

EFFECTS OF BRIDGEHEAD SUBSTITUENTS ON THE STABILITY OF THE 1-NORBORNYL RADICAL

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Dedicated to Professor Otto Exner on the occasion of his 75th birthday in recognition of his outstanding contributions to the areas of physical organic chemistry and chemometrics.

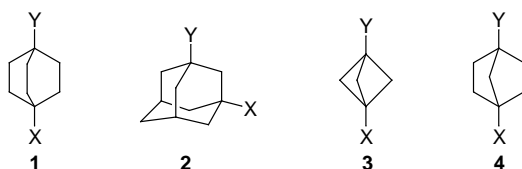
The electrochemical reductive cleavage of a series of 4-X-substituted bicyclo[2.2.1]heptan-1-yl bromides and iodides (X = H, F, Cl, Br, I, SnMe₃) was investigated by means of cyclic voltammetry. By application of the dissociative electron-transfer theory, the variations in the peak reduction potentials translate to values for the weakening of the C–Br and C–I bond dissociation energies (ΔD) upon replacement of H by all the substituents (X). The ΔD values suggest significant through-space stabilizing interactions (homohyperconjugation) in the 4-X-substituted bicyclo[2.2.1]heptane radical species.

Key words: Cyclic voltammetry; Dissociative electron transfer; 4-Substituted 1-norbornyl radicals; Spin delocalization; Radical stabilization; Electrochemistry; Reduction cleavage.

Cyclic voltammetry studies coupled with a newly developed dissociative electron-transfer model allows for the determination of changes in the bond dissociation energy value (D) for the cleavage of a common nucleofuge, within series of structurally similar compounds¹. The methodology is useful since the effects of remote substituents on the stability of relatively large radical species can be readily and conveniently assessed. It is significant to note that such pertinent information is extremely difficult, if not impossible, to obtain by other experimental means.

Previously, we have reported the application of the aforementioned electrochemical technique to series of dihalobicyclo[2.2.2]octanes (**1**), dihalo-adamantanes (**2**), and dihalobicyclopentanes (**3**) (Y = Br or I; X = F, Cl, Br, I)² as well as to tin substituted derivatives of **1** and **2** (Y = Br or I; X = SnMe₃)³. Substantial variations in the ΔD values of the first carbon–halogen bond to be cleaved (C–Br or C–I) were revealed. The overall trends were rationalized in terms of dominant through-space (adamantanes and bicyclopentanes)

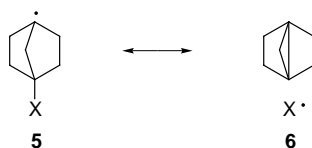
and through-bond (bicyclooctanes) stabilizing interactions in the respective radical species and, to a lesser extent, in the precursor halide. Herein we report an extension of these studies to a similar series of 1,4-disubstituted



In compounds **1**, **2**, and **4**: X = H, F, Cl, Br, I, SnMe₃; Y = Br, I

In compound **3**: X = H, F, Cl, Br, I; Y = Br, I

bicyclo[2.2.1]heptanes (**4**) (Y = Br or I; X = F, Cl, Br, I, SnMe₃). The study of **4** is particularly relevant since several years ago, solution⁴ and matrix⁵ ESR investigations of the 1-norbornyl (**5**; X = H) and 4-halo-1-norbornyl radicals (**5**; X = Br and I), respectively, revealed large long-range hydrogen and halogen coupling which suggests the operation of a facile spin-delocalization mechanism. Moreover, the *hfsc* and *g* values indicated enhanced delocalization of the unpaired electron as the 4-substituent is varied from hydrogen through bromine to iodine. This has been ascribed to a "through-space" interaction (homohyperconjugation) as depicted by the following resonance structures. As we shall see below, the radical stabilization associated with this spin-delocalization mechanism is clearly exposed and placed on a quantitative footing by the present studies.



RESULTS AND DISCUSSION

The cyclic voltammograms of the various iodides and bromides of **4** (see above) were obtained in acetonitrile at a glassy carbon electrode. Tetra-butylammonium tetrafluoroborate (0.1 mol l⁻¹) was used as the supporting electrolyte. A single irreversible cathodic wave was observed in all cases except for the parent bromide (**4**; X = H, Y = Br). The latter compound exhibited no reduction peak before the current rise due to the supporting electrolyte discharge. It should be noted that thorough studies of the electrochemical reduction of 1-iodo- and 1-bromonorbornane (**4**; X = H, Y = I

and Br, respectively) as well as 1,4-dihalonorbornanes (**4**; X = Y = Br and I) at a mercury cathode in DMF have been reported⁶.

The most relevant information pertaining to the cyclic voltammograms of **4** is presented in Table I. The E_p value listed for the parent bromide (**4**; X = H, Y = Br) is an estimate based on the assumption that the ΔE_p value for the chloro substituent (X = Cl) is identical for both the bromo and iodo series of compounds (**4**; Y = Br and I, respectively). This is reasonable given that this was found to be the case for systems **1**, **2**, and **3** (X = Cl, Y = Br and I)². It can be seen (Table I) that the values of the transfer coefficient (α) derived from the cyclic voltammetric peak widths are of the order 0.24–0.33, *i.e.*, considerably less than 0.5. Thus, the reductive cleavage follows a concerted mechanism rather than a pathway involving the formation of an anion radical. Similar observations were noted for **1**, **2**, and **3** (Y = Br and I)^{2,3} and other simple saturated halides¹. An examination of the E_p values (Table I) reveals that there is a definite positive shift of the peak potential in both series of compounds on replacing H by the various substituents (X). Central to translating these perturbations of the reduction potential to values for the weakening of the C–Br or C–I bond dissociation energy (ΔD) is a quadratic activation-driving force relationship shown (Eq. (1)) in its electrochemical

TABLE I
Cyclic voltammetric peak potentials (E_p) and transfer coefficients (α) for compounds (**4**)

X	$E_p^{a,b}$, V vs SCE		α^c	
	Y = Br	Y = I	Y = Br	Y = I
H	-2.98 ^d (0.00)	-2.42(0.00)	–	0.24
F	-2.88(0.10)	-2.29(0.13)	0.24	0.29
Cl	-2.81(0.17)	-2.25(0.17)	0.20	0.27
Br	-2.61(0.37)	-2.19(0.23)	0.24	0.24
I	–	-2.04(0.38)	–	0.24
SnMe ₃	-2.84(0.14)	-2.34(0.08)	0.27	0.33

^a Measured in acetonitrile at 20 °C at 0.1 V s⁻¹, accurate to ± 5 mV. ^b In parentheses: $\Delta E_p = E_p(Y) - E_p(H)$. ^c Determined from the cyclic voltammetric peak widths assuming the Butler–Volmer kinetics applies $\alpha = (1.85 RT/F)/E_{p/2} - E_p$ (ref.^{1f}). ^d Estimated value (see the text). No reduction observed due to the concomitant reduction of either the solvent or the supporting electrolyte (*ca* -2.90 V).

version¹ (expressing the potential in volts and the Gibbs energies in electronvolts and

$$\Delta G^\# = \Delta G_0^\# \left(1 + \frac{E_p - E^0}{4\Delta G_0^\#} \right)^2 \quad (1)$$

where E_p is the electrode peak potential, and E^0 is the standard potential of the $\text{RX}/\text{R}^\bullet + \text{X}^-$ couple). The intrinsic barrier Gibbs energy ($\Delta G_0^\#$; see Eq. (2)) is the sum of a solvent reorganization factor (λ_0) and a contribution of bond breaking equal to one-fourth of the bond dissociation energy ($D_{\text{RX} \rightarrow \text{R}^\bullet + \text{X}^-}$).

$$\Delta G_0^\# = \frac{D_{\text{RX} \rightarrow \text{R}^\bullet + \text{X}^-} + \lambda_0}{4} \quad (2)$$

The standard potential (E^0) for the dissociative electron transfer is related to the bond dissociation energy as shown in Eq. (3).

$$E^0 = -D_{\text{RX} \rightarrow \text{R}^\bullet + \text{X}^-} + E_{\text{X}^\bullet/\text{X}^-}^0 + T\Delta S \quad (3)$$

Since the change in driving force between compounds within a structurally similar series is small, the above quadratic equation (Eq. (1)) can be linearized (Eq. (4)) to a good first-order approximation.

$$\Delta G^\# = \Delta G_0^\# + \frac{E_p - E^0}{2} \quad (4)$$

Thus, if it is assumed that ΔS and λ_0 do not vary much and if the leaving group is the same, then it follows that ΔD is directly related to ΔE_p (Eq. (5)),

$$\Delta D = 2/3\Delta E_p \quad (5)$$

given that $\Delta G^\#$ has a fixed value at a constant scan rate. It should be noted that the results for these approximations are not too different from those obtained from a more rigorous procedure for determining D used previously^{1f,2,3}.

The ΔD values for the two series of **4** ($Y = \text{Br}$ and I) determined from the corresponding ΔE_p parameters (Table I) by use of Eq. (5) are listed in Table II. In order to facilitate comparisons, the corresponding values of **2** determined similarly are also presented together with those previously calculated by a more rigorous procedure (in parentheses)^{2,3}. A comparison between **2** and **4** is pertinent because of their structural semblance, namely, the 1,3-geometrical relationship of the bridgehead groups. The experimental precision of the ΔD values is of the order ± 10 meV. However, additional errors may result from the inaccuracy of the dissociative electron-transfer model itself as well as the inherent assumptions in deriving Eq. (5).

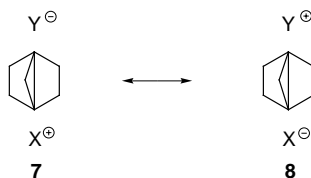
It can be seen (Table II) that in the iodide series of **4** ($Y = \text{I}$), the ΔD variations for the halogen substituents is $\text{I} > \text{Br} > \text{Cl} > \text{F} > \text{H}$. A similar pattern of effects is also revealed for the bromide series (**4**; $Y = \text{Br}$). However, it is noteworthy that ΔD for $X = \text{Br}$ is significantly smaller in **4** ($Y = \text{I}$) than the corresponding value in **4** ($Y = \text{Br}$). These overall trends for the halogen substituents are practically identical to those previously observed in **2** (ref.²) and may be similarly rationalized in terms of a combination of the effects of through-space stabilizing interactions in the monohalo radical ($\sigma_{\text{cx}}^* - \sigma_{\text{c}}$; depicted by canonical structure **6**) and the precursor dihalide ($\sigma_{\text{cx}} - \sigma_{\text{cy}}$ and $\sigma_{\text{cx}}^* - \sigma_{\text{cy}}$; depicted by canonical structures **7** and **8**, respectively). The latter interactions are certainly weaker than those in the former and appear only significant for $X = Y = \text{I}$ and $X = \text{Br}, Y = \text{I}$, leading only to a partial

TABLE II
Bond dissociation energy changes (ΔD)^a for systems **2** and **4**

X	ΔD^b , meV for 2		ΔD^c , meV for 4	
	Y = Br	Y = I	Y = Br	Y = I
H	0	0	0	0
F	33(31)	33(31)	66	86
Cl	133(124)	133(125)	113	113
Br	266(245)	146(140)	246	153
I	-	266(251)	-	253
SnMe ₃	113(116)	66(73)	93	53

^a $\Delta D = 2/3 \Delta E_p$. ^b Values in parentheses taken from refs^{2,3}. ^c ΔE_p values taken from Table I.

compensation. The relative magnitude of the through-space interactions in **5** when going from X = H to F, to Cl, to Br, and to I is in accord with orbital energy level considerations⁷. The significantly larger value of ΔD for SnMe₃ in the bromide *versus* the iodide **4** (X = Br and I, respectively), which was previously noted for **2** (ref.³) (X = SnMe₃; Y = Br and I; see Table II), suggests a greater stabilizing interaction in the precursor for the latter compound.



Given that homohyperconjugation is dependent on the extent of overlap of the “back-lobe” orbitals and, hence, on their relative orientation (interorbital angle and internuclear distance between the bridgehead positions)⁸ and state of hybridization, the very similar electron delocalization effects in **2** and **4** and in their respective monosubstituted radicals, as mirrored by their ΔD values is somewhat surprising. Consequently, because one-bond carbon-tin coupling constants ($^1J(^{13}\text{C}, ^{119}\text{Sn})$) are NMR parameters which are directly related to the bond order of the C–Sn bond⁹ and, therefore, likely to be responsive to “back-lobe” interactions as depicted by

TABLE III
One-bond carbon-tin coupling constants ($^1J(^{13}\text{C}, ^{119}\text{Sn})$) for **2**^a and **4** (Y = SnMe₃)

X	σ_{F}^b	$^1J(^{13}\text{C}, ^{119}\text{Sn})$, Hz		$^1J(^{13}\text{CH}_3, ^{119}\text{Sn})$, Hz		Σ^1J , Hz	
		2	4	2	4	2	4
H	0.00	455	460	291	312	1 328	1 396
F	0.42	433	445	304	322	1 345	1 411
Cl	0.43	424	431	304	323	1 336	1 400
Br	0.44	417	426	304	323	1 329	1 395
I	0.43	416	422	303	323	1 325	1 391
SnMe ₃	0.02	441	445	289	311	1 308	1 378

^a From ref.³; ^b from ref.¹⁰

structure **8** ($X = \text{halogen}$, $Y = \text{SnMe}_3$), a comparison of these parameters for **2** ($Y = \text{SnMe}_3$) and **4** ($Y = \text{SnMe}_3$) seemed appropriate. These are listed in Table III together with the σ_F values¹⁰ of the substituents. It can be seen (Table III) that the $^1J(^{13}\text{C}, ^{119}\text{Sn})$ values of the halogens in both series increase by a constant amount in response to an electrostatic field polarizing influence (σ_F effect), which effects a redistribution of s character in the binding Sn hybrid orbitals. This was to be expected on the basis of previous studies of **1** and **4** for which a diverse range of substituents are available for the former^{3,11,12}. However, if this was the only remote electronic influence operating then a concomitant constant decrease ($F \approx \text{Cl} \approx \text{Br} \approx \text{I}$) in the $^1J(^{13}\text{C}, ^{119}\text{Sn})$ values should also be observed. This expectation is obviously not realized. Clearly, the order of the decrease ($\text{I} > \text{Br} > \text{Cl} > \text{F} > \text{H}$) is that expected of a homohyperconjugative influence overlaying the σ_F effect and, moreover, is very similar for both systems. It is of interest to note that except for the F and SnMe_3 derivatives, Σ^1J (Hz) about Sn (Table III) for the other compounds ($X = \text{Cl}, \text{Br}, \text{and I}$) differ little (<10 Hz) from that for the parent system ($X = \text{H}$). Moreover, the perturbations of $^1J(^{13}\text{C}, ^{119}\text{Sn})$ and $^1J(^{13}\text{CH}_3, ^{119}\text{Sn})$ by SnMe_3 are considerably larger than the negligible influence expected on the basis of its σ_F constant. Thus, for F and SnMe_3 an electronegativity-induced change in the 1,3-nonbonded repulsion interaction between the bridgehead positions is probably significant and translates into a strengthening and weakening of the bridgehead C–Sn bond, respectively. This particular phenomenon is most pronounced in system **3** and several manifestations of its influence have been recently observed^{2,12,13}.

CONCLUSIONS

The main conclusion to emerge from this study is that changes in the bond dissociation energies (ΔD) determined by cyclic voltammetry/dissociative electron-transfer theory provide minimal estimates of the order of magnitude of stabilizing through-space interactions on 4-X-substituted bicyclo[2.2.1]heptan-1-yl radicals (**5**; $X = \text{F}, \text{Cl}, \text{Br}, \text{I}, \text{SnMe}_3$). The interaction energies reach considerable values for $X = \text{Br}$ and I (>5 kcal mol⁻¹). Hence, early inferences regarding stabilization due to enhanced delocalization of the unpaired electron based on ESR studies of **5** ($X = \text{Br}$ and I ; see above) are confirmed and quantified.

EXPERIMENTAL

General

Melting and boiling points are uncorrected. Liquid samples were purified by distillation in a kugelrohr apparatus (Büchi, GKR-50). Hence, boiling points pertain to this instrument. NMR spectra were recorded on a Varian Gemini-300 spectrometer operating at 300.75 (^1H), 111.9 (^{119}Sn), and 75.46 MHz (^{13}C) in CDCl_3 solutions (δ -scale, ppm; J , Hz). Mass spectra and high-resolution mass spectra (HR MS) were recorded on a Kratos MS25RF spectrometer. GC MS analyses were run on a Varian Saturn 4D instrument (column: 30 m, 0.22 mm, 0.25 μm film thickness; 5% poly[methyl(phenyl)siloxane] as stationary phase with helium (15 psi) as the carrier gas). Acetonitrile (Aldrich, HPLC grade, 99.93+%) and the supporting electrolyte, Bu_4NBF_4 (Aldrich), were used as received.

Compounds. 1-Iodobicyclo[2.2.1]heptane (**4**; X = H, Y = I) was prepared from bicyclo[2.2.1]heptane-1-carboxylic acid as recently described¹⁴. The corresponding bromo compound (**4**; X = H, Y = Br) was prepared from the acid¹⁴ following a procedure recently described for the preparation of 1-bromo-3-chloroadamantane (**2**; X = Cl, Y = Br) from 3-chloroadamantane-1-carboxylic acid¹⁵. The compound displayed identical properties with that reported in the literature¹⁶. All the 1,4-dihalo derivatives (**4**; X = F, Y = Br and I; X = Cl, Y = Br and I; X = Br, Y = Br and I; X = Y = I) were prepared by literature procedures^{17,18} except that the decarboxylation methods for Y = Br and I were replaced by the procedures of Barton *et al.*¹⁹ as recently described for the preparation of 1,3-dihalodamantanes¹⁵. Samples of 1-fluoro-4-(trimethylstannyl)bicyclo[2.2.1]heptane (**4**; X = F, Y = SnMe_3) and 1,4-bis(trimethylstannyl)bicyclo[2.2.1]heptane (**4**; X = Y = SnMe_3) were available from other studies^{11,17,18}. 1-Chloro-, 1-bromo-, and 1-iodo-4-(trimethylstannyl)bicyclo[2.2.1]heptanes (**4**; X = SnMe_3 , Y = Cl, Br, and I) were prepared as described below.

4-(Trimethylstannyl)bicyclo[2.2.1]heptane-1-carboxylic Acid (**4**; X = SnMe_3 , Y = COOH)

By use of the procedure of Brown *et al.*²⁰, a solution of 4-iodobicyclo[2.2.1]heptane-1-carboxylic acid (**4**; X = I, Y = COOH; 3.4 g, 12.8 mmol)^{14,18} in dry tetrahydrofuran (35 ml) was treated dropwise with borane-dimethyl sulfide (2.5 mol equivalents), and the resulting mixture was allowed to stir overnight under a nitrogen atmosphere. Methanol (20–30 ml) was then carefully added to the reaction mixture and the resulting solution was then heated under reflux for 1 h. The residue obtained after removal of the solvent under vacuum was then further treated with sodium methoxide (0.1 mol l^{-1}) in methanol (100 ml) under reflux to effect complete hydrolysis of the intermediate borate complex. After removal of the solvent *in vacuo* the residue was extracted with diethyl ether and the combined extracts washed with water. After drying (MgSO_4), the solvent was removed *in vacuo* to afford a residue which, after distillation (110 $^\circ\text{C}/0.05 \text{ mm}$), gave 1-hydroxymethyl-4-iodobicyclo[2.2.1]heptane as a white solid (3.0 g, 93%). Without further purification the crude alcohol was silylated and stannylated following procedures previously deployed for the conversion of **1** (X = I, Y = CH_2OH) to **1** (X = SnMe_3 , Y = $\text{CH}_2\text{OSiMe}_3$)³. The crude product (**4**; X = SnMe_3 , Y = $\text{CH}_2\text{OSiMe}_3$) was then desilylated ($\text{THF}/\text{Bu}_4\text{NF}$) following a literature procedure²¹. Fractional kugelrohr distillation (90 $^\circ\text{C}/0.1 \text{ mm}$) afforded the stannyl alcohol (1.5 g, 50%) as a white solid, m.p. 40–44 $^\circ\text{C}$. ^{13}C NMR (CDCl_3): 66.96, 50.94 ($J_{\text{SnC}} = 58.02$ and 60.45), 44.69 ($J_{\text{SnC}} = 11.6$), 35.35 ($J_{\text{SnC}} = 429.8$ and 449.7), 35.20 ($J_{\text{SnC}} = 16.7$), 33.08 ($J_{\text{SnC}} = 49.1$), -11.8 ($J_{\text{SnC}} = 300.5$ and 314.5).

A solution of Jones reagent²² (H₂O (10 ml), H₂SO₄ (2.0 ml), and CrO₃ (2.4 g)) was added dropwise to a well-stirred solution of the stannyl alcohol (**4**; X = SnMe₃, Y = CH₂OH; 1.5 g, 5.2 mmol) in acetone (160 ml) until the initial blue-green colour of the reaction mixture had changed to a distinct orange-yellow appearance. A large volume of dichloromethane (250 ml) was added, and the chromium salts were removed by filtration. After the mixture was washed with water and dried (MgSO₄), the solvent was removed *in vacuo* to afford the crude acid. Sublimation (100 °C/0.05 mm) followed by recrystallization from tetrachloromethane gave the title compound (1.36 g, 87%) as white crystals, m.p. 119–121 °C. ¹³C NMR (CDCl₃): 183.82, 52.94 (*J*_{SnC} = 60.9), 47.12 (*J*_{SnC} = 15.2), 36.25 (*J*_{SnC} = 414 and 433), 35.03 (*J*_{SnC} = 16.2), 34.32 (*J*_{SnC} = 48.1), -11.62 (*J*_{SnC} = 306.8 and 321.1). For C₁₁H₂₀O₂Sn (303.0) calculated: 43.61% C, 6.65% H; found: 43.57% C, 6.76% H.

1-Chloro-4-(trimethylstannyl)bicyclo[2.2.1]heptane (**4**; X = SnMe₃, Y = Cl)

Following a procedure recently described for the preparation of the *O*-acyl-*N*-hydroxypyridine-2-thione derivative (Barton PTOC ester)^{19,22} of 3-chloroadamantane-1-carboxylic acid (**2**; X = Cl, Y = COOH)¹⁵, 4-(trimethylstannyl)bicyclo[2.2.1]heptane-1-carboxylic acid (**4**; X = SnMe₃, Y = COOH; 250 mg, 0.8 mmol) was similarly converted. The thioester was then dissolved in CFCl₃ (30 ml) and the solution irradiated (300 W lamp) under nitrogen for 1 h. The solution was then diluted with dichloromethane (50 ml) followed by successive washings with concentrated hydrochloric acid at 0 °C (15 ml), saturated aqueous sodium hydrogencarbonate (15 ml), and water (2–10 ml). After drying (MgSO₄), the solvent was removed *in vacuo* to afford the crude product, which after kugelrohr distillation (70 °C/0.1 mm), gave the title compound as a colourless oil (150 mg, 62%). ¹³C NMR (CDCl₃): 69.94 (*J*_{SnC} = 76.4), 50.53 (*J*_{SnC} = 9.1), 39.23 (*J*_{SnC} = 42.2), 35.39 (*J*_{SnC} = 11.8), 32.65 (*J*_{SnC} = 411.6 and 431.0), -11.94 (308.5 and 322.8). HR MS (EI): calculated for C₁₀H₁₉ClSn 294.0197, found 294.0195.

1-Bromo-4-(trimethylstannyl)bicyclo[2.2.1]heptane (**4**; X = SnMe₃, Y = Br)

Following procedures recently described for the preparation of 1-bromo-3-chloroadamantane (**2**; X = Cl, Y = Br) from 3-chloroadamantane-1-carboxylic acid¹⁵, 4-(trimethylstannyl)bicyclo[2.2.1]heptane-1-carboxylic acid (250 mg, 0.8 mmol) was converted into the title compound. Kugelrohr distillation (70 °C/0.1 mm) gave the compound as a colourless oil (190 mg, 70%). ¹³C NMR (CDCl₃): 62.19 (*J*_{SnC} = 75.9), 51.98 (*J*_{SnC} = 9.6), 40.67 (*J*_{SnC} = 43.0), 36.06 (*J*_{SnC} = 12.3), 32.56 (*J*_{SnC} = 407.1 and 426.1), -11.70 (*J*_{SnC} = 308.9 and 323.2). HR MS (EI): calculated for C₁₀H₁₉BrSn 339.9673 and 337.9693, found 339.9699 and 337.9694.

1-Iodo-4-(trimethylstannyl)bicyclo[2.2.1]heptane (**4**; X = SnMe₃, Y = I)

Following procedures recently described for the preparation of 1-chloro-3-iodoadamantane (**2**; X = Cl, Y = I) from 3-chloroadamantane-1-carboxylic acid¹⁵, 4-(trimethylstannyl)bicyclo[2.2.1]heptane-1-carboxylic acid (400 mg, 1.3 mmol) was converted into the title compound. Kugelrohr distillation (70 °C/0.1 mm) gave the compound as a colourless oil which solidified to a white solid (370 mg, 74%) on standing, m.p. 34–36 °C. ¹³C NMR (CDCl₃): 58.84 (*J*_{SnC} = 10.4), 43.66 (*J*_{SnC} = 44.2), 38.21 (*J*_{SnC} = 72.1 and 75.2), 36.52 (*J*_{SnC} = 13.2), 32.33 (*J*_{SnC} = 403 and 422), -11.61 (*J*_{SnC} = 308.3 and 322.6). HR MS (EI): calculated for C₁₀H₁₉ISn 385.9555, found 385.9556.

Cyclic Voltammetry

Cyclic voltammetry experiments were performed at 20 °C using a Bioanalytical Systems Inc. apparatus (Electrochemical Analyser BAS100B). The working electrode was a glassy carbon disc of 3 mm diameter and the counter-electrode was a platinum wire. The reference electrode was an aqueous Ag/AgCl electrode which was isolated from the cell by a double junction.

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