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Electrochemical Reduction of *exo*-5-Acetyl-*endo*-6-trichloromethylbicyclo[2.2.1]hept-2-ene

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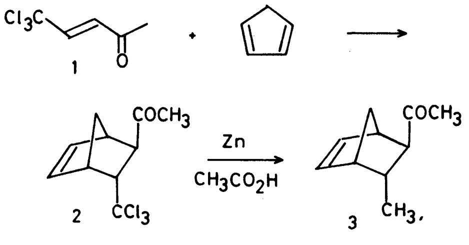
Synopsis. Electrochemical reduction of exo-5-acetyl-endo-6-trichloromethylbicyclo[2.2.1]hept-2-ene (**2**) using a mercury cathode gave chemoselectively either the corresponding monochloromethyl or dichloromethyl derivatives in high yields by selecting supporting electrolyte. The reduction of **2** using a lead cathode gave 2-acetyl-3-methylbicyclo[2.2.1]-hepta-2,5-diene and *cis*-1-(4-vinyl-2-cyclopentenyl)-2-propanone together with by-products.

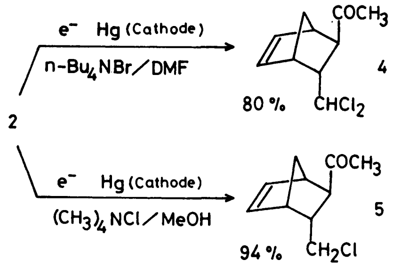
As our continuing studies on the chemistry of 5,5,5-trichloro-3-penten-2-one (**1**),[1] we reported that **1** reacted with cyclopentadiene giving stereospeciffically exo-5-acetyl-endo-6-trichloromethylbicyclo[2.2.1]hept-2-ene (**2**) in a high yield.[1d] If conversion of the trichloromethyl group of **2** to a chloromethyl or a methyl group could be accomplished, the stereospecific introduction of these groups into the endo position of norbornene will become possible. This conversion was poorly accomplished by conventional reduction of **2** with zinc in acetic acid affording *exo*-5-acetyl-*endo*-6-methylbicyclo[2.2.1]hept-2-ene (**3**) in 13% yield,[1d] which is a minor component of the mixture obtained from the reaction of 3-penten-2-one with cyclopentadiene.[2] As an electrochemical method may be profitable in conversion of compound **2** to **3**, we investigated the cathodic reduction of **2** under various conditions.



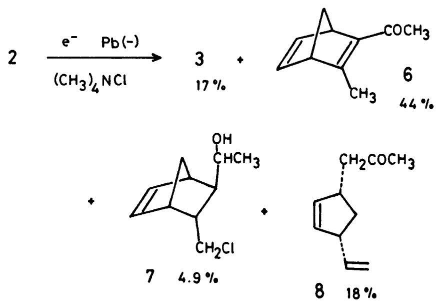
Results and Discussion

Only a few investigations have been made on the electrochemical reduction of trichloromethyl compounds. Nagao, et al.[3] have reported that $\alpha,\alpha,\alpha,\omega$-tetrachloroalkanes can be converted to either α,ω-dichloroalkanes or α,α,ω-trichloroalkanes by selecting cathodic supporting electrolyte. We carried out the reduction of **2** under the similar conditions.

When norbornene **2** was reduced electrolytically at the mercury cathode using tetrabutylammonium bromide as a supporting electrolyte in *N,N*-dimethylformamide (DMF), *exo*-5-acetyl-*endo*-6-dichloromethylbicyclo[2.2.1]hept-2-ene (**4**) was obtained in 80% yield. Compound **4** was identical with the major component of the products obtained from the Diels-Alder reaction[1d] of 5,5-dichloro-3-penten-2-one with cyclopentadiene. On the other hand, *exo*-5-acetyl-*endo*-6-chloromethylbicyclo[2.2.1]hept-2-ene (**5**) was formed in 94% yield when tetramethylammonium chloride was used in a 90% methanol solution. It is clear that a supporting electrolyte plays an important role in the present chemoselectivity in the reduction of trichloromethyl group.

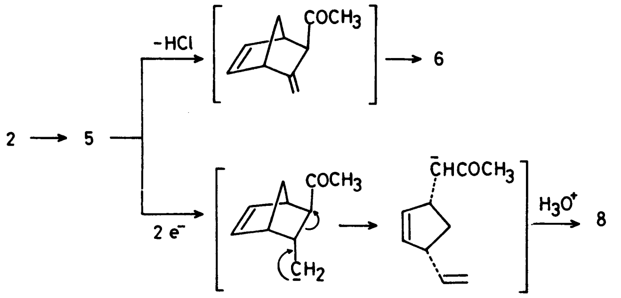


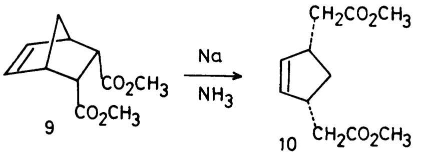
However, the reduction of compound **2** with a lead cathode using tetramethylammonium chloride gave nonchemoselectively 2-acetyl-3-methylbicyclo[2.2.1]-hepta-2,5-diene (**6**) in 44% yield together with **3** (17%), *exo*-5-(1-hydroxyethyl)-*endo*-6-chloromethylbicyclo-[2.2.1]hept-2-ene (**7**) (4.9%) (1 : 1 diastereomeric mixture) and *cis*-1-(4-vinyl-2-cyclopentenyl)-2-propanone (**8**) (18%). The structure of **6** was elucidated by spectral data. Mass spectrum showed a clear peak of molecular ion at *m/z* 148. The IR bands of **6** at 1665 cm^{-1} are characteristic of the α,β-unsaturated ketone. The structure of **7** was confirmed by the fact that the oxidation with chromium trioxide gave ketone **5**.



Reduction of **2** with zinc in acetic acid also has afforded cyclopentene **8** as a minor product in addition to **3**, although the structure has not been clarified.[1d] The structure of **8** was determined on the basis of IR, NMR, MS, and elemental analyses. The NMR spectrum of **8** was very similar to that of methyl 4-vinyl-2-cyclopentene-1-acetate with the exception of a singlet (2.15 ppm, $COCH_3$).[4] A signal due to olefin protons of cyclopentene appeared as a singlet at 5.68 ppm along with the disappearence of a signal (ca. 6.2 ppm) due to olefin protons of norbornene. Two multiplets (4.80—5.23 and 5.5—6.1 ppm) due to three olefin protons show the existence of a vinyl group. The unusual high δ value of cis proton of cyclopentene methylene is undoubtedly due to shielding effect of both vinyl and carbonyl groups. In mass spectrum of **8** (MW 150), the peaks at m/z 107 and 93 show the existence of an acetonyl group. The base peak at m/z 92 must be due to ions of vinylcyclopentadiene.

The following mechanism can be postulated for the formation of **6** and **8**. Compound **6** would be presumably formed from **5** via dehydrochlorination and prototropic shift. Cyclopentene **8** would be produced from **5** via C-C bond cleavage induced by anion. The C-C bond cleavage of norbornene derivatives under electroreductive conditions is interesting and is similar to a cleavage of diester **9** to produce **10** upon treatment with Na/NH_3.[5,6]





In conclusion, the electrochemical method using mercury cathode could reduce trichloromethyl compound **2** either to dichloromethyl compound **4** or monochloromethyl compound **5** chemoselectively in high yields. In contrast to the conventional method such as the reduction with $Zn-CH_3CO_2H$, the reaction proceeded with no contamination of resinous materials.

Experimental

The melting points and boiling points are uncorrected. Analytical determinations by GLPC were performed on a Hitachi model K-53 gas chromatograph using columns filled with 10% Apiezone Grease L on Chromosorb W (3 mm $\phi \times 1$ m) or 10% polyneopentyl glycol succinate on Chromosorb W (3 mm $\phi \times 1$ m). Preparative GLC was performed on a Yanagimoto model GCG-550 T gas chromatograph. IR spectra were determined on a Hitachi model EPI-S2 spectrometer. ^1H NMR spectra (60 MHz) were obtained with a Hitachi model R-24 apparatus. The mass spectra were measured on a Hitachi model RMS-4 mass spectrometer at 70 ev.

Electrolysis. The electrochemical cell consisted of an anode porcelain cylinder (35 mm in diameter; 150 mm in height) fitted with a calcium chloride tube, and of a cathode glass vessel (80 mm in diameter, ca. 300 ml content) fitted with a gas lead pipe, a thermometer, and a magnetic stirrer. All electrolyses were carried out at room temperature under N_2. Mercury (300 g; surface area, 50 cm^2) or lead (60 mm in diameter; 1.5 mm in thickness; surface area, ca. 58 cm^2) was used as the cathod, while a platinum wire (1.0 mm $\phi \times 75$ mm) was used as an anode.

Material. *exo*-5-Acetyl-*endo*-6-trichloromethylbicyclo[2.2.1]hept-2-ene (**2**) was prepared from 5,5,5-trichloro-3-penten-2-one (**1**) and cyclopentadiene.[1d)]

Reduction of 2 with $Zn-CH_3CO_2H$. This reaction was reported in the previous paper.[1d)] The structure of the minor component was newly determined as **8**: 10% yield: IR (neat) 1710 (C=O), 1636 (C=C), 1360, 1160, 910; ^1H NMR ($CDCl_3$) δ=0.8—1.4 (m, 2H, ring CH_2), 2.15 (s, 3H, $COCH_3$), 2.25—2.7 (m, 2H, $C\underline{H}_2COCH_3$), 2.8—3.5 (m, ring methyne), 4.80—5.23 (m, 2H, $CH=C\underline{H}_2$), 5.68 (s, 2H, CH=CH), 5.5—6.1 ppm (m, 1H, $C\underline{H}=CH_2$); MS (70 ev) m/z (rel intensity) 150 (M^+, 2), 135 (10), 107 ($M-COCH_3$, 38), 93 (56), 92 (100), 91 (86), 79 (58), 77 (60), 66 (58), 43 (72). Found: C, 79.73; H, 9.56%. Calcd for $C_{10}H_{14}O$: C, 79.96; H, 9.39%.

Electrochemical Reduction of 2. (a) Mercury was used as the cathode. A mixture of **2** (2.00 g, 8 mmol), tetrabutylammonium bromide (1.935 g, 6 mmol), and *N,N*-dimethylformamide (100 ml) was charged in a cathode cell. Tetrabutylammonium bromide (0.967 g, 3 mmol) and *N,N*-dimethylformamide (50 ml) was charged in an anode cell. The electrolysis with terminal voltage 27.0 V (current, 40—200 mA) was continued until the starting material **2** was consumed (24 h). The organic materials of the cathode cell were extracted with ether. The combined extracts were washed with water, dried over $MgSO_4$, and concentrated to give 1.43 g (80% yield) of **4** as crystals: 98% pure by GLC analysis (column, polyneopentyl glycol succinate, 150 °C; carrier gas, N_2, 0.5 kg cm^{-2}); mp 68—70 °C (from hexane)(lit,[1d)] 66—67.5 °C). IR and ^1H NMR data were identical with those reported previously.[1d)] No trace of the isomers was detected by ^1H NMR.

(b) Mercury was used as the cathode. In a cathode cell a mixture of **2** (2.00 g, 8 mmol) tetramethylammonium chloride (2.19 g, 20 mmol), and 90% methanol (100 ml) was charged. In an anode cell a solution of tetramethylammonium chloride (1.10 g, 10 mmol) in 90% methanol (50 ml) was charged. The electrolysis with terminal voltage 27.0 V (44—219 mA) was carried out at room temperature until the starting material **2** was consumed (24 h). The organic materials in the cathode cell were extracted with ether and worked up as described above, giving 1.39 g (94% yield) of **5** as a clean oil: 99% pure by GLC analysis (column, polyneopentyl glycol succinate, 150 °C; carrier gas, N_2, 0.5 kg cm^{-2}); bp 85—87 °C/3 Torr; IR (neat) 1709, 1570 cm^{-1}; MS (70 eV) m/z (rel intensity) 184 (M^+, 7), 149 (M—Cl, 79), 145 (80), 121 (66), 119 (95), 105 (84), 91 (69), 77 (69), 66 (100); ^1H NMR ($CDCl_3$) δ= 1.18—1.74 (m, 2H, C_7-H), 1.87—2.08 (m, 1H, $C\underline{H}COCH_3$), 2.22 (s, 3H, $COCH_3$), 2.5—3.8 (m, 1H, $C\underline{H}CH_2Cl$), 2.85—3.13 (m, 2H, C_1-H, C_4-H), 3.27 (d, 2H, J=6.5 Hz, CH_2Cl), 5.95—6.50 ppm (m, 2H, CH=CH). Found: C, 65.13; H, 7.11%. Calcd for $C_{10}H_{13}ClO$: C, 65.04; H, 7.09%.

(c) Lead was used as the cathode. A mixture of **2** (2.00 g, 8.0 mmol), tetramethylammonium chloride (2.19 g, 20 mmol), and 90% methanol (100 ml) was charged in a cathode cell. A solution of tetramethylammonium chloride (1.10 g, 10 mmol) in 90% methanol was charged in an anode cell. The electrolysis was carried out at terminal voltage 15 V (0.1—0.5 A) at room temperature. Every one hour the reaction mixture was analyzed by GLC. After 10 h, the organic materials in the cathode cell were extracted with ether. The combined extracts were washed with water and dried over $MgSO_4$. Removal of the solvent gave 1.22 g of an oil. GLC (column, Apiezone Grease L, 160 °C; carrier gas N_2, 0.5 kg cm^{-2}) analysis showed five peaks. Peaks, retention times (min), and percentages of peak area are as follows: 1, 1.4, 17%; 2, 1.6, 18%; 3, 2.3, 16%; 4, 3.6, 43%; 5, 7.6, 6%. Each component was separated by preparative GLC and identified. Peak 1: **3**; 17% yield. The retention time, and IR and ^1H NMR data were identical with those of the sample prepared from the reduction of **2** with $Zn-CH_3CO_2H$. Peak 2: **8**; 18% yield. Spectral data were identical with those described above. Peak 3: the structure was unidentified. Peak 4: **6**; 44% yield; IR (neat) 1665 (C=O), 1562 cm^{-1} (C=C); ^1H NMR ($CDCl_3$) δ=1.82 (s, 3H, CH_3), 2.05 (s, 3H, $COCH_3$), 2.12 (m, 2H, CH_2), 2.94 (br. s, 1H, methyne), 3.40 (m, 1H, methyne), 5.92 (m, 2H, CH=CH); MS (70 eV) m/z (rel intensity) 148 (M^+, 29), 133 ($M-CH_3$, 27), 105 ($M-COCH_3$, 100), 103 (47), 79 (73), 77 (69), 70 (82). Found: C, 81.05; H, 8.21%. Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16%. Peak 5: **7**; 4.9% yield; IR (neat) 3380 (OH), 2960, 1330, 900, 715 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.29 (d, 3H, J=6 Hz, CH_3), 1.50 (br. s, 1H, ring CH_2), 1.65 (s, 1H, OH), 2.0—4.0 (m, 7H, 5 methyne, CH_2Cl), 6.2 ppm (m, 2H, CH=CH). Found: C, 64.10; H, 8.08%. Calcd for $C_{10}H_{15}ClO$: C, 64.34; H, 8.10%.

Conversion of 7 to 5. To 3 ml of dry pyridine was added CrO_3 (0.31 g, 3.1 mmol) at 15—20 °C with stirring. A solution of **7** (0.199 g, 1.07 mmol) in dry pyridine (3 ml) was added and the mixture was stirred overnight at room temperature, and then poured into cold water. The organic materials were extracted with benzene-ether (1 : 1), washed with water, dried over $MgSO_4$, and concentrated. The residue was chromatographed on SiO_2 (hexane/acetone, 10 : 1), giving 80 mg (40%) of **5**: TLC (SiO_2; hexane/acetone, 3 : 1) R_f 0.54. IR and ^1H NMR spectra were identical with those of the sample prepared above.

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