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# Stereochemical Control in Electron-transfer Induced Reactions. Cyclic Voltammetry and Cathodic Reduction of Epimeric 3-Halogeno-6-nitro-5-cholestenes[1]

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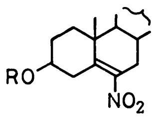
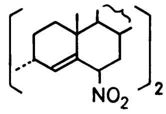
The cathodic electrolyses and cyclic voltammetric measurements were carried out for epimeric 3-halogeno-6-nitro-5-cholestenes. The stability and the fate of anion radicals were found to be highly dependent on the stereochemistry of homoallylic halogen groups. Half-lives of the anion radical from 3α-chloro- and 3α-bromo derivatives were found to be 12.5 and 1.6 s, respectively, while those of 3β-halogeno derivatives were much shorter. On cathodic reduction 3β-derivatives gave a cyclosteroid, 6β-nitro-3α,5α-cyclo-5α-cholestane in a two-electron process, whereas 3α-derivatives gave a dimer, 6β,6′β-dinitro-3α,3′α-cholesta-4,4′-diene, as the major product *via* a one-electron process. Detailed CV studies were carried out for 6-nitro-5-cholestene as a model. The stereochemistry of 3,3′-dimer was established by the $^1$H NMR measurements.

In a previous paper of this series[2] we have shown that the cathodic reduction of nitro olefinic esters **1** in *N,N*-dimethylformamide (DMF) gives two types of products, namely, a 3,3′-dimer, 6β,6′β-dinitro-3α,3′α-cholesta-4,4′-diene (**2**), and a cyclosteroid, 6β-nitro-3α,5α-cyclo-5α-cholestane (**3**), depending on a leaving-group ability of an equatorial ester group at C-3. For example, tosylate **1a** gave **3** as the major product while acetate **1b** gave only the dimer **2**. Trifluoroacetate **1c** showed an intermediate behavior and gave equimolar amounts of **2** and **3**. In these reactions a nitro olefinic moiety served as an electron inlet and no reduction of the nitro group itself occurred.



R
1a p-Ts
1b $CH_3CO$
1c $CF_3CO$



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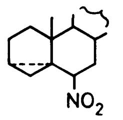

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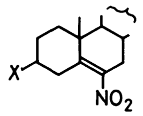
Recently, Yates and coworker[3] reported that the reaction of **1b** with lithium dimethylcuprate(I) in ether gave 3α,5α-cyclooxime but no dimeric product. The reaction was assumed to occur *via* a one-electron reduction mechanism.

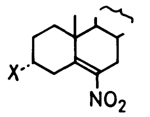
We have shown[1,2] that the cyclic voltammogram (CV) is highly dependent on the C-3 ester groups. Indeed the CV method has been shown to be used effectively to predict the reaction course which was dependent on the stability of an initially-formed anion radicals.

In this paper we describe further substituent effects on the CV behavior and cathodic reactions using epimeric 3α- and 3β-halogeno-6-nitro-5-cholestenes (**4a**), (**4b**), (**5a**), and (**5b**). We also describe the stereochemistry of dimer **2** studied by using proton NMR.

*Preparation.* 3β-Chloro- and 3β-bromo-6-nitro-5-cholestenes (**4a**) and (**4b**) were prepared from cholesterol by halogenation followed by nitration according to the literature.[4a,b] We found 3α derivatives **5a** and **5b** could be prepared simply by reversing the reaction order. Namely, **5a** and **5b** were obtained by the halogenation of 6-nitrocholesterol with phosphorus pentachloride or phosphorus tribromide which gave the corresponding halogeno products with inversion of stereochemistry at C-3 in 38 and 20% yields respectively. Low yields were outweighed by shorter reaction steps. The conventional route for 3α derivatives required lengthy steps involving halogenation with inversion at C-3 of 3β-hydroxy-5α-cholestan-6-one followed by lithium aluminum hydride reduction, dehydration, and nitration.



4a X=Cl
4b X=Br



5a X=Cl
5b X=Br

The stereochemistry of substitution at C-3 has been known to be controlled by the π electron density at C-5.[4c] In the present case, low-electron density at C-5 in nitro-olefinic group directed the reaction course toward inversion which was common both for halogenation of cholestanol[4c] and also for acetoxylation of 3-chlorocholest-5-en-7-one.[5]

*Cyclic Voltammetry.* The CV measurements were carried out in DMF containing 0.1 mol dm$^{-3}$ of tetrabutylammonium perchlorate (TBAP) for solutions with concn $10^{-3}$—$10^{-4}$ mol dm$^{-3}$. For a reversible wave $E=E_{pc}-(E_{pc}-E_{pa})/2$ was calculated. When no anodic peak was recorded $E$ was approximated by the potential at which $i=0.85\ i_{pc}$.[6] The results are summarized in Tables 1 and 2. Table 1 shows data for compound **6** in detail together with those for **1a**, **1b**, and **1c** for comparison purpose.[2] Table 2 summarizes the data for **4a**, **4b**, **5a**, and **5b**. With compounds **6**, **4b**, and **5b** a series of measurements

Table 1. The cyclic voltammetry data for the nitro steroids **1a**—**c** and **6**[a)]

| Compound | Scan rate mV s$^{-1}$ | Peak potetial/-V | | Peak pot. diff. $E_{pa}-E_{pc}$/mV | $E$/-V | Current ratio $i_{pa}/i_{pc}$ | Peak current $i_{pc}$/μA |
|---|---|---|---|---|---|---|---|
| | | $E_{pc}$ | $E_{pa}$ | | | | |
| **1a**[b)] | 50 | 1.49 | | | 1.44[c)] | | |
| | 100 | 1.55 | | | 1.48[c)] | | |
| | 250 | 1.69 | | | 1.58[c)] | | |
| | 500 | 1.74 | | | 1.55[c)] | | |
| **1b**[b)] | 50 | 1.47 | 1.23 | 240 | 1.35 | 0.84 | |
| | 100 | 1.55 | 1.18 | 370 | 1.36 | 0.82 | |
| | 250 | 1.63 | 1.10 | 530 | 1.37 | 0.72 | |
| | 500 | 1.70 | 1.01 | 690 | 1.36 | 0.55 | |
| **1c**[b)] | 500 | 1.61 | 1.10 | 510 | 1.36 | 0.55 | |
| **6**[d)] | 5 | 1.52 | 1.45 | 70 | 1.49 | 0.93 | 7.5 |
| | 10 | 1.53 | 1.44 | 90 | 1.49 | 0.94 | 9.5 |
| | 15 | 1.54 | 1.43 | 110 | 1.49 | 0.94 | 11.2 |
| | 25 | 1.55 | 1.42 | 130 | 1.49 | 0.89 | 14.0 |
| | 50 | 1.56 | 1.41 | 150 | 1.49 | 0.89 | 19.0 |
| | 100 | 1.58 | 1.40 | 180 | 1.49 | 0.90 | 25.0 |
| | 150 | 1.59 | 1.39 | 200 | 1.49 | 0.91 | 29.8 |
| | 250 | 1.62 | 1.37 | 250 | 1.50 | 0.89 | 36.0 |
| | 500 | 1.67 | 1.34 | 330 | 1.51 | 0.84 | 47.8 |
| | 750 | 1.72 | 1.33 | 390 | 1.53 | 0.78 | 57.8 |
| | 1000 | 1.74 | 1.32 | 420 | 1.53 | 0.79 | 66.5 |
| | 2500 | 1.85 | 1.25 | 600 | 1.55 | 0.70 | 105.7 |
| | 5000 | 1.92 | 1.20 | 720 | 1.56 | 0.56 | 139.3 |
| | 7000 | 2.00 | 1.16 | 840 | 1.58 | 0.65 | 168.0 |

a) The cyclic voltammetry was carried out in DMF–TBAP (0.1 mol dm$^{-3}$) using a platinum inlay electrode (Beckman No. 39273) and platinum wire as cathode and reference electrodes, respectively. An SCE was used as reference. b) Data from Ref. 2. c) The potential at which $i=0.85\ i_{pc}$ is shown. d) The concentration of solution, $1.0\times10^3$ mol dm$^{-3}$.

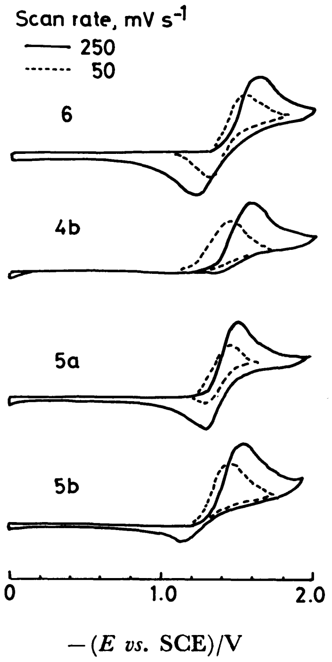


Fig. 1. The cyclic voltammograms for compounds **4b**, **5a**, **5b**, and **6** determined in DMF–TBAP; Scan rates, 50 and 250 mV s$^{-1}$.

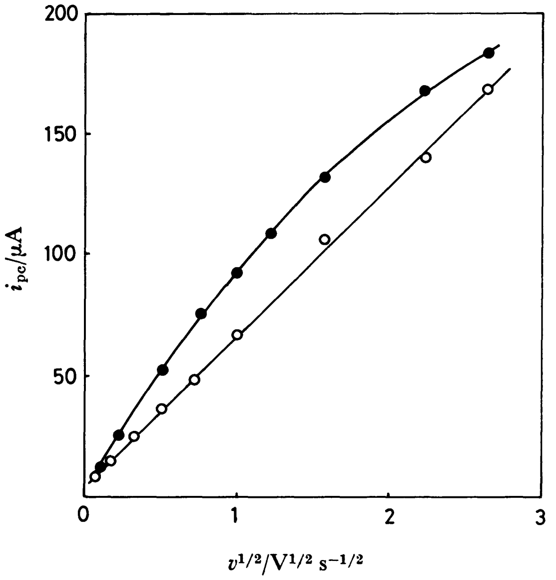


Fig. 2. The plot of square root of scan rate, $v^{1/2}$, vs. peak current, $i_{pc}$, for compounds **5b** (—●—) and **6** (—○—). The slope for compound **6**, $i_{pc}\ v^{-1/2}=61.7$/ μA s$^{1/2}$ V$^{-1/2}$.

TABLE 2. THE CYCLIC VOLTAMMETRY DATA FOR THE NITRO STEROIDS **4a**, **4b**, **5a**, AND **5b**[a]

| Compound | Scan rate mV s$^{-1}$ | Peak potential/-V | | Peak pot. diff. $E_{pa}-E_{pc}$/mV | $E$/-V | Current ratio $i_{pa}/i_{pc}$ | Peak current $i_{pc}$/μA |
|---|---|---|---|---|---|---|---|
| | | $E_{pc}$ | $E_{pa}$ | | | | |
| **4a** | 50 | 1.48 | | | 1.43[b] | | |
| | 100 | 1.52 | | | 1.56[b] | | |
| | 150 | 1.54 | | | 1.48[b] | | |
| | 250 | 1.56 | | | 1.49[b] | | |
| | 500 | 1.58 | | | 1.50[b] | | |
| **4b** | 10 | 1.42 | | | 1.36[b] | | 11.0[c] |
| | 25 | 1.43 | | | 1.37[b] | | 16.9[c] |
| | 50 | 1.47 | | | 1.40[b] | | 23.7[c] |
| | 100 | 1.50 | | | 1.43[b] | | 32.8[c] |
| | 150 | 1.52 | | | 1.45[b] | | 39.7[c] |
| | 250 | 1.55 | | | 1.49[b] | | 49.8[c] |
| | 500 | 1.59 | | | 1.52[b] | | 67.8[c] |
| | 750 | 1.61 | | | 1.53[b] | | 83.2[c] |
| | 1000 | 1.64 | | | 1.55[b] | | 93.8[c] |
| | 2500 | 1.72 | | | 1.61[b] | | 134.4[c] |
| | 5000 | 1.80 | | | 1.69[b] | | 182.0[c] |
| | 7000 | 1.89 | | | 1.73[b] | | 210.0[c] |
| | 10000 | 1.93 | | | 1.76[b] | | 259.0[c] |
| **5a** | 50 | 1.47 | 1.34 | 130 | 1.41 | 0.48 | |
| | 100 | 1.50 | 1.33 | 170 | 1.42 | 0.49 | |
| | 150 | 1.51 | 1.31 | 200 | 1.41 | 0.58 | |
| | 250 | 1.52 | 1.30 | 220 | 1.41 | 0.63 | |
| | 500 | 1.56 | 1.25 | 310 | 1.41 | 0.81 | |
| **5b** | 10 | 1.50 | | | 1.42[b] | | 11.9[c] |
| | 25 | 1.56 | | | 1.49[b] | | 17.7[c] |
| | 50 | 1.61 | | | 1.54[b] | | 25.1[c] |
| | 75 | 1.63 | 1.19 | 440 | 1.41 | 0.37 | 30.4[c] |
| | 100 | 1.65 | 1.17 | 480 | 1.41 | 0.37 | 35.1[c] |
| | 150 | 1.67 | 1.15 | 520 | 1.41 | 0.38 | 42.0[c] |
| | 250 | 1.70 | 1.13 | 570 | 1.42 | 0.42 | 52.0[c] |
| | 500 | 1.74 | 1.09 | 650 | 1.42 | 0.46 | 71.0[c] |
| | 600 | 1.76 | 1.07 | 690 | 1.42 | 0.49 | 76.4[c] |
| | 700 | 1.77 | 1.06 | 710 | 1.42 | 0.50 | 82.0[c] |
| | 750 | 1.78 | 1.05 | 730 | 1.42 | 0.51 | 83.6[c] |
| | 1000 | 1.83 | 1.00 | 830 | 1.42 | 0.56 | 92.4[c] |
| | 1500 | 1.86 | 0.96 | 900 | 1.41 | 0.61 | 108.0[c] |
| | 2500 | 1.90 | 0.94 | 960 | 1.42 | 0.81 | 132.0[c] |
| | 5000 | 1.95 | 0.90 | 1050 | 1.43 | 0.76 | 168.0[c] |
| | 7000 | 1.98 | 0.87 | 1110 | 1.43 | 0.74 | 184.0[c] |

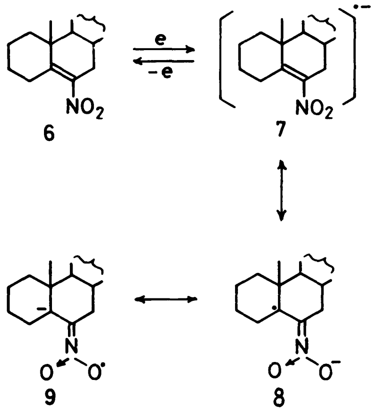
a) The measurements were carried out similarly as those in Table 1. b) The potential at which $i=0.85\ i_{pc}$ is shown. c) The concentration of solution, $6.7\times10^{-4}$ mol dm$^{-3}$.

were conducted using a single solution and the peak current data are tabulated together with the other parameters.

In order to examine the effect of C-3 substituents and its stereochemistry on the electron-transfer process we first investigated the CV of 6-nitro-5-cholestene (**6**) in detail as the model (Table 1, Figs. 1 and 2).

Compound **6** showed a reversible wave for varied scan rates indicating reversible electron-transfer between **6** and its anion radical **7**. The CV curves for 50 and 250 mV s$^{-1}$ are shown in Fig. 1. The cathodic potential $E$ was found to be −1.5 V. The anion radical is fairly stable and assumed to be composed of a resonance hybrid between **8** and **9**. At lower scan rates the current ratio $i_{pa}/i_{pc}$ became almost unity. The peak potential difference, $E_{pa}-E_{pc}$, was 70 mV at the scan rate of 5 mV s$^{-1}$, the value of which was close to 56 mV required for an ideal one-electron transfer process.[6]

When higher scan rates were used, however, the peak potential difference showed a steady increase, reflecting limited electron-transfer rate. At the scan rate of 7V s$^{-1}$ recorded using a wave-memory technique, the peak potential difference reached 840 mV, while the peak current ratio decreased to 0.65.



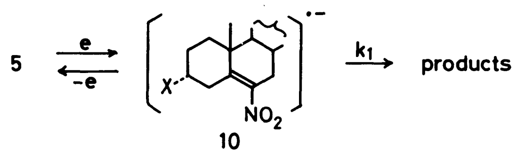
6 7 9 8

Figure 2 shows the dependence of the cathodic current $i_{pc}$ on the square root of the scan rate. A good linear relation was obtained as expected from the Randles-Sevcik equation,[6]

$$i_p = 2.687\times10^5 n^{3/2} A D^{1/2} C v^{1/2}$$

The effect of a homoallylic substituent at C-3 was then investigated using substrates **4** and **5** (Table 2, Fig. 1). The CV curves for 3-axial halogeno derivatives **5a** and **5b** recorded in two speeds, 50 and 250 mV s$^{-1}$, are shown in Fig. 1. 3-Axial chloro derivative **5a** showed a reversible wave for both scan rates. The corresponding bromo derivative **5b**, however, showed no anodic peak at the scan rate of 50 mV s$^{-1}$ but it appeared as a small peak at −1.42 V on increasing the scan rate fivefold indicating the presence of coupled chemical reactions. Reversibility was increased markedly by employing higher scan rates. The plot between $i_{pc}$ and $v^{1/2}$ for 3α-bromo derivative **5b** results in a nonlinear correlation unlike the case of compound **6** (Fig. 2).

In 3α-derivatives a reversible electron-transfer process is assumed to be coupled with chemical reactions with the rate of $k_1$. The CV behavior indicated that $k_1$ was larger for bromo derivative than for chloro derivative. These results indicate the anion radical formed from **5a** and **5b** have a limited stability.



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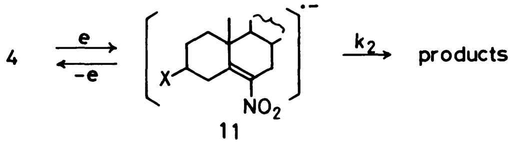
For 3β-chloro and 3β-bromo derivatives, **4a** and **4b**, no anodic peak was recorded even when high speed CV determination was carried out. This indicates a higher reactivity of the 3β-halogeno anion radical **11** compared with the 3α-halogeno anion radical **10** ($k_2 > k_1$). The CV behavior of **4** resembles to that of 3β-tosylate **1a**.[2] Figure 1 shows voltammograms at two speeds of **4b**. Compound **4a** also showed similar voltammograms.



11

Whereas halogeno substituents at C-3 and its stereochemistry were found to affect the voltammograms in various ways, the cathodic potentials for these compounds were found to fall within a narrow range of −1.4—−1.5 V.

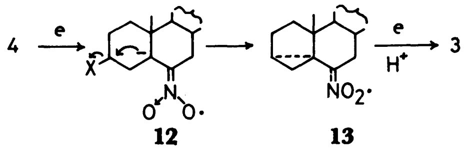
Half lives for these anion radical can be estimated by using the House method.[7] One assumes a simple EC reaction composed of a reversible electron transfer coupled with an irreversible chemical reaction. By carrying out the CV determination at various speeds one can obtain a voltammogram with $i_{pa}$ just half of $i_{pc}$. The half-life of an anion radical can be regarded as the elapsed time between the cathodic peak and the anodic peak on potential reversal.

Compound **6** showed a good reversible wave throughout the scan ranges used even when a very slow sweep rate was employed. By contrast, equatorial halogeno derivatives **4a** and **4b** showed no anodic peak even when higher scan rates were employed, the situation is similar to tosylate **1a**, indicative of short life of the corresponding anion radicals. Axial isomers **5a** and **5b** showed an intermediate behavior and half-lives for anion radicals **10** were estimated to be 12.5 s for chloro derivative **5a** and 1.6 s for bromo derivative **5b**. Thus the stability of the anion radicals from the following compounds decreases in the order;

**6>5a>5b>4a, 4b, 1a**

*Cathodic Reaction.* The cathodic reduction was carried out in DMF containing 0.1 mol dm$^{-3}$ of tetrabutylammonium perchlorate (TBAP) as a supporting electrolyte using a divided cell under nitrogen. Constant current conditions (0.45 mA cm$^{-2}$) were employed to compare with the results for esters **1** which were electrolyzed similarly. The results are summarized in Table 3.

When 1 F mol$^{-1}$ of electricity had been consumed the reaction was stopped: Both equatorial compounds **4a** and **4b** gave cyclosteroid **3** in 40 and 43% yields, respectively. On further electrolysis **4a** gave 61% yield of **3** when 1.8 F mol$^{-1}$ of electricity was passed. The yield of **3** from **4b** reached 70% when 1.9 F mol$^{-1}$ was consumed. Apparently the reaction proceeds in a two-electron scheme involving an anion radical **12** to give **13** followed by further electron transfer and protonation as proposed before.[2]



**12** **13**

TABLE 3. CONTROLLED-CURRENT ELECTROLYSES OF NITRO ESTERS **4a**,**4b**,**5a**, AND **5b**[a)]

| Compound | Concn/mmol dm$^{-3}$ | Electricity F mol$^{-1}$ | Yield/% | | Recovery/% |
|---|---|---|---|---|---|
| | | | **2** | **3** | |
| **4a** | 22.2 | 1.0 | 5 | 40 | 45 |
| | 22.2 | 1.8 | 8 | 61 | 0 |
| | 25.6[b)] | 1.3 | 4 | 52 | 0 |
| **4b** | 20.2 | 1.0 | Trace | 43 | 49 |
| | 20.2 | 1.9 | Trace | 70 | Trace |
| **5a** | 20.0 | 1.0 | 37 | 0 | 0 |
| **5b** | 20.2 | 1.0 | 35 | 0 | 0 |

a) The electrolysis reactions were carried out at constant-current conditions in DMF–TBAP (0.1 mol dm$^{-3}$) using platinum electrodes. SCE was used as a reference. Current density was 0.45 mA cm$^{-2}$ except for b) for which 0.85 mA cm$^{-2}$ was used.

Similarly, axial isomers **5a** and **5b** were electrolyzed cathodically under conditions shown in Table 3. These gave dimer **2** in 37 and 35% yields, respectively possibly *via* a radical species as depicted in a previous paper.[2)]

Epimeric compounds were found to behave differently and the two competing reactions leading to **2** and **3** were dependent not only on the leaving group ability but also on the stereochemistry. The equatorial chloro and bromo derivatives behaved similarly to tosylate **1a** indicating the importance of leaving group ability on cyclosteroid formation. By contrast, the axial halogeno derivatives underwent dimerization reaction typical to acetate **1b**. The results can be rationalized by assuming that a favorite geometry for concerted elimination to form the cyclosteroid is possible only for an equatorial leaving group as in **12**.

The CV results again were found to be instructive: Those with reversible wave tend to give the dimer whereas those with irreversible wave the cyclosteroid. In other words those compounds forming short-lived anion radicals such as tosylate **1a** and equatorial halogeno derivatives **4a** and **4b** were lost rapidly in an intramolecular cyclosteroid formation, whereas those with long-lived anion radicals such as acetate **1b**, **5a**, and **5b** underwent an intermolecular coupling.

*The Stereochemistry of 6β,6′β-Dinitro-3α,3′α-cholesta-4,4′-diene (2).* Although the orientation of the 6-nitro group in compound **2** was established to be axial based on the NMR evidence the stereochemistry of ring junction between C-3 and C-3′ has remained unsettled.[2)]

There are several reports on the formation of dimeric steroids. Fried and Abraham[8)] reported the formation of a pinacol by the modified Birch reduction of estrone methyl ether. The stereochmistry at the ring juncture was deduced to be 3α,3′α by comparing the NMR spectra with those of monomeric compounds. Other examples of reductive coupling in steroidal ketones include dehydroepiandrosterone[9)] and some α,β-unsaturated ketones.[10)]

TABLE 4. THE 360 MHz $^1$H NMR SPECTRAL DATA FOR DIMER **2**

| Proton | Chemical shift/δ | Coupling constant/Hz | |
|---|---|---|---|
| C-2H$_{eq}$ | 2.020 | $J_{2a,3e}$ | 3 |
| C-3H$_{eq}$ | 2.175 | $J_{3e,4}$ | 3 |
| C-4H | 5.905 | | |
| C-6H$_{eq}$ | 4.678 | $J_{6e,7a}$ | 5.3 |
| C-7H$_{eq}$ | 2.635 | | |

Grignard reaction of 3-chlorocholestane[11)] or 3-chloro-5-cholestene[12)] produced a dimeric product, which was structually closely related to our dimer **2**, in a low yield but the configuration at C-3 and C-3′ remained unsettled.

The cathodic reaction of nitro olefin **1b** produced[2)] dimer **2** in a 54% yield, which separated out from the solution during the electrolysis. The examination of crude material by using NMR spectroscopy revealed that the material was a single compound although three stereoisomers, 3α,3′α-, 3α,3′β-, and 3β,3′β-types, were possible.

The proton NMR spectra of **2** were determined in $CDCl_3$ at the frequency of 360 MHz where nearly all proton signals in rings A and B were observed as separate signals. Five one-proton signals, C-2, 3, 4, 6, and 7H, were assigned by the first order analysis as shown in Table 4. The absorption due to C-3H appeared as a narrow peak at δ 2.175. The expanded spectrum clearly showed that it consisted of a double-doublet with J=3 Hz. The configuration of C-3H was deduced to be equatorial since $J_{2a,3e}=J^3{}_{e,4}=3$ Hz. Accordingly the stereochemistry of bonding between C-3 and C-3′ was established as α,α′-type.

## Experimental

*3β-Halogeno-6-nitro-5-cholestene (4a and 4b).* 3β-Chloro-6-nitro-5-cholestene (**4a**) was prepared by the nitration of 3$\beta$-chloro-5-cholestene,[4a)] recrystallized from acetone, colorless needles, mp 153.5—154.5 °C. Similarly, 3$\beta$-bromo-6-nitro-5-cholestene (**4b**) was prepared,[4b)] colorless needles from acetone, mp 158—159 °C.

*3α-Chloro-6-nitro-5-cholestene (5a).* To a stirred chloroform suspension (750 cm$^3$) containing 6-nitrocholestrol (20 g, 46 mmol) and barium carbonate (40 g), phosphorus pentachloride (37 g, 0.18 mol) was added under cooling in an ice bath. After 1.5 h stirring, water (400 cm$^3$) was added and the chloroform layer was washed with water, aq sodium carbonate, and water. Evaporation of chloroform, after being dried over calcium chloride, gave a solid which was purified by passing through a silica-gel column using hexane–benzene (4:1) as an eluent. Recrystallization from acetone gave **5a** (7.9 g, 38% yield) as colorless plates, mp 163—164 °C; IR (nujol) 1660 (C=C) and 1515 cm$^{-1}$ (conj $NO_2$); $^1$H NMR ($CDCl_3$) $\delta$=0.72 (3H, s, C-18H), 1.15 (3H, s, C-19H), and 4.51 (1H, m, $w_{1/2}$=8.0 Hz, C-3H$_{eq}$).

Found: C, 72.13; H, 9.83; N, 3.20%. Calcd for $C_{27}H_{44}NO_2Cl$: C, 72.05; H, 9.85; N, 3.11%.

*3α-Bromo-6-nitro-5-cholestene (5b).* To a refluxing benzene solution (70 cm$^3$) of 6-nitrocholesterol (25 g, 58 mmol) was added phosphorus tribromide (7.5 cm$^3$, 79 mmol) in benzene (10 cm$^3$). After 2 h refluxing benzene was removed by evaporation and the residue was taken up in ether. The ethereal layer was washed with aq sodium hydroxide and water, and dried over magnesium sulfate. The product was purified by passing through a silica-gel column using hexane–benzene (2:1) as an eluent to give **5b** (5.7 g, 20%) after recrystallization from acetone, mp 154—155 °C; IR (nujol) 1660 (C=C) and 1515 cm$^{-1}$ (conj $NO_2$); $^1$H NMR ($CDCl_3$) $\delta$=0.72 (3H, s, C-18H), 1.14 (3H, s, C-19H), and 4.65 (1H, m, $w_{1/2}$=8.0 Hz, C-3H$_{eq}$)

Found: C, 65.53; H, 8.83; N, 2.85%. Calcd for $C_{27}H_{44}NO_2Br$: C, 65.57; H, 8.97; N, 2.83%.

*Electrolyses.* The controlled current electrolysis, using either 0.45 mA/cm$^2$ or 0.85 mA/cm$^2$, was carried out for **4a**, **4b**, **5a**, and **5b**. A Hokuto potentiostat/galvanostat HA-101 apparatus with max. output 30 V (1 A) was used. The cylindrical cell used previously[2)] was equipped with a side arm for connecting the reference electrode, SCE, with the aid of two junction bridges, filled with satd KCl and DMF–TBAP (0.1 mol dm$^{-3}$) solutions. A ceramic thimble was used as a divider and was placed over a glass spacer to allow efficient stirring by a magnetic stirrer. A punched platinum electrode with an area of 118 cm$^2$ was used as the cathode together with a platinum wire anode placed in the above thimble. Representative examples are summarised in Table 3.

As an example the cathodic reduction of 3$\beta$-chloro-6-nitro-5-cholestene (**4a**) is described.

*a) Electricity; 1 F mol$^{-1}$.* After passing purified nitrogen for 20 m, a solution of **4a** (0.5 g, 1.1 mmol) in DMF (50 cm$^3$) containing 0.1 mol dm$^{-3}$ of TBAP was electrolyzed at the current density of 0.42 mA cm$^{-2}$ until 1 F mol$^{-1}$ of electricity was consumed. DMF was evaporated *in vacuo* and the residue was extracted with ether. When the etherial solution was washed with water a part of TBAP was separated out, which was filtered off. The ethereal solution was washed with water again and dried. The ether extract contained **4a** ($R_f$=0.38) and a cyclosteroid **3** ($R_f$=0.35) together with dimer **6** as a slow moving fraction on examination by TLC. The mixture **4a** and **3** was separated on a Merck Lobar column using hexane–benzene (4:1) as an eluent. Recovery of **4a** was 45% while compounds **2**[2)] and **3**[2)] were obtained in 5 and 40% yields respectively.

*b) Electricity; 1.8 F mol$^{-1}$.* When the electrolysis was further continued, the voltage between the working and the reference electrodes was raised steadily. The electrolysis was switched to a controlled potential mode when the voltage reached −1.55 V. Current stopped essentially when 1.8F mol$^{-1}$ of electricity had been consumed. The reaction mixture contained **2** (8%) and **3** (61%), no starting material being left.

*Cyclic Voltammetry.* The cyclic voltammetry measurements were carried out using the combination of a function generator, Hokuto HB-107A, and a potantiostat, Hokuto HA-101. For high-speed record, the output was stored in a wave-memory device, NF Circuit Block WM-812A. A modified H-type cell, separated by a sintered glass divider, is equipped with two side arms for connecting a nitrogen bubbler and a reference electrode, SCE, which is connected using two junction bridges filled with KCl and DMF–TBAP solutions. Molecular sieve 1A (Wako chemicals) was added to the bridge directly immersed in the cell to avoid contamination by water. Results are summarized in Tables 1 and 2. Representative CV curves are shown in Figure 1.

*NMR Spectra.* The $^1$H NMR spectra were recorded with a Bruker WM-360 spectrometer.

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