Electroreduction of Organic Compounds, 37 [1]. Electroreduction of 1,4-Dichlorobicyclo[2.2.2]octane-2-carboxamides

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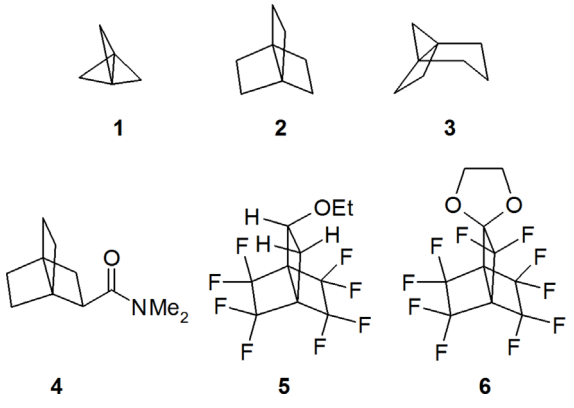
Several 1,4-dichlorobicyclo[2.2.2]octanecarboxamides were prepared, which were expected to be suitable precursors for the electrochemical synthesis of [2.2.2]propellanes. Their potentiostatic electroreduction at extremely negative potentials in THF, however, did not lead to the expected [2.2.2]propellanes. Instead, protio-dechlorination to form the corresponding bicyclo[2.2.2]octanecarboxamides occurred, even under rigorous exclusion of moisture and oxygen. Ring-opened olefins were produced as by-products. Polytetrahydrofuran was formed when the supporting electrolyte tetrabutylammonium hexafluorophosphate was electrolyzed at −3.5 V in the absence of an organic chloro compound as depolarizer. The experimental results are interpreted in terms of *semi*-empirical MO calculations.

Key words: Bicyclo[2.2.2]octanes, [2.2.2]Propellanes, Elimination, Electroreduction, X-Ray Structure, MO Calculations

Introduction

The highly strained [1.1.1]propellane (**1**) is a well characterized stable compound which can be conveniently prepared on a preparative scale [2]. The homologous [2.2.2]propellane (**2**), on the other hand, has resisted all attempts of a synthesis. This fact is somewhat surprising at first naive sight because one would expect the strain energy of **2** to be considerably lower compared with **1**. One stable derivative, the amide **4** was prepared in 1973 by Eaton's ingenious route [3]. It remained the only one until decades later Lemal's group described the successful synthesis of the persistent oligofluoro derivatives **5** [4] and **6** [5].

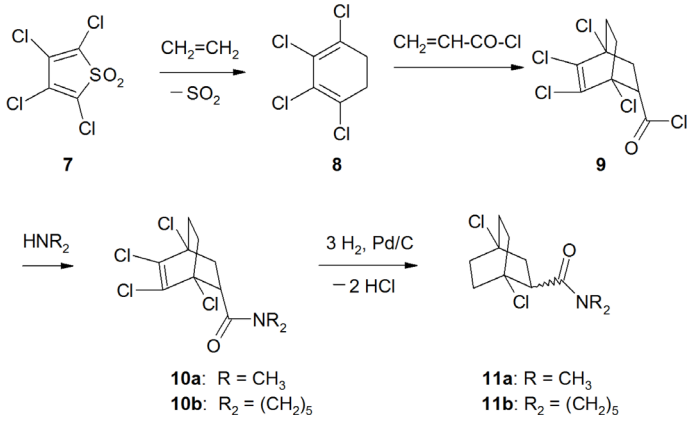


As we were interested in the electroreductive dehalogenation of dihalides under formation of small ring compounds [6] and because, furthermore, Rifi had described the formation of [3.2.1]propellane (**3**) by electrochemical reduction of 1.5-dibromobicyclo-[3.2.1]octane [7], we started an investigation which aimed at the electrochemical formation of a [2.2.2]propellane.

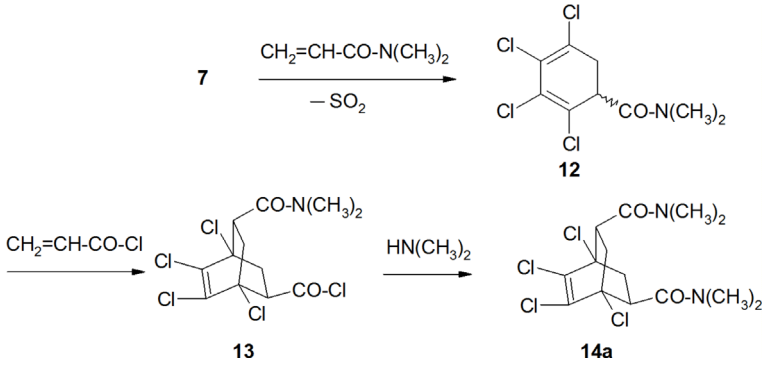
Results and Discussion

Preparation of starting compounds

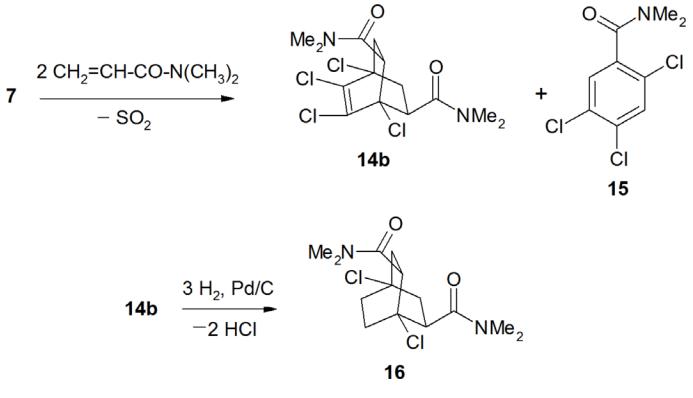
1,4-Dichlorobicyclo[2.2.2]octane-2-carboxamides seemed to be suitable substrates for the electroreductive 1,4-elimination of chloride under formation of the corresponding [2.2.2]propellanes, since Eaton's carboxamide **4** [3] represents one of the only three known stable [2.2.2]propellanes. We therefore decided to synthesize **11a** as the precursor of **4**, and furthermore the two related carboxamides **11b** and **16**. The *N,N*-dimethylcarboxamide **11a** was prepared from tetrachlorothiophene *S,S*-dioxide (**7**) *via* tetrachlorocyclohexadiene (**8**) and the bicyclic acid chloride **9**, and catalytic reduction of the corresponding carboxamide **10a** according to Eaton's description [3, 8]. The acid chloride **9** was also used for the preparation of the *endo*-piperidide **10b**. Finally, the two amides **10a** and **10b**



Scheme 1.



Scheme 2.



Scheme 3.

were hydrogenated on palladium/charcoal to yield the saturated amides **11a** and **11b** (Scheme 1).

A first [4+2]-cycloaddtion reaction of **7** with *N,N*-dimethylacrylamide under elimination of sulfur dioxide gave **12**. The subsequent second [4+2]-cycloaddition step with acryloyl chloride was rather sluggish. Only after five days of heating at 130 °C, cyclohexadiene **12** was completely consumed. The intermediate acid chloride **13** was not purified but directly transformed into a bis-carboxamide by reaction with dimethylamine (Scheme 2).

Its structure and configuration cannot be established straightforward from the ^{1}H and ^{13}C NMR spectra, which show two magnetically equivalent dimethylamide groups at the bridges of the molecular skeleton, because the regioselectivity of the cycloaddition leading to **13** or its 2,6-regioisomer, and therefore the constitution of the resulting bis-carboxamide is not

clear. The latter could either be the C_2-symmetric 2,5-isomer **14a** shown in Scheme 2 or the corresponding 2,6-regioisomer exhibiting mirror symmetry. We assume structure **14a** to be the correct one, as the formation of **13** should be favored compared with the 2,6-isomer because it exhibits less sterical hindrance. Since **14a** is only very sparingly soluble in boiling methanol it is anyway not a suitable intermediate for the intended synthesis. Fortunately however, we were able to obtain the unsymmetrical stereoisomer **14b** by simply reacting **7** with a six-fold excess of *N,N*-dimethylacrylamide for three days in boiling xylene (Scheme 3).

According to its ^{1}H NMR spectrum, **14b** represents a *racemic* and not a *meso* compound. Remarkably, one of the bridge hydrogen signals appears at δ = 4.90 ppm. This extreme downfield shift is quite unusual even for a bicyclo[2.2.2] system. We explain this effect with the strong anisotropic shift resulting from the close distance between the proton 2-H and the two neighboring carbonyl groups, which is only possible in the stereoisomer **14b**. As **14b** can be easily re-crystallized from a hexane-methanol mixture, we could grow a suitable single crystal and perform an X-ray structure analysis, which unequivocally proved its structure (Fig. 1).

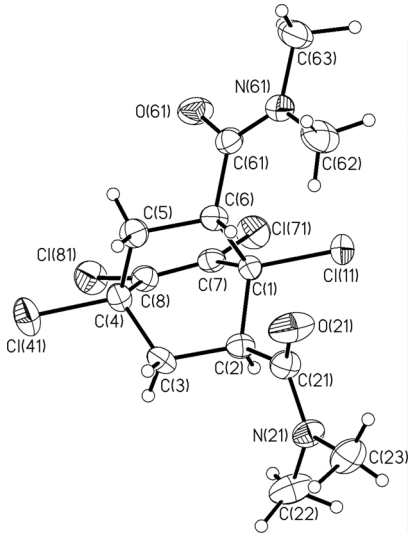


Fig. 1. ORTEP view of the molecular structure of **14b** in the crystal. The (*2R,6R*)-enantiomer of the racemic crystal is shown. Thermal ellipsoids are drawn at the 30 % probability level. Selected characteristic bond lengths (pm): C(7)–C(8) 131.5(4), C(1)–Cl(11) 178.9(3), C(4)–Cl(41) 179.1(3), C(7)–Cl(71) 171.1(3), C(8)–Cl(81) 171.4(3); non-bonding distance between the bridgeheads: C(1)···C(4) 254.3(3).

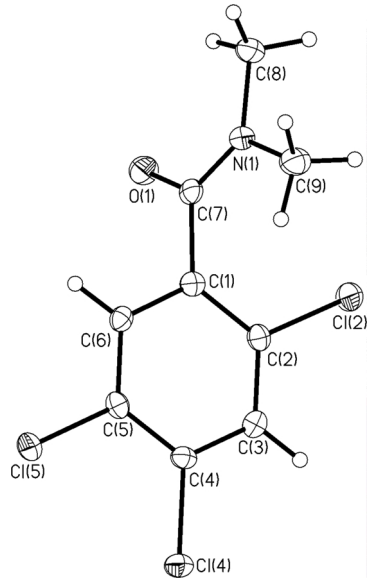
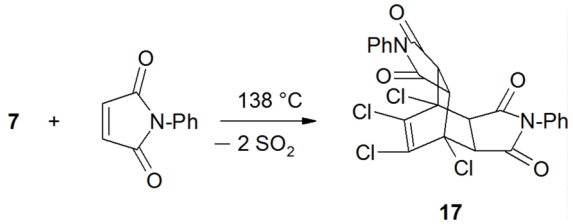


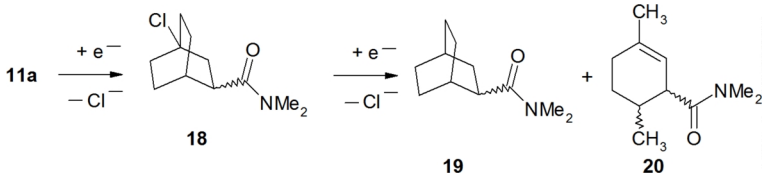
Fig. 2. ORTEP view of the molecular structure of **15** in the crystal. Thermal ellipsoids are drawn at the 50 % probability level. Selected characteristic bond lengths (pm): C(1)–C(7) 151.3(2); C(7)–O(1) 123.2(2); C(7)–N(1) 134.4(2); torsion angles (deg): C(2)–(C1)–(C7)–(N1) –75.2(2); C(9)–N(1)–C(7)–(O1) 176.6(1).

Besides 11 % of **14b**, 2,4,5-trichloro-*N*,*N*-dimethylbenzamide **15** (9 %) was formed as a by-product. The structure of **15** was deduced from its ^{1}H NMR spectrum and was confirmed by an X-ray structure analysis (Fig. 2). The substitution pattern of **15**, in particular the displacement of the chloro substituent in the 3-position, is unexpected. It can be explained by assuming that first **12** is formed by loss of sulfur dioxide from a primary cycloadduct (*cf.* Scheme 2). Under the rather harsh reaction conditions two subsequent, thermally symmetry-allowed 1→5 hydrogen shifts lead to the corresponding 5,6-dihydrobenzamide, which then undergoes 1,2-elimination of hydrogen chloride to form **15**.

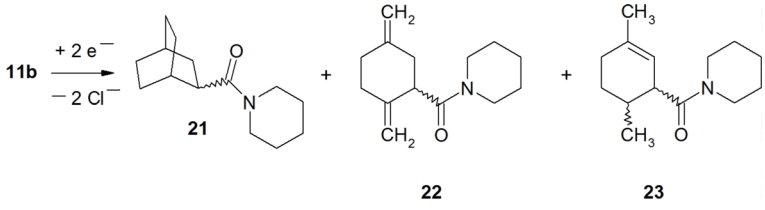
Compound **14b** was easily reduced by catalytic hydrogenation to form the desired substrate **16** for the intended electrolysis (Scheme 3).



Scheme 4.



Scheme 5.



Scheme 6.

The double Diels-Alder reaction of **7** with the "super-dienophile" *N*-phenylmaleimide yielded the bis-cycloadduct **17** (Scheme 4). But **17** turned out to be also not sufficiently soluble for the catalytic hydrogenation, and it was thus ruled out as a precursor.

Electroreductions

Electroanalytical measurements such as polarography or cyclovoltammetry were not possible with the bridge-head chlorinated bicyclic carboxamides **11a**, **11b** and **16** since their reduction potentials are beyond the decomposition potential of the solvent-supporting electrolyte. A cathodic dechlorination of the bicyclic substrates could nevertheless be achieved at reduction potentials as negative as ≈ -4.0 V by use of tetrabutylammonium hexafluorophosphate (TBPF) in dry THF as electrolyte. The formation of insoluble oxidation products at the anode that would interrupt the circuit was suppressed by the addition of tetrabutylammonium iodide to the anolyte. The preparative electrolyses were performed galvanostatically at potentials which were determined empirically: a preliminary electrolysis was carried out at a potential which was sufficiently negative to yield a gaschromatographically detectable reaction product.

We used a divided cylindrical cell described earlier [9] which allowed strict exclusion of moisture and air. Mercury was used as working electrode (cathode) and platinum as counter electrode (anode).

Electroreduction of the *N,N*-dimethylamide **11a** at -3.7 V (*vs.* Ag/Ag^+) led to the monochloro derivative **18** as the only product with 26 % yield. When **18** was further electrolyzed at a potential of -4.0 V, complete dechlorination to form **19** occurred. Expectedly, the direct electroreduction of **11a** at -4.0 V also led to **19** (29 %) together with a small amount (9 %) of the cyclohexenecarboxamide **20** (Scheme 5).

The constitution of the products was proved by their ^{1}H and ^{13}C NMR spectra. The amide **20** was obtained as one pure diastereoisomer the configuration of which could not be determined.

A similar result was obtained when the piperidide **11b** was electrolyzed. Complete dechlorination occurred when a reduction potential of -4.0 V was applied. Bicyclo[2.2.2]octane-2-carboxypiperidide (**21**) was isolated as the main product with 30 % yield by preparative gas chromatography besides an inseparable mixture of two minor monocyclic by-products **22** and **23** (Scheme 6).

The NMR spectra of the bicyclic piperidide **21** were in agreement with its structure. The ^{1}H and ^{13}C NMR signals of the bicyclic skeleton appeared close to the corresponding lines of the dimethylamide **19**. The spectra of the monocyclic piperidides **22** and **23** could not be completely analyzed since the signals of the numerous aliphatic centers give rise to a multitude of multiplets. However, the vinylic protons and carbon centers could be identified and assigned to the individual species and positions. In particular, the NMR spectra of **23** compared with the fully assigned spectra of the related dimethylamide **20**, and the ^{1}H NMR signals of the vinylic protons of **22** were in agreement with the data of Eaton's dimethylamide **4** [3].

The formation of the observed electrolysis products requires the presence of a proton source. Since we applied dry THF as solvent the protons can only be provided by the tetrabutylammonium cations which may undergo a Hofmann-type elimination under the attack of the strong electro-generated bases [10]. Although the cationic decomposition of TBPF can be detected

only at −3.7 V by polarography, prolonged electrolyses in fact yield tributylamine even at −2.5 V. Its formation is due to the high concentration of the electrolyte which shifts the reduction potential in positive direction according to the Nernst equation. In addition, pronounced field inhomogeneities within the cell favor the formation of the amine. Kariv-Miller *et al.* [11] have shown that neither the mercury cathode nor the supporting electrolyte are inert at very negative potentials. They found tetraalkylammonium amalgams to be formed and to represent even more reactive reductive agents compared with alkali amalgams.

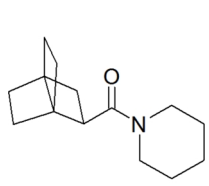
The formation of the 1,4-dimethylenecyclohexane **22** may be explained by assuming the corresponding [2.2.2]propellane to be the primary electrolysis product, which immediately undergoes a Grob-type fragmentation reaction [12]. Eaton and Temme also observed this type of fragmentation for **4** and found its activation energy to be only 22 kcal mol^{-1} [3]. Electroreduction of 1,4-dibromobicyclo[2.2.2]octane also ends up with 1,4-dimethylenecyclohexane which can be taken as indicative of the intermediate formation of **2** [13]. Further reduction of **22** and a proton shift step would yield **23**. An analogous reaction sequence should lead to the formation of **20** from **11a**.

Electroreduction of the bis-carboxamide **16** at −3.8 or −4.0 V led to a complex mixture of products the structures of which could not be determined. However, the mass spectrum of the product mixture at least showed that complete dechlorination had taken place.

We would like to mention that poly-tetrahydrofuran {poly-THF, [-O-$(CH_2)_4$-]$_n$} was formed when the electrolysis of the solvent-supporting electrolyte was performed in the absence of a depolarizer in the catholyte and without TBAI in the anolyte. The anodic polymerization of THF has also been observed in the presence of tetraethylammonium perchlorate as anolyte [14].

Theoretical considerations

Eckert-Maksić *et al.* have performed a comprehensive *ab-initio* MO calculation (MR-AQCC method) on the unsubstituted [2.2.2]propellane (**2**) and its rearrangement by Grob fragmentation [12]. They found that an activation energy of 97 kJ mol^{-1} (22.7 kcal mol^{-1}) is required for the conversion of **2** into the corresponding 1,4-biradical, in excellent agreement with Eaton's experimental value for the rearrangement of **4**. The stability of this "artificial" biradical is however negligible. "It undergoes barrierless cage-opening resulting in the thermodynamically more stable [by 48 kcal mol^{-1} (207 kJ mol^{-1})] 1,4-dimethylenecyclohexane" [12].



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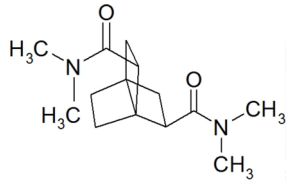

25

Since **4**, **5** and **6** are persistent compounds, the [2.2.2]propellane system seems to be stabilized by suitable substituents (*cf.* also [15]), for instance by the carboxamide group. In order to get a better understanding of this effect, we performed MO calculations on *N,N*-dimethyl[2.2.2]propellane-2-carboxamide (**4**), [2.2.2]propellane-2-carboxypiperidide (**24**) and *N,N,N′,N′*-tetramethyl[2.2.2]propellane-2.6-bis-carboxamide (**25**).

To keep the frame of the calculations within reasonable limits, we used the MNDO model. The electronic and geometric structure of the closed-shell molecules was determined by use of the RHF approximation. The open-shell singlet biradical state was taken into account by CI and the triplet states by UHF calculations. The minima on the energy hypersurface were calculated with fully optimized geometries, and the dependence of the energies on the length of the C1–C4 bond between the bridgeheads was determined with strictly fixed three-dimensional structures of the tricyclic systems.

The *N,N*-dimethylcarboxamide **4** exhibits a bonding, symmetric linear combination of the bridgehead carbon atomic orbitals at a C1–C4 distance of 158 pm (RHF calculation) with a σ bond order of 0.98 which is evidence for significant overlap. This orbital does however not represent the HOMO, which is rather a non-bonding MO with high electron density at the nitrogen atom. Further elongation of the C1–C4 distance leads to level crossing of the symmetric and the antisymmetric LCAO at 220 pm where the σ^* MO becomes the HOMO. Since the consideration of CI yields a significant stabilization we conclude the second minimum observed at a C1–C4 distance of 240 pm to represent a biradical state (Fig. 3).

In principle, the same situation as for **4** is observed for the carboxypiperidide **24** with a calculated bond length of 157 pm, which is in excellent agreement

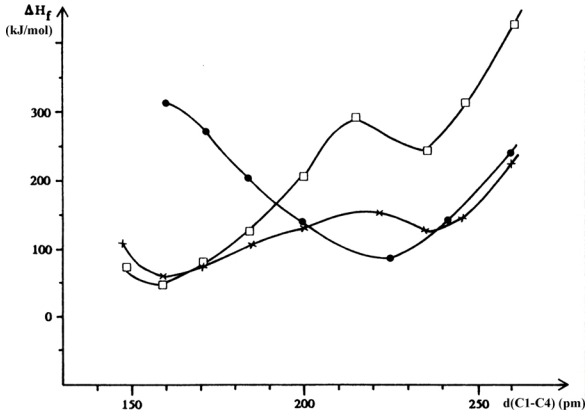

Fig. 3. Heat of formation ΔH_f (kJ mol^{-1}) *vs.* bridgehead distance *d*(C1–C4) (pm) of *N,N*-dimethyl[2.2.2]propellane-2-carboxamide (**4**). □ = RHF calculation; • = UHF calculation; × = CI calculation.

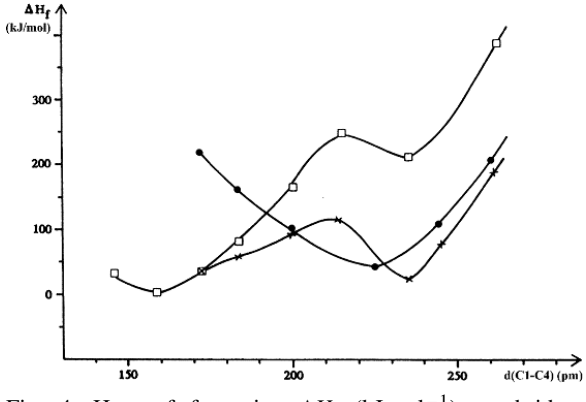

Fig. 4. Heat of formation ΔH_f (kJ mol^{-1}) *vs.* bridgehead distance *d*(C1–C4) (pm) of [2.2.2]propellane-2-carboxypiperidide (**24**). □ = RHF calculation; • = UHF calculation; × = CI calculation.

with the value of 157.3 pm found experimentally by X-ray structural analysis of the crystalline **6** [5]. The stabilization of **24** by the substituent is however more pronounced. The increased stability of the piperidide **24** also appears from its higher activation energy of 113 kJ mol^{-1} for the formation of the biradical state with a C1–C4 distance of 236 pm as compared with 102 kJ mol^{-1} calculated for **4** (Fig. 4).

Expectedly, the stabilization effect is even more pronounced for the bis-*N,N*-dimethylcarboxamide **25**. Its heat of formation ΔH_f amounts to −47.6 kJ mol^{-1} at a C1–C4 distance of 157 pm with a σ bond order of 0.98. Thus, according to our calculations, **25** represents the only thermodynamically stable molecule in the series. The barrier height of 136 kJ mol^{-1} between the propellane **25** and the corresponding biradical isomer

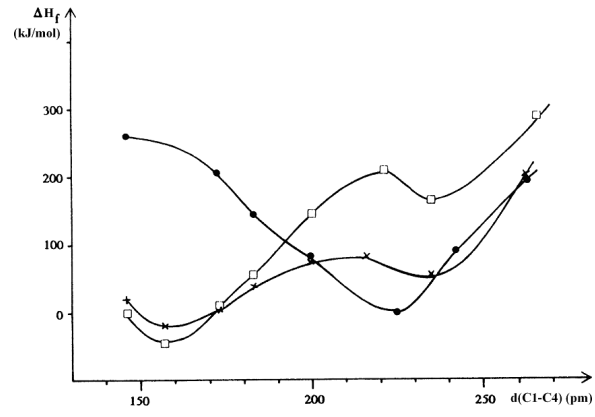

Fig. 5. Heat of formation ΔH_f (kJ mol^{-1}) *vs.* bridgehead distance *d*(C1–C4) (pm) of *N,N,N′,N′*-tetramethyl [2.2.2]propellane-2,5-bis(carboxamide) (**25**).

with a C1–C4 distance of 236 pm is higher then for the other propellanes which also points to a certain kinetic stabilization of **25** (Fig. 5). Nevertheless, we could not detect **24** or **25** experimentally after electrolyses of **11b** or **16**, respectively.

In agreement with Eaton's [3], and Lemal's experimental results [4, 5] and with Imamura's [15] presumption, our calculations reveal a significant effect of substituents, in particular of carboxamide substituents, on the energy level of the central σ bond, on the barrier height for the formation of the singlet biradical, and on the total stabilization of the [2.2.2]propellane system. On the other hand, a synthetic approach to a [2,2,2]propellane *via* formation of the central bond as the final step seems not feasible. Since the C1–C4 distance in the starting molecule, *e. g.* in a 1,4-dihalide, is as large as ≈ 260 pm, a pronounced shortening of this distance to form the central propellane bond with *d*(C1–C4) ≈ 160 pm [5] would be necessary. This would however lead to the intermediate formation of an unstable biradical at a distance of ≈ 210 pm which then would undergo spontaneous decomposition. We assume that our attempts to produce [2.2.2]propellanes by electroreduction of the 1,4-dichlorobicyclo[2.2.2]octanes failed for this reason, in spite of the presence of stabilizing carboxamide substituents.

Conclusion

The electrochemical generation of [2.2.2]propellanecarboxamides by reductive 1,4-dechlorination of the corresponding bicyclo[2.2.2]octanes is not more viable than related conventional methods for this transformation, although the expected propellanes

should be stable products. Instead, simply protiodechlorination or fragmentation of the bicyclic substrates occur. This experimental result can be rationalized by semiempirical MO calculations.

Experimental Section

General

Melting points (corrected): Electrothermal. NMR spectra (δ in ppm *vs*. Me_4Si) were recorded on WH 270 or WM 400 spectrometers (Bruker) at 250 or 400 MHz (^1H) and 62.9 or 100.6 MHz (^{13}C) in $CDCl_3$ if not stated otherwise. Assignments were performed by the DEPT method. IR spectra (KBr pellets): FT-IR 1720X (Perkin-Elmer). MS: CH 7 (EI, 70 eV, Varian), HRMS: 70-250S (VG-Analytical). Analytical thin layer chromatography (TLC): Al-foils coated with silica $60F_{254}$ (Merck). Column chromatography (CC): silica 60 (70 – 230 mesh, Merck). Analytical GLC: GC 6000 (Carlo Erba) equipped with a 25 m fused silica capillary SE 54 column (Macherey & Nagel). Preparative GLC: GC-8A (Shimadzu) equipped with a 3 m steel column packed with 15 % SE 30 on Chromosorb WAW and heat conductance detector.

X-Ray structure analyses

The crystal data of **14b** and **15** and a summary of experimental details are given in Table 1. The structure of **14b** was solved by Direct Methods (MULTAN) [16]. An absorption correction [17] was performed by use of SADABS [18], refinement by least-squares methods. All non-hydrogen atoms were localized. After refinement of these parameters the hydrogen atoms were localized by differential Fourier synthesis [19].

The structure of **15** was solved with SHELXS-97 [20]. All non-hydrogen atoms were localized and refined by using SHELXL-97 [21]. The positions of the hydrogen atoms were calculated and refined using a riding model.

CCDC 773016 (**14b**) and 773017 (**15**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Preparations

*(1RS,2SR,4SR)-1,4,5,6-Tetrachloro-N,N-dimethylbicyclo-[2.2.2]oct-5-ene-2-carboxamide (**10a**)* and *(2RS)-1,4-dichloro-N,N-dimethylbicyclo[2.2.2]octane-2-carboxamide (**11a**)* were prepared as described by Eaton and Temme [3, 8].

***10a*:** Colorless needles (78 %), m. p. 196 °C (hexane/EtOH 30 : 1), (lit. [3]: 196 – 197 °C). – IR: ν = 2958, 1652 (C=O), 1595 (C=C), 1143, 1034, 980 cm^{-1}. – ^1H NMR (250 MHz): δ = 1.9 – 2.3 (m, 5 H), 2.50 (dd, J = 9.0/11.5.0 Hz, 1 H, 3a-H), 3.00 (s, 3 H, CH_3), 3.10 (s, 3 H, CH_3), 3.55 (dd, J = 6.0/9.0 Hz, 1 H, 2-H).

***11a*:** Colorless needles (75 %), m. p. 119 °C (hexane/EtOH 30 : 1), (lit. [3]: 121 – 122 °C). – IR: ν = 2950, 1653 (C=O), 1149, 973, 581 (C-Cl) cm^{-1}. – ^1H NMR (250 MHz): δ = 1.93 (m, 1 H, 5a-H), 2.1 – 2.3 (m, 6 H), 2.40 (m, 1 H, 5b-H), 2.53 (m, 1 H, 3a-H), 2.96 (m, 1 H, 3b-H), 3.00 (s, 3 H, CH_3), 3.10 (s, 3 H, CH_3), 3.53 (dd, J = 6.0/11.5.0 Hz, 1 H, 2-H).

Table 1. Crystal data and parameters pertinent to data collection and structure refinement for **14b** and **15**.

	14b	**15**
Formula	$C_{14}H_{18}Cl_4N_2O_2$	$C_9H_8Cl_3NO$
Formula weight, M_r	388.12	252.51
Crystal system	orthorhombic	orthorhombic
Space group	*Pbca*	*Pbcn*
Z	8	8
a, pm	1231.4 (1)	1357.10 (14)
b, pm	1527.6 (3)	950.63 (10)
c, pm	1821.4 (2)	1601.74 (16)
Cell volume V, pm^3	3.426×10^9	$2.0664(4) \times 10^9$
Temperature, K	298	100
Density $\rho_{calcd.}$, g cm^{-3}	1.51	1.62
$F(000)$, e	1600	1024
Diffractometer	CAD4-SDP (Enraf Nonius)	Bruker AXS, 1998
Radiation; monochromator	CuK_α; graphite	MoK_α; graphite
Wavelength λ, Å	1.54184	0.71073
Absorption coeff. μ, cm^{-1}	65.0	8.5
Scan mode	ϑ-2ϑ	ω
ϑ range, deg	2.0 – 65.0	2.5 – 27.5
Index range *hkl*	+14, +17, +21	±17, ±12, ±20
Refl. collected / unique	unknown	19122 / 2370
Refl. observed [$I \geq 3\ \sigma(I)$]	2151	2088
Ref. parameters	271	129
$R1$ [$I \geq 3\ \sigma(I)$]	0.041	0.024
wR[($I \geq 3\ \sigma(I)$; $w = \sigma^{-2}$)]	0.039	–
$wR2$ (all data)	–	0.062
$\Delta\rho_{fin}$ (max / min), e $Å^{-3}$	+0.40	+0.38 / –0.20

*(1RS,2SR,4SR)-1,4,5,6-Tetrachlorobicyclo[2.2.2]oct-5-ene-2-carboxypiperidide (**10b**)*

1,2,3,4-Tetrachloro-1,3-cyclohexadiene (**8**) [22] (2.0 g, 9.3 mmol) and acryloyl chloride (3.3 g, 33 mmol) were heated to 130 °C for 72 h under N_2. Excessive acryloyl chloride was distilled off under N_2. The residue (**9**) was dissolved in dry $CHCl_3$. A solution of piperidine (3.0 g, 35 mmol) in $CHCl_3$ (30 mL) was slowly dropped in. The reaction mixture was stirred for 2 h and then washed twice with H_2O. After drying over Na_2SO_4, the solvent was removed. The remaining red-brown oil was crystallized from MeOH/hexane (1 : 35) to yield colorless crystals of **10b** (1.2 g, 35.5 %), m. p. 148 °C. – IR: ν = 2942, 2861, 1635 (C=O), 1593 (C=C), 1442, 1283, 1245, 1222, 1008 cm^{-1}. – ^1H NMR (250 MHz): δ = 1.5 – 1.8 (m, 6 H), 2.0 – 2.3 (m, 5 H), 2.45 (dd, J = 12.0/11.5 Hz, 1 H, 3-H), 3.4 – 3.6 (m, 5 H). –

^{13}C NMR (62.9 MHz): δ = 24.5 (CH_2), 25.6 (CH_2), 26.7 (CH_2), 36.8 (CH_2), 38.7 (CH_2), 43.3 (NCH_2), 43.8 (NCH_2), 47.2 (C-3), 48.2 (C-2), 66.2 (C-1), 68.5 (C-4), 127.3 (C-8), 130.4 (C-7), 168.8 (C=O). – $C_{14}H_{17}Cl_4NO$ (357.1): calcd. C 47.09, H 4.80, Cl 39.71, N 3.92; found C 47.16, H 4.84, Cl 39.35, N 3.77.

*(2RS)-1,4-Dichlorobicyclo[2.2.2]octane-2-carboxypiperidide (**11b**)*

The piperidide **10b** (1.0 g, 2.8 mmol) and NaOH (0.88 g, 22 mmol) were dissolved in MeOH (50 mL) and hydrogenated at r. t. under atmospheric pressure by use of a Pd/charcoal catalyst (5 %). After the consumption of 198 mL (8.8 mmol) of H_2 (8 h), the solution was neutralized with AcOH. MeOH was removed under vacuum, and the residue was dissolved in CH_2Cl_2. The solution was washed with H_2O, dried over Na_2SO_4 and evaporated to dryness. The solid residue was re-crystallized from MeOH/hexane (1 : 30) to yield colorless crystals of **11b** (0.56 g, 71 %), m. p. 111 °C. – IR: ν = 2938, 2857, 1631 (C=O), 1451, 1245, 1140, 1121, 991, 972, 849, 730 (C-Cl) cm^{-1}. – ^{1}H NMR (250 MHz): δ = 1.5 – 1.8 (m, 6 H), 1.9 – 2.0 (m, 1 H), 2.1 – 2.3 (m, 6 H), 2.3 – 2.5 (m, 1 H), 2.6 (m, 1 H), 3.0 (m, 1 H), 3.50 – 3.65 (m, 5 H). – ^{13}C NMR (100.6 MHz): δ = 24.5 (CH_2), 25.7 (CH_2), 26.5 (CH_2), 34.1 (CH_2), 37.69 (CH_2), 37.73 (CH_2), 40.1 (CH_2), 42.2 (NCH_2), 43.3 (NCH_2), 45.5 (C-2), 47.8 (C-3), 63.7 (C-1), 66.1 (C-4), 170.3 (C=O). – $C_{14}H_{21}Cl_2NO$ (290.2): calcd. C 57.94, H 7.29, Cl 24.43, N 4.83; found C 58.30, H 7.25, Cl 24.02, N 4.76.

*(1RS)-2,3,4,5-Tetrachloro-N,N-dimethylcyclohexa-2,4-diene-1-carboxamide (**12**)*

Tetrachlorothiophene *S,S*-dioxide (**7**) [22] (2.3 g, 9.2 mmol) and *N,N*-dimethylacrylamide (2.0 g, 20.0 mmol) were refluxed in *p*-xylene (50 mL) for 4 h. The solvent and the excess of acrylamide were removed under vacuum (0.1 torr) at 20 °C. The oily, yellow residue was crystallized from hexane/EtOH (30 : 1) at −20 °C to yield **12** (1.5 g, 57 %), m. p. 82 °C. – IR: ν = 2955, 1651 (C=O), 1494 (C=C), 1415, 1401, 1220, 1200, 1147, 1059, 826 (C-Cl) cm^{-1}. – ^{1}H NMR (250 MHz): δ = 2.95 (dd, J = 17.8/11.8 Hz, 1 H, 6a-H), 3.05 (s, 3 H, CH_3), 3.10 (s, 3 H, CH_3), 3.15 (dd, J = 17.8/8.9 Hz, 1 H, 6b-H), 4.15 (dd, J = 11.8/8.9 Hz, 1 H, 1-H). – ^{13}C NMR (62.9 MHz): δ = 35.7 (C-6), 36.2 (CH_3), 38.0 (CH_3), 43.7 (C-1), 123.6 (C_q), 126.5 (C_q), 127.1 (Cq), 128.5 (Cq), 168.7 (C=O). – $C_9H_9Cl_4NO$ (289.0): calcd. C 37.41, H 3.14, Cl 49.07, N 4.85; found C 37.41, H 3.02, Cl 48.97, N 4.71.

*(1RS,2SR,4RS,5SR)-1,4,7,8-Tetrachloro-N,N,N′,N′-tetramethylbicyclo[2.2.2]oct-7-ene-2,5-dicarboxamide (**14a**)*

The amide **12** (0.90 g, 3.1 mmol) and acryloyl chloride (3.30 g, 33 mmol) were refluxed (130 °C) for 120 h under N_2. The excess of acryloyl chloride was removed under vacuum (0.1 torr), and the residue (**13**) was dissolved in $CHCl_3$. An excess (50 mL at −40 °C) of gaseous Me_2NH was slowly passed through the solution. The reaction mixture was washed with H_2O three times, and the solvent was distilled off. The brown, highly viscous residue was crystallized from MeOH (100 mL) to yield **14a** (0.54 g, 45 %) as a colorless solid (sparingly soluble in MeOH and DMSO), m. p. 330 °C (decomp.). – IR: ν = 2934, 1730 (C=O), 1651 (C=O), 1593 (C=C), 1423, 1404, 1293, 1179, 1144, 981, 960, 751 (C-Cl) cm^{-1}. – ^{1}H NMR (250 MHz, DMSO): δ = 1.85 (dd, J = 6/12 Hz, 2 H, 3a/6a-H), 2.35 (dd, J = 10/12 Hz, 2 H, 3b/6b-H), 2.80 (s, 6 H, 2 CH_3), 3.05 (s, 6 H, 2 CH_3), 3.85 (dd, J = 6/10 Hz, 2 H, 2/6-H). – ^{13}C NMR (62.9 MHz, DMSO): δ = 35.1 (CH_3), 37.0 (CH_3), 43.6 (C-3/6), 46.0 (C-2/5), 68.6 (C-1/4), 127.5 (C-7/8), 169.9 (C=O). – $C_{14}H_{18}Cl_4N_2O_2$ (388.1): calcd. C 43.33, H 4.67, Cl 36.54, N 7.22; found C 43.50, H 4.80, Cl 36.80, N 7.18.

*(1RS,2SR,4SR,6SR)-1,4,7,8-Tetrachloro-N,N,N′,N′-tetramethylbicyclo[2.2.2]oct-7-ene-2,6-dicarboxamide (**14b**)*

Tetrachlorothiophene *S,S*-dioxide (**7**) [22] (4.0 g, 16.0 mmol) and *N,N*-dimethylacrylamide (5.0 g, 50 mmol) were refluxed in *p*-xylene (100 mL) for 72 h. Xylene was removed under vacuum (0.4 Torr). Column chromatography (CH_2Cl_2) of the black residue gave two fractions, F_1 and F_2.

F_1: Re-crystallization from toluene gave 2,4,5-trichloro-*N,N*-dimethylbenzamide (**15**) as colorless crystals (0.36 g, 9 %), m. p. 99 °C. – IR: ν = 2961, 1652 (C=O), 1456, 1434, 1402, 1332, 1105, 1060, 912, 856, 765 (C-Cl), 599 (C-Cl) cm^{-1}. – ^{1}H NMR (400 MHz): δ = 2.89 (s, 3 H, CH_3), 3.12 (s, 3 H, CH_3), 7.40 (s, 1 H, 3-H), 7.52 (s, 1 H, 6-H). – ^{13}C NMR (62.9 MHz): δ = 34.7 (CH_3), 38.1 (CH_3), 129.3 (CH), 131.0 (CH), 131.9 (C_q), 133.8 (C_q), 136.0 (C_q), 166.0 (C=O). – $C_9H_8Cl_3NO$ (252.5): calcd. C 42.81, H 3.19, Cl 42.12, N 5.55; found C 42.62, H 3.08, Cl 43.08, N 5.68.

F_2: Re-crystallization from MeOH/hexane (1 : 35) gave colorless crystals of **14b** (0.65 g, 10.5 %), m. p. 188 °C. – IR: ν = 2943, 1653 (C=O), 1500 (C=C), 1456, 1421, 1398, 1261, 1167, 1152, 1032, 740 (C-Cl) cm^{-1}. – ^{1}H NMR (250 MHz, DMSO): δ = 2.10 (m, 2 H, 3a/5a-H), 2.50 (dd, J = 6/12 Hz, 1 H, 5b-H), 2.65 (dd, J = 12/11 Hz, 1 H, 3b-H), 2.95 (s, 3 H, CH_3), 3.05 (s, 3 H, CH_3), 3.10 (s, 3 H, CH_3), 3.15 (s, 3 H, CH_3), 3.35 (dd, J = 12/6 Hz, 1 H, 2-H), 4.90 (dd, J = 11/6 Hz, 1 H, 6-H). – ^{13}C NMR (62.9 MHz, DMSO): δ = 35.8 (CH_3), 36.5 (CH_3), 37.7 (CH_3), 38.5 (CH_3), 41.2 (C-3), 41.9 (C-2), 43.5 (C-5), 46.7 (C-6), 66.3 (C-4), 71.0 (C-1), 128.6 (C-8), 131.0 (C-7), 170.3 (C=O), 171.1 (C=O). – $C_{14}H_{18}Cl_4N_2O_2$ (388.12): calcd. C 43.33, H 4.67, Cl 36.54, N 7.22; found C 43.48, H 4.70, Cl 36.40, N 7.22. – MS: *m/z* (%) = 394, 392, 390, 388, 386 (0.1, 0.1, 1.4, 3.1, 2.3) $[M]^+$, 355, 353, 351 (0.4, 1.5, 1.1) $[M–Cl]^+$, 317, 316, 315 (1.1,

1.6, 1.7) $[M–2Cl]^+$, 280, 278 (5, 5) $[M–3Cl]^+$, 182 (5), 101 (7), 100 (100) $[C_5H_{10}NO]^+$.

*(2RS,6RS)-1,4-Dichlorobicyclo-N,N,N′,N′-tetramethylbicyclo[2.2.2]octane-2,6-dicarboxamide (**16**)*

Compound **14b** (350 mg, 0.91 mmol) was hydrogenated as described for **11b** to yield **16** as colorless needles (220 mg, 68.5 %), m. p. 126 °C (MeOH/H_2O). – IR: ν = 2943, 1637 (C=O), 1494 (C=C), 1418, 1398, 1339, 1255, 1160, 990, 951, 860, 692 (C-Cl) cm^{-1}. – ^1H NMR (400 MHz): δ = 1.85 (m, 1 H), 2.15 (m, 1 H), 2.30 (m, 2 H), 2.40 (m, 1 H), 2.60 (m, 2 H), 2.95 (s, 3 H, CH_3), 3.00 (s, 3 H, CH_3), 3.10 (s, 3 H, CH_3), 3.15 (s, 3 H, CH_3), 3.20 (m, 1 H), 3.50 (dd, J = 7.2/10.8 Hz, 1 H, 2-H), 4.90 (m, 1 H, 6-H). – ^{13}C NMR (62.9 MHz): δ = 35.5 (C-7), 36.0 (CH_3), 36.3 (CH_3), 37.6 (C-8), 38.36 (CH_3), 38.43 (CH_3), 39.4 (C-2), 41.7 (C-3/5), 46.7 (C-6), 63.2 (C-4), 68.2 (C-1), 172.0 (C=O), 172.1 (C=O). – $C_{14}H_{22}Cl_2N_2O_2$ (321.2): calcd. C 52.33, H 6.85, Cl 22.12, N 8.72; found C 52.57, H 6.07, Cl 22.43, N 8.88.

*(2RS,6SR)-1,4,7,8-Tetrachloro-N,N′-diphenylbicyclo[2.2.2]-oct-7-ene-2,3,5,6-tetracarboxydiimide (**17**)*

Tetrachlorothiophene *S,S*-dioxide (**7**) [22] (0.5 g, 1.9 mmol) and *N*-phenylmaleimide (0.7 g, 4.0 mmol) were refluxed in *p*-xylene (50 mL) for 4 h. A colorless solid precipitated from the solution which was filtered off and re-crystallized from acetone to yield **17** (0.4 g, 39 %), m. p. 370 °C (decomp.). – IR: ν = 2943, 1728 (C=O), 1637 (C=O), 1499 (C=C), 1384, 1340, 1204, 1168, 990, 951, 743 (C-Cl), 693 (C-Cl) cm^{-1}. – ^1H NMR (250 MHz, [D_6]acetone): δ = 4.10 (s, 4 H, 2/3/5/6-H), 7.2 – 7.6 (m, 10 H, H_{ar}). – ^{13}C NMR (62.9 MHz, [D_6]acetone): δ = 52.2 (C-2/3/5/6), 67.9 (C-1/4), 127.8 (CH), 129.7 (CH), 129.9 (CH), 130.1 (C-7/8), 133.0 (C_q), 170.7 (C=O). – $C_{24}H_{14}Cl_4N_2O_4$ (536.2): calcd. C 53.76, H 2.63, Cl 26.45, N 5.22; found C 53.84, H 2.67, Cl 26.40, N 5.19.

Electrolyses, General

The preparative-scale electrolyses were performed in a cylindrical cell (40 mL volume) [9]. The anodic and cathodic departments were divided by a sintered glass (G3) diaphragm. The cell was equipped with a Luggin capillary and a salt bridge. A [Ag/Ag^+ (sat. $AgNO_3$)] reference electrode was used according to the constant-ionic-medium concept. Mercury (special grade III, Degussa) and platinum were applied as working cathode and anode, respectively. Tetrabutylammonium hexafluorophosphate, *puriss.*, Fluka (TBPF), and tetrabutylammonium iodide, *puriss.*, Fluka (TBAI) were dried at 60 °C over P_2O_5 under vacuum (0.1 Torr) before use as supporting electrolytes. The solvent THF was refluxed over Na/K-alloy until the blue color of benzophenone ketyl appeared and was then distilled off. A Wenking ST72 potentiostat (Bank Elektronik, Göttingen) equipped with a 80V/1A-cartridge was used.

*Electroreduction of **11a***

A solution of the amide **11a** (150 mg, 0.60 mmol) and TBPF (0.20 M, 30 mL) in THF was introduced into the cathodic compartment of the cell under N_2. A solution of TBAI (4.8 mmol) in dry THF was used as anolyte. The electroreduction was performed potentiostatically at −30 °C. A potential of −3.7 V was applied which led to a starting current of 15 mA. The progress of the reduction was monitored by GLC. The substrate was consumed after 6 h, and the current had dropped to 12 mA. The electrolyte was removed from the cell and evaporated under vacuum. The residue was stirred with pentane for 24 h. Solids were filtered off, and the filtrate was evaporated to dryness. Preparative GLC of the residue gave **18**.

*(2RS)-4-chloro-N,N-dimethylbicyclo[2.2.2]octane-2-carboxamide (**18**)* (34 mg, 26 %). – ^1H NMR (250 MHz): δ = 1.5 – 1.6 (m, 1 H), 1.7 – 2.2 (m, 9 H), 2.60 – 2.75 (m, 1 H), 2.90 (s, 3 H, CH_3), 2.90 (m, 1 H, 2-H), 3.00 (s, 3 H, CH_3). – ^{13}C NMR (62.9 MHz): δ = 24.1 (CH_2), 26.4 (C-1), 28.6 (CH_2), 35.5 (CH_2), 35.6 (CH_2), 36.0 (CH_3), 37.1 (CH_3), 38.2 (CH_2), 41.3 (C-2), 67.0 (C-4), 173.6 (C=O). – MS: *m/z* (%) = 215 (0.1) $[M]^+$, 181 (11) $[M–Cl]^+$, 101 (14), 100 (100) $[C_5H_{10}NO]^+$, 91 (8) $[C_7H_7]^+$, 87 (25), 72 (23) $[CON(CH_3)_2]^+$.

Electroreduction of **11a** (150 mg, 0.60 mmol) or **18** (25 mg, 0.12 mmol) at a potential of −4.0 V and a current of 48 mA with work-up as before led to a mixture of **19** and **20** being separated by preparative GLC.

*(2RS)-N,N-dimethylbicyclo[2.2.2]octane-2-carboxamide (**19**)* (32 mg, 29 %) as a colorless solid. – ^1H NMR (250 MHz): δ = 1.9 – 2.0 (m, 8 H), 2.1 – 2.2 (m, 2 H), 2.2 – 2.4 (m, 1 H), 2.80 (dd, 1 H, 3-H), 2.90 (s, 3 H, CH_3), 3.05 (s, 3 H, CH_3), 3.05 (m, 1 H, 2-H). – ^{13}C NMR (62.9 MHz): δ = 21.5 (CH_2), 23.9 (C-4), 25.2 (CH_2), 25.3 (CH_2), 26.6 (CH_2), 27.2 (C-1), 28.4 (CH_2), 35.8 (CH_3), 37.1 (CH_3), 38.9 (C-2), 175.5 (C=O). – MS: *m/z* (%) = 181 (11) $[M]^+$, 109 (9) $[M–CONMe_2]^+$, 101 (14), 100 (100) $[C_5H_{10}NO]^+$, 87 (25), 72 (23).

*(1RS,6SR)-3,6,N,N-tetramethylcyclohex-2-ene-1-carboxamide (**20**)* (10 mg, 9 %) as a colorless liquid. – ^1H NMR (250 MHz): δ = 0.90 (d, 3 H, 6-CH_3), 1.3 – 1.5 (m, 2 H), 1.6 – 2.2 (m, 6 H), 2.95 (m, 1 H), 3.00 (s, 3 H, NCH_3), 3.10 (s, 3 H, NCH_3), 5.15 (m, 1 H, 1-H). – ^{13}C NMR (62.9 MHz): δ = 20.5 (3-CH_3), 23.6 (6-CH_3), 29.9 (CH_2), 30.2 (CH_2), 30.9 (C-6), 35.8 (NCH_3), 37.4 (NCH_3), 47.2 (C-1), 118.6 (C-2), 136.9 (C-3), 174.8 (C=O). – MS: *m/z* (%) = 181 (11) $[M]^+$, 142 (3), 109 (84) $[M–CONMe_2]^+$, 91 (38), 72 (23).

*Electroreduction of **11b***

The amide **11b** (100 mg, 0.35 mmol) was electrolyzed at −4.0 V (40 mA) as described for **11a**. Pure **21** was isolated from the product mixture by preparative GLC.

*(RS)-Bicyclo[2.2.2]octane-2-carboxypiperidide (**21**)*

(23 mg, 30 %), colorless solid. – ^{1}H NMR (250 MHz): δ = 1.2 – 1.9 (m, 16 H, CH_2-3/5/6/7/8/3′/4′/5′), 2.1 – 2.3 (m, 2 H, 1/4-H), 2.75 (m, 1 H, 2-H), 3.30 – 3.50 (m, 2 H, 2′/6′-H), 3.50 – 3.70 (m, 2 H, 2′/6′-H). – ^{13}C NMR (62.9 MHz): δ = 21.6 (CH_2), 24.0 (C-4), 24.8 (CH_2), 25.3 (CH_2), 25.4 (CH_2), 25.8 (CH_2), 26.6 (CH_2), 26.8 (CH_2), 27.5 (C-1), 34.5 (C-3), 38.7 (C-2), 42.7 (NCH_2), 46.5 (NCH_2), 173.7 (C=O). – MS: *m/z* (%) = 221 (30) $[M]^+$, 192 (3), 141 (17) $[M–C_6H_8]^+$, 140 (100) $[CH_3CHCON(CH_2)_5]^+$, 138 (3), 127 (61), 112 (23) $[CON(CH_2)_5]^+$, 109 (12) $[M–CON(CH_2)_5]^+$.

*(RS)-2,5-Dimethylenecyclohexane-1-carboxypiperidide (**22**)* and *(1RS,6RS)-3,6-dimethylcyclohex-2-ene-1-carboxypiperidide (**23**)* formed as by-products could not be separated from each other by the GS-MS coupling technique. The ^{1}H NMR spectra, characteristic ^{13}C NMR signals and MS data of the components were detected, however, in the mixture.

22: ^{1}H NMR (250 MHz): δ = 1.5 – 3.7 (m, 17 H), 4.60 (s, 1 H, =CH), 4.75 (s, 2 H, =CH), 4.90 (s, 1 H, =CH). – ^{13}C NMR (62.9 MHz): δ = 109.0 (CH_2), 109.2 (CH_2), 145.9 (C_q), 147.3 (C_q), 170.7 (C=O).

23: ^{1}H NMR (250 MHz): δ = 0.90 (d, 3 H, CHCH_3), 1.5 – 3.7 (m, 19 H), 5.15 (m, 1 H, 2-H). – ^{13}C NMR (62.9 MHz): δ = 119.1 (C-2), 136.7 (C-3), 173.2 (C=O).

MS of the mixture: *m/z* (%) = 222 (4) $[M(\mathbf{23}) + 1]^+$, 221 (23) $[M(\mathbf{23})]^+$, 220 (0.7) $[M(\mathbf{22}) + 1]^+$, 219 (0.2) $[M(\mathbf{22})]^+$, 206 (4) $[M(\mathbf{23})–CH_3]^+$, 178 (1.2), 114 (4), 113 (7), 112 (100) $[CON(CH_2)_5]^+$, 109 (25) $[M–CON(CH_2)_5]^+$, 108 (6), 93 (7), 84 (12), 69 (58).

Polytetrahydrofuran

A 0.2 M solution of TBPF in THF was electrolyzed at −3.0 V for 2 h. A polymer precipitated in the anolyte, and the current dropped to zero. The viscous black mass was dissolved in hot $CHCl_3$. A colorless solid precipitated from the solution upon cooling to −30 °C. It was purified by repeated dissolution in boiling $CHCl_3$/acetone (1 : 30) and precipitation to form a tough, flexible, milky-white foil in the cold. – IR: ν = 2921, 2079, 1490, 1372, 1210, 114, 845 cm^{-1}. – ^{1}H NMR (400 MHz): δ = 1.62 (dt, 4 H, 2 CH_2), 3.41 (t, 4 H, 2 OCH_2). – ^{13}C NMR (100.6 MHz): δ = 26.5 (CH_2), 70.62 (OCH_2).

Quantum chemical calculations

Semi-empirical MO calculations were performed by use of the QCPE software MOPAC 2.0 (no. 464) on the Siemens 7.882 computer of the University of Hamburg.

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