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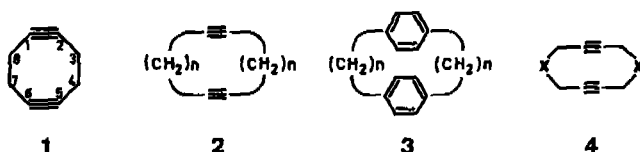
20. 1,5-Cyclooctadiyne. Preparation and Reactivity

by Else Kloster-Jensen¹⁾ and Jakob WirzPhysikalisch-chemisches Institut der Universität Basel
Klingelbergstrasse 80, CH-4056 Basel, Switzerland

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Summary. 1,5-Cyclooctadiyne **1** was isolated in 2 percent yield from polymerized butatriene **5**. Other oligomers of **5** were detected in the reaction mixture by combined GLC./MS. analysis but have not been identified. *Diels-Alder* adducts of **1** with two equivalents of 1,3-butadiene and of 2,3-dimethyl-1,3-butadiene have been prepared. In the presence of strong base **1** isomerized to cyclooctatetraene. **5** was reformed by photolysis of **1**. Attempts to prepare transition metal complexes of **1** failed. Effects of ring strain and of transannular interaction on the reactivity of **1** are discussed. The dimerization of **5** to **1** is predicted to be strongly exothermic.

The synthesis of medium-sized cyclic alkynes [1] and the investigation of their chemical reactivity as a function of geometric ring strain have been the object of considerable effort during the past twenty years. The smallest unsubstituted cycloalkyne yet isolated is cyclooctyne which was first prepared by *Blomquist* in 1953 [2]. Evidence for the intermediate existence of the lower homologues cycloheptyne, -hexyne, and -pentyne is limited to trapping and self-trapping reactions [3a].



¹⁾ Permanent address: Department of Chemistry, University of Oslo, Blindern, Oslo 3, Norway.

The first carbocyclic diyne, 1,7-cyclododecadiyne **2** ($n = 4$), was synthesized in 1956 by *Cram & Allinger* [4] in the course of their classical investigation of the related $[n.n]$ paracyclophanes **3**. The same authors attempted to prepare the lower homologue 1,6-cyclodecadiyne **2** ($n = 3$) 'in the hope that in this compound the two acetylenic functions would be forced into one another's electronic environment and would perhaps possess some cyclobutadiene-like character.' Unlike its higher homologue, however, the precursor dimethyl-5-decyne dioate failed to undergo acyloin ring closure and it is only recently that substituted derivatives of **2** ($n = 3$) have been obtained by alternative routes [5] [6]. Although the heterocyclic analogue **4** ($X = O$) has been synthesized by *Lespiau* [7] as early as 1929 this claim was not generally accepted until 1960 when *Sondheimer et al.* [8] provided rigorous structural proof for its formation. The corresponding dithio compound **4** ($X = S$) was described in 1964 [9]. Extended studies of intramolecular interactions between spatially close triple bonds have been undertaken since 1965 by the groups of *Müller* [10] and *Staab* [11].

During recent investigations of the photoelectron spectrum of butatriene **5** [12] highly purified samples were repeatedly prepared from several grams of raw product. Instead of destroying residual quantities by reaction with bromine, we found it of interest to follow the reactions of **5** in dilute solution to see if any oligomers of low molecular weight would be formed. 1,5-Cyclooctadiyne **1**, a remarkably stable crystalline compound (Fig. 1), was isolated in low yield from the largely polymeric

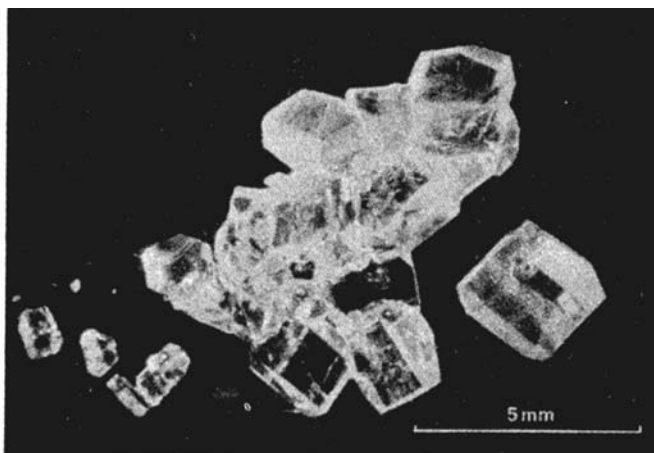
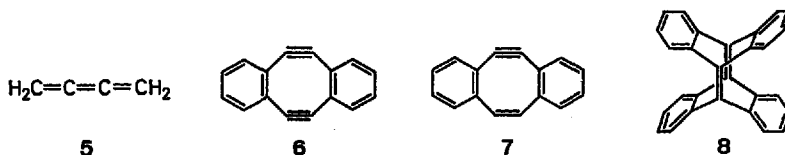


Fig. 1. Crystals of 1,5-cyclooctadiyne stored under vacuum at 0°

product²⁾. The identification of **1** has been briefly reported [13]. *Wong, Garratt & Sondheimer* [15] have now achieved the synthesis of the conjugated, 8-membered cycloalkynes *sym*-dibenzo-1,5-cyclooctadiene-3,7-diyne (**6**) and *sym*-dibenzo-1,3,5-cyclooctatriene-7-yne (**7**).



²⁾ Curiously enough, the related $[2.2]$ paracyclophane (**3**, $n = 2$) was first obtained in an analogous manner by *Brown & Farthing* [14] from polymers of *p*-xylylene.

The nonbonded approach of the π -systems in 1,5-cyclooctadiyne (**1**) to an interatomic distance of 2.60 Å (C(1)–C(6)) [16] is closer than in any of the cyclophanes known³⁾. The effects of the *cis*-bending and the transannular interaction of the triple bonds in **1**, as displayed by the photoelectron spectrum, have been discussed [18]. In this paper we describe in detail the preparation and isolation of **1**. The reactivity of **1** under various conditions has been studied in an exploratory manner. Some negative results are briefly mentioned which should, however, not be considered as definitive. These topics were not pursued any further in view of the limited quantities of **1** available at present.

Results. – 1. *Preparation and General Properties.* Since *Schubert et al.* [19] first described the synthesis of butatriene (**5**) by reaction of 1,4-dibromo-2-butyne with zinc, further investigation of the chemistry of **5** has been scarce [20–22] being restricted by its easy polymerization. Treatment with maleic anhydride, cyclopentadiene, diazoacetic ester, or phenyl azide was reported [19] to yield polymers and no clear-cut products.

5 was synthesized according to [19] using a technically modified procedure [23]. The raw material trapped in a cooled receiver on a vacuum line was found to contain considerable amounts of the slightly less volatile 2-bromo-1,3-butadiene (**9**). The same impurity appears to have been present in the sample of *Schubert et al.* as indicated by their mass spectrum [19]. Likewise, in the synthesis of **5-d₄** [12] we obtained isotopically pure C₄HD₄Br as a by-product. Pure samples of **5** were prepared by repeated fractionation at –78° on the vacuum line. Neat **5** is a water-clear liquid at –78° which polymerizes above –40° under exclusion of air. In the presence of air it is known [19] to ignite spontaneously and may cause violent explosions.

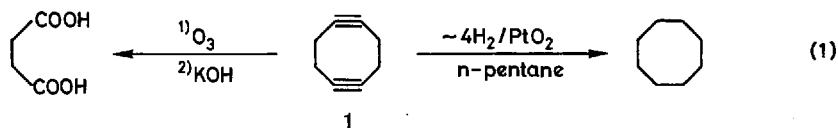
In order to favour the intended formation of oligomeric products the polymerization of **5** was performed in dilute solution under mild, controllable conditions. In a preliminary experiment, 50 ml of degassed *n*-pentane were vacuum transferred to a cooled sample of **5** (1 g). The resulting clear solution turned yellow to red on standing under vacuum at room temperature and slowly deposited a flocculent, yellow-brownish precipitate. After four days, volatiles were removed in the cold. The residue was kept under vacuum at ambient temperature. During the next days, a few transparent crystals, later identified as 1,5-cyclooctadiyne (**1**), appeared on the glass wall above the dry polymeric deposits. On the vacuum line the crystals sublimed into a cooled receiver.

The above procedure was slightly modified (Exper. Part, Procedure A) and repeated a number of times yielding around two percent of recrystallized and sublimed **1**. Variation of reaction parameters such as concentration (Procedures B, C), temperature, or solvent viscosity (Procedure D) did not give improved yields. Attempts to prepare **1** by thermal ([24], Procedure E) or photochemical ([25], Procedure F) extrusion of sulfur from 1,6-dithiacyclodeca-3,8-diyne (**4**, X = S) were unsuccessful. Irradiation of **5** at –78° with 229 nm light (Procedure G) promoted polymerization but did not yield detectable quantities of **1**. Finally, an experiment (Procedure H)

³⁾ Shorter yet is the distance between the central double bonds of 9,9',10,10'-tetrahydrodianthracene (**8**) [17] where the atoms C(9) and C(10) are only 2.42 Å apart.

aimed at the detection of any **1** which might form during the synthesis of **5** gave negative results.

The structure of **1** was tentatively assigned on the basis of its spectral characteristics given in the Experimental Part. Chemical evidence was obtained by catalytic hydrogenation of **1** which by uptake of *ca.* four equivalents of hydrogen yielded cyclooctane. Furthermore, ozonolysis of **1** followed by alkaline hydrolysis furnished succinic acid as the only isolable product. Definite proof for the structure of **1** was provided by an X-ray structure analysis by *Römming* [13] [16]. Recent diffractometer data obtained at -170° have furnished the molecular dimensions shown in Fig. 2, which are slightly different from the data in [13]. The monoclinic crystal has



2 molecules per unit cell in space group $P2_1/c$ (cell dimensions $a = 4.409$, $b = 6.688$, $c = 9.982 \text{ \AA}$, $\beta = 97.73^\circ$, $V = 291.6 \text{ \AA}^3$, calculated density 1.18 g/cm^3 , R value = 0.053). The molecule has in average a center of symmetry and the carbon skeleton is essentially planar, the average distance from the regression plane of the acetylenic and methylenic carbons being 0.02 and 0.04 \AA , respectively (Fig. 2b).

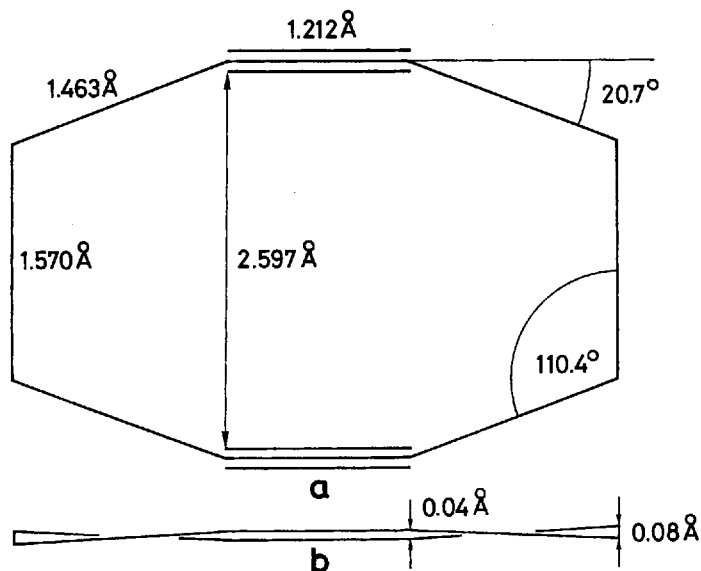
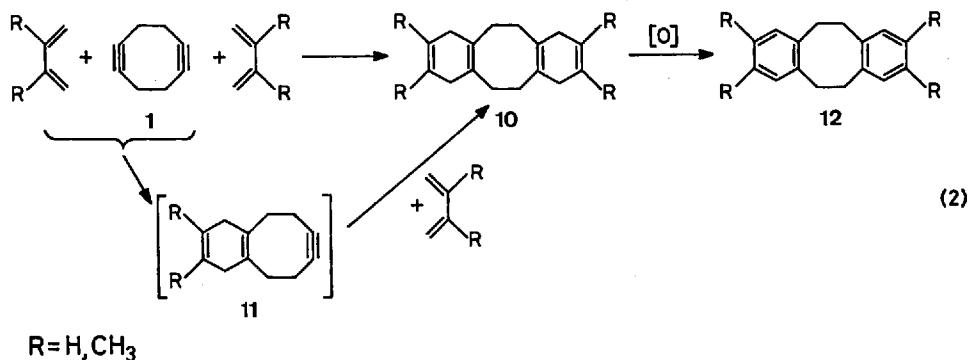


Fig. 2. Molecular dimensions of 1,5-cyclooctadiene from X-ray crystal structure determination at -170° [16]. a) Front view and b) side view of the carbon skeleton

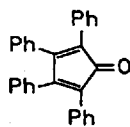
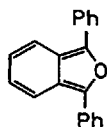
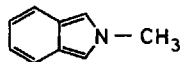
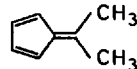
1,5-Cyclooctadiene (**1**) is a readily crystallizable solid which decomposes at 105° without melting. Its solubility in hydrocarbon solvents is surprisingly low. The latter fact allows effective purification of **1** by low-temperature recrystallization from *ca.* 1% *n*-pentane solutions. Under exclusion of air **1** is stable indefinitely at

0°. On storing, evacuated samples of **1** tend to grow to large prisms (Fig. 1). When exposed to daylight at ambient temperature for prolonged periods, the crystals take on a blue luster; in the presence of air they are rapidly covered by a white film which gradually turns black. On resublimation of **1** even after prolonged exposure to air this film is left behind as thin nearly weightless skins which keep the shape of the original crystals. Due to its characteristic, disagreeable odour the presence of **1** even in trace quantities is readily detected⁴).

2. Diels-Alder Reactions. 1,3-Butadiene as well as 2,3-dimethyl-1,3-butadiene smoothly reacted with **1** in benzene solution at 75° to form the diadducts 1,4,5,6,7,10,11,12-octahydro-dibenzo[*a,e*]cyclooctene [**14**] (**10**, R = H), and 1,4,5,6,7,10,11,12-octahydro-2,3,8,9-tetramethyldibenzo[*a,e*]cyclooctene (**10**, R = CH₃), respectively (2). Interestingly, the intermediate mono-adducts **11** could not be isolated from the reaction mixture even when **1** was present in excess of the diene. When the progress of the reaction was monitored by intermittent NMR, analysis no peaks attributable to the intermediates **11** (R = H) or **11** (R = CH₃) were detected at any time. In the presence of air the adducts **10** (R = H) and **10** (R = CH₃) oxidized to 5,6,11,12-tetrahydrodibenzo[*a,e*]cyclooctene (**12**, R = H) and 5,6,11,12-tetrahydro-2,3,8,9-tetramethyldibenzo[*a,e*]cyclooctene (**12**, R = CH₃), respectively (2).



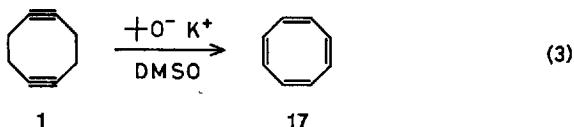
The reactivity of **1** as a dienophile was further explored by the following qualitative tests in which the diene concentration was monitored by UV./Vis. absorption spectrophotometry. Degassed benzene solutions of **1** (*c*₀ = 10⁻² M) were used in each case. Tetracyclone (**13**) (*c*₀ = 1 · 10⁻⁴ M) and 1,3-diphenylbenzo[*c*]furan (**14**) (*c*₀ = 3 · 10⁻⁵ M) were consumed with pseudo-first order rates of about 3 · 10⁻⁵ and 10⁻⁴ s⁻¹, respectively, at room temperature. The products have not been identified. N-Methyliso-

**13****14****15****16**

⁴) Tobacco appears to have a disgusting taste when smoked within some six hours after inhalation of vapours from traces of **1**. This effect was discovered independently by at least five involuntary test persons (patents pending).

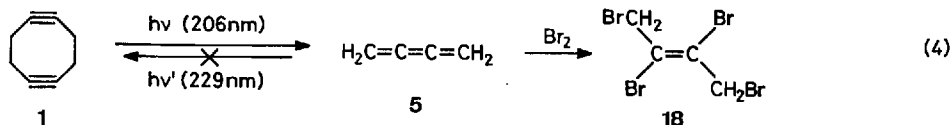
indole (**15**) ($c_0 = 4 \cdot 10^{-4} \text{M}$) and 6,6-dimethylfulvene (**16**) ($c_0 = 1 \cdot 10^{-2} \text{M}$) did not react with **1** within 24 hours at room temperature or within 5 hours at 75°.

3. *Reactions with Acid and Base.* 1,5-Cyclooctadiyne (**1**) was found to be fairly stable to both acid and base. Solutions of **1** in methanol containing 1% trifluoroacetic acid or in *t*-butyl alcohol containing 1% potassium *t*-butoxide kept unchanged for at least 24 hours at room temperature. In dry dimethylsulfoxide **1** rapidly isomerized to cyclooctatetraene (**17**) when potassium *t*-butoxide was added (3).



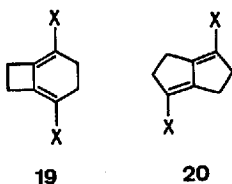
When a solution of **1** in absolute benzene was acidified with trifluoroacetic acid **1** was rapidly consumed in a complex sequence of reactions (Exper. Part) from which no products have been isolated.

4. *Photolysis.* By irradiation of a degassed solution of **1** in *n*-pentane at 206 nm **5** formed rapidly, as shown by the appearance of the characteristic UV. absorption of **5** (λ_{max} 241 nm) (4). In a preparative run the product **5** was identified as its tetrabromo derivative **18** [19] [26]. As mentioned above (Sect. 1) the reverse cycloaddition could not be induced by low temperature 229 nm irradiation of **5**. (Exper. Part, Procedure G).



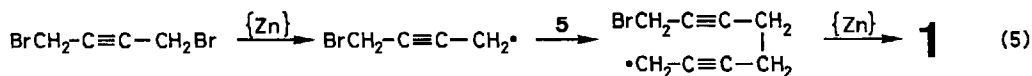
5. *Reactions with Transition Metal Complexes.* A series of exploratory experiments has been carried out reacting small quantities of **1** (ca. 5 mg each) in perdeuterio-benzene solution with the following transition metal complexes: $\text{Fe}(\text{CO})_5$, $\text{Fe}_2(\text{CO})_9$, $(\text{C}_6\text{H}_5)_2\text{Co}(\text{CO})_2$, $(\text{Ph}_3\text{P})_2\text{Ni}(\text{CO})_2$, $[(\text{PhO})_3\text{P}]_2\text{Ni}(\text{CO})_2$, and Ph_2AgBF_4 . In each case an amorphous precipitate slowly formed on warming, concomitant with the disappearance of the singlet NMR. peak of **1** but no distinct new peaks could be detected. IR. spectra of the filtered precipitates did not reveal the presence of a complex. When a 45 mg sample of **1** was heated with 2 equiv. of $\text{Fe}_2(\text{CO})_9$ in anhydrous ether, $\text{Fe}_3(\text{CO})_{12}$ (100 mg) was isolated in addition to a yellowish product (80 mg), m.p. $\sim 0^\circ$, the UV. spectrum of which exhibited a $\lambda_{\text{max}} = 240 \text{ nm}$. Attempts on recrystallization at -70° over night furnished only polymeric material.

6. *Transannular Addition Reactions.* Highly complex mixtures were obtained when bromine, iodine, dimethyl acetylenedicarboxylate, and tetracyanoethylene,



respectively, were allowed to react with **1** in benzene solution at room temperature. Conceivably, some of these reagents reacted to give transannular addition products of type **19** or **20** in a primary step. However, no identifiable products could be isolated in any case.

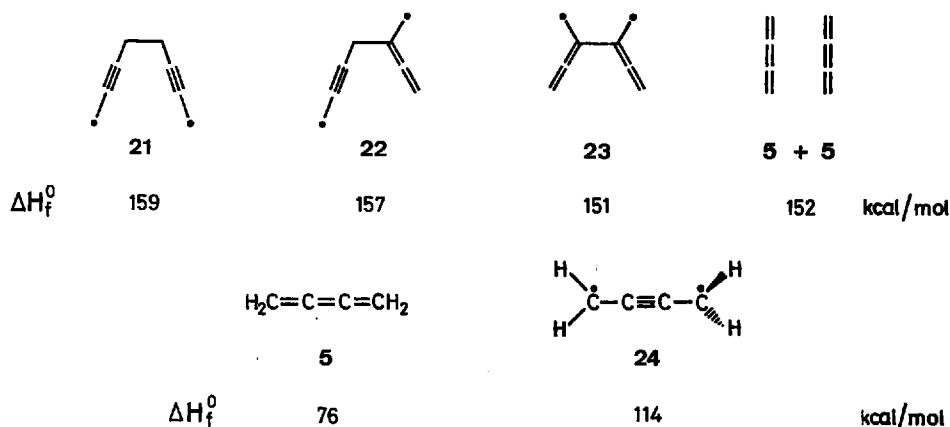
Discussion. – In our preliminary communication [13] reporting the isolation and identification of 1,5-cyclooctadiyne (**1**) the origin of the compound was not specified. It was at that time open to question whether the small amounts of **1** isolated from polymerized butatriene **5** were formed by dimerization of **5**, particularly in view of the fact that the thermal $\pi 4_s + \pi 4_s$ cycloaddition of two butatriene molecules is formally forbidden according to the *Woodward-Hoffmann* rules. As an alternative possibility, we considered the formation of **1** as a by-product during the synthesis



of **5**, *e.g.* by the pathway shown in (5). However, a search for the presence of **1** in the raw product from the preparation of **5** was negative. Also, the yield of **1** did not decrease when **5** was carefully purified prior to its polymerization. GLC./MS. analysis of the volatiles isolated from polymeric **5** revealed the presence of at least two dimers, five trimers, and three tetramers of **5**. Hence we conclude that **1**, along with other oligomers, is indeed formed during the polymerization of **5** in dilute solution.

It is evident from the structure diagram (Fig. 2) that **1** is a highly strained molecule. Moreover, the heat of formation of hypothetical strainfree **1**, as obtained by summation of the appropriate group contributions tabulated by *Benson et al.* [27], is itself rather high (91.3 kcal/mol) due to the presence of two triple bonds. For comparison, the experimentally determined [27] [28] heat of formation of the isomer cyclooctatetraene (**17**) is 71.3 kcal/mol. We may thus ask the question: Is the dimerization of **5** to **1** thermochemically feasible? In the absence of experimental data we have estimated the heats of formation of **1** and **5** by a number of essentially independent semiempirical and empirical methods which are described below. For **1** a strain energy of *ca.* 30 kcal/mol was evaluated which arises largely from the bending of the C≡C–C bond angles and the opposing transannular repulsion of the π -systems. This yields ΔH_f° (**1**) = 120 kcal/mol. Various estimates for the heat of formation of **5** fall in the range of 76 ± 3 kcal/mol. The high energy of cumulated double bonds thus provides the driving force for the reaction $\mathbf{5} + \mathbf{5} \rightarrow \mathbf{1}$ which is predicted to be exothermic by some 30 kcal/mol.

According to the *Bell-Evans-Polanyi* principle [29], the more exothermic a reaction, the lower will be its activation energy and the closer the transition state structure will resemble that of the reactants. Concomitantly, the distinction between allowed and forbidden pericyclic reactions should diminish [30] [31]. A stepwise addition of two butatriene molecules can proceed *via* either of the biradical intermediates **21**, **22**, or **23**. Their enthalpies have been estimated from the group additivity tables of *O'Neal & Benson* [32]. The striking result is that these biradicals are approximately isoenthalpic with two butatriene molecules. For comparison, the same method predicts an energy difference of 38 kcal/mol between planar (**5**) and



twisted (**24**) butatriene. This value compares very well with experimental activation energies of *ca.* 30 kcal/mol for the *cis/trans* isomerization of substituted butatrienes [33] [34]. A qualitative reaction diagram for the dimerization of **5** to **1** is shown in Fig. 3 which illustrates the results of the thermochemical estimates discussed above.

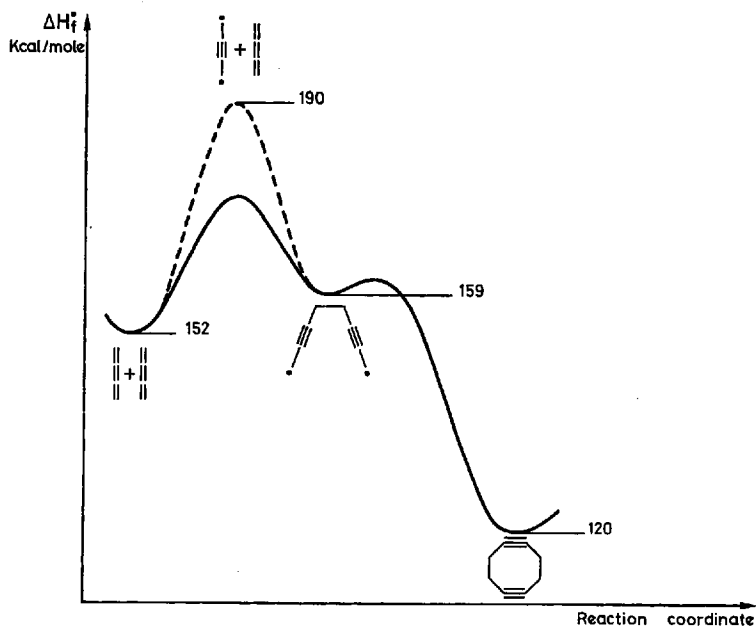
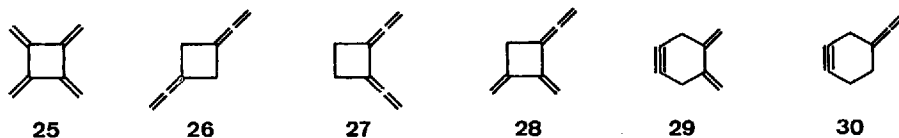


Fig. 3. Potential energy diagram for the dimerization of **5**

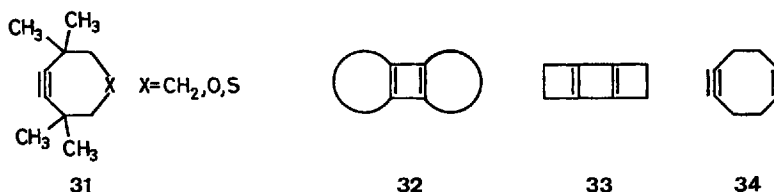
The differences between the calculated energies of the isomeric biradicals **21** to **23** arise largely from the different stabilization energies attributed to allylic ($E_s = 9.6$ kcal/mol) and propargylic ($E_s = 6.5$ kcal/mol) resonance [35]. The precursor of **1**, biradical **21**, is calculated to be less stable than **22** and **23**. A preponderant formation

of the latter biradicals in the first step may thus be responsible for the low yield of **1**. This hypothesis immediately explains our finding that the yield of **1** is not increased by reacting **5** in highly dilute solution. Some of the dimers **25** through **30** which can formally be derived from the biradicals **22** and/or **23** may have escaped isolation due to further reaction with butatriene.



The spectral characteristics of **1** are essentially in accord with expectation. Some features worth noting follow. The unsaturated carbon atoms appear at relatively low field in the ^{13}C -NMR. spectrum of **1**. Their chemical shift (95.8 ppm) falls between the usual range given for olefinic and acetylenic carbon atoms, respectively [36]. This may be attributed⁵⁾ to the $\text{C}\equiv\text{C}-\text{C}$ bond angle deformation of 21° . A detailed discussion of the IR. spectrum does not seem expedient in the absence of further data. The near UV. spectrum, showing only end absorption up to *ca.* 230 nm, does not provide clearcut evidence for a transannular interaction of the triple bonds let alone a 'cyclobutadienoid' character of **1**. The prominent peak observed in the mass spectrum at *m/e* 52 (C_4H_4 , intensity 90% of molecular base peak) indicates that the cleavage of $\mathbf{1}^+$ to $\mathbf{5} + \mathbf{5}^+$ is a major fragmentation pathway, in analogy to the photochemical cleavage of **1**. The photoelectron spectrum of **1** has been discussed previously [18]. As a point relating to the reactivity of **1**, it may be mentioned that the lowest ionization potential of **1** is nearly identical to that of cyclooctyne ($I_v = 9.16$ and 9.18 eV, respectively).

The thermal stability of cycloalkynes is known to be a sensitive function of ring strain. It is tempting to generalize from the bulk of chemical experience [1] [3a] that the borderline between isolable and (at room temperature) non-isolable strained alkynes passes somewhere near a $\text{C}\equiv\text{C}-\text{C}$ angle of 155° . Notable exceptions are the cycloheptyne derivatives **31** synthesized by *Krebs et al.* [38] in which the triple bond



is shielded by neighbouring methyl groups. The acetylenic bond angle in **31** ($\text{X} = \text{CH}_2$) amounts to 146° [39]. Evidence is accumulating [40–42] that the oligo- or polymerization of strained, unshielded cycloalkynes proceeds *via* $\pi_2 + \pi_2$ adducts of type **32**. The $\text{C}\equiv\text{C}-\text{C}$ bond angles in cyclooctyne and **1** are 158.5 [43] and 159.3° , respectively, and, indeed, their reactivities are qualitatively comparable. Never-

⁵⁾ A correlation between angle strain and ^{13}C chemical shifts in cycloalkynes has been noted by *Krebs* [37].

theless, it is surprising that **1** which is stable in solution up to at least 80° shows no tendency to react *via* the intramolecular cycloaddition product **33**. Apparently, the *cis*-bending of acetylenes favours an attack from the outside.

The *Diels-Alder* addition reaction of **1** with butadiene (**2**) has provided evidence that the cyclooct-1-ene-5-yne derivative **11** is more reactive than **1**. The parent compound **34** has now been isolated [44] and preliminary results support the inference. Also, as stated by *Sondheimer et al.* [15], the *sym*-dibenzo-1,3,5-cyclooctatriene-7-yne (**7**) is much less stable than the corresponding diyne **6**.

The photochemistry of **1** is under continued investigation and will be discussed in connection with the photochemistry of **34** and 1,5-cyclooctadiene [44].

Thermochemical Estimates. – *Dewar & Kohn* [45] predict ΔH_f (**5**) = 73.3 kcal/mol from a MINDO/2 calculation with complete energy minimization. A MINDO/2 calculation for **1** [18] yielded ΔH_f (**1**) = 92.8 kcal/mol using the experimental [13] [16] geometry of the carbon skeleton and normal C–H bond lengths and angles. On the MINDO/2 surface the reaction **5** + **5** → **1** is thus exothermic by at least 54 kcal/mol. It should be noted, however, that the heats of formation of strained molecules are generally underestimated by the MINDO/2 method [46] [47].

A direct evaluation of the strain energy of **1** was considered both instructive and useful since apart from strain the thermochemical data of hydrocarbons are very accurately predicted by group additivity rules [27]. Comparison of the molecular dimensions of **1** with those of related strainfree molecules reveals the following contributions to the strain energy of **1**: (1) The bending by 20.7° of the C≡C–C bond angles, (2) the eclipsed conformation of the dimethylene bridges, (3) the transannular repulsion between the π -moieties, and (4) the elongation of the CH₂–CH₂ bonds by 0.03 Å. Contributions (1) and (4) were estimated as 13.1 and 0.6 kcal/mol, respectively, using the bending and stretching force constants compiled by *Dale* [3b]. The strain due to the eclipsed hydrogens should be comparable to the rotational barrier in ethane (2.93 kcal/mol [48]). Contribution (2) thus adds *ca.* 5.9 kcal/mol of strain energy. For the nonbonded repulsion between the π -systems no experimental data are at hand which can be applied to **1** in a straightforward manner.

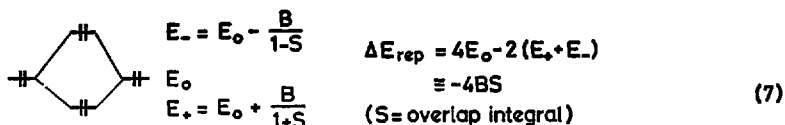
The presence of a strong transannular repulsion in **1** is obvious from the fact that the C–C–C bond angles in the dimethylene bridges (110.4°) happen to be quite normal. This implies that at the equilibrium geometry of **1** the transannular repulsion is approximately balanced by the restoring force resulting from the *cis*-bending of the acetylenes. The latter is calculated as 26.5 kcal/mol Å using the same harmonic bending potential as above [3b]. *Boyd*, in his empirical valence force calculations of cyclophanes [49], has attributed 8.1 kcal/mol to the nonbonded repulsion between the aromatic rings in [2.2]paracyclophane (**3**, *n* = 2). He represented the repulsion between each pair of carbon atoms on opposite rings by the exponential potential (6).

$$U(r_{ij}) = A \exp(-Br_{ij}). \quad (6)$$

The parameters $A = 1.5 \cdot 10^{-7}$ erg/molecule and $B = 5.0 \text{ \AA}^{-1}$ were chosen by trial and error to fit the results of the overall calculation to structural and heat-of-formation data of **3** (*n* = 2). Application of eq. (6) to **1** yields 12.5 kcal/mol for the strain energy due to π -repulsion. However, the steep rise of *Boyd's* potential function is unrealistic

for interatomic distances below 3 Å. The repulsive force at the experimental transannular distance of 2.6 Å is calculated from the potential given by eq. 6 as 62.5 kcal/mol Å, more than twice the value deduced above.

A more direct approach to the nonbonded π -repulsion is derived from the photoelectron spectrum of **1**. The analysis of this spectrum (Fig. 5 and 6 in [18]) on the basis of *Koopmans'* theorem has provided an estimate of 1.0 ± 0.3 eV for the resonance integral B between the strongly overlapping, localized in plane π -orbitals of **1** which can be regarded as a measure of the through space interaction. Now, the energy change due to the interaction of occupied orbitals is invariably destabilizing (closed shell repulsion). In the case of degenerate basis orbitals an approximation for the repulsion ΔE_{rep} is given by eq. 7 [50] [51].



In general, further mixing between occupied and unoccupied orbitals may lead to an overall stabilization of the combined system, *e.g.* when two double bonds are coupled in butadiene. The symmetric approach of the π -systems in **1** precludes any mixing with antibonding π -orbitals. Hence, eq. (7) should be a useful approximation in the present case. The overlap integral S between the in plane π -MO's of **1**, approximated by the overlap between two colinear carbon 2p AO's (*Slater* exponent 1.625), is shown as a function of interatomic distance in Fig. 4. With $B = 1.0$ eV and $S(2.6 \text{ \AA}) = 0.107$ we obtain $\Delta E_{\text{rep}} \cong 9.9$ kcal/mol. A potential function for the π -repulsion in **1** and related systems is obtained upon introducing the *Mulliken* approximation [52] $B \cong k \cdot S$. The value $k = -8.55$ eV recommended by *Salem* [51] yields the eq. (8).

$$\Delta E_{\text{rep}} \cong 4 \cdot 8.55 \cdot S^2 \text{ eV} = 7.9 \cdot 10^2 \cdot S^2 \text{ kcal/mol.} \quad (8)$$

Eq. (8) yields an estimate of 9.1 kcal/mol for contribution (8) to the strain energy of **1** and 19 kcal/mol Å for the repulsive force between the π -moieties. We suggest that a suitable simple function fitted to reproduce the potential function eq. (8) in the region of interest might be used in force field calculations of **1** and related compounds.

Summing up, we obtain an estimate of *ca.* 30 kcal/mol for the total strain energy of **1** which, together with the group additivity prediction [27] for 'strainfree' **1** yields $\Delta H_f^\circ(\mathbf{1}) \cong 120$ kcal/mol. This value should be accurate within ± 10 kcal/mol, allowing for a 30% error in the calculated strain energy.

The heat of formation of butatriene **5** is predicted to be 80.9 kcal/mol using the group additivity tables [27] which include a contribution for allenic sp hybridized carbon atoms. This value does not account for any resonance stabilization in **5** which in 1,3-butadiene amounts to *ca.* 3.6 kcal/mol [53]. Since the splitting of the bonding π orbitals in **5** and 1,3-butadiene is nearly identical according to photoelectron spectroscopic data ($\Delta I_V = 2.48$ and 2.43, respectively [12] [54]) we may infer that the resonance energy is also of similar magnitude in the two compounds. The corrected value is then $\Delta H_f^\circ(\mathbf{5}) = 77.3$ kcal/mol.

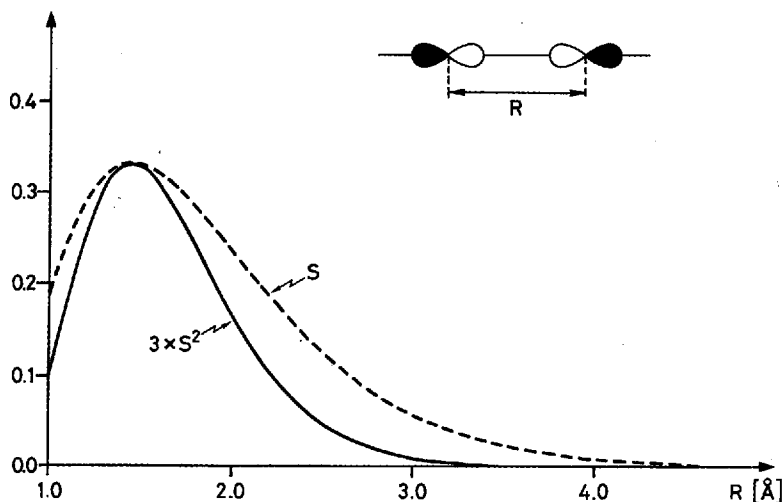


Fig. 4. Overlap integral S (---) and S^2 (—) of two colinear carbon $2p$ AO's (Slater exponent 1.625). S^2 is roughly proportional to the transannular π -repulsion of **1** (eq. 8).

Last not least, the results of an *ab initio* calculation of **5** [12] have been used to predict ΔH_f° (**5**) by the bond separation method [55]. The total energy obtained by the 4-31 G basis set calculation on the STO-3G optimized geometry of **5** is -153.47496 a. u.⁶⁾ Combined with the appropriate theoretical data [56] of methane and ethylene the isodesmic reaction (9)



is thus calculated to be exothermic by 7.0 kcal/mol at 0° K. This value is corrected to 3.6 kcal/mol when the change of the zero point vibrational energy in the isodesmic reaction is accounted for on the basis of experimental data for methane, ethylene [55], and **5** ($\sum \nu_i = 24500 \text{ cm}^{-1}$ [57]). Insertion of the appropriate heat-of-formation data [58] yields $\Delta H_{f,0}^\circ$ (**5**) = 79.1 kcal/mol and $\Delta H_{f,298}^\circ$ (**5**) = 76.9 kcal/mol.

Experimental Part. – All manipulations with air-sensitive compounds **1** and **5** were carried out under vacuum (10^{-3} Torr) in all-glass apparatus. Vapour pressures were monitored with a Balzers NV 3 thermoelectric Pirani vacuum gauge and values given for gases other than air cannot be considered to be accurate. Melting points are uncorrected. Spectra were taken with the following instruments: NMR.: Varian HA-100 D and Bruker 90 (δ values in ppm), IR.: Perkin-Elmer 457, (values in cm^{-1}), MS.: Hitachi Perkin-Elmer RMU-7 operated at 70 eV, UV.: Cary 14, Far UV.: McPherson 225.

Preparation of Butatriene 5. **5** was synthesized from 1,4-dibromo-2-butyne according to Morse [23]. Zinc powder (10 g) in diethyleneglycol dibutylether (30 ml, distilled twice from colloidal sodium) was degassed at 80°. 1,4-Dibromobutyne (15 g) was added in small portions over a period of 40 min while the solution was vigorously stirred at 80°. The volatiles escaping through a water-cooled vertical reflux condenser were collected in a cold trap kept at 77° K. The contents of the trap were then fractionated by vacuum distillation at -78° (vapour pressure of **5** ca. 1 Torr at -78°). The distillate **5** was subsequently redistilled twice at -78° , leaving little residue

⁶⁾ We are indebted to Dr. L. Radom for communicating this value which was not published in [12] and for comments concerning the isodesmic reaction.

(yield of pure **5**: 1.9 g, 50%). IR., NMR., UV.⁷⁾, and MS. (see below) were in accord with literature [12] [19] [57] [59]. A second fraction of 0.9 g distilled from the cold trap at up to -60° contained ca. 25% of 2-bromo-1,3-butadiene (**9**) as first recognized by a MS. of the sample. Schubert *et al.* [19] had found it 'difficult to account for the large mass 53 ($M^+ + 1$) peak'. The high intensity of the mass 53, 27, and 26 peaks in their spectrum is most probably due to the presence of **9** in their sample of **5**.

Pure **9** was isolated by GC. and identified by the following spectroscopic data: NMR. (CCl_4/TMS , coupling constants ≤ 2 Hz ignored): δ 5.33 (*d*, 1H, $J = 10$ Hz); 5.6₀ (*d*, 1H, $J' = 16$ Hz); 5.6₆ (*s*, 1H); 5.81 (*s*, 1H); 6.29 (*q*, 1H, $J = 10$, $J' = 16$ Hz); MS. (*m/e*, intensity in percent of base peak): 134 and 132 (15 each, M^+), 81 and 79 (2 each), 54 (6), 53 (100), 52 (9), 51 (15), 50 (14), 44 (24), 27 (40), 26 (12); IR. (gas phase, CsI windows, 10 cm path length; the letters w, m, s, and vs relate to intensity): 3110 s, 3025 s, 1845 m, 1770 m, 1632 s, 1586 vs, 1418 w, 1386 m, 1355 m, 1270 w, 1210 vs, 1120 m, 1020 m, 971 vs, 922 vs, 882 vs, 734 m, 670 w, 578 s, 520 w, 477 m, 390 s.

Preparation of 1,5-Cyclooctadiyne 1. - Procedure A: The freshly prepared sample of **5** above (1.9 g) was distributed in about equal proportions into three 20 ml tubes equipped with vacuum stopcocks. Degassed *n*-pentane was distilled into the tubes (ca. 18 ml each) and the contents were mixed by shaking as they were allowed to warm up slowly. The clear solutions became coloured within a few hours on standing under vacuum at room temperature, turning yellow to blood red while yellow-brownish fluffy material was deposited in increasing amounts. After a period of 5 to 7 days the solvent and unreacted **5** were evaporated at -78° . The dry ice cooling bath was then removed and remaining volatiles were vacuum transferred to a liquid nitrogen cooled tube. After additional heating of the residues in a water bath to no more than 50° (further heating may cause violent decomposition of the polymers) for about 1 h the distillate was refractionated at -60° . Ca. 10 ml of degassed *n*-pentane were then transferred to the partly crystalline residue in the cold trap. The clear pale yellow solution obtained on warming was cooled down slowly in an air bath immersed into dry ice/acetone whereby colourless transparent needles deposited, up to 10 mm in length. Nitrogen gas was let in and the cold mother liquor was removed with a pipette under a stream of nitrogen. Residual solvent was removed under vacuum in the cold and the crystalline product **1** was sublimed into a weighed vacuum tube (vapour pressure of **1** at room temperature 0.2 Torr, yield 50 mg, 2.6%).

The mother liquor was concentrated at $-50^\circ/10^{-8}$ Torr leaving a yellow oily residue (30 mg) containing minor quantities of crystalline **1**. This mixture was subjected to a combined GC./MS. analysis. Using a 1m Apiezon column, programmed to run from 100° to 230° in 10 min, more than twenty peaks were separated in the chromatogram. The corresponding MS. revealed that the mixture contained two isomeric butatriene-dimers (C_8H_8), five trimers ($\text{C}_{12}\text{H}_{12}$), and at least three tetramers ($\text{C}_{16}\text{H}_{16}$).

When heated above 95° in a sealed capillary **1** turned sooty black and rapidly carbonized at 105° without melting. It is characterized by the following spectroscopic data [13]: $^1\text{H-NMR}$. (δ vs. int. TMS): one single peak at 2.62, 2.53, or 2.21 ppm in CDCl_3 , CCl_4 , or C_6D_6 , respectively; $^{13}\text{C-NMR}$. (δ calibrated by the solvent, C_6D_6 , δ 128.0 ppm, but quoted vs. δ (TMS) \equiv 0): 20.2 (t , $J_{\text{CH}} = 140$ Hz) and 95.8 ppm (*s*); MS. (*m/e* (intensity in percent of base peak): 105 (8), 104.0611 \pm 0.002⁸⁾ (100), 103 (96), 102 (11), 78 (82), 77 (48), 76 (33), 75 (15), 74 (18), 65 (13), 64 (20), 63 (20), 52 (90), 51 (45), 50 (40), 39 (18), $m^* = 58.5$ corresponding to $104^+ \rightarrow 78^+ + 26$. - IR. (ca. 5% solution in CCl_4 , KBr windows): 2910 vs, 2865 m, 2832 s, 2237 vw, 2175 w, 1436 m, 1423 m, 1115 m, 552 s, 434 s; attempts to record a Raman spectrum⁹⁾ failed due to carbonization of **1** in the laser beam (515 or 448 nm). - UV. (gas phase or *n*-pentane solution: only end absorption $\lambda < 230$ nm; Far-UV. (gas phase, preliminary data, extinction coefficients not determined): weak broad band λ_{max} ca. 197 nm (extending to 230 nm), weak peak λ_{max} 194 nm, medium intensity broad band λ_{max} ca. 183 nm, strong structured band λ_{max} 166 nm; the photoelectron spectrum has been discussed [18].

⁷⁾ Correct for **5** in [12] is λ_{max} 250, 232, 203, 183 nm.

⁸⁾ Calculated for C_8H_8 104.0626; we are grateful to Dr. H. Hürzeler, Ciba-Geigy SA for calibration of the molecular peak.

⁹⁾ We wish to thank Drs. Else Augdahl, University of Oslo, and J. Bersier, Ciba-Geigy SA for their contributions.

Procedure B: In a degassed solution of 0.5 g **5** in 250 ml *n*-pentane the formation of polymeric deposits took place very slowly on standing at room temperature. After three weeks considerable amounts of unreacted **5** were still present. Work-up as above yielded only a trace of **1**.

Procedure C: A clear solution of 0.5 g **5** in 0.5 ml *n*-pentane remained unchanged in a dry ice box for eight days. On warming to room temperature it polymerized within a few hours to a hard colourless solid. No **1** could be isolated from this sample.

Procedure D: 2 ml *n*-pentane and 1 g of **5** were transferred to 20 ml of cooled, deaerated liquid paraffin. The cooling bath was removed and the liquid layer was gradually mixed with the melting paraffin by shaking. On standing over night at room temperature the clear solution became opaque and gel-like. After one week the volatiles were removed by repeated flash distillation. Fractionation and recrystallization of the distillate yielded *ca.* 3 mg of **1**.

Procedure E: 100 mg **1**, 6-dithiacyclodeca-3,8-diyne (**4**, X = S) were mixed with 1 g triphenylphosphine and slowly heated to 200° under vacuum. A few mg of volatile material condensed into a cooled receiver. No **1** was detected by NMR. analysis.

Procedure F: Upon irradiation of **4** (X = S) in triethyl phosphite with a low pressure mercury arc the extinction at wavelength $\lambda < 320$ nm rapidly increased, presumably due to the formation of triethyl thiophosphate. The photolysis was then performed in a sealed quartz NMR. tube. After prolonged irradiation a number of new peaks appeared in the spectrum at the expense of the singlet peak at δ 3.4 ppm arising from **4** (X = S). However, no peak at δ 2.5 ppm, attributable to **1**, was detected although authentic **1** was stable under the conditions used.

Procedure G: Two solutions of 250 mg **5** in 1 and 5 ml *n*-pentane, respectively, were irradiated for 4 h at -78° through quartz with unfiltered light from a Philips Cd spectral lamp 93107 E. Solvent and unreacted **5** were evaporated at -78° from the polymers formed. Work-up as in Procedure A did not yield detectable amounts of **1**.

Procedure H: The synthesis of **5** was repeated as described above but without cooling the reflux condenser between the reaction vessel and the cold trap. **5** and **9** were removed from the raw distillate by evaporation at up to -30°. 5 ml of *n*-pentane were transferred to the residue and the resulting clear solution was slowly cooled to -78° whereby a crystalline solid precipitated. Removal of the mother liquor and recrystallization from pentane yielded colourless needles of 1,4-dibromobutyne, m.p. 0-1°, NMR. (CDCl₃/TMS): δ 4.45 ppm (s). Concentration of the combined mother liquors left an oil the NMR. spectrum of which revealed the presence of diethyleneglycol dibutylether (δ 2.4-2.8 ppm, complex), but no trace of **1**.

Catalytic Hydrogenation of 1. A deaerated solution of 9 ± 1 mg **1** in 10 ml *n*-pentane and 10 mg of PtO₂ catalyst were equilibrated with hydrogen (1 atm.) at 0°. When the catalyst was dipped into the solution 8 ± 1 ml of hydrogen (4.2 ± 1 equivalents, uncorrected) were rapidly consumed. The single product detected by analytical vpc was shown to be cyclooctane by coinjection with an authentic sample (Carbowax column, 65000 theor. plates) and by MS.

Ozonization of 1. Ozone (3% in O₂) was conducted through a solution of *ca.* 10 mg **1** in 1 ml carbon tetrachloride for 1 min. The solvent was removed under vacuum leaving a dry residue (m.p. *ca.* 100°) the IR. spectrum of which indicated the presence of an anhydride. The solids were dissolved in 10% potassium hydroxide and the solution acidified with dilute sulfuric acid. Extraction with ether and removal of the solvent gave a pale yellow solid. Vacuum sublimation at 70° yielded colourless crystals, m.p. 187°, shown to be succinic acid by comparison with an authentic sample (mixed m.p., MS.).

Diels-Alder Reaction with 1,3-Butadiene and with 2,3-Dimethyl-1,3-butadiene. Perdeuterio-benzene (0.5 ml), TMS (0.02 ml), diene (0.1 ml), and **1** (20 mg) were vacuum transferred into a NMR. tube which was sealed and kept at 75°. Occasionally, the progress of the reaction was monitored by NMR. After three days more than 90% of **1** had reacted. The sealed tube was broken under an atmosphere of nitrogen and the solution transferred to a small flask which was fitted to a glass tube equipped with a stopcock. Evaporation of the solvent followed by vacuum sublimation of the solid residue into the glass tube yielded colourless crystals of **10** (R = H) and **10** (R = CH₃), respectively, in nearly quantitative yield. In aerated solutions **10** (R = H) and **10** (R = CH₃) were oxidized to the corresponding tetrahydrodibenzocyclooctenes **12** (R = H) and **12** (R = CH₃), respectively. M.p.: **10** (R = H) 37-37.5°, **10** (R = CH₃) *ca.* 173° (dec.?),

12 (R = H) 107–107.5° (109.4–109.9° [60]), **12** (R = CH₃) 242–243°. – MS. **10** (R = H): M⁺ (*m/e* 212) 25% of base peak *m/e* 91; **10** (R = CH₃): M⁺ (*m/e* 268) 45% of base peak *m/e* 119; **12** (R = H): M⁺ (*m/e* 208) 80% of base peak *m/e* 193; **12** (R = CH₃): M⁺ (*m/e* 264) 70% of base peak *m/e* 249. – NMR.: **10** (R = H) (C₆D₆/TMS): 2.16 (sharp *s*, 2 H); 2.54 (br. *s*, 2 H); 5.63 ppm (br. *s*, 1 H); **10** (CH₃) (C₆D₆/TMS): 1.55 (*s*, 3 H); 2.28 (*s*, 2 H); 2.53 (*s*, 2 H); **12** (R = H) (CCl₄/TMS): 3.05 (*s*, 1 H); 6.90 (*s*, 1 H); **12** (R = CH₃) (C₆D₆/TMS): 1.90 (*s*, 3 H); 2.95 (*s*, 2 H); 6.72 (*s*, 1 H).

Base Catalyzed Isomerization to Cyclooctatetraene **17**. Perdeuteriodimethylsulfoxide (0.5 ml, dried over CaH₂) and **1** (20 mg) were vacuum transferred to a NMR. tube. A spectrum recorded without locking the instrument showed the singlet peak of **1** on top of the solvent multiplet (DMSO-d₆, δ ca. 2.6 ppm). One drop of DMSO-d₆, saturated with potassium *t*-butoxide, was then added under an atmosphere of nitrogen. Within 5 min **1** had completely isomerized to **17** (*s* at δ 4.75 ppm vs. int. *t*-butoxide, corresponding to ca. δ 5.8 vs. TMS). The mixture was quenched with water and extracted with *n*-pentane. The product **17** was identified as partly deuteriated cyclooctatetraene by comparison with an authentic sample (GLC., UV./VIS., MS.).

Reaction with Trifluoroacetic Acid. A solution of **1** (10 mg) in dry perdeuteriobenzene immediately turned red (λ_{\max} 548 nm) when acidified with trifluoroacetic acid. A NMR. spectrum taken within 3 min after addition of the acid exhibited complex absorptions in the region of δ 1.2 to 3.2 ppm. The sharp singlet peak of **1** at δ 2.2 ppm was absent. The red solution did not give rise to an EPR. signal. On standing, the colour of the solution gradually changed to blue (λ_{\max} ca. 770 nm) within a few hours and after a few days a brown precipitate was deposited.

Photolysis. A deaerated solution of **1** (15 mg) in *n*-pentane (200 ml) was irradiated through quartz for 90 min with unfiltered light from a homebuilt 500 W iodine discharge lamp which emits a strong line at 206 nm. The solution was cooled to –20° and treated with excess bromine (250 mg in 10 ml pentane). Volatiles were evaporated up to room temperature. Vacuum sublimation at 50° and low temperature recrystallization from *n*-pentane yielded 12 mg of 1,2,3,4-tetra-bromo-2-butene (**18**) [19] [26], m.p. 69°, identical with a sample prepared from authentic butatriene. – NMR. (CDCl₃/TMS): one singlet at δ 4.45 ppm.

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