POLYFLUOROBICYCLO(2,2,1)HEPTANES
PART VIII*. BIS(UNDECAFLUOROBICYCLO(2,2,1)HEPTAN-1-YL)- AND BIS(4*H*-DECAFLUOROBICYCLO(2,2,1)HEPTAN-1-YL)-MERCURY

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SUMMARY

The title compounds were prepared from 1-lithio-undecafluorobicyclo(2,2,1)-heptane, and from 1*H*,4-lithio-decafluorobicyclo(2,2,1)heptane and 1*H*-deca-fluorobicyclo(2,2,1)hept-4-yl magnesium iodide with mercuric chloride. With sulphur and caesium fluoride in dimethyl formamide, both mercurials gave the corresponding thioxides and these on hydrolysis gave the known bridgehead thiols. With sulphur alone, the undecafluoro mercurial gave mainly the disulphide and a range of polysulphides, under conditions which left the 4*H*-decafluoro mercurial unchanged. Conventional d.c. polarography of the mercurials indicated an inconsistency in the use of this method for determining the acidities of highly fluorinated hydrocarbons.

INTRODUCTION

Perfluoroalkyl mercurials in the presence of alkali metal fluorides have been used as sources of perfluorocarbanions[2]. This paper describes analogous studies with polyfluoronorbornane mercurials. The geometry at the bridgehead position of the norbornane system confers additional interest on the reactions.

RESULTS AND DISCUSSION

We have already described the preparation of bridgehead mercurials (VI) and (IX) directly from (I)[3,4] and (II)[3], respectively, by reaction with mercury salts in a medium of KOH–H₂O–DMSO. Mercurials (VI) and (IX) were used in the

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* For Part VII, see ref. 1.

present study, but were prepared by alternative routes from mercuric chloride and 1-lithio-undecafluorobicyclo(2,2,1)heptane (III) and 1*H*,4-lithio-decafluoro-bicyclo(2,2,1)heptane (IV) or 1*H*-decafluorobicyclo(2,2,1)hept-4-yl magnesium iodide (V) and mercuric iodide.

Since various polyfluoro-organo mercurials have been shown to react with sulphur at elevated temperatures[5–7], it was of interest to examine these bridgehead analogues.
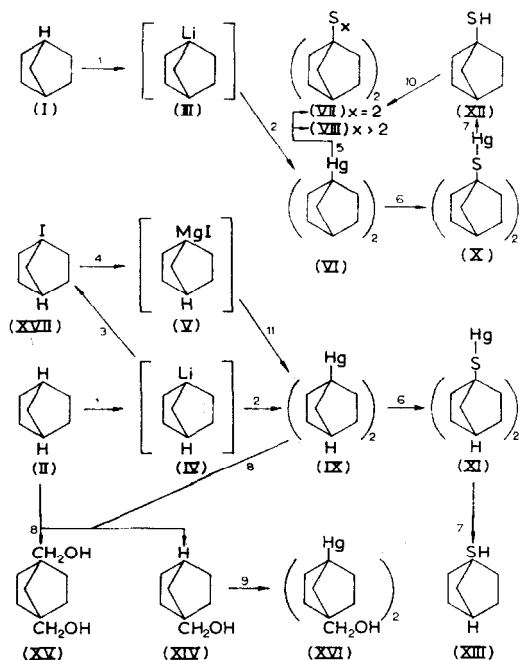

Fig. 1. Polyfluorobicyclo(2,2,1)heptane bridgehead mercurials.

1, BuLi; 2, HgCl₂; 3, I₂; 4, Mg; 5, S; 6, S–CsF–DMF; 7, H₂O⁺; 8, H₂O–KOH–DMSO–HCHO; 9, HgCl₂–NaBr–KOH–H₂O–DMSO; 10, Br₂–AcOH; 11, HgI₂. (All unmarked substituents are fluorine.)

Bis (undecafluorobicyclo[2,2,1]heptan-1-yl)mercury (VI) (1 mol) was largely unaffected by sulphur (2 mol) after 4 days at 250 °C, but an excess of sulphur after 1 week at 250 °C gave mainly the disulphide[1] (VII) and a range of polysulphides (VIII), thought to have the general structure $(C_7F_{11})_2S_x$, but none of the known[1] thio-ether, $(C_7F_{11})_2S$. A process of the type:

$$C_7F_{11}-Hg-C_7F_{11} + S_8 \rightarrow C_7F_{11}Hg^+ + C_7F_{11}S_8^-$$
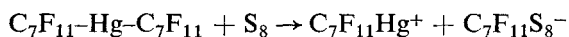
is suggested, in which the carbanionic character of the fluoroalkyl group is the decisive influence. It thus resembles the reaction of bis(perfluoro-isopropyl)mercury with sulphur at 200 °C which gave[5] a mixture of perfluoro-isopropyl-disulphide

and -polysulphides, $(C_3F_7)_2S_x$, and differs from that[6] between bis(pentafluoro-phenyl)mercury and sulphur at 250 °C which gave only the thio-ether $(C_6F_5)_2S$. There is evidence for the formation of a polysulphide in addition to the thio-ether from pentafluorophenyl mercuric chloride and sulphur[8].
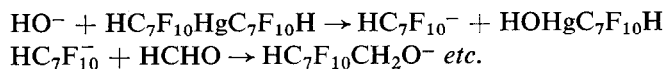
In contrast to (VI), bis(4*H*-decafluorobicyclo[2,2,1]heptan-1-yl)mercury (IX) did not react with an excess of sulphur alone at 250 °C. When the temperature was raised to 340 °C, only a small amount of the mercurial was recovered from the charred residue.

The difference in reactivity between (VI) and (IX) presumably arises from a reduction in the anionoid character of the mercury-bonded carbon atom resulting from replacement of the fluorine at C_4 by hydrogen (see later). A comparable difference in reactivity was observed[2] between bis(perfluoro-isopropyl)mercury and bis(perfluoro-t-butyl)mercury, though it was thought that this might be explained by a higher stability of the perfluoro-t-butyl carbanion as compared with the perfluoro-isopropyl analogue[2].

Both mercurials (VI) and (IX) reacted with sulphur in dimethyl formamide in the presence of caesium fluoride[2] to give, respectively, mercury bis(undeca-fluorobicyclo[2,2,1]heptan-1-yl)thioxide (X) and mercury bis(4*H*-decafluoro-bicyclo[2,2,1]heptan-1-yl)thioxide (XI), the latter as a crystalline complex with dimethyl formamide. It is perhaps pertinent to the difference in reactivity between (VI) and (IX) with sulphur, mentioned previously, that this caesium-fluoride-catalysed reaction is thought[2] to be facilitated by enhancement of the anionoid properties of the mercury-bonded carbon atom through coordination of fluoride ion with mercury.

The thioxides (X) and (XI) gave the known[1] thiols (XII) and (XIII), respec-tively, on acid hydrolysis. Thiol (XII) was characterised by oxidation to the disulphide (VII). Thiol (XIII) was identical with an authentic specimen prepared from the lithio compound (IV) and sulphur[1].

The synthetic utility of the bridgehead hydrogen in the decafluoro mercurial (IX) appears to be circumscribed by nucleophilic attack on mercury. Thus (IX) with base in aqueous dimethyl sulphoxide containing formalin gave 1*H*,4-hydroxy-methyl- and 1,4-bis(hydroxymethyl)-decafluorobicyclo(2,2,1)heptane, (XIV) and (XV), respectively, the same products as obtained[3] from (II). Presumably the process is of the type depicted by:

$$HO^- + HC_7F_{10}HgC_7F_{10}H \rightarrow HC_7F_{10}^- + HOHgC_7F_{10}H$$
$$HC_7F_{10}^- + HCHO \rightarrow HC_7F_{10}CH_2O^- \text{ etc.}$$

However, bis(4-hydroxymethyldecafluorobicyclo[2,2,1]hept-1-yl)mercury (XVI) was prepared from the 1*H*,4-hydroxymethyldecafluoride (XIV) and mercuric chloride in aqueous potassium hydroxide containing dimethyl sulphoxide and an excess of sodium bromide; this approach should provide a route to a wider range of 4-substituted decafluorobicyclo(2,2,1)heptane mercurials.

In an attempted aqueous hydrolysis of the undecafluoro mercurial (VI) in dimethyl sulphoxide, a crystalline complex of the mercurial and dimethyl sulphoxide was produced.

The acidities of bridgehead hydrogen substituents in polyfluorobicyclo(2,2,1)-heptanes are of considerable interest and have been demonstrated qualitatively[3, 4] and quantitatively[9, 10]. The latter work used the relative rates of hydrogen isotope exchange and revealed[10] an unexpectedly large difference between the $1H$-undeca-fluoride (I) and the $1H,4H$-decafluoride (II).

Recently Butin *et al.*[11] have reported electrochemical reductions of some fluorocarbon-type mercurials, $(R_f)_2Hg$, and they used these polarographic results to calculate the acidities of the corresponding fluorocarbon hydrides R_fH. These polarographic data did not always correlate very precisely with the rate constants of hydrogen isotopic exchange of R_fH in methanol, however.

It was of considerable interest therefore to apply the polarographic procedure of Butin *et al.*[11] to the mercurials (VI) and (IX) and arrive at the acidities of (I) and (II) as given by their method. As a standard, electrochemical reduction of bis(pentafluorophenyl)mercury was carried out to give $n\alpha E_{1/2} = 0.49 \pm 0.04$ V. Butin *et al.*[11] quoted 0.55 V but did not give the limits of experimental error associated with their measurements.

TABLE 1

POLAROGRAPHIC CONSTANTS OF MERCURIALS

	$(C_7F_{11})_2Hg$	$(HC_7F_{10})_2Hg$
$-E_{1/2}$ (*vs.* S.C.E.)	0.752 ± 0.001 V	1.33 ± 0.02 V
$n\alpha$	0.73 ± 0.02	0.9 ± 0.1
$-n\alpha E_{1/2}$	0.55 ± 0.02 V	1.2 ± 0.2 V

The polarographic values obtained for our mercurials are set out in Table 1, and if they are applied to the calibration graph of Butin *et al.*[11] the resultant pK_a values are 16.0 ± 0.5 for the undecafluoride (I) and 27 ± 3 for the decafluoride (II). These values are different, both in relative and absolute terms, to those obtained by hydrogen isotope exchange[10], *viz.*, pK_a 22 (I) and pK_a 26 (II), although the considerable difference in acidity, $C_7F_{11}H > HC_7F_{10}H$, is maintained.

In so far that electron transfer to the mercurial from the electrode would be expected to be influenced mainly by inductive effects, the above difference in calculated pK_a values between the undecafluoride (I) and the decafluoride (II) could be interpreted to support a substantial inductive effect through the molecular cavity in the perfluoro mercurial (VI). We have made similar postulates to explain other effects in bicyclo(2,2,1)heptane systems, though it is noteworthy that, despite acidity differences, the hydrogen in both (I) and (II) can be replaced synthetically.

A major discrepancy stands out from these results however; whereas the isotope exchange process indicated a comparable acidity for $C_7F_{11}H$ (I) (pK_a 20 or 22) and $(CF_3)_3CH$ (pK_a 20)[10], Butin *et al.*[11] report a much higher acidity determined by polarography for $(CF_3)_3CH$ (pK_a 7) than our figure for (I) (pK_a 16).

The absolute values of pK_a determined by the two techniques may well not be strictly comparable, but the similarity in experimentally-determined results for (I) and $(CF_3)_3CH$ found by isotope exchange, and the significant difference between the values determined by polarography, are not reconcilable if both techniques measure the same effect. This is a vital issue since the similarity of the results from (I) and $(CF_3)_3CH$ by isotope exchange has been used by Streitweiser[9] and by Holtz[10] and by ourselves as arguments against negative hyperconjugation in fluorocarbon derivatives (such effects in (I) would require contributions from species with unsaturation at the bridgehead). From studies on other fluorocarbon hydrides, Klabunde and Burton[12] have also decided that fluorine hyperconjugation is not a necessary rationale. We have some reservations about the polarographic approach since we have found that experimental problems arise with it. We have further reservations about the theoretical relationships of the polarographic results on mercury compounds to acidities of fluorocarbon hydrides. We still believe therefore that the isotope exchange results of Streitweiser and Holtz are the more reliable, and that the acidities of $C_7F_{11}H$ and $(CF_3)_3CH$ are of the same general order.

It has been suggested[12] that the tris(trifluoromethyl) carbanion might be planar, but it seems most unlikely that secondary effects of this sort could explain the discrepancy.

Obviously, more information on the purely inductive effects of the tris(trifluoromethyl), undecafluoronorbornyl and 4*H*-decafluoronorbornyl groups is required; this is currently being sought.

EXPERIMENTAL

Gas chromatography

Analytical work was carried out using 2 m glass columns (4 mm diam.) packed with silicone gum (SE 301)–Universal B (col. A).

Mass spectra

These were measured on an A.E.I. MS9 instrument.

NMR spectroscopy

The proton and fluorine spectra were measured with a Varian HA-100 instrument at 100 MHz using tetramethylsilane as internal standard and at 94.07 MHz using trichlorofluoromethane as internal standard, respectively, except as otherwise stated.

Bis(undecafluorobicyclo[2,2,1]heptan-1-yl)mercury (VI)

     To a solution of 1*H*-undecafluorobicyclo(2,2,1)heptane (I) (3.0 g) in ether
(10 cm³) at −78 °C, butyl-lithium (5.5 cm³; 2.35 mol l⁻¹ in hexane) was added
slowly. The mixture was stirred for 0.5 h, mercuric chloride (1.3 g) added, and
stirring continued for 2 h at −78 °C and for 18 h at 15 °C. It was then washed
with water (50 cm³), the ether layer dried (MgSO₄) and shown by GLC (col. A;
100 °C; N₂, 3 l h⁻¹) to contain ether, hexane, starting material, bis(undecafluoro-
bicyclo[2,2,1]heptan-1-yl)mercury and one other small unidentified peak. The
solution was evaporated to dryness and the residue recrystallised from CCl₄ to give
bis(undecafluorobicyclo[2,2,1]heptan-1-yl)mercury (VI) (0.6 g), m.p. 162.5–163 °C
(lit.[3] : 164.5–165.5 °C) with a correct IR spectrum. In an earlier paper[4], a lower
m.p. was recorded but the synthesis used (C₇F₁₁I + Hg in UV light) gave material
contaminated with C₇F₁₁HgI.

*Bis(*4H*-decafluorobicyclo[2,2,1]heptan-1-yl)mercury (IX)*

     (i) Via *the lithio derivative (IV)*

     Butyl-lithium (5.0 cm³; 2.35 mol l⁻¹ in hexane) was slowly added to a
solution of 1*H*,4*H*-decafluorobicyclo(2,2,1)heptane (II) (3.0 g) in ether (10 cm³)
at −78 °C, the mixture stirred for 0.5 h and mercuric chloride (1.5 g) added to
the solution. Isolation as above afforded a paste which was recrystallised from
CCl₄ to give bis(4*H*-decafluorobicyclo[2,2,1]heptan-1-yl)mercury (IX) (1.2 g),
m.p. 215–216 °C, with a correct IR spectrum[3].

     (ii) Via *a Grignard reagent*

     1*H*,4-Iodo-decafluorobicyclo(2,2,1)heptane[13] (XVII) (1.4 g) in ether (10 cm³)
was slowly added to magnesium (1.0 g) in refluxing ether. After 2.5 h, mercuric
iodide (0.75 g) was added in small portions to the refluxing solution. After a
further 1 h under reflux, water was added carefully (vigorous reaction), the ethereal
layer separated, dried (MgSO₄), filtered and evaporated to dryness. The residue
was sublimed (140 °C/14 mmHg) to give bis(4*H*-decafluorobicyclo[2,2,1]heptan-
1-yl)mercury (IX) (0.2 g) with a correct IR spectrum[3].

Bis(4-hydroxymethyldecafluorobicyclo[2,2,1]heptan-1-yl)mercury (XVI)

     To a solution of sodium bromide (12 g) in water (30 cm³) was added mercuric
chloride (1.3 g) and potassium hydroxide (0.5 g). The mixture was stirred until
homogeneous and dimethyl sulphoxide (40 cm³) added, followed by 1*H*,4-hydroxy-
methyldecafluorobicyclo(2,2,1)heptane[3] (XIV) (2.0 g), stirred for 3 h, poured into
water (100 cm³) and extracted with ether (1 × 40 cm³ and 2 × 20 cm³). The
combined extracts were dried (MgSO₄), filtered and evaporated. The resultant
mixture was fractionally sublimed to give the starting material (0.2 g), a very impure
mercurial (0.2 g) and the mercurial (0.7 g) which was recrystallised from CCl₄ to
give bis(4-hydroxymethyldecafluorobicyclo[2,2,1]heptan-1-yl)mercury (XVI) (nc)

(0.6 g), m.p. 231–232 °C, (Found: C, 23.4; H, 0.5; F, 46.4%. $C_{16}H_6F_{20}HgO_2$ requires C, 23.7; H, 0.7; F, 46.8%), $\nu_{max.}$ 3400 cm^{-1} (OH); the ^{1}H and ^{19}F NMR spectra (in hexadeuteroacetone) were consistent with the proposed structure.

Reaction of bis(4H-decafluorobicyclo[2,2,1]heptan-1-yl)mercury (IX) with formaldehyde in aqueous base

To the mercurial (0.5 g), dimethyl sulphoxide (10 cm^3) and water (20 cm^3) was added KOH (0.1 g) and formalin (1 cm^3; 40% w/v) and the mixture stirred for 30 min. The solution was poured into water (100 cm^3) and extracted with ether. The combined extracts were dried (MgSO$_4$), filtered and evaporated and the small bulk (*ca.* 5 cm^3) of residue shown by GLC and IR spectroscopy to contain 1*H*,4-hydroxymethyl- and 1,4-bis(hydroxymethyl)-decafluorobicyclo(2,2,1)heptane[3].

Reaction of bis(undecafluorobicyclo[2,2,1]heptan-1-yl)mercury (VI) with aqueous base

To the mercurial (0.9 g), dimethyl sulphoxide (25 cm^3) and water (5 cm^3) was added KOH (2 g) and the solution shaken for 30 min, when a black precipitate had formed. The solution was poured into water (60 cm^3) and extracted with ether. The extract was dried (MgSO$_4$), filtered, evaporated to dryness and the residue sublimed (80 °C/14 mmHg) to give a crystalline sublimate (0.33 g), m.p. 66–67 °C, which was recrystallised from CCl$_4$ to give bis(dimethylsulphoxido)bis-(undecafluorobicyclo[2,2,1]heptan-1-yl)mercury (nc) (0.2 g), m.p. 74–75 °C, (Found: C, 22.8; F, 44.5%. $C_{18}H_{12}F_{22}HgO_2S_2$ requires C, 22.9; F, 44.3%), m/e 769 (P) ($C_{14}F_{21}$ ^{202}Hg), 495 (C_7F_{11} ^{202}Hg), 78 ((CH$_3$)$_2$SO), 32 (S).

Reaction of bis(undecafluorobicyclo[2,2,1]heptan-1-yl)mercury (VI) with sulphur alone

The mercurial (VI) (0.5 g) and sulphur (0.5 g) were intimately mixed and kept at 250 °C for 1 week in a Carius tube. After cooling, the contents of the tube were extracted with several small portions of ether and the combined extracts evaporated to dryness and sublimed (100 °C/14 mmHg) to yield a solid (0.2 g), m.p. 105–120 °C, with an IR spectrum almost identical to that of bis(undecafluoro-bicyclo[2,2,1]heptan-1-yl)disulphide[1] (VII); $m/e = 650$ (P) (P:P+2 ratio was consistent with the presence of the disulphide). By GLC analysis (col. A; 148 °C; N$_2$, 5 l h^{-1}), it was shown to contain a major component with the same retention time as an authentic specimen of (VII) and one minor component. TLC analysis (silica gel plate, irrigated with $C_6F_{11}CF_3$ (5 parts) and C_6F_6 (1 part), developed with iodine vapour) indicated five components (with R_f values of 0.67, 0.58, 0.52, 0.46 and 0.34, the amounts of the last four being very small. The R_f value of an authentic specimen of the disulphide (VII) in this system was 0.68.

Attempted reaction of bis(4H-decafluorobicyclo[2,2,1]heptan-1-yl)mercury (IX) with sulphur alone

The mercurial (0.5 g) and sulphur after 1 week in a Carius tube at 250 °C gave a solid (0.2 g) with an IR spectrum similar to that of the starting material. A portion (0.18 g) was recrystallised from aqueous ethanol to yield unchanged mercurial (IX) (0.09 g), m.p. 216–218 °C.

The mercurial (IX) (0.5 g) and sulphur (0.5 g) at 340 °C under an atmosphere of nitrogen gave small quantities of unchanged mercurial and a large amount of charred material.

Mercury bis(undecafluorobicyclo[2,2,1]heptan-1-yl)thioxide (X)

Bis(undecafluorobicyclo[2,2,1]heptan-1-yl)mercury (VI) (2.9 g), dimethyl formamide (20 cm^3) and sulphur (0.5 g; dried at 14 mmHg over P_2O_5 for 24 h) were stirred together at 80 °C and caesium fluoride (0.2 g; freshly calcined and ground) added. After stirring for 0.5 h, the solution was cooled, filtered, poured into water (70 cm^3) and extracted with ether (20 cm^3). The extract was dried (MgSO$_4$), filtered and evaporated to a residue which was sublimed (130 °C/ 14 mmHg) to give mercury bis(undecafluorobicyclo[2,2,1]heptan-1-yl)thioxide (X) (nc) (0.37 g), m.p. 162–165 °C, (Found: C, 19.9; F, 49.3%. $C_{14}F_{22}HgS_2$ requires C, 19.7; F, 49.1%).

The mercury thioxide (X) (0.2 g), ether (15 cm^3) and 4 mol l^{-1} HCl (20 cm^3) were shaken together for 5 min and left for 1 h. The ethereal layer was dried (MgSO$_4$), filtered and evaporated to leave a residue (0.18 g) which slowly solidified. The latter solid, glacial acetic acid (1.0 cm^3) and bromine (3 drops) gave bis-(undecafluorobicyclo[2,2,1]heptan-1-yl)disulphide (VII) (0.06 g), m.p. 98–99 °C, with a correct IR spectrum[1].

Mercury bis(4H-decafluorobicyclo[2,2,1]heptan-1-yl)thioxide (XI)

Treated as described previously, bis(4*H*-decafluorobicyclo[2,2,1]heptan-1-yl)mercury (IX) (1.10 g), dimethyl formamide (20 cm^3), sulphur (0.3 g) and caesium fluoride (0.1 g) afforded a complex of dimethyl formamide with mercury bis-(4*H*-decafluorobicyclo[2,2,1]heptan-1-yl)thioxide (XI) (nc) (from hexane) (0.18 g), m.p. 153–156 °C, (Found: C, 22.6; H, 1.0; F, 44.0%. $C_{14}H_2F_{20}HgS_2$•$(C_3H_7NO)_{0.7}$ requires C, 22.3; H, 0.8; F, 43.8%).

The mercury thioxide–dimethyl formamide complex (0.08 g) was dissolved in ether (7 cm^3) and shaken with 4 mol l^{-1} HCl (10 cm^3) for 5 min. After a further 10 min, the ethereal layer was dried (MgSO$_4$), filtered and evaporated to leave a residue of 4*H*-decafluorobicyclo(2,2,1)heptan-1-yl thiol (XIII) (0.05 g) with a correct IR spectrum[1].

Polarography

Polarographic measurements were made automatically using an Amel polarograph and a capillary with an enforced drop time of 2 s. Dimethyl formamide

(distilled from P_2O_5 and stored over CaH_2) was used as solvent with tetra(n-butyl)-ammonium perchlorate as base electrolyte (0.2 mol l^{-1} solution): solutions were deoxygenated with N_2. All potentials were measured against a saturated calomel electrode and were corrected for the i_r drop in the cell. For bis(undecafluoro-bicyclo[2,2,1]heptan-1-yl)mercury (VI), polarograms were recorded at a 0.11×10^{-3} mol l^{-1} concentration of the organo mercurial: at higher concentrations the polarograms showed the presence of maxima. Observed values are given in Table 2.

TABLE 2

Concentration/ 10^3 mol l^{-1}	$E\frac{1}{2}$(V)	na	$-naE\frac{1}{2}$(V)
0.11	$\begin{cases} -0.752 \\ -0.753 \end{cases}$	0.715 0.741	0.538 0.557

Bis(4*H*-decafluorobicyclo[2,2,1]heptan-1-yl)mercury (IX) was studied in a similar manner; solutions of concentration greater than 0.3×10^{-3} mol l^{-1} gave non-linear plots of $\log(i_d-i)/i$ vs. E so that $naE\frac{1}{2}$ could not be calculated. The results obtained are recorded in Table 3.

TABLE 3

Concentration/ 10^3 mol l^{-1}	i_d(μA)	$E\frac{1}{2}$(V)	na	$-naE\frac{1}{2}$(V)
0.214	0.061	−1.301	0.86	1.12
0.32	0.108	−1.290	1.07	1.38
0.53	0.197	−1.262	—	—
1.07	0.485	−1.253	—	—

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