Diels-Alder Reactions of 5,5,5-Trichloro-3-penten-2-one and Related Compounds[1]

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The Diels-Alder reaction of 5,5,5-trichloro-3-penten-2-one (**1a**) with cyclopentadiene afforded *exo*-2-acetyl-*endo*-3-trichloromethylbicyclo[2.2.1]hept-5-ene (**2a**) stereoselectively. The stereochemistry of the reactions of cyclopentadiene with several γ-chlorinated α,β-unsaturated ketones was examined. The *endo*-directive abilities decreased in the following order: $CCl_3 > CCl_2CH_3$, $CHCl_2$, $CCl(CH_3)_2 > CH(CH_3)_2 > CH_3$. Compound **1a** reacted with butadiene and furan to give 4-acetyl-5-trichloromethylcyclohexene (**3**) and 4-(2-furyl)-5,5,5-trichloropentan-2-one (**7**) respectively.

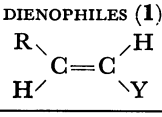
We have recently published several works on the allylic rearrangement of 5,5,5-trichloro-3-penten-2-one (**1a**)[2,3] and on the reaction of **1a** with nucleophiles.[4] To expand the knowledge of its chemical properties, especially its dienophilic reactivity, we have now carried out the reaction of the compound **1a** and related compounds with such dienes as cyclopentadiene, butadiene, and furan.

A great number of examples have manifested a wide applicability of the well-known rule[5] of *endo* addition in the Diels-Alder reaction. However, many examples have also disclosed deviations from the *endo* rule.[6-8] Williamson and Hsu have reported that pentachlorocyclopentadiene with many dienophiles gives bicycloheptene Diels-Alder adducts in which the predominant isomer has the chlorine atom on the bridge *anti* to the double bond.[9] Recently, McBee *et al.* have reported that fluorine substituents dominate the stereochemical course of the Diels-Alder reactions.[10]

Results and Discussion

A list of dienophiles prepared for this study is given in Table 1. The methyl ketone **1d** was prepared by the reaction of triethylphosphonoacetone with 2-chloro-2-methylpropanal in the presence of sodium hydride. Compound **1i** was prepared by the condensation of chloral with 4-methyl-2-pentanone. Other α,β-unsaturated ketones were prepared by the methods described in the literature. All the dienophiles listed here were assigned to the *trans* configuration on the basis of the large coupling constants (J=14—17 Hz) observed of olefin protons and the infrared absorption at *ca.* 970 cm^{-1}.

Table 1. Preparation and properties of dienophiles (**1**)



Compd.	R	Y	Yield %	Bp, °C/mmHg (Mp, °C)	Ref.
1a	CCl_3	$COCH_3$	80	95—100/20	a
1b	$CHCl_2$	$COCH_3$	65	91—92/17	b
1c	CCl_2CH_3	$COCH_3$	52	77—80/6	b
1d	$CCl(CH_3)_2$	$COCH_3$	55	53—55/4	g
1e	$CH(CH_3)_2$	$COCH_3$	13	59—61/25	c
1f	CH_3	$COCH_3$	41	119—125	d
1g	CCl_3	COC_6H_5	86	(97—99)	e
1h	CH_3	COC_6H_5	12	140—145/30	f
1i	CCl_3	$COCH_2$-$CH(CH_3)_2$	83	96—97/6	g

a) Ref. 2. b) Ref. 3. c) E. N. Eccot and R. P. Linstead, *J. Chem. Soc.*, **1930**, 905. d) Ref. 17. e) W. Koenigs, *Chem. Ber.*, **25**, 795 (1892). f) Ref. 18. g) New compound.

When the trichloromethyl compound **1a** (*trans*) was allowed to react with cyclopentadiene at 90—100 °C for 40 hr, a cycloaddition product (**2a**) was formed in a high yield. The yield was quantitative when the reaction was conducted for 3 day, even at room temperature. The elemental analysis and mass spectral data clearly indicated the formation of the 1 : 1 adduct of **1a** and cyclopentadiene (see Table 3). The infrared spectrum of **2a** showed a strong band at 1724 cm^{-1} due to an isolated carbonyl group and a weak band at 1583 cm^{-1} due to a norbornene ring double bond. In the NMR spectrum of **2a**, which is shown in Fig. 1, the signals at 2.32 ppm (clean singlet, 3H) and at 4.01 ppm (q, 1H, J=3.4 and 5.5 Hz) are attributable to acetyl protons and a C_3-methine proton[11] respectively. The signals of two olefin protons appeared at 6.28 ppm (t, 2H, J=1.3 Hz). It is reasonable to conclude that the adduct **2a** has an *exo*-2-acetyl-*endo*-3-trichloromethyl structure, because signals of olefin protons in *endo*-2-acetylbicyclo[2.2.1]hept-5-ene tend to appear as two multiplets, with the result that the resonance due to the C_6-olefin proton is shifted to a higher field than that of the *exo*-acetyl isomer.[12] The

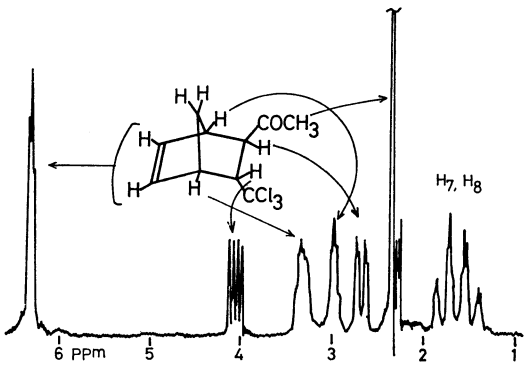
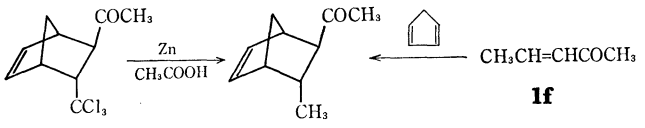


Fig. 1. NMR spectrum of *exo*-2-acetyl-*endo*-3-trichloromethylbicyclo[2.2.1]hept-5-ene (**2a**) in $CDCl_3$.

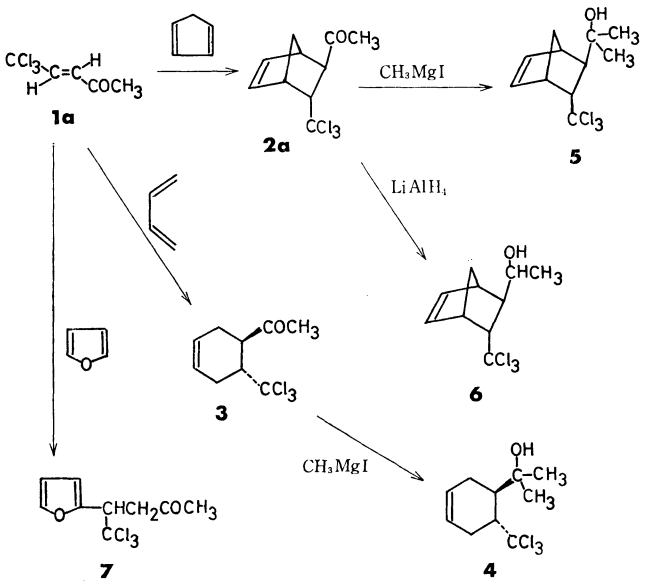
endo structure of **2a** was further substantiated by the fact that it was reduced with zinc in acetic acid, giving *exo*-2-acetyl-*endo*-3-methylbicyclo[2.2.1]hept-5-ene (*endo* **2f**), one of the two isomers derived from the reaction of 3-penten-2-one (**1f**) with cyclopentadiene, whose structure has been unambiguously established. The NMR spectrum ($COCH_3$, 2.20 ppm; CH_3, 0.93 ppm) of the compound **2f** which we obtained was identical with that of the authentic sample of the *endo* **2f** prepared independently by Kobuke's procedure.[8]



2a *endo*-**2f** **1f**

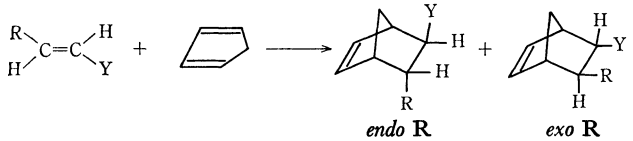
The yields, *endo* percentages, and physical properties of the adducts of cyclopentadiene with ketones listed in Table 1 are summarized in Table 2. Their elemental analyses and the spectral data are tabulated in Table 3. The configurational determination of the Diels-Alder adducts was accomplished by analyzing the NMR spectrum. The NMR spectra of trichloromethyl compounds, **2a**, **2g**, and **2i**, which were free from an *exo* component, showed clear patterns of chemical shifts and coupling constants. Those of other compounds containing both *endo* and *exo* components showed more complicated patterns. The C_3-protons of compounds **2a**, **2c**, **2g**, and **2i** showed a sharp quartet with a small width of the peak at half-height (*ca.* 0.75 Hz),[13] indicating that these protons are in the *exo* configuration. If they were in the *endo* configuration, a long-range coupling between the C_3-proton and the bridge proton would be expected to work over the coplanar W in the order of 1—2 Hz.[9] The signals of the C_2-protons of the adducts **2** usually appeared at 2.5—3 ppm. The methyl protons of the *exo*-acetyl isomers appeared as a singlet at a lower field than those of the *endo*-acetyl isomers.[14] The configurations of compounds **2b**, **2d**, **2e**, and **2f** were determined on the basis of the signals due to acetyl and olefin protons, while that of **2h** was determined by comparing its NMR spectrum with that of **2f**, especially on the basis of the signals due to olefin and methyl protons.

From the data given in Table 2, it is apparent that chlorine substituents exert the principal influence on the stereochemical course of the Diels-Alder reaction.[15] It should be noted as remarkable that the dienophiles **1a**, **1g**, and **1i**, each possessing a trichloromethyl group, afforded *endo* products exclusively. When we compare the *endo* percentages of **2a**, **2g**, and **2i** with each other, and also those of **2f** and **2h** with each other, it is understandable that the group Y is of minor importance in predicting the stereochemical course of the reaction of the dienophiles **1** with cyclopentadiene. Thus, the *endo*-directive abilities of substituents in the Diels-Alder reactions of a series of γ-chlorinated α,β-unsaturated ketones with cyclopentadiene may be regarded as decreasing in this order: $CCl_3 > CCl_2CH_3$, $CHCl_2$,



Scheme 1.

Table 2. The *endo* percentage and properties of Diels-Alder adducts (**2**)

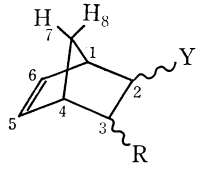


endo R *exo* R

Compd.	R	Y	Yield %	*endo* R, %	Bp, °C/mmHg[a] (Mp, °C)
2a	CCl_3	$COCH_3$	83—96	100[c]	131—132/7 (49.0—50.5)[d]
2b	$CHCl_2$	$COCH_3$	65	72	102—112/5 (66.0—67.5)[d]
2c	CCl_2CH_3	$COCH_3$	72	76	117—118/0.6
2d	$CCl(CH_3)_2$	$COCH_3$	9	70	94—95/4
2e	$CH(CH_3)_2$	$COCH_3$	11	60	70—81/4
2f	CH_3	$COCH_3$	62	35[b]	
2g	CCl_3	COC_6H_5	59	100	(65.0—67.5)[d]
2h	CH_3	COC_6H_5	68	31	119—121/0.5
2i	CCl_3	$COCH_2CH(CH_3)_2$	62	100	108/0.42

a) Data of the *exo*:*endo* mixture. b) The *endo* percentage was determined by glpc analysis, and it was nearly identical with that of Kobuke's experiment.[8] c) The configuration of the adduct obtained from the reaction at room temperature for 3 day was the same one. d) Recrystallized from petroleum ether (bp 45—51°C).

TABLE 3. ANALYSES AND PROPERTIES OF DIELS-ALDER ADDUCTS (**2**)



Compd.[a]	Anal (Calcd), % C	H	IR[b] and MS *m/e* (rel. intensity)	NMR[c] δ ppm
2a	47.17 (47.37	4.77 4.37)	IR 1724, 1583, 795 cm^{-1} MS 252 (0.2, M^+), 217 (5, M^+-Cl), 173 (10), 139 (22), 135 (100)	1.42 (dq, H_8), 1.73 (dt, H_7), 2.32 (s, *exo* $COCH_3$), 2.65 (dd, H_2), 2.98 (dt, H_1), 3.27 (m, H_4), 4.01 (dd, H_3), 6.28 (t, H_5 and H_6), J_{34}=3.4 Hz, J_{23}=5.5 Hz, J_{56}=1.3 Hz, J_{78}=8.8 Hz
2b	54.60 (54.81	5.58 5.52)	IR 1715, 1577, 742 cm^{-1}	1.30—1.90 (m, H_7 and H_8), 2.15 (s, 0.9 H, *endo* $COCH_3$), 2.24 (s, 2.1 H, *exo* $COCH_3$), 2.30—3.20 (m, H_1, H_2, and H_4), 3.20—3.60 (m, H_3), 5.01 (d, 0.72H, J=11 Hz, *endo* $CHCl_2$), 5.59 (d, 0.28 H, J=9 Hz, *exo* $CHCl_2$), 5.80—6.60 (m, H_5 and H_6)
2c	56.97 (56.69	6.10 6.05)	IR 1720, 1580, 700 cm^{-1}	1.22—1.93 (m, H_7 and H_8), 2.05 (s, 2.28 H, *endo* CCl_2CH_3), 2.12 (s, 0.72H, *exo* CCl_2CH_3), 2.21 (s, 0.72H, *endo* $COCH_3$), 2.29 (s, 2.28H, *exo* $COCH_3$), 3.54 (q, 0.76H, *exo* H_3), 5.83—6.56 (m, H_5 and H_6)
2d	67.68 (67.76	8.20 8.06)	IR 1710, 1575 cm^{-1}	1.21—1.87 (m, H_7 and H_8), 1.48 (d, 4.2H, J=2 Hz, *endo* $CCl(CH_3)_2$), 1.69 (d, 1.8H, J=7 Hz, *exo* $CCl(CH_3)_2$), 2.22 (s, 0.9H, *endo* $COCH_3$), 2.31 (s, 2.1H, *exo* $COCH_3$), 2.42—2.63 (m, H_2), 2.69—3.32 (m, H_1, H_4 and H_3), 5.77—6.55 (m, H_5 and H_6)
2e[d]			IR 1710, 1575 cm^{-1}	0.89 (d, 3.6H, J=8 Hz, *endo* $CH(C\underline{H}_3)_2$), 0.98 (d, 2.4H, J=7 Hz, *exo* $CH(C\underline{H}_3)_2$), 1.10—1.30 (m, $C\underline{H}(CH_3)_2$), 1.30—1.60 (m, H_7 and H_8), 2.12 (s, 1.2H, *endo* $COCH_3$), 2.23 (s, 1.8H, *exo* $COCH_3$), 2.50—3.00 (m, H_1 and H_4), 1.90—3.30 (m, H_2 and H_3), 5.70—6.53 (m, H_5 and H_6)
2g	56.80 (57.08	4.10 4.15)	IR 1680, 1604, 1585 cm^{-1} MS 314 (0.5, M^+), 279 (7, M^+-Cl), 278 (8, M^+-HCl), 196 (100)	1.33—2.21 (m, H_7 and H_8), 3.00 (m, H_2), 3.31—3.61 (m, H_1 and H_4), 4.30 (dd, H_3), 6.36 (t, H_5 and H_6), 7.43—8.20 (m, COC_6H_5); J_{34}=3 Hz, J_{23}=6 Hz, J_{16}=J_{45}=J_{56}=2 Hz
2h	84.52 (84.87	7.96 7.60)	IR 1680, 1601, 1582 cm^{-1}	0.89 (d, 0.9H, J=8 Hz, CH_3), 1.17 (d, 2.1H, J=8 Hz, CH_5), 1.30—1.95 (m, H_7 and H_8), 5.60—6.45(m, H_5 and H_6), 7.19—8.24 (m, COC_6H_5)
2i	58.90 (58.82	5.73 5.80)	IR 1715, 1578 cm^{-1}	0.94 (d, J=7 Hz, $CH(C\underline{H}_3)_2$), 1.26—1.90 (m, H_7 and H_8), 1.90—2.30 (m, $C\underline{H}(CH_3)_2$), 2.48 (d, J=5 Hz, $COCH_2$–), 2.60 (dd, H_2), 2.90 (m, H_1), 3.30 (m, H_4), 4.39 (dd, H_3), 6.24 (t, H_5 and H_6); J_{12}=2 Hz, J_{23}=6 Hz, J_{34}=3 Hz, J_{16}=J_{56}=J_{45}=2 Hz

a) *Endo* and *exo* materials from **2f** were separated by glpc and each component was analyzed. NMR spectra were identical with those of authentic samples.[8] b) Compound **2g** was measured by a Nujol method. All the others were measured in neat. c) Measured in $CDCl_3$. d) This compound was too volatile to be analyzed.

$CCl(CH_3)_2$>$CH(CH_3)_2$>CH_3.

Compound **1a** further gave the Diels-Alder adduct **3** with butadiene, as is shown in Scheme 1. The adduct **3** was converted to 4-(1-hydroxy-1-methylethyl)-5-trichloromethylcyclohexene (**4**) in a 50% yield by the action of methylmagnesium iodide. On the other hand, the Grignard reaction of the adduct **2a** afforded 2-(1-hydroxy-1-methylethyl)-3-trichloromethylbicyclo[2.2.1]hept-5-ene (**5**) in only a 5% yield, probably because of the steric restriction of the norbornene skeleton. The reduction of **2a** with lithium aluminum hydride gave the corresponding carbinol **6** in a 38% yield. When the dienophile **1a** was allowed to react with furan, a substitution-addition product **7** was obtained in a low yield.[16] The structural assignments of these compounds were accomplished by the aid of the IR, NMR, and Mass spectra and by elemental analyses (see Experimental).

Experimental

The melting points and boiling points are uncorrected. The elemental analyses were carried out by Mr. Eiichiro Amano. The analytical determinations by glpc were performed on a Hitachi K-53 model gas chromatograph fitted with 10% Apiezon Grease L on Chromosorb W (3 mm o.d.×1 m). The preparative isolations by glpc were performed on 10% Apiezon Grease L on Chromosorb W (3 mm o.d.×2.25 m). The mass spectra were measured on a Hitachi RMS-4 model mass spectrometer with an ionization energy of 70 eV. We are indebted to Mr. Heizan Kawamoto and Miss Hiromi Ootani for the NMR (60 MHz) measurement.

Compounds **1a**, **1b**, and **1g** were prepared by the procedures described in the literature. Compound **1f** was prepared by the method of Claisen[17] by dehydrating 4-hydroxypentan-2-one: bp 119—125 °C; IR (cm^{-1}, liquid) 1675 (C=O) and 1635 (C=C). Ethylideneacetophenone (**1h**) was prepared by the method of Kohler from crotonyl chloride and benzene[18]: bp 140—145 °C/30 mmHg; IR (cm^{-1}, liquid) 1670 (C=O), 1628 (C=C), 1603, 1585 (benzene C=C). Cyclopentadiene was generated from its dimer by a standard procedure[19] just prior to use.

*5-Chloro-5-methyl-3-hexen-2-one (**1d**).* To a mixed solution of 1.9 g (0.04 mol) of sodium hydride (52% in mineral oil) in 40 ml of dry tetrahydrofuran (THF) was added 7.8 g (0.04 mol) of diethylphosphonoacetone at 30—35 °C with stirring. Freshly-distilled 2-chloro-2-methylpropanal (4.3g, 0.04 mol) was then added at 20—25 °C, and the mixture was stirred for 15 min at 45 °C. After 50 ml of water had then been added, the organic layer was extracted with ether. The ethereal layer was washed with water and dried over $MgSO_4$. After the removal of the solvent, the residue was distilled to give 3.1 g (55%) of **1d**: bp 53—55 °C/4 mmHg; IR (cm^{-1}, liquid) 1695 (cisoid C=O), 1670 (transoid C=O), 1625 (C=C); NMR ($CDCl_3$) δ 1.73 (s, 6H, $CCl(CH_3)_2$), 2.28 (s, 3H, $COCH_3$), 6.21 and 6.92 (2d, 2H, J=17 Hz, -CH=CH-).

Found: C, 57.10; H, 7.70. Calcd for $C_7H_{11}ClO$: C, 57.34; H, 7.56.

*6-Methyl-1,1,1-trichloro-2-hepten-4-one (**1i**).* A mixture of chloral hydrate (82 g, 0.5 mol), 4-methyl-2-pentanone (60 g, 0.6 mol), acetic anhydride (50 g, 0.5 mol), glacial acetic acid (30 g, 0.5 mol), and sodium acetate (2.0 g, 0.024 mol) was refluxed for 24 hr. After the removal of the solvent, the residue was dissolved in ether and the ether solution was treated with charcoal. After most of the ether had been removed, the precipitate was collected and recrystallized from ether to give 51.4 g (42%) of 2-hydroxy-6-methyl-1,1,1-trichloroheptan-4-one:[20] mp 86—87 °C; IR (cm^{-1}, nujol) 3400 (OH), 1710 (C=O), 820, 793; NMR ($CDCl_3$) δ 0.97 (d, 6H, J=6 Hz, $-CH(C\underline{H}_3)_2$), 2.23 (m, 1H, $-C\underline{H}(CH_3)_2$), 2.27 (d, 2H, J=12 Hz, $C\underline{H}_2CH(CH_3)_2$), 3.00 (m, 2H, $-CH(OH)C\underline{H}_2-$), 3.60 (broad s, 1H, OH), and 4.69 (dd, 1H, J=4 and 7 Hz, $>C\underline{H}(OH)$).

Found: C, 38.75; H, 5.30. Calcd for $C_8H_{13}Cl_3O_2$: C, 38.82; H, 5.29.

To 320 ml of conc. H_2SO_4 was added 51 g (0.21 mol) of 2-hydroxy-6-methyl-1,1,1-trichloroheptan-4-one at −5—0 °C with stirring. After the mixture had been stirred for 4 hr at room temperature, it was poured onto crashed ice. The organic layer was extracted with ether, and the ethereal layer was washed with water and then dried over $MgSO_4$. After the evaporation of the solvent, the residue was distilled to yield 40.4 g (83%) of **1i**: bp 96—97 °C/6 mmHg; IR (cm^{-1}, liquid) 1705 (cisoid C=O), 1678 (transoid C=O), 1632 (C=C); NMR ($CDCl_3$) δ 0.98 (d, 6H, J=6 Hz, $2CH_3$), 1.80—2.70 (m, 1H, $-C\underline{H}(CH_3)_2$), 2.50 (d, 2H, J=5 Hz, $-C\underline{H}_2CH(CH_3)_2$), 6.51 (d, 1H, J=17 Hz, $-CH=C\underline{H}CO$), 7.01 (d, 1H, J=17 Hz, $CCl_3C\underline{H}=CH-$).

Found: C, 41.85; H, 4.78. Calcd for $C_8H_{11}Cl_3O$: C, 41.87; H, 4.83.

Diels-Alder Additions. Most of the reactions were conducted in autoclaves or ampoules. A solution of two mols of diene and one mol of dienophile in benzene ([c]=*ca.* 10 mol/l) was heated at 90—100 °C for 40 hr,[21] under an atmosphere of nitrogen. After the solvent had then been evaporated, the residue was distilled to give nearly pure Diels-Alder adducts. The crystallized materials were collected and purified by recrystallization from petroleum ether (bp 45—50 °C). If necessary, the microanalyses and spectral measurements were performed on samples collected by glpc or tlc.

exo-*2-Acetyl*-endo-*3-methylbicyclo[2.2.1]hept-5-ene* (*endo* **2f**). To a solution of 5.1 g (0.02 mol) of **2a** in 10 ml of acetic acid was added, in several portions, 5.2 g (0.08 mol) of zinc powder at 0—5 °C. The mixture was then stirred at 5 °C for 30 min. Zinc chloride and the resinous material were filtered off, and the filtrate was extracted with ether. The ethereal layer was washed with water and dried over $MgSO_4$. The removal of the solvent left 1.9 g of a brown oil which, on distillation, gave 0.7 g of a clean oil: bp 67—69 °C/7 mmHg. The glpc analysis (column temp., 110 °C; carrier gas, N_2, 0.5 kg/cm², 40 ml/min) of this oil showed two peaks. The peaks, retention times (min), and peak areas were as follows: 1, 7.3, 57%; 2, 8.0, 43%.

The component 1 collected by preparative glpc was identified as the *endo* **2f** by comparison of the NMR spectrum and retention time with that of the *endo* isomer isolated from the Diels-Alder adducts (see Table 2) of 3-penten-2-one (**1f**) with cyclopentadiene: yield, 13%: IR (cm^{-1}, liquid) 1700 (C=O), 1570 (C=C); NMR ($CDCl_3$)[8] δ 0.93 (d, 3H, J=7 Hz, *endo*-CH_3), 2.20 (s, 3H, *exo*-$COCH_3$), 6.02—6.35 (m, 2H, olefin protons); Mass *m/e* (rel. intensity) 150 (M^+, 20), 135 (M^+-CH_3, 31), 126 (66), 117 (M^+-COCH_3, 26), 107 (71), 105 (56), 92 (56), 91 (79), 85 (100), 79 (75).

The structure of the component 2 collected by preparative glpc was not resolved: IR (cm^{-1}, liquid) 1710, 1635, 1360, 1160, 910, 740; NMR ($CDCl_3$) δ 0.80—1.35 (m, 1H), 2.15 (s, 3H, $COCH_3$), 2.0—3.6 (m, 5H), 4.85—5.22 (m, 2H), 5.68 (s, 2H), 5.52—6.15 (m, 1H); Mass *m/e* (rel. intensity) 150 (2), 135 (10), 117 (38), 93 (56), 92 (100), 91 (86), 79 (58), 77 (60), 66 (58).

4-Acetyl-5-trichloromethylcyclohexene (**3**) was prepared by the Diels-Alder reaction of **1a** with butadiene: yield, 77%; bp 114—117 °C/3 mmHg; IR (cm^{-1}, liquid) 1718 (C=O), 1670 (C=C); NMR ($CDCl_3$) δ 1.88—3.96 (m, 4H, H_3 and H_6), 2.30 (s, 3H, $COCH_3$), 3.17 (q, 1H, $>C\underline{H}COCH_3$), 3.41 (q, 1H, $CHCCl_3$), 5.79 (t, 2H, -CH=CH-); Mass *m/e* (rel. intensity) 240 (0.6, M^+), 204 (4, M^+-HCl), 169 (39), 162 (39), 127 (100), 123 (58), 105 (44), 91 (87), 79 (90).

Found: C, 44.42; H, 4.23. Calcd for $C_9H_{11}Cl_3O$: C, 44.75; H, 4.59.

*4-(1-Hydroxy-1-methylethyl)-5-trichloromethylcyclohexene (**4**).* The ethereal solution of methyl magnesium iodide was prepared from magnesium (0.61 g, 0.025 mol), methyl iodide (4.3 g, 0.030 mol), and ether (20 ml) in the usual manner. To this solution was added a solution of 3.0 g (0.015 mol) of **3** in 20 ml of dry ether at −10—−5 °C. After the complete addition, the mixture was stirred for 30 min at room temperature. It was then acidified with 10% HCl at −5 °C, and the organic layer was extracted with ether. The extract was washed with saturated sodium chloride solution and dried

over $MgSO_4$. The subsequent removal of the solvent gave 2.8 g of a brown oil. The tlc analysis[22] of this oil showed two spots at R_f values of 0.42 and 0.52 in the ratio of 3: 1. The spot of **3** appeared at R_f 0.52. The component with the R_f value of 0.42 separated by preparative tlc was identified as **4**: yield, 50%; IR (cm^{-1}, liquid) 3500 (OH), 1677 (C=C); NMR ($CDCl_3$) δ 1.26 (s, 3H, CH_3), 1.34 (s, 3H, CH_3), 1.68 (s, 1H, OH), 2.20—2.80 (m, 5H, H_3, H_4 and H_6), 3.14—3.40 (m, 1H, >$CHCCl_3$), 5.78 (broad s, 2H, -CH=CH-).

Found: C, 46.43; H, 5.82. Calcd for $C_{10}H_{15}Cl_3O$: C, 46.63; H, 5.87.

2-(1-Hydroxy-1-methylethyl)-3-trichloromethylbicyclo[2, 2, 1]hept-5-ene (5). The adduct **2a** (2.5 g, 0.01 mol) was allowed to react with methyl magnesium iodide (methyl iodide, 0.018 mol; magnesium, 0.015 mol) in ether. When the mixture was treated as usual, 1.98 g of a clean oil was obtained. The tlc analysis[22] of this oil showed two spots at R_f values of 0.37 and 0.51 in the ratio of 1: 4. The spot of **2a** appeared at R_f 0.51. The component with the R_f value of 0.37 was separated by preparative tlc and was identified as **5**: yield 5%; IR (cm^{-1}, liquid) 3530 (OH), 1571 (C=C); NMR ($CDCl_3$) δ 1.12—1.77 (m, 2H, $2H_7$), 1.33 and 1.42 (2s, 6, -C(C$\underline{H}_3$)$_2$), 1.77—2.10 (m, 1H, H_2), 1.87 (s, 1H, OH), 2.90 (m, 1H, H_1), 3.40 (m, 2H, H_3 and H_4), 6.20 (m, 2H, -CH=CH-).

Found: C, 49.28; H, 5.57. Calcd for $C_{11}H_{15}Cl_3O$: C, 49.01; H, 5.56.

2-(1-Hydroxyethyl)-3-trichloromethylbicyclo[2.2.1]hept-5-ene (6). To a mixture of 30 ml of dry ether and 0.75 g (0.02 mol) of lithium aluminum hydride was added dropwise a solution of 10.1 g (0.04 mol) of **2a** in 30 ml of dry ether at reflux temperature. After the complete addition, the mixture was refluxed for a further 30 min. To the mixture was added 10 ml of ice-water, and it was acidified with 10% H_2SO_4. The organic layer was extracted with ether. The extract was washed with water and dried over $MgSO_4$. The subsequent removal of the solvent left a residue which, on distillation, gave 3.8 g (38%) of **6**: bp 124 °C/0.25 mmHg; IR (cm^{-1}, liquid) 3375 (OH), 1572 (C=C); NMR ($CDCl_3$) δ 1.28 and 1.34 (2d, 3H, J=7 Hz, -CH(OH)C$\underline{H}_3$), 1.40—1.60 (m, 2H, $2H_7$), 1.79—1.95 (m, 1H, H_2), 2.01 (s, 1H, OH), 2.82—3.55 (m, 3H, H_1, H_3, and H_4), 3.91—4.73 (m, 1H, >C$\underline{H}$(OH)), 6.23 (m, 2H, -CH=CH-).

Found: C, 47.26; H, 5.26. Calcd for $C_{10}H_{13}Cl_3O$: C, 47.00; H, 5.13.

4-(2-Furyl)-5,5,5-trichloropentan-2-one (7). A mixed solution of **1a** (5.6 g, 0.3 mol) and furan (4.1 g, 0.06 mol) in benzene (20 ml) was heated for 40 hr at 80 °C under an atmosphere of nitrogen. The solvent and excess furan were then removed *in vacuo*; the residue, on distillation, gave 0.9 g (11%) of **7**: bp 111 °C/4 mmHg; IR (cm^{-1}, liquid) 1730 (C=O), 1506 (furan C=C); NMR ($CDCl_4$) δ 2.14 (s, 3H, $COCH_3$), 3.34 (d, 2H, J=7 Hz, $-CH_2-$), 4.49 (t, 1H, J= 7 Hz, >CH), 6.37 (m, 2H, furan H_3 and H_4), 7.37 (m, 1H, furan H_5); MS *m/e* (rel. intensity) 218 (49, M^+-HCl), 183 (40), 162 (10), 149 (37), 141 (27), 137 (11), 81 (10), 43 (100).

Found: C, 42.43; H, 4.02. Calcd for $C_9H_9Cl_3O_2$: C, 42.30; H, 3.55.

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14) The electrochemical reduction of **2a** afforded the *endo* **2b**, whose *exo*-acetyl protons in NMR sppeared as a singlet at a lower field (2.24 ppm) than did the *endo*-acetyl protons (2.15 ppm) of the *exo* **2b**, the minor component of the two isomers derived from the reaction of **1b** with cyclopentadiene. The details of the electrochemical reduction of **2a** and related compounds will be published elsewhere.

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21) The reaction of **1f** was discontinued after heating for 20 hr.

22) Conditions of tlc: support, Silica gel GF_{254} (E. Merck AG, Darmstadt), 0.2 mm; developer, *n*-hexane–acetone (5:1 v/v).