Articles

Improved Syntheses and Some Selective Transformations of 2,2,4,4-Tetrachloro-8-oxabicyclo[3.2.1]oct-6-en-3-ones

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The methyl- and alkenyl-substituted furans **1b**−**h** react with pentachloroacetone (**2**) and sodium 2,2,2-trifluoroethoxide solution to form the title compounds **3b**−**h** in good yield. With the furans **1i**−**m** bearing an oxygen or a sulfur heteroatom in the side chain, moderate yields are obtained. Dechlorination of the [4+3] cycloadducts **3** with the Zn−Cu couple leads to the corresponding oxabicyclic ketones **4**. On catalytic hydrogenation of the tetrachlorooxabicyclooctenones **3a**−**c** hydrogenolysis of the *exo*-carbon−chlorine bonds occurs, leading to the *endo*-2,*endo*-4-dichloro-8-oxabicyclooctan-3-ones **8a**−**c**. With lithium aluminum hydride and Grignard reagents, **8a** and **3a** form the *endo*-3-alcohols **12a**−**c** and **13**, respectively, the latter with uncertain configuration at C-3, in a highly stereoselective manner. The ether bridge in the dechlorinated oxabicyclooctenones **4b**, **4f**, and **4g** can be cleaved by means of trimethylsilyl triflate/triethylamine to produce the tropones **5b**, **5f**, and **5g**. Hydrogenation of 1,5-dimethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (**4c**), followed by Wolff−Kishner reduction, affords 1,5-dimethyl-8-oxabicyclo[3.2.1]octane (**7**). *m*-Chloroperbenzoic acid epoxidizes the alkenyl side chain of the tetrachlorinated oxabicycles **3d**, **3e**, **3g**, and **3h** in a site-selective reaction. In contrast, from the dehalogenated oxabicyclic ketone **4g** the bis(epoxide) **14** is obtained.

8-Oxabicyclo[3.2.1]oct-6-en-3-ones, readily available by [4+3] cycloaddition of oxyallyl intermediates to furans, are valuable building blocks for organic synthesis.[1,2] Until now, the preferred procedure for the preparation of these oxabicyclics, *unsubstituted at C-2 and C-4*, seems to be the debromination of 2,4-dibromo derivatives which result from the reaction of furans with tetrabromoacetone in the presence of nonacarbonyl diiron,[3] zinc/triethyl borate,[4] or zinc/silver couple.[5] Recently, diethyl zinc has been recommended as a debrominating agent.[6]

Chloro-substituted 8-oxabicyclo[3.2.1]oct-6-en-3-ones are available from furans and trichloro-, tetrachloro-, and pentachloroacetones in methanol, 2,2,2-trifluoroethanol (TFE), or 2,2,3,3-tetrafluoropropan-1-ol (TFP) in the presence of bases, preferrably the corresponding sodium alkoxides.[7−10] For further transformations the chlorinated oxabicyclics have been used comparatively seldom.[11] Recently, we have disclosed a procedure for the preparation of the unsubstituted 8-oxabicyclo[3.2.1]oct-6-en-3-one (**4a**) from its 2,2,4,4-tetrachloro derivative (**3a**).[10] The cycloaddition of the tetrachloro-substituted oxyallyl intermediate, generated from 1,1,1,3,3-pentachloro-2-propanone (pentachloroacetone, PCA), to cyclic 1,3-dienes has the advantage that no *endo*-/*exo*-stereoisomers can be formed, thus facilitating workup by crystallization.

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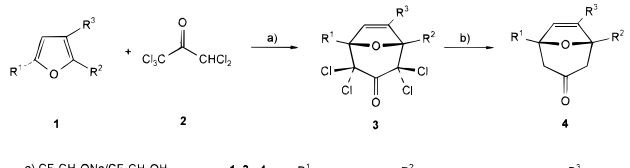
Table 1. Oxabicyclo[3.2.1]oct-6-en-3-ones (4) and Their Tetrachloro-Derivatives (3) by Reaction of Furans (1) with Pentachloroacetone (2) in TFE/NaTFE (Column A) and in $LiClO_4$/Diethyl Ether/Triethylamine (Column B)

	3 [% yield]		
furan (**1**)	A	B	**4** [% yield]
furan (**1a**)	57	42[a]	97[a]
-2-methyl (**1b**)	66	42	65
-2,5-dimethyl (**1c**)	81	62	87
-2-vinyl (**1d**)	83	38	71
-2-vinyl-5-methyl (**1e**)	84		60
-3-methyl (**1f**)	86		87
-2-(but-3-enyl)-3-methyl (**1g**)	88		65
-2-(3-methylbut-3-enyl)-3-methyl (**1h**)	87		74
-2-hydroxymethyl (**1i**)	not isolated		21
-2-hydroxymethyl-5-methyl (**1j**)	not isolated		26
-2-phenoxymethyl-5-methyl (**1k**)	not isolated		6
-2-dimethoxymethyl-5-methyl (**1l**)	not isolated		41
-2-methylthiomethyl (**1m**)	not isolated		10

[a] Reference 10.

To explore the scope and limitation of this [4+3] cycloaddition, we have investigated the reactions of several substituted furans (**1b**−**m**) with PCA in TFE in the presence of sodium 2,2,2-trifluoroethoxide (NaTFE). TFE was preferred as the solvent since TFP apparently is not generally available at a lower price, but there is no doubt that the reactions could be performed in TFP as well. Moreover, we have worked out a procedure for recycling TFE from the waste of the reactions's workup (see Experimental Section).



a) CF_3CH_2ONa/CF_3CH_2OH

b) Zn-Cu, NH_4Cl, CH_3OH

1, **3**, **4**	R^1	R^2	R^3
a	H	H	H
b	CH_3	H	H
c	CH_3	CH_3	H
d	CH_2=CH	H	H
e	CH_2=CH	CH_3	H
f	H	H	CH_3
g	H	CH_2=$CHCH_2CH_2$	CH_3
h	H	CH_2=$C(CH_3)CH_2CH_2$	CH_3
i	$HOCH_2$	H	H
j	$HOCH_2$	CH_3	H
k	$C_6H_5OCH_2$	CH_3	H
l	$(CH_3O)_2CH$	CH_3	H
m	CH_3SCH_2	H	H

Since furan (**1a**) and 2-methylfuran (**1b**) are volatile liquids and cheap by comparison with PCA, they may be used as cosolvents, i.e., in stoichiometric excess. Under these conditions, the cycloadduct **3a** is formed with yields of more than 50%.[9,10] However, in the case of the substituted furans **1c**−**m** economy should prohibit their use in excess. We have found that these furans should be made to react in the following way: a 1−2 M solution of NaTFE in TFE is added dropwise to a mixture of the furan with a slight excess of PCA (see Experimental Section). This procedure also reduces the amount of the expensive TFE. For the same reason we prefer a 2 M solution of NaTFE/TFE. Solutions of higher concentration are no more homogeneous and, therefore, are less convenient to add. As shown in Table 1, high yields of tetrachloro-substituted 8-oxabicyclo[3.2.1]oct-6-en-3-ones are obtained with the alkyl- or alkenyl-substituted furans **1b**−**h**. Note that 2-vinylfuran (**1d**) undergoes a site-specific (perispecific) cycloaddition; the vinyl substituent is not attacked by the oxyallyl intermediate.

As reported repeatedly for other cases,[9−12] the tetrachlorinated oxabicyclics are dechlorinated by zinc or the zinc−copper couple reagent, according to the standard method advanced by Noyori[3,5] to give the oxabicyclics **4** (Table 1).

In the case of the furans **1i**−**m** functionalized at the side chain in the 2-position, the yields of cycloadducts are distinctly lower. Byproducts arise, presumably of polymeric structure, that retard crystallization of the bicyclics. Consequently, we have dechlorinated the crude product mixtures with zinc powder or zinc−copper couple. The 8-oxabicyclo[3.2.1]oct-6-en-3-ones **4i**−**m** could be isolated in low yields (Table 1).

Fortunately, the bicyclics with an alkenyl substituent (**3d**,**e**,**g**,**h**) are formed in high yield. Undoubtedly, a functionalization of the unsaturated appendix can be performed at a later stage (for one example vide infra).

At present, TFE is an expensive solvent; hence we have tried to substitute it for lithium perchlorate−diethyl ether solution, with triethylamine as the base.[12] With 2-methyl- and 2,5-dimethylfuran, the yields were slightly lower (42%, 62%); however, in the reactions of the furans **1d**−**h** unsatisfactory yields of the bicyclics were encountered (see Experimental Section and Table 1).

From a synthetic point of view the bicyclics **3** and **4** can be regarded as 4-cycloheptenones with an oxygen bridge between C-3 and C-6. Concerning the stereostructure, however, these molecules preferably are related to the (4-oxa)cyclohexanone chair conformation in which the axial bonds at C-3 and C-5 are bridged by a vinylene group.

Indeed, in the ^{13}C NMR spectrum ($CDCl_3$) of the dechlorinated bicyclics **4** the resonance of the carbonyl carbon atom (C-3) (δ = 205−206 ppm, see Experimental Section) is close to that of 4-oxacyclohexanone (tetrahydro-4*H*-pyran-4-one; δ = 206.2 ppm) and occurs at higher field than the corresponding one of cyclohexanone (δ = 211.3, $CDCl_3$; 208.8 ppm, neat).[13] The tetrachloro-substituted bicyclics **3** show an upfield shift of the carbonyl resonance to δ = ca. 185 ppm. Almost the same effect is found comparing cyclohexanone with its 2,2,6,6-tetrachloro derivative (δ = 184.5).[14]

In the IR spectrum the carbonyl absorption of the bicyclics **3** characteristically occur at higher wavenumbers than that of **4**. Tetrahydro-4*H*-pyran-4-one shows 1715−1718 cm^{-1} (film),[15] a value not far from cyclohexanone (1712 cm^{-1})[16] and the bicyclics **4a**−**c** (1710−1720 cm^{-1}). 2,2,6,6-Tetrachlorocyclohexanone is reported to absorb at 1766 cm^{-1}.[16] However, in the carbonyl region of the IR spectrum of the tetrachlorinated bicyclics **3** two bands occur; for example, **3a** shows a strong band at 1772 (CCl_4), 1765 (in $CHCl_3$) cm^{-1} accompanied by a weak one at 1733 (CCl_4), 1730 cm^{-1} (in $CHCl_3$). In KBr we observe 1760 and 1730 cm^{-1}, the latter band appearing relatively more intense than in CCl_4 or $CHCl_3$ solution. At first sight the two bands in the carbonyl region might originate from the presence of different conformers, e.g., chair and boat forms of the bridged (oxa)cyclohexanones.[17]

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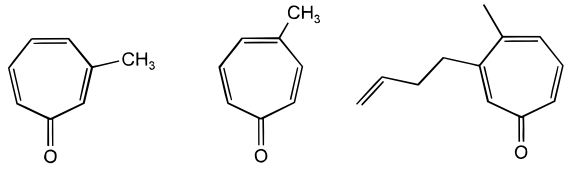
However, it cannot be excluded that this phenomenon is caused by a Fermi resonance.[18] Strong absorptions at approximately half of these wavenumbers occur in the "fingerprint region", and the corresponding vibrations may be coupled with the C=O stretching modes. The spectrum of bicycle **3a**, for example, shows strong bands at 880 and 920 cm^{-1} (skeleton vibrations?) and at 710 cm^{-1} (C−Cl stretching vibration?).

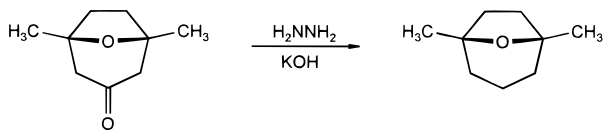
Cleavage of Oxabicyclics 4 to Tropones 5. We have recently shown that the ether bridge in the parent oxabicyle **4a** and some of its alkyl derivatives, substituted at C-2 and/or C-4, are cleaved by reaction with trimethylsilyl trifluoromethanesulfonate/triethylamine (TMSOTf/Et_3N) in tetrachloromethane, to form tropone and its 2,7-dialkyl derivatives, respectively.[19] However, these conjugated systems are accessible by more efficient routes.[20] A more interesting result is that the cleavage of oxabicycles substituted at the bridgehead carbon (C-1) or at the 6,7-double bond leads to 3- or 4-substituted tropones, since these are more difficult to obtain by existing, rather lengthy procedures. The oxabicycles **4b**, **4f**, and **4g** undergo cleavage with TMSOTf/Et_3N, to afford 3-methyltropone (**5b**), 4-methyltropone (**5f**), and 3-(but-3-enyl)-4-methyltropone (**5g**) with yields of 55, 62, and 66%, respectively. Presumably these tropones should be valuable building blocks in organic synthesis. For 4-methyltropone (**5f**), alternative routes exist.[21−23] So far, we were not able to transform the 1,5-dimethyl derivative **4c** and the vinyl derivative **4d** to 3,6-dimethyltropone or 3-vinyltropone, respectively, on treatment with TMSOTf/Et_3N. In both cases a complex product mixture resulted, which has not been investigated further.



5b **5f** **5g**

Catalytic Hydrogenation and Hydrogenolysis of Oxabicyclics 3a−c and 4c. The 6,7-double bond of 8-oxabicyclo[3.2.1]oct-6-en-3-ones is known to be saturated readily by catalytic hydrogenation.[3,4b,18−20] Several hydrogenated oxabicycles have been transformed to other useful products.[1,2b,25,26]

Our interest concentrated upon the oxabicycle **7**, which is structurally related to the olfactory compound 1,5-dimethylbicyclo[3.2.1]octan-8-one.[27] The oxime of the latter ketone is a commercial fragrance ingredient ("buccoxime").[28] To obtain **7**, **4c** was hydrogenated over Pd/C catalyst. The highly volatile ketone product **6** showed a peculiar herbaceous odor. Wolff−Kishner reduction of **6** gave the parent oxabicycle **7**, a compound with a camphor-like smell, but of more pungent and acidulous character.



6 **7**

Catalytic hydrogenation of chloro-substituted norbornene derivatives is known to saturate the C=C double bond without affecting the halogen substituents.[29] On the other hand, numerous organic chlorides undergo hydrogenolysis of the carbon−chlorine bond(s) in the presence of a variety of heterogeneous hydrogenation catalysts, preferably palladium on carbon.[30−32] To our knowledge, very few papers in fact deal with the behavior of α-chloroketones under the conditions of catalytic hydrogenation.[33] Expecting that both dechlorination and hydrogenation of the tetrachloro-substituted oxabicycles would occur, we hydrogenated compounds **3a,b,c** over palladium−carbon catalyst in methanol. As expected, saturation of the C=C double bond did occur; however, to our surprise, only two of the four chlorine atoms had been removed. The spectra showed that the *exo*, i.e., *axial* carbon−halogen bonds had stereoselectively undergone hydrogenolysis with the exclusive formation of the *endo*-2,*endo*-4-8-oxabicyclo[3.2.1]octan-3-ones (**8a,b,c**). The NMR spectra of **8a** and **8c** reflect the C_s symmetry of these products, and the coupling constants of 2-H and 4-H with the bridgehead hydrogens in the ^1H NMR spectra clearly show the *endo*-arrangement of both chlorine substituents ($^3J_{1,2}$ and $^3J_{4,5}$ = ca. 5 Hz), which is consistent with the corresponding coupling constant in *endo*-2,*endo*-4-dichloro-8-oxabicyclo[3.2.1]oct-6-en-3-on (J = 4.6 Hz).[8]

To secure the structure and to corroborate this difference in reactivity of the C−Cl bonds, we also hydrogenated *endo*-2,*endo*-4-dichloro-1,5-dimethyl-8-oxabicyclo-[3.2.1]oct-6-en-3-one (**9αα**) and its *exo*-2,*exo*-4 isomer (**9*ββ***).[8] The latter gave the dechlorinated oxabicycle **6** (vide ante) and its *exo*-monochloro (2-chloro) derivative (**10**). Catalytic hydrogenation of the former (**9αα**) occurred rapidly and exclusively at the C=C double bond with formation of **8c**.

One might speculate that a stereoelectronic effect might be responsible for the higher reactivity of the *exo*

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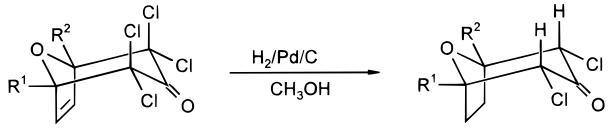
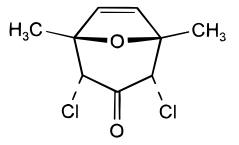


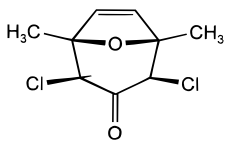
3 **8**

3 , 8	R^1	R^2
a	H	H
b	CH_3	H
c	CH_3	CH_3

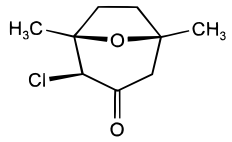
carbon−chlorine bonds. Namely, in the preferred chair conformation of the bicycles the better overlap between the axial C−Cl σ bond(s) and the C=O π bonds would facilitate cleavage of the carbon−halogen bond(s). To check this, we prepared the carbon-bridged analogue **11**, by reaction of cyclopentadiene with PCA. The hydrogenolytic dechlorination of **11** was nonselective, yielding a mixture of bicyclic compounds. From this we conclude that the oxygen bridge atom of the bicyclics interacts with the catalyst surface, leading to selective hydrogenolysis of the *exo* C−Cl bond(s) situated at the same face.



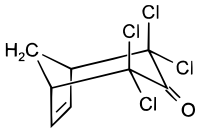
9ααα



9βββ



10



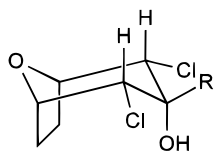
11

Hydride Reductions and Grignard Additions of 3a and 8a. Bicyclo[3.2.1]oct-6-en-3-one, the parent carbocyclic analogue of ketone **4a**, is known to be reduced by sodium borohydride or lithium aluminum hydride to form a mixture of *endo*- and *exo*-bicyclo[3.2.1]oct-6-en-3-ol.[34] Likewise, the 8-oxa analogue **4a**, its alkyl derivatives, substituted at C-2 and C-4, and 6,7-dihydro derivatives of them, on reaction with sodium borohydride, afford a mixture of the bicyclic *endo*- and *exo*-alcohols with the former predominating.[1c] Reductions with bulky metal hydrides such as diisobutylaluminum hydride (DIBALH) or potassium tri-*sec*-butyl borohydride (K-Selectride) give enhanced proportions of the *endo*-alcohols.[35]

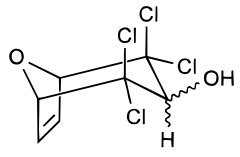
We have observed that lithium aluminum hydride causes highly stereoselective reduction of the *endo*-dichlorinated oxabicycle **8a**: Only one of the expected *endo*/*exo*-isomers of the α,α′-dichlorohydrin **12a** was found. Concerning the product conformation, the coupling constant between the *exo*-protons at the chloro-substituted carbons C-2 and C-4 and the proton α to the OH group (3-H) should reflect the *endo*- or *exo*-orientation of the OH group.[34] Unfortunately, the protons 2-H, 3-H, and 4-H gave rise to an absorption of a narrow multiplet (δ = 4.18); that is, all these have nearly equal chemical shifts; for this reason the vicinal coupling constants $^3J_{2,3} = {}^3J_{3,4}$ could not be derived.

The reduction of the bicyclic α,α′-dichloroketone **8a** may also be compared with the behavior of 2-chlorocyclohexanone. This monocyclic, nonbridged analogue, which is conformationally more flexible, is reported to give rise to a mixture of equal amounts of *cis*- and *trans*-2-chlorocyclohexanol on reduction with lithium aluminum hydride.[36]

The reaction of **8a** with methylmagnesium iodide, isopropenylmagnesium bromide, or isopropenyllithium (lithium 2-propenide) gave the bicyclic dichloro alcohols **12b** and **12c**, respectively. There should be little doubt that the three dichlorohydrins are the result of an equatorial, i.e., *exo*, attack of the hydride or RMgX, respectively, upon the bridged chair conformer of **8a**. The axial (i.e., *endo*) attack on the carbonyl group is expected to be hindered by the *endo*-chloro substituents. We conclude therefore that the hydroxy group in the bicyclic alcohols **12a**−**c** is *endo*-oriented, i.e., in a *cis*-relationship with the chlorine atoms at C-2, C-4.



12



13

12	R
a	H
b	CH_3
c	$CH_2=C(CH_3)-$

The *endo*-orientation of the OH group in the compounds **12a**−**c** is indicated by the pronounced downfield shift of the resonances of one pair of the four protons at C-6 and C-7 ($\Delta\delta$ = ca. 0.65 ppm); this is in full accord with the expected deshielding of the *endo* protons 6-H and 7-H by the *endo*-OH group.

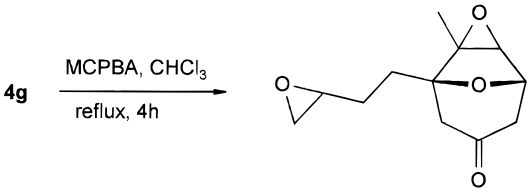
Similarly, 2-chlorocyclohexanone upon reaction with methylmagnesium bromide gives predominantly the *cis*-chlorohydrin.[37]

The above model reactions with the dichloroketone **8a** may open a path for stereoselective transformations using the chlorohydrin functionality. However, treatment of **12c** with sodium hydroxide or silver oxide gave none of the expected epoxide, in accord with the postulated *cis*-relationship of the 3-OH (*endo*, i.e., *axial*) and the vicinal chloro atoms (*endo*, i.e., *equatorial*).[38,39]

(34) LeBel, N. A.; Maxwell, R. J. *J. Am. Chem. Soc.* **1969**, *91*, 2307.
(35) (a) Bowers, K. G.; Mann, J. *Tetrahedron Lett.* **1985**, 4411. For further examples see ref 1c and, for example: (b) Treu, J.; Hoffmann, H. M. R. *J. Org. Chem.* **1997**, *62*, 4650.
(36) Felkin, H. *Ct. R. Acad. Sci.* **1950**, *231*, 1316; *Chem. Abstr.* **1951**, *45*, 7029f.
(37) Bartlett, P. D.; Rosenwald, R. H. *J. Am. Chem. Soc.* **1934**, *56*, 1990.
(38) Bartlett, P. D. *J. Am. Chem. Soc.* **1935**, *57*, 224.
(39) Bodot, H.; Jullien, J.; Mousseron, M. *Bull. Soc. Chim. Fr.* **1958**, 1097.

By the way, the sterically more hindered unsaturated tetrachloroketone **3a** did not lead to an addition product with isopropenyllithium. Instead, **3a** was reduced by lithium aluminum hydride, affording a single tetrachlorohydrin **13**. Considering the limited information from the spectra, we do not like to speculate upon the configuration at C-3.

Epoxidation of 3d,e,g,h and 4g. The unsatisfactory yields of [4+3] cycloadducts obtained from the heterosubstituted furans **1i**−**m** prompted us to find a way to functionalize the exocyclic double bond in the alkenyl-substituted oxabicycles derived from the furans **1d,e,g** and **1h**. It was recorded earlier that *m*-chloroperbenzoic acid (MCPBA) readily epoxidizes the 6,7-double bond of bicyclo[3.2.1]oct-6-en-3-one and its 8-oxa derivatives.[40]



14

Not unexpectedly, the butenyl-substituted oxabicycle **4g**, for example, is converted to the bis-epoxide **14** on 4 h reflux with MCPBA in chloroform (71% yield). However, treating the tetrachloro-substituted precursor **3g** with MCPBA, we obtained the monoepoxide **15g** (73%). The NMR spectra of the epoxides **14** and **15g** show that both epoxidations give rise to a 1:1 mixture of diastereomers, as expected. Apparently, the electron-attracting chlorine substituents decrease the reactivity of the endocyclic C=C double bond against electrophilic attack of the peracid. In line with this phenomenon is the observation that no defined product could be obtained from the reaction of the simplest tetrachloride, **3a**, with MCPBA, even after 40 h at reflux in chloroform.

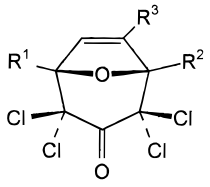
The site-selective epoxidation of the *exocyclic* C=C double bond described is also observed with the tetrachlorobicycles **3d**,**e**,**h**. However, with the vinyl-substituted derivatives **3d**,**e** the reaction proceeded at a slower rate, and yields—not optimized—were lower.

Conclusions. The cyclocondensation of pentachloroacetone (PCA) with cyclopentadiene or methyl- and alkenyl-substituted furans constitutes an efficient synthesis of 2,2,4,4-tetrachlorobicyclo[3.2.1]oct-6-en-3-one and its 8-oxa analogues. The yields of the [4+3] cycloadducts with the tetrachlorooxyallyl intermediate are good and compare favorably with those of related Diels−Alder reactions. By means of dehalogenations and reactions at the carbonyl group these cycloadducts can be transformed into bicyclic products that should be useful building blocks in organic synthesis. Presently, we are exploring both the utilizations of the bicyclics as well as the reactions of acyclic 1,3-dienes with PCA.

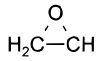
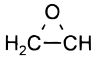
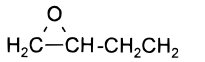
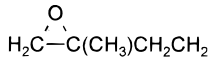
Experimental Section

General Comments. Equipment for spectrometric analysis, materials, and general conditions for chromatographic separations are described in refs 8 and 10.

1,1,1,3,3-Pentachloro-2-propanone (PCA) (**2**) was purchased (Aldrich or Janssen) or synthesized by reaction of acetone with



15

15	R^1	R^2	R^3
d		H	H
e		CH_3	H
g	H		CH_3
h	H		CH_3

chlorine gas in the presence of pyridine catalyst.[41] The chlorination products were separated by distillation on a Vigreux column followed by distillation on a spaltrohr or spinning band column. The furans **1a**, **1b**, and **1i** were commercially available. The other furans, except **1k** and **1l**, were prepared by the procedures of the references cited in the text. 2,2,2-Trifluoroethanol (TFE) was commercially available in high purity (GC >99%, Fluka, *puriss.*, or ABCR, Karlsruhe, Germany) and was used directly, without further purification. Solutions of sodium 2,2,2-trifluoroethoxide (NaTFE) were prepared by adding small (!) cut pieces of sodium to TFE at room temperature. **Caution**: If the sodium is added too rapidly, i.e., the local amount of sodium is too large, overheating can occur; in one of some dozens of preparations, the reaction mixture decomposed with charring and ignition, even under inert gas!

Methanol was dried by refluxing with magnesium turnings and distillation.[42] For the zinc dechlorination we preferred Merck grade zinc powder, particle size > 60 μm. Zinc powder of undefined quality may react slower and gives lower yields. In this case it is preferable to prepare the zinc/copper couple by the procedures of Le Goff[43] or Jäger.[44]

2,2,4,4-Tetrachloro-8-oxabicyclo[3.2.1]oct-6-en-3-one (3a) was prepared according to the procedure published previously.[10] Instead of the sodium 2,2,3,3-tetrafluoropropoxide solution, a 2 M solution of sodium 2,2,2-trifluoroethoxide in 2,2,2-trifluoroethanol was used. The yield was approximately the same (57%). An IR sample was purified by repeated (3 ×) fractional sublimation at 75 °C/0.005 Torr. The first fractions were discarded. The last fractions showed a mp 89.5−90.5 °C (ref:[10] 88−89 °C). IR (KBr): 3080 (m-w), 2970 (w), 1760 (s), 1730 (m), 1590 (w) cm^{-1}. IR (CCl_4): 3105 (w), 2980 (w), 1772 (s), 1733 (w), 1598 (w) cm^{-1}.

2,2,4,4-Tetrachloro-1-methyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (3b). A mixture of 2-methylfuran (**1b**) (3.28 g, 40.0 mmol) and 1,1,1,3,3-pentachloro-2-propanone (PCA) (**2**) (10.13 g, 44.0 mmol) was cooled in an ice bath. With magnetic stirring, a solution of sodium 2,2,2-trifluoroethoxide (NaTFE) in 2,2,2-trifluoroethanol (TFE) (c = 2 mol/L, 22 mL) was added dropwise, within ca. 25 min. Sodium chloride precipitated. The ice bath was removed, and stirring was continued for 2 h at room temperature. Be sure that the reaction mixture shows a

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(41) Bugrova, L. V.; Rudnev, G. K.; Kristich, A. I.; Radchenko, V. I.; Mishchenko, L. F. *Zh. Prikl. Khim. (Leningrad)* **1973**, *46*, 1529; *J. Appl. Chem. USSR* **1973**, *2*, 1627.

(42) Vogel, A. I. *A Textbook of Practical Organic Chemistry*, 3rd ed.; Longmans: London, 1957; p 169.

(43) Le Goff, E. *J. Org. Chem.* **1964**, *29*, 2048.

(44) Jäger, V.; Häfele, B. *Synthesis* **1987**, 801.

basic reaction against pH paper (pH 9−10). Otherwise some drops of NaTFE solution should be added. Water (40 mL) was added to the reaction mixture, and the layers separated. The aqueous layer was extracted with five 20 mL portions of dichloromethane. The combined organic layers were dried (sodium sulfate) and concentrated in a rotary evaporator to afford a brown oil (11.03 g) that was dissolved in a minimal amount of petroleum ether. After cooling in a refrigerator overnight slightly yellow crystals separated that were sucked off and washed with cold petroleum ether. Yield: 7.24 g (66%), mp. 53−54 °C. ^{1}H NMR (80 MHz, $CDCl_3$): δ 1.81 (s, 3 H), 5.21 (split s, 1 H), 6.49 (split s, 2 H). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ 16.9, 82.1, 87.7, 91.8, 132.9, 137.9, 185.1. IR (KBr, cm^{-1}): 1760, 1750, 1740, 1595. Anal. Calcd for $C_8H_6Cl_4O_2$: C, 34.82; H, 2.19; Cl, 51.39. Found: C, 34.97; H, 2.19; Cl, 51.23.

2,2,4,4-Tetrachloro-1,5-dimethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (3c). 2,5-Dimethylfuran[47] (**1c**) (10.12 g, 105.2 mmol) was reacted with PCA (26.66 g, 115.8 mmol) as described for compound **3b**. Recrystallization of the crude product from petroleum ether gave slightly yellow crystals (20.80 g, 68%) of **3c** with mp 111−112 °C. ^{1}H NMR (60 MHz, $CDCl_3$): δ 1.76 (s, 6 H), 6.36 (s, 2 H). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ 17.2, 87.3, 91.6, 136.9, 185.7. IR (CCl_4, cm^{-1}): 1770, 1740. EIMS (20 eV): *m*/*z* (%) 294 (0.4, M^+ from $C_9H_8{}^{35}Cl^{37}Cl_3O_2$), 292 (0.8, M^+ from $C_9H_8{}^{35}Cl_2{}^{37}Cl_2O_2$), 290 (1.6, M^+ from $C_9H_8{}^{35}Cl_3{}^{37}ClO_2$), 288 (1.3, M^+ from $C_9H_8{}^{35}Cl_4O_2$), 255 (26), 254 (21), 253 (27), 252 (19), 219 (52), 217 (79), 182 (10), 178 (14), 143 (13), 96 (100). Anal. Calcd for $C_9H_8Cl_4O_2$: C, 37.28; H, 2.78; Cl, 48.91. Found: C, 37.38; H, 2.86; Cl, 48.73.

2,2,4,4-Tetrachloro-1-vinyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (3d). 2-Vinylfuran[48] (**1d**) (9.41 g, 100 mmol) was reacted with PCA (25.33 g, 110 mmol) and NaTFE solution (c = 2 mol/L, 55 mL) as decribed for compound **3b**. The dark brown oil (27.74 g) was filtrated with 250 mL of petroleum ether/ethyl acetate (5:1) over 40 g of silica. After concentration of the eluate the amber-colored oil was distilled in a kugelrohr at 170 °C/ 0.01 Torr. The distillate, a slightly yellow oil crystallized in the refrigerator. Yield: 23.87 g (83%) of **3d** with mp 31−32 °C. ^{1}H NMR (80 MHz, $CDCl_3$): δ 5.31 (s, 1 H), 5.57−5.86 (m, 2 H), and 6.22−6.45 (m, 1 H), 6.56 (s, 2 H). IR (neat, cm^{-1}): 3100, 1760, 1595. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ 82.2, 86.7, 87.8, 122.1, 128.8, 132.6, 136.7, 184.9. Anal. Calcd for $C_9H_6Cl_4O_2$: C, 37.54; H, 2.10; Cl, 49.25. Found: C, 37.40; H, 2.30; Cl, 49.49.

2,2,4,4-Tetrachloro-1-methyl-5-vinyl-8-oxabicyclo[3.2.1]-oct-6-en-3-one (3e). 2-Methyl-5-vinylfuran[49] (**1e**) (2.16 g, 20.0 mmol) was reacted with PCA (5.07 g, 22.0 mmol) as described for compound **3b**. The crude dark brown oil was purified by kugelrohr distillation at 140 °C/0.005 Torr. The distillate crystallized on standing, to afford 5.08 g (84%) of a yellow solid with mp 56−57 °C. For analysis, a sample was recrystallized from a small amount of *n*-pentane to give a colorless solid with mp 60−61 °C. ^{1}H NMR (60 MHz, $CDCl_3$) δ 1.83 (s, 3 H), 5.50−5.83 (m, 2 H), 6.15−6.33 (m, 1 H), 6.40 (s, 2 H). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ 17.2, 91.6, 93.0, 121.9, 129.2, 135.6, 136.5, 185.5. IR (KBr, cm^{-1}): 3110, 3000, 2950, 1890, 1780, 1750, 1645, 1610. Anal. Calcd for $C_{10}H_8Cl_4O_2$: C, 39.77; H, 2.67; Cl, 46.96. Found: C, 39.74; H, 2.65; Cl, 46.94.

2,2,4,4-Tetrachloro-6-methyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (3f). 3-Methylfuran[50] (**1f**) (9.56 g, 116 mmol) was reacted with PCA (29.39 g, 128 mmol) as described for compound **3b**. Recrystallization of the crude product from methanol/water (9:1) gave coarse colorless crystals (27.73 g, 86%) of **3f** with mp 90−90.5 °C. For analysis, a small sample was sublimed to give long white needles with the same melting point. ^{1}H NMR (250 MHz, $CDCl_3$): δ 2.09 (s, 3 H), 4.93 (s, 1 H), 5.09 (m, 4 lines with splitting of ca. 1 Hz, 1 H), 6.19 (m, 5 lines with splitting of ca. 1.7 Hz, 1 H). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ 15.7, 82.7, 83.1, 88.0, 90.1, 128.8, 145.5, 184.8. IR (KBr, cm^{-1}): 3080, 2960, 2900, 1760, 1750, 1730, 1640. Anal. Calcd for $C_8H_6Cl_4O_2$: C, 34.82; H, 2.19; Cl, 51.39. Found: C, 34.88; H, 2.15; Cl, 51.47.

1-(3-Butenyl)-2,2,4,4-tetrachloro-7-methyl-8-oxabicyclo-[3.2.1]oct-6-en-3-one (3g). A mixture of 2-(3-butenyl)-3-methylfuran (**1g**)[51] (27.2 g, 200 mmol) and PCA (53.0 g, 230 mmol) was cooled in an ice bath. With magnetic stirring, a NaTFE solution (c = 2 mol/L, 115 mL) was added dropwise, within 2 h. Sodium chloride precipitated, together with part of the yellow solid product **3g**. After completion of the addition the ice bath was removed, and stirring was continued at room temperature for 15 min. A test with pH paper showed an alkaline reaction. The mixture was poured into saturated brine (250 mL). Small amounts of water and dichloromethane were added to dissolve the solid. The mixture was extracted with five 100 mL portions of dichloromethane. The combined organic layers were washed with saturated brine, dried with magnesium sulfate, and concentrated in a rotary evaporator. In the air, the remaining yellow solid turned black immediately. The solid was washed with a small amount of hexane until the crystals were nearly colorless. The washing solution was concentrated in a rotary evaporator and filtrated through silica (30 g) with petroleum ether/ethyl acetate (20:1). After evaporation of the solvent, the remaining solid was combined with the crystals (see above) and sublimed at 70 °C/ 0.005 Torr. Colorless and odorless crystals of **3g** were obtained (58.1 g, 88%) with mp 67 °C. ^{1}H NMR (60 MHz, $CDCl_3$): δ 1.7−2.7 (m, 4 H), with a finely split singlet at 2.00 (3 H), 4.9−5.3 (m, 3 H), 5.6−6.2 (m, 1 H), 6.23 (m, 1 H). ^{13}C NMR (75.75 MHz, $CDCl_3$): δ 14.9, 26.7, 26.8, 82.4, 86.1, 88.6, 94.5, 115.5, 129.7, 137.0, 146.1, 184.9. IR (KBr, cm^{-1}): 3080, 3000, 2980, 2960, 2940, 2915, 2895, 2840, 1765, 1750, 1635. Anal. Calcd for $C_{12}H_{12}Cl_4O_2$: C, 43.67; H, 3.66; Cl, 42.97. Found: C, 43.76; H, 3.45; Cl, 43.30.

2,2,4,4-Tetrachloro-7-methyl-1-(3-methylbut-3-en-1-yl)-8-oxabicyclo[3.2.1]oct-6-en-3-one (3h). 3-Methyl-2-(3-methylbut-3-en-1-yl)furan (**1h**)[52] (7.51 g, 50.0 mmol) was reacted with PCA (12.67 g, 55.0 mmol) and NaTFE solution (28 mL, 56 mmol) as described for compound **3b**. Crystallization of the crude product from 130 mL of petroleum ether gave slightly yellow crystals (14.91 g, 87%) of **3h** with mp 101−102 °C. ^{1}H NMR (80 MHz, $CDCl_3$): δ 1.86 (s, 3 H), 2.06 (finely split singlet, 3 H), 1.9−2.9 (m, 4 H), 5.00 (bs, 2 H), 5.25 (bs, 1 H), 6.44 (bs, 1 H). IR (KBr, cm^{-1}): 3090, 3070, 2970, 2940, 2860, 1805, 1750, 1640, 1450, 1440, 1375. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ 14.9, 22.7, 25.6, 30.5, 82.3, 86.1, 88.6, 94.4, 110.1, 129.6, 144.4, 146.1, 185.0. Anal. Calcd for $C_{13}H_{14}Cl_4O_2$: C, 45.38; H, 4.10; Cl, 41.22. Found: C, 45.46; H, 4.28; Cl, 40.98.

8-Oxabicyclo[3.2.1]oct-6-en-3-one (4a) was prepared from the tetrachloroketone **3a** according to our procedure previously published.[10]

1-Methyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (4b). Tetrachloroketone **3b** (2.00 g, 7.25 mmol) was dissolved in methanol (28 mL) saturated with ammonium chloride. Zinc powder (7.58 g, 116 mmol) was added in portions with magnetic stirring. The mixture was refluxed for 6 h and stirred overnight at room temperature. Unreacted zinc powder and inorganic salts were removed by suction and washed with methanol. To the combined filtrates a solution of EDTA disodium salt (4.83 g in 60 mL water) was added. The mixture was extracted with dichloromethane (5 × 25 mL). The combined extracts were dried with sodium sulfate, and the solvent was evaporated. Kugelrohr distillation of the residue at 100 °C/0.01 Torr gave **4b** as a colorless oil (0.65 g, 65%), which was identified by

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(48) Schmidt, U.; Werner, J. *Synthesis* **1986**, 986.
(49) Alvarez, R.; Gandini, A.; Martinez, R. *Makromol. Chem.* **1982**, *183*, 2399.
(50) Cornforth, J. W.; Firth, M. E. *J. Chem. Soc.* **1958**, 1091. Cornforth, J. *J. Chem. Soc.* **1958**, 1310.
(51) Kaiser, R.; Föhlisch, B. *Helv. Chim. Acta* **1990**, *73*, 1504.
(52) (a) Firmenich SA (Schulte-Elte, K. H. Inventor); Swiss Patent 603614 (6.10.1975) (*Chem. Abstr.* **1979**, *90*, P 6234j). (b) Kaiser, R. Dissertation, University Stuttgart, 1986.

comparison of the ^{1}H NMR spectrum with the reported data[53] and by the following spectra. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ 23.0, 45.1, 52.6, 77.6, 83.4, 133.2, 136.4, 205.9. EIMS (70 eV): *m/z* (%) 138 (71, M^+), 109 (5), 96 (38), 95 (100), 82 (7), 81 (47), 67 (12), 54 (5), 53 (19), 51 (5), 43 (42), 42 (6), 41 (10), 39 (15). Anal. Calcd for $C_8H_{10}O_2$: C, 69.54; H, 7.30. Found: C, 69.11; H, 7.52.

1,5-Dimethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (4c). Tetrachloroketone **3c** (17.2 g, 60 mmol), dissolved in methanol (450 mL) saturated with ammonium chloride, was dehalogenated with zinc powder (65.3 g, 1 mol) in 43 h, as described for compound **4b**. The dark brown raw product (8.5 g) was purified by sublimation at <55 °C/atmospheric pressure to give colorless crystals (7.8 g, 87%) with mp 59.5−60.5 °C (sealed capillary); lit:[8] mp 61−62 °C. The ^{1}H and the ^{13}C NMR spectra agreed with those of a substance obtained earlier by us.[8]

1-Vinyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (4d). Tetrachloroketone **3d** (1.75 g, 60.7 mmol) in methanol saturated with ammonium chloride (50 mL) was treated with zinc powder (3.5 g, 54 mmol) as described for compound **4b**. The mixture was stirred for 4 days at room temperature and worked up as usual. Kugelrohr distillation at 50 °C/0.01 Torr gave **4d** as a colorless oil (648 mg, 71%). ^{1}H NMR (60 MHz, $CDCl_3$): δ 2.1−3.0 (m, 4 H), 5.1−5.6 (m, 3 H), 5.9−6.5 (m, 3 H). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ 45.5, 50.7, 77.6, 85.6, 116.0, 133.3, 137.1, 138.0, 205.0. IR (neat, cm^{-1}): 3080, 3000, 2950, 2890, 1710, 1635. EIMS (70 eV): *m/z* (%) 150 (62, M^+), 108 (33), 107 (100) Anal. Calcd for $C_9H_{10}O_2$: C, 71.98; H, 6.71. Found: C, 71.76; H, 7.00.

1-Methyl-5-vinyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (4e). Tetrachloroketone **3e** (3.02 g, 10.0 mmol) in methanol saturated with ammonium chloride (40 mL) was treated in portions with zinc powder (Merck, particle size > 60 μm, 10.46 g, 160 mmol). The flask was cooled in an ice bath. When the exothermic reaction was over, stirring was continued for 24 h at room temperature. Workup as described for **4b** afforded an oil that was distilled in a kugelrohr at 110 °C/0.02 Torr. The distillate, a slightly yellow oil (1.00 g), consisted of nearly pure **4e**, according to the ^{1}H NMR. The yield corresponded to ca. 60%. A part of the oil (700 mg) was purified by chromatography on alumina (activity 3, 70.0 g) with petroleum ether/ethyl acetate (10:1) to give 530 mg of a colorless oil. Nevertheless, the ^{1}H NMR spectrum showed an impurity. ^{1}H NMR (80 MHz, $CDCl_3$): δ 1.53 (s, 3 H), 2.0−3.0 (m, 4 H), 5.2−5.6 (m, 2 H), 5.7−6.6 (m, 3 H). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ 23.2, 49.0, 51.3, 83.8, 85.8, 116.0, 134.7, 136.4, 137.3, 206.0. IR (neat, cm^{-1}): 3090, 3020, 2980, 2960, 2940, 2900, 2880, 1715, 1645, 1600. EIMS (70 eV): *m/z* (%) 164 (92, M^+ from $C_{10}H_{12}O_2$); 122 (30); 121 (100); 109 (45); 108 (27); 107 (86); 95 (29); 93 (21); 92 (11); 91 (15); 81 (20); 79 (47); 78 (10); 77 (36); 67 (13); 65 (11); 55 (63); 53 (14); 51 (16); 43 (94); 41 (22); 39 (33); 28 (20); 27 (40). HRMS calcd for $C_{10}H_{12}O_2$: 164.0837, found 164.0838.

6-Methyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (4f). Tetrachloroketone **3f** (11.04 g, 40 mmol) in methanol saturated with ammonium chloride (160 mL) was treated in portions with zinc/copper couple[44] (40 g). The flask was cooled in an ice bath. When the exothermic reaction was over, stirring was continued for 22 h at room temperature. Workup as described for **4b** afforded an oil that was distilled in a kugelrohr at 52 °C/0.01 Torr to give a colorless oil (4.88 g, 87%). The ^{1}H and ^{13}C NMR data were in agreement with those reported for compound **4f**.[53] Anal. Calcd for $C_8H_{10}O_2$: C, 69.55; H, 7.29. Found: C, 69.38; H, 7.28.

1-(3-Butenyl)-7-methyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (4g). Tetrachloroketone **3g** (270 mg, 0.82 mmol) in methanol saturated with ammonium chloride (10 mL) was treated with zinc powder (643 mg, 9.8 mmol) as described for compound **4b**. The mixture was stirred for 5 days at room temperature and worked up as usual. Kugelrohr distillation at 70−80 °C/0.01 Torr gave **4g** as a colorless oil (102 mg, 65%), which solidified on standing. The white crystalline mass melted at 43 °C. ^{1}H NMR (80 MHz, $CDCl_3$): δ 1.73 (s, 3 H), 1.60−2.85 (m, 8 H), 4.80−5.25 (m, 3 H), 5.60−6.20 (m, 2 H). ^{13}C NMR (75.75 MHz, $CDCl_3$): δ 11.9, 27.7, 34.0, 44.8, 50.1, 76.0, 86.7, 114.7, 127.9, 138.2, 143.7, 206.4. IR (KBr cm^{-1}): 3060, 2960, 2940, 2900, 2840, 1710 (C=O), 1635. Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.74; H, 8.65.

7-Methyl-1-(3-methylbut-3-enyl)-8-oxabicyclo[3.2.1]oct-6-en-3-one (4h). A solution of tetrachloroketone **3h** (1.72 g, 5.00 mmol) in methanol saturated with ammonium chloride (20 mL) was treated with zinc/copper couple[43] (5.27 g) in portions under magnetic stirring and cooling in an ice bath. When the exothermic reaction was over, the mixture was refluxed for 6.5 h and stirred for a further 20 h at room temperature. Workup as described for **4b** gave a residue that was distilled in a kugelrohr at 120 °C/0.005 Torr. The distillate (760 mg, 74%) solidified on standing and melted at 46−47 °C. However, it was not possible to obtain an acceptable elemental analysis. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.7−1.95 (m, 10 H, with split singlets at 1.72 and 1.76, 2.2−2.7 (m, 4 H), 4.72 (m, 2 H), 4.93 (m, 1 H), 5.80 (m, 1 H). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ 11.9, 22.7, 31.4, 33.0, 44.8, 50.2, 76.0, 86.7, 109.9, 127.9, 143.7, 145.5, 206.4. IR (CH_2Cl_2, cm^{-1}): 3030, 3010, 2920, 2900, 2840, 1710, 1640. EIMS (20 eV): *m/z* (%) 206 (86); 163 (10); 151 (100); 150 (17); 148 (16). HRMS calcd for $C_{13}H_{18}O_2$: 206.1307, found 206.1306.

8-Oxabicyclo[3.2.1]oct-6-en-3-ones 4i−m, Prepared from the Furans 1i−m without Isolation of the Tetrachlorides 3. 1-Hydroxymethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (4i). 2-Furfuryl alcohol (**1i**) (3.04 g, 31 mmol) was reacted with PCA (7.7 g, 33 mmol) and NaTFE solution (23 mL, c = 2 mol/L) as described for compound **3b**. The reaction mixture was stirred for 2 h. Dry diethyl ether (100 mL) was added and the precipitated sodium chloride filtered off. The filtrate was concentrated in a rotary evaporator. The remaining brown oil (7.0 g) containing tetrachloride **3i** was dissolved in methanol (230 mL) saturated with ammonium chloride. Zinc powder (33 g, 505 mmol) was added in portions with magnetic stirring. When the exothermic reaction was over, the mixture was refluxed for 24 h. Workup with EDTA disodium salt solution and extraction with dichloromethane (10 100 mL portions) afforded 2.0 g of a dark oil that was purified by chromatography on silica (60 g) with petroleum ether/ethyl acetate (3:2). From the middle fractions compound **4i** (0.98 g, 21%) was isolated as a colorless oil. An analytically pure substance was obtained by kugelrohr distillation at 110−130 °C/0.001 Torr. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.19 (bs, 1 H, $-CH_2-OH$, the chemical shift may occur between 2.19 and 3.62, depending on temperature and concentration of the probe), 2.30−2.78 (m, 4 H), 3.82 (s, 2 H), 5.12 (dd, J = 4.6 Hz and J = 1.1 Hz, 1 H); AB-system with center at δ = 6.21, δ_A = 6.29 and δ_B = 6.12, J_{AB} = 6.0 Hz, the lines of the A-part are doubled with J = 1.8 Hz. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ 45.5, 47.4, 64.9, 77.8, 87.1, 133.4, 134.8, 205.2. IR (neat, cm^{-1}): 3440 (br), 3075, 2950, 2910, 1710, 1590, 1446, 1402, 1370, 1341, 1289, 1246, 1217, 1199, 1175, 1146, 1084, 1037, 1020, 985, 937, 918, 855, 830, 815, 757, 735, 680, 633, 600. GC/CIMS (CH_4): *m/z* (%) 155 (24, MH^+), 153 (15, $M - H^+$), 151 (13), 149 (14), 125 (77), 123 (42), 121 (73), 119 (11), 97 (16), 95 (100), 94 (15), 93 (26), 91 (18), 83 (20), 81 (23), 79 (15), 67 (29). Anal. Calcd for $C_8H_{10}O_3$: C, 62.33; H, 6.54. Found: C, 62.53; H, 6.67.

1-Hydroxymethyl-5-methyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (4j). 2-Hydroxymethyl-5-methylfuran (**1j**)[45] (1.20 g, 10.7 mmol) was reacted with PCA (2.72 g, 11.8 mmol) and NaTFE solution (7 mL, c = 1.74 mol/L) as described for compound **3b**. The reaction mixture was stirred for 1.5 h. Workup as described for **3b** gave a yellow oil (2.42 g) containing **3j** that was treated as usual with zinc powder (8.26 g, 126.4 mmol) in methanol (31 mL) saturated with ammonium chloride. Workup as decribed for **4i** afforded 1.03 g of a yellow oil that was purified by kugelrohr distillation at 150 °C/0.1 Torr. According to the NMR spectra, the yellow liquid (0.42 g, 25%) contained mainly compound **4j**, but was not pure. ^{1}H NMR (80 MHz, $CDCl_3$): δ 1.50 (s, 3 H), 2.15−2.7 (m, 5 H), 3.78 (s, 2 H), 5.9−6.2 (m, 2 H), and further weak signals from byproducts. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ 23.1, 45.9, 51.5,

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65.1, 84.2, 87.4, 133.2, 137.9, 206.0, and further weak signals from byproducts. IR (neat, cm^{-1}): 3085, 3700−3140 (br), 1700. EIMS (20 eV): *m/z* (%) 168 (25, M^+); 138 (67); 137 (15); 122 (19); 111 (17); 109 (23); 108 (26); 96 (34); 95 (100); 43 (10); peaks from byproducts at 281, 232 and 176. EIMS (70 eV): *m/z* (%) 168 (8, M^+); 138 (20); 109 (13); 108 (13); 96 (20); 95 (100); 67 (17); 43 (44); 41 (17); 39 (12).

1-Benzyloxymethyl-5-methyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (4k). 5-Benzyloxymethyl-2-methylfuran (**1k**) (2.02 g, 10 mmol) was reacted with PCA (2.53 g, 11 mmol) and NaTFE solution (8.3 mL, c = 1.74 mol/L) as described for compound **3b**. The reaction mixture was stirred for 1 h. Workup as decribed for **3b** gave a yellow oil (3.40 g) containing **3k** that was treated as usual with zinc powder (8.98 g, 137.4 mmol) in methanol (34 mL) saturated with ammonium chloride. Workup as decribed for **4b** and chromatography with petroleum ether/ethyl acetate (4:1) gave 0.26 g of a colorless oil that was distilled in a kugelrohr at 150 °C/0.1 Torr. Yield: 0.16 g (6%) **4k**. IR (neat, cm^{-1}): 3080, 3050, 3020, 1705 (C=O). ^{1}H NMR (80 MHz, $CDCl_3$): δ 1.49 (s, 3 H), 2.0−2.8 (m, 4 H), 3.64 (s, 2 H), 4.61 (s, 2 H), 5.99 (s, 2 H), 7.33 (s, 5 H). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ 23.1, 46.6, 51.4, 72.1, 73.6, 84.2, 86.4, 127.7, 127.8, 128.4, 133.5, 137.1, 137.9, 206.5. EIMS (20 eV): *m/z* (%) 258 (37, M^+); 153 (13); 152 (100); 110 (21); 109 (85); 95 (30). EIMS (70 eV): *m/z* (%) 258 (11, M^+); 152 (25); 110 (14); 109 (44); 95 (45); 92 (12); 91 (100); 43 (15). HRMS calcd for $C_{16}H_{18}O_3$: 258.1256, found 258.1257.

1-Dimethoxymethyl-5-methyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (4l). 2-Dimethoxymethyl-5-methylfuran (**1l**) (3.77 g, 24.2 mmol) was reacted with PCA (6.12 g, 26.6 mmol) and NaTFE solution (18 mL, c = 1.9 mol/L) as described for compound **3b**. The reaction mixture was stirred for 1.5 h. Workup as decribed for **3b** gave a residue (6.34 g) that was filtrated over basic alumina (30 g, activity 3) with petroleum ether/ethyl acetate (30:1). The solvent was evaporated, and the residue (4.47 g) containing the tetrachloride **3l** was treated with zinc−copper couple (prepared from 13.62 g (204.8 mmol) of zinc powder and 0.83 g (4.2 mmol) of cupric acetate monohydrate) in methanol (50 mL) saturated with ammonium chloride (6 h reflux, then stirring overnight) and worked up as described for **3b**. Kugelrohr distillation at 140 °C/0.1 Torr gave impure **4l** as a white solid (0.56 g, 21%) with mp 78−79 °C. ^{1}H NMR (60 MHz, $CDCl_3$): δ 1.50 (s, 3 H); 2.35−2.55 (m, 4 H); 3.57 (s, 6 H); 4.38 (s, 1 H), AB-spectrum with center at 6.07, δ_A 6.03 and δ_B 6.11, J_{AB} = 6 Hz; and further weak signals from byproducts. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.51 (s, 3 H), two AB-spectra with δ_A 2.65, δ_B 2.51, J_{AB} = 16.4 Hz, and δ_A 2.40, δ_B 2.34, J_{AB} = 16.3 Hz, 3.55 (s, 3 H), 3.56 (s, 3 H), 4.38 (s, 1 H); AB-spectrum with center at δ 6.07, δ_A 6.10 and δ_B 6.03, J_{AB} = 5.9 Hz. ^{13}C NMR (75.47 MHz, $CDCl_3$) δ 23.1, 44.4, 51.5, 57.0, 57.3, 84.2, 88.5, 106.2, 133.1, 137.0, 206.5. IR (KBr, cm^{-1}): 2845, 1705. EIMS (70 eV): *m/z* (%) 212 (1, M^+); 75 (100); 47 (12). EIMS (20 eV): *m/z* (%) 212 (1, M^+); 75 (100). HRMS calcd for $C_{11}H_{16}O_4$: 212.1049, found 212.1047.

1-[(Methylthio)methyl]-8-oxabicyclo[3.2.1]oct-6-en-3-one (4m). 2-[(Methylthio)methyl]furan (**1m**)[54] (12.8 g, 0.1 mol) was reacted with PCA (25.3 g, 0.11 mol) and NaTFE solution (58 mL, c = 2 mol/L) as described for compound **3b**. The reaction mixture was stirred for 2 h. Workup as described for **3b** gave a dark oil (30.7 g). A part of the oil (18.7 g) was treated with zinc powder (65.3 g, 1.0 mol) in methanol (450 mL) saturated with ammonium chloride and worked up as described for **3b**. The resulting dark yellow oil (1.80 g) consisted mainly of **4m**, as shown by the NMR spectrum. Yield: ca. 15%. ^{1}H NMR (80 MHz, $CDCl_3$): δ 2.21 (s, 3 H), 2.2−2.9 (m, 4 H), 2.90 (split s, 2 H), 5.0−5.15 (m, 1 H), 6.05−6.3 (m, 2 H). GC/CIMS (CH_4): **4m** with t_R 15.74 min; *m/z* (%) 185 (74, MH^+), 167 (9), 165 (22), 143 (8), 139 (10), 138 (13), 137 (100, $MH^+ - CH_3SH$), 121 (6), 109 (10, $MH^+ - CH_3SH - CO$), 103 (31), 97 (7), 95 (32), 91 (11), 83 (7), 81 (16), 75 (14), 67 (6), 63 (13), 61 (71).

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Recycling of 2,2,2-Trifluoroethanol from the Waste of Cycloaddition Reactions. The liquid waste resulting from concentration of the dichloromethane or diethyl ether phases by distillation in the rotary evaporator was collected. It turned yellow to brown on storing. Combined waste (2 L) containing trifluoroethanol (TFE) was shaken with tap water (500 mL) in a separating funnel (4 L). The organic layer (dichlormethane or diethyl ether, respectively) was extracted 5 times with water (200 mL) and disposed or recycled after drying. The water layers containing the TFE (ca. 1.6−1.8 L) were combined, adjusted to pH 7 if necessary, and extracted with *n*-heptane (3 × 100 mL) in order to remove nonpolar byproducts. The heptane layers were disposed. Activated charcoal powder (10 g) was stirred into the aqueous phase and the mixture left overnight for settling. The charcoal was removed by gravity filtration.

The filtrate, collected in a distillation flask (2 L), was distilled over a vacuum jacketed column, packed with glass rings (effective length 100 cm), and equipped with a rectification still-head. As heating device, an electric heating mantle with voltage regulator was used.

After a few drops of the forerun, with bp 68−71 °C, which was given back to the waste-bottle, the main fraction distilled at 72−74 °C. The distillation was continued until the head-temperature rose near the boiling point of water (95−96 °C).

In three recycling operations the amount of the crude TFE/water distillate was 200−235 mL.

To the distillates obtained from three batches (665 mL) was added anhydrous calcium chloride (33.3 g, i.e., 5 wt %) using a tightly closed bottle. Occasionally the mixture was swirled. The calcium chloride party dissolved, forming the lower layer of the heterogeneous mixture. After 48 h the upper layer (TFE) was isolated by decantation and by use of a separating funnel and dried once more with the same amount of calcium chloride. The dried crude TFE was distilled over a 20 cm Vigreux column (bp 72−74 °C).

To remove traces of water (which would react with the sodium needed for the preparation of the NaTFE solution, see above), the predried TFE was treated overnight with freshly activated calcium sulfate (Drierite) (10 wt %), using a tightly stoppered round-bottom flask. TFE was distilled off directly from the heterogeneous mixture over a 20 cm Vigreux column with magnetic stirring in an oil bath. The vent of the distillation apparatus was protected against moisture by a calcium chloride drying tube.

3-Methylcyclohepta-2,4,6-trienone (3-Methyltropone) (5b). A 100 mL three-necked flask with a magnetic stirring bar was flamed dry, closed with three septa, and flushed with dry argon. Oxabicycle **4b** (2.00 g, 14.5 mmol) dissolved in dry tetrachloromethane (14 mL) was introduced by syringe, followed by dry triethylamine (3.66 g, 36.2 mmol). The flask was cooled to −3 °C (temperature of the ice salt bath). Under vigorous stirring trimethylsilyl trifluoromethanesulfonate (TMSOTf, 7.50 g, 33.7 mmol) was slowly added dropwise by syringe, within 30 min; the mixture turned orange. Stirring was continued for 3 h and 45 min at −3 °C to +3 °C. The ice/water bath was removed, and saturated $NaHCO_3$ solution (50 mL) was added. After 15 min stirring the mixture was extracted with five 40 mL portions of tetrachloromethane. The combined extracts were dried with sodium sulfate and concentrated in a rotary evaporator. The resulting liquid was filtered over silica (120 g) with petroleum ether/ethyl acetate (1:1). The elution was completed with neat ethyl acetate. The solvent was removed in a rotary evaporator. Kugelrohr distillation at 150 °C/0.1 Torr gave **5b** (0.95 g, 55%) as a slightly yellow oil. ^{1}H NMR (80 MHz, $CDCl_3$): δ 2.34 (s, 3 H), 6.84−7.10 (m, 5 H). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ 26.8, 132.8, 135.4, 138.5, 141.1, 142.1, 147.2, 187.1. IR (neat, cm^{-1}): 3010, 1630, 1570, 1518. EIMS (70 eV): *m/z* (%) 120 (63, M^+); 92 (47); 91 (100); 65 (18); 51 (15); 50 (10); 39 (20). HRMS calcd for C_8H_8O: 120.0575, found 120.0574.

4-Methylcyclohepta-2,4,6-trienone (4-Methyltropone) (5f). A solution of **4f** (0.69 g, 5 mmol) in dry tetrachloromethane (11 mL) was treated with triethylamine (1.27 g, 12.5 mmol) and TMSOTf (2.56 g, 11.5 mmol) as described for

5b. The reaction temperature was −13 °C (30 min); stirring was continued for 3 h at 0−3 °C. Filtration of the crude product over silica (40 g) with ethyl acetate, concentration of the eluate, and kugelrohr distillation at 74 °C/0.004 Torr gave **5f** (0.37 g, 62%) as a slightly yellow oil. The ^{1}H NMR data were in agreement with those of refs 21 and 22.

3-(But-3-enyl)-4-methylcyclohepta-2,4,6-trienone (3-(But-3-enyl)-4-methyltropone) (5g). A solution of **4g** (1.92 g, 10 mmol) in dry tetrachloromethane (5 mL) was treated with triethylamine (2.53 g, 25 mmol) and TMSOTf (5.17 g, 23 mmol) as described for **5b**. The reaction temperature was +3 °C (30 min); stirring was continued for 2 h at room temperature. Filtration of the crude product over silica (80 g) with petroleum ether/ethyl acetate (1:1), further elution with petroleum ether/ethyl acetate (1:2), and kugelrohr distillation at 120−140 °C/0.005 Torr gave **5g** (1.14 g, 66%) as a yellow viscous oil that solidified in the refrigerator at −18 °C. ^{1}H NMR (80 MHz, $CDCl_3$): δ 2.32 (s, 3 H), 2.1−2.8 (m, 4 H), 4.9−5.2 (m, 2 H), 5.6−6.15 (m, 1 H), 6.7−7.2 (m, 4 H). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ 25.2, 34.1, 37.4, 116.0, 133.5, 135.9, 136.6, 139.1, 141.7, 146.3, 150.8, 167.3. IR (Neat, cm^{-1}): 3062, 2961, 2905, 1625, 1568, 1512, 1230, 909, 803. Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.67; H, 8.03.

1,5-Dimethyl-8-oxabicyclo[3.2.1]octan-3-one (6). A solution of **4c** (1.51 g, 9.92 mmol) in ethyl acetate (30 mL) was shaken with palladium on carbon catalyst (10% Pd) (296 mg) in an atmosphere of hydrogen, at normal pressure and room temperature. When the uptake of hydrogen had stopped (60 min), the catalyst was removed by filtration and washed with ethyl acetate. The filtrates were concentrated in a rotary evaporator and the remaining liquid distilled in a kugelrohr at 110 °C/0.03 Torr. The colorless oil (1.21 g, 79% yield) showed a peculiar herbaceous odor. ^{1}H NMR (80 MHz, $CDCl_3$): δ 1.45 (s, 6 H), 1.83 (s, 4 H), 2.36−2.40 (m, 4 H). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ 26.4, 37.0, 54.1, 81.4, 208.3, and further weak signals of an impurity. IR (neat, cm^{-1}): 2970, 2920, 2890, 2870, 1720−1700 (broad). Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 69.87; H, 9.26.

1,5-Dimethyl-8-oxabicyclo[3.2.1]octane (7). Potassium hydroxide (1.22 g, 21.8 mmol) was dissolved in diethylene glycol (9 mL) with gentle heating. The ketone **6** (1.11 g, 7.20 mmol) was added, followed by hydrazine hydrate (0.90 g, 18.0 mmol). The mixture was refluxed for 2 h at 185 °C (bath temperature), with magnetic stirring. The bath temperature was raised to 195 °C, and heating was continued for a further 2.5 h. After cooling to room temperature, water (15 mL) was added to the reaction mixture, and the layers separated. The aqueous layer was extracted with five 20 mL portions of diethyl ether. The ether extracts were dried with sodium sulfate and concentrated in a rotary evaporator, and the remaining liquid was filtered over silica (70 g) with petroleum ether/ethyl acetate (6:1). The filtrates were concentrated by rotary evaporation. Distillation in a kugelrohr at 70 °C/0.01 Torr gave 0.29 g of **7** (29%) as a volatile colorless oil with a smell of camphor, but of more pungent and acidulous character. ^{1}H NMR (80 MHz, $CDCl_3$): δ 1.30 (s, 6 H) 1.38−1.88 (m, 10 H). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ 19.0; 27.0; 36.4, 36.5, 80.6. EIMS (70 eV): *m*/*z* (%) 140 (38, M^+); 111 (19); 97 (31); 83 (10); 82 (75); 71 (17); 70 (27); 69 (41); 67 (22); 55 (18); 43 (100); 41 (17). HRMS calcd for $C_9H_{16}O$: 140.1201, found 140.1200.

***endo*-2,*endo*-4-Dichloro-8-oxabicyclo[3.2.1]octan-3-one (8a).** A solution of tetrachloroketone **3a** (5.24 g, 20.0 mmol) in dry methanol (100 mL) was shaken with palladium on carbon catalyst (10% Pd) (600 mg) in an atmosphere of hydrogen, at normal pressure and room temperature. When the uptake of hydrogen had stopped (2 h and 25 min), the catalyst was removed by filtration and washed with methanol. The filtrates were concentrated in a rotary evaporator and the remaining solid purified by sublimation at 85 °C/0.02 Torr. The colorless solid (3.48 g, 89%) showed mp 119−120 °C. ^{1}H NMR (80 MHz, $CDCl_3$): δ 2.01 (apparent s, 4 H), 4.66−4.88 (m, 4 H). ^{1}H NMR (300 MHz, C_6D_6): δ 1.20−1.35 and 1.53−1.62 (m, 4 H), 3.88 (d, J = 5.0 Hz, 2 H), 4.11−4.15 (m, 2 H). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ 24.7, 64.4, 81.1, 191.5. IR (KBr, cm^{-1}) 2965, 2940, 2880, 1770, 1735, 1475, 1455. Anal. Calcd for $C_7H_8Cl_2O_2$: C, 43.11; H, 4.13 Cl, 36.3. Found: C, 43.33; H, 4.15; Cl, 36.55.

***endo*-2,*endo*-4-Dichloro-1-methyl-8-oxabicyclo[3.2.1]-octan-3-one (8b).** A solution of **3b** (5.52 g, 20.0 mmol) in methanol (107 mL) was hydrogenated over Pd/C catalyst (607 mg) as described for **8a**. Sublimation at 85 °C/0.04 Torr gave 3.66 g of **8b** (88%) as a colorless solid with mp 73−74 °C. A sample for analysis was crystalized from petroleum ether (bp 60−80 °C) and had mp 82−83 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.57−1.74 (m, with s at δ 1.61, 4 H), 1.91−2.02 (m, 1 H), 2.05−2.17 (m, 2 H), 4.45 (s, 1 H), 4.70−4.74 (m, 2 H). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ 24.1, 25.9, 30.7, 64.5, 70.1, 80.3, 88.1, 191.7. IR (KBr, cm^{-1}): 2980−2910, 2890−2860, 1735, 1465, 1445. Anal. Calcd for $C_8H_{10}Cl_2O_2$: C, 45.96; H, 4.82; Cl, 33.91. Found C, 46.13; H, 4.88; Cl, 34.08.

***endo*-2,*endo*-4-Dichloro-1,5-dimethyl-8-oxabicyclo[3.2.1]-octan-3-one (8c).** (a) *endo*-2,*endo*-4-Dichloro-1,5-dimethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (**9**$\alpha\alpha$)[8] (0.42 g, 1.90 mmol) in dry methanol (13 mL) was hydrogenated over Pd/C catalyst (70 mg) as described for **8a**. Sublimation at 100 °C/0.03 Torr gave 0.31 g of **8c** (73%) as a colorless solid with mp 137.5−138.5 °C.

(b) Tetrachloroketone **3c** (6.00 g, 20.7 mmol) in dry methanol (90 mL) was hydrogenated over Pd/C catalyst (614 mg) as described for **8a**. Sublimation at 100 °C/0.02 Torr gave 3.96 g of **8c** (86%) as a colorless solid with mp 135−136 °C. ^{1}H NMR (60 MHz, $CDCl_3$): δ 1.58 (s, 6 H), 1.75−2.20 (m, 4 H), 4.45 (s, 2 H). ^{1}H NMR (80 MHz, $CDCl_3$): δ 1.60 (s, 6 H), 1.68−2.21 (m, 4 H), 4.51 (s, 2 H). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ 24.4, 31.9, 70.1, 86.9, 191.8; and some weaker signals of an impurity. IR (KBr, cm^{-1}): 2980, 2930, 2900−2860, 1740, 1470, 1450. Anal. Calcd for $C_9H_{12}Cl_2O_2$: C, 48.45; H, 5.42; Cl, 31.78. Found: C, 48.26; H, 5.37; Cl, 31.61.

Catalytic Hydrogenation of *exo*-2,*exo*-4-Dichloro-1,5-dimethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (9$\beta\beta$). 1,5-Dimethyl-8-oxabicyclo[3.2.1]octan-3-one (6) and *exo*-2-Chloro-1,5-dimethyl-8-oxabicyclo[3.2.1]octan-3-one (10). A solution of **9**$\beta\beta$ in methanol (13 mL) was shaken with palladium on carbon catalyst (10% Pd) (70 mg) in an atmosphere of hydrogen, at normal pressure and room temperature. After 50 min the uptake of hydrogen became very slow. Therefore, the catalyst was removed by filtration and washed with methanol. The filtrates were concentrated in a rotary evaporator, and the remaining oil was distilled in a kugelrohr at 140 °C/0.02 Torr. The distillate, a colorless wax (0.21 g), was dissolved in methanol (15 mL) and hydrogenated once more over Pd/C catalyst (70 mg). Kugelrohr distillation gave a colorless oil (0.12 g) that was subjected to GC and GC/MS analysis. The GC (20 m OV 1701 capillary column, 40/5/300 °C, on column injection) showed two peaks at t_R 9.4 (**6**) and t_R 13.7 min (**10**) in the integral ratio of 1:2.5. CIMS (methane, 0.5 Torr, 70 eV, 20 m OV 1701, 40/5/300 °C): t_R 11.5 min, **6**; *m*/*z* (%) 155 (91, MH^+ from $C_9H_{14}O_2$), 149 (10), 139 (12), 137 (71), 135 (12), 123 (15), 121 (18), 113 (37), 111 (11), 109 (13), 107 (13), 97 (22), 96 (19), 95 (100), 71 (20), 69 (24). t_R 14.9 min, **10**, *m*/*z* (%) 191 (27%, MH^+ from $C_9H_{13}{}^{37}ClO_2$), 189 (73, MH^+ from $C_9H_{13}{}^{35}ClO_2$), 183 (17), 171 (21), 165 (10), 155 (75), 153 (89, $MH^+ - HCl$ from $C_9H_{13}{}^{35}ClO_2$), 151 (15), 149 (15), 147 (11), 139 (16), 137 (92), 135 (27), 129 (12), 123 (23), 121 (18), 113 (28), 111 (39), 109 (29), 107 (19), 97 (37), 96 (16), 95 (100), 93 (49), 85 (13), 83 (17), 81 (17), 73 (11), 71 (15), 69 (41), 67 (11), 61 (11). ^{1}H NMR (80 MHz, $CDCl_3$): **6**, δ 1.48 (s, 6 H), 1.83 (s, 4 H), 2.36−2.40 (m, 4 H). **10**, δ 1.45 (s, 3 H), 1.51 (s, 3 H); 1.89 (s, 4 H); AB-spectrum centered at δ 2.61 with δ_A 2.98 and δ_B 2.23, J_{AB} = 15 Hz, the signals of the B-part are finely split with J = 1 Hz, 2 H; 3.78 (s, 1 H).

2,2,4,4-Tetrachlorobicyclo[3.2.1]oct-6-en-3-one (11). Freshly distilled cyclopentadiene (6.61 g, 100 mmol) and PCA (**2**, 25.33 g, 110 mmol) were mixed and cooled in an ice bath. With magnetic stirring, a solution of NaTFE in TFE (c = 2 mol/L, 58 mL) was added dropwise. The ice bath was removed, and stirring was continued for 30 min at room temperature. Water (150 mL) was added to the reaction mixture, and the layers were separated. The aqueous layer was extracted with five 50 mL portions of dichloromethane. The combined organic

phases were dried with sodium sulfate and concentrated in a rotary evaporator. The brown oily residue was distilled in a kugelrohr at 110 °C/0.001 Torr to give a slightly yellow solid (19.4 g). Crystallization from a small amount of petroleum ether gave **11** (14.8 g, 57%) as a nearly colorless solid with mp 47−48 °C. ^{1}H NMR (80 MHz, $CDCl_3$): AB-spectrum centered at $\delta = 2.68$ with δ_A 2.97 and δ_B 2.39, $J_{AB} = 12.8$ Hz; the B-part is split to give a triplet with $J = 5$ Hz; δ 3.58 (dd, $J = 5$ Hz, $J = 1$ Hz, 2 H), 6.36 (split s, 2 H). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ 37.2, 56.1, 86.3, 136.8, 186.9. IR (KBr, cm^{-1}): 3070, 2980, 2950, 1755 and 1730, 1680, 1675, 1670, 1585, 1445. Anal. Calcd for $C_8H_6Cl_4O$: C, 36.96; H, 2.33; Cl, 54.55. Found: C, 37.08; H, 2.35; Cl, 54.47.

***endo*-2,*endo*-4-Dichloro-8-oxabicyclo[3.2.1]octan-3-ol (12a).** To a stirred solution of lithium aluminum hydride (0.30 g, 7.90 mmol) in dry THF (10 mL) under an atmosphere of argon was added a solution of ketone **8a** (2.93 g, 15.0 mmol) in dry THF (12 mL) dropwise and with cooling in an ice bath. The ice bath was removed, and stirring was continued at room temperature for 3 h and 20 min. Then an aqueous solution of sodium hydroxide (20%, 130 mL) was added; the first 15 mL were added dropwise with ice cooling. The two layers were separated, and the aqueous phase extracted with eight 25 mL portions of diethyl ether. The combined organic phases were dried with magnesium sulfate. Removal of the solvent in a rotary evaporator gave a colorless solid (2.45 g) that was recrystallized from petroleum ether (170 mL) to afford the alcohol **12a** as a colorless solid (2.22 g, 75%) with mp 112−113 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.87 (mc, 2 H), 2.50 (m, 12 signals, 2 H), 2.62 (split s, 1 H), 4.18 (mc, 3 H), 4.34 (mc, 2 H). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ 24.6, 59.3, 69.8, 77.6. IR (KBr, cm^{-1}): 3440 (s, O−H). Anal. Calcd for $C_7H_{10}Cl_2O_2$: C, 42.67; H, 5.12; Cl, 35.9. Found: C, 42.83; H, 5.10; Cl, 35.75.

***endo*-2,*endo*-4-Dichloro-3-methyl-8-oxabicyclo[3.2.1]-octan-3-ol (12b).** A solution of CH_3MgI Grignard reagent was prepared under nitrogen from magnesium turnings (0.73 g, 30.0 mmol) and iodomethane (4.26 g, 30.0 mmol) in 60 mL of dry diethyl ether. To the Grignard reagent, cooled in a bath of −3 to 0 °C was added a solution of dichloroketone **8a** (2.93 g, 15.0 mmol) in dry diethyl ether (100 mL) dropwise for 15 min with stirring. The mixture was stirred in the cooling bath (−3 to 0 °C) for 2.5 h and poured into a saturated aqueous solution of ammonium chloride (150 mL). After separation of the layers, the aqueous layer was extracted with five 25 mL portions of ethyl acetate. The combined phases were dried with magnesium sulfate and concentrated in a rotary evaporator. The reddish brown residue was filtered over silica (30 g) with petroleum ether/ethyl acetate (5:1). The solvent was removed, whereupon the slightly reddish oil (2.63 g) crystallized slowly. Recrystallization from petroleum ether (60 mL) gave **12b** as a colorless solid (2.05 g, 65%) with mp 96−97 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.39 (s, 3 H), 1.84 (mc, 2 H), 2.17 (s, 1 H), 2.50 (m, 2 H), 4.03 (d, $J = 4.2$ Hz, 2 H), 4.36 (m, 2 H). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ 24.3, 27.5, 64.7, 72.8, 78.7. IR (KBr, cm^{-1}): 3480, 3450 (s, O−H). Anal. Calcd for $C_8H_{12}Cl_2O_2$: C, 45.52; H, 5.73; Cl, 33.59. Found: C, 45.62; H, 5.85; Cl, 33.73.

***endo*-2,*endo*-4-Dichloro-3-isopropenyl-8-oxabicyclo-[3.2.1]octan-3-ol (12c).** (a) In a two-necked flask equipped with a thermometer and a pressure equalizing dropping funnel, dichloroketone **8a** (2.00 g, 10.25 mmol) was dissolved in dry diethyl ether (150 mL) under argon. The solution was cooled to −78 °C, whereby a part of the educt **8a** precipitated again. To this mixture was added dropwise with magnetic stirring a solution of freshly prepared isopropenyllithium in diethyl ether, prepared from 2-bromopropene (4.00 g, 33 mmol) and lithium dispersion (5.00 g of 30% lithium dispersion in vaseline, 3 × washed with hexane) in dry ethyl ether (50 mL).[55] Stirring was continued for 30 min at −78 °C. The cooling bath was removed and the mixture stirred for 16 h at room temperature. At ca. 0 °C the precipitated solid dissolved completely. The dark solution was poured into aqueous hydrochloric acid (100 mL, $c = 1$ mol/L). The aqueous lower layer was extracted with diethyl ether (3 × 20 mL). The upper layer was combined with the ether extracts and washed neutral with saturated aqueous sodium bicarbonate solution (50 mL) and with water (50 mL). The solution was dried with magnesium sulfate and concentrated in a rotary evaporator. The yellow solid (2.81 g) was recrystallized from a mixture of petroleum ether (50 mL) and ethyl acetate (5 mL). One obtained colorless crystals (1.55 g, 64% yield) with mp 117−118 °C.

(b) A solution of isopropenylmagnesium bromide was prepared from magnesium turnings (1.24 g, 51 mmol) and 2-bromopropene (6.00 g, 49.5 mmol) in dry THF (20 mL).[56] The solution was cooled to 0 °C, whereby a part of the Grignard reagent precipitated as a white solid. The suspension was diluted with dry THF (30 mL). A solution of dichloroketone **8a** (7.80 g, 40 mmol) in THF (30 mL) was added dropwise at 0 °C in such a rate that the temperature of the mixture was between 0 and 5 °C. The mixture became slowly homogeneous. The cooling bath was removed and the mixture stirred for 2 h at room temperature. Saturated aqueous ammonium chloride solution (40 mL) was added, and the layers were separated. The aqueous layer was extracted with diethyl ether (4 × 10 mL). The extracts were combined with the THF layer and dried with magnesium sulfate. The solvent was removed by rotary evaporation and the remaining yellow solid (10.71 g) dissolved in a hot mixture of petroleum ether (60 mL) and *tert*-butyl methyl ether (50 mL). On cooling, 4.32 g (45% yield) of slightly yellow crystals separated, with mp 115−117 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.82 (finely split s, 3 H), 1.88 (m, 2 H), 2.43 (s, 1 H), 2.54 (m, 2 H), 4.25 (d, $J = 4.2$ Hz), 4.43 (m, 2 H), 5.17 (finely split s, 1 H), 5.26 (s, 1 H). IR (KBr, cm^{-1}): 3440 (broad, HO−), 3100 (w, −CH=). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ 19.1, 24.5, 60.9, 77.2, 78.6, 116.0, 143.9. Anal. Calcd for $C_{10}H_{14}Cl_2O_2$: C, 50.65; H, 5.95; Cl, 29.90. Found: C, 50.90; H, 6.10; Cl, 29.81.

2,2,4,4-Tetrachloro-8-oxabicyclo[3.2.1]oct-6-en-3-ol (13). To a stirred solution of lithium aluminum hydride (0.20 g (5.30 mmol) in dry THF (10 mL) under an atmosphere of nitrogen was added dropwise a solution of tetrachloroketone **3a** (2.62 g, 10.0 mmol) in dry THF (12 mL) with cooling in an ice bath. The ice bath was removed and stirring was continued at room temperature for 4.5 h before adding water (30 mL), dropwise and cautiously, under cooling in an ice bath. The inorganic precipitate was filtered off and washed with diethyl ether (20 mL). The two liquid layers formed were separated, and the aqueous layer was extracted with six 20 mL portions of diethyl ether. The combined organic phases were dried with magnesium sulfate. Removal of the solvent in a rotary evaporator gave a colorless solid (0.92 g) that was recrystallized from diethyl ether (20 mL) to afford the alcohol **13** as a colorless solid (0.84 g, 32%) with mp 165−166 °C. ^{1}H NMR (80 MHz, DMSO-d_6): δ 4.31 (d, $J = 8.0$ Hz, 1 H), 5.18 (s, 2 H), 6.70 (s, 2 H), 7.28 (d, $J = 8.0$ Hz, 1 H). ^{13}C NMR (62.90 MHz, DMSO-d_6): δ 83.9, 92.4, 93.8, 138.4. IR (KBr, cm^{-1}): 3460 (s, O−H), 3200, 3110, 2990, 2960, 1600. Anal. Calcd for $C_7H_6Cl_4O_2$: C, 31.86; H, 2.29; Cl, 53.73. Found: C, 32.05; H, 2.28; Cl, 53.73.

1-(3,4-Epoxybutyl)-2-methyl-3,9-dioxatricyclo[3.3.1.0^{2,4}]-nonan-7-one (14). A solution of oxabicycle **4g** (0.58 g, 3.00 mmol) and *m*-chloroperoxybenzoic acid (*m*-CPBA, 70%, 1.63 g, 6.61 mmol) in chloroform (10 mL) was refluxed for 4 h. After cooling to room temperature, the mixture was filtrated to remove the precipitated *m*-CPBA. The filtrate was poured into a mixture of saturated aqueous sodium carbonate solution (30 mL) and water (30 mL) and extracted with chloroform (3 × 20 mL). The combined organic phases were washed with saturated sodium chloride solution (2 × 20 mL) and dried over magnesium sulfate. Evaporation of the solvent gave a colorless oil (870 mg) that was purified by chromatography on silica (100 g) with petroleum ether/ethyl acetate (1:1) and kugelrohr distillation of the fraction with R_f 0.31 at 150 °C/0.005 Torr.

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(56) House, H. O.; Latham, R. A.; Slater, C. D. *J. Org. Chem.* **1966**, *31*, 2667.

The colorless oil (480 mg) consisted of a ca. 1:1 mixture of diastereomers **14**, according to several doubled signals of almost equal intensity in the NMR spectra; yield 71%. ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.39/1.41 (two s, 3 H), 1.5−3.0 (m, 11 H), 3.30/3.32 (two s, 1 H), 4.43 (d, J = 5.4 Hz, 1 H). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ 12.1/12.2, 26.5, 28.9/29.1, 43.1, 47.1/47.2, 48.2/48.7, 52.0/52.1, 60.0/60.3, 61.9/62.1, 71.3, 80.2/80.3, 205.1; the chemical shift values separated by diagonal strokes are due to signals of diastereomers. IR ($CDCl_3$, cm^{-1}): 3060, 2980, 2970, 2930, 1720. EIMS (70 eV): *m*/*z* (%) 224 (2, M^+ from $C_{12}H_{16}O_4$), 181 (22), 168 (12), 151 (10), 139 (22), 137 (10), 127 (19), 125 (41), 123 (16), 121 (12), 112 (10), 111 (19), 109 (17), 108 (15), 99 (43), 97 (30), 95 (22), 93 (10), 85 (10), 84 (33), 83 (45), 82 (12), 81 (24), 79 (16), 71 (49), 69 (37), 67 (12), 57 (25), 55 (64), 54 (12), 53 (14), 43 (100), 41 (55), 39 (29), 31 (11). HRMS Calcd for $C_{12}H_{16}O_4$: 224.1049, found 224.1048.

2,2,4,4-Tetrachloro-1-epoxyethyl-8-oxabicyclo[3.2.1]-oct-6-en-3-one (15d). To a stirred solution of **3d** (5.76 g, 20.0 mmol) in chloroform (70 mL) was added *m*-CPBA (70%, 11.9 g, ca. 48.0 mmol) in portions. The mixture was refluxed for 6 h and worked up as described for compound **14** (see preceding experiment). Examination of the reaction mixture by GC showed some unreacted **3d**. Therefore the chloroform solution was refluxed with a further portion of *m*-CPBA (5.93 g, ca. 24 mmol) and refluxed for 4 h. A second workup as described for compound **14** gave an oily residue that was layered with a little petroleum ether. In the refrigerator crystallization occurred. The solid (3.51 g) was dissolved in petroleum ether/ethyl acetate (5:1) and filtered over alumina (150 g, activity 3). The solvent was removed and the remaining colorless solid dried in vacuo. Yield: 1.44 g (24%) of **15d** with mp 65−66 °C. ^{1}H NMR (60 MHz, $CDCl_3$): δ 2.96 (d, J = 3 Hz, 2 H), 3.75 (t, J = 3 Hz, 1 H), 5.18 (finely split s, 1 H), 6.48 (finely split s, 2 H). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ 44.0, 49.1, 81.9, 85.4, 87.8, 91.9, 134.2, 134.7, 184.2; weaker peaks at 44.2, 49.3, and 132.9 may be due to the presence of a minor diastereomer. IR (KBr, cm^{-1}): 3110, 3090, 3020, 2940, 1770, 1760, 1605. Anal. Calcd for $C_9H_6Cl_4O_3$: C, 35.56; H, 1.99; Cl, 46.65. Found: C, 35.66; H, 2.03; Cl, 46.64.

2,2,4,4-Tetrachloro-1-epoxyethyl-5-methyl-8-oxabicyclo-[3.2.1]oct-6-en-3-one (15e). To a stirred solution of **3e** (2.72 g, 9.00 mmol) in chloroform (35 mL) was added *m*-CPBA (70%, 5.94 g, ca. 24.0 mmol) in portions. The mixture was refluxed for 4 h, and a further portion of *m*-CPBA (70%, 2.97 g, ca. 12.0 mmol) was added. After 2 h refluxing the reaction mixture was worked up as described for compound **15d** (see preceding experiment). Yield: 0.73 g (26%) of **15e** as a colorless solid with mp 79−80 °C. ^{1}H NMR (60 MHz, $CDCl_3$): δ 1.73 (s, 3 H), 2.90 (finely split d, J = 3 Hz, 2 H), 3.68 (t, J = 3 Hz, 1 H), 6.28 (s, 2 H). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ 16.9, 43.9, 49.2, 84.9, 87.2, 91.7, 92.0, 133.5, 138.1, 184.8. IR (KBr, cm^{-1}): 3115, 3020, 3010, 1780, 1760, 1750, 1615. Anal. Calcd for $C_{10}H_8Cl_4O_3$: C, 37.77; H, 2.53; Cl, 44.60. Found: C, 37.66; H, 2.50; Cl, 44.74.

2,2,4,4-Tetrachloro-1-(3,4-epoxybutyl)-7-methyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (15g). Tetrachlorobicycle **3g** (1.06 g, 3.20 mmol) dissolved in chloroform (6 mL) and *m*-CPBA (70%, 0.80 g, 3.25 mmol) was refluxed for 2 h. TLC showed complete conversion of **3g**. Work up as described for compound **14** gave a white solid (1.10 g) that was recrystallized from petroleum ether (bp 60−80 °C, 100 mL). Yield: 0.81 g (73%), white crystals with mp 86 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.15−1.28/1.43−1.53 (m, 1 H), 1.76−2.04 (m, 1 H), 1.97 (finely split s, 3 H), 2.13−2.23/2.28−2.38 (m, 1 H), 2.45−2.59 (m, 2 H), 2.79−2.84/2.98−3.07 (m, 2 H), 5.05 (finely split s, 1 H), 6.19 (finely split s, 1 H); the chemical shift values separated by diagonal strokes are due to signals of diastereomers. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ 14.8, 23.0/24.0, 25.4/26.3, 46.7/47.5, 51.3/51.8, 82.2, 86.0, 88.36/88.41, 94.17/94.23, 129.8/129.9, 145.86/145.93, 184.8; the chemical shift values separated by diagonal strokes are due to signals of diastereomers. IR (KBr, cm^{-1}): 3060, 2990, 2930, 2880, 2860, 1760, 1645. Anal. Calcd for $C_{12}H_{12}Cl_4O_3$: C, 41.62; H, 3.47; Cl, 41.04. Found: C, 41.85; H, 3.56; Cl, 41.02.

2,2,4,4-Tetrachloro-1-(3,4-epoxy-3-methylbutyl)-7-methyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (15h). To a stirred solution of **3h** (3.44 g, 10 mmol) in chloroform (35 mL) was added *m*-CPBA (ca. 70%, 3.21 g, ca. 13 mmol). The mixture was refluxed for 3.5 h and worked up as described for compound **14**. The remaining solid was recrystallized from a small amount of diethyl ether to give 2.56 g (71%) of a colorless solid with mp 111−112 °C, according to the ^{13}C NMR spectrum a mixture of diastereomers. ^{1}H NMR (60 MHz, $CDCl_3$): δ 1.37 (s, 3 H), 1.50−2.45 (m, 7 H, surmounted by a finely split s of the 7-CH_3 at δ = 1.93), 2.53−2.72 (m, 2 H), 5.00 (mc, 1 H), 6.15 (mc, 1 H). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ 14.8, 20.6/21.7, 22.4/23.0, 29.1/30.1, 52.9/54.6, 56.2/56.4, 82.2, 86.0, 88.4, 94.3, 129.75/129.83, 145.8/146.0, 184.8; the chemical shift values separated by diagonal strokes are due to signals of diastereomers. IR (KBr, cm^{-1}): 3110, 3060, 2990, 2970, 2930, 1755, 1645. Anal. Calcd for $C_{13}H_{14}Cl_4O_3$: C, 43.37; H, 3.92; Cl, 39.38. Found: C, 43.73; H, 3.92; Cl, 39.57.

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Supporting Information Available: Describes the preparation of the furans **1k** and **1l**. Cyclocondensations with lithium perchlorate/triethylamine in diethyl ether. 8-Oxabicyclo-[3.2.1]oct-6-en-3-one **4g**, prepared from the furan **1g** without isolation of the tetrachloride **3g**. ^{1}H and ^{13}C NMR data with peak assignments. This material is available free of charge via the Internet at http://pubs.acs.org.

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