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134. Reductions of Tetrahalo-1,3,5,7-tetramethyl-*anti*-tricyclo[5.1.0.0^{3,5}]octane-2,6-diones. 1,3,5,7-Tetramethyl-*anti*-tricyclo[5.1.0.0^{3,5}]octane-2,6-dione[1)2)]

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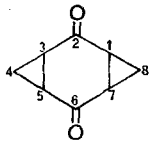
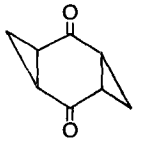
Zusammenfassung. Methoden zur Entfernung von Halogenatomen aus den leicht zugänglichen (Bis-homo-*p*-chinon)-Derivaten 4,4,8,8-Tetrachlor- (**4**) und 4,4,8,8-Tetrabrom-1,3,5,7-tetramethyl-*anti*-tricyclo[5.1.0.0^{3,5}]octan-2,6-dion (**5**) wurden untersucht. Mit $LiAlH_4$ bzw. mit $KFeH(CO)_4$, $NaBH_3CN$ oder $CrCl_2$ entstanden Diole bzw. Diketone, in denen ohne Gerüstveränderung verschiedene Halogenatome durch Wasserstoffatome ersetzt worden waren. Die Diole wurden entweder isoliert oder zu den Diketonen aufoxydiert. Von den neun möglichen Dehalogenierungsmustern (Diketone mit unverändertem C-Skelett) liessen sich acht beobachten, sechs davon (**8** bis **13**) aus **4** und sechs (**14** bis **18**, **6**) aus **5**. Nur $KFeH(CO)_4$ entfernte alle vier Halogenatome und dies nur aus dem Tetrabrom-dion **5**, wobei das noch unbekannte *anti*-Isomere von 1,3,5,7-Tetramethyl-tricyclo[5.1.0.0^{3,5}]octan-2,6-dion (**6**) entstand.

Die Zuordnung der *endo*- oder *exo*-Konfigurationen der nicht-entfernten Halogenatome an den Cyclopropanringen erfolgte auf Grund von ^{1}H-NMR.-Spektraleigenschaften. Als Basisargument diente eine H/^{13}C-Kopplung von 4,5 Hz zwischen *exo*-H—C(4) und den *cis-vicinalen* Methyl-Kohlenstoffatomen, welche im ^{13}C-NMR.-Spektrum von **12** beobachtbar ist. Daraus und aus unterschiedlichen Linienbreiten der ^{1}H-NMR.-Signale von *endo*- und *exo*-Protonen wurde abgeleitet, dass *endo*-H immer bei tieferem Feld absorbiert als *exo*-H. Im Fall von **6** liess sich dies durch geeignete Vergleiche unter Anwendung eines abschirmenden Effektes der angulären Methylgruppen auf *exo*-H bestätigen. Die Konfigurationen der Hydroxylgruppen in den Diolen **19** bis **22** und **24** bis **27** wurden aufgrund von Symmetrieüberlegungen bestimmt.

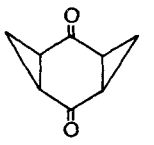
1. Introduction. – Addition of two one-carbon-atom units to appropriately functionalized 6-membered rings [1–3] leads to the tricyclo[5.1.0.0^{3,5}]octane-2,6-dione system **1** of which the two isomers **2** and **3** are possible. However, only the



1



2

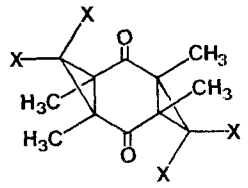


3

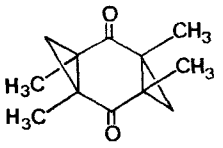
1) The trivial name is *anti*-bis-homoduroquinone; this nomenclature was used in previous publications (compare [1]).
2) In part from the planned dissertation of *R. A. Dyllick-Brenzinger,* ETH Zürich.
3) Post-doctoral fellow, University of Zürich, 1972–1975.

procedure reported in [1] gives the *anti*-isomer **2**, and in that case the 4,4,8,8-tetrahalo-1,3,5,7-tetramethyl-derivatives **4** and **5** are obtained.

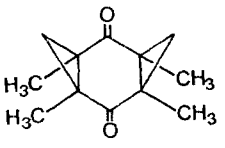
We now report our experience of attempts to remove the halogen atoms from **4** and **5**. This includes the preparation of 1,3,5,7-tetramethyl-*anti*-tricyclo[5.1.0.$0^{3,5}$]-octane-2,6-dione (**6**), the *syn*-isomer **7** already having been prepared by one of the other methods [3].



4 X = Cl
5 X = Br



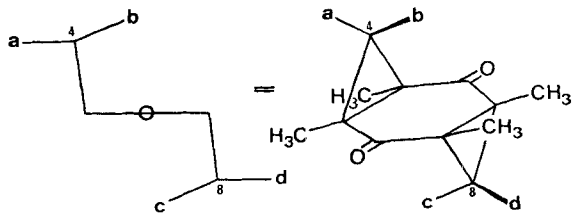
6



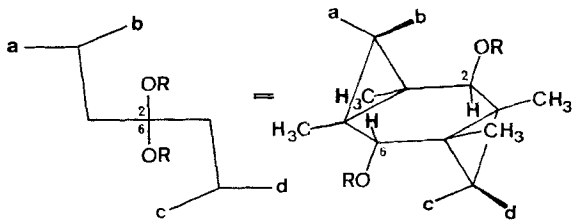
7

2. Stereochemical relationships. – Compounds **4**–**6** and **8**–**27**, which are dealt with in the present work, are shown in the *Scheme*. They are also represented by

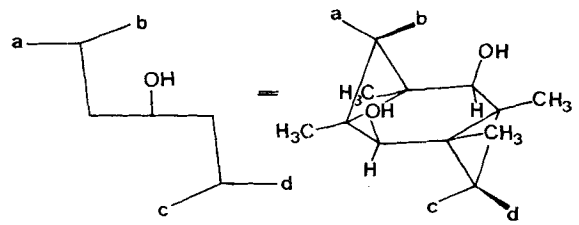
Scheme



4: a = b = c = d = Cl
5: a = b = c = d = Br
6: a = b = c = d = H
8: a = b = c = Cl, d = H
9: a = b = d = Cl, c = H
10: b = c = Cl, a = d = H
11: a = d = Cl, b = c = H
12: b = d = Cl, a = c = H
13: a = Cl, b = c = d = H
14: a = b = c = Br, d = H
15: b = c = Br, a = d = H
16: a = d = Br, b = c = H
17: b = Br, a = c = d = H
18: a = Br, b = c = d = H



19: a = b = c = d = Cl, R = H
20: a = b = c = d = Br, R = H
21: a = b = c = d = R = H
22: a = d = Cl, b = c = R = H
23: a = d = Cl, b = c = H, R = CH_3CO
24: a = d = Br, b = c = R = H



25: a = b = c = d = Cl
26: a = b = c = d = Br
27: a = b = c = d = H

simplified diagrams (left side of the *Scheme*), which emphasize the stereochemistry of the substituents at C(4) and C(8), and at C(2) and C(6). For the designation of isomers we use the term *anti* to specify the configuration of the two 3-membered rings on the 6-membered ring; the expressions *endo/exo* refer to the position of the halogen atoms at C(4) and C(8) relative to the 6-membered ring and *cis/trans* to that of the OH or OR groups at C(2) and C(6) relative to each other.

3. Reduction procedures and products. – Four reducing agents were used under different conditions to remove one to four halogen atoms from the two 4,4,8,8-tetrahalo-1,3,5,7-tetramethyl-*anti*-tricyclo[5.1.0.0^{3,5}]octane-2,6-diones **4** and **5** (in short tetrahalo-diones). Agents, conditions, products observed, and their yields are listed in Table 1. Three of the reducing agents, namely $KFeH(CO)_4$, $NaBH_3CN$ and $CrCl_2$, left the two carbonyl groups untouched while $LiAlH_4$ produced diols, which were either isolated or immediately oxidized to the corresponding diones. The arguments leading to the structures given are discussed in section 4.

Treatment of the tetrabromo- and tetrachloro-diones **5** and **4** with $LiAlH_4$ under mild conditions did not remove halogen atoms. This and reduction of the de-halo-dione **6** with $NaBH_4$ gave mixtures of *trans* and *cis*-diols in the ratios 17:1 (**20**:**26**), 2.7:1 (**19**:**25**)[4], and 1:1 (**21**:**27**), respectively.

Table 1 emphasizes the pattern of halogen atom removal under different conditions. The occasionally low yields, especially under some of the more energetic conditions, may be due to uncontrolled rearrangements of the tricyclic carbon skeleton. No defined products of such rearrangements could be isolated, but their formation is suspected from the ^{1}H-NMR. spectra of the crude reaction mixtures. They sometimes showed signals in the vinyl- and CH_3-region. A few conditions not mentioned in Table 1 gave only such products.

Two trends noticeable from the qualitative results shown in Table 1 may be worth mentioning:

1. Removal of all four halogen atoms was achieved only with the tetrabromo-dione **5** and only with $KFeH(CO)_4$ as reducing agent to give 73% of the hitherto unknown 1,3,5,7-tetramethyl-*anti*-tricyclo[5.1.0.0^{3,5}]octane-2,6-dione (**6**), m.p. 144°. $LiAlH_4$ was able to remove up to three halogen atoms from both the tetrabromo- and the tetrachloro-dione **5** (8%) and **4** (18%); less energetic conditions removed only two or one halogen atom.
2. While $KFeH(CO)_4$, $NaBH_3CN$ and $CrCl_2$ show a certain preference in the formation of products with a single halogen atom on a cyclopropane ring in the *endo*-position, $LiAlH_4$ gives mostly *exo*-halo-diones. It has been suggested that halogen atom removal from cyclopropane rings by $LiAlH_4$ proceeds with retention [5] and those by $KFeH(CO)_4$ with inversion of configuration [6]. Our results cannot shed any further light on these proposals since a single halogen atom remaining in either of the two positions (*endo* or *exo*) could have resulted from removal of a halogen atom in the same position with inversion or in the other position with retention of configuration.

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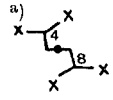
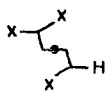
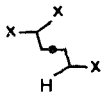
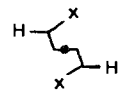
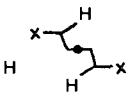
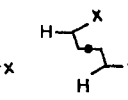
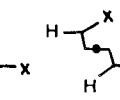
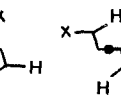
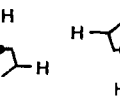
[4] Recently the tetrachloro-diols **19** and **25** have been described [4] as the products of $NaBH_4$ reduction of the tetrachloro-dione **4**, and their configurations have been assigned on the basis of Eu(fod)$_3$ shifted ^{1}H-NMR. spectra.

Table 1. *Product distributions*[a] *obtained from different reduction procedures applied to 4,4,8,8-tetrahalo-1,3,5,7-tetramethyl-*anti*-tricyclo[5.1.0.0^{3,5}]-octane-2,6-diones* **4** *and* **5** *and to the dehalo-dione* **6**

Educt dione	Conditions: reagent, solvent	time (h)	total yield (%)	[a] 								
	$LiAlH_4$ Ether	$2^1/_2$	96	70% **19** 26% **25**								
4 (X = Cl)	$LiAlH_4$ THF	24	52					52% **22**				
		60[b]	21					3% **11**			18% **13**	
	$KFeH(CO)_4$ EtOH/DME	24	34				10% **10**	5% **11**	19% **12**			
		48	68		2% **8**	1% **9**	32% **10**	9% **11**	24% **12**			
		96	51				38% **10**	4% **11**	9% **12**			
	$LiAlH_4$ Ether	4–7	89	84% **20** 5% **26**								
		16	29					29% **24**				
	$LiAlH_4$ THF	2[b]	31		14% **14**		17% **15**					
		24[b]	11					3% **16**			8% **18**	
5 (X = Br)	$KFeH(CO)_4$ EtOH/DME	3	58							34% **17**		24% **6**
		24	50									50% **6**
		48	70									70% **6**
		60	73									73% **6**
	$NaBH_3CN$ HMPA	24	12							12% **17**		
	$CrCl_2$ THF	24	14				14% **15**					
6 (X = H)	$NaBH_4$ H_2O/MeOH	20	95									47% **21** 48% **27**

[a] Products are diones or diols; distributions are expressed as yields in %.
[b] Initially formed diol oxidized to dione before analysis.

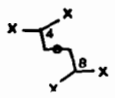
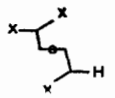
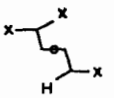
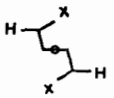
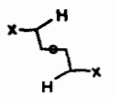
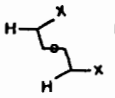
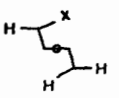
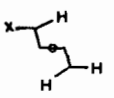
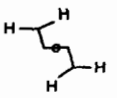
4. Structural assignments. – All products discussed here must have the *anti*-configuration of the two 3-membered rings on the 6-membered ring (compare [1]), as an *anti* to *syn* interconversion is hardly expected under the reaction conditions used. This is confirmed by the fact that the fully dehalogenated dione **6** is different from the previously described *syn*-isomer **7** [3].

4.1. *Diones.* Eight of the nine possible types of dehalogenated diones were obtained; six out of nine from the tetrachloro- **4**, and six out of nine from the tetrabromo-dione **5**. Most of them were obtained pure or almost pure, but two (**9** and **14**) were observed only in mixtures. Some of their properties and the assigned structures are listed in Table 2. The constitutions are evident from the results of the elemental analysis and from the properties, in particular since only one constitution is possible for the de-, mono- and trihalo-diones. In the case of the dihalo-diones the *gem*-dihalo arrangement can be excluded from the nature of the cyclopropyl-proton NMR. signals. Thus the 4,4-dihalo-dione is the only dehalogenated species not observed.

The assignment of configurations at the centres bearing halogen atoms in all partial reduction products is based on the assignment made for the *endo,exo*-dichloro-dione **12** according to ^{1}H- and ^{13}C-NMR. spectroscopic results. **12** was chosen as a model because of the presence of both stereochemical arrangements of halogen atoms at the cyclopropane ring within the same molecule. The *endo,exo*-configuration of **12** is evident from the fact that the ^{1}H-NMR. spectrum shows two singlets ($\delta = 3.97$ and 3.04) for the two protons of the CHCl groups. The former signal is slightly sharper than the latter (see below). It was important to know which of these signals belongs to the *endo*- and which to the *exo*-hydrogen atom. A decision was possible with the help of the difference in the coupling of these two hydrogen atoms with the ^{13}C-atoms of the *vicinal* methyl groups. This coupling ($J = 4.5$) is visible in the non-decoupled ^{13}C-NMR. spectrum of **12**, which shows two different kinds of methyl-carbon-atom signals, one as a quartet ($J = 130$) of doublets ($J = 4.5$) at $\delta = 14.8$, and the other as a quartet ($J = 131$, other couplings < 1) at 8.5. Selective decoupling revealed that the hydrogen atom absorbing at $\delta = 3.04$ was responsible for the 4.5 Hz coupling in the methyl signal at $\delta = 14.8$. We now propose that the signal at $\delta = 3.04$ should be assigned to the hydrogen atom in the *exo*-configuration on the basis of the following argument: 1) *Vögeli & v. Philipsborn* [7] (compare [8]) have shown that the ^{13}C/H *vicinal* coupling on a double bond is larger when the carbon-atom substituent and the hydrogen atom are located *trans* rather than *cis*. This behaviour parallels that of two H-atoms in the same relative positions. 2) On a cyclopropane ring, on the other hand, it is the *cis*-relationship of two *vicinal* H-atoms which give rise to a larger coupling than the corresponding *trans*-relationship [9]. We now assume that in this respect *vicinal* ^{13}C- and H-atoms on a cyclopropane ring behave similarly to two H-atoms, just as in the case of the atoms on a double bond, an assumption which is justified on theoretical grounds [10]. This implies that the coupling of $J = 4.5$ involves that hydrogen atom which lies *cis* to the methyl groups[5]), *i.e.* the one in the *exo*-position.

[5]) This method of assigning configurations to carbon-atom substituents *vicinal* to hydrogen atoms on a cyclopropane ring receives support from our observation with a bis-homobenzene derivative, in which the conclusion could be checked by an additional *vicinal* H/H coupling. Details will be reported later. It is possible that this method will turn out to be of general utility.

Table 2. *IR.-Carbonyl and ^{1}H-NMR. absorptions of the tetra-, tri-, di-, mono- and dehalo-1,3,5,7-tetramethyl-*anti*-tricyclo[5.1.0.0^{3,5}]octane-2,6-diones*

	Melting point and spectral data		Dione									
(X = Cl)	Cpd. no.			**4**	**8**	**9**	**10**	**11**	**12**		**13**	
	m.p.			256°	210°	in mixt.	273°	261°	165°		138°	
	IR.: C=O [a] (CHCl$_3$)			1698	1695		1695 1690	1695	1695 1690		1690	
	^{1}H-NMR.: (CDCl$_3$)	H_3C—C [b]		1.45 (12)	1.38 (6) 1.44 (6)	1.32 (6) 1.46 (6)	1.40 (12)	1.34 (12)	1.33 (6) 1.46 (6)		1.34 (6) 1.40 (6)	
		H—C(4)					3.17 (2) [d]	3.55 (2) [c]	3.04 (1) [d]		3.15 (1) [c]	
		H—C(8)			3.30 (1) [d]	4.00 (1) [c]			3.97 (1) [c]		1.72 (1) 1.16 (1) } 5	
		Δδ endo-exo			← 0.70 →		← 0.38 →		0.93		0.56	
	Cpd. no.			**5**	**14**		**15**	**16**	**17**	**18**	**6**	
	m.p.			> 220° dec.	in mixt.		267° dec.	230° dec.	149°	133°	144°	
	IR.: C=O (CHCl$_3$)			1695			1692	1693	1690	1685	1690 1675	
(X = Br)	^{1}H-NMR.: (CDCl$_3$)	H_3C—C		1.44 (12)	1.43 (6) 1.50 (6)		1.43 (12)	1.37 (12)	1.38 (6) 1.44 (6)	1.36 (6) 1.41 (6)	1.38 (12)	
		H—C(4)							2.74 (1) [d]	3.30 (1) [c]	1.36 (2) } 5	
		H—C(8)			3.06 (1) [d]		2.96 (2) [d]	3.58 (2) [c]	1.90 (1) } 5 1.24 (1)	1.75 (1) } 5 1.23 (1)	0.98 (2)	
		Δδ endo-exo					← 0.62 →		0.66	0.52	0.38	
									← 0.56 →			

[a] In cm^{-1}. [b] δ-Values (no. of protons); } J-Value in Hz. [c] With ringing. [d] Without ringing.

Thus the assignments of the ^{13}C- and ^{1}H-NMR. data of the *endo,exo*-dichloro-dione **12** are those shown in Fig. 1. The ^{1}H-NMR. signal of the *endo*-H not only occurs at lower field than that of the *exo*-H but is also sharper. The slight broadening of the

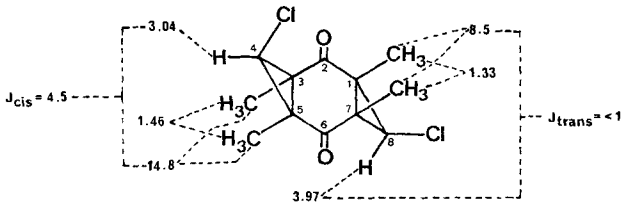


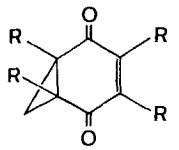
Fig. 1. ^{13}C- *and* ^{1}H-*NMR. assignments for the* endo, exo-*dichloro-dione* **12** (values without units are chemical shifts on the δ-scale, J-values are in Hz)

exo-H signal is attributed to a long range coupling with the protons of the *cis*-methyl groups, since only this signal ($\delta = 3.04$) is sharpened on irradiation of one of the methyl proton absorptions[6]), namely the one at $\delta = 1.46$.

These two aspects, namely position at lower field and greater sharpness *vs.* position at higher field and slight broadening, were observed in all signals due to protons of CHX groups. The sharper signal could invariably be distinguished from the other one by its ringing (described as 'with ringing' in Table 2 and in the Exper. Part). The relative chemical shifts are used as criteria for the assignment of signals to *endo*- (lower field) or *exo*-positions (higher field) of protons on the cyclopropane rings and thus to the configurational assignments of the diones shown in Table 2. The signal occurring at lower field of all comparable *endo*/*exo*-H-pairs was assigned to the *endo*-H, whether these signals belong to two hydrogen atoms within the same molecule (cases **6**, **13**, **17** and **18**, aside from **12**) or to two stereoisomeric molecules (cases **8/9**, **10/11**, **15/16** and **17/18**). The $\Delta\delta$-values (δ_{endo}-δ_{exo}), which are also listed in Table 2, vary from 0.93 to 0.38. The occasional low $\Delta\delta$-values diminish the validity of the chemical shift criterion but, since always the low field signal is sharp in the diones with CHX groups, more confidence in the assignments is gained. The assignment made to *endo*-H and *exo*-H of CH_2 groups (compounds **6**, **13**, **17** and **18**) on the basis of chemical shift only (no difference in line width observed) is further substantiated by an argument for the dehalo-dione **6** given below. The totally dehalogenated dione **6** shows the expected properties of a bis-homo-*p*-quinone[1]) derivative (*cf.* [1] [11]): Multiple absorptions in the carbonyl region (1690, 1675 and 1608 cm^{-1}) of the IR. spectrum are observed, and the mass spectrum reveals a molecular ion (*m/e* 192) as well as the characteristic fragmentations, namely two consecutive losses of CO (*i.e.* *m/e* 164, (M – CO) and *m/e* 121, (M – 2(CO)–CH_3)) and fragmentation into equal parts (*m/e* 96). The assignment of ^{1}H-NMR. signals to the protons of the CH_2 groups

[6]) This effect was noted while attempting to confirm by an NOE-experiment the *exo*-configuration of one of the protons of the CHCl groups in **12**. Selective methyl signal irradiation was difficult, but could be achieved to some extent: irradiation at $\delta = 1.46$ produced enhancements of 30 and 20% of the two H—C(Cl) signals, while irradiation at $\delta = 1.33$ led to enhancements of 10 and 13% of the same signals. Thus it appears that both the *exo*- and the *endo*-H—C(Cl) are close to one of the methyl group pairs, namely to the one situated at C(3) and C(5) with a chemical shift of $\delta = 1.46$.

in **6** can be made by applying a modification of the previously observed [12] effect of the angular methyl groups on the methylene protons of homo-*p*-quinone derivatives: Comparison of the chemical shift (in $CDCl_3$) of *exo*-H in *syn*-bishomo-*p*-quinone (**3**, $\delta = 1.37$) with that in *syn*-bishomo-duroquinone (**7**, $\delta = 0.81$), and in homo-*p*-quinone (**28**, $\delta = 1.73$) with that in homo-duroquinone (**29**, $\delta = 1.05$) shows



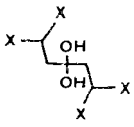
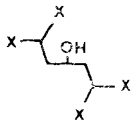
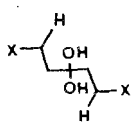
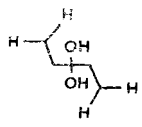
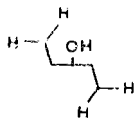
28: R = H
29: R = CH_3

a shielding effect due to two methyl groups of $\Delta\delta = -0.56$ to -0.68. When this value is added to the well established [11] chemical shift of *exo*-H in *anti*-bishomo-*p*-quinone (**2**, $\delta = 1.65$), a chemical shift of $\delta = 0.97$ to 1.09 is calculated for *exo*-H in *anti*-bishomo-duroquinone (**6**). This is in good agreement with the observed signal of one of the CH_2 protons in **6**, namely the one with $\delta = 0.98$, to which the *exo*-position is assigned; it is not in agreement with $\delta = 1.36$ for the other CH_2 proton in **6**, which must be *endo*-H (for comparison: *endo*-H in **2** has $\delta = 1.23$).

4.2. *Diols.* Three constitutional types of diols were observed: The tetrahalo-diols as *trans*- and *cis*-isomers **19** and **25** as well as **20** and **26**, the *exo,exo*-dihalo-diols as *trans*-isomers **22** as well as **24**, and the dehalo-diols as *trans*- and *cis*-isomers **21** and **27**. Some of their properties are summarized in Table 3. The constitutions of the isomer pairs **19**/**25**, **20**/**26** and **21**/**27** are evident because they were obtained by mild reductions ($LiAlH_4$ and $NaBH_4$) of the parent ketones **4**, **5** and **6**. The constitution and the configuration at C(4) and C(8) of the dihalo-diols **22** and **24** may be deduced from their properties, and in the case of **22** from the fact that oxidation afforded the *exo,exo*-dichloro-dione **11**. The configurations at C(2) and C(6) in these diols are derived from symmetry considerations. All the diols observed here have equivalent substitution patterns at both cyclopropane rings. Such derivatives possess C_i symmetry when the hydroxyl groups are *trans*, but only C_s symmetry when they are *cis*: The two *endo*-hydrogen atoms on the two cyclopropane rings are enantiotopic in the *trans*-, but diastereotopic in the *cis*-diols; this is also the case for the two *exo*-hydrogen atoms in **21** and **27**. Thus, of the two diols obtained from the dehalo-dione **6**, the one with four signals for cyclopropyl hydrogen atoms is the *cis*-isomer **27**, and the one with only two such signals the *trans*-isomer **21**. Both dihalo-diols **22** and **24** show only one sharp singlet for the cyclopropyl hydrogen atoms, indicating the *trans*-configuration. Accidental signal coincidence can be excluded in the case of **22** since change of solvent and conversion to the diacetate **23** did not alter the number of ^{1}H-NMR. signals.

In the case of the tetrahalo-diols a yield argument leads to configurational assignments (compare [4]). The tetrahalo-diol isomers were formed in yields of 70 and 26% in the tetrachloro-, and of 84 and 5% in the tetrabromo-case (see Table 1). But the dichloro- and the dibromo-*trans*-diol **22** and **24** were obtained in 52 and 29%

Table 3. *^1H-NMR. Absorptions of the tetra-, di- and dehalo-diols*

^{1}H-NMR. ($CDCl_3$) [a]	Diol [b]					
	Cpd. no.	**19**	**25**	**22**	**21**	**27**
	m.p.	189°	in mixt.	164°	126°	134°
(X = Cl)	H_3C—C	1.22/*s* (6H) 1.41/*s* (6H)	1.28/*s* (6H) 1.38/*s* (6H)	1.16/*s* (6H) 1.17/*s* (6H)	1.10/*s* (12H)	1.08/*s* (6H) 1.28/*s* (6H)
	H—C(4) H—C(8)			3.24/*s* (2H) [b]	0.05/*d* (2H) 0.68/*d* (2H) (both J = 5)	1.12/*d* (1H) 0.75/*d* (1H) 0.20/*d* (1H) −0.03/*d* (1H) (all J = 5)
	H—C(2) H—C(6)	4.08/*d* (2H) (J = 12)	4.01/*d* (2H) (J = 12)	3.80/*d* (2H) (J = 5)	3.74/*d* (2H) (J = 5)	3.88/*d* (2H) (J = 7)
	Cpd. no.	**20**	**26**	**24**		
	m.p.	> 130° dec.	in mixt.	132° dec.		
(X = Br)	H_3C—C	1.26/*s* (6H) 1.45/*s* (6H)	1.29/*s* (6H) 1.42/*s* (6H)	1.14/*s* (12H)		
	H—C(4) H—C(8)			3.28/*s* (2H) [c]		
	H—C(2) H—C(6)	4.07/*d* (2H) (J = 12)	4.01/*d* (2H) (J = 12)	3.86/*d* (2H) (J = 5)		

[a] δ-Values/multiplicity (intensity) (J in Hz). [b] See scheme at p. 1312. [c] With ringing.

yield, respectively. If we accept that the tetrahalo-diols (obtained by mild $LiAlH_4$ reduction) are the intermediates for the corresponding dihalo-diols (obtained under the same, but more energetic conditions), and that no isomerization of the hydroxyl groups takes place (see below), the minor tetrachloro- and tetrabromo-diol isomers cannot have the same configuration at C(2) and C(6) as the isolated dichloro- and dibromo-diols (shown to be *trans*) and, therefore, must be the *cis*-isomers **25** and **26**, respectively. Conversely the major tetrachloro- and tetrabromo-diol isomer must have the *trans*-configurations, as shown in **19** and **20**.

It was desirable (see above) to test whether an isomerization of hydroxyl groups in the diols could take place with lithium aluminium hydride. This has been shown [13] to be the case for cyclohexanols, albeit there in the presence of aluminium chloride. Therefore the dehalo-diols **21** and **27** were treated under the (more energetic) conditions which were capable of converting the tetrahalo-diones **4** and **5** to the dihalo-diols **22** and **24**. Both the pure *trans*-diol **21**, and a 1:1 mixture of the *trans*- and *cis*-diols (**21** and **27**) were recovered unisomerized.

The diacetate **23** was synthesized in the hope that an independent conclusion could be drawn on the configuration (*endo* or *exo*) of the hydrogen atom of the CHCl group from the effect of these acetoxy groups on the chemical shift of the *endo*-hydrogen atom. However, the change observed (0.10 ppm) was not significant enough to add to the argument.

5. Preparation of the tetrabromo-dione 5. – A procedure different from the one described in [1] was used here. Treatment of duroquinone and carbon tetrabromide with a sixfold excess of methyl lithium in ether[7]) afforded 63% of 4,4,8,8-tetrabromo-1,3,5,7-tetramethyl-*anti*-tricyclo[5.1.0.$0^{3,5}$]octane-2,6-dione (**5**)[1]).

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Experimental part

1. General. – For abbreviations and the spectral data, see [9] [12]. In the ^{1}H-NMR. spectra of certain compounds singlets due to H–C(X) (X = Cl, Br) were observed to be either so sharp that they showed ringing or slightly broadened so that they showed no ringing. They are described here as 'with ringing' or 'without ringing', respectively, after the multiplicity of the signal. These features were reproducible on different instruments.

The mass, (100 MHz)-^{1}H-NMR., ^{13}C-NMR. and IR. spectra were measured in the laboratories for mass spectrometry (under Prof. *M. Hesse* and Prof. *J. Seibl*), for nuclear magnetic resonance (under Prof. *W. v. Philipsborn* and Prof. *J. F. M. Oth*) and for micro-analysis (under Mr. *H. Frohofer* and Mr. *W. Manser*), of the University and of the ETH, respectively. Elemental analyses were performed in the last mentioned laboratories. The (60 MHz)-^{1}H-NMR. spectra were measured on a *Varian* EM-360 instrument.

2. Products from 4,4,8,8-tetrachloro-1,3,5,7-tetramethyl-*anti*-tricyclo[5.1.0.$0^{3,5}$]-octane-2,6-dione (4). – 2.1. *Lithium aluminium hydride reduction in ether.* A mixture of 0.31 g (0.94 mmol) of **4** and 0.04 g (1.10 mmol) of lithium aluminium hydride in 25 ml of anhydrous ether was stirred under reflux for 2½ h. After cooling 1 ml of water was added followed by 10 ml of dilute hydrochloric acid, and the resulting solution was extracted with chloroform. The combined

[7]) Preliminary experiments with this method were carried out by Dr. *Ch. E. Dahl* in this laboratory.

extracts were washed with water, dried, and evaporated to leave 0.30 g (96%) of a powder which was recrystallized from chloroform to give 0.172 g (55%) of *4,4,8,8-tetrachloro-1,3,5,7-tetramethyl*-anti-*tricyclo*[*5.1.0.0*^{3,5}]*octane-2,6*-trans-*diol* (**19**) as colourless plates, m.p. 187–189° (dec.). – IR. (KBr): 3550*s*, 3430*s*, 3020*m*, 3010*m*, 2970*m*, 2940*m*, 1470*m*, 1440*m*, 1430*m*, 1400*m*, 1310*m*, 1280*m*, 1238*m*, 1182*m*, 1160*m*, 1085*m*, 1070*m*, 1060*m*, 1038*s*, 1023*s*, 935*m*, 915*m*, 878*m*, 790*m*, 770*m*, 752*m*. – IR. ($CHCl_3$): 3580*s*. – MS.: 301/299/297 (1/2.5/3, $M^+ - Cl$),.283/281/279 (4/10/11, $M^+ - Cl - H_2O$), 265/263/261 (0.75/1.75/2.0, $M^+ - Cl - 2(H_2O)$), 161 (33), 159 (100), 157 (34), 143 (26), 141 (58), 139 (92), 137 (30), 131 (32), 129 (29), 123 (25), 105 (16), 103 (26), 101 (34), 95 (22), 91 (15). – ^{1}H-NMR. (100 MHz, $CDCl_3$): 4.08/*d* (J = 12), 2H (H—C(2), H—C(6)); 2.39/*d* (J = 12), 2H (2OH); 1.41/*s*, 6H ($2CH_3$); 1.22/*s*, 6H ($2CH_3$). Addition of D_2O removed the signal at δ = 2.39 and converted the signal at 4.08 to a *s*.

$C_{12}H_{16}Cl_4O_2$ (334.07) Calc. C 43.13 H 4.81 Cl 42.45% Found C 42.96 H 4.55 Cl 42.60%

The residue from the crystallization mother liquor (0.128 g, 41%) was shown by its ^{1}H-NMR. spectrum to be a 3:5 mixture of the two isomeric diols, the minor component being the *trans*-isomer **19** described above. The major component in this residue was *4,4,8,8-tetrachloro-1,3,5,7-tetramethyl*-anti-*tricyclo*[*5.1.0.0*^{3,5}]*octane-2,6*-cis-*diol* (**25**). It was recognized by ^{1}H-NMR. (100 MHz, $CDCl_3$): 4.01/*d* (J = 12), 2H (H—C(2), H—C(6)); 2.34/*d* (J = 12), 2H (2OH); 1.38/*s*, 6H ($2CH_3$); 1.28/*s*, 6H ($2CH_3$).

2.2. *Lithium aluminium hydride reduction in tetrahydrofuran.* 2.2.1. *For 24 and 40 h.* A solution of 2.0 g (6.2 mmol) of **4** in 50 ml of anhydrous tetrahydrofuran was treated with an excess of lithium aluminium hydride (4.5 g), and the stirred mixture was heated under reflux for 24 h. After a further 16 h at RT. 5 ml of water were added followed by 150 ml of dilute hydrochloric acid. The resulting solution was extracted with chloroform and the combined extracts were washed with water, dried, and evaporated to leave 1.2 g of a semisolid residue. Crystallization from chloroform/hexane gave 0.83 g (52%) of *4*-exo,*8*-exo-*dichloro-1,3,5,7-tetramethyl*-anti-*tricyclo*[*5.1.0.0*^{3,5}]*octane-2,6*-trans-*diol* (**22**) as colourless needles, m.p. 162.5–163.5°. – IR. ($CHCl_3$): 3600*m*, 3410*m*, 3000*w*, 2920*s*, 2850*w*, 1468*m*, 1398*w*, 1165*m*, 1032*s*, 1000*m*, 918*w*, 905*w*. – MS.: 250/248/246 (0.04/1.5/2, $M^+ - H_2O$), 231/229 (3/3, $M^+ - Cl$), 213/211 (20/50, $M^+ - Cl - H_2O$), 175 (30), 171 (10), 161 (25), 160 (30), 159 (55), 157 (16), 155 (31), 147 (30), 142 (20), 137 (19), 135 (17), 134 (20), 133 (20), 132 (55), 131 (15), 125 (100), 124 (25), 123 (50), 121 (22), 119 (30), 109 (30), 107 (48), 105 (70), 103 (40), 101 (30), 98 (15), 97 (50), 95 (45), 93 (15), 91 (30). – ^{1}H-NMR. (100 MHz, $CDCl_3$): 3.80/*d* (J = 5), 2H (H—C(2), H—C(6)); 3.24/*s* with ringing, 2H (*endo*-H—C(4), *endo*-H—C(8)); 1.75/*d* (J = 5), 2H (2OH); 1.17/*s*, 6H ($2CH_3$); 1.16/*s*, 6H ($2CH_3$). – ^{1}H-NMR. (100 MHz, C_6D_6): 3.27/*d* (J = 5), 2H (H—C(2), H—C(6)); 3.12/*s*, 2H (*endo*-H—C(4), *endo*-H—C(8)); 1.00/*s*, 6H ($2CH_3$); 0.93/*s*, 6H ($2CH_3$); 0.78/*d* (J = 5), 2H (2OH).

$C_{12}H_{18}Cl_2O_2$ (265.18) Calc. C 54.36 H 6.84 Cl 26.74% Found C 54.08 H 6.83 Cl 26.56%

A solution of 0.22 g (0.83 mmol) of dichloro-diol **22** in 2 ml of pyridine was treated with 2 ml of acetic anhydride. After 20 h at RT. the solution was diluted with 100 ml of water and extracted with chloroform. The combined extracts were washed with dilute hydrochloric acid, aqueous sodiumhydrogen carbonate solution and water, dried, and evaporated to leave a yellow oil which on distillation gave 0.27 g (93%) of *4*-exo,*8*-exo-*dichloro-1,3,5,7-tetramethyl*-anti-*tricyclo*[*5.1.0.0*^{3,5}]-*oct-2,6-ylene*-trans-*diacetate* (**23**) as a viscous colourless oil, b.p. 90–95°/0.1 Torr. – IR. ($CHCl_3$): 3010*m*, 2975*m*, 2940*m*, 1740*s*, 1472*m*, 1375*s*, 1250–1205*s*, 1170*m*, 1025*s*, 990*s*, 915*m*, 830*m*. – MS.: 315/313 (10/4, $M^+ - Cl$), 278 (0.7, $M^+ - 2Cl$), 211 (23), 175 (13), 147 (12), 43 (100). – ^{1}H-NMR. (100 MHz, $CDCl_3$): 4.82/*s*, 2H (H—C(2), H—C(6)); 3.14/*s* with ringing, 2H (*endo*-H—C(4), *endo*-H—C(8)); 2.16/*s*, 6H (2OAc); 1.19/*s*, 6H ($2CH_3$); 1.07/*s*, 6H ($2CH_3$).

$C_{16}H_{22}Cl_2O_4$ (349.27) Calc. C 55.01 H 6.35 Cl 20.30% Found C 55.23 H 6.42 Cl 19.77%

When the reduction was repeated with 0.15 g (0.45 mmol) of **4** and 0.35 g of reducing agent in 15 ml of solvent for 40 h under reflux, 0.04 g (33%) of the diol **22** were isolated which had identical spectral properties to those described above. To a solution of the residue from the mother liquor of the crystallization in 2 ml of acetone was added dropwise *Jones'* reagent [14] until the orange colour persisted. After 1 h at RT. the mixture was diluted with 50 ml of water and extracted with chloroform. The combined extracts were washed with aqueous sodium carbonate,

water, dried and evaporated to leave a semisolid residue. Crystallization from chloroform/hexane gave 15 mg (13%) *4*-exo,*8*-exo-*dichloro-1,3,5,7-tetramethyl*-anti-*tricyclo*[*5.1.0.0*^{3,5}]*octane-2,6-dione* (**11**) as transparent needles, m.p. 260–261°, whose spectral properties are described in 2.2.3.

2.2.2. *For 60 h.* The reduction (0.30 g (0.9 mmol) of **4** for 60 h) and the subsequent oxidation were repeated using the same procedures as described in 2.2.1 to give 0.18 g of a brown oil. Crystallization from chloroform/hexane gave two fractions. The first (11 mg, 9%) was shown by its ^{1}H-NMR. spectrum to be a 2:1 mixture of the chloro-dione **13** (see below) and the dichloro-dione **11** (see 2.2.3). The second fraction (26 mg, 12%) was *4*-exo-*chloro-1,3,5,7-tetramethyl*-anti-*tricyclo*[*5.1.0.0*^{3,5}]*octane-2,6-dione* (**13**), m.p. 136–138°. – IR. ($CHCl_3$): 3000*w*, 2940*w*, 2920*w*, 2860*w*, 1690*s*, 1468*m*, 1392*w*, 1300*s*, 1055*m*, 840*m*. – MS.: 228/226 (15/40, M^+), 200/198 (5/15, M^+-CO), 191 (25, M^+-Cl), 163 (63), 162 (87), 158 (15), 157 (27), 156 (16), 155 (17), 147 (22), 140 (17), 135 (35), 134 (15), 130 (20), 123 (30), 122 (65), 121 (22), 120 (20), 119 (47), 107 (22), 105 (23), 96 (35), 93 (15), 91 (27), 69 (100). – ^{1}H-NMR. (60 MHz, $CDCl_3$): 3.15/*s* with ringing, 1H (*endo*-H–C(4)); 1.72/*d* (J = 5), 1H (*endo*-H–C(8)); 1.40/*s*, 6H ($2CH_3$); 1.34/*s*, 6H ($2CH_3$); 1.16/*d* (J = 5), 1H (*exo*-H–C(8)).

$C_{12}H_{15}ClO_2$ (226.70) Calc. C 63.60 H 6.67 Cl 15.64% Found C 63.97 H 6.68 Cl 15.18%

2.2.3. *Oxidation of the dichloro-diol* **22**. A stirred solution of 44 mg (0.17 mmol) of **22** in 3 ml of acetone was treated with *Jones'* reagent [14] until the orange colour persisted. After 1 h at RT. the reaction was worked-up as described in 2.2.1 to give 41 mg (95%) of *4*-exo,*8*-exo-*dichloro-1,3,5,7-tetramethyl*-anti-*tricyclo*[*5.1.0.0*^{3,5}]*octane-2,6-dione* (**11**) as needles, m.p. 259–261°. – IR. ($CHCl_3$): 3030*w*, 2940*w*, 2920*w*, 2850*w*, 1695*s*, 1465*m*, 1295*s*, 1045*w*, 940*w*, 850*m*. – MS.: 264/262/260 (3/12/18, M^+), 227/225 (28/80, M^+-Cl), 199/197 (11/34, $M^+-Cl-CO$), 196 (20), 169 (25), 161 (50), 134 (15), 133 (35), 130 (30), 119 (18), 105 (18), 103 (20), 91 (19), 67 (100), 39 (85). – ^{1}H-NMR. (60 MHz, $CDCl_3$): 3.55/*s* with ringing, 2H (*endo*-H–C(4), *endo*-H–C(8)); 1.34/*s*, 12H ($4CH_3$).

$C_{12}H_{14}Cl_2O_2$ (261.15) Calc. C 55.18 H 5.40 Cl 27.15% Found C 55.16 H 5.21 Cl 27.66%

2.3. *Potassium hydridotetracarbonylferrate* [6] *reductions.* 2.3.1. *Of the tetrachloro-dione* **4**. The iron hydride was generated by refluxing a mixture of 6 ml (44.4 mmol) of iron pentacarbonyl, 7.4 g (132 mmol) of potassium hydroxide and 750 ml of ethanol for 2 h. The tetrachloro-dione **4** (3 g, 9.1 mmol) was added as a slurry in 50 ml of dimethoxy-ethane and the resulting mixture was heated under reflux for 48 h. On cooling the solids were filtered off, and the filtrate evaporated to dryness. The residue was shaken with water and chloroform, and the organic phase was dried and evaporated to leave 2.20 g of a green solid residue. Crystallization from chloroform/hexane yielded 0.84 g (35%) of a 4:1 mixture of the *endo,endo-* and *exo,exo*-dichloro-diones **10** and **11** which was fractionally crystallized from chloroform/hexane at 0° to give 0.21 g (8%) of *4*-endo,*8*-endo-*dichloro-1,3,5,7-tetramethyl*-anti-*tricyclo*[*5.1.0.0*^{3,5}]*octane-2,6-dione* (**10**) as transparent needles, m.p. 271–273°. – IR. ($CHCl_3$): 3030*m*; 3018*m*; 2990*w*, 2947*w*, 1695*s*, 1690*s*, 1605*w*, 1470*m*, 1392*m*, 1320*m*, 1230–1200*s* br., 1085*w*, 1048*m*, 930*m*, 885*m*. – MS.: 264/262/260 (0.5/2/3, M^+), 227/225 (6/18, M^+-Cl), 199/197 (4/10, $M^+-Cl-CO$), 161 (18), 133 (17), 69 (95), 39 (100). – ^{1}H-NMR. (60 MHz, $CDCl_3$): 3.17/*s* without ringing, 2H (*exo*-H–C(4), *exo*-H–C(8)); 1.40/*s*, 12H ($4\ CH_3$).

$C_{12}H_{14}Cl_2O_2$ (261.15) Calc. C 55.18 H 5.40 Cl 27.15% Found C 54.95 H 5.63 Cl 26.89%

The remaining 1.36 g of the green residue obtained initially was chromatographed on a silica gel column using chloroform/hexane 7:3 and gave four fractions, the two minor ones being described further below. The two major fractions consisted of 0.36 g (15%) of a 4:2:1 mixture of the three stereoisomeric *endo,exo-*, *endo,endo-* and *exo,exo*-dichloro-diones **12**, **10** and **11**, and 0.38 g (15%) of the *endo,exo*-isomer **12**. Recrystallization of the mixture from carbon tetrachloride gave more pure isomer **12** (0.1 g) making a total of 0.48 g (24%) of *4*-endo,*8*-exo-*dichloro-1,3,5,7-tetramethyl*-anti-*tricyclo*[*5.1.0.0*^{3,5}]*octane-2,6-dione* (**12**) as white needles, m.p. 163–165°. – IR. ($CHCl_3$): 3030*m*, 3020*m*, 2980*w*, 2945*w*, 1695*s*, 1690*s* sh, 1605*w*, 1468*m*, 1395*m*, 1305*s*, 1240–1200*s* br., 1048*s*, 930*m*, 875*m*. – MS.: 264/262/260 (1/3/5, M^+), 227/225 (10/25, M^+-Cl), 199/197 (6/20, $M^+-Cl-CO$), 169 (18), 161 (33), 133 (30),130 (24), 119 (15), 105 (15), 91 (17), 67 (100), 39 (80). – ^{1}H-NMR. (100 MHz, $CDCl_3$ degassed): 3.97/*s* with ringing, 1H (*endo*-H–C(8)); 3.04/*s* without ringing, 1 H (*exo*-H–C(4)); 1.46/*s*, 6H (H_3C–C(3), H_3C–C(5)); 1.33/*s*, 6H (H_3C–C(1), H_3C–C(7)).

Spin decoupling: Irradiation at 1.46 (H_3C—C(3), H_3C—C(5)) enhanced the singlet at 3.04 (*exo*-H—C(4)) by 30% and the one at 3.97 (*endo*-H—C(8)) by 20%; irradiation at 1.33 (H_3C—C(1), H_3C—C(7)) enhanced the singlets at 3.04 and 3.97 (*exo*-H—C(4) and *endo*-H—C(8)) by 10% and 13%, respectively. In addition, it was observed that the slightly broader singlet at 3.04 (*exo*-H—C(4)) was sharpened only by the irradiation at 1.46 (H_3C—C(3), H_3C—C(5)), and not by the one at 1.33 (H_3C—C(1), H_3C—C(7)). The singlet at 3.97 (*endo*-H—C(8)) was not affected with respect to sharpness by either of the irradiations. This experiment, apart from establishing a slight coupling between *exo*-H—C(4) and the two CH_3's at C(3) and C(5), shows that a certain selectivity was indeed achieved in the two irradiations. The enhancements were determined from the integration curves for each signal and the term 'sharpened' refers to the signal showing ringing as a result of the irradiation. – ^{13}C-NMR. (25.2 MHz, $CDCl_3$): 198.9 (C(2), C(6)); 46.0 (C(4) or C(8)); 45.5 (C(8) or C(4)); 41.3 (C(3), C(5) or C(1), C(7)); 36.1 (C(1), C(7) or C(3), C(5)); 14.8 (CH_3—C(3), CH_3—C(5)); 8.5 (CH_3—C(1), CH_3—C(7)). Selective decoupling: Irradiation at 3.04 (*exo*-H—C(4)) converted the $q \times d$ (J = 130 & 4.5) at 14.8 (CH_3—C(3), CH_3—C(5)) to q, whereas the q (J = 131, other couplings < 1) at 8.5 (CH_3—C(1), CH_3—C(7)) remained unchanged; irradiation at 3.97 (*endo*-H—C(8)) did not change the signal at 14.8 (CH_3—C(3), CH_3—C(5)) but slightly sharpened the one at 8.5 (CH_3—C(1), CH_3—C(7)).

$C_{12}H_{14}Cl_2O_2$ (261.15) Calc. C 55.18 H 5.40 Cl 27.15% Found C 55.01 H 5.57 Cl 27.36%

The first minor fraction of the chromatogram consisted of 20 mg (1%) of *4,4,8*-endo-*trichloro-1,3,5,7-tetramethyl*-anti-*tricyclo*[*5.1.0.0*^{3,5}]*octane-2,6-dione* (**8**), m.p. 208–210°. – IR. ($CHCl_3$): 3020*m*, 2948*w*, 1695*s*, 1605*w*, 1465*m*, 1390*w*, 1375*w*, 1300*m*, 1230–1200*m* br., 1195*m*, 1045*w*, 995*w*, 925*w*, 905*w*, 881*m*. – MS.: 263/261/259 (0.5/1.5/2.0, M^+ – Cl), 235/233/231 (0.5/1.5/2.0, M^+ – Cl – CO), 225/223 (0.1/0.3, M^+ – Cl – HCl), 207/205/203 (1/3/5, M^+ – Cl – 2(CO)), 197/195 (2/6, M^+ – Cl – CO – HCl), 169/167 (3/9, M^+ – Cl – 2(CO) – HCl), 131 (6, M^+ – Cl – 2(CO) – 2(HCl)), 101 (36), 91 (15), 67 (75), 39 (100). – ^{1}H-NMR. (100 MHz, $CDCl_3$): 3.30/*s* without ringing, 1H (*exo*-H—C(8)); 1.44/*s*, 6H ($2CH_3$); 1.38/*s*, 6H ($2CH_3$).

$C_{12}H_{13}Cl_3O_2$ (295.59) Calc. C 48.76 H 4.43 Cl 35.98% Found C 48.86 H 5.10 Cl 35.82%

The second minor fraction of the chromatogram (60 mg, 2%), m.p. 105–115°, was shown by its ^{1}H-NMR. spectrum to be a 1:1 mixture of two isomeric trichloro-diones, one being the isomer **8** described above. The other was *4,4,8*-exo-*trichloro-1,3,5,7-tetramethyl*-anti-*tricyclo*[*5.1.0.0*^{3,5}]-*octane-2,6-dione* (**9**). It was recognized by ^{1}H-NMR. (100 MHz, $CDCl_3$): 4.00/*s* with ringing, 1H (*endo*-H—C(8)); 1.46/*s*, 6H ($2CH_3$); 1.32/*s*, 6H ($2CH_3$).

When the reaction was repeated for 24 h a yield of 34% of a 4:2:1 mixture (*endo,exo*/*endo,endo*/*exo,exo*) of the dichloro-diones **12**, **10** and **11** was obtained. A reaction of 96 h resulted in a 51% yield of a 9:2:1 mixture (*endo, endo*/*endo,exo*/*exo,exo*) of the stereoisomeric dichloro-diones **10**, **12** and **11**.

2.3.2. *Of the dichloro-diones* **10**, **11**, *and* **12**. The reduction (for 48 h) of the dichloro-diones was attempted using the same procedure as described in 2.3.1. with 0.13 g (0.5 mmol) of an about 1:1:1 mixture of the stereoisomeric diones **10**, **11**, and **12**, 0.6 ml (4.4 mmol) of iron pentacarbonyl, 0.74 g (13.2 mmol) of potassium hydroxide, 45 ml of ethanol, and 8 ml of dimethoxy-ethane. Purification of the green residue (0.13 g) by preparative TLC. on silica gel using chloroform/hexane 7:3 lead to the recovery of 70 mg (54%) of a 3:1:1 (*endo,endo*/*exo,exo*/*endo,exo*)-mixture (according to the ^{1}H-NMR. spectrum integration) of the stereoisomeric dichloro-diones **10**, **11**, and **12**. A second fraction (40 mg) obtained from the chromatography was shown by its ^{1}H-NMR. spectrum to be a complex mixture containing about 20% of the *endo,exo* isomer **12** and possibly also a small amount of *1,3,5,7-tetramethyl*-anti-*tricyclo*[*5.1.0.0*^{3,5}]*octane-2,6-dione* (**6**) (see 3.5.1.).

3. Products from 4,4,8,8-tetrabromo-1,3,5,7-tetramethyl-*anti*-tricyclo[5.1.0.0^{3,5}]-octane-2,6-dione (5). – 3.1. *Lithium aluminium hydride reduction in ether.* 3.1.1. *For 4–7 h.* A mixture of 0.3 g (0.59 mmol) of **5**, and 0.05 g (1.3 mmol) of lithium aluminium hydride in 20 ml of anhydrous ether was stirred under reflux for 4–7 h. The procedure described in 2.1. was used for the work-up to leave 0.28 g of a mixture consisting of ~90% of **20** and ~5% of **26** (^{1}H-NMR., see below) as a powder which was recrystallized from chloroform to give 0.09 g (30%) of *4,4,8,8-*

tetrabromo-1,3,5,7-tetramethyl-anti-*tricyclo*[*5.1.0.0*^{3,5}]*octane-2,6*-trans-*diol* (**20**) as white plates. M.p. determination: darkening above 130° until black at 160°, accompanied by sublimation. – IR. (KBr): 3495*s*, 3440*s*, 3020*w*, 2965*w*, 2935*w*, 1395*m*, 1235*w*, 1180*m*, 1152*w*, 1045*s*, 1030*m*, 910*m*, 833*m*, 755*m*, 745*m*. – MS.: 435/433/431/429 (0.7/2/2/0.7, M^+ – Br), 417/415/413/411 (7/20/20/7, M^+ – Br – H_2O), 335/333/331 (6/6/2, M^+ – Br – HBr – H_2O), 336/334/332 (3/6/3, M^+ – 2 Br – H_2O), 231 (40), 229 (100), 227 (100), 225 (40), 205 (55), 204 (20), 203 (70), 201 (20), 175 (15), 174 (20), 173 (15), 149 (23), 147 (35), 145 (30), 125 (50), 124 (85), 123 (85), 119 (22), 105 (22), 97 (22), 96 (26), 95 (30), 91 (40). – ^{1}H-NMR. (60 MHz, $CDCl_3$): 4.07/*d* (J = 12), 2H (H–C(2), H–C(6)); 2.63/*d* (J = 12), 2H (2OH); 1.45/*s*, 6H (2CH_3); 1.26/*s*, 6H (2CH_3).

$C_{12}H_{16}Br_4O_2$ (511.90) Calc. C 28.15 H 3.15 Br 62.43% Found C 28.54 H 3.42 Br 60.79%

The ^{1}H-NMR. spectrum (60 MHz, $CDCl_3$) of the crude product permitted the recognition (~5%) of the minor component, *4,4,8,8-tetrabromo-1,3,5,7-tetramethyl*-anti-*tricyclo*[*5.1.0.0*^{3,5}]*octane-2,6-cis*-diol (**26**), which could not be isolated, by 4.01/*d* (J = 12), 2H (H–C(2), H–C(6)); 2.57/*d* (J = 12), 2H (2 OH); 1.42/*s*, 6H (2 CH_3); 1.29/*s*, 6H (2 CH_3).

The yields of **20** and **26** were thus ~84 and ~5%. The pure tetrabromo-*trans*-diol **20** was quite stable, but the crude reaction product gradually darkened to become black after 7 days. Aside from the two diols **20** and **26** it contained small amounts of the starting tetrabromo-dione **5**, and more highly reduced products. The ratio of these products depended on the reaction time; this may be due to the insolubility of the starting dione **5**.

3.1.2. *For 16 h.* The reduction of 0.3 g (0.59 mmol) of **5** with 0.09 g (2.4 mmol) of lithium aluminium hydride was repeated for 16 h using the same procedure as described in 3.1.1. to give 0.24 g of a semisolid residue. Its ^{1}H-NMR. spectrum suggests the presence of about 10% of the educt **5**, and not more than 30% of the dibromo-*trans*-diol **24** (see below). The remaining signals could not be identified. Recrystallization from chloroform/hexane gave 0.06 g (29%) of not quite pure *4*-exo,*8*-exo-*dibromo-1,3,5,7-tetramethyl*-anti-*tricyclo*[*5.1.0.0*^{3,5}]*octane-2,6*-trans-*diol* (**24**) as white needles, m.p. 129–132° (dec.). Further attempts to purify were not successful and the ^{1}H-NMR. spectrum indicated the sample to be ~90% pure. – IR. (KBr): 3380*s*, 2990*w*, 2960*w*, 2925*m*, 2870*w*, 1460*m*, 1395*m*, 1250*m*, 1230*m*, 1165*m*, 1045*s*, 1025*s*, 1005*s*, 905*m*. – ^{1}H-NMR. (60 MHz, $CDCl_3$): 3.86/*d* (J = 5), 2H (H–C(2), H–C(6)); 3.28/*s* with ringing, 2H (*endo*-H–C(4), *endo*-H–C(8)); 1.84/*d* (J = 5), 2H (2OH); 1.14/*s*, 12H (4CH_3). In one spectrum the signals at 3.86 and 1.84 were seen as singlets. The isolated dibromo-diol **24** darkened on standing to become black after 2 days.

3.2. *Lithium aluminium hydride reduction in tetrahydrofuran.* 3.2.1. *For 2 h.* A stirred mixture of 0.30 g (0.59 mmol) of **5** and 0.08 g (2.11 mmol) of lithium aluminium hydride in 25 ml of anhydrous tetrahydrofuran was heated under reflux for 2 h. The procedure described in 2.1. was used for the work-up to leave 0.21 g of a brown oil which was oxidized with *Jones'* reagent [14] as in 2.2.1. to give 0.2 g of a semisolid residue. Crystallization from carbon tetrachloride gave 0.07 g (31%) of a 1:1 mixture of *4,4,8*-endo-*tribromo*- and *4*-endo,*8*-endo-*dibromo-1,3,5,7-tetramethyl*-anti-*tricyclo*[*5.1.0.0*^{3,5}]*octane-2,6-dione* (**14** and **15**) as white plates, m.p. 215–230°. – IR. ($CHCl_3$): 1695*s*. – ^{1}H-NMR. (60 MHz, $CDCl_3$): The dibromo-dione **15** had signals at 2.96/*s*; 1.43/*s*, as described in 3.4. The tribromo-dione **14** had signals at 3.06/*s* with out ringing (*exo*-H–C(8)), 1.50/*s* and 1.43/*s* (overlapping with signal due to **15**) (4CH_3). In the mixture the two *s* of H–C(Br) at 3.06 and 2.96 were in an intensity ratio of 1:2 with each other and of ~1:9 with the two methyl *s*; the latter two at 1.50 and 1.43 were in an intensity ratio of ~1:3. From these ratios both the component ratio and the signal assignments given above were deduced. Attempts to separate the components by crystallizations were unsuccessful.

3.2.2. *For 24 h.* The same reduction of 0.5 g (1 mmol) of **5** for 24 h and the subsequent oxidation by the procedure described in 2.2.1. gave 0.11 g of a brown oil, which failed to crystallize. Purification was effected by chromatography on silica gel with chloroform/hexane 4:1. The resultant 0.03 g solid was recrystallized from carbon tetrachloride/hexane giving 0.02 g (8%) of *4*-exo-*bromo-1,3,5,7-tetramethyl*-anti-*tricyclo*[*5.1.0.0*^{3,5}]*octane-2,6-dione* (**18**), m.p. 130–133°, as white plates. – IR. ($CHCl_3$): 3030*w* sh., 2995*w*, 2980*w*, 2940*w*, 2870*w*, 1685*s*, 1460*m*, 1390*m*, 1295*m*, 1045*m*, 835*m*. – MS.: 272/270 (15/16, M^+), 244/242 (1/1, M^+ – CO), 229/227 (0.75/0.75, M^+ – CH_3 – CO), 191 (48, M^+ – Br), 162 (62), 161 (30), 135 (25, M^+ – Br – 2(CO)), 123 (32), 122

(50), 121 (25), 119 (30), 107 (16), 105 (24), 96 (25), 91 (25), 41 (100). – ^{1}H-NMR. (100 MHz, $CDCl_3$): 3.30/*s* with ringing, 1H (*endo*-H–C(4)); 1.75/*d* (J = 5), 1H (*endo*-H–C(8)); 1.41/*s*, 6H ($2CH_3$); 1.36/*s*, 6H ($2CH_3$); 1.23/*d* (J = 5), 1H (*exo*-H–C(8)).

$C_{12}H_{15}BrO_2$ (271.16) Calc. C 53.15 H 5.58 Br 29.46% Found C 53.83 H 5.75 Br 27.99%

When this reduction followed by oxidation was repeated on a larger scale (3 g of **5**) the crude product crystallized to give 55 mg (3%) of slightly impure *4*-exo,*8*-exo-*dibromo-1,3,5,7-tetramethyl-anti-tricyclo*[*5.1.0.0*^{3,5}]*octane-2,6-dione* (**16**), m.p. 220–230° (dec.). – IR. ($CHCl_3$): 1693*s*. – IR. (KBr): 1685*s*. – ^{1}H-NMR. (60 MHz, $CDCl_3$): 3.58/*s* with ringing, 2H (*endo*-H–C(4), *endo*-H–C(8)); 1.37/*s*, 12H ($4CH_3$). The ^{1}H-NMR. spectrum indicated the sample to be ~90% pure; further attempts to purify were unsuccessful.

3.3. *Sodium cyanoborohydride reduction.* A mixture of 0.40 g (0.79 mmol) of **5** and 1 g (159 mmol) of sodium cyanoborohydride in 15 ml of hexamethylphosphoramide was heated at 100° for 24 h. Water was added after cooling, and the mixture extracted with ether. The extracts were washed well with water and with saturated sodium chloride solution, dried, and evaporated to leave 0.27 g of an oil. Purification by preparative TLC. gave 50 mg of a semisolid (along with a number of fractions consisting of unidentified mixtures). Recrystallization from carbon tetrachloride/hexane afforded 25 mg (12%) of *4*-endo-*bromo-1,3,5,7-tetramethyl*-anti-*tricyclo*[*5.1.0.0*^{3,5}]*octane-2,6-dione* (**17**), shown by its m.p. and ^{1}H-NMR. spectrum to be identical with the sample described in 3.5.2. No other tetramethyl-tricyclo[5.1.0.0^{3,5}]octane-2,6-dione derivative could be detected in the ^{1}H-NMR. spectra of the crude product and of the other chromatography fractions.

3.4. *Chromium(II)chloride reduction.* A stirred mixture of 0.40 g (0.79 mmol) **5**, and 2.0 g (16.3 mmol) of chromium(II)chloride in 35 ml of anhydrous tetrahydrofuran was refluxed for 24 h under nitrogen. On cooling 200 ml of water were added, and the solution was extracted with chloroform. The extracts were washed with water, dried, and evaporated to leave 0.2 g of a semisolid residue. Its ^{1}H-NMR. spectrum showed only the signals due to the isomer **15**. Crystallization from carbon tetrachloride resulted in the isolation of 40 mg (14%) of *4*-endo,*8*-endo-*dibromo-1,3,5,7-tetramethyl*-anti-*tricyclo*[*5.1.0.0*^{3,5}]*octane-2,6-dione* (**15**) as white plates, m.p. 265–267° (dec.). – IR. (KBr): 3040*m*, 2990*m*, 2940*m*, 1680*s*, 1647*w*, 1460*m*, 1387*m*, 1370*m*, 1313*s*, 1193*s*, 1085*w*, 1077*w*, 1048*m*, 920*w*, 880*s*, 857*m*, 695 *m*, 685*m*. – IR. ($CHCl_3$): 1692*s*. – MS.: 352/350/348 (7/15/7, M^+), 271/269 (45/44, $M^+ - Br$), 243/241 (55/54, $M^+ - Br - CO$), 215/213 (7/6, $M^+ - Br - 2(CO)$), 191 (18), 190 (90, $M^+ - 2Br$), 189 (30), 176 (16), 175 (25, $M^+ - 2Br - CH_3$), 174 (15), 162 (55, $M^+ - 2Br - CO$), 161 (45), 147 (70, $M^+ - 2Br - CH_3 - CO$), 135 (20), 134 (68, $M^+ - 2Br - 2(CO)$), 133 (35), 119 (100, $M^+ - 2Br - CH_3 - 2(CO)$), 117 (15), 105 (27), 91 (38). – ^{1}H-NMR. (60 MHz, $CDCl_3$): 2.96/*s* without ringing, 2H (*exo*-H–C(4), *exo*-H–C(8)); 1.43/*s*, 12H ($4CH_3$).

$C_{12}H_{14}Br_2O_2$ (350.06) Calc. C 41.17 H 4.03 Br 45.65% Found C 41.11 H 4.19 Br 45.09%

3.5. *Potassium hydridotetracarbonylferrate* [6] *reductions.* – 3.5.1. *For 24–60 h.* The same procedure as described in 2.3.1. was used with 3.0 g (5.9 mmol) of **5**, 9 ml (66.6 mmol) of iron pentacarbonyl, 11.1 g (198 mmol) of potassium hydroxide, 750 ml of ethanol, and 50 ml of dimethoxyethane. After 60 h the reaction was worked up to give 1.5 g of a green solid residue which was purified on a silica gel column using chloroform/hexane 7:3. After the green material (~ 0.2 g) had been eluted the solvent was changed to chloroform which led to the isolation of 0.83 g (73%) of *1,3,5,7-tetramethyl*-anti-*tricyclo*[*5.1.0.0*^{3,5}]*octane-2,6-dione* (**6**), m.p. 125–135°. Recrystallization from carbontetrachloride/hexane raised the m.p. to 142–143.5°. – IR. (KBr): 3085*w*, 3002*w*, 2980*m*, 2940*w*, 2882*w*, 1670*s*, 1640*w*, 1475*m*, 1390*m*, 1332*m*, 1318*m*, 1308*m*, 1095*m*, 1085*m*, 1065*m*, 981*w*, 941*w*, 830*m*, 755*m*, 692*m*. – IR. ($CHCl_3$): 1690*s*, 1675*s* sh., 1608*w*. – MS.: 192 (27, M^+), 177 (12, $M^+ - CH_3$), 164 (22, $M^+ - CO$), 149 (46, $M^+ - CH_3 - CO$), 124 (22), 123 (36), 122 (20), 121 (48, $M^+ - CH_3 - 2(CO)$), 109 (25), 107 (16), 105 (23), 96 (40, $^1/_2M^+$), 95 (17), 93 (18), 91 (22), 69 (100), 41 (90). – ^{1}H-NMR. (100 MHz, $CDCl_3$): 1.38/*s*, 12H ($4CH_3$); 1.36/*d* (J = 5) part of the signal is covered by the singlet at 1.38, 2H (*endo*-H–C(4), *endo*-H–C(8)); 0.98/*d* (J = 5), 2H (*exo*-H–C(4), *exo*-H–C(8)). – ^{1}H-NMR. (60 MHz, C_6D_6): 1.10/*s*, 12H ($4CH_3$); 0.85/*d* (J = 5), 2H (*endo*-H–C(4), *endo*-H–C(8)); 0.32/*d* (J = 5), 2H (*exo*-H–C(4), *exo*-H–C(8)).

$C_{12}H_{16}O_2$ (192.26) Calc. C 74.97 H 8.39% Found C 74.53 H 8.32%

When the reaction was repeated for 24 and for 48 h, 50 and 70% of **6** were isolated together with varying amounts of a second product which is described in 3.5.2.

3.5.2. *For 3 h.* The reduction of 0.33 g (0.66 mmol) of **5** was carried out for 3 h using the procedure described in 2.3.1. Purification of the isolated green residue (0.3 g) by preparative TLC. on silica gel using chloroform/hexane 7:3 gave two main fractions. Recrystallization of the first fraction (70 mg) from carbon tetrachloride/hexane afforded 30 mg (24%) of **6**, identical with the sample obtained in 3.5.1. The second chromatography fraction (0.12 g) was recrystallized from carbon tetrachloride/hexane to give 60 mg (34%) of *4-endo-bromo-1,3,5,7-tetramethyl*-anti-*tricyclo*[*5.1.0.0*^{3,5}]*octane-2,6-dione* (**17**), m.p. 147–149°, as white plates. – IR. ($CHCl_3$): 3030*w* sh., 3010*w*, 2940*w*, 1690*s*, 1468*m*, 1390*w*, 1310*m*, 1145*w*, 1080*w*, 865*w*. – MS.: 272/270 (15/16, M^+), 244/242 (1/1, $M^+ - CO$), 192 (23), 191 (100, $M^+ - Br$), 163 (35, $M^+ - Br - CO$), 149 (16), 135 (43, $M^+ - Br - 2(CO)$), 123 (19), 122 (22), 121 (18), 119 (24), 105 (17), 96 (16), 91 (15). – ^{1}H-NMR. (100 MHz, $CDCl_3$): 2.74/*s* without ringing, 1 H (*exo*-H–C(4)); 1.90/*d* (J = 5), 1 H (*endo*-H–C(8)); 1.44/*s*, 6 H ($2CH_3$); 1.38/*s*, 6 H ($2CH_3$); 1.24/*d* (J = 5), 1 H (*exo*-H–C(8)). This product was identical with the one obtained in 3.3.

$C_{12}H_{15}BrO_2$ (271.16) Calc. C 53.15 H 5.58 Br 29.46% Found C 52.65 H 5.58 Br 29.40%

4. Products from 1,3,5,7-tetramethyl-*anti*-tricyclo[5.1.0.0^{3,5}]octane-2,6-dione (6). – 4.1. *Sodium borohydride reduction.* To a solution of 0.41 g (2.1 mmol) of **6** in 25 ml of methanol was added dropwise a solution of 0.82 g (21.6 mmol) of sodium borohydride in 25 ml of water. After 20 h at RT. the solution was evaporated to dryness, and the residue was washed five times with acetone. Filtration of the solvent, and evaporation gave 0.4 g (95%) of an approximately 1:1 mixture (from the ^{1}H-NMR. spectrum) of the *cis*- and *trans*-diols as a solid. Recrystallization from carbon tetrachloride gave 0.13 g (31%) of *1,3,5,7-tetramethyl*-anti-*tricyclo*[*5.1.0.0*^{3,5}]*octane-2,6*-trans-*diol* (**21**) as white needles, m.p. 124–126°. – IR. ($CHCl_3$): 3610*s*, 3450*m* br., 3000*s*, 2880*s*, 1472*m*, 1452*s*, 1392*s*, 1240–1200*s* br., 1168*m*, 1045–1030*s* br., 978*m*, 958*m*, 928*m*, 892*m*, 880*m*. – MS.: 196 (1, M^+), 178 (10, $M^+ - H_2O$), 163 (*19*, $M^+ - CH_3 - H_2O$), 137 (20), 136 (36, $M^+ - 4(CH_3)$), 135 (20), 125 (60), 123 (25), 122 (18), 121 (28), 111 (16), 109 (87), 108 (50), 107 (37), 98 (50, $^1/_2M^+$), 97 (27), 96 (20), 95 (16), 93 (28), 91 (24), 43 (100). – ^{1}H-NMR. (100 MHz, $CDCl_3$): 3.74/*d* (J = 5), 2 H (H–C(2), H–C(6)); 1.48/*d* (J = 5), 2 H (2OH); 1.10/*s*, 12 H ($4CH_3$); 0.68/*d* (J = 5), 2 H (H–C(4), H–C(8), both possibly *endo*); 0.05/*d* (J = 5), 2 H (H–C(4), H–C(8), both possibly *exo*).

$C_{12}H_{20}O_2$ (196.29) Calc. C 73.43 H 10.27% Found C 73.06 H 10.29%

Recrystallization of the residue obtained from the crystallization mother liquors (see above) gave 30 mg (7%) of *1,3,5,7-tetramethyl*-anti-*tricyclo*[*5.1.0.0*^{3,5}]*octane-2,6*-cis-*diol* (**27**) as white needles, m.p. 132–134°. – IR. ($CHCl_3$): 3600*m*, 3420*s* br., 3080*w*, 2980*s*, 2925*s*, 2870*s*, 2735*w*, 1460*s*, 1390*m*, 1255–1190*m* br., 1075*w*, 1032*s*, 1000*m*, 970*m*, 940*w*, 918*w*, 885*m*, 840*w*. – MS. 196 (1, M^+), 178 (8, $M^+ - H_2O$), 163 (19, $M^+ - CH_3 - H_2O$), 136 (45, $M^+ - 4(CH_3)$), 135 (21), 125 (39), 123 (36), 122 (20), 121 (30), 109 (88), 108 (88), 107 (50), 105 (17), 98 (38, $^1/_2M^+$), 97 (21), 96 (16), 95 (20), 94 (20), 93 (36), 91 (23), 43 (100). – ^{1}H-NMR. (100 MHz, $CDCl_3$): 3.88/*d* (J = 7), 2 H (H–C(2), H–C(6)); 2.38/*d* (J = 7), 2 H (2OH); 1.28/*s*, 6 H ($2CH_3$); 1.12/*d*, half covered by signal at 1.08, (J = 5), 1 H (H–C(4) or H–C(8), possibly *endo*); 1.08/*s*, 6 H ($2CH_3$); 0.75/*d* (J = 5), 1 H (H–C(8) or H–C(4), possibly *endo*); 0.20/*d* (J = 5), 1 H (H–C(4) or H–C(8), possibly *exo*); –0.03/*d* (J = 5), 1 H (H–C(8) or H–C(4), possibly *exo*).

$C_{12}H_{20}O_2$ (196.29) Calc. C 73.43 H 10.27% Found C 73.22 H 10.20%

5. Absence of *cis-trans* Isomerization of 21 and 27 using $LiAlH_4$ in THF. – 200 mg (1.02 mmol) of a 1:1 mixture of **21** and **27** were dissolved in 10 ml of absolute tetrahydrofuran, and mixed with 450 mg (11.9 mmol) of lithium aluminium hydride. After refluxing for 24 h, water was added slowly and then dilute hydrochloric acid. The aqueous layer was extracted 3 times with ether, the extracts were washed with aqueous sodium hydrogen carbonate solution, and dried. Solvent removal furnished 190 mg of an oil. ^{1}H-NMR. integration of the CH_3 signals showed an unchanged 1:1 ratio of *cis*- to *trans*-diol; other signals indicated the sample to be 80% pure.

When the reaction was repeated with 200 mg (1.02 mmol) of pure *trans*-diol **21** by refluxing for 22 h, 190 mg of oily crystals were isolated after the same work-up. In the ^{1}H-NMR. spectrum only the signals of the *trans*-diol could be identified (no *cis*-diol); but signals of other unidentified compounds were present to the extent of about 40%.

6. 4,4,8,8-Tetrabromo-1,3,5,7-tetramethyl-*anti*-tricyclo[5,1,0,0^{3,5}]octane-2,6-dione (5). – To a stirred solution of 6.05 g (18,4 mmol) of carbon tetrabromide and 0.5 g (3.1 mmol) of duroquinone in 15 ml of anhydrous ether, cooled to $-78°$ and under nitrogen, were added 9 ml of a 2M (18 mmol) solution of methyl lithium in ether during 10 min. After 2 h the mixture was allowed to warm to RT., and after 20 h water was added. The resultant solution was extracted with chloroform, and the combined extracts were washed with dilute hydrochloric acid, dried, and evaporated to leave a brown residue. Recrystallization from chloroform yielded 0.98 g (63%) of *4,4,8,8-tetrabromo-1,3,5,7-tetramethyl*-anti-*tricyclo[5.1.0.0^{3,5}]octane-2,6-dione* (**5**), as off-white plates. The IR. and ^{1}H-NMR. spectra as well as the m.p. behaviour of this sample were in agreement with those reported [1].

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