140. Reactions of 1,3,5,7-Tetramethyl-*anti*-tricyclo[5.1.0.0^{3,5}]octane-2,6-diols and their 4,4,8,8-Tetrachloro- and 4,8-Dichloro-Derivatives with Diphosphorus Tetraiodide[1])

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(18. III. 77)

Reaktionen von 1,3,5,7-Tetramethyl-*anti*-tricyclo[5.1.0.0^{3,5}]octan-2,6-diolen und deren 4,4,8,8-Tetrachlor- und 4,8-Dichlorderivaten mit Diphosphortetrajodid

Zusammenfassung

Es wurden die P_2I_4-Reaktionen mit 1,3,5,7-Tetramethyl-*anti*-tricyclo[5.1.0.0^{3,5}]-octan-2,6-diolen (**3**/**6**), mit dem 4,8-Dichlorderivat **4** und mit den 4,4,8,8-Tetrachlorderivaten **5**/**7** untersucht. Dabei entstanden die Styrolderivate **9** und **12**, die *anti*-Bishomobenzolderivate **8** und **11**, ein Homotropylidenderivat **10**, ein Cyclooctatetraenderivat **13** und ein 9-Oxabicyclo[4.2.1]nona-2,4,7-trienderivat **15**. Die Ausbeuten lagen zwischen 1 und 10%. Die Bildung aller dieser Produkte liess sich unter der Annahme der primären Umwandlung einer oder beider Hydroxylgruppen in Abgangsgruppen X oder X und Y (wahrscheinlich X=Y=I) mechanistisch deuten. Die Reaktion der Deschlorderivate **3**/**6** lieferte nach Substitution beider Hydroxylgruppen durch X und Y: a) unter Abspaltung von HX und HY das Styrolderivat **9** (*Schema 2*) und b) unter Abspaltung von XY das Homotropylidenderivat **10** (*Schema 3a*)) und das Bishomobenzolderivat **8** (*Schema 3b*)). Die Reaktion des 4,8-Dichlorderivates **4** lieferte nach Substitution beider Hydroxylgruppen durch X und Y: a) unter Abspaltung von HX und HY das Styrolderivat **12** (*Schema 2*), und b) unter Abspaltung von XY das Bishomobenzolderivat **11** (*Schema 3b*)). Die Reaktion mit den 4,4,8,8-Tetrachlorderivaten **5**/**7** lieferte: a) nach Substitution beider Hydroxylgruppen durch X und Y unter Abspaltung von XCl und YCl das Cyclooctatetraenderivat **13** (*Schema 4*), und b) nach Substitution nur einer Hydroxylgruppe durch X unter Abspaltung von XCl und HCl das bicyclische Derivat **15** (*Schema 5*). Alle diese Reaktionen sind zusätzlich zu den angegebenen Fragmentierungen und Eliminierungen noch teilweise von Umlagerungen des Kohlenstoffgerüstes begleitet.

Die thermische Umlagerung von 1,5-Dichlor-2,4,6,8-tetramethyl-cycloocta-1,3,5,7-tetraen (**13**) in das Styrolderivat **12** wurde in Abhängigkeit der Lösungsmittelpolarität untersucht und mit der analogen thermischen Umlagerung von Brom-cyclooctatetraen und Chlor-cyclooctatetraen verglichen.

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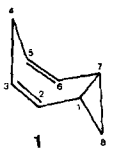
[1]) From the planned dissertation of *R. A. Dyllick-Brenzinger*, ETH Zürich.

[2]) Post-doctoral fellow, University of Zürich 1972–1975.

1. Introduction. – Among the methods used to obtain the homotropylidene syste **1** [1], the one involving reactions of *anti*-tricyclo[5.1.0.0^{3,5}]octane-2,6-diols (**2**, r duced *anti*-bishomo-*p*-quinones) with diphosphorus tetraiodide (P_2I_4) and pyridin in carbon disulfide at 0 to 10° [2][3]), promised to be generally applicable. We inve tigated the P_2I_4-method with the substituted reduced *anti*-bishomo-*p*-quinones **3** to



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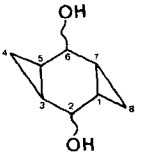

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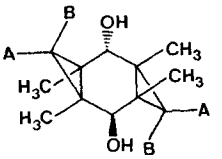
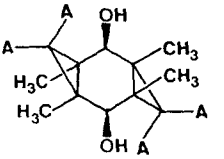
[3]. Experiments showed that the method has its limitations giving very low yields o products and only in one case a substituted homotropylidene. We present the product obtained from the reaction of **3** to **7** (*sections 2* to *4*), a study of one of the produc transformations (*section 5*) and a discussion of the possible mechanisms of thei formation (*section 6*).

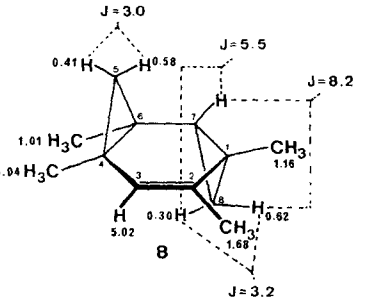


3 A = B = H
4 A = Cl; B = H
5 A = B = Cl



6 A = H
7 A = Cl

2. Products from 1,3,5,7-tetramethyl-*anti*-tricyclo[5.1.0.0^{3,5}]octane-2,6-*trans*- (3) and *cis*-diols (6). – The P_2I_4-reaction of a 1:1 mixture of **3** and **6** gave at least eight products, each in less than 3% yield. The GC./MS. analysis suggested that six of the compounds had a molecular weight of 162, one of 164 and one of 160. Three were partially purified by preparative TLC. The main component (2.3%) was identified as 1,2,4,6-tetramethyl-*anti*-tricyclo[5.1.0.0^{4,6}]oct-2-ene (**8**, 1,2,4,6-tetramethyl-*anti*-bishomobenzene). Its constitution and the *anti*-configuration of the two cyclopropane rings were assigned by analogy with the corresponding dichloro-derivative (*section 3*). Its MS. (M^+·162) and the ^{1}H-NMR. data indicated on the formula are in accord with structure **8**.

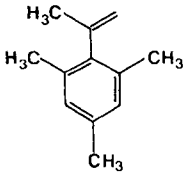


8

(with the δ-values of the ^{1}H-shifts)

[3]) We thank Prof. *H. Kessler* for a detailed description of the P_2I_4-procedure [2].

The second component (1.9%) was the known α,2,4,6-tetramethylstyrene (**9**) [4][4]). A third component (0.5%) was the known 1,3,5,7-tetramethyl-bicyclo[5.1.0]-octa-2,5-diene (**10**, 1,3,5,7-tetramethyl-homotropylidene) [5] identified by its MS. (M^+·162) and its typical temperature-dependent ^{1}H-NMR. spectrum.



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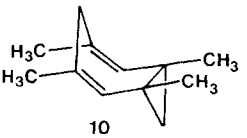

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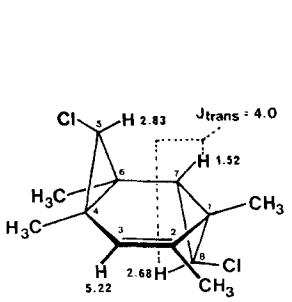
3. Products from 4-*exo*,8-*exo*-dichloro-1,3,5,7-tetramethyl-*anti*-tricyclo[5.1.0.0^{3,5}]-octane-2,6-*trans*-diol (4). – Treatment of **4** under the P_2I_4-conditions gave at least two products, the major component being 5-*exo*,8-*exo*-dichloro-1,2,4,6-tetramethyl-*anti*-tricyclo[5.1.0.0^{4,6}]oct-2-ene (**11**, a bishomobenzene-derivative), m.p. 43° (10%). Its structure was derived from the ^{1}H-NMR. and ^{13}C-NMR. data (*cf.* formulae) using the following arguments: 1. Assuming the most plausible rearrangement of such



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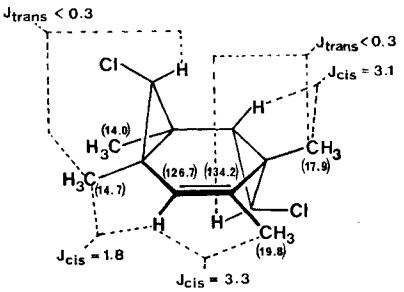


11

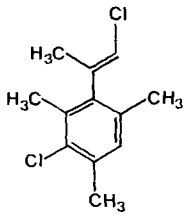
(with the δ-values of the ^{1}H- and, in parentheses, those of ^{13}C-shifts)

systems as well as the absence of subsequent methyl and chlorine migrations, the observed change in composition (loss of two hydroxyls) leads (*section 6*) to the bishomobenzene-constitution **11**; 2. the *anti*-configuration of the two cyclopropane rings follows from the absence of a rearrangement when **11** was heated to 220° in perchlorobutadiene: *syn*-bishomobenzenes are known to undergo rapid thermal isomerisation to cyclooctatrienes [6]. 3. the *exo*, *exo*-configuration of the two chlorine atoms is indicated by the size of three ^{13}C-^{1}H-coupling constants between methyl carbon and hydrogen atoms which are located vicinally on the same cyclopropane ring: it had been argued previously [3] that couplings between such atoms are smaller in *trans*-($J<1$ Hz), than in *cis*-arrangements ($J=4.5$ Hz). The coupling constants between $^{13}CH_3$–C(1) and ^{1}H–C(8), $^{13}CH_3$–C(4) and ^{1}H–C(5), $^{13}CH_3$–C(6) and ^{1}H–C(5) are all smaller than 0.3 Hz, suggesting *trans*-arrangements of these atom pairs and thus *exo*-positions of the chlorine atoms on both cyclopropane rings. In the case of the cyclopropane ring involving C(8), this is confirmed by the larger coupling constant (3.1 Hz) between $^{13}CH_3$–C(1) and ^{1}H–C(7), which must have the *cis*-arrangement, and especially by

[4]) We thank Prof. *A. Mannschreck* for a sample of this compound.

the ^1H–^1H-coupling constant of 4 Hz between ^1H–C(7) and ^1H–C(8), showing *trans* arrangement of this atom pair[5]). As expected from previous experience in similar cases [3], the ^1H-NMR. signals of the two H–C(Cl) at $\delta = 2.83$ and 2.68 ppm were both sharp (showing ringing, see experimental part) due to their *trans*-position relative to the vicinal methyl groups on the cyclopropane ring. The signal at 1.52 ppm (H–C(7)), however, was broader, suggesting a *cis*-arrangement of H_3C–C(1) and H–C(7).

The minor product from the P_2I_4-reaction with **4** was (*E*)-β,3-dichloro-α,2,4,6-tetramethylstyrene (**12**), isolated as a 3:1 mixture (2%) with **11**. Spectroscopic and other properties of **12** were identical with those of a sample, described in *section 4*.



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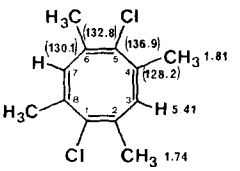

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(with δ-values of ^1H- and, in parentheses, those of ^{13}C-shifts)

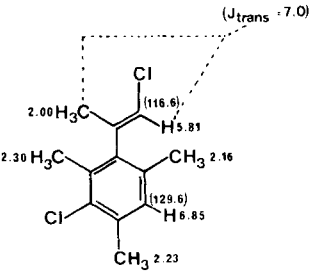
4. Products from 4,4,8,8-tetrachloro-1,3,5,7-tetramethyl-*anti*-tricyclo[5.1.0.0^{3,5}]-octane-2,6-*trans*- (5) and *cis*-diol (7). – The P_2I_4-procedure with a mixture of **5** and **7** or with pure **5** gave at least three products, two of which were isolated in pure form. The main product (6%) was 1,5-dichloro-2,4,6,8-tetramethyl-cycloocta-1,3,5,7-tetraene (**13**), m.p. 72°. Its structure was assigned on the basis of the ^{13}C-NMR. spectrum (see formula), showing the presence of four types of olefinic C atoms (1 *d* and 3 *s*) and two types of methyl groups (twofold symmetry), thus excluding all structures but **13**. The ^1H-NMR. data shown further support the assignment. The chlorine and methyl substitution pattern in **13** shows that no migrations of methyl groups or chlorine atoms have taken place during the P_2I_4-reaction in this case.

It was expected that **13** would show coalescence of the two methyl-^1H-NMR.-signals at elevated temperatures due to a fast bond shift, analogous to the observation [7] with 1,3,5,7-tetramethyl-cyclooctatetraene at about 120°. However, compound **13** rearranged irreversibly at about 150° in d_8-toluene (*section 5*) before any broadening of the two methyl-signals could be observed, so the free enthalpy of activation of the bond shift in **13** at 423°K is larger than 26 kcal/mol.

The only rearranged product isolated from the thermolysis of **13** in d_8-toluene was (*E*)-β,3-dichloro-α,2,4,6-tetramethylstyrene (**12**). Its structure was derived from the ^{13}C- and ^1H-NMR. data (see formula **12**) and from its catalytic hydrogenation; the former reflect the absence of molecular symmetry and indicate the number of olefinic carbon atoms in accord with structure **12**. Conclusive evidence comes from an independent synthesis of 3-chloro-isopropylmesitylene (**14**), the hydrogenation product of **12** *via* electrophilic chlorination [8] of isopropylmesitylene[4]). The ^{1} H-NMR. data of **14**

[5]) This confirmation lends support to the generality of the method [3] for assigning configurations to carbon atom substituents vicinal to hydrogen atoms on a cyclopropane ring (compare footnote 5 in [3]).

(see formula), is in accord with the structure proposed. The (*E*)-configuration of **12** was derived from a 7.0 Hz ^{13}C–^{1}H-coupling [9] between the methyl carbon atom at C(α) and the hydrogen atom at C(β). A mechanism for the conversion of **13** to **12** is discussed in *section 5*.



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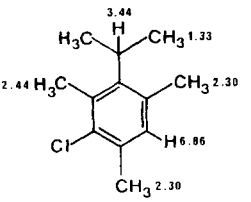

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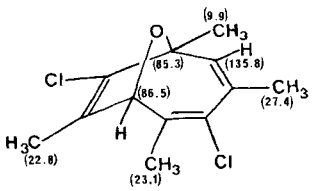
(with the δ-values of the ^{1}H- and, in parentheses, those of ^{13}C-shifts)

4,8-Dichloro-1,3,5,7-tetramethyl-9-oxabicyclo[4.2.1]nona-2,4,7-triene (**15**), m.p. 95°, was isolated as a minor product (1%) from the P_2I_4-reaction with **5** or **7**. Structural evidence comes from its UV., ^{1}H-NMR. and ^{13}C-NMR. spectra. The UV. spectrum is similar to that reported for 9-oxabicyclo[4.2.1]nona-2,4,7 triene [10]. The ^{13}C-NMR. spectrum (see formula) exhibits four olefinic C-atom signals (1 *d* and 3 *s*; two *s* were not observed), two signals at 86.5/*d* and 85.3/*s* which apparently belong to C(1) and C(6) (*cf.* [11]), and four signals due to methyl carbon atoms. The ^{1}H-NMR. spectrum (see formula) supports the proposed structure. Further evidence comes



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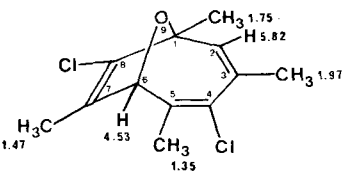

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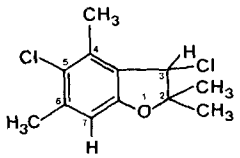
(with the δ-values of the ^{1}H- and, in parentheses, those of ^{13}C-shifts)

from catalytic hydrogenation of **15**, which resulted in a mixture of products (GC./MS.) showing ^{1}H-NMR. signals all at δ-values smaller than 3.0 ppm. This experiment excluded an alternative structure, 3,5-dichloro-2,2,4,6-tetramethyl-2,3-dihydrobenzo[*b*]furan (**16**), which would have retained its aromatic ring after hydrogenation under the conditions used. Model compounds **17**, **18** and **19**, related to **16**, showed UV. spectra similar to that of **15**, but their aromatic ^{1}H-NMR. signal (H–C(7)) appeared at δ-values larger than 6.4 and never at 5.8 ppm. Another minor product (0.3%) was observed in a fraction as a 1:1 mixture with **15**. Its composition (MS.) is $C_{12}H_{13}Cl_3O$, but its structure could not be determined.

5. Thermal rearrangement of the cyclooctatetraene-derivative 13. – The rate of thermolysis of **13** to **12** in four solvents of different polarities (d_8-toluene, $CDCl_3$, CD_3CN and CD_3COOD; ascending E_T values [12]) follows a first order law and in-



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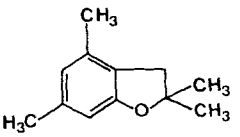

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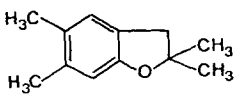

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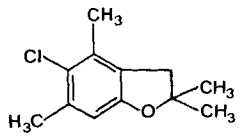

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creases strongly from d_8-toluene to $CDCl_3$, then leveling off towards CD_3CN and CD_3COOD (see *Table*). This solvent dependence («*plateau* effect» [13]) of the rate of rearrangement is similar to that observed with bromo- [13] and chloro-cyclooctatetraene [14]. Three features are notable; a) the higher reactivity of **13** compared with chloro-cyclooctatetraene, b) an almost identical «*plateau* effect» observed with **13** and with bromo-cyclo octatetraene, but a displaced one on the E_T-scale with chloro-cyclooctatetraene, and c) an $E_T/\log k$ plot much steeper for **13** than for bromo-cyclooctatetraene showing that the transition state is more polar in the former than in the latter case. The mechanism proposed for conversion of bromo-cyclooctatetraene to *trans*-β-bromostyrene [13] is illustrated for **13** in *Scheme 1*; it involves electrocyclic ring closure to **20**, allylic chlorine migration *via* **21** to give **22** and subsequent conrotatory electrocyclic ring opening to **12**.

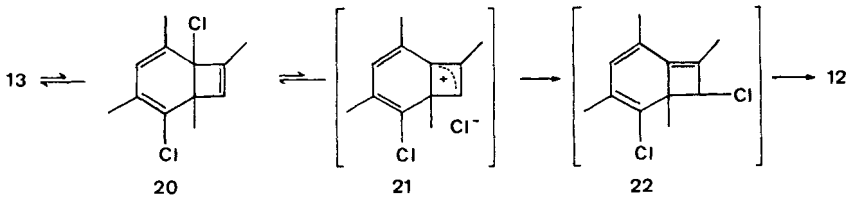
Table. *Rates of thermolysis in solvents of different polarities* (E_T)

Compound	$k(120°)$[a]	Solvent	E_T-value [12]	Ref.
13	1.6×10^{-5}	d_8-toluene	33.9	
	1.5×10^{-2}	$CDCl_3$	39.1	
	5.3×10^{-2}	CD_3CN	46.0	
	1.0×10^{-1}	CD_3COOD	51.2	
Chloro-cyclooctatetraene	2.1×10^{-4}	CH_3CN	46.0	[14]
	6.3×10^{-3}	CH_3COOH	51.2	
Bromo-cyclooctatetraene	3.3×10^{-4}	d_6-benzene	34.5	[13]
	2.7×10^{-3}	$CDCl_3$	39.1	
	1.4×10^{-2}	CH_3CN	46.0	
	1.6×10^{-2}	CH_3COOH	51.2	

[a]) The rate constants for **13** and for bromo-cyclooctatetraene are extrapolated from values obtained in the temperature range between 60 and 150°.

6. Mechanistic considerations concerning P_2I_4-reactions. – Although our P_2I_4-reactions furnished only low yields of products, the observed structures – of great

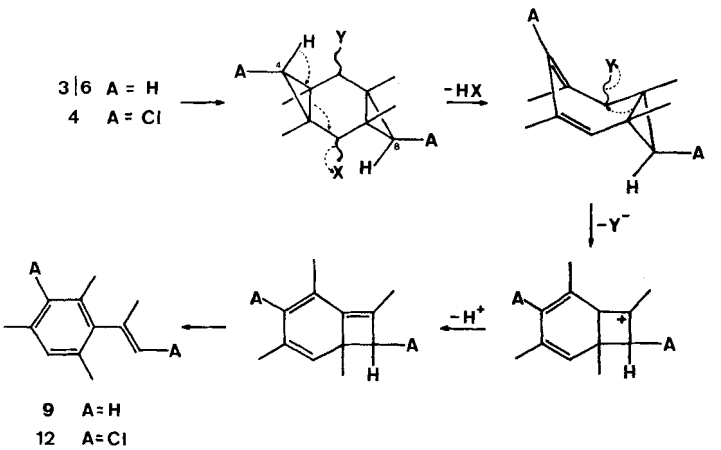
Scheme 1



diversity – are of interest. Their formation can be rationalized by assuming that the hydroxyl functions are first converted by P_2I_4 into cationic or anionic leaving groups. Since the nature of these leaving groups is not known, we call them X and Y. We shall discuss four mechanistic *Schemes* which explain the formation of the products of *sections 2* to *4*. In these *Schemes*, species like XY, HX, HY, XCl and YCl or combinations thereof are eliminated.

Scheme 2 explains formation of the styrene derivatives **9** and **12** from the dehalo-diols **3**/**6** and from the dichloro-diol **4**, respectively, assuming that X and Y leave as anions. This pathway requires at least one hydrogen atom to be present in both positions 4 and 8 in the educt diols; no styrene is observed in the P_2I_4-reaction of **5** and **7**.

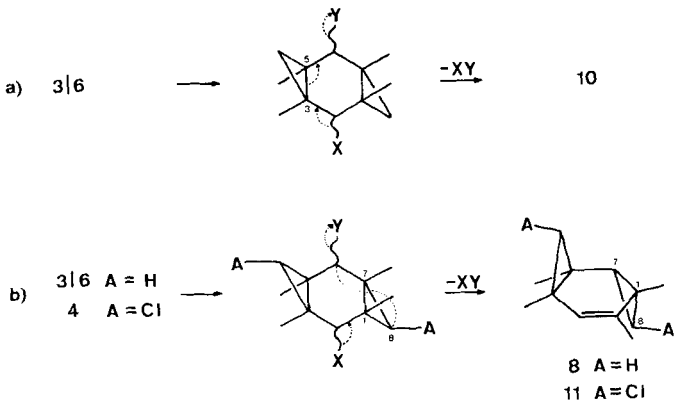
Scheme 2



Scheme 3 involves loss of X^+ and Y^-. It comprises two pathways, one (a) explaining the formation of the substituted homotropylidene **10** from the dehalo-diols **3**/**6** with fragmentation of the C(3)–C(5) bond, the other (b) the formation of the substituted bishomobenzenes **8** and **11** from **3**/**6** and from the dichloro-diol **4** with fragmentation of the C(1)–C(8) bond, migration of C(8) to form a new C(7)–C(8) bond and inversion of the C(8) configuration.

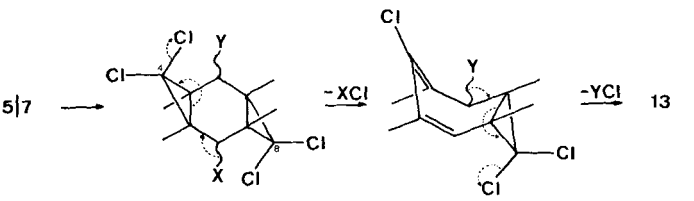
Scheme 4 was devised to explain the formation of **13** from the tetrachloro-diols **5**/**7** assuming that X and Y leave as cations together with chloride ions. The formation of a cyclooctatetraene derivative according to *Scheme 4* is only possible if there is at least one chlorine atom present at C(4) and C(8) of the educt diol. The fact that formation of a cyclooctatetraene derivative is only observed from the tetra-

Scheme 3



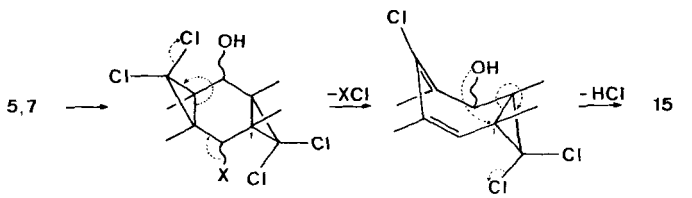
chloro-diols **5**/**7** with two chlorine atoms at these two positions and not from the 4-*exo*,8-*exo*-dichloro derivative **4** might mean that loss of chlorine can only occur from an *endo*-position.

Scheme 4



Scheme 5 indicates a reasonable route for the formation of **15**. It involves conversion of only one hydroxyl function into X followed by cationic loss of X together with a chloride ion. The oxygen atom of the remaining hydroxyl group attacks C(1), thus opening the cyclopropane ring and inducing loss of HCl to give **15**.

Schema 5



A reasonable candidate for both leaving groups X and Y is iodine, which can depart either as a cation – assisted by pyridine – or as an anion. The anionic leaving group could also be of the type =P–O–.

Diiodo compounds in P_2I_4-reactions of similar diols were proposed [2] as intermediates in order to explain the formation of homotropylidenes: The P_2I_4-reaction with 2,6-dimethyl-*anti*-tricyclo[5.1.0.0^{3,5}]octane-2,6-diol [2] had afforded di(3,6-iodomethyl)-1,4-dimethyl-cyclohexa-1,4-diene as a minor product. We attempted the

P_2I_4-reaction with cyclohexanol and with a mixture of stereoisomers of cyclohexane-1,4-diol. In the first case we isolated cyclohexyliodide and a phosphorus-containing compound (phosphate or phosphite), in the second *cis*- and *trans*-1,4-diiodocyclohexane and 4-iodo-cyclohex-1-ene; all five products were obtained in low yields. These results lend slight support to the previously proposed [2] hypothesis that the substitutents X and Y may indeed be iodine atoms.

This work was supported by the *Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung* and by *Sandoz AG*, Basel.

Experimental Part

1. General. – For abbreviations and presentation of the spectral data, see [15] [16]. In the ^{1}H-NMR. spectrum of one compound one singlet and two doublets due to cyclopropane H-atoms were observed to be either so sharp that they showed ringing or slightly broadened that they showed no ringing. An analogous feature has been observed previously [3] and the same notation is used. Metastable ions in the mass spectra (MS.) are abbreviated as (*m**). The conditions for gas-liquid chromatography (GC.) are recorded as follows: (column temperature or program, injector temperature, retention time). For thin layer chromatography (TLC.) *Merck* precoated PLC. plates, silica gel F-254 were used. Spectroscopic measurements were made with the following instruments: IR. spectra, *Perkin Elmer* 125 or 577 spectrometer; MS., *Hitachi Perkin Elmer* RMU 6M instrument (ionization energy 70 eV); ^{1}H-NMR. spectra, *Varian* HA-100 or XL-100; ^{13}C-NMR. spectra, *Varian* XL-100 instrument (Fourier transform mode); GC./MS. analyses, *Carlo Erba* Fractovap model G1 equipped with a SE 52 (Dr. *Grob*, Dübendorf) capillary glass-column (37 m × 0.25 mm and 1.6 atm. Helium) and connected with a *Varian* MAT 112 mass spectrometer (ionization energy 82 eV); Preparative GC., *Varian* Aerograph model 90-P with a 5% Carbowax 20M on 60/80 Chromosorb G Reg metal column 10′ × 3/8″ 1.5 atm. He; UV. spectra, *Cary* 14 spectrometer. The UV., IR., ^{1}H-NMR., ^{13}C-NMR. and mass spectra were measured in our laboratories for mass spectrometry (under Prof. *J. Seibl* and Prof. *M. Hesse*), for IR. and UV. spectroscopy (under Prof. *W. Simon*), for NMR. (under Prof. *J. F. M. Oth* and Prof. *W. v. Philipsborn*). Microanalyses were performed in the ETH and the University Laboratories (under Mr. *W. Manser* and Mr. *H. Frohofer*, respectively).

2. Reactions of diols with diphosphorus tetraiodide. – 2.1. *Products from 1,3,5,7-tetramethyl*-anti-*tricyclo* [*5.1.0.0*^{3,5}] *octane-2,6*-cis- *and* trans-*diols* (**6**) *and* (**3**). In a Soxhlet apparatus, 6.0 g (9.7 mmol) of freshly prepared anhydrous diphosphorus tetraiodide [17] was extracted with 180 ml of anhydrous carbon disulfide. After cooling the deep orange solution to 20°, a solution of 510 mg (2.6 mmol) of a 1:1 mixture (^{1}H-NMR.) of *cis*- and *trans*-dehalo-diols **6** and **3** in 15 ml of warm anhydrous pyridine was added dropwise with stirring and cooling in an ice-water bath. Immediately after the addition of the first few drops a dark brown precipitate formed. After a further 2 h, stirring at 0–5° the solvent from the decanted supernatant solution was removed under reduced pressure at 15–20°. The residue in 300 ml of ether was washed at 0°, three times with 10% aqueous NaOH-solution, three times with a saturated aqueous $Na_2S_2O_3$-solution and seven times with 2_N HCl. Drying and evaporation of the solvent (cold) gave 180 mg of an oily residue, which showed ^{1}H-NMR. signals of three main products in the approximate ratio of 10:5:1. A sample of the crude mixture was analysed by capillary GC./MS. (column 75°; injector 150°) and showed eight fractions. The following figures in sequence, represent fraction, molecular ion, retention time (min.) and structure (in brackets) if known: 1) 162, 7.1 (**8**); 2) 162, 8.3; 3) 162, 9.2; 4) 162, 10.8; 5) 162, 11.6; 6) 162, 13.1; 7) 164, 14.3; 8) 160, 16.4 (**9**). Preparative TLC. of the crude reaction product on silica gel (4 times pentane) gave 5 fractions as oils: 1) 10 mg; 2) 14 mg; 3) 15 mg; 4) 16 mg; 5) 12 mg. Only fractions 2, 3 and 4 contained identifiable products. *Fraction 2* was shown by its ^{1}H-NMR. spectrum to be *ca.* 70% *1,2,4,6-tetramethyl*-anti-*tricyclo* [*5.1.0.0*^{4,6}] *oct-2-ene* (**8**, 2.3%). – ^{1}H-NMR. (100 MHz, CCl_4): 5.02/br. *s*, 1H, H-C(3); 1.68/*d* (*J* = 1.5), 3H, H_3C–C(2); 1.16/*s*, 1.04/*s* and 1.01/*s*, 3H each, H_3C–C(1), H_3C–C(4) and H_3C–C(6); 0.62/*d* × *d* (*J* = 8.2 and 3.2), 1H, *exo*-H–C(8); 0.58/*d* (*J* = 3.0) and 0.41/*d* (*J* = 3.0), 1 H each, *endo*-H–C(5) and *exo*-H–C(5); 0.30/*d* × *d* (*J* = 5.5 and 3.2), 1H, *endo*-H–C(8); the signal due to H–C(7) could not be seen. – MS. (82 eV): 162 (20, $M^{+\cdot}$), 147 (45, $M^+ - CH_3$), 134 (5), 133 (13), 132 (7), 121 (22), 120 (100), 119 (45), 117 (5), 116 (10), 115 (7), 106 (22), 105 (15), 104 (69), 91 (30), 77

(15). – *Fraction 3* contained *ca.* 20% (0.5%) of *1,3,5,7-tetramethyl-bicyclo [5.1.0]octa-2,5-diene* (**10**) [5]. The temperature-dependent ^{1}H-NMR. spectrum of **10** in the mixture was in agreement with that reported: the broad signal at 1.37 due to the exchange of two CH_3 signals, visible in $CDCl_3$ at 30°, disappeared on cooling to −35°. The two sharp CH_3 signals were hidden by signals of various other olefinic products (GC./MS.). – *Fraction 4* consisted of *ca.* 50% *α,2,4,6-tetramethyl-styrene* (**9**) (1.9%); its IR., ^{1}H-NMR. and MS. were identical with those of a sample independently synthesized [4]. – IR. (CCl_4): 3075*m*, 2970*s*, 2940*s*, 2920*s*, 2860*m*, 1642*m*, 1612*m*, 1482*m*, 1448*m*, 1430*m*, 1378*m*, 1370*m*, 1095*m*, 902*s*, 850*s*. – ^{1}H-NMR. (100 MHz, CCl_4): 6.70/br.*s*, 2H, H–C(3) and H–C(5); 5.2–5.1/*m* and 4.7–4.6/*m*, 2H, *Z*–H–C(*β*) and *E*–H–C(*β*); 2.22/*s*, 3H, H_3C–C(4); 2.17/*s*, 6H, H_3C–C(2) and H_3C–C(6); 1.88/*m*, 3H, H_3C–C(*α*). – MS. 160 (93, $M^{+\cdot}$), 145 (100, $M^+ - CH_3$), 130 (35), 129 (27), 128 (27), 127 (12), 117 (25), 115 (20), 105 (25), 91 (15).

2.2. *Products from 4*-exo,*8*-exo-*dichloro-1,3,5,7-tetramethyl*-anti-*tricyclo[5.1.0.0^{3,5}]octane-2,6-trans-diol* (**4**). The reaction and work-up conditions described in 2.1 were applied to 1.4 g (5.3 mmol) of *trans*-dichloro-diol **4**. The dried and evaporated ether extracts left a residue which quickly turned brown. The ^{1}H-NMR. spectrum indicated mostly an 8:1 mixture of two compounds (see below). Purification by column chromatography using aluminium oxide (grade 1) and eluting with pentane (500 ml each) at 6° gave a *first fraction* (0.28 g) of a 6:1 mixture (by ^{1}H-NMR. spectrum) of the two products and a *second fraction* (0.16 g) of a mixture containing *ca.* 30% of the major product of fraction 1. The *first fraction* was rechromatographed (85 × 2 cm) using 4% silver nitrate impregnated silica gel and eluting with pentane to give 0.124 g (10%) of *5*-exo,*8*-exo-*dichloro-1,2,4,6-tetramethyl*-anti-*tricyclo[5.1.0.0^{4,6}]oct-2-ene* (**11**) as colourless prisms, m.p. 42–43°, b.p. 100°/1 Torr. – IR. (CCl_4): 3040*w*, 2980*m*, 2960*m*, 2930*m*, 2910*m*, 2875*m*, 1460*m*, 1447*m*, 1443*m*, 1392*w*, 1385*w*, 1378*m*, 1260*w*, 1250*w*, 1038*m*, 1018*m*, 997*m*, 915*m*, 895*s*, 862*m*. – ^{1}H-NMR. (100 MHz, CCl_4): 5.22/br.*s*, 1H, H–C(3); 2.83/*s* with ringing, 1H *endo*-H–C(5); 2.68/*d* with ringing (J = 4), 1H, *endo*-H–C(8); 1.75/*d* (J = 1.5), 3H, H_3C–C(2); 1.52/*d* without ringing (J = 4), 1H, H–C(7); 1.30/*s*, 1.24/*s* and 1.09/*s*, 3H each, H_3C–C(1), H_3C–C(4) and H_3C–C(6). – ^{13}C-NMR. (25.2 MHz, $CDCl_3$): 134.2/*s*, C(2); 126.7/*d*, C(3); 50.5/*d*, C(5) or C(8); 45.2/*d*, C(8) or C(5); 40.0/*d*, C(7); 28.6/*s*, 25.7/*s* and 24.4/*s*, C(1), C(4) and C(6); 19.8/*qa* × *d* (J^1 = 127 and J^3 = 3.3), CH_3–C(2); 17.9/*qa* × *d* (J^1 = 127 and J^3 = 3.1), CH_3–C(1); 14.7/*qa* × *d* (J^1 = 127 and J^3 = 1.8), CH_3–C(4); 14.0/*qa* (J^1 = 128 and $J^3 < 0.3$), CH_3–C(6). – *Selective decoupling*: Irradiation at 5.25 (H–C(3)) converted the *qa* × *d* at 19.8 (CH_3–C(2)) to *qa* and the *qa* × *d* at 14.7 (CH_3–C(4)) to *qa*; irradiation at 2.78 (between H–C(5) and H–C(8)) did not alter the multiplicity of the CH_3–^{13}C-signals; irradiation at 1.52 (H–C(7)) produced a complicated non first order spectrum because of the proximity of the ^{1}H-absorptions of the CH_3 groups but left unchanged two CH_3–^{13}C-absorptions: *qa* × *d* 14.7 and *qa* 14.0. – MS.: 232/230/228 (4/21/29, $M^+ - 2H$), 219/217/215 (0.3/1/2, $M^+ - CH_3$), 197/195 (27/90, $M^+ - Cl$), 182/180 (3/9, $M^+ - CH_3 - Cl$), 181/179 (6/13, $M^+ - CH_3 - HCl$), 163.5 (*m**), 160 (21, $M^+ - 2Cl$), 159 (100, $M^+ - Cl - HCl$), 158 (40, $M^+ - 2((HCl))$), 145 (33, $M^+ - CH_3 - 2(HCl)$), 129 (*m**), 115.5 (*m**), 91 (39), 77 (37).

$C_{12}H_{16}Cl_2$ (231.16) Calc. C 62.35 H 6.98 Cl 30.68% Found C 62.26 H 6.97 Cl 30.74%

When a ^{1}H-NMR. sample of **11** was heated for 0.5 h at 210° in perchlorobutadiene no rearrangement was observed. The first eluates from the silver nitrate-impregnated silica gel column contained about 15 mg of a 3:1 mixture of (E)-*β*, *3-dichloro-α,2,4,6-tetramethyl-styrene* (**12**) and **11**. The major component of this mixture had the same retention time (GC.) and ^{1}H-NMR. signals as a pure sample of the dichlorostyrene **12**, prepared as described in experiment 3.

2.3. *Products from 4,4,8,8-tetrachloro-1,3,5,7-tetramethyl*-anti-*tricyclo [5.1.0.0^{3,5}]octane-2,6*-trans-*diol* (**5**). The reaction and work-up conditions described in 2.1 applied to 1.4 g (4.2 mmol) of **5** in 15 ml of pyridine yielded 0.65 g of a semisolid residue after solvent removal. Partial separation of the mixture was achieved by column chromatography (50 × 1.5 cm) on aluminium oxide (grade 1) in pentane, then pentane/ether 2:1.

The *first fraction* (600 ml pentane) yielded 50 mg (5%) of *1,5-dichloro-2,4,6,8-tetramethyl-cycloocta-1,3,5,7-tetraene* (**13**) which was *ca.* 95% pure (^{1}H-NMR.); recrystallization from acetonitrile (−40°) gave 8 mg of colourless prisms, m.p. 71–72°. – IR. (KBr): 3010*w*, 2978*w*, 2950*w*, 2918*w*, 1633*w*, 1433*w*, 938*s*, 856*w*. – ^{1}H-NMR. (100 MHz, $CDCl_3$): 5.61/br.*s*, 2H, H–C(3) and H–C(7); 1.90/br.*s*, 12 H, H_3C–C(2), H_3C–C(4), H_3C–C(6) and H_3C–C(8). – ^{1}H-NMR. (100 MHz, d_8-toluene): 5.41/br.*s*, 2H, H-C(3) and H–C(7); 1.81/*d* (J = 1.5), 6H, H_3C–C(4) and H_3C–C(8); 1.74/*d* (J = 0.75),

6H, H_3C–C(2) and H_3C–C(6). – *Spin decoupling*: irradiation at 5.41 (H–C(3), H–C(7)) converted the *d* at 1.81 (H_3C–C(4) and H_3C–C(8)) to *s* and the *d* at 1.74 (H_3C–C(2) and H_3C–C(6)) to *s*. – ^{13}C-NMR. (25.2 MHz, $CDCl_3$): 136.9/*s*, 132.8/*s*, 128.2/*s*, C(1) and C(5), C(2) and C(6), C(4) and C(8); 130.1/*d*, C(3) and C(7); 21.1/*q*, 19.7/*q*, CH_3–C(2), CH_3–C(4), CH_3–C(6) and CH_3–C(8). – MS.: 232/230/228 (0.6/4.3/6.9, $M^{+\cdot}$), 217/215/213 (0.3/1.1/1.7, $M^+ - CH_3$),195/193 (25/27, $M^+ - Cl$), 194/192 (39/91, $M^+ - HCl$), 158 (58), 157 (100, $M^+ - Cl - HCl$), 143 (19, $M^+ - CH_3 - 2Cl$), 142 (73), 141 (47), 128.5 (*m**), 128 (16), 115 (22).

$C_{12}H_{14}Cl_2$ (229.15) Calc. C 62.89 H 6.12 Cl 30.95% Found C 62.95 H 6.23 Cl 31.00%

The *second chromatography fraction* (250 ml pentane) yielded 30 mg of a mixture which contained (^{1}H-NMR.) about 50% of **13** (the total yield of **13** was thus about 6%). The *third chromatography fraction* (300 ml pentane/ ether 2:1) gave 70 mg of oily crystals. Preparative TLC. on silica gel with pentane/benzene 1:1 (twice) separated 40 mg of a solid containing (^{1}H-NMR.) a 4:1 mixture of **15** and an unidentified compound **X** (see below). Recrystallization from acetonitrile afforded 5 mg (1%) of *4,8-dichloro-1,3,5,7-tetramethyl-9-oxabicyclo[4.2.1]nona-2,4,7-triene* (**15**) as colourless needles, m.p. 94–95°. – UV. (heptane): max. 289 (1960), max. 278 (3330), max. 268.5 (3480), sh. 260 (2930), min. 240 (1650). – IR. (KBr): 3020*w*, 2980*m*, 2950*m*, 2920*m*, 1658*m*, 1572*m*, 1452*s*, 1438*m*, 1378*m*, 1029*s*, 965*m*, 875*s*. – ^{1}H-NMR. (100 MHz, $CDCl_3$): 5.94/br.*s*, 1H, H–C(2); 4.85/br.*s*, 1H, H–C(6); 2.11/br.*s*, 6H, H_3C–C(7) and H_3C–C(5); 1.80/br.*s*, 3H, H_3C–C(3); 1.53/*s*, 3H, H_3C–C(1). – ^{1}H-NMR. (100 MHz, d_8-toluene): 5.82/br.*s*, 1H, H–C(2); 4.53/br.*s*, 1H, H–C(6); 1.97/*d* (J=1.2), 3H, H_3C–C(3); 1.75/br.*s*, 3H, H_3C–C(1); 1.47/*d* (J=0.75), 3H, H_3C–C(7); 1.35/*s*, 3H, H_3C–C(5). – *Spin decoupling*: irradiation at 5.82 (H–C(2)) converted the *d* at 1.97 (H_3C–C(3)) to *s* and sharpened the br.*s* at 1.75 (H_3C–C(1)); irradiation at 4.53 (H–C(6)) converted the *d* at 1.47 (H_3C–C(7)) to *s*. – ^{13}C-NMR. (25.2 MHz, $CDCl_3$): 143.1/*s*, 132.1/*s*, 125.5/*s*, C(3), C(4), C(5), C(7), C(8), two signals were not observed; 135.8/*d*, C(2); 86.5/*d*, C(6); 85.3/*s*, C(1); 27.4/*qa*, 23.1/*qa*, 22.8/*qa*, 9.9/*qa*, CH_3–C(7), CH_3–C(5), CH_3–C(3) and CH_3–C(1). – MS.: 248/246/244 (0.2/0.4/0.6, $M^{+\cdot}$), 233/231/229 (0.1/0.4/0.5, $M^+ - CH_3$), 205/203/201 (13/72/100, $M^+ - CH_3 - CO$), 91 (8), 77 (8).

$C_{12}H_{14}Cl_2O$ (245.15) Calc. C 58.79 H 5.75 Cl 28.92% Found C 58.51 H 5.73 Cl 28.55%

Compound **X** was partially characterized in the 4:1 mixture by capillary GC./MS. (column 100–170°, 3°/min., injector 175°, retention time 22.5 min.). – MS. (82 eV): 282/280/278 (2/2/4, $M^{+\cdot}$), 267/265/263 (1/8/10, $M^+ - CH_3$), 247/245/243 (12/82/100, $M^+ - Cl$), 219/217/215 (8/30/63, $M^+ - Cl - CO$), 210/208 (13/39, $M^+ - 2Cl$), 209/207 (20/53, $M^+ - Cl - HCl$), 181/179 (21/63, $M^+ - HCl - Cl - CO$), 91 (20), 77 (27). The molecular ion corresponds to the composition $C_{12}H_{13}Cl_3O$. In the ^{1}H-NMR. spectrum of a 1:1 mixture of **15** and **X** the following signals are attributed to the latter. – ^{1}H-NMR. (100 MHz, d_8-toluene): 5.51/br.*s* 1H; 1.94/s, 3H; 1.67/*d* (J=1.5), 3H; 1.10/*s*, 3H; 0.95/*s*, 3H. – *Spin decoupling*: Irradiation at 5.51 converted the *d* at 1.67 to *s*.

A solution of 20 mg of the 4:1 mixture of **15** and **X** in acetic acid was hydrogenated for 2.5 h, over platinum oxide at RT. The ^{1}H-NMR. spectrum of the crude product mixture showed that all signals at larger δ-values than 3.0 had disappeared. This mixture was further characterized by capillary GC./MS. (column program 80–180°, 6°/min., injector 175°). Fraction number, molecular ion, and retention time in min. are given in that sequence for the 5 main fractions: 1) 216/214, 4.0; 2) 215/213, 9.3; 3) 214/212, 10.0; 4) 215/213, 10.2; 5) 296/294/292, 13.2. When the hydrogenation of a 1:1 mixture of **15** and compound **X** was carried out at 60° for 2 h and the product mixture analysed by capillary GC./MS. (column program 70–170°, 5°/min., injector 175°) 4 main fractions were observed. Reported as above: 1) 215/213, 14.0; 2) 215/213, 14.2; 3) 215/213, 15.0; 4) 296/294/292, 18.7.

2.4. *Products from cyclohexanol.* The reaction and work-up conditions described in 2.1 were applied to 3 g (30 mmol) of distilled cyclohexanol in 7 ml of pyridine using 18 g (32 mmol) of freshly prepared P_2I_4. Preparative TLC. of 180 mg of crude product on silica gel (3 times pentane) gave 10 mg of *iodocyclohexane*, identical to an authentic sample (^{1}H-NMR., MS.). Extraction of the start zone with CH_2Cl_2 and sublimation of the oily residue gave 10 mg of a phosphorus-containing product of *unknown structure* (as a colourless oil). – IR. (CCl_4): 2940*s*, 2860*m*, 1450*w*, 1285*m*, 1015*s*, 1000*s*, 955*m*. – ^{1}H-NMR. (60 MHz, CCl_4): 4.8–4.2/m; 1.95/br.*s*; 1.50/br.*s*. – ^{31}P-NMR. (36.43 MHz, $CDCl_3/H_3PO_4$) two signals at + 0.1 and −15.2 ppm in an approximate 1:5 ratio. – MS.: 507 (0.2/ presumably $M^{+\cdot}$), 425 (3), 343 (12), 289/288 (2/1.5), 227 (*m**), 261/260 (36/28), 235 (5.5), 207 (12.5), 198.5 (*m**), 179 (100), 127 (7), 122.8 (*m**), 99 (31.5).

The yield of iodocyclohexane increased when more pyridine was used.

2.5. *Products from cyclohexane-1,4-diol.* The reaction and work-up conditions described in 2.1 were applied to 1.8 g (15.5 mmol) of cyclohexane-1,4-diol (*Fluka*, mixture of *cis* and *trans*, m.p. 101–103°) using 17 g (30 mmol) of freshly prepared P_2I_4. Preparative TLC. of 270 mg of crude product on silica gel with pentane gave 3 fractions. *Fraction 1* (30 mg = 1%) was subjected to a bulb distillation (100°/20 Torr) giving 7 mg of a colourless oil, rapidly turning mauve (I_2). Its ^{1}H-NMR. and mass spectra were in agreement with those reported for *4-iodo-cyclohex-1-ene* [18]. *Fraction 2* (10 mg = 0.2%) was a crystalline solid, whose m.p. (136–137°, Lit. [19]: 142–143°), IR., ^{1}H-NMR., and mass spectrum showed it to be trans-*1,4-diiodo-cyclohexane*. *Fraction 3* (10 mg = 0.2%) was cis-*1,4-diiodo-cyclohexane*: crystalline solid, m.p. 64–65°, (Lit. [19]: 68–69°), IR., ^{1}H-NMR., and mass spectrum.

3. (*E*)-β,3-dichloro-α-2,4,6-tetramethyl-styrene (12). – Samples of 1,5-dichloro-2,4,6,8-tetramethyl-cycloocta-1,3,5,7-tetraene (**13**) were heated in different degassed solvents in closed tubes. The disappearance of the ^{1}H-NMR. signals of **13** were measured relative to an internal standard (benzene or TMS) as a function of time. In all cases this was found to follow a first order rate law. The following half lives of **13** and the yields of product **12** (after the disappearance of **13**) were determined: In CD_3CN at 61.3° $t_{1/2}$ was 80 min. (60% yield); in CD_3COOD at 61.3° $t_{1/2}$ was 40 min. (60%); in $CDCl_3$ at 88.0° $t_{1/2}$ was 20 min. (95%); in toluene-d_8 at 143° $t_{1/2}$ was *ca.* 70 min. (15%). In all the thermolyses no ^{1}H-NMR. signals of other products except polymeric material and in particular none of the other isomer (*Z*) of the styrene derivative were observed. An almost pure sample of **12** was obtained as an oil by preparative TLC. on silica gel. – GC. (column 152°, injector 167°, retention time 2.5 min.). – IR. (KBr): 3075*w*, 2980*w*, 2950*w*, 2930*w*, 1620*w*, 1190*m*, 1000*m*, 868*m*, 800*m*. – ^{1}H-NMR. (100 MHz, CCl_4); 6.85/br.*s*, 1 H, H–C(5); 5.81/*qa* (*J* = 1.5), 1 H, H–C(β); 2.30/*s*, 2.23/*s* and 2.16/*s*, 3 H each, H_3C–C(2), H_3C–C(4) and H_3C–C(6); 2.00/*d* (*J* = 1.5), 3 H, H_3C–C(α). – ^{13}C-NMR. (25.2 MHz, $CDCl_3$): 139.0/*s*, 138.0/*s*, 135.0/*s*, 133.7/*s*, 133.4/*s* and 132.4/*s*, C(1), C(2), C(3), C(4), C(6) and C(α); 129.6/*d*, C(5); 116.6/*d*, C(β); 20.6/*qa* (J^1 = 128.5 and J^3 = 5.0), CH_3–C(4) or CH_3–C(6); 19.4/*qa* (J^1 = 127 and J^3 = 5.0), CH_3–C(6) or CH_3–C(4); 18.2/*qa* (J^1 = 129 and J^3 = 7.0), CH_3–C(α); 17.7/*qa* (J^1 = 129 and $J^3 < 0.3$), CH_3–C(2). – *Selective decoupling*: Irradiation at 5.81 (H–C(β)) converted the *qa* × *d* at 18.2 to *qa*. – MS.: 232/230/228 (11/55/87, $M^{+\cdot}$), 217/215/213 (0.9/3.4/5.3, $M^+ - CH_3$), 195/193 (33/100, M^+–Cl), 180/178 (8/16, M^+–CH_3–Cl), 163.5 (*m**), 158 (98, M^+–2Cl), 157 (66, M^+–Cl–HCl), 143 (53, M^+–CH_3–2Cl), 129 (*m**), 128 (41, M^+–2(CH_3)–2Cl), 115 (42), 91 (16), 77 (26).

Catalytic hydrogenation of **12** for 1.5 h over PtO_2 in acetic acid at 60° and purification of the product by preparative TLC. on silica gel (pentane) gave *ca.* 60% of *3-chloro-1-isopropyl-2,4,6,-trimethyl-benzene* (**14**) as a colourless oil, with spectroscopic properties identical to a sample of **14** synthesized as described in experiment 4.

4. 3-Chloro-1-isopropyl-2,4,6-trimethyl-benzene (14). – To a solution of 29 mg (0.18 mmol) 1-isopropyl-2,4,6-trimethyl-benzene [20] and 25 mg (0.19 mmol) of sulfuryl chloride in 3 ml hexane was added 30 mg of silica gel (mesh: 70–230) and the mixture was stirred at RT. for 20 h. Filtration, evaporation of the solvent and distillation of the residue gave 28 mg (80%) of oily **14**, b.p. 85–90°/11 Torr. – IR. ($CHCl_3$): 2980*m*, 2965*s*, 2935*m*, 2880*m*, 1470*s*, 1460*s*, 1390*w*, 1380*w*, 1370*w*, 1355*w*, 1190*w*, 1080*w*, 990*s*, 870*m*. – ^{1}H-NMR. (100 MHz, $CDCl_3$): 6.86/*s*, 1H, H–C(5); 3.44/*septet* (*J* = 7.5), 1H, isopropyl-CH; 2.44/*s*, 3H and 2.30/*s*, 6H, H_3C–C(2), H_3C–C(4) and H_3C–C(6); 1.33/*d* (*J* = 7.5), 6H, isopropyl-CH_3. – MS.: 198/196 (0.3/1, $M^{+\cdot}$), 183/181 (2/6, M^+–CH_3), 168/166 (3/9, M^+–2(CH_3)), 153/151 (3/9, M^+–3(CH_3)), 115 (26, M^+–3(CH_3)–HCl), 91 (20), 43 (100).

$C_{12}H_{17}Cl$ (196.72) Calc. C 73.27 H 8.71% Found C 73.20 H 8.60%

5. Synthesis of some derivatives of 2,2-dimethyl-2,3-dihydrobenzo(b)furan. – 5.1. *2,2,4,6-Tetramethyl-2,3-dihydrobenzo(b)furan* (**17**) [21] [22] was prepared from 2,5-dimethyl-phenol and isobutyraldehyde [21]. Preparative GC. (column 172°, injector 195°, retention time 4 min) gave an analytically pure sample. – UV. (heptane): max. 289 (3060), max. 285 (2800), max. 280 (2670), min. 250 (193), max. 223 (6160). – IR. (CCl_4): 3020*w*, 2987*s*, 2920*s*, 2855*s*, 1620*m*, 1600*s*, 1494*m*, 1460*m*, 1445*m*, 1370*m*, 1333*m*, 1285*m*, 1118*m*, 1084*m*, 833*s*. – ^{1}H-NMR. as reported [22]. – MS.: 176 (67, $M^{+\cdot}$), 161 (100, M^+–CH_3), 146 (9, M^+–2(CH_3)), 133 (32, M^+–CO–CH_3), 115 (11), 91 (21), 77 (11).

$C_{12}H_{16}O$ (176.26) Calc. C 81.77 H 9.15% Found C 81.63 H 9.26%

5.2. *2,2,5,6-Tetramethyl-2,3-dihydrobenzo(b)furan* (**18**). 24.4 g (0.2 mol) 3,4-Dimethyl-phenol, 14.4 g (0.2 mol) isobutyraldehyde and 0.8 g conc. sulfuric acid in 30 ml of toluene were refluxed for 3 h while removing the water azeotropically (12 ml). The cooled mixture was washed 4 times with

10% KOH-solution and once with $NaHCO_3$-solution and dried. After removal of the solvent the residue was distilled, b.p. 50–65°/1 Torr, giving 7 g (16%) of a liquid consisting of 80% **18**(^{1}H-NMR.). Prep. GC. (column 175°, injector 200°, retention time 4.2 min.) afforded an analytically pure sample of **18**. – UV. (heptane): max. 297 (3480), max. 291.5 (4250), max. 287.5 (4150), sh. 282.5 (2660), min. 251 (96), sh. 230 (4680), sh. 220 (5750). – IR. (CCl_4): 3020*w*, 2975*s*, 2930*m*, 2860*w*, 1625*m*, 1592*m*, 1495*s*, 1462*s*, 1402*m*, 1370*s*, 1265*m*, 1065*m*, 882*m*, 870*m*, 855*m*. – ^{1}H-NMR. (100 MHz, $CDCl_3$): 6.88/br. *s* and 6.53/br. *s*, 1H each, H–C(7) and H–C(4); 2.95/br. *s*, 2H, 2H–C(3); 1,20/*s* and 1.18/*s*, 3H each, H_3C–C(5) and H_3C–C(6); 1.45/*s*, 6H, $2H_3C$–C(2). – ^{13}C-NMR. (25.2 MHz, $CDCl_3$): 157.2/*s*, C(7a); 135.8/*s*, 127.3/*s*, 124.0/*s*, C(5), C(6) and C(3a); 126.0/*d* and 110.6/*d*, C(4) and C(7); 86.0/*s*, C(2); 42.8/*t*, C(3); 28.15/*qa*, $2CH_3$–C(2); 20.0/*qa* and 19.1/*qa*, CH_3–C(5) and CH_3–C(6). – MS.: 176 (83, M^+·), 161 (100, M^+–CH_3), 146 (10, M^+–2(CH_3)), 133 (27, M^+–CO–CH_3), 91 (18).

$C_{12}H_{16}O$ (176.26) Calc. C 81.77 H 9.15% Found C 81.67 H 9.25%

5.3. *2,2,4,6-Tetramethyl-5-chloro-2,3-dihydrobenzo(b)furan* (**19**). The procedure described in 5.2 was applied to 31.3 g (0.2 mol) of 4-chloro-3,5-dimethyl-phenol to give 7 g of a mixture containing 30% of **19** (5% yield). Prep. GC. (column 190°, injector 210, retention time 4.3 min.) afforded 80% pure **19** (^{1}H-NMR.), colourless needles, m.p. 37–38° (from EtOH). An alternative synthesis of **19** following section 4 and using **17** as starting material, also gave **19** as the only product. The two samples of **19** had identical spectral properties (as follows). – UV. (heptane): max. 296.5 (2820), max. 292 (2880), max. 286.5 (2770), min. 255 (142), max. 235.5 (5950). – IR. (CCl_4): 3040*w*, 2975*s*, 2925*m*, 2850*m*, 1612*w*, 1592*m*, 1475*s*, 1458*s*, 1368*s*, 1280*s*, 1138*s*, 1050*s*, 875*m*, 845*m*. – ^{1}H-NMR. (100 MHz, $CDCl_3$): 6.47/br. *s*, 1H, H–C(7); 2.94/br. *s*, 2H, 2H–C(3); 2.31/*s*, and 2.24/*s*, 3H each, H_3C–C(4) and H_3C–C(6); 1.46/*s*, 6H, $2H_3C$–C(2). – ^{13}C-NMR. (25.2 MHz, $CDCl_3$): 156.8/*s*, C(7a); 135.3/*s*, 132.2/*s*, 125.1/*s* and 124.9/*s*, C(3a), C(4), C(5) and C(6); 109.2/*d*, C(7); 86.5/*s*, C(2); 42.5/*t*, C(3); 28.2/*qa*, $2CH_3$–C(2); 21.0/*qa* and 17.1/*qa*, CH_3–C(4) and CH_3–C(6). – MS.: 212/210 (33/100, M^+·), 197/195 (29/88, M^+–CH_3), 175 (17, M^+–Cl), 169/167 (18/22, M^+–CO–CH_3), 160 (33, M^+–Cl–CH_3), 145 (8, M^+–Cl–2(CH_3)), 115 (13, M^+–Cl–4(CH_3)), 91 (11).

$C_{12}H_{15}ClO$ (210.70) Calc. C 68.40 H 7.18 Cl 16.83% Found C 68.23 H 7.25 Cl 16.70%

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