are refluxed in 100 ml xylene for several hours until no more selenadiazole can be detected by TLC. Evaporation of the solvent under reduced pressure furnishes a solid residue, which is purified by chromatography on silica gel (column 3, 5 × 100 cm, toluene–petroleum ether (30–50°) 3:10). After some fast moving impurities the cycloadducts are eluted. (The excess tetracyclone remains on the column.) Recrystallization from MeOH gives analytical pure samples (for yields see Table 4).

Of course, the cycloadducts can also be prepared from the isolated cycloalkenynes. Toluene, which is refluxed towards the end of the reaction, is a suitable medium. The purification is done in the same fashion as described before. Compound **26**, the cycloadduct of **19**, can only be obtained in that way (yield 44%).

Bicyclo[7.3.0]*dodeca*-2,4-*dien*-7-*yne* **19**

Colourless liquid. ^{1}H-NMR ($CDCl_3$):† δ 1.48 (m, 2H, 10-H), 1.73 (m, 2H, 11-H), 1.90 (m, 2H, 12-H), 2.23 (m, 2H, 1-H and 9-H), 2.70 (dd, 1H, $^2J_{6,6}$ = 18.8 Hz, $^3J_{5,6}$ = 7.6 Hz, 6-H), 2.94 (m, 1H, 6-H), 5.28 (m, 1H, 2-H), 5.71 (m, 1H, 5-H), 5.91 (dq, 1H, $^3J_{4,5}$ = 11.4 Hz, 4-H), 6.00 (dq, 1H, $^3J_{2,3}$ = 11.6 Hz, 3-H). ^{13}C-NMR ($CDCl_3$):† δ 19.3 (C-6), 23.3 (C-11), 29.2/30.0 (C-10/C-12), 43.1 (C-9), 53.4 (C-1), 89.7 (C-8), 91.8 (C-7), 128.6/128.9/129.1/133.0 (C-2/C-3/C-4/C-5). MS *m/e* 157 $(M-H]^+$, 16%), 143 $(M-CH_3]^+$, 44), 130 $(M-C_2H_4]^{+\cdot}$, 96), 129 $(M-C_2H_5]^+$, 100), 128 $(M-C_2H_6]^{+\cdot}$, 66), 115 $(M-C_3H_7]^+$,

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† The assignment of the NMR signals is based on double resonance and INDOR experiments.

82), 57 ($C_4H_9^+$, 32). (Found: C, 90.85; H, 9.18. Calc for $C_{12}H_{14}$: C, 91.08; H, 8.92%.)

(1Z,5Z,9E)-Cyclododecatrien-3-yne 22

Colourless liquid. ^{1}H-NMR ($CDCl_3$): δ 2.11 (m, 4H, 8-H and 11-H), 2.37 (m, 4H, 7-H and 12-H), 5.58 (d, 2H, $^3J_{1,2}$ = 10.2 Hz, 2-H and 5-H), 5.71 (m, 2H, 9-H and 10-H), 6.03 (dt, 2H, $^3J_{1,2}$ = 10.2 Hz, $^3J_{1,12}$ = 9.2 Hz, 1-H and 6-H). ^{13}C-NMR ($CDCl_3$): δ 30.5/32.1 (C-7/C-8/C-11/C-12), 91.9 (C-3 and C-4), 110.8 (C-2 and C-5), 129.8 (C-9 and C-10), 142.9 (C-1 and C-6). MS *m/e* 158 ($M^{+\cdot}$, 26%), 143 ($M-CH_3\rceil^+$, 34), 130 ($M-C_2H_4\rceil^+$, 25), 103 ($M-C_4H_7\rceil^+$, 46), 91 ($C_7H_7^+$, 32), 86 ($M-C_6H_{12}\rceil^{+\cdot}$, 100), 79 ($M-C_7H_7\rceil^+$, 17), 78 ($C_6H_6^{+\cdot}$, 31). (Found: C, 90.75; H, 9.29. Calc for $C_{12}H_{14}$: C, 91.08; H, 8.92%.)

6,7-Dihydro-1,2,3,4-tetraphenyl-5H-benzocycloheptene 23

Trapping product of **1**. Colourless crystals, m.p. 209–212°. IR (KBr) cm^{-1}: 3030, 1600, 1495, 1440, 695. ^{1}H-NMR ($CDCl_3$): δ 2.01 (m, 2H, 6-H), 2.23 (m, 2H, 7-H), 2.52 (m, 2H, 5-H), 5.99 (m, 1H, 8-H), 6.26 (d, 1H, ^3J = 11.2 Hz, 9-H), 6.78 (m, 10H, phenyl-H), 7.10 (m, 10H, phenyl-H). MS *m/e* 448 ($M^{+\cdot}$, 100%). (Found: C, 93.44; H, 6.25. Calc for $C_{35}H_{28}$: C, 93.71; H, 6.29%.)

4,5,6,7-Tetraphenyltricyclo[9.1.0.0^{3,8}]*dodeca-3^8,4,6,9-tetraene* 14

Trapping product of **2**. Colourless crystals, m.p. 203°. IR (KBr) cm^{-1}: 3020, 1600, 1495, 1440, 1070, 1025, 750, 695. ^{1}H-NMR ($CDCl_3$): δ 0.20–0.65 (m, 2H, 12-H), 1.17–1.77 (m, 2H, 1-H and 11-H), 2.34 (dd, 1H, $^2J_{2,2}$ = 13.4 Hz, $^3J_{1,2}$ = 9.1 Hz, 2-H), 2.95 (dd, 1H, $^2J_{2,2}$ = 13.4 Hz, $^3J_{1,2}$ = 9.1 Hz, 2-H), 2.95 (dd, 1H, $^2J_{2,2}$ = 13.4 Hz, $^3J_{1,2}$ = 4.1 Hz, 2-H), 6.03 (m, 2H, 9-H and 10-H), 6.78 (narrow m, 10H, phenyl-H), 7.13 (narrow m, 10H, phenyl-H). MS *m/e* 460 ($M^{+\cdot}$, 100%), between 445 and 241 groups of signals of low intensity ($\leqslant$ 16%). (Found: C, 93.49; H, 6.05. Calc for $C_{36}H_{28}$: C, 93.87; H, 6.13%.)

(E,E,E)-7,8,11,12-Tetrahydro-1,2,3,4-tetraphenylbenzocyclododecene 25

Trapping product of **21**. Colourless crystals, m.p. 236–238°. IR (KBr) cm^{-1}: 3020, 2915, 1600, 1495, 1440, 1070, 1025, 955, 745, 695. ^{1}H-NMR ($CDCl_3$): δ 2.07 (m, 8H, 7-H, 8-H, 11-H and 12-H), 5.09 (m, 2H, 9-H and 10-H), 5.22 (dt, 2H, $^3J_{5,6} = {}^3J_{13,14}$ = 16.0 Hz, $^3J_{6,7} = {}^3J_{12,13}$ = 6.8 Hz, 6-H and 13-H), 5.95 (d, 2H, $^3J_{5,6} = {}^3J_{13,14}$ 16.0 Hz, 5-H and 14-H), 7.02 (narrow m, 10H, phenyl-H), 6.75 (narrow m, 10H, phenyl-H). MS *m/e* 514 ($M^{+\cdot}$, 100%), 486 ($M-C_2H_4\rceil^{+\cdot}$, 10), 433 ($M-C_4H_5\rceil^+$, 40), 367 (12), 355 (10), 341 (11). (Found: C, 93.17; H, 6.48. Calc for $C_{40}H_{34}$: C, 93.34; H, 6.66%.)

13,14,15,16-Tetraphenyltricyclo[10.4.0.0^{7,11}]*hexadeca-3Z,5Z,12,14,16-pentaen* 26

Colourless crystals, m.p. 232–234°. ^{1}H-NMR ($CDCl_3$): δ 1.06 (m, 1H), 1.54 (m, 1H), 1.75 (m, 3H), 2.04 (m, 1H), (8-H, 9-H and 10H), 2.72 (m, 1H, 11-H),† 3.13 (dd, 1H, $^2J_{2,2}$ = 16.2 Hz, $^3J_{2,3}$ = 9.6 Hz, 2-H), 3.41 (m, 1H, 7-H), 3.61 (d, 1H, $^2J_{2,2}$ = 16.2 Hz, 2-H), 5.18 (t, 1H, $^3J_{5,6} = {}^3J_{6,7}$ = 10.5 Hz, 6-H), 5.22 (m, 1H, 3-H), 5.76 (dd, 1H, $^3J_{5,6}$ = 10.5 Hz, $^3J_{4,5}$ = 5.3 Hz, 5-H), 5.85 (dq, 1H, $^3J_{3,4}$ = 12.5 Hz, 4-H), 6.72 (m, 10H, phenyl-H), 6.79 (m, 1H, phenyl-H), 6.87 (m, 1H, phenyl-H), 7.02 (m, 3H, phenyl-H), 7.17 (m, 5H, phenyl-H). ^{13}C-NMR ($CDCl_3$): δ 22.8 (C-2), 31.1/33.2/34.0 (C-8, 9, 10), 46.3 (C-11), 54.1 (C-7), 124.8/124.8/125.8/125.8/125.8/126.2/126.2/126.2/126.3/126.5/126.9/127.0/127.3/128.2/129.2/130.0/130.2/130.6/131.1/131.1/131.3/131.4/132.4/135.3 (C_{sp^2}—H), 135.9/137.6/139.3/139.4/140.9/141.1/141.3/142.1/142.3/142.5 (C_q). MS *m/e* 514 ($M^{+\cdot}$, 100%), 460 ($M-C_4H_6\rceil^{+\cdot}$, 16), 355 (17), 341 (21), 315 (17), 289 (11), 265 (13), 95 (18), 77 ($C_6H_5^+$, 24). (Found: C, 93.34; H, 6.66. Calc for $C_{40}H_{34}$: C, 93.34; H, 6.66%.)

The enynes **5**,[45] **6**,[45] **7**,[45] **10**[32] and **20**[40] and the tetracyclone adducts of **5**,[45] **6**,[45] **7**,[45] **8**,[37] **9**,[37] **10**[32] and **20**[40], which have been prepared by the selenadiazole method, too, are already spectroscopically characterized.

Flash thermolysis

The flash pyrolysis experiments with **5** were performed at 300–600° and 3–7 × 10^{-2} Torr in a quartz tube filled with quartz chips in order to study also secondary processes, provoked by the high number of collisions in the hot zone (350 × 29 mm). The temps, measured with a PtRh–Pt element, are controlled at the inner wall of the tube. Compound **5** and the other isolable enynes **10** and **11** are introduced by molecular distillation. An alternative possibility is to introduce the precursors, the corresponding 1,2,3-selenadiazoles, in an N_2 stream. Of course, the latter variant has to be applied for the short-lived systems **2**, **8** and **9**. In the C_8H_8 series the pyrolysis conditions were adjusted to the observation of the primary processes: **2** (480°, 3 × 10^{-1} Torr), **8** (640°, 3 × 10^{-1} Torr), **9** (520°, 3 × 10^{-1} Torr), **10** (500°, 1 × 10^{-1} Torr), **11** (490°, 1 × 10^{-1} Torr). The volatile products are collected in a trap at −196° and analysed by GLC, GLC–MS, ^{1}H- and ^{13}C-NMR spectroscopy. The identification of **27**, **32**, **34**, **38**–**41** was made by comparison with authentic samples. (The postulated intermediates **33** and **35**–**37** are in our experiments below the limit of proof).‡ Principally, compounds **28**,[41,49] **29**,[41] **30**[50] and **31**[51] are known; yet an assignment of the NMR signals completing or correcting the published data shall be given.† A preparative GLC was made for this purpose.

5-Ethenyl-1,3-cyclohexadiene 28

^{1}H-NMR ($CDCl_3$): δ 5.80–5.66 (m, 3H, 2-H, 3-H and 7-H), 5.60 (m, 1H, 4-H), 5.51 (m, 1H, 1-H), 4.89 (m, 1H, $^3J_{trans}$ = 17.2 Hz, 8-H), 4.82 (m, 1H, $^3J_{cis}$ = 10.2 Hz, 8-H), 2.78 (m, 1H, 5-H), 2.15 (m, 1H, 6-H), 1.96 (m, 1H, 6-H). ^{13}C-NMR ($CDCl_3$): δ 140.6 (C-7), 129.1/125.5/124.1/124.1 (C-1, C-2, C-3 and C-4), 113.6 (C-8), 37.3 (C-5), 28.7 (C-6).

1-Ethenyl-1,3-cyclohexadiene 29

^{1}H-NMR ($CDCl_3$): δ 6.41 (q, 1H, 7-H), 5.99–5.93 (m, 1H, 2-H), 5.89–5.83 (m, 2H, 3-H and 4-H), 5.21 (d, 1H, $^3J_{trans}$ = 17.4 Hz, 8-H), 5.03 (d, 1H, $^3J_{cis}$ = 10.7 Hz, 8-H), 2.38–2.30 (m, 2H, 6-H), 2.30–2.20 (m, 2H, 5-H). ^{13}C-NMR ($CDCl_3$): δ 138.6 (C-7), 135.6 (C-1), 127.4/124.9/124.8 (C-2, C-3 and C-4), 111.7 (C-8), 22.8 (C-6), 21.3 (C-5).

2-Ethenyl-1,3-cyclohexadiene 30

^{1}H-NMR ($CDCl_3$): δ 6.29 (q, 1H, 7-H), 6.25 (dd, 1H, 3-H), 5.99–5.93 (m, 1H, 1-H), 5.77 (dt, 1H, 4-H), 5.22 (d, 1H, $^3J_{trans}$ = 17.5 Hz, 8-H), 4.94 (d, 1H, $^3J_{cis}$ = 10.8 Hz, 8-H), 2.30–2.20 (m, 2H, 6-H), 2.20–2.11 (m, 2H, 5-H). ^{13}C-NMR ($CDCl_3$): δ 136.9 (C-7), 133.6 (C-2), 127.7/128.6/121.9 (C-1, C-3 and C-4), 110.4 (C-8), 22.7/22.4 (C-5 and C-6).

Tricyclo[3.2.1.0^{2,7}]*oct-3-ene* 31

^{1}H-NMR ($CDCl_3$): δ 5.95–5.93 (m, 2H, 3-H and 4-H), 2.56 (m, 1H, 5-H), 1.66 (m, 1H, $^3J_{2,3}$ = 4.7 Hz, 2-H), 1.60 (q, 2H, $^3J_{5,6} = {}^3J_{5,8}$ = 4.2 Hz, $^2J_{6,6} = {}^2J_{8,8}$ = 11.3 Hz, 6-H, 8-H, *exo*-position in relation to the double bond), 1.46 (d, 2H, $^3J_{1,2} = {}^3J_{2,7}$ = 7.1 Hz, 1-H and 7-H), 0.79 (d, 2H, 6-H and 8-H, *endo*-position in relation to the double bond). ^{13}C-NMR ($CDCl_3$): δ 129.1/121.9 (C-3 and C-4), 32.1 (C-5), 27.8 (C-6 and C-8), 15.7 (C-2), 13.8 (C-1 and C-7).

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