Synthesis of *trans,trans*-1,5-Cycloundecadiene

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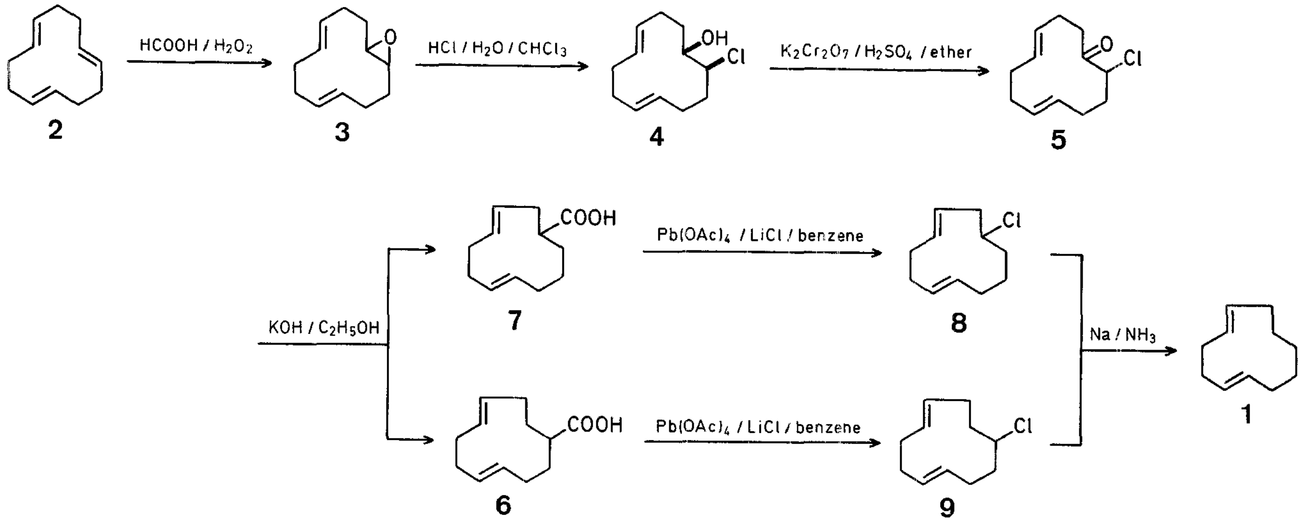
Up to now, the only known cycloundecadienes are the allene[1], the *cis/trans* isomeric 1,3-dienes[2], the *cis,cis*-1,4-diene[3], and *cis,cis*-1,6-cycloundecadiene[4]. In connection with our investigations on the transannular reactivity of medium-sized and large-ring dienes and trienes[5,6,7] we are interested in 1,5-cycloundecadienes. We describe here the synthesis of *trans,trans*-1,5-cycloundecadiene **(1)** from *trans,trans,trans*-1,5,9-cyclododecatriene **(2)**.



The triene **2** is transformed into its monoepoxide **3**[8] by the procedure of Ref.[9]. Ring cleavage of epoxide **3** with concentrated hydrochloric acid[10] leads to the *cis*-chlorohydrin **4** which is oxidized with dichromate in dilute sulfuric acid to give the 12-chloroketone **5**. Favorskii rearrangement of **5** using potassium hydroxide in ethanol gives two isomeric cycloundecadienecarboxylic acids **6** and **7** which are decarboxylated with lead(IV) acetate/lithium chloride in benzene[11] to give the chloro-1,5-cycloundecadienes **8** and **9** in a ratio of 62:38. Reduction of **8** + **9** with sodium in ammonia affords *trans,trans*-1,5-cycloundecadiene (**1**) in >95% purity and 18–20% yield (based on **2**).

cis-12-Chloro-*trans,trans*-4,8-cyclododecadienol (4):

A mixture of *trans*-9,10-epoxy-*trans,trans*-1,5-cyclododecadiene (**3**; 44 g, 0.25 mol), concentrated hydrochloric acid (100 ml), and chloroform (150 ml) is stirred vigorously at room temperature for 5 h. The organic layer is separated, the aqueous phase is extracted with chloroform (2 × 50 ml), and the combined extracts are washed with water (2 × 100 ml), sodium hydrogen carbonate solution (5%; 2 × 50 ml), and again with water (50 ml). The organic solution is dried with sodium sulfate, the solvent is evaporated, and the residue is distilled in vacuo to afford **4** as a colorless viscous oil; yield: 45.8 g (88%); b.p. 113–115 °C/0.5 torr; n_D^{20}: 1.5271.

$C_{12}H_{19}ClO$	calc.	C 67.12	H 8.92	Cl 16.51
(214.7)	found	67.49	8.54	16.57

M.S.: *m/e* = 214 (M^+, 6%), 196 ($M^+ - H_2O$, 3), 179 ($M^+ - Cl$, 12), 54 (100).

I.R. (film): $\nu = 3432, 3028, 1662, 983\ cm^{-1}$.

I.R. (CCl_4): $\nu = 3579\ cm^{-1}$ (intramolecular H bridge).

^{1}H-N.M.R. ($CDCl_3/TMS_{int}$): $\delta = 5.17$ (m, 4H, 2 $\underline{H}C{=}C\underline{H}$); 4.40 (m, 1H, $C\underline{H}Cl$); 3.76 (m, 1H, $C\underline{H}OH$); 2.5–1.5 ppm (m, 13H, $O\underline{H}$, 6 $C\underline{H}_2$).

12-Chloro-*trans,trans*-4,8-cyclododecadienone (5):

A mixture of potassium dichromate (29.4 g, 0.1 mol), concentrated sulfuric acid (50 ml), and water (125 ml) is added dropwise to a vigorously stirred solution of dienol **4** (45.8 g, 0.22 mol) in ether (200 ml) at a temperature below 15 °C. The mixture is stirred for a further 15 min and then diluted with water (1000 ml). The ethereal layer is separated, the aqueous phase is extracted with ether (2 × 100 ml), and the combined extracts are washed with water (50 ml), sodium hydrogen carbonate solution (5%; 2 × 50 ml), and again with water (50 ml). The organic solution is dried with sodium sulfate, the solvent is evaporated, and the residue is distilled in vacuo to afford **5** as a yellow oil; yield: 33.2 g (70%); b.p. 91–93 °C/0.7 torr; n_D^{20}: 1.5158 [in addition, 4.5 g (10%) of **4** are recovered].

$C_{12}H_{17}ClO$	calc.	C 67.76	H 8.06	Cl 16.67
(212.7)	found	67.76	7.99	16.35

M.S.: *m/e* = 212 (M^+, 13%), 177 ($M^+ - Cl$, 20), 67 (100).

I.R. (film): $\nu = 3032, 1720, 1640, 983\ cm^{-1}$.

^{1}H-N.M.R. ($CDCl_3/TMS_{int}$): $\delta = 5.05$ (m, 4H, 2 $\underline{H}C{=}C\underline{H}$); 4.20 (dd, 1H, $C\underline{H}Cl$); 3.0–1.5 ppm (m, 12H, 6 $C\underline{H}_2$).

trans,trans-4,8-Cycloundecadienecarboxylic Acid (6) and *trans,trans*-3,7-Cycloundecadienecarboxylic Acid (7):

To a stirred solution of potassium hydroxide (28 g, 0.5 mol) in ethanol (150 ml) is added dropwise a solution of dienone **5** (33.2 g, 0.14 mol) in ethanol (100 ml) at 70 °C. The mixture is heated under reflux for 2 h. The salt is separated, most of the solvent (200 ml) evaporated, and the residue poured into water (1000 ml). The aqueous solution is extracted with ether (3 × 100 ml) (to separate the neutral compounds), acidified with concentrated hydrochloric acid, and again extracted with ether (3 × 100 ml). The acidic ethereal solution is washed with water (2 × 50 ml) and dried with sodium sulfate. The solvent is evaporated and the residue distilled in vacuo to afford a mixture of the carboxylic acids **5** and **6** as a colorless, viscous oil; yield: 17.4 g (64%); b.p. 132 °C/0.6 torr; n_D^{20}: 1.5095. The product crystallizes upon standing for several days; m.p. 32–40 °C.

$C_{12}H_{18}O_2$	calc.	C 74.19	H 9.34
(194.3)	found	74.30	9.06

M.S.: *m/e* = 194 (M^+), 176 ($M^+ - H_2O$), 148 ($M^+ - H_2CO_2$).

I.R. (CCl_4): $\nu = \sim 3000$ (broat), 1705, 983 cm^{-1}.

^{1}H-N.M.R. ($CDCl_3/TMS_{int}$): $\delta = 11.14$ (bs, 1H, $COO\underline{H}$); 5.06 (m, 4H, 2 $\underline{H}C{=}C\underline{H}$); 2.31 (m, 1H, $C\underline{H}{-}COOH$); 2.03 (bs, 8H, 2 $CH{=}CH{-}C\underline{H}_2$); 1.65–1.05 ppm (m, 4H, 2 $C\underline{H}_2$).

8-Chloro-*trans,trans*-1,5-cycloundecadiene (8) and 9-Chloro-*trans,trans*-1,5-cycloundecadiene (9):

To a stirred solution of the carboxylic acids **6** and **7** (24.0 g, 124 mmol) in dry benzene (250 ml), lead(IV) acetate (88.6 g, 0.2 mol) is added under a nitrogen atmosphere. The mixture is stirred at room temperature until homogeneous, treated with lithium chloride (8.5 g, 0.2 mol), and stirred for a further 15 min while the flask is flushed with nitrogen. The mixture is then heated at 80 °C (rapid evolution of carbon dioxide). Gas evolution ceases after 15–30 min. The clear solution is decanted from the amorphous solid, washed with water (50 ml), sodium hydrogen carbonate solution (5%; 50 ml), and again water (50 ml). The organic solution is dried with sodium sulfate, the solvent evaporated and the residue distilled in vacuo to afford the chlorides **8** and **9** as a colorless oil; yield: 14.3 g (62%); b.p. 68–71 °C/0.5 torr; n_D^{20}: 1.5095. [In addition, 5.0 g (20%) of an acetate mixture is isolated.]

$C_{11}H_{17}Cl$	calc.	C 71.53	H 9.28	Cl 19.19
(184.7)	found	71.69	9.04	18.96

M.S.: *m/e* = 184 (M^+), 149 ($M^+ - Cl$), 148 ($M^+ - HCl$).

I.R. (film): $\nu = 3012, 1648, 964\ cm^{-1}$.

^{1}H-N.M.R. ($CDCl_3/TMS_{int}$): $\delta = 5.03$ (m, 4H, 2 $\underline{H}C{=}C\underline{H}$); 3.89 (m, 1H, $C\underline{H}Cl$); 2.5–1.3 ppm (m, 12H, 6 $C\underline{H}_2$).

***trans,trans*-1,5-Cycloundecadiene (1):**

Sodium (11.5 g, 0.5 mol) is added in portions to stirred liquid ammonia (250 ml) at −70 °C. To this solution is added dropwise a solution of the chlorides **8** and **9** (14.3 g, 78 mmol) in dry ether (125 ml) at −70 °C and stirring is continued for 2 h. Then, ammonium chloride (54 g, 0.5 mol) is added in portions at −70 to −50 °C and the ammonia allowed to evaporate overnight. Moist ether (150 ml) and then water (100 ml) are added dropwise. The ether layer is separated and the aqueous layer extracted with ether (2 × 50 ml). The combined organic solutions are washed with highly diluted hydrochloric acid (2 × 25 ml), sodium hydrogen carbonate solution (5%; 25 ml), and water (25 ml), and are dried with sodium sulfate. The solvent is evaporated and the residue distilled in vacuo; yield: 9.0 g (77%); b.p. 90–92 °C/15 torr; n_D^{20}: 1.4914; purity: >95% (G.L.C., glass capillary column, 100 × 0.24 mm I.D., Carbowax 20 M, 120 °C.

$C_{11}H_{18}$	calc.	C 87.93	H 12.07
(150.3)	found	87.90	12.15

M.S.: $m/e = 150$ (M^+, 50%), 135 ($M^+ - CH_3$, 25), 121 ($M^+ - C_2H_5$, 12), 67 (100).

I.R. (film): $\nu = 3015, 1653, 970\ cm^{-1}$.

^{1}H-N.M.R. ($CDCl_3/TMS_{int}$): $\delta = 5.05$ (m, 4H, 2 $\underline{H}C{=}C\underline{H}$); 2.02 (m, 4H); 1.88 (m, 4H); 1.25 ppm (bs, 6H).

^{13}C-N.M.R. ($CDCl_3/TMS_{int}$): $\delta = 132.8, 130.2, 32.3, 31.6, 28.5, 22.5$ ppm.

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