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The Cyclic Voltammetry and Cathodic Reduction of Steroidal Homoallylic Nitro Esters. Dimerization *vs.* Cyclopropane Formation[1]

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The cathodic reduction of homoallylic nitro esters was carried out in DMF–TBAP using platinum electrodes. The reaction was found to be highly dependent on the ester-leaving group: Whereas 6-nitrocholest-5-en-3β-yl acetate (**3a**) gave a 3,3′-dimer **4**, 3β-tosylate **3d** gave a cyclosteroid, 6β-nitro-3α,5-cyclo-5α-cholestane (**7**). 3β-Trifluoroacetate showed intermediate behavior and gave both **4** and **7**. Similarly, 6-nitrocholest-5-ene-3β,19-diol 3-acetate 19-tosylate gave 5β,19-cyclosteroid. The cyclic voltammetry was carried out for these and related compounds. A reversible cyclic voltammogram was recorded for **3a**, but **3d** showed no anodic peak on potential reversal. A possible electron-transfer and the following chemical-reaction mechanism was discussed.

The cathodic reactions of conjugated or homoconjugated systems in aprotic media are potentially useful as a means to induce remote reactions without reducing or protonating the electroactive group which itself is serving as the electron inlet. In this investigation we carried out the cathodic reduction of homoallylic nitro esters, such as **1**, in a steroid series. We found two

$$RO\dot{C}HCH_2\dot{C}{=}\dot{C}NO_2$$

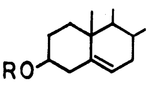
1, R = Ac, Ts *etc.*

types of reactions, namely, dimerization and cyclopropane-ring formation, which were highly dependent on the nature of the ester-leaving groups. The results are discussed in relation to the electrochemical parameters, as determined by cyclic voltammetry.

Results

*Controlled-potential Electrolyses of Two Nitro Esters, **3a** and **3d**.* 6-Nitrocholest-5-en-3β-yl acetate (**3a**) was obtained by the nitration reaction of cholesteryl acetate (**2a**).[2] The acylation or sulfonylation of 6-nitrocholest-5-en-3β-ol (**3**, R=H) gave benzoate **3b**, trifluoroacetate **3c**, and tosylate **3d**. For comparison, some cholesteryl esters **2a**—**d** were also prepared.

The cathodic reduction was carried out in a divided cell using platinum electrodes. Anhydrous DMF containing tetrabutylammonium perchlorate (TBAP, 0.1 mol dm^{-3}) was used as the reaction medium; it had been purged with nitrogen before the electrolysis. As reference, a saturated calomel electrode (SCE) was used.



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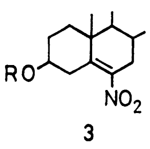

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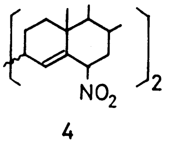
a, R = Ac
b, R = PhCO
c, R = CF$_3$CO
d, R = Ts

The controlled-potential electrolysis of the acetate **3a** supplied from a potentiostat at −1.44 V gave a precipitate after 1 F mol^{-1} of electricity had been consumed. We thus obtained a high-melting material with a molecular weight of 826 (the Rast method), for which a dimeric structure **4** (MW 829) was assigned based on the spectral evidence to be presented below. The yield of **4** was 45%.

Compound **4** showed an IR absorption at 1550 cm^{-1}, indicating the presence of a nitro group substituted on a saturated carbon. The proton NMR spectrum showed two single-proton resonances due to a vinylic proton (C-4H) at δ 5.90 as a multiplet and a proton attached to a saturated carbon carrying a nitro group (C-6H) at δ 4.67 (multiplet).

The location of the olefinic linkage and the configuration of the nitro group were determined by spectral comparison with related materials, 6β-nitrocholest-4-ene (**5**)[3] and 6α-nitrocholest-4-en-3-one (**6**).[4] Compound **5** showed the C-4H proton resonance at δ 5.90. The half-band width of C-5H in **4** (7.5 Hz, H$_{eq}$) can be compared with that of **6** (16.5 Hz, H$_{ax}$). The configuration at C-3 could not be determined.[5]



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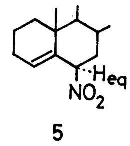

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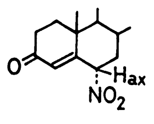

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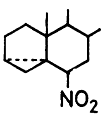
The use of a lead cathode instead of platinum reduced the yield of **4**. When tetrabutylammonium tetrafluoroborate (TBAF) was used as a supporting electrolyte instead of TBAP, the yield of **4** was also reduced. The addition of methanol to the reaction mixture caused intense coloration and greatly reduced the yield of **4**, indicating that a reduction of the nitro group occurred.

When the tosylate **3d** was electrolyzed at −1.45 V as above (1.5 F mol^{-1}), we obtained only a 4% yield of the dimer **4**. Instead, a new compound was formed which showed the IR maxima at 3030, 3070, and 3080 cm^{-1}, indicating the presence of a cyclopropane ring. A nitro group was assumed to be attached to a saturated carbon (1550 cm^{-1}). The proton NMR spectrum showed no vinylic proton resonance, but it did show a one-proton absorption at δ 3.87 with a half-band width of 8.3 Hz, which was attributable to an equatorial proton at C-6. Accordingly, the nitro group exists in an axial configuration. The compound showed the highest-field carbon-13 NMR resonance at δ 12.3. For comparison, compound **8**[6] showed the C-4 carbon resonance at δ 12.1. These results indicate the compound

Table 1. Controlled-current electrolyses of nitro esters **3a**—**3d**[a)]

Compound	Concn/mmol dm^{-3}	Potential variation/$-$V[b)]	Yield/% 4	Yield/% 7
3a	5.1	1.23—2.00	13.8	—
3a	25.6	1.23—2.00	29	—
3a	50.8	1.23—2.00	54	—
3b	25.4	1.54—2.00	30	—
3c	50.0	1.28—2.00	12	10
3d	39.2	1.10—2.00	2	36

a) The electrolysis was carried out at a constant current of 0.85 mA cm^{-2} in DMF–TBAP (0.1 mol dm^{-3}) using platinum elctrodes. The yields shown were obtained after 1.0—1.2 F mol^{-1} of electricity had been passed through (for **3c** 1.9 F mol^{-1}). b) Reference electrode, SCE.



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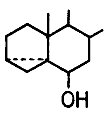

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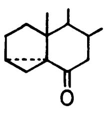

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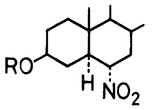
obtained is 6β-nitro-3α,5-cyclo-5α-cholestane (**7**). Chemical evidence for the suggested structure, including the stereochemistry of the cyclopropane ring, comes from the conversion of **7** into the known 3α,5-cyclo-5α-cholestan-6-one (**9**)[7)] (see below). The yield of **7** from **3d** was 43%.

Controlled-current Electrolyses of Nitro Esters ***3a—d***. In order to investigate the effect of C-3 substituents on the course of the cathodic reaction, we further examined the reaction of the benzoate **3b** and the trifluoroacetate **3c**. During the controlled-potential electrolyses of these nitro esters, the current showed a wide variation. In order to avoid current-density variation during the dimerization reaction, we employed controlled-current conditions for the purposes of comparison. The compounds **3a**—**d** were reduced cathodically under the same current density of 0.85 mA cm^{-2} until 1.0—1.2 F mol^{-1} of electricity had been consumed (with **3c** 1.9 F mol^{-1}). The results are summarized in Table 1.

The concentration of the substrate had a marked effect on the yield of the intermolecular reaction product **4**. Table 1 shows several experiments carried out for **3a** using 5 to 50 mmol dm^{-3} solutions which gave yields of **4** ranging from 14 to 54%. For **3c** and **3d**, 40—50 mmol dm^{-3} solutions were used, but for the benzoate **3b** a more dilute solution had to be used because of the limited solubility. The course of the reaction appeared to be primarily determined by the leaving-group ability for the nucleophilic reactions;[8)] the compound with a good leaving group such as tosylate gave a high yield of **7**. Both the acetate **3a** and the benzoate **3b** gave only a dimer ever when a dilute solution was used. The trifluoroacetate **3c** showed an intermediate behavior and gave comparable yields of **4** and **7**.

Both the dimer and cyclosteroid are stable under the present electrolytic conditions. No interconversion between **4** and **7** was observed in the control experiments, suggesting that they were formed by independent routes (see Discussion). The rest of the material was a colored matter which could not be characterized.

Cyclic Voltammetry. To obtain further insight into the structural dependence on the one-electron transfer reaction, we carried out cyclic voltammetric measurements in DMF containing 0.1 mol dm^{-3} TBAP using the cell and instruments as has been described before.[1)] The measurements were carried out for related compounds, including the starting esters **2a**—**d**, **5**, **7**, and 6α-nitro-5α-cholestan-3β-yl acetate (**11**).[9)]



10, R = H
11, R = Ac

The results are summarized in Table 2. When an anodic peak was recorded on a potential reversal, the cathodic potential, $E^0 = E_{pc} - (E_{pc} - E_{pa})/2$, was calculated. As a measure of reversibility, the current ratio, i_{pa}/i_{pc}, was also calculated. In cases where no anodic peak was recorded, the potential at which $i = 0.85 i_{pc}$ was taken as E^0.[10)]

As the control, the CV curves of the starting cholesteryl esters **2a**—**d** were determined. None of these materials showed a cathodic peak in the potential range of 0—−2 V, indicating that the ester carbonyl or sulfonyl groups were not reducible at the potentials used for the reduction of the nitro esters **3**.

Saturated nitro acetate **11** showed a cathodic potential, E^0, at −1.6 V. The β,γ-unsaturated nitro compound **5** and cyclosteroid **7** showed E_{pc}'s higher than −2.0 V and had no corresponding E_{pa}. Their cathodic potentials were estimated[10)] to be −1.9 V and *ca.* −2 V respectively. Whereas compound **11**, with an equatorial nitro group, gave a quasi-reversible wave, compound **5** and **7**, with a nitro group in an axial geometry, showed no anodic wave. Figure 1 records

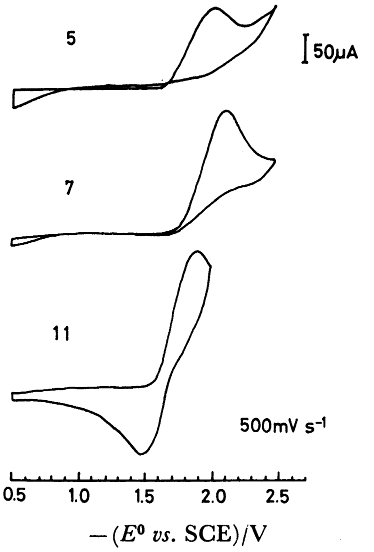


Fig. 1. Cyclic voltammograms for compounds **5**, **7**, and **11** determined in DMF using TBAP as supporting electrolyte.

Table 2. The cyclic voltammetry data for the nitro esters **3a**—**d** and related compounds **5**, **7**, **11**, **33a**, and **33b**[a]

Compound	Scan rate mV s^{-1}	Peak potential/−V[b] E_{pc}	E_{pa}	Peak pot. diff. $(E_{pa}-E_{pc})$/mV	E^0/−V[b]	Current ratio i_{pa}/i_{pc}
3a	50	1.47	1.23	240	1.35	0.84
	100	1.55	1.18	370	1.36	0.83
	150	1.59	1.14	450	1.37	0.77
	250	1.63	1.10	530	1.37	0.72
	500	1.70	1.01	690	1.36	0.55
3b	250	1.50	1.21	290	1.36	0.85
	500	1.52	1.21	310	1.36	0.88
	1000	1.55	1.18	370	1.37	0.87
3c	500	1.61	1.10	510	1.36	0.55
	750	1.65	1.08	570	1.37	0.53
	1000	1.66	1.06	600	1.36	0.50
3d	50	1.49	—		1.44[c]	
	100	1.55	—		1.48[c]	
	150	1.63	—		1.54[c]	
	250	1.69	—		1.58[c]	
	500	1.74	—		1.55[c]	
5	500	2.01	—		1.90[c]	
7	250	2.06	—		1.96[c]	
	500	2.10	—		2.00[c]	
	1000	2.18	—		2.06[c]	
11	500	1.89	1.47	420	1.68	
33a	50	1.59	1.07	520	1.33	0.68
	150	1.61	1.01	600	1.31	0.63
	250	1.63	1.00	630	1.32	0.64
	500	1.69	0.96	730	1.33	0.50
33b	50	1.46	—		1.39[c]	
	100	1.50	—		1.44[c]	
	150	1.53	—		1.46[c]	
	250	1.61	—		1.53[c]	
	500	1.66	—		1.56[c]	

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 the counter electrode respectively. b) Reference electrode, SCE. c) When no anodic peak was recorded on potential reversal, the potential at which $i=0.85\ i_{pc}$[10] was calculated.

the voltammograms for compounds **5**, **7**, and **11**, determined at the scan rate of 500 mV s^{-1}.

The α,β-unsaturated nitro esters **3a**—**d** showed E_{pc} values at considerably anodic potentials. Compounds **3a**, **3b**, and **3c** showed a quasi-reversible wave with quite similar $E^{0\prime}$'s at −1.35— −1.37 V. Compound **3d**, on the other hand, showed only a cathodic wave with *ca.* −1.5 V (Table 2). Figure 2 shows the CV curves for **3a** at 50 and 250 mV s^{-1} and for **3b**—**d** either at 250 or 500 mV s^{-1}.

At the slow scan rate of 50 mV s^{-1}, for example, **3a** showed a fairly good reversible wave with $E^0=-1.35$ V. The peak potential difference, $\Delta E_p=E_{pc}-E_{pa}$, was 240 mV, whereas the current ratio, i_{pa}/i_{pc} was 0.84. When higher scan rates were used, the peak separation increased, and, unexpectedly, the current ratio showed a decrease. These phenomena were supposed to be caused both by a limited electron-transfer rate and a coupled chemical reaction.[10] Based on the Randles-Cevcik equation[10] the ratio, $i_p/269\,ACv^{1/2}=D^{1/2}n^{3/2}$, was calculated; it was found to be essentially unchanged on scan-speed variation.

The benzoate **3b** showed an even more prominent reversible wave with respect both to the peak separation and the current ratio (Fig. 2, Table 2). The current ratio for these compounds showed no change at the scan rates employed.

With the tosylate **3d** no anodic wave was recorded, not even when a high speed scan was used. The anion radical formed at this potential was shown to be highly reactive and was lost by the following chemical reaction in the time scale of the CV measurements. When the CV of **3a** and **3d** was determined under the same conditions using a similar concentration of the substrates, the cathodic current of **3d** was larger than that of **3a**, suggesting that the cathodic wave for **3d** might involve a two-electron transfer, whereas those for **3a**—**c** were quasi-reversible one-electron transfer processes.

Discussion

Whereas the electrochemical reduction of nitro compounds in protic media provides a useful synthetic process,[11] a similar reaction under aprotic conditions results only in a reversible electron-transfer process involving an anion radical, as is shown by cyclic voltam-

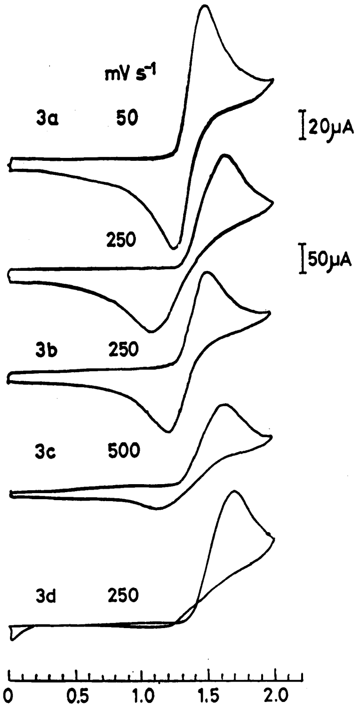


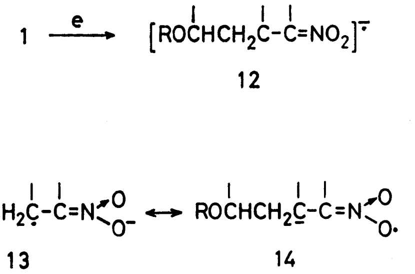
Fig. 2. Cyclic voltammograms for compounds **3a**, **3b**, **3c**, and **3d** determined in DMF using TBAP as supporting electrolyte. Current units (ordinate) for **3b**, **3c**, and **3d** are 20, 10, and 50 μA, respectively for the range shown for **3a**.

metry and ESR spectroscopy.[12,13] Accordingly, not much is known about the behavior of the anion radical in aprotic solvents. The anion radical of 2-methyl-2-nitropropiononitrile has been reported[14] to be cleaved into an alkyl radical and a nitrate ion.

The cathodic reactions of the homoallylic nitro esters **3a**—**d** were found to give a dimer and/or a cyclosteroid, depending on the nature of the ester group. The situation was found to be well reflected in the CV curves: those compounds that show a reversible wave tend to give the dimerization reaction product, whereas, those which fail to show an anodic wave tend to give the cyclosteroid. The time-dependent CV behavior of **3a** and **3b** suggests that the reaction involves an EC step, in which a reversible electron-transfer process is followed by the chemical reaction with the rate constant k_1. When k_1 is small and the scan rate is low,

$$\mathrm{O} \underset{-\mathrm{e}}{\overset{\mathrm{e}}{\rightleftharpoons}} \mathrm{R} \xrightarrow{k_1} \mathrm{P}$$

the reversibility is good and the current ratio becomes nearly unity. The CV measurements carried out for related model compounds, such as **2a**—**d**, **5**, **7**, and **11** revealed that electrophores in these compounds could be reduced only at considerably cathodic potentials. On the other hand, **3a**—**d** were reduced at less cathodic potentials, indicating that the reduction occurred on an α,β-unsaturated nitro electrophore. As a result of the one-electron reduction, the electrophore is converted to an anion radical **12**, which is a resonance hybrid **13**↔**14**.



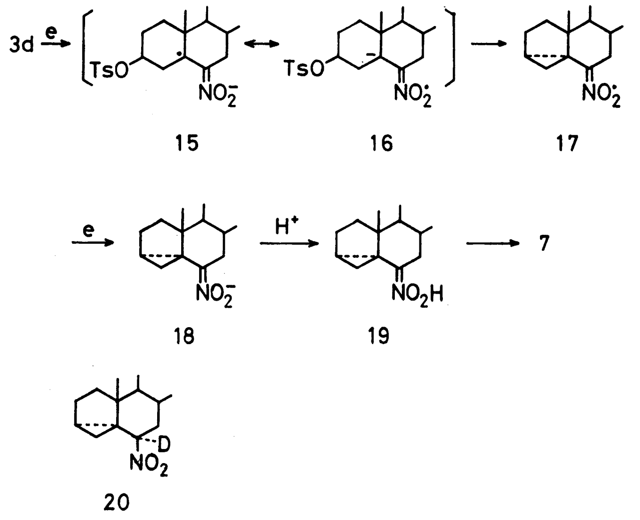
$$1 \xrightarrow{e} [\mathrm{ROCHCH_2C\text{-}C{=}NO_2}]^{\bar{\cdot}}$$

12

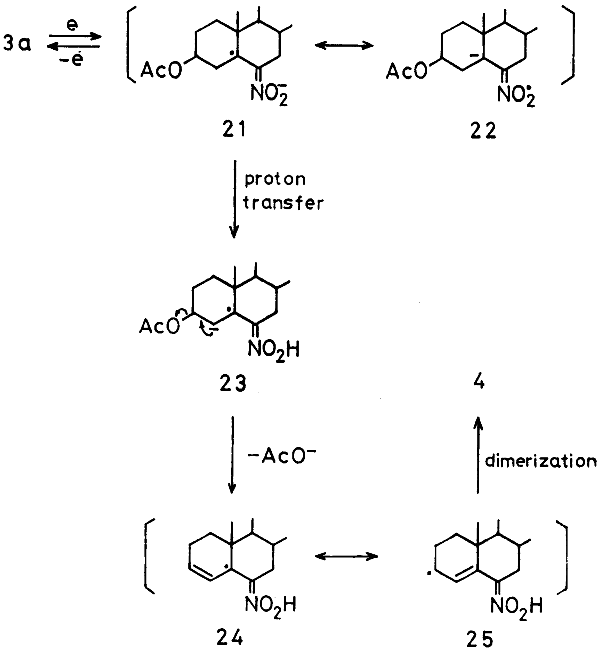
$$\mathrm{ROCHCH_2\dot{C}\text{-}C{=}N{\overset{\nearrow O}{\underset{\searrow O^-}{}}}} \longleftrightarrow \mathrm{ROCHCH_2\bar{C}\text{-}C{=}N{\overset{\nearrow O}{\underset{\searrow O\cdot}{}}}}$$

13 14

The tosylate **3d** showed no corresponding anodic peak on potential reversal, not even when the scan speed was increased by using a storage-memory technique. This indicates that the anion radical derived from **3d** is short-lived and hence possesses a high reactivity. The anion radicals equivalent to **13** and **14** can be written as **15** and **16**. The high reactivity of **16** can be expected, since a tosylate anion is an extremely good leaving group. An intramolecular nucleophilic displacement reaction gives **17**, which, on further one-electron reduction, forms an aci-anion **18**, the protonation of which gives **7** *via* **19**. The protonation of **18** appeared to occur in the isolation step, since the addition of D_2O, after the reaction was over, gave a deuterated product **20**. The mass-spectral analysis indicated the formation of **20** in up to a 60% yield by quenching the electrolysis reaction with D_2O. Before the addition of water, the reaction mixture remained colored, suggesting the stability of the aci-anion species **18**. No deuterium incorporation was observed in the control experiments in which **7** was treated with D_2O after electrolysis. The preferential formation of the thermodynamically unstable 6β-nitro compound **7** with an axial nitro group suggests that the proton attack occurs from a less hindered α-side for steric reasons.

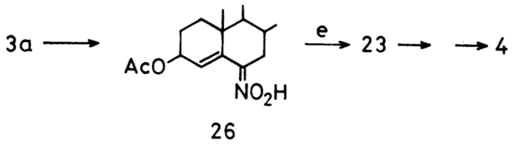


In the case of the acetate **3a** the corresponding anion radical exists as a resonance hybrid **21**↔**22**. Since an acetate ion is a less efficient leaving group, prototropy precedes to give **23** from **21**. The C-4 proton is sufficiently acidic, and its abstraction by the aci-anion is favored by the proximity effect.[3] The elimination of an acetate ion gives the corresponding allyl radical (**24**↔**25**).



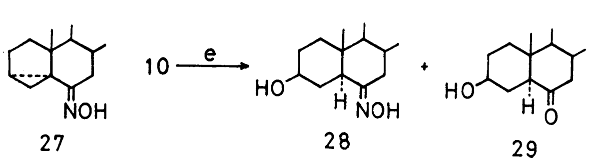
Dimerization is expected to occur on **25** to iveg **4**.

Alternatively, it is also possible to assume the isomerization of **3a** to give **26** prior to the one-electron reduction. The radical anion **23** can be derived from **26** by means of a cathodic reaction.

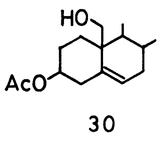


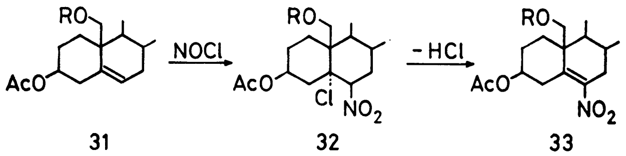
It might be possible that the dimer **4** was formed *via* the cyclosteroid **7** as an intermediate. That this is not likely is shown by the electrolysis reaction of **7**, coupled with the CV data indicating that it was reducible only at a more cathodic potential than that used for the actual electrolysis. Moreover, the controlled potential electrolysis of **7** at −1.90 V gave no trace of **4**, but instead gave the cyclosteroidal ketone **9** in a 16% yield, 72% of the starting material being recovered. Compound **9** was identical with the authentic material[7] and thus served as chemical evidence for the structure of **7**.

The ketone **9** may be formed *via* the oxime **27**. As support of this idea, we have observed that 6β-nitro-5α-cholestan-3β-ol (**10**) gives a hydroxy oxime **28** and a hydroxy ketone **29** upon controlled potential electrolysis in DMF–TBAP containing methanol at −1.70 V.[15]

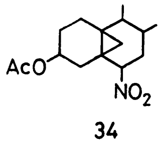


Related Reactions





a, R = Ac
b, R = Ts



The homoallylic nitro ester electrophore can be constructed in the steroidal system in another disposition. We further investigated the CV and controlled-potential electrolyses of 19-acetate **33a** and -tosylate **33b**. These were obtained by the above scheme.

Cholest-5-ene-3β,19-diol 3-acetate (**30**)[16] was converted to 19-acetate **31a** and 19-tosylate **31b**, which were then treated with nitrosyl chloride using the method previously reported from these laboratories[17] to give two nitro chlorides **32a** and **32b**; this was followed by dehydrochlorination with pyridine.

The CV data of **33a** and **33b** are shown in Table 2. Whereas compound **33a** showed a quasi-reversible couple, $E^0 = -1.33$ V, the tosylate **33b** showed a cathodic peak at -1.5—-1.7 V, but not any anodic peak, on potential reversal (Fig. 3). In view of the data found for **3a**—**d**, the CV results suggested that the tosylate **33b** might be highly reactive and might give the corresponding cyclosteroid. In fact, the electrolysis of **33b** carried out at −1.30 V in DMF–TBAP gave a 27% yield of 6β-nitro-5,19-cyclo-5β-cholestan-3β-ol acetate (**34**). The electricity consumed amounted to 1.7 F mol^{-1}. The structure was supported by the IR spectral data, which showed absorptions at 3070 (cyclopropane ring), 1730 (acetoxy), and 1545 cm^{-1} (nitro group on saturated carbon), and also by the NMR spectra, which showed a one-proton multiplet at δ 4.77 with a half-band width of 9 Hz. On the other

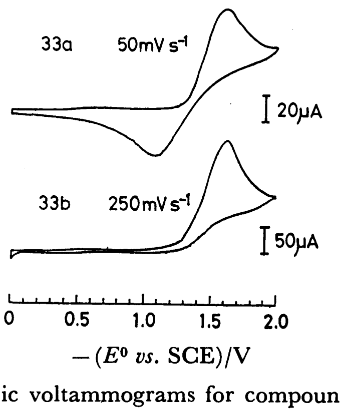


Fig. 3. Cyclic voltammograms for compounds **33a** and **33b** determined in DMF using TBAP as supporting electrolyte.

hand, no isolable compounds were obtained by similar experiments carried out for **33a**.

Experimental

6-Nitrocholest-5-en-3β-yl Acetate (3a). Cholesteryl acetate was nitrated with concd nitric acid and potassium nitrite according to the method of Shoppee *et al.*,[2] to give **3a**: mp 103.5—104.5 °C. The hydrolysis of **3a** with 60% perchloric acid in methanol gave **3** (R=H); mp 129—131 °C.[18]

6-Nitrocholest-5-en-3β-yl Benzoate (3b). A mixture of 14.6 g (27 mmol) of **3** (R=H) and 12 cm^3 (54 mmol) of benzoyl chloride, in 10 cm^3 of pyridine, was left to stand overnight. A subsequent usual work-up gave benzoate **3b** in an 86% yield; recrystallized from ethyl acetate: mp 191—196 °C; IR (KBr) 1510, 1710 cm^{-1}; NMR (CDCl$_3$) δ 0.72 (3H, s, C-18H), 1.18 (3H, s, C-19H), 6.35 (1H, m, $W_{1/2}$=16.8 Hz, C-3αH), 7.35—8.15 (5H, m, ArH).

Found: C, 75.90; H, 9.37; N, 2.62%. Calcd for $C_{34}H_{49}NO_4$: C, 76.20; H, 9.22; N, 2.61%.

6-Nitrocholest-5-en-3β-yl Trifluoroacetate (3c). A mixture of 9.2 g (21 mmol) of **3** (R=H) and 11 cm^3 (78 mmol) of trifluoroacetic anhydride in 80 cm^3 of pyridine was left to stand overnight; recrystallization from methanol then gave 49% of **3c**: mp 110.5—111.5 °C; IR (KBr) 1510, 1780 cm^{-1}; NMR (CDCl$_3$) δ 0.69 (3H, s, C-18H), 1.18 (3H, s, C-19H), 4.87 (1H, m, $W_{1/2}$=17.4 Hz, C-3αH).

Found: C, 65.68; H, 8.14; N, 2.65%. Calcd for $C_{29}H_{44}NO_4F_3$: C, 66.00; H, 8.40; N, 2.65%.

6-Nitrocholest-5-en-3β-yl Tosylate (3d). A mixture of 15 g (31.7 mmol) of **3** (R=H), 7.5 g (39.3 mmol) of tosyl chloride, and 100 cm^3 of pyridine was warmed at 50 °C for 1 h. A usual work-up subsequently gave an 88% yield of **3d** after recrystallization from acetone–methanol: mp 168—169 °C (dec); IR (KBr) 1510, 1780 cm^{-1}; NMR (CDCl$_3$) δ 0.67 (3H, s, C-18H), 1.10 (3H, s, C-19H), 2.47 (3H, s, ArMe), 4.35 (1H, m, $W_{1/2}$=16.2 Hz, C-3αH), 7.55 (4H, m, ArH).

Found: C, 69.92; H, 8.95; N, 2.31%. Calcd for $C_{34}H_{51}NO_5S$: C, 69.72; H, 8.79; N, 2.39%.

Electrolyses. Both controlled-potential and controlled-current electrolyses were carried out for **3a**—**d**. As representative examples, the controlled-potential electrolysis of **3a** and **3d** and the controlled-current electrolysis of **3d** will be described. The results of the controlled-current electrolysis are summarized in Table 2.

The cylindrical cell used for the electrolysis was equipped with a side arm for connecting the reference electrode, SCE, using two junction bridges, filled with saturated KCl and DMF–TBAP (0.1 mol dm^{-3}) solutions. A ceramic thimble (o. d. 3 cm) was used as a divider and was placed on a spacer to allow stirring using a magnetic bar. A punched platinum electrode with an area of 60 cm^2 was used as the cathode, while a platinum wire was used as the anode. Before the electrolysis, the reaction mixture was purged with nitrogen for at least 20 min. A Hokuto potentiostat/galvanostat HA-101 apparatus (max. output 30 V, 1 A) was used, together with a Hokuto digital coulometer HF-102.

The Controlled-potential Cathodic Reduction of 3a. 6β,6′β-Dinitro-3,3′-cholesta-4,4′-diene (4): A solution of 600 mg (12.7 mmol) of **3a** in 250 cm^3 of purified DMF containing TBAP (0.1 mol dm^{-3}) was purged with nitrogen and electrolyzed at the controlled potential of −1.44 V. During the reaction, a solid material was separated out as a precipitate. After 1 F mol^{-1} of electricity had been consumed, the precipitate was filtered, washed with DMF, water, and dried. Recrystallization from benzene gave colorless needles; mp 234—235 °C. The filtrate was evaporated to dryness, extracted with ether, and washed with water to eliminate TBAP. The residue was dissolved in benzene and passed through a Florisil column to give a second crop (mp 233—235 °C) of **4**; the total yield was 45%: IR (KBr) 1550, 1635 cm^{-1}; NMR (CDCl$_3$) δ 0.72 (3H, s, C-18H), 0.92 (3H, s, C-19H), 4.67 (1H, m, $W_{1/2}$=8.25 Hz, C-6αH), 5.90 (1H, m, $W_{1/2}$=4.2 Hz, C-4H); MW 829 (Rast).

Found: C, 77.81; H, 10.69; N, 3.24%. Calcd for $C_{54}H_{88}N_2O_4$: C, 78.02; H, 10.91; N, 3.37%.

The Controlled-potential/current Cathodic Reduction of 3d. A solution of 1.0 g (1.7 mmol) of **3d** in 100 cm^3 of DMF–TBAP was electrolyzed at the controlled potential of −1.45 V. After 1.5 F mol^{-1} of electricity had been consumed, the product was purified by silica-gel chromatography and eluted with hexane containing an increasing amount of benzene. Compound **7** was thus obtained in a 43% yield (mp 102—102.5 °C), after recrystallization from methanol: IR (KBr) 3080, 3030, 3007, 1550 cm^{-1}; NMR (CDCl$_3$) δ 0.73 (3H, s, C-18H), 0.94 (3H, s, C-19H), 3.87 (1H, m, $W_{1/2}$=8.25 Hz, C-6αH).

Found: C, 77.84; H, 10.77; N, 3.27%. Calcd for $C_{27}H_{45}NO_2$: C, 78.03; H, 10.91; N, 3.37%.

The controlled-current reduction of **3d** was carried out using a solution of 5.8 g (9.8 mmol) of **3d** in 250 cm^3 of DMF–TBAP at the current density of 0.85 mA cm^{-2}. The electrolysis was continued until the potential between the working and reference electrodes reached −2.0 V and 1 F mol^{-1} of electricity had been consumed. A 36% yield of **7** and a 2% yield of **4** were obtained.

When D$_2$O (1 cm^3) was added after the electrolysis was over, a 6α-deuterio compound **20** was isolated. Compound **20** was characterized by means of its mass spectrum; *m/e* 370. NMR analysis showed that **20** was present in a 60% quantity together with 40% of **7**.

The Controlled-potential Reduction of 7. A solution of 430 mg (1.0 mmol) of **7** in 100 cm^3 of DMF–TBAP was electrolyzed at −1.90 V. A usual work-up, followed by silica-gel chromatography and eluting with benzene–hexane (1 : 4), gave 310 mg of colorless needles; mp 101—102 °C; recrystallized from acetone–methanol. It was identical with the **10** prepared by the known route.[11] The yield was 16%.

5-Chloro-6β-nitro-5α-cholestane-3β,19-diol Diacetate (32a). Nitrosyl chloride (4.9 g, 75 mmol) was added to a solution of 3.7 g (7.6 mmol) of cholest-5-ene-3β,19-diol diacetate (**31a**) in 41 cm^3 of ether at 0 °C. After 2.9 g of potassium acetate had then been added, the mixture was left to stand for 4 d in a refrigerator. Filtration and then evaporation gave a blue oil, which, after solidification, was recrystallized from acetone–methanol; mp 120.5—121.5 °C. The yield was 58%: IR (KBr) 1745, 1550 cm^{-1}; NMR (CDCl$_3$) δ 0.73 (3H, s, C-18H), 2.04 (6H, s, CH$_3$COO), 5.35 (1H, m, $W_{1/2}$=28.5 Hz, C-3αH).

Found: C, 65.80; H, 8.97; N, 2.39%. Calcd for $C_{31}H_{50}NO_6Cl$: C, 65.52; H, 8.87; N, 2.46%.

6-Nitrocholest-5-ene-3β,19-diol Diacetate (33a). Compound **32a** was dissolved in pyridine, warmed at 50 °C for 30 min, and then left to stand overnight. The product was recrystallized from acetone–methanol; mp 114.5—115.5 °C (69%): IR (KBr) 1740, 1520 cm^{-1}; NMR (CDCl$_3$) δ 0.73 (3H, s, C-18H), 2.03 (3H, s, CH$_3$COO), 2.07 (3H, s, CH$_3$COO), 4.32 (2H, dd, C-19H), 4.60 (1H, m, $W_{1/2}$=21 Hz, C-3αH).

Found: C, 70.15; H, 9.34; N, 2.56%. Calcd for $C_{31}H_{49}NO_6$: C, 70.02; H, 9.29; N, 2.63%.

5-Chloro-6β-nitro-5α-cholestane-3β,19-diol 3-Acetate 19-Tosylate (32b). To a solution of 2.6 g (4.3 mmol) of cholest-5-ene-3β,19-diol 3-acetate 19-tosylate (**31b**) in ether (94 cm^3), were added nitrosyl chloride (2.8 g) and potassium acetate (1.7 g) at 0 °C. The product was then recrystallized from acetone–methanol; mp 131—132 °C (47% yield): IR (KBr) 1735, 1565 cm^{-1}; NMR ($CDCl_3$) δ 0.41 (3H, s, C-18H), 2.04 (3H, s, CH_3COO), 5.32 (1H, m, C-3αH), 7.38—7.80 (4H, m, ArH).

Found: C, 63.55; H, 8.05; N, 1.88%. Calcd for $C_{36}H_{54}O_7NSCl$: C, 63.55; H, 8.00; N, 2.06%.

*6-Nitrocholest-5-ene-3β,19-diol 3-Acetate 19-Tosylate (**33b**).* The dehydrochlorination of **32b** with pyridine gave **33b**, mp 116.5—117.5 °C (85%, recrystallized from acetone–methanol): IR (KBr) 1735, 1520 cm^{-1}; NMR ($CDCl_3$) δ 0.63 (3H, s, C-18H), 1.98 (3H, s, CH_3COO), 2.44 (3H, s, ArMe), 7.35—7.79 (4H, m, ArH), 4.53 (1H, m, $W_{1/2}=25.5$ Hz, C-3αH).

Found: C, 67.43; H, 8.37; N, 2.10%. Calcd for $C_{36}H_{53}O_7NS$: C, 67.15; H, 8.29; N, 2.17%.

*Controlled-potential Reduction of **33b**.* A solution of 590 mg (0.91 mmol) of **33b** in 60 cm^3 of DMF–TBAP was electrolyzed at −1.30 V until 1.7 F mol^{-1} of electricity had been consumed. Chromatography on silica gel eluted with benzene–hexane (1 : 4) gave a 27% yield of 5β,19-cyclo-6β-nitro-5β-cholestan-3β-ol 3-acetate (**34**); mp 88—89 °C (recrystallized from methanol): IR (KBr) 1730, 1545 cm^{-1}; NMR ($CDCl_3$) δ 0.52 and 0.98 (2H, dd, $J=6$ Hz, cyclopropyl CH_2), 2.05 (3H, s, CH_3COO).

Found: C, 73.48; H, 10.01; N, 2.80%. Calcd for $C_{29}H_{47}O_4N$: C, 73.53; H, 10.00; N, 2.96%.

Cyclic Voltammetry. The measurements were carried out using a generator, Hokuto HB-107A and a potentiostat, Hokuto HA-101. As a cathode, a platinum inlay electrode, Beckman No. 39273, was used. Samples are dissolved in DMF containing 0.1 mol dm^{-3} of TBAP. The results are shown in Table 2 and Figs. 1—3. For high-speed scans, the output was stored in a wave-memory unit, NF Circuit Block WM-812A.

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