Cycloaddition of Acyclic Conjugated Dienes with a Tetrachloro-Substituted Oxyallyl Intermediate Generated from Pentachloroacetone

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Pentachloroacetone (**1**) reacts with several conjugated dienes in the presence of sodium trifluoroethoxide/trifluoroethanol to form cycloadducts of a tetrachlorooxyallyl intermediate **6**, mainly in the [4+3] mode. Representative [4+3] cycloadducts, i.e. $\alpha,\alpha,\alpha',\alpha'$-tetrachlorocycloheptenones **9**, have been dehalogenated and dehydrohalogenated, furnishing α,α'-dichlorotropones **15** in high yields.

Introduction

A host of bicyclic [4+3] cycloadducts have been prepared from furans and oxyallyl intermediates, which, in turn, have been generated from α-halogeno ketones by various methods. In contrast, the number of monocyclic 4-cycloheptenones obtained from acyclic 1,3-dienes is comparatively small.[1] Moreover, in several cases, by-products resulting from competing [3+2] cycloaddition have been observed, necessitating chromatographic separation, and hence only modest yields of the monocyclic [4+3] cycloadducts have been achieved.

In order to undergo a concerted [4+3] cycloaddition, the short-living oxyallyl intermediates should encounter a large population of the 1,3-diene in the *s-cis* (*synperiplanar*, *sp*) or *gauche* (*synclinal*, *sc*) conformation. This prerequisite is met with cyclic 1,3-dienes, but not with butadiene and its simple substituted derivatives.

Having shown that cycloaddition of the oxyallyl intermediate generated from pentachloropropan-2-one (pentachloroacetone, PCA, **1**)[2] with furans and cyclopentadiene often gives very good yields, provided that the appropriate procedure is used,[3] we were curious to investigate reactions of PCA with acyclic 1,3-dienes in the presence of sodium 2,2,2-trifluoroethoxide/2,2,2-trifluoroethanol (NaTFE/TFE). We had a faint hope that 2,2,7,7-tetrachloro-4-cycloheptenones (**9**) would result (Scheme 1) which, ultimately, could be dehalogenated by the usual methods.

Results and Discussion

A priori, the solvolysis of PCA by TFE/NaTFE would be expected to compete with the cycloaddition (for the trifluoroethanolysis of α-monohalogeno ketones in the presence of base, see ref.[4]). Reaction of PCA with NaTFE/TFE in the absence of a diene component led to a mixture that could not be separated by liquid chromatography. A substantial amount of the resulting product consisted of an intractable non-volatile oil. Among the volatile components, two could be identified as 2,2,2-trifluoroethyl dichloroacetate (**4**) and 2,2,2-trifluoroethyl 2,3,3-trichloropropenoate (**7**). The ester **7** is the product of a Favorskii rearrangement proceeding by the oxyallyl–cyclopropanone mechanism, induced by cleavage of the tetrachlorocyclopropanone intermediate by the trifluoroethoxide anion (**5** → **8**). Evidently, this anion also attacks the carbonyl carbon atom of PCA forming the ester **4** under haloform cleavage.

Reaction of the prototype conjugated diene, i.e. 1,3-butadiene, with PCA and NaTFE/TFE at ca. 0 °C also led to a mixture, from which the expected 2,2,7,7-tetrachloro-4-cycloheptenone (**9a**) could be isolated by chromatography in 5% yield. A carbonyl absorption band in the IR spectrum at 1740 cm^{-1}, i.e. at a comparatively high wavenumber, clearly proves the ketonic structure of the cycloadduct.

The ^{13}C-NMR spectrum ($CDCl_3$) shows four signals at $\delta = 45.6$, 86.9, 126.0, and 183.6, thus indicating a species with C_s or C_2 symmetry; the chemical shifts are in accord with the resonances of the carbon atoms C-3/C-6, C-2/C-7, C-4/C-5, and C-1, as verified by the DEPT technique.

For the unsubstituted 4-cycloheptenone (**12a**, vide infra), a chair and/or a boat conformation has been discussed.[5] An X-ray structure determination could be carried out on a crystal of the tetrachloro ketone, which showed that in the solid state the seven-membered ring of **9a** adopts a twist-chair conformation (Figure 1).[6]

Reaction of 3-methyl-1,3-butadiene (isoprene) resulted in a much better yield of the desired product **9b** (42%), but this [4+3] cycloadduct was accompanied by two minor [3+2] cycloadducts, namely the dichloromethylenetetrahydrofuran **10b** (4%) and the tetrachlorocyclopentanone **11b** (2%). The occurrence and structure of these minor products is consistent with a non-concerted, i.e. stepwise mechanism of the cycloaddition.[7]

With 2-isopropyl-1,3-butadiene, 2,3-dimethyl-1,3-butadiene, and 1,2,3-trimethyl-1,3-butadiene (i.e. 2,3-dimethyl-1,3-pentadiene), only the [4+3] cycloadducts (**9c–e**) could be isolated in ca. 60% yield. The latter diene was obtained as a mixture with its isomer, 3,4-dimethyl-1,3-pentadiene, by dehydration of 3,4-dimethylpent-1-en-3-ol.[8] However, this isomer, which bears two methyl groups at one terminus, cannot compete with 2,3-dimethyl-1,3-pentadiene in cyclo-

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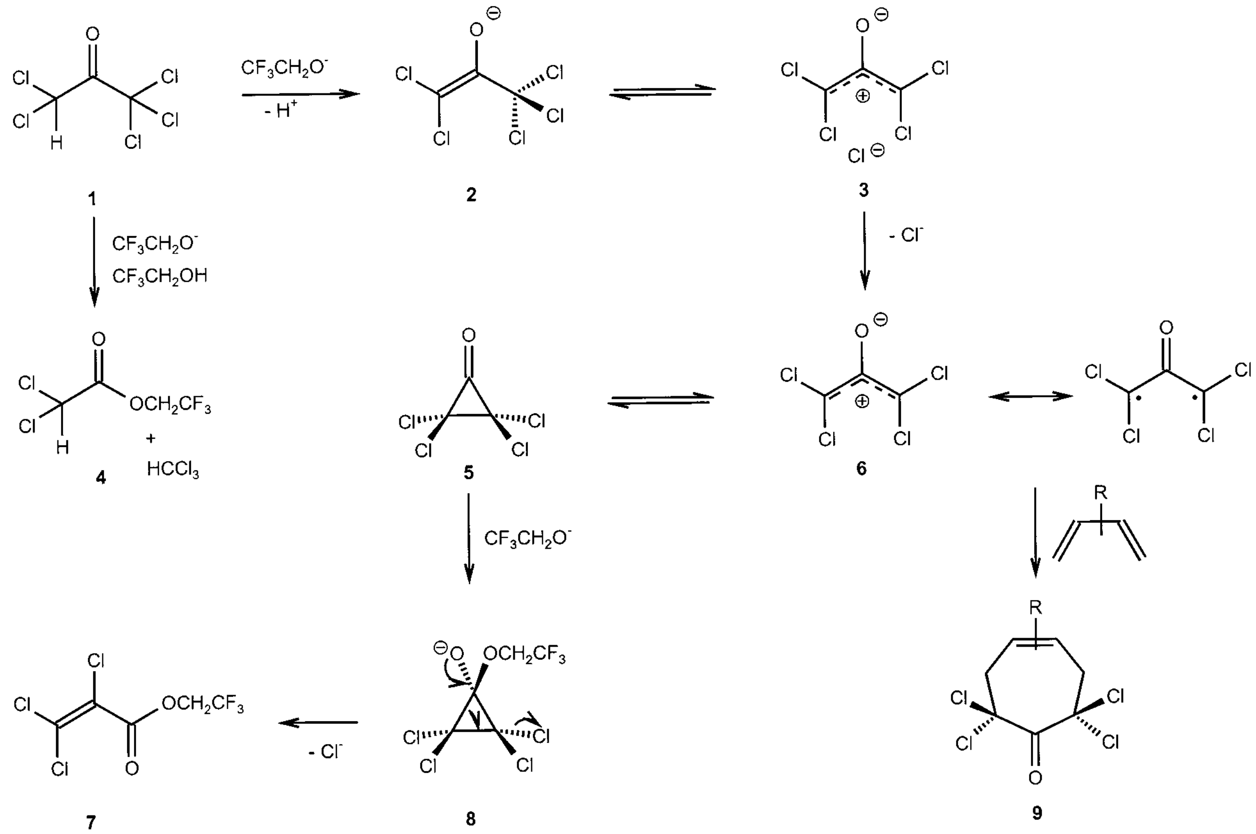


Scheme 1

addition with the oxyallyl intermediates **3** or **6**; only **9e** was found after exposing the isomeric mixture of dienes to PCA and NaTFE/TFE.

It cannot be excluded that, as with isoprene, minor amounts of the [3+2] cycloadducts are also formed in these cases, although we could not isolate any such products. Even with 1,2-dimethylenecyclohexane, a diene fixed in the *gauche* (*sc*) conformation,[9] the dichloromethylenetetrahydrofuran **10f** is formed (2% isolated yield) besides the [4+3] cycloadduct **9f** (65% yield). The results of the cycloaddition reactions are summarized in Table 1.

Dehalogenation of Some Tetrachloro-Substituted [4+3] Cycloadducts

Fortunately, from a synthetic point of view, the unsubstituted 4-cycloheptenone (**12a**) and the 4-methyl derivative (**12b**), the expected products of dehalogenation of **9a** and **9b**, respectively, may be obtained more efficiently by other, albeit lengthy, routes.[10,11]

In order to obtain **12b** by dechlorination, **9b** was treated with zinc/copper couple in methanol saturated with ammonium chloride.[1c] In contrast to the smooth dehalogenation of the rigid bicyclic tetrachlorooxyallyl cycloadducts, i.e. tetrachlorobicyclo[3.2.1]oct-6-en-3-ones, achieved using zinc/copper couple,[3] dechlorination of **9b** with this reagent led to a mixture of products. The ^{1}H-NMR spectrum of this mixture showed the presence of only a few percent of 4-methyl-4-cycloheptenone (**12b**).

A more quantitative investigation using the 2,3-dimethylbutadiene [4+3] cycloadduct **9d** revealed that the main product was the 1,4-cyclohexadiene derivative **13**, accompanied by the anticipated 3,4-dimethyl-4-cycloheptenone **12d** (21% yield). On standing in air, the main product **13** is eventually dehydrogenated to methyl 2-chloro-4,5-dimethylbenzoate (**14**). On reduction of the more flexible tetrachlorocycloheptenone, Favorskii intermediates can be formed, which lead to ring contraction (Scheme 2). It was found that the dechlorination of **9d** and **9f** could be accomplished with improved yields by means of zinc in aqueous THF using ammonium acetate as a mild proton source.[12]

α,α′-Dichlorotropones

Dehydrobromination of 2,2,7-tribromocycloheptanone with lithium carbonate in boiling dimethylformamide (DMF) was reported by Jones to give 2,4,6-cycloheptatrienone (tropone) in 53% yield.[13] In the course of this reaction, migration of C=C double bonds, i.e. isomerization, occurs.[14] Jones' protocol has been used by Noyori's group to synthesize 2,7-dialkyltropones.[15]

Applying this method to the tetrachlorocycloheptenones **9b–f**, a double dehydrochlorination could be achieved, resulting in the expected 2,7-dichlorotropones **15b–f** in very good yields. A lack of material prohibited the dehydrochlorination of **9a**, but anyway a more efficient approach to 2,7-dichlorotropone (**15a**) already exists.[16]

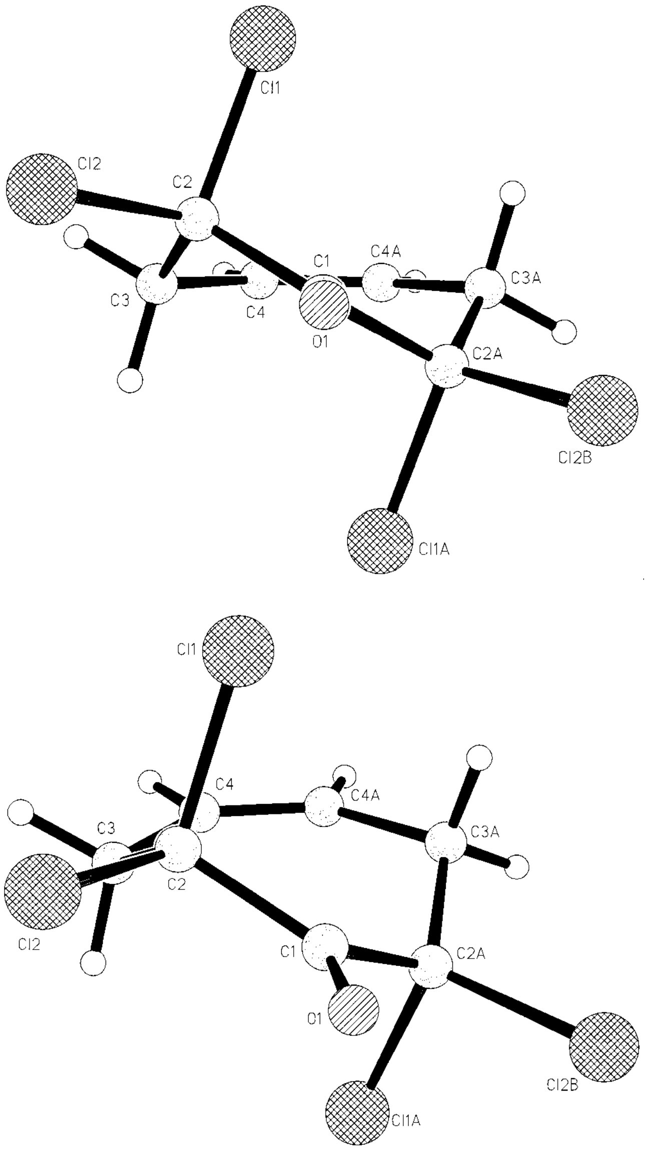
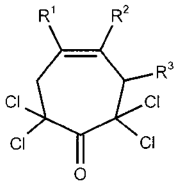


Figure 1. Structure of tetrachloro ketone **9a** in two views as determined by X-ray diffraction



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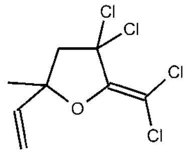
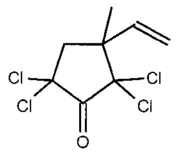
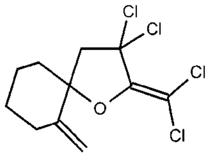


10b

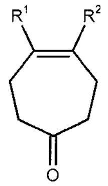


11b

9	R^1	R^2	R^3
a	H	H	H
b	CH_3	H	H
c	$(CH_3)_2CH$	H	H
d	CH_3	CH_3	H
e	CH_3	CH_3	CH_3
f	—$(CH_2)_4$—		H



10f



12

12	R^1	R^2
a	H	H
b	CH_3	H
d	CH_3	CH_3
f	—$(CH_2)_4$—	

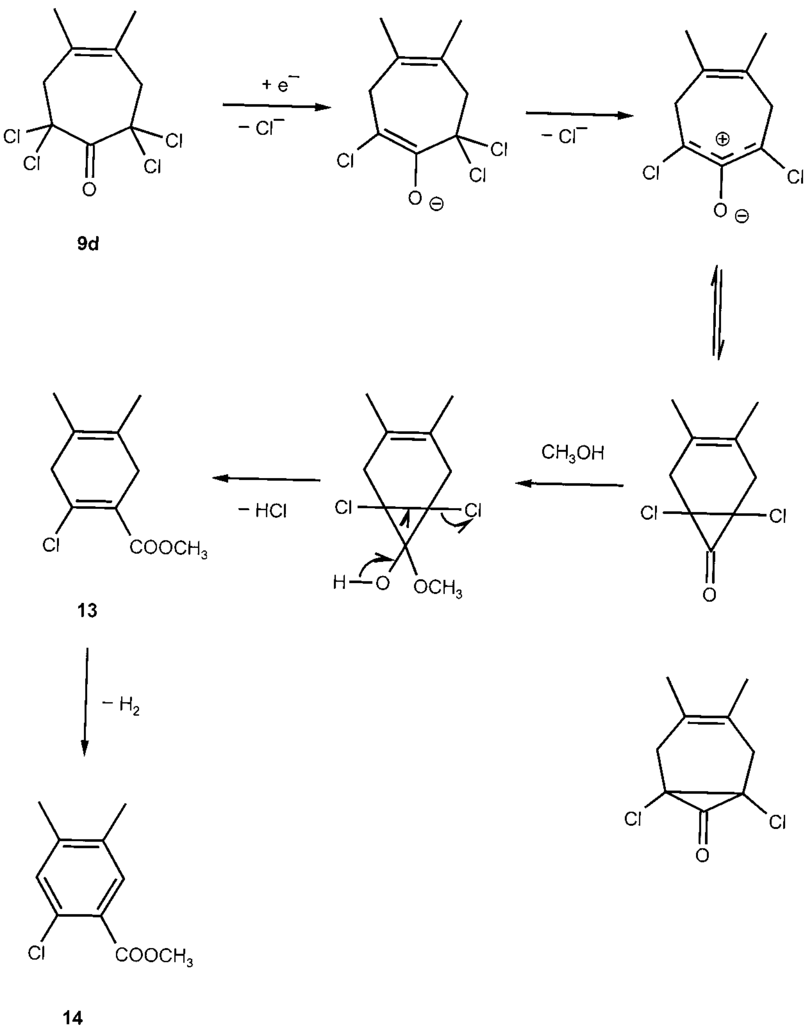
Table 1. 2,2,7,7-Tetrachlorocyclohept-4-enones (**9**) from conjugated dienes and pentachloroacetone

Diene	Cycloadduct	Yield (%)
1,3-Butadiene	**9a**	5
2-Methyl-1,3-butadiene	**9b**	42
2-Isopropyl-1,3-butadiene	**9c**	65
2,3-Dimethyl-1,3-butadiene	**9d**	57
2,3-Dimethyl-1,3-pentadiene	**9e**	62
3,4-Dimethyl-1,3-pentadiene	–	0
1,2-Dimethylidenecyclohexane	**9f**	65

In order to obtain a dechlorinated tropone, the tetrachloro ketone **9c** was treated with two equivalents of tributylstannane and the radical initiator azoisobutyronitrile (AIBN) in benzene at 60 °C. After removal of organotin species, the crude reaction product was heated with lithium carbonate in DMF. Subsequent chromatography afforded the natural product nezukone[17] (4-isopropyltropone) in ca. 30% yield.

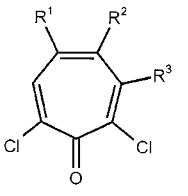
Displacement of the chloro substituent of 2-chlorotropone by a hydroxy group, i.e. transformation to tropolone, can be effected by boiling with aqueous formic acid.[16] We applied this protocol to the symmetric (C_{2v}) dichlorotropone **15d** in the expectation that dihydroxytropone **17** would be formed. However, after reflux for 13 days in 60% formic acid, essentially only one of the chloro substituents had been displaced; the chlorotropolone **18** (2-chloro-7-hydroxy-4,5-dimethyltropone) was isolated in 88% yield along with just 5% of **17**. Eventually, it was found that **18** could be dehydrochlorinated in alkaline solution, i.e. via the chlorotroponolate anion, by catalytic hydrogenation in the presence of palladium on carbon,[18] thereby affording 4,5-dimethyltropolone **19**.

It is well known that tropolone undergoes rapid tautomerism in solution through proton-transfer between the two oxygen atoms; this degenerate isomerization leads to averaged signals in its NMR spectra.[19] In the case of **17** and **18**, however, the NMR spectra give no indication of the tautomers **20** and **21**, respectively, as seen with 2-bromo-7-hydroxytropone.[20] As for **19**, the comparatively large coupling constant in the ^{1}H-NMR spectrum, J_{vic} = 11.4 Hz, points to **19** ($^3J_{6,7}$) rather than to **22**; a smaller value would be expected for the vicinal coupling ($^3J_{3,4}$) in the latter case.[21] In the ^{13}C-NMR spectrum, the high-field resonance at δ = 121.4 ($CDCl_3$) may be assigned to C-3 of the tautomer **19**. Of course, these arguments, based on small differ-



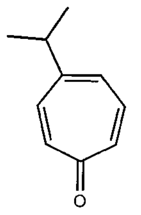
Scheme 2

ences, do not give unequivocal proof of the **19/22** tautomeric equilibrium.



15

15	R¹	R²	R³
b	CH₃	H	H
c	(CH₃)₂CH	H	H
d	CH₃	CH₃	H
e	CH₃	CH₃	CH₃
f	— (CH₂)₄ —		H



16

As expected, hydrolysis of the monoalkylated dichlorotropones **15b** and **15c** gave mixtures of 2-chloro-7-hydroxytropones with the methyl and isopropyl substituents, respectively, in both the 4- and 5-positions. In both cases, the corresponding dihydroxytropones were detected as minor products.[22]

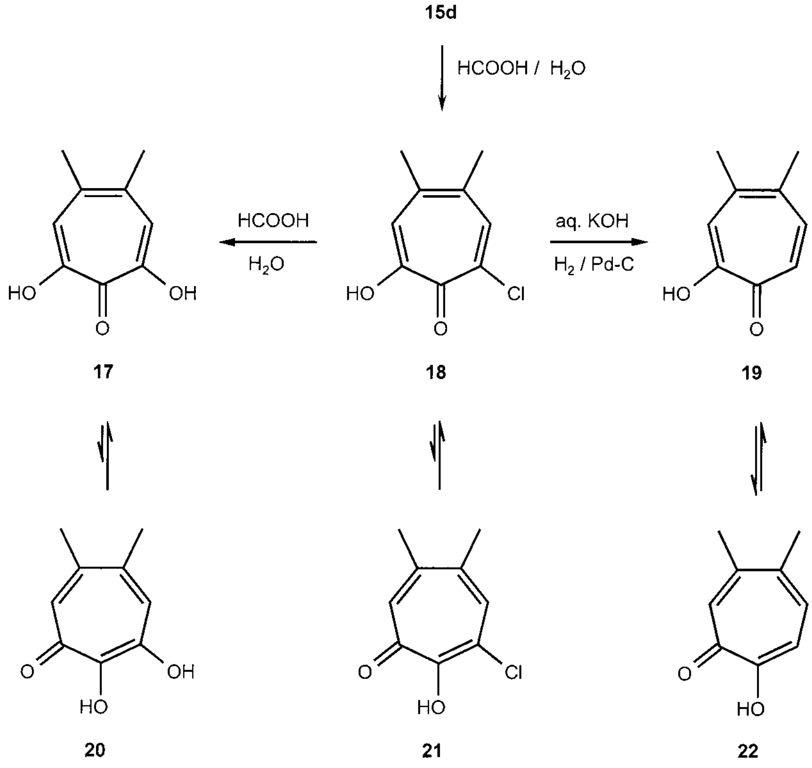
To sum up, the [4+3] cycloaddition of tetrachlorooxyallyl intermediate to acyclic 1,3-dienes is, in principle, feasible. In some cases, acceptable yields of tetrachlorocycloheptenones can be obtained. This reaction also offers a novel access to hetero-substituted tropones.

However, [3+2] cycloaddition emerges as a minor side reaction that is obviously not followed with cyclopentadiene and furans. Our results show once more that the nature of the diene component is of crucial importance to the successful outcome of the [4+3] cycloaddition. Clearly, *s-cis*-fixed dienes such as cyclopentadiene and electron-rich furans react most rapidly, giving other reactions of PCA no chance to compete. From this, one may conclude that the diene combines with the intermediate(s) generated from PCA at an early stage.

With these observations in mind, it is interesting to speculate as to how appropriate the "simple" oxyallyl structure **6** is for an interpretation of the [4+3] cyclocondensation with PCA (Scheme 1). A more realistic description may be as follows: The diene reacts with the oxyallyl ion-pair **3**, derived from the enolate **2**, displacing the chloride ion by nucleophilic attack of its π-system. If the nucleophilicity of the diene is weak,[23] or the *s-trans* conformers are strongly preferred, side reactions become predominant.

Experimental Section

General Remarks: IR: Perkin–Elmer 457 spectrometer. – NMR: Bruker AC 250 for 250 MHz ^{1}H-NMR and 62.9 MHz ^{13}C-NMR



spectra; Bruker AC 500 for 500 MHz ^{1}H-NMR and 125.77 MHz ^{13}C-NMR spectra; $CDCl_3$ or [D$_6$]DMSO as solvent; TMS as internal standard. Assignments of the ^{13}C-NMR signals of the cycloadducts and the products derived therefrom were made with the aid of DEPT spectra. – EI-MS: Varian MAT 711 with AMD data system DP 10. – GC/MS: Carlo Erba Fractovap 2151 AC-Special gas chromatograph, distributed by Brechbühler AG, Urdorf, Switzerland, coupled directly with a Finnigan 4023 mass spectrometer using the Incos 2300 data system. In chemical ionization mode (CI-MS), methane was used as reactand gas; pressure 0.5 Torr (66.8 Pa). The temperature of the ion source was 130 °C. – Gas chromatography: Carlo Erba Fractovap 4160 GI or Carlo Erba HRGC 5300 Mega Series with integrator; 20-m glass capillary column coated with PS 086. Temperature program: 40 °C → 300 °C, heating rate 10 K/min. The percent values refer to the relative peak areas obtained by integration of the FID signals. – Analytical TLC: Precoated sheets, Polygram Sil G/UV$_{254}$ (silica) or Polygram N/UV$_{254}$ (alumina), distributed by Macherey Nagel, Düren, Germany; detection by UV extinction, or by spraying with 0.5% aqueous $KMnO_4$ solution or with vanillin/H_2SO_4 solution and subsequent warming. – Preparative column chromatography: Silica 60 (63–200 μm), distributed by Macherey Nagel, Düren, Germany. – Dry petroleum ether (PE) was distilled (b.p. 40–65 °C). Ethyl acetate (EA) was dried with calcium chloride, distilled, and stored over 4-Å molecular sieves. – Melting points were determined with a Büchi 510 apparatus, Büchi Laboratoriumstechnik AG, Flawil, Switzerland, and are uncorrected. – Elemental analyses were performed by the service of the Institut für Organische Chemie, University of Stuttgart. – Dichloromethane and dimethylformamide (DMF) were dried by refluxing with powdered calcium hydride and then distilled. For sodium trifluoroethoxide/trifluoroethanol (NaTFE/TFE) reagent and pentachloropropan-2-one (PCA, **1**), see ref.[3] 1,3-Butadiene, 2-methyl-1,3-butadiene (isoprene), and 2,3-dimethyl-1,3-butadiene were purchased from Fluka. The other dienes were prepared according to literature procedures. Ethylenediaminetetraacetic acid disodium salt dihydrate (EDTA) and tributylstannane were purchased from Merck; the hydrogenation catalyst 10% palladium on activated charcoal was obtained from Fluka.

Reaction of Pentachloropropan-2-one (PCA, 1) with Sodium Trifluoroethoxide (NaTFE) in Trifluoroethanol (TFE): To a solution of 2.30 g (10 mmol) of **1** in TFE (5 mL), cooled in an ice bath, a solution of NaTFE in TFE (2 M) was added dropwise with magnetic stirring, which led to the precipitation of sodium chloride. The progress of the reaction was monitored by spotting samples of the mixture on pH indicator paper. When 15 mL (30 mmol) of the NaTFE solution had been added, the reaction mixture was seen to be alkaline. The ice bath was then removed, and the mixture was stirred for 5 d at room temperature under protection from moisture. The precipitated sodium chloride was then allowed to settle, and the supernatant solution was examined by GC using a 20-m glass capillary column coated with PS 086 and a temperature program of 40 → 300 °C, 10 K/min. The GC trace showed at least eleven peaks with t_R = 1.2 min (4%), 1.3 (5), 2.8 (5), 3.3 (12), 5.7 (28), 6.1 (9), 6.5 (20), 7.9 (3), 10.9 (4), 11.5 (6), and 13.9 (4). The peaks at t_R = 2.8 and t_R = 6.1 min showed enhancements upon co-injection with the reference compounds **4** and **7**, respectively (vide infra). GC/MS analysis of the solution after 120 h using the same column and temperature program (40 → 300 °C, 10 K/min) as above gave the following masses and fragmentations of six major volatile products in chemical ionization (CI) mode with methane as the reactant gas:

Component with t_R = 2.0 min (**4**): CI-MS (70 eV, CH_4, 0.5 Torr); *m/z* (%) = 215 (7) [MH^+ from $C_4H_3{}^{37}Cl_2F_2O_2$], 213 (63) [MH^+ from $C_4H_3{}^{37}Cl^{35}ClF_2O_2$], 211 (100) [$MH^+$ from $C_4H_3{}^{35}Cl_2F_2O_2$], 195 (0.5) [MH^+ – HF], 193 (11) [MH^+ – HF], 191 (23) [MH^+ – HF], 177 (28), 175 (20) [MH^+ – HCl], 147 (22), 111 (12), 101 (33) [$CF_3CH_2OH_2{}^+$], 85 (14), 83 (12), 81 (28).

Component with t_R = 2.3 min: CI-MS; *m/z* (%) = 417 (12), 337 (95), 309 (12), 101 (100).

Component with t_R = 4.6 min: CI-MS; *m/z* (%) = 449 (5), 421 (8), 401 (12), 385 (15), 321 (35), 323 (21), 309 (10), 239 (11), 211 (55), 101 (100).

Component with t_R = 5.4 min (**7**): CI-MS (CH_4, 70 eV); *m/z* (%) = 263 (2) [MH^+ from $C_5H_2Cl_3F_3O_2$], 261 (26) [MH^+ from $C_5H_2Cl_3F_3O_2$], 259 (90) [MH^+ from $C_5H_2Cl_3F_3O_2$], 257 (100) [MH^+ from $C_5H_2Cl_3F_3O_2$], 239 (20) [$MH^+ - HF$], 237 (22) [$MH^+ - HF$], 187 (24), 161 (12), 159 (47) 157 (44), 101 (10) [$CF_3CH_2OH_2^+$].

Component with t_R = 5.8 min: CI-MS; *m/z* (%) = 467 (2), 465 (6), 387 (17), 385 (52), 309 (28), 169 (11), 101 (100).

Component with t_R = 9.3 min: CI-MS; *m/z* (%) = 599 (1), 309 (4), 227 (1), 101 (100).

2,2,2-Trifluoroethyl Dichloroacetate (4): To a solution of NaTFE in TFE (10 mL, *c* = 2 mol/L), cooled in an ice bath, 2.95 g (20 mmol) of dichloroacetyl chloride was added dropwise by means of a syringe. The mixture was stirred overnight at room temperature under protection from moisture. After allowing the precipitated sodium chloride to settle, the supernatant solution was decanted off and fractionally distilled using a 14-cm Vigreux column. The colourless mobile distillate (1.7 g, 81%, **4**) had b.p. 138 °C (ref.[24] 138.5 °C). – IR ($CDCl_3$): $\tilde{\nu}$ = 1775 cm^{-1} (C=O). – ^1H NMR (250 MHz, $CDCl_3$): δ = 4.64 (q, $^3J_{H,F}$ = 8.1 Hz, 2 H, CF_3CH_2O), 6.05 (s, 1 H, $CHCl_2$). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 62.31 (q, $^2J_{C,F}$ = 37.7 Hz, CF_3CH_2O), 63.17 (s, $CHCl_2$), 122.18 (q, $^1J_{C,F}$ = 277.3 Hz, CF_3), 163.26 (s, C=O). – $C_4H_3Cl_2F_3O_2$ (211.0): calcd. C 22.77, H 1.43, Cl 33.61; found C 22.63, H 1.53, Cl 33.49.

2,2,2-Trifluoroethyl 2,3,3-Trichloropropenoate (7): With magnetic stirring and cooling in an ice bath, a 2 M NaTFE/TFE solution (8.5 mL, 16 mmol) was added dropwise by means of a syringe to 3.30 g (17 mmol) of 2,3,3-trichloropropenoyl chloride.[25] The ice bath was then removed and the mixture was stirred for 1 h at room temperature. Water (4 mL) and *tert*-butyl methyl ether (20 mL) were then added to the heterogeneous mixture and the layers were separated. The organic layer was dried with magnesium sulfate, filtered, and concentrated in a rotary evaporator at 20 °C. The remaining liquid was distilled using a 14-cm Vigreux column. The colourless mobile distillate (2.72 g, 42%, **7**) had b.p. 70–71 °C/11 Torr. – IR ($CDCl_3$): $\tilde{\nu}$ = 1745 cm^{-1} (C=O), 1550 (C=C). – ^1H NMR (250 MHz, $CDCl_3$): δ = 4.63 (q, $^3J_{C,F}$ = 8.1 Hz, 2 H, CF_3CH_2O). – ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 61.89 (q, $^2J_{C,F}$ = 37.7 Hz, CF_3CH_2O), 120.81 (s, C-2), 122.39 (q, $^1J_{C,F}$ = 277.5 Hz, CF_3), 133.38 (s, C-3), 159.12 (s, C=O). – $C_5H_2Cl_3F_3O_2$ (257.4): calcd. C 23.33, H 0.78, Cl 41.32; found C 23.13, H 0.81, Cl 41.57.

Reaction of 1,3-Butadiene with PCA (1) and NaTFE/TFE: Preparation of 2,2,7,7-Tetrachlorocyclohept-4-enone (9a). – Procedure A: A 100-mL three-necked flask, equipped with a dropping funnel, a dry-ice condenser, a septum, and a magnetic stirring bar was cooled in a dry-ice bath and ca. 20 mL of 1,3-butadiene was liquefied therein. A solution of 2.30 g (10 mmol) of PCA in TFE (10 mL) was then added by means of a syringe and the dry-ice bath was replaced with an ice bath. To the boiling butadiene solution, 10 mL of NaTFE/TFE solution (1 M) was added dropwise over a period of 3 h. Stirring was continued for 30 min at ice-bath temperature and then overnight at room temperature. Water (50 mL) and dichloromethane (20 mL) were then added and the layers were separated. The aqueous layer was extracted with dichloromethane (5 × 10 mL) and the combined dichloromethane phases were washed with brine (2 × 30 mL), dried with sodium sulfate, and concentrated in a rotary evaporator. The residue was subjected to chromatography on silica (30 g) eluting with PE. A colourless solid (117 mg, **9a**, 5%) was isolated, which showed m.p. 47–47.5 °C after crystallization from pentane. One of the crystals was selected for X-ray analysis.[6]

Procedure B: A stream of 1,3-butadiene gas was slowly passed into an ice-cooled solution of PCA (2.30 g, 10 mmol) in TFE (10 mL). NaTFE/TFE solution (10 mL, *c* = 1 mol/L) was then added over a period of 3 h with magnetic stirring and cooling in an ice bath. Work-up and chromatography as described above gave 126 mg of **9a** (5%) as a colourless solid with m.p. 47–47.5 °C. – IR ($CDCl_3$): $\tilde{\nu}$ = 1745 cm^{-1} (C=O), 1670 (C=C). – ^1H NMR (250 MHz, $CDCl_3$): δ = 3.43 (d, *J* = 2.9 Hz, 4 H, 3-H_2 and 6-H_2), 5.70 (t, *J* = 2.8 Hz, 2 H, 4-H and 5-H). – ^{13}C NMR/DEPT (62.9 MHz, $CDCl_3$): δ = 45.63 (CH_2, C-3 and C-6), 86.91 (C_q, C-2 and C-7), 125.97 (CH, C-4 and C-5), 183.64 (C_q, C-1). – $C_7H_6Cl_4O$ (247.9): calcd. C 33.91, H 2.44, Cl 57.20; found C 33.92, H 2.39, Cl 57.44.

Reaction of 2-Methyl-1,3-butadiene (Isoprene) with PCA (1) and NaTFE/TFE: Preparation of 2,2,7,7-Tetrachloro-4-methylcyclohept-4-enone (9b), 3,3-Dichloro-2-(dichloromethylene)-5-methyl-5-vinyltetrahydrofuran (10b), and 2,2,5,5-Tetrachloro-3-methyl-3-vinylcyclopentanone (11b): A mixture of 2-methyl-1,3-butadiene (6.81 g, 100 mmol) and PCA (**1**) (6.81 g, 100 mmol) was cooled in an ice bath. A solution of NaTFE in TFE (1 M) was then added dropwise under magnetic stirring over a period of 4 h. Stirring was continued for 1 h at ice-bath temperature and then for a further 1 h at room temperature. Water (60 mL) and dichloromethane (30 mL) were added and the layers were separated. The aqueous layer was extracted with dichloromethane (5 × 15 mL) and the combined dichloromethane phases were washed with brine (2 × 50 mL), dried with sodium sulfate, and concentrated in a rotary evaporator. The residue was dried in vacuo (oil pump) and then subjected to chromatography on silica (250 g) eluting with PE/EA (30:1). From the first fraction, a pale-yellow liquid (320 mg) was obtained, which was found to consist of a mixture of **10b** and **11b** on the basis of its NMR spectra (vide infra). From the second fraction, 2.19 g of a colourless oil (**9b**, 42%) was obtained.

9b: IR (film): $\tilde{\nu}$ = 1800 cm^{-1}, 1750 (C=O). – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.90 (d, *J* = 0.5 Hz, 3 H, CH_3), 3.44–3.50 (m, 4 H, 3-H_2 and 6-H_2), 5.56–5.61 (m, 1 H, 5-H). – ^{13}C NMR/DEPT (62.9 MHz, $CDCl_3$): δ = 26.03 (CH_3), 45.04 (CH_2, C-6), 50.04 (CH_2, C-3), 86.23 (C_q, C-2), 86.69 (C_q, C-7), 120.98 (CH, C-5), 135.43 (C_q, C-4), 184.42 (C_q, C-1). – $C_8H_8Cl_4O$ (262.0): calcd. C 36.68, H 3.08, Cl 54.13; found C 36.70, H 3.05, Cl 54.28.

The mixture of **10b** and **11b** (320 mg) was further chromatographed on silica (40 g); elution with PE gave first 198 mg of a colourless liquid (**10b**, 4%) and then 97 mg of a pale-yellow liquid (**11b**, 2%). The products were, however, still not sufficiently pure to obtain correct elemental analyses.

10b: ^1H NMR (250 MHz, $CDCl_3$): δ = 1.57 (s, 3 H, CH_3); AB subspectrum, centered at δ = 3.18 with δ_A = 3.11 and δ_B = 3.25, J_{AB} = 14.3 Hz (4-H_2); 5.18−5.37 (2 H, 6 lines of the AB part of an ABX sub-spectrum, $H_aH_bC{=}CH$); 5.86−5.97 (1 H, 4 lines of the X part of the ABX sub-spectrum, $H_2C{=}CH$). – ^{13}C NMR/DEPT (62.9 MHz, $CDCl_3$): δ = 25.92 (CH_3), 60.68 (CH_2, C-4), 80.52 (C_q, C-5), 86.14 (C_q, C-3), 104.03 (C_q, $Cl_2C{=}$), 114.91 (CH_2, $H_2C{=}CH$), 139.08 (CH, $H_2C{=}CH$), 152.68 (C_q, C-2).

11b: IR ($CDCl_3$): $\tilde{\nu}$ = 1790 cm^{-1} (C=O), 1750, 1640 (C=C). – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.41 (s, 3 H, CH_3); AB sub-spectrum, centered at δ = 3.13 with δ_A = 3.06 and δ_B = 3.19, J_{AB} = 15.2 Hz (4-CH_2); 5.27 (d, *J* = 17.3 Hz, 1 H, $H_a\mathrm{H}_b$C=CH); 5.40 (d, *J* = 10.9 Hz, 1 H, H_aH_bC=CH); 6.07 (dd, *J* = 10.9 Hz, *J* = 17.3 Hz, 1 H, H_2C=C*H*). – ^{13}C NMR/DEPT (62.9 MHz, $CDCl_3$): δ = 23.21 (CH_3), 49.65 (C_q, C-3), 52.92 (CH_2, C-4), 76.14 (CH_2, C-5), 89.30 (CH_2, C-2), 117.71 (CH_2, H_2*C*=CH), 136.68 (CH, H_2C=*C*H), 191.53 (C_q, C-1).

2,2,7,7-Tetrachloro-4-isopropylcyclohept-4-enone (9c): Prepared from 1.92 g (20 mmol) of 2-isopropylbuta-1,3-diene,[8] 7.34 g (32 mmol) of PCA (**1**), and NaTFE/TFE solution (32 mL, 1 M) as described for **9b** (preceding experiment). Chromatography on silica (250 g) eluting with PE/EA (30:1) gave 3.71 g of a colourless oil (**9c**, 65%). – IR ($CDCl_3$): $\tilde{\nu}$ = 1750 cm^{-1} (C=O). – ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.07 [d, *J* = 6.9 Hz, 6 H, $(CH_3)_2$CH], 2.38 [m_c, *J* = 6.8 Hz, 1 H, $(CH_3)_2$C*H*], 3.45–3.49 (m, 4 H, 3-H_2 and 6-H_2), 5.55–5.57 (m, 1 H, 5-H). – ^{13}C NMR/DEPT (125.77 MHz, $CDCl_3$): δ = 21.01 (CH_3), 37.03 [CH, $(CH_3)_2$*C*H], 45.03 (CH_2, C-6), 47.23 (CH_2, C-3), 86.58 (C_q, C-7), 86.82 (C_q, C-2), 118.51 (CH, C-5), 144.54 (C_q, C-4), 184.28 (C-1). – $C_{10}H_{12}Cl_4O$ (290.0): calcd. C 41.41, H 4.17, Cl 48.90; found C 41.34, H 4.16, Cl 48.74.

2,2,7,7-Tetrachloro-4,5-dimethylcyclohept-4-enone (9d): Prepared from 1.80 g (22 mmol) of 2,3-dimethylbuta-1,3-diene, 4.61 g (20 mmol) of PCA (**1**), and NaTFE/TFE solution (20 mL, 1 M) as described for **9b**. The residue obtained following rotary evaporation was dried at oil-pump pressure and then recrystallized from hexane. Thin white needles of **9d** with m.p. 90.5–91 °C (3.12 g, 57%) were obtained. – IR (KBr): $\tilde{\nu}$ = 1740 cm^{-1} (C=O), 1650 (C=C). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.92 (s, 6 H, CH_3), 3.45 (s, 4 H, 3-H_2 and 6-H_2). – ^{13}C NMR/DEPT (62.9 MHz, $CDCl_3$): δ = 21.68 (CH_3), 51.32 (CH_2, C-3 and C-6), 85.98 (C_q, C-2 and C-7), 131.55 (C_q, C-4 and C-5), 186.63 (C_q, C-1). – $C_9H_{10}Cl_4O$ (276.0): calcd. C 39.17, H 3.65, Cl 51.38; found C 39.31, H 3.75, Cl 51.10.

2,2,7,7-Tetrachloro-3,4,5-trimethylcyclohept-4-enone (9e): A mixture of 2,3-dimethylpenta-1,3-diene and 3,4-dimethylpenta-1,3-diene (ca. 3:2, 960 mg, 10 mmol), prepared from 3,4-dimethylpent-1-en-3-ol by dehydration with $KHSO_4$ and subsequent fractional distillation,[8] was added to PCA (**1**) (2.30 g, 10 mmol). Treatment with 10 mL of NaTFE/TFE solution (1 M) and work-up as described for **9b** gave an oily residue, which was chromatographed on silica (130 g) eluting with PE/EA (30:1). From the eluate, a white solid (1.54 g) was isolated. Recrystallization from pentane gave 1.08 g of white crystals (**9e**, 62%) with m.p. 92–93 °C. – IR ($CDCl_3$): $\tilde{\nu}$ = 1745 cm^{-1} (C=O), 1640 (C=C). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.54 (d, *J* = 6.6 Hz, 3 H, 3-CH_3), 1.76 (s, 3 H, 4-CH_3), 1.91 (s, 3 H, 5-CH_3); AB sub-spectrum, centred at δ = 3.63 with δ_A = 3.39 and δ_B = 3.87, J_{AB} = 15.8 Hz, the lines of the B part appear as doublets with *J* = 0.6 Hz (6-H_2); 3.71 (q, *J* = 6.5 Hz, 1 H, 3-H). – ^{13}C NMR/DEPT (62.9 MHz, $CDCl_3$): δ = 13.57 (CH_3, 4-CH_3), 15.37 (CH_3, 3-CH_3), 21.15 (CH_3, 5-CH_3), 48.59 (CH, C-3), 52.15 (CH_2, C-6), 92.44 (C_q, C-2), 86.20 (C_q, C-7), 135.93 (C_q, C-4), 131.89 (C_q, C-5), 186.74 (C_q, C-1). – $C_{10}H_{12}Cl_4O$ (290.0): calcd. C 41.41, H 4.17, Cl 48.90; found C 41.46, H 4.13, Cl 48.63.

Reaction of 1,2-Bis(methylene)cyclohexane with PCA (1) and NaTFE/TFE: Preparation of 3,3,5,5-Tetrachlorobicyclo[5.4.0]undec-1(7)-en-4-one (9f) and 3,3-Dichloro-2-dichloromethylene-6-methylene-1-oxaspiro[4.5]decane (10f): A mixture of 1,2-bis(methylene)cyclohexane[26] (1.19 g, 11 mmol) and PCA (**1**) (2.30 g, 10 mmol) was cooled in an ice bath. A solution of NaTFE in TFE (10 mL, 1 M) was then added dropwise with magnetic stirring over a period of 2 h. Stirring was continued for 15 min at ice-bath temperature and then for 1 h at room temperature. Water (30 mL) and dichloromethane (15 mL) were then added and the layers were separated. The aqueous layer was extracted with dichloromethane (5 × 15 mL) and the combined dichloromethane phases were washed with brine (5 × 10 mL), dried with sodium sulfate, and concentrated in a rotary evaporator. The residue was dried in vacuo (oil pump) and then subjected to chromatography on silica (180 g) eluting with PE/EA (10:1). The first fraction gave 71 mg of **10f** (2%) as a pale-yellow oil, identified on the basis of its NMR spectra (vide infra). From the second fraction, 1.95 g of **9f** (65%) was obtained as a colourless solid with m.p. 59–60 °C. A sample for analysis was purified by crystallization from pentane; the thin white needles showed m.p. 61–62 °C.

9f: IR (KBr): $\tilde{\nu}$ = 1740 cm^{-1} (C=O). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.59–1.68 (m, 4 H, 9-H_2 and 10-H_2), 2.16–2.21 (m, 4 H, 8-H_2 and 11-H_2), 3.37 (s, 4 H, 2-H_2 and 6-H_2). – ^{13}C NMR/DEPT (62.9 MHz, $CDCl_3$): δ = 22.36 (CH_2, C-9 and C-10), 31.88 (CH_2, C-8 and C-11), 50.21 (CH_2, C-2 and C-6), 86.25 (C_q, C-3 and C-5), 132.32 (C_q, C-1 and C-7), 186.05 (C_q, C-4). – $C_{11}H_{12}Cl_4O$ (276.0): calcd. C 43.74, H 4.00, Cl 46.95; found C 43.75, H 4.03, Cl 46.98.

10f: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.31–2.50 (m, 8 H, 7-H_2, 8-H_2, 9-H_2, and 10-H_2); AB sub-spectrum, centred at δ = 3.26 with δ_A = 3.14 and δ_B = 3.37, J_{AB} = 14.4 Hz (4-H_2); 4.85 (s, 1 H, $H_a\mathrm{H}_b$C=); 4.97 (s, 1 H, H_aH_bC=). – ^{13}C NMR/DEPT (62.9 MHz, $CDCl_3$): δ = 23.94 (CH_2, C-9), 27.32 (CH_2, C-8), 33.82 (CH_2, C-7,), 39.27 (CH_2, C-10), 58.15 (CH_2, C-4), 80.41 (C_q, C-5), 88.54 (C_q, C-3), 107.78 (CH_2, H_2C=), 147.11 (C_q, C-6), 152.54 (C_q, C-2). – The oily substance was not sufficiently pure to give a correct elemental analysis.

4,5-Dimethylcyclohept-4-enone (12d): To a stirred, ice-cooled suspension of zinc powder (1.25 g, 19 mmol) in a mixture of aqueous ammonium acetate solution (2 M, 20 mL) and THF (10 mL), a solution of **9d** (1.10 g, 4 mmol) in THF (10 mL) was added dropwise over a period of 30 min. Stirring was continued for 15 min at ice-bath temperature and then for 2 h at room temperature. The mixture was then filtered through Celite, the Celite was washed with THF, and the filtrate and washings combined. The aqueous layer was separated and extracted with dichloromethane (3 × 10 mL). The combined organic layers (THF and dichloromethane) were concentrated in a rotary evaporator, the residue was taken up in dichloromethane (20 mL), and this solution was washed with brine (20 mL) and dried with sodium sulfate. After filtration and rotary evaporation of the solvent, the residue was chromatographed on silica (40 g) eluting with PE/EA (10:1). From the eluate, a clear colourless liquid (0.37 g, 67%, **12d**) was isolated. – IR ($CDCl_3$): $\tilde{\nu}$ = 1700 cm^{-1} (C=O). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.74 (s, 6 H, CH_3), 2.27–2.32 (m, 4 H), 2.48–2.53 (m, 4 H). – ^{13}C NMR/DEPT (62.9 MHz, $CDCl_3$): δ = 21.08 (CH_3), 30.63 (CH_2, C-3 and C-6), 42.40 (CH_2, C-2 and C-7), 129.73 (C_q, C-4 and C-5), 213.25 (C_q, C-1). – For analysis, a semicarbazone was prepared according to the general procedure given in ref.[27] Recrystallization from 25% ethanol gave an analytically pure solid with m.p. 180–181 °C. – $C_{10}H_{17}N_3O$ (195.3): calcd. C 61.51, H 8.78, N 21.52; found C 61.46, H 8.78, N 21.31.

Bicyclo[5.4.0]undec-1(7)-en-4-one (12f): Prepared from 1.25 g (19 mmol) of zinc powder and 1.21 g (4 mmol) of **9f** as described for **12d** (preceding experiment). Chromatography on silica (50 g) eluting with PE/EA (30:1) gave 0.37 g (58%) of **12f** as a clear, colourless liquid. – IR ($CDCl_3$): $\tilde{\nu}$ = 1705 cm^{-1} (C=O). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.55–1.62 (m, 4 H), 1.98 (br. s, 4 H), 2.20–

2.25 (m, 4 H), 2.52–2.57 (m, 4 H). – ^{13}C NMR/DEPT (62.9 MHz, $CDCl_3$): δ = 23.05 (CH_2, C-9 and C-10), 29.96 (CH_2), 31.94 (CH_2) [C-2, C-6, C-8, and C-11], 42.27 (CH_2, C-3 and C-5), 131.44 (C_q, C-1 and C-7), 213.79 (C_q, C-4). – Semicarbazone (from 25% ethanol): m.p. 198–199 °C (dec.). – $C_{12}H_{19}N_3O$ (221.3): calcd. C 65.13, H 8.65, N 18.99; found C 65.03, H 8.74, N 18.83.

Reaction of 2,2,7,7-Tetrachloro-4,5-dimethylcyclohept-4-enone (9d) with Zinc/Copper Couple: Methyl 2-Chloro-4,5-dimethylcyclohexa-1,4-diene-1-carboxylate (13) and 4,5-Dimethylcyclohept-4-enone (12d): A solution of **9d** in methanol (5 mL), saturated with ammonium chloride, was cooled in an ice bath. To this, zinc/copper couple (1.0 g)[28] was added portionwise under magnetic stirring. The mixture was stirred for 15 min. at ice-bath temperature and then for 17 h at room temperature. The inorganic solid was then filtered off and washed with methanol. The filtrate and washings were combined and treated with a solution of EDTA disodium salt dihydrate (1.5 g) in water (15 mL). After 10 min, the mixture was filtered and the filtrate was diluted with water (15 mL) and extracted with diethyl ether (5 × 10 mL). The combined organic extracts were washed with brine (40 mL) and dried with sodium sulfate. After filtration and concentration in a rotary evaporator, the residue was chromatographed on silica (20 g) eluting with PE/EA (10:1). From the first fraction, 98 mg of a colourless liquid was obtained, the ^{1}H-NMR spectrum of which showed it to consist of **13** (49% yield) contaminated with minor amounts of impurities. The second fraction was found to consist of **12d** (29 mg, 21%) on the basis of its NMR spectra (see above).

13: IR ($CDCl_3$): ṽ = 1720 cm^{-1} (C=O), 1640 (C=C). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.63–1.68 (m, 6 H, 4-CH_3 and 5-CH_3), 2.98–3.00 (m, 4 H, 3-H_2 and 6-H_2), 3.79 (s, 3 H, CH_3O). – ^{13}C NMR/DEPT (62.9 MHz, $CDCl_3$): δ = 17.67 (CH_3, 4-CH_3 and 5-CH_3), 35.98 (CH_2, C-6), 42.28 (CH_2, C-3), 51.82 (CH_3, CH_3O), 121.68 (C_q), 122.38 (C_q), 124.22 (C_q), 135.24 (C_q) [C-1, C-2, C-4, and C-5], 166.56 (C_q, CO_2R). – A satisfactory combustion analysis could not be obtained. GC/EI-MS analysis (50 °C → 250 °C, 10 K/min, t_R = 14.7 min) showed that the substance had been dehydrogenated to methyl 2-chloro-4,5-dimethylbenzoate (**14**) through exposure to air. – EI-MS (70 eV): *m/z* (%) = 200 (18) [M$^+$ from $C_{10}H_{11}{}^{37}ClO_2$], 198 (49) [M$^+$ from $C_{10}H_{11}{}^{35}ClO_2$], 169 (34) [M$^+$ − CH_3O from $C_{10}H_{11}{}^{37}ClO_2$], 168 (23), 167 (100) [M$^+$ − CH_3O from $C_{10}H_{11}{}^{35}ClO_2$], 139 (12), 103 (22), 77 (18), 50 (18). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.25 (s, 3 H), 2.27 (s, 3 H) [4-CH_3 and 5-CH_3], 3.91 (s, 3 H, CH_3O), 7.22 (s, 1 H, 3-H), 7.63 (s, 1 H, 6-H). – ^{13}C NMR/DEPT (62.9 MHz, $CDCl_3$): δ = 19.05 (CH_3), 19.65 (CH_3) [4-CH_3 and 5-CH_3], 52.22 (CH_3, CH_3O), 131.93 (CH, C-3 and C-6), 126.69 (C_q), 130.88 (C_q), 135.27 (C_q), 142.39 (C_q) [C-1, C-2, C-4, and C-5], 166.20 (C_q, CO_2R).

2,7-Dichlorocyclohepta-2,4,6-trienones (2,7-Dichlorotropones) 15 by Dehydrochlorination of 2,2,7,7-Tetrachlorocyclohept-4-enones (9) – General Procedure: Lithium carbonate (2 equiv.) was added to a solution of **9** in dry dimethylformamide (DMF). The mixture was protected from moisture with a calcium chloride guard tube and heated in an oil bath at 90 °C for 1 h under magnetic stirring. After cooling to room temperature, the inorganic salts were filtered off and washed with dichloromethane. The combined filtrate and washings were then treated with water (50 mL) and dichloromethane (20 mL) and the layers were separated. The aqueous layer was extracted with dichloromethane (5 × 20 mL) and the combined organic extracts were washed with water (50 mL) and brine (50 mL), and dried with sodium sulfate. After filtration, the solvent was evaporated and the residue was purified by adsorptive filtration through silica (10 g) eluting with PE/EA (3:1). The filtrate was concentrated and the residue was sublimed at 100 °C/0.001 Torr.

2,7-Dichloro-4-methylcyclohepta-2,4,6-trienone (15b): Prepared from 0.64 g (2.4 mmol) of **9b** and 0.37 g (5 mmol) of lithium carbonate in 10 mL of DMF. The pale-yellow solid (0.42 g, 92%, **15b**) had m.p. 106–107 °C. – IR (KBr): ṽ = 1610 cm^{-1} (C=O), 1590 (C=C). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.49 (d, *J* = 1 Hz, 3 H, CH_3), 6.78 (dd, *J* = 9.9 Hz, 1 H, 5-H), 7.76 (d, *J* = 9.9 Hz, 1 H, 6-H), 7.84 (d, *J* = 1.5 Hz, 1 H, 3-H). – ^{13}C NMR/DEPT (62.9 MHz, $CDCl_3$): δ = 26.24 (CH_3), 129.93 (CH, C-5), 135.74 (CH, C-6), 138.98 (CH, C-3), 142.97 (C_q, C-4), 144.28 (C_q, C-2), 146.06 (C_q, C-7), 173.15 (C_q, C-1). – $C_8H_6Cl_2O$ (189.0): calcd. C 50.83, H 3.20, Cl 37.51; found C 50.59, H 3.29, Cl 37.33.

2,7-Dichloro-4-isopropylcyclohepta-2,4,6-trienone (15c): Prepared from 2.90 g (10 mmol) of **9c** and 1.77 g (24 mmol) of lithium carbonate in 30 mL of DMF. The crude product was purified by chromatography on silica (140 g) eluting with PE/EA (10:1). The pale-yellow solid thus obtained (1.95 g, 90%, **15c**) had m.p. 81.5–82 °C. – IR ($CDCl_3$): ṽ = 1620 cm^{-1} (C=O), 1600 (C=C). – ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.27 [d, *J* = 6.8 Hz, 6 H, $(CH_3)_2CH$], 2.85 [sept, *J* = 6.9 Hz, 1 H, $(CH_3)_2CH$], 6.78 (dd, *J* = 10 Hz, *J* = 1.2 Hz, 1 H, 5-H), 7.82 (d, *J* = 10.1 Hz, 1 H, 6-H), 7.84 (d, *J* = 1.6 Hz, 1 H, 3-H). – ^{13}C NMR/DEPT (62.9 MHz, $CDCl_3$): δ = 22.99 (CH_3), 37.99 [CH, $(CH_3)_2CH$], 127.50 (CH, C-5), 136.03 (CH, C-3), 137.06 (CH, C-6), 144.38 (C_q, C-2), 146.74 (C_q, C-7), 153.05 (C_q, C-4), 173.17 (C_q, C-1). – $C_{10}H_{10}Cl_2O$ (217.1): calcd. C 55.33, H 4.64, Cl 32.66; found C 55.40, H 4.64, Cl 32.56.

2,7-Dichloro-4,5-dimethylcyclohepta-2,4,6-trienone (15d): Prepared from 4.14 g (15 mmol) of **9d** and 2.22 g (30 mmol) of lithium carbonate in 30 mL of DMF. The crude product was filtered through silica (30 g) eluting with PE/EA (3:1). The filtrate was concentrated in vacuo and the residual yellow solid was sublimed at 110 °C/0.001 Torr. The pale-yellow solid thus obtained (2.91 g, 95%, **15d**) had m.p. 161–162 °C. – IR (KBr): ṽ = 1610 cm^{-1}, 1600 (C=O), 1570 (C=C). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.34 (s, 6 H, CH_3), 7.88 (s, 2 H, 3-H and 6-H). – ^{13}C NMR/DEPT (62.9 MHz, $CDCl_3$): δ = 24.75 (CH_3), 140.04 (C_q, C-4 and C-5), 140.51 (CH, C-3 and C-6), 143.05 (C_q, C-2 and C-7), 171.92 (C_q, C-1). – $C_9H_8Cl_2O$ (203.1): calcd. C 53.23, H 3.97, Cl 34.92; found C 53.17, H 3.89, Cl 35.22.

2,7-Dichloro-3,4,5-trimethylcyclohepta-2,4,6-trienone (15e): Prepared from 0.29 g (1 mmol) of **9e** and 0.30 g (4 mmol) of lithium carbonate in 10 mL of DMF. The crude product was purified by chromatography on silica (30 g) eluting with PE/EA (7:1). The eluate was concentrated in vacuo and the residual pale-yellow solid (0.15 g) was sublimed at 90 °C/0.005 Torr. The almost colourless solid (0.14 g, 65%, **15e**) had m.p. 128–129 °C. – IR ($CDCl_3$): ṽ = 1620 cm^{-1} (C=O), 1590 (sh, C=C). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.25 (s, 3 H, 4-CH_3), 2.30 (d, *J* = 0.7 Hz, 3 H, 5-CH_3), 2.52 (s, 3 H, 3-CH_3), 7.60 (s, 1 H, 6-H). – ^{13}C NMR/DEPT (125.77 MHz, $CDCl_3$): δ = 22.32 (3-CH_3), 25.17 (CH_3), 25.28 (CH_3) [4-CH_3 and 5-CH_3], 138.64 (CH, C-6), 135.31 (C_q), 138.57 (C_q), 140.91 (C_q), 141.08 (C_q) [C-3, C-4, C-5, and C-7], 146.75 (C_q, C-2), 174.90 (C_q, C-1). – $C_{10}H_{10}Cl_2O$ (217.1): calcd. C 55.33, H 4.64, Cl 32.66; found C 55.40, H 4.71, Cl 32.90.

3,5-Dichlorobicyclo[5.4.0]undeca-1(7),2,5-trien-4-one (15f): Prepared from 0.62 g (2 mmol) of **9f** and 0.30 g (4 mmol) of lithium carbonate in 10 mL of DMF. The crude product was sublimed at 110 °C/0.001 Torr to give 0.45 g (98%) of **15f** as lemon-coloured crystals from diethyl ether with m.p. 149.5–150 °C. – IR ($CDCl_3$): ṽ = 1620 cm^{-1} (C=O), 1590 (C=C). – ^{1}H NMR (250 MHz,

$CDCl_3$): δ = 1.76–1.82 (m, 4 H), 2.70–2.75 (m, 4 H), 7.68 (s, 2 H, 2-H and 6-H). – ^{13}C NMR/DEPT (62.9 MHz, $CDCl_3$): δ = 21.73 (CH_2, C-9 and C-10), 33.54 (CH_2, C-8 and C-11), 140.49 (C_q, C-1 and C-7), 140.59 (CH, C-2 and C-6), 142.26 (C_q, C-3 and C-5), 172.54 (C_q, C-4). – $C_{11}H_{10}Cl_2O$ (229.1): calcd. C 57.67, H 4.40, Cl 30.95; found C 57.65, H 4.42, Cl 31.22.

4-Isopropylcyclohepta-2,4,6-trienone (16, Nezukone): To a solution of 0.58 g (2 mmol) of **9c** in 10 mL of dry benzene, 10 mg of azoisobutyronitrile and 1 mL (4 mmol) of freshly distilled tributylstannane were added under argon. The stirred mixture was heated to 60 °C in an oil bath and maintained at this temperature for 3 h. The bulk of the solvent was then removed by rotary evaporation. The residue was treated with diethyl ether (20 mL) and 10% aqueous potassium fluoride solution (20 mL). The resulting mixture was stirred for 1 h and then suction-filtered. The inorganic solid was thoroughly washed with diethyl ether. The aqueous layer was extracted with diethyl ether (3 × 10 mL) and the combined organic phases were washed with brine (20 mL). After drying with sodium sulfate and filtration, the solvent was removed by rotary evaporation. Dry DMF (10 mL) and lithium carbonate (0.18 g, 2.4 mmol) were then added to the residue and the mixture was heated at 120 °C in an oil bath for 3 h under protection from moisture. After cooling, the inorganic solid was filtered off and washed with dichloromethane. Water (20 mL) and dichloromethane (20 mL) were added to the filtrate and the layers were separated. The aqueous layer was extracted with dichloromethane (5 × 10 mL) and the combined organic phases were washed with water (20 mL) and brine (20 mL), and dried with sodium sulfate. After filtration, the solvent was removed by rotary evaporation and the residue was purified by chromatography on silica (25 g) eluting with PE/EA (3:1). A yellow oil (100 mg) was isolated. The ^1H- and ^{13}C-NMR spectra were in agreement with the data given for **16** in ref.[17] and ref.[29], apart from signals due to a slight impurity that could not be removed by chromatography; yield ca. 33%.

Reaction of 2,7-Dichloro-4,5-dimethylcyclohepta-2,4,6-trienone (15d) with Aqueous Formic Acid: Preparation of 2-Chloro-7-hydroxy-4,5-dimethylcyclohepta-2,4,6-trienone (18) and 2,7-Dihydroxy-4,5-dimethylcyclohepta-2,4,6-trienone (17): To a solution of 2.03 g (10 mmol) of **15d** in formic acid (36 mL) was added water (24 mL) and the mixture was refluxed for 13 d. Thereafter, the starting material **15d** could no longer be detected by TLC. The solution was concentrated under reduced pressure and the remaining formic acid was removed by azeotropic distillation with toluene in a rotary evaporator. The residue was dried in vacuo (oil pump) and then sublimed at 100 °C/0.001 Torr to give 1.74 g of a yellow solid. It was dissolved in a few mL of dichloromethane and this solution was filtered through Celite (7 g) that had been pretreated with phosphoric acid. Elution with dichloromethane gave two fractions, from which the solvent was removed in vacuo and the residues were purified by sublimation. Sublimation of the first fraction at 100 °C/0.001 Torr gave 1.62 g (88%) of 2-chloro-7-hydroxy-4,5-dimethylcyclohepta-2,4,6-trienone (**18**) as a yellow solid with m.p. 165.5–166.5 °C. – IR (KBr): $\tilde{\nu}$ = 3200 cm^{-1} (OH), 1700, 1590, 1570, 1540 (C=O and C=C). – ^1H NMR (250 MHz, $[D_6]$DMSO): δ = 2.29 (s, 3 H), 2.33 (s, 3 H), [4-CH_3 and 5-CH_3], 7.33 (s, 1 H, 3-H), 7.92 (s, 1 H, 6-H). – ^{13}C NMR/DEPT (62.9 MHz, $[D_6]$DMSO): δ = 23.91 (CH_3), 25.15 (CH_3) [4-CH_3 and 5-CH_3], 124.45 (CH, C-6), 133.76 (C_q, C-2), 134.69 (C_q, C-4), 139.58 (CH, C-3), 146.99 (C_q, C-5), 164.03 (C_q, C-7), 166.67 (C_q, C-1). – $C_9H_9ClO_2$ (184.6): calcd. C 58.55, H 4.91, Cl 19.20; found C 58.66, H 4.90, Cl 18.95. – Sublimation of the second fraction at 60 °C/0.001 Torr yielded 79 mg (5%) of 2,7-dihydroxy-4,5-dimethylcyclohepta-2,4,6-trienone (**17**) as a pale-yellow solid with m.p. 174–176 °C. – IR (KBr): $\tilde{\nu}$ = 3220 cm^{-1} (OH), 1600, 1500 (C=O and C=C). – ^1H NMR (250 MHz, $CDCl_3$): δ = 2.40 (s, 6 H, 4-CH_3 and 5-CH_3), 7.50 (s, 2 H, 3-H and 6-H), 8.00 (v. br. s, 2 H, OH). – ^{13}C NMR/DEPT (62.9 MHz, $CDCl_3$): δ = 25.69 (CH_3, 4-CH_3 and 5-CH_3), 124.58 (CH, C-3 and C-6), 139.48 (C_q, C-4 and C-5), 157.23 (C_q, C-2 and C-7), 166.07 (C_q, C-1). – EI-MS (70 eV): *m/z* (%): = 166 (100) [M^+ from $C_9H_{10}O_3$], 138 (57) [M^+ − CO], 137 (28), 123 (62), 120 (13), 92 (27), 91 (24), 77 (13), 65 (18), 51 (13), 41 (13), 39 (24), 28 (24). – HRMS: calcd. for $C_9H_{10}O_3$ 166.0630; found 166.0630.

2-Hydroxy-4,5-dimethylcyclohepta-2,4,6-trienone (19): Palladium (10%) on charcoal (Fluka) (55 mg) was added to a solution of **18** (184 mg, 1 mmol) in aqueous potassium hydroxide solution (10 mL, 0.5 M). The resulting mixture was subsequently stirred under hydrogen at room temperature. When 23 cm^3 of hydrogen gas had been taken up, the solution was filtered and the catalyst was washed with aqueous potassium hydroxide solution (0.5 M). The combined filtrate and washings were acidified to pH = 2 with hydrochloric acid (2 M) and then extracted with dichloromethane (5 × 10 mL). The combined organic extracts were washed with brine (20 mL) and dried with sodium sulfate. After filtration, the solvent was removed in a rotary evaporator and the residue was sublimed at 70 °C/0.001 Torr to give a pale-yellow solid (133 mg, 90%, **19**) with m.p. 153.5–154.5 °C. – IR ($CDCl_3$): $\tilde{\nu}$ = 3190 cm^{-1} (OH), 1700, 1610, 1600 (C=O and C=C). – ^1H NMR (500 MHz, $CDCl_3$): δ = 2.34 (s, 3 H), 2.39 (s, 3 H), [4-CH_3 and 5-CH_3]; AB sub-spectrum, centred at δ = 7.20 with δ_A = 7.13, δ_B = 7.27, J_{AB} = 11.4 Hz, 2 H [6-H and 7-H], 7.39 (s, 1 H, 3-H), 8.65 (v. br. s, 1 H, OH). – ^{13}C NMR/DEPT (125.77 MHz, $CDCl_3$): δ = 25.19 (CH_3), 26.52 (CH_3) [4-CH_3 and 5-CH_3], 121.43 (CH, C-3), 127.91 (CH, C-7), 138.17 (C_q, C-5), 137.76 (CH, C-6), 148.48 (C_q, C-4), 168.80 (C_q, C-2), 169.99 (C_q, C-1). – $C_9H_{10}O_2$ (150.2): calcd. C 71.98, H 6.71; found C 71.97, H 6.85.

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