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THERMAL [2 + 2] CYCLODIMERISATION OF STRAINED OLEFINS. *CIS, TRANS*-1,5-CYCLO-OCTADIENE AND TRANS-CYCLO-OCTENE

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Abstract—The title reaction in the absence of catalysts has been investigated both with the racemic and with the optically active cycloolefins. Both title olefins form [2 + 2] dimers of the *trans* double bonds with complete retention of configuration (*trans-syn-trans* **2** by R + S and *trans-anti-trans* **3** by R + R combination) and with mono-inversion (*cis,trans* **4**, both by R + S and R + R combinations), but almost none with di-inversion (*cis-syn-cis* **5** and *cis-anti-cis* **6**), together with *trans-cis* isomerised starting olefins.

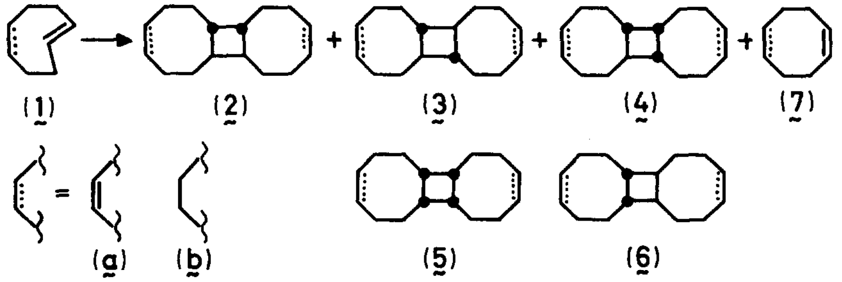
INTRODUCTION

Willstätter[1] and Ziegler *et al.*[2] found *cis,trans*-1,5-cyclo-octadiene (**1a**) to give a crystalline dimer at room temperature to which Ziegler (correctly, as will be shown in this paper) assigned the constitution of a [2 + 2] cyclodimer of the two strained *trans* double bonds. The configuration of the dimer molecule, however, remained undetermined and no search for other dimers was carried out. No investigation into the uncatalysed thermal dimerisation of *trans*-cyclo-octene (**1b**) has been reported so far. In the meantime it has been found that, due to restricted ring mobilities, both **1a**[3] and **1b**[4] can be obtained optically active. The present paper reports constitution, configurations, and relative yields of all dimers obtained from **1a** and **1b**, both from the racemic and from the >99% enantiomerically pure forms, in uncatalysed thermal reactions.

Reaction products

cis,trans-1,5-cyclo-octadiene (**1a**) and *trans*-cyclo-octene (**1b**), on standing neat in the dark under an argon atmosphere, at room temperature and at > 100°, respectively, (preferably in the presence of polymerisation inhibitors), change into the products whose structures are shown in Scheme 1. The relative yields of these products, both from racemic **1a** and **1b** and from the pure antipodes *R*-**1a** and *R*-**1b**, are presented in Table 1. The rates of formation (which will be reported in a subsequent paper) and the relative yields of the dimers are uninfluenced by light and by additives such as atmospheric oxygen, sodium metal, 0.1 M of acidic or basic stabilizers (phenols or amines), 0.1 M of π-acids (maleic anhydride, fumaronitrile), and 0.4–4 M of stable free radicals (phenoxyls and nitroxyls). Hence, the dimerisations are thermal and uncatalysed.

No other products could be detected by capillary glc, in particular none of the isomers of **1a**: 4-vinyl-cyclohexene, syn- and anti-tricyclo[4.2.0.0^{2,5}]octane, and tricyclo[3.3.0.0^{2,6}]octane. Varying amounts of polymers tended to form along with products **2–7(a,b)**; however, when **1(a,b)**, freshly distilled from sodium, was used with 1,4-diaminobenzene plus triethylamine as stabilisers and oxygen was excluded from the reaction, polymer formation could be kept between nil and a few percent of the other reactions when working in >1 M solutions. No material boiling higher than the dimers **2–6** could be detected in the hexane soluble (i.e. non polymeric) fraction of the product mixture. Material balances, gauged by quantitative capillary glc using n-undecane and n-hexadecane as internal standards, confirmed that in most solvents no products besides **2–7** and polymer were formed. In a few solvents the material balances derived from **1a** showed strong deficits (in diiodomethane, in the nitroxyl 2,2,4,4-tetramethylisoxazolidine-N-oxyl) or noticeable deficits (in the nitroxyl 2,2,6,6-tetramethylpiperidine-N-oxyl (TEMPO)) which increased with the reaction time. In these solvents not even traces of polymer formation were detected, which can be explained by the fact that these solvents are good free radical scavengers. In the case of the nitroxyls, the



Scheme 1.

Table 1. Relative yields of products from *RS*-**1(a,b)** and *R*-(−)-**1(a,b)**. The sum of relative yields ≡ 100 for **2a** through **7a** in cases **a** and for **2b** through **6b** in cases **b**. a) ≪1. b) similar magnitude as with *RS*-**1b**

Starting material	% Products						T/°C
	2a	**3a**	**4a**	**5a**	**6a**	**7a**	
RS-**1a**	64	8.6	26.4	0.013	0.037	1	30
R-(−)-**1a**	0.5	71	24.5	a	a	4.	30
	2b	**3b**	**4b**	**5b**	**6b**	**7b**	
RS-**1b**	25.2	7.7	66	0.062	0.97	35	150
R-(−)-**1b**	5.1	25.8	65.3	a	3.8	b	150

deficit is due to an addition of two nitroxyl molecules across the reactive double bond[5]. This adduct was obtained crystalline, in 5% yield besides **2a**–**7a**, from a solution of **1a** in TEMPO which had been left standing. In the case of diiodomethane, the deficit can be explained by noting that scavenging of a growing polymer radical by diiodomethane will form a free iodomethyl radical which will trigger a radical chain addition of the elements I and iodomethyl across the reactive double bond of **1a**. No search for this addition product was carried out.

2a, m.p. 123–4°, readily crystallises from the product mixture obtained from plain (*RS*–) **1a**. It is the dimer that has already been isolated by Willstätter[1] and by Ziegler *et al.*[2] in the course of their early investigations on the chemical behavior of **1a**. The other dimers, *RS*-**3a**, m.p. 33°, and *RS*-**4a**, m.p. 52–3.5°, from *RS*-**1a**, *S*–(+)–**3*a***, m.p. 52–3°, $[\alpha]_D^{29} = +360°$ (dichloromethane, c 0.64), and (+)–**4a**, m.p. 60–1°, $\{\alpha]_D^{28} = +199°$ (dichloromethane, c 0.23), from *R*–(−)–**1a**, and **2b**, m.p. 72–3°C[2], *RS*–**3b**, liquid, and *RS*–**4b**, m.p. 56°, from *RS*–**1b**, were isolated by preparative glc. Dimers **5** and **6** were not isolated but identified, after catalytic hydrogenation in case **a**, in the reaction mixtures by capillary glc comparison with authentic samples of **5b**[6] and **6b**[7]. *S*–(+)–**3b**, obtained by catalytic hydrogenation of S–(+)–**3a**, was a liquid, $[\alpha]_D^{26} = +114.5°$ (dichloromethane, c 0.37).

The 0.5% yield of **2a** obtained from R–(−)–**1a** indicates[8] that **1a** was 99.9% enantiomerically pure. R–(−)–**1b** was prepared in a conparable enantiomeric purity by repeated recrystallisation to constant optical rotation of a platinum complex[4]. Still, as is evident from Table 1, this sample of R–(−)–**1b** formed much higher relative amounts of **2b** than the R–(−)–**1a** formed **2a**. The ratio of **2b** to **3b** and **4b**, however, was not constant when derived from R–(−)–**1b** but increased with the conversion of the **1b** to dimers; extrapolation suggests that at zero conversion the ratio of **2b** to **3b** and **4b** should be close to zero. The effect can be quantitatively explained by the known slow racemisation of **1b** at the dimerisation temperatures[9]. (The data in Table 1 are averaged values for several runs).

From the signs of optical rotation of (+)–**3a**, (+)–**3b** and (+)–**4a** their absolute configurations, as displayed in Scheme 1, can be inferred[10].† Together with the known absolute configuration of R–(−)**1a**[8,12], from which these dimers were formed, their absolute configurations demonstrate that, as expected, dimerisations take place on the sterically unhindered "outside" face of the *trans* double bond. The reaction kinetics described in a subsequent paper will confirm that **3a** is exclusively formed by combination of two molecules of **1a** of like chirality even when derived from *RS*–**1a**.

Structure determinations

CH-analyses and molecular weight determinations showed compounds **2**–**4** to be dimers of **1**. Catalytic hydrogenation using 10% Pd/C in ethanol cleanly converted **2a** to **2b**, **3a** to **3b**, and **4a** to **4b**, thus showing the presence of one C=C double bond per C_8-unit in the dimers **a** and the absence of double bonds in the dimers **b**.

The structure determination of dimers (**2b**–**4b**) was based on the proven structures of dimers **5b**[6] and **6b**[7]. In the gas phase at 400–500° cyclobutanes suffer epimerisations of ring positions and competing cleavage whereas larger ring and open chain saturated hydrocarbons are unaffected under these conditions in the absence of catalysts[13]. At 460° and 20–200 Torr dimer pressure in quartz bulbs every one of the five dimers **2b**–**6b** gave the following products: **7b**, 1,7-octadiene (which is known to arise both from **7b** and **1b** thermally[14]), the three Z,E-isomeric 1,9-cyclohexadecadienes‡ and all four other dimers.§ These results show that **2b**–**4b** are the three possible epimers of **5b** and **6b**. Of these three epimers, two must feature 2×2 fold molecular symmetries (C_{2h} and D_2) and one must be asymmetric. ^{13}C-NMR spectra (see Table 2) show **2a** and **3a** to possess the required

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†Estimated $[M]_D$ values (with $x \equiv K(c\text{–}H)^2 = 60°$[10]): **3a**, 4x = +240° (found: +777°); **4a**, 2x = +120° (found: +430°); **3b**, 2x = +120° (found: +252°). In these estimates, the boat-chair conformation was adopted for the eight-membered rings in **3b**[11] while in **3a** and **4a** the conformations are unambiguously fixed. Although these estimates are quantitatively less satisfying than those in other cases[10] (which may be due to the involvement of cyclobutane rings) they predict correctly that the $[M]_D$ value of **3a** should be about twice that of the other two compounds.

‡Identified by capillary glc comparison, both before and after catalytic hydrogenation, with an authentic mixture prepared by olefin metathesis from **7b**[15]; hydrogenation effected the merger of the three glc peaks due to the cyclohexadecadienes into a single peak.

§From **2b** and **5b**, dimer **4b** was formed in *ca.* 35 fold and 5 fold preference, respectively, over the other three dimers. The sum of other unidentified $C_{16}H_{28}$ isomers amounted to *ca.* 10% of **4b**.

2×2 fold symmetries, exhibiting only four resonances for sixteen carbon atoms, and identify **4(a,b)** as the asymmetric epimer. Furthermore, the observed 2×2 fold molecular symmetries prove the locations of the C=C double bonds in **2a** and **3a**. Indeed, the observed symmetries, δ values, multiplicities, and the relatively high J_{CH} value of the saturated CH which is characteristic of a cyclobutane ring allow an independent deduction of the constitutions (not of the configurations) of **2a** and **3a** solely from their ^{13}C-NMR spectra.

Table 3 shows ^{1}H-NMR data of dimers **2a**–**4a** and **2b**–**6b**. The symmetric olefinic portions of the ^{1}H-NMR spectra of **2a** and **3a** are virtually superimposable and represent an A_2 part of an $A_2X_2Y_2$ system with $J_{AA'}=11.1$, $J_{AX}=J_{AY}=8.3$, $J_{AX'}=J_{AY'}=-0.6$, $J_{XY'}=-0.1$, $J_{XX'}$ and $J_{YY'}\cong 0$ cps, and J_{XY} undetermined (values obtained by LAOCOON[16] analysis). Since J values of 9.5–12.5 cps have been observed in *cis* and 15.4–18 cps in *trans* HC=CH arrangements in C_8 rings[17], the value of $J_{AA'}$ shows the HC=CH arrangement in **2a** and **3a** to be *cis*, as expected. The original structural proposal put forward by Ziegler[2] for dimer **2a** is thus verified. The *cis* arrangements also follow from the unreactivity of **2a**–**4a** towards added cyclopentadiene; **1b** with cyclopentadiene at room temperature forms a Diels–Alder adduct immediately.

Since the two symmetric dimers with proven configurations, **5b** and **6b**, both have the eight- and the four-membered rings *cis* fused, the other two symmetric dimers, **2** and **3(a,b)**, must both have these rings *trans* fused. This follows independently from the fact that the olefinic portions of the ^{1}H-NMR spectra of **2a** and **3a** are virtually superimposable on that of 1,8-*trans*-bicyclo[6.2.0]deca-4,9-diene but are quite different from that of the corresponding *cis* isomer[18]. On cooling below 0°, the same freezing of the C_8-ring flip process is observed with **2a** and **3a** as with the *trans* adduct of **1a** to benzyne whereas no such phenomenon is observed with the corresponding *cis* adduct[19]. A final proof of the *trans* fusion in **2a** is provided by the diepoxides of **2a**. Any epoxide protons derived from the *cis* fused symmetric dimer structures (**5a** and **6a**) should be equivalent when located on the same ring. Hence, no coupling between ^{1}H-NMR signals of nonequivalent expoxide protons in a diepoxide mixture obtained from either structure **5a** or **6a** should be observed. By contrast, when derived from the *trans* fused symmetric dimer structures (**2a** and **3a**), any two diepoxide protons located on the same ring should be nonequivalent and show a mutual coupling of ca. 4.5 cps.[20]. The raw epoxidation product obtained from dimer **2a** by treatment with 2.2 equivalents of peracetic acid in dichloromethane was crystalline, m.p. 211–5°; one recrystallisation gave a product with m.p. 218° which was not raised by further recrystallisations. Both the raw and the most recrystallised product showed only one peak in capillary glc under various conditions and one spot by tlc. CH analysis, molecular weight, UV, IR (no C=O present), and ^{1}H-NMR spectra were fully in accord

Table 2. ^{13}C-NMR data: δ values (ppm relative to internal TMS) and J_{CH} values (cps) obtained from undecoupled and broad band decoupled 67.89 MHz spectra in $CDCl_3$

	$=\mathrm{C}{<}^{\mathrm{H}}$	$-\mathrm{CH_2}-$	$-\mathrm{CH}{<}$
2a	130.3(d,J=153)	27.4 (t,J=126) 24.5 (t,J=125)	39.1 (d,J=133)
3a	130.5(d,J=154)	34.0 (t,J=124) 24.8 (t,J=126)	45.2 (d,J=130)
4a	131.2,130.2,130.2, 128.9 (each: d, J=153	34.0,30.3,28.0 27.5,24.7,24.6 24.5,24.5 (each: t, J=123-126)	44.5, 44.0,40.2 37.3, (each: d, J=129-132)
4b	—	35.7,31.8,30.9 28.9,28.7,28.2 28.0,27.9,26.1 26.0,25.6,23.9 (each:t, J≃125)	46.6,43.8,42.8, 41.4 (each: d, J=127-137)

Table 3. ^{1}H-NMR data: δ values in $CDCl_3$, obtained at 270 MHz. All signals are multiplets. a) broadened d, J ≅ 8 cps b) dddd, J ≅ 11, 9, 9, 3 cps

	$=/^{\mathrm{H}}$	tert. CH	residual H
2a	5.55(4H)	2.24(4H)	2.24(4H),2.00(4H),1.46(8H)
3a	5.57(4H)	1.50(4H)	2.17,1.99,1.76,1.14(4H each)
4a	∼ 5.57(4H)		2.51(1H),1.41-2.32(18H),1.14(1H)
2b	—	2.21$^{a)}$(4H)	1.26-1.77(24 H)
3b	—	1.75 (4H)	1.75(8H),1.19-1.24(16 H)
4b	—	2.16$^{b)}$,1.98$^{b)}$ (1 H each)	1.10-1.73(26 H)
5b	—	2.32$^{a)}$(4H)	1.15-1.59 (24 H)
6b	—	1.20-1.66	

with a diepoxide structure. The ^{13}C-NMR spectra also showed the δ and J_{CH} values expected for a diepoxide; however, some of the resonances, in broad band proton decoupled spectra of the most recrystallised product, appeared as narrowly spaced doublets of equal intensity, so that there were actually more resonance lines than to be expected of any single diepoxide. Obviously two stereoisomeric diepoxides were formed from dimer **2a** in almost equal amount (with structures **2a** or **3a**, two stereoisomeric diepoxides are possible, with structures **5a** or **6a** three). These would appear to give a 1:1 crystalline compound, to have very similar ^{13}C-NMR spectra, and to be chromatographically indistinguishable. The 270 MHz ^{1}H-NMR spectra, too, of this diepoxide mixture appear essentially as though derived of a single diepoxide; only the cyclobutane signals (as expected) and the δ = 1.22/1.26 signal betray that they are suprapositions of two different spectra. 270 MHz spectra taken in different solvents and extensive decoupling experiments allowed an almost complete assignment of the observed resonances as shown in Table 4.

The mutual coupling of 4 cps between the epoxide signals at 2.76 and 2.86 as determined by decoupling proves the *trans* fusion of the eight- and the four-membered rings in **2a**.†

Dimer **3a** upon similar treatment with peracetic acid give a mixture of diepoxides, m.p. 96–122°, which was not separated. In contrast to dimer **2a**, the epoxide proton signals in the 270 MHz-^{1}H-NMR spectrum of this mixture were not sufficiently separated (δ = 2.82, 2.87) to allow a conclusive decoupling experiment. The complete relative configuration of dimer **3a**, however, follows unambiguously from the fact that **3a** has been obtained strongly optically active in 97% purity, the only impurity being dimer **4a** which shows a smaller molar rotation. Of the four dimer structures with 2×2 fold molecular symmetries (**2a**, **3a**, **5a**, **6a**), only structure **3a** is chiral (D_2 symmetry)* and therefore capable of showing optical activity.

With one of the two *trans* fused symmetric structures thus being assigned to dimer **3a**, dimer **2a** is unambigously left with the other one.

The structure of 2:1 adduct of TEMPO to **1a**, 5,6-bis-(2,2,6,6-tetramethylpiperidinyl-1-oxy)-cis-cyclooctene, m.p. 117-125°, follows from CHN analyses, mol. wt., and the 270-MHz-^{1}H-NMR spectrum which shows a twofold symmetry of the molecule.

Related dimerisation experiments

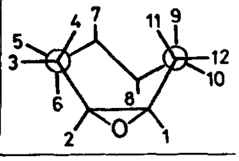
7a and **7b** slowly form dimeric fractions when kept in the liquid phase at 300° for several hours in an autoclave. These dimeric fractions, however, are very complex mixtures (as shown by capillary glc) which contain only traces, if any, of the dimers **2–6**. The rates of formation and the composition of these mixtures appeared to be essentially the same no matter how well **7a** and **7b** had been purified, how well oxygen has been excluded, or which wall material (stainless steel or pyrex) has been chosen.

Dimerisation of **1a** in **7a** as the solvent at room temperature proceeds with the same rate and gives the same dimer distribution as in other solvents. This shows that **1a** and **7a** do not codimerise, and hence, that formation of the dimers from **1a** does not involve rearrangement of **1a** to **7a** and addition of the latter to a second molecule of **1a**.

In the same manner, due to the great difference in ease of dimerisation between **1a** and **1b**, no mixed dimers were observed when **1a**, dissolved in **1b**, was left standing at room temperature. Instead, the dimers **2a–4a** were formed in the usual ratio. Likewise, no codimerisation occurred between **1a** and cyclopropene (which underwent fast oligomerisation) and 3,3-dimethylcyclopropene (which was inert), only the dimers of **1a** being formed. Codimers were found, however, by glc, with mixtures of **1a** and 1,2-cyclononadiene (along with the three dimers of the latter[21] and the dimers of **1a**), of **1a** and *cis,trans*-1,3-cyclo-octadiene (along with the three dimers of the latter[7] and the dimers of **1a**), and of **1a** and cyclooctyne (along with the dimers of **1a**). The thermal [2+2] cycloadditions of benzyne to **1b** and **7b**[22], and to **1a** and **7a**[19], and of the three dichlorodifluoroethenes to **1b** and **7b**[23] have been described.

Attempts to effect dimerisation of either **1a**, **1b**, **7a** or **7b** photochemically either by direct irradiation with 254 nm or by sensitation with acetophenone, led only to slow formation of complex mixtures.

Table 4. ^{1}H-NMR data ($CDCl_3$) of the diepoxide obtained from **2a**

H	δ/ppm	H,H	$\vert J_{HH}\vert$/cps	H,H	$\vert J_{HH}\vert$/cps
1	2.76	1,2	4	5,7	~3
2	2.86	1,11	11.5	6.7	12
3	2.31	1,12	3	7,8	12
4	1.07	2,3	4.5	9,12	3
5	1.61	2,4	11	10,12	3
6	1.44	3,4	14	11,12	14
7	1.90/1.94	3,5	~5.5		
8	2.22/2.26	3,6	~0-1.5		
9,10	~1.61	4,5	~0-2		
11	1.22/1.26	4,6	12		
12	2.07	5,6	14		

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†The analysis of the couplings was complicated by protons 1 and 2 exhibiting some virtual coupling (proton 1:4 cps in $CDCl_3$, different in C_6D_6) which could not be assigned to a specific partner proton but changed or disappeared when various other protons were irradiated. All couplings of protons 1 and 2 could nevertheless be determined with sufficient accuracy.

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EXPERIMENTAL

Much of the experimental information is contained in the theoretical sections and will not be repeated in this chapter.

Melting points: Kofler hot stage, uncorrected. IR and UV spectra: Perkin Elmer instruments. ^1H-NMR spectra: Varian A 60 A, Varian HA 100, Bruker WH 270. ^{13}C-NMR spectra: Bruker WH 270. LAOCOON calculation on computer PDP 10 by Digital Equipment. Elementary analyses and molecular weights: Dornis & Kolbe, D-4330 Mülheim a.d. Ruhr.

Preparation of cis,trans-1,5-cyclo-octadiene (**1a**). Several useful procedures exist for this purpose[2,24,25]. We used the following procedure: 230 g (2.13 mol) *cis,cis*-1,5-cyclo-octadiene (**7a**) and 230 g (2.09 mol) thiophenol are heated at 60° for 48 hr with occasional addition of small amounts of α,α'-azoisobutyronitrile. Distillation yields 390 g 4-cycloocten-1-yl phenyl sulfide[26], b.p. 120° at 0.2 mm Hg. 300 g (1.38 mol) of this material, 135 ml dimethyl sulfate, and 2200 ml acetonitrile are refluxed for 5 hr, the acetonitrile is distilled off and the dark viscous residue shaken with several portions of ether which are discarded. The residue is mixed with a cold solution of 200 g KOH in 210 ml water in a 2 1 round bottom flask. This flask is fitted with an efficient magnetic stirrer and built into a vacuum distillation apparatus having wide inner diameters and two consecutive receivers cooled at −80° by acetone/CO_2. At 11 Torr the flask is heated in an oil bath under stirring and gradual increase of the temperature to sustain quick distillation till at about 160° bath temperature the distillation fades away and the operation is stopped. The contents of the receivers at room temperature are distributed between water and 200 ml hexane. The hexane layer is transferred into a flask which is kept on dry ice overnight whereupon thioanisol crystallises compactly at the bottom of the flask. The hexane layer, still at −70°, is decanted from the solid thioanisol and shaken for several min. at room temp. with a solution of 30 g silver nitrate in 60 ml water to give 75 g (moist) $AgNO_3$·(**1a**)[24] as greyish crystals which are isolated by filtration and washed with hexane. They are decomposed as described[24] with aqueous ammonia in a separatory funnel and the oil which separates is dried over Na_2SO_4 and distilled from sodium (because of strong foaming a wide flask and vigorous magnetic stirring are advisable) to give 11 g **1a**, b.p. 30°/11 mm Hg, *ca.* 99% pure (glc: polypropyleneglycol, 55 m glass capillary, injection 200°, colum 70°, 1.2 at N_2, appearance time/min. after injection: **1a** 8.1, **7a** 9.2, thioanisol 18.2. The contaminations are **7a** and thioanisol). Residual thioanisol present will boil at 70°/11 mm Hg.

R-(−)-**1a** was prepared according to lit.[3] and its enantiomeric purity (>98% with all samples used in this work) determined as described previously[8].

trans-cyclo-octene (**1b**) was prepared according to lit.[27]

R-(−)-**1b** was prepared according to lit.[4] from the dichlorophenylethylamineplatinum complex which had been recrystallised to constant optical rotation ($[\alpha]_D^{20} = +69.3°$ in CH_2Cl_2) and m.p. (130–131.5°). **5b**[6], **6b**[7], syn- and anti-tricyclo[4.2.0.$0^{2,5}$]-octanes[28], tricyclo[3.3.0.$0^{2,6}$]octane[29], and 2,2,6,6-tetramethylpiperidine-N-oxyl (TEMPO)[30] were prepared according to the literature.

2,2,4,4-*tetramethylisoxazolidine-N-oxyl* (*DOPR*) was prepared according to lit.[31] using a changed workup procedure: the reaction mixture obtained from 35 g tetramethylisoxazolidine, 100 g m-chloroperbenzoic acid (Aldrich), and 30 g anhydrous magnesium sulfate in 200 ml ether was washed well with aqueous sodium carbonate solutions till acid free. The aqueous layers were reextracted with ether and the combined ether layers dried over magnesium sulfate. After evaporation of the ether the residue was distilled using a short Vigreux column to give 9.4 g of an orange liquid, b.p.: 50–60°/11 mm Hg (higher boiling material was colorless and was discarded). This liquid gave crystals from ether/pentane at −70° which were isolated in the cold, recrystallised and finally redistilled to give 6.2 g DOPR, b.p. 47°/11 mm Hg. The material is highly sensitive to aqueous acids in the cold and to organic acids at elevated temperatures.

1,2-*cis*-2,9-*trans*-9,10-*cis*- and 1,2-*trans*-2,9-*trans*-9,10-*trans*- and 1,2-*cis*-9,10-*trans-tricyclo*[8.6.0.$0^{2,9}$]*hexadeca-cis-5-cis-13-diene* (**2a**, **3a**, and **4a**). The following preparation was typical. 2.16 g (0.02 mol) **1a** with a drop of triethylamine and a few crystals of 1,4-diaminobenzene added was left standing in a bulb tube (Kugelrohr) at room temp. in the dark under an argon atmosphere for 10 days. Distillation from that bulb tube at 0.1 mm Hg and a bath temp. of 110–140° gave 2.00 g of a largely crystalline distillate which was slightly yellow due to the 1,4-diaminobenzene. The solution of the distillate in ether, after filtration from small amounts of insolubles, yielded crystals upon immersion in an acetone/solid CO_2 bath which were recrystallised to give 1.00 g **2a**, m.p. 121–123°, 99% pure by glc. Further recrystallisations would raise the m.p. to 123–124°. The mother liquors were combined and the residue after evaporation of the ether was separated by preparative glc using a column of 6 m length and 10 mm inner diameter filled with 10% XE 60 (Cyanoethylmethyl-phenylmethyl-silicone) on Chromosorb B and heated to 180° and a nitrogen stream of 350 ml/min. The residue 1 : 1 diluted with chloroform was injected in 0.5 ml portions to give, in order of increasing retention times, 120 mg **3a**, m.p. 25–26°, 98.2% pure by glc, 110 mg of **4a**, 84.8% pure, 190 mg of a 2 : 1 mixture of **4a** and **2a**, and 150 mg of a 1 : 1 mixture of **4a** and **2a**. Recrystallisations at low temperatures as described for **2a** raised the m.p. of **3a** to 33° and that of **4a** to 52–53.5°. UV spectra (hexane): λ_{max} < 220 nm for all three compounds. ^1H- and ^{13}C-NMR spectra: see Tables 2 and 3. The mass spectra of all three compounds are almost superimposable except that *m/e* = 188, which is the strongest signal for both **2a** and **3a**, is only of average intensity for **4a** and that *m/e* = 80, which is very strong for **3a** and **4a**, is only of average intensity for **2a**. *m/e* (13 and 70 eV) = 216(M^+), 201, 187–189, 173–176, 159–162, 145–149, 131–136, 117–123, 104–110, 91–96, 78–83, < 70. IR(KBr): **2a**: 3000(m), 2910(s), 2850(m), 1638(w), 1460(s), 1450(w), 1440(m), 1345(m), 1310(w), 1295(w), 1254(m), 1240(m), 1225(m), < 1200, > 900(≤ m), 875(m), 830(w), 810(w), 775(m), 735(s), <600 cm^{-1}. **3a**: 3000(m), 2900(s), 2840(m), 1462(s), 1448(w), 1439(m), 1350(m), 1345(m), 1330(m), 1317(w), 1295(m), 1245(m), 1230(w), < 1200, > 900(≤ m), 869(m), 771(m), 764(m), 717(s), <600 cm^{-1}. **4a**: 3000(m), 2910(s), 2860(m), 1646(w), 1471(m), 1461(s), 1439(m), 1350(m), 1319(w), 1295(w), 1265(w), 1250(m), 1225(w) <1200, >900(≤m), 875(m), 865(m), 855(w), 820(w), 769(w), 740(s), < 600 cm^{-1}. Found: **3a**: C 88.70, H 11.21, m.w. 216(MS); **3a** 89.03, H 11.17, m.w. 216(MS); $C_{16}H_{24}$ requires C 88.82, H 11.18, m.w. 216.35.

Catalytic hydrogenations of **2a**, **3a**, *and* **4a**: 10% Pd on charcoal (Fluka) in ethanol, rapid uptake of 1 mol H_2/equivalent C_8, no further uptake of H_2, less than 0.5% epimerisations on the cyclobutane ring (glc: polypropyleneglycol, 30 m glass capillary, injection 250°, column 130°, 0.8 at H_2, appearance time/min. after injection: **3b** 13.0, **6b** 15.9, **4b** 19.6, **2b** 25.8, **5b** 29.6)-NMR: see Tables 2 and 3. **2b** has been described before[2] and **4b** is identical to a compound prepared by different routes[7]. **3b**: liquid; found: C 87.38, H 12.72, m.w. 220 (MS); $C_{16}H_{28}$ requires C 87.19, H 12.81, m.w. 220.38.

Epoxidation of **2a**. To a stirred suspension of 120 mg anhydrous sodium acetate in a solution of 160 mg **2a** in 4 ml dichloromethane at room temp. was added 320 mg of a 40% solution of peracetic acid in acetic acid and stirring was continued for 4 hr. Water and dichloromethane were added and the dichloromethane layer was washed with aqueous $NaCHO_3$ solution till acid free and with water and dried over magnesium sulfate. Evaporation of the dichloromethane left 147.4 mg colorless crystals, m.p. 211–215°. After recrystallisation from toluene 47 mg, m.p. 218°. UV (hexane): λ_{max} < 204 nm. IR(KBr): 2970(m), 2910(s), 2870(m), 2845(s), 1461(s), 1450(s), 1428(m), < 1400, > 1050(≤ m), 1015(s), 909(s), 843(m), 835(m), 769(s), 739(m), < 520 cm^{-1}. ^{13}C-NMR ($CDCl_3$): $\delta = 56.1, 55.5$ (d, J = 166 Hz, each), 40.1, 39.9, 39.9, 39.8 (d, J = 127 Hz, each), 29.1, 29.0, 25.9, 25.6,

Table 5. Products from thermolysis of **2b** and **5b**. x = not determined

Starting Dimer	mg	volume/cm^3 of bulb	T/^{o}C	t/h	relative amount of (2b -6b ≡ 100) 2b	3b	4b	5b	6b	7b	1,7-octadiene	sum of other $C_{16}H_{28}$ isomers including cyclohexadecadienes
5b (100%)	20	18	460	4	0.05	0.02	0.48	99.4	< 0.01	4.18	0.95	0.04
"	"	"	"	8	0.13	0.05	1.21	98.6	0.01	3.04	0.53	0.1
"	"	100	"	4	0.05	0.04	0.45	99.5	< 0.01	3.33	0.76	0.04
"	"	"	"	8	0.14	0.05	0.95	98.9	x	x	x	0.1
"	"	250	"	4	0.05	0.06	0.46	99.4	0.02	x	x	0.04
"	"	"	"	8	0.12	0.03	0.96	98.9	x	6.68	1.82	0.1
2b (containing 0.1% 3b and 1.91% 4b)	50	18	"	2	90.6	0.18	8.61	0.09	x	x	x	0.8
	"	"	"	4	82.8	0.26	15.55	0.18	0.06	x	x	1.5
	"	"	"	6	73.8	0.39	23.36	0.24	0.08	x	x	2.3
	"	"	472	2	81.6	0.11	17.04	0.17	0.06	x	x	1.7
	"	"	"	4	63.3	0.59	32.49	0.25	< 0.2	x	x	3.2
	"	"	"	6	47.6	0.97	43.91	0.30	< 0.3	x	x	4.4

23.6, 23.5, 23.1, 23.0 (t, J = 124 Hz, each). ^{1}H-NMR see Table 4. Found: C 77.26, H 9.76, O 12.78, m.w. 248 (MS), 256 (vaporimetr. in benzene); $C_{16}H_{24}O_2$ requires C 77.37, H 9.74, O 12.88, m.w. 248.35.

Epoxidation of **3a**. Analogous to **2a** with 32.8 mg **3a**, 50 mg anhydrous sodium acetate, and 0.5 ml 40% peracetic acid in 2 ml dichloromethane, Crude product: colorless crystals, m.p. 96–122°. IR(KBr): 2970(s), 2930(s), 2900(s), 2885(s), 2845(s), 1455(s), 1423(m), < 1400, > 950 (≤ m), 934(s), 920(s), 900(m), 862(m), 835(m), 779(s), 740(m), < 560 cm^{-1}. ^{1}H-NMR ($CDCl_3$): $\delta = 1.09$, 1.14, 2 × 1.25, 1.30, 1.47, 2 × 1.88, 2.03, 2.19, 2.82, 2.87 (m, 1H, each).

Dimerisation of **1a** *in* 2,2,6,6,-*tetramethylpiperidine-N-oxyl* (*TEMPO*). A liquid mixture of 3.0 g **1a** and 3.0 g TEMPO was left in the dark at room temp. under an Ar atmosphere for 12 days. Kugelrohr distillation afforded 2.4 g of a dark red liquid consisting mainly of TEMPO with minor amounts of **7a** and **1a** (≤100°/11 mg Hg), 2.4 g of a colourless crystallising mixture of dimers **2a–6a** in the usual proportion (100–130°/0.1 mm Hg), 827 mg of a highly viscous colourless liquid, **A**, (150–180°/0.1 mm Hg) and 190 mg of dark residue **B**. A solution of **A** in ether deposited 520 mg of colourless crystalline 1:2 adduct, 5,6-*bis*(2,2,6,6-*tetramethyl*-1-*piperidinyloxy*)-*c*-*cyclo*-*octene*, m.p. 117–125°. 270 MHz-^{1}H-NMR ($CDCl_3$, 25°): $\delta = 0.95$–1.65 (broad with two broad methyl singlets, 36 H), 1.87 (40 Hz wide, 2H), 2.10 (80 Hz wide, 4H), 2.65 (broad t, 40 Hz wide, 2H), 4.22 (80 Hz wide, 2H) 5.66 (quasi t, 20 Hz wide, 2H). Found: C 75.00, H 11.10, N 8.03, m.w. 420 (MS); $C_{26}N_{48}N_2O_2$ requires C 74.23, H 11.50, N 6.66; m.w. 420.66. The mother liquor on chromatography (silica gel, CH_2Cl_2) yielded another 61 mg of the same substance and 29 and 13 mg, respectively, of two other substances of m.w. 420 (MS), but no 2:2 adduct (MS). **B** on treatment with benzene/methanol left 30 mg of dark, amorphous, insoluble material which was discarded. The 160 mg soluble material on chromatography (silica gel, CH_2Cl_2) yielded 11, 23, and 15 mg, respectively, of three substances of m.w. 528 (MS; 2:2 adducts **1a**: TEMPO) followed by 80 mg of the 1:2 adducts also contained in **A**.

Thermolyses of **2b–6b**.

The following examples serve as illustrations.

Method A. Dimer samples were weighed into quartz bulbs. The bulbs were evacuated to 0.2 Torr under external cooling by liquid nitrogen, sealed by the flame, and kept in an air bath, thermostated to 460 or 472°, for 2–8 hr. The seals were then broken, again under external cooling, the contents collected by rinsing with hexane and the hexane solutions analysed by glc as above to give the results presented in Table 5.

Method B. 0.1 Torr of dimer vapors without added gases were passed through a quartz tube which was externally wrapped by an electric heating coil and thermal insulation material and whose temperature was monitored using a thermocouple. The vapours were condensed in a trap cooled by liquid nitrogen and the condensate was taken up in hexane and analysed by glc as above. Thus, passing **5b** at 610° gave a condensate composed of 1.05% **2b**, 24.67% **4b**, 11.16 **5b**, 25.56% **7b**, 17.88% 1,7-octadiene, 1.82, 4.36, and 1.98% respectively, of the three cyclohexadecadienes, and 11.53% of other $C_{16}H_{28}$ compounds (**3b** and **6b** were not determined). Analogously **2b** at 650° gave 22.6 **2b**, 51.75% **4b**, 0.36% **5b**, 8.05% **7b**, 2.76% 1,7-octadiene, 0.88, 2.53, and 1.48%, respectively, of the three cyclohexadecadienes, and 9.6% of other $C_{16}H_{28}$ compounds.

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