CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200600859

Dehalogenation of 1,3-Diiodotricyclo[3.3.0.0^{3,7}]octane: Generation of 1,3-Dehydrotricyclo[3.3.0.0^{3,7}]octane, a 2,5-Methano-Bridged [2.2.1]Propellane

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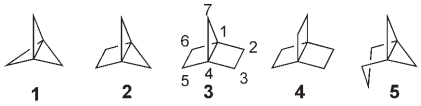
Abstract: Compounds isolated from the reaction of (±)-1,3-diiodotricyclo[3.3.0.0^{3,7}]octane with molten sodium or *t*BuLi suggest the intermediate formation of (±)-1,3-dehydrotricyclo[3.3.0.0^{3,7}]octane. Worthy of note is the formation of stereoisomeric bi(5-methylenebicyclo[2.2.1]hept-2-ylidene) derivatives, probably by coupling of two units of (±)-1,3-dehydrotricyclo[3.3.0.0^{3,7}]octane of the same or different absolute configuration followed by fragmentation, processes that have been studied by theoretical calculations.

Keywords: dehalogenation · density functional calculations · propellanes · strained molecules

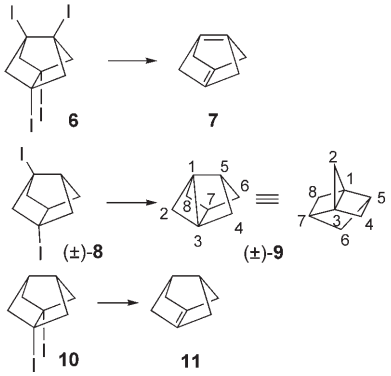
Introduction

In 1966, Ginsburg coined the name *propellane* for compounds with three nonzero bridges and one zero bridge between a pair of bridgehead carbon atoms.[1] Small-ring propellanes,[2] such as **1**–**5**, are particularly interesting, mainly



because of the presence of two carbon atoms with inverted geometries, that is, all of the groups attached to the bridgehead carbon atoms lie on one side of a plane, with a consequent unusual degree of reactivity.[3] The unusual structure of these compounds has attracted,[4] and still attracts,[5] much attention from both experimental and theoretical chemists.

For more than 20 years, our group has been working on the synthesis of bisnoradamantane derivatives. We have developed two general entries to this strained carbocyclic skeleton,[6] and have generated, trapped, and dimerized several highly pyramidalized alkenes by dehalogenation of 1,2-diiodobisnoradamantanes.[7] We have also recently published an attempt to generate tricyclo[3.3.0.0^{3,7}]octa-1(5),3(7)-diene (**7**) by deiodination of **6** (Scheme 1).[8] This reaction led to a



Scheme 1. 1,3-Dehydrotricyclo[3.3.0.0^{3,7}]octane [(±)-**9**] and highly pyramidalized alkenes **7** and **11**.

complex mixture of products, probably because 1,2-deiodination to give the pyramidalized alkene can compete with 1,3-deiodination to give 1,3-dehydro derivatives. In fact, **9** was predicted to be more stable [9.0 kcal mol^{-1}, UB3LYP/6-31G(d); 10.2 kcal mol^{-1}, UMP2/6-31G(d)] than the highly pyramidalized tricyclo[3.3.0.0^{3,7}]oct-1(5)-ene (**11**), a very reactive intermediate already generated by our group by deiodination of compound **10** (Scheme 1).[7b,9]

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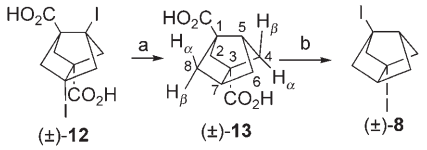
To get more insight into this 1,3-deiodination, we have now prepared (±)-**8** (Scheme 2), and studied its possible deiodination to 1,3-dehydrotricyclo[3.3.0.0^{3,7}]octane ((±)-**9**, Scheme 1). The isolated compounds from the deiodination of (±)-**8** suggest the intermediate formation of (±)-**9** (Schemes 3 and 4).



Scheme 2. Preparation of (±)-**8**: a) Li, *t*BuOH, THF, Δ, 6 h, 80%; b) IBDA, I_2, *hν*, acetonitrile, 24 h, 76%. IBDA = iodosobenzene diacetate

Although, at first sight, **9** can be seen as an irrelevant derivative of the known [2.2.1]propellane **3**,[4] the additional methano bridge connecting positions 5 and 7 in **9** strongly distorts the molecular structure of **3** (Figure 1). Thus, while

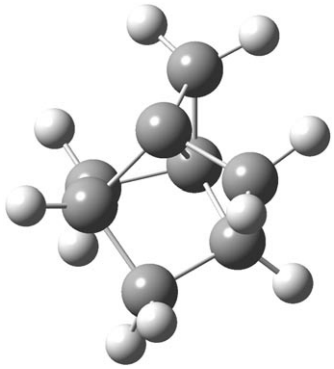


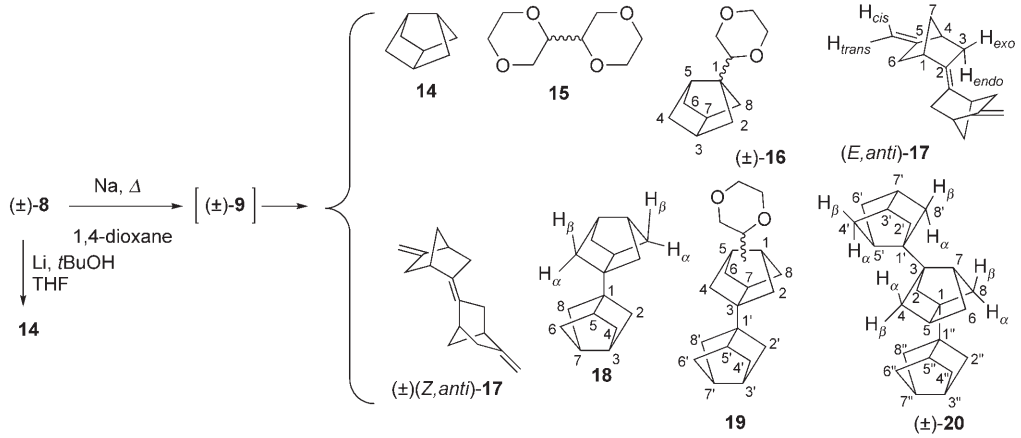
Figure 1. Minimum energy conformation [UMP2/6-31G(d)] of propellane **9**.

the dihedral C1-C2-C3-C4 angle in **3** was calculated to be 0° (UB3LYP/6-31G(d) or UMP2/6-31G(d)), the corresponding angle in **9** (C1-C5-C4-C3) was calculated to be 31° (UB3LYP/6-31G(d)) or 32° (UMP2/6-31G(d)). Although the energy change resulting from hydrogenolysis of the C1–C3 bond in **9** was found to be only slightly higher (1.4 kcal mol^{-1}, UB3LYP/6-31G(d); 2.5 kcal mol^{-1}, UMP2/6-31G(d)) than that of the corresponding bond (C1–C4) in **3**, the zero-bridge propellane bond length in **9** was calculated to be 1.725 Å (UB3LYP/6-31G(d)) and 1.789 Å (UMP2/6-31G(d)), clearly larger than the corresponding bond in **3** of 1.583 Å (UB3LYP/6-31G(d)) and 1.619 Å (UMP2/6-31G(d)). Taking into account that **3** is a very unstable compound, an even more reactive behavior should be expected for **9**, if it can be generated at all.

Results and Discussion

Diiodide (±)-**8** was prepared from diiododiacid (±)-**12**[8] by reduction with Li/*t*BuOH to the known diacid (±)-**13**,[10] followed by double iododecarboxylation of (±)-**13** using our improved conditions in acetonitrile as solvent (Scheme 2).[7e] Notably, compounds **8**, **12**, and **13** are chiral 1,3-disubstituted tricyclo[3.3.0.0^{3,7}]octane derivatives. All of them contain four stereogenic centers, which correspond to the bridgehead positions. However, in a more simple way, they can be considered as having a chiral axis passing through the middle of the C1–C5 and C3–C7 bonds. Their chirality could then be defined in the same way as for chiral allenes. The same is true for dehydro compound **9**.

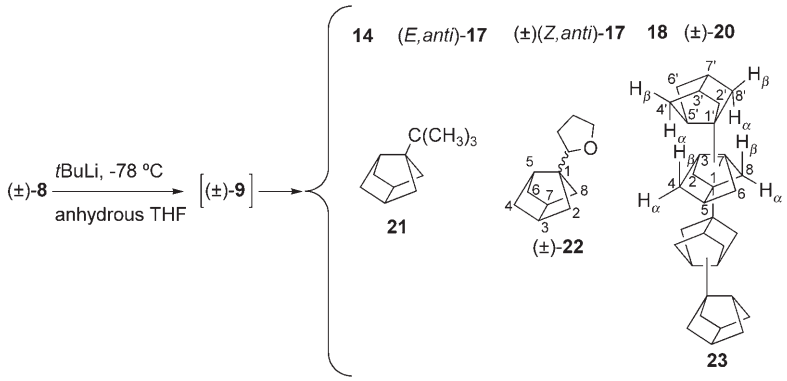
Reaction of (±)-**8** with molten sodium in boiling 1,4-dioxane gave a complex mixture (Scheme 3), which by GC–MS showed, in order of elution, the presence of the following compounds (% area ratio (a.r.)): **14** (1.2), *meso*- and *dl*-**15** (4.7 and 5.2), (±)-**16** (33.5), (±)(*Z*,*anti*)-**17** (1.5), (*E*,*anti*)-**17** (2.4), **18** (32.3), stereoisomers of **19** (13.7), and (±)-**20** (5.5). From this mixture, compounds (±)-**16**, a mixture of two stereoisomers of **17**, for which we propose the structures (*E*,*anti*)-**17** and (±)(*Z*,*anti*)-**17** (see later), **18**, the stereoisomeric mixture **19**, and (±)-**20** were isolated in 20, 3.5, 27, 11, and 2% yield, respectively, and fully characterized.



Scheme 3. Reaction of (±)-**8** with molten sodium in boiling 1,4-dioxane.

Moreover, the formation of the known products **14**[11] and *meso*- and *dl*-**15**[12] was detected by GC–MS analysis. To secure the structure of **14**, it was prepared by reduction of (±)-**8** with Li/*t*BuOH.

Similarly, reaction of (±)-**8** with *t*BuLi in anhydrous THF gave a complex mixture (Scheme 4), which by GC–MS showed the presence, in order of elution, of the following



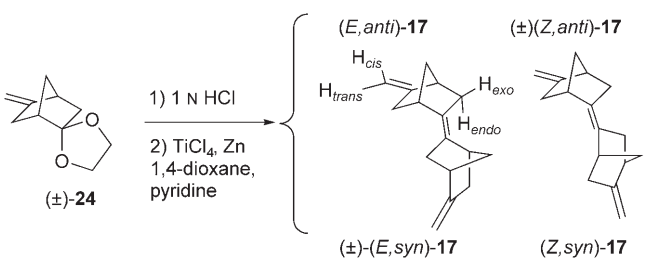
Scheme 4. Reaction of (±)-**8** with *t*BuLi in THF.

compounds (% a.r.): **21** (7.2), (±)-**22** (24.5), (±)(*Z*,*anti*)-**17** (0.1), (*E*,*anti*)-**17** (0.6), **18** (40.6), (±)-**20** (14.3), and the stereoisomeric mixture **23** (2.0). Traces of **14** were detected in the organic extracts before concentration. From the above mixture, compounds **18**, (±)-**20**, (±)-**22**, and a stereoisomeric mixture of **23** were isolated in pure form in 20, 6, 7, and 3% yield, respectively. The structure of compound **21**, which could not be isolated due to its high volatility, is proposed on the basis of its mass spectrum and by analogy with previous related results.[4,13]

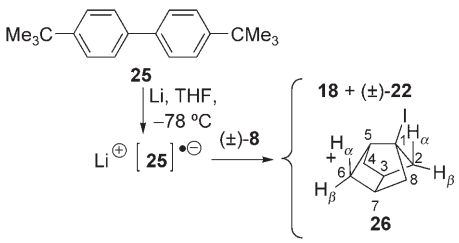
To confirm the structure of the stereoisomers of **17**, we carried out an alternative synthesis (Scheme 5), starting from the known ene ketal (±)-**24**.[14] After acidic hydrolysis of (±)-**24**, the obtained ketone was submitted to the McMurry reduction. In this way, a new mixture of stereoisomers of **17** was obtained and characterized by ^{1}H and ^{13}C NMR spectroscopy. Achiral GC–MS analysis of this mixture showed the presence of four components with similar area ratios, whose mass spectra were essentially identical and coincidental with those of the components of the mixture **17** obtained from (±)-**8**. Since the starting material in the McMurry reaction was racemic, the four dimers shown in Scheme 5 could be formed. Two of them are *meso* compounds, formed from starting compounds of opposite absolute configuration, while the other two are chiral, being formed from starting compounds of the same absolute configuration and, consequently, they should be racemic. In fact, chiral GC–MS analysis showed the presence of six components in the above mixture, confirming the presence of two racemic and two *meso* components. Achiral GC–MS analysis of mixed samples of **17** from the two reactions showed that the minor and main components of the mixture of **17** from (±)-**8** coincide with the second and third eluted components of the McMurry reaction, respectively. Similarly, chiral GC–MS analysis showed the main and minor components of the mixture **17** from (±)-**8** to be *meso* (corresponding to the fifth eluted component of the McMurry reaction) and racemic (corresponding to the third and fourth eluted components of the McMurry reaction), respectively.

We also carried out several reactions of (±)-**8** with different reagents to obtain more information about the possible formation of the bridged propellane (±)-**9**, without additional results to those described above. Thus, reaction of (±)-**8** with the radical anion derived from 4,4′-di-*tert*-butylbiphenyl (**25**), by treatment with lithium under ultrasound irradiation in anhydrous THF at −78 °C[15] followed by quenching of the reaction mixture by bubbling CO_2 (g), did not give an acidic fraction. Instead, a neutral fraction containing mainly **25** was obtained. GC–MS analysis of this mixture showed the presence, in order of elution, of the following significant components (% a.r.): **26** (0.1), (±)-**22** (0.6), **18** (1.4), and **25** (87.6) (Scheme 6). An analytical sample of the new compound **26** was obtained by controlled catalytic hydrogenation of the starting diiodide (±)-**8**.

Moreover, (±)-**8** was reacted with *t*BuLi in anhydrous diethyl ether[4a,16] at −78 °C, which gave similar results to those described above for the reaction carried out in THF

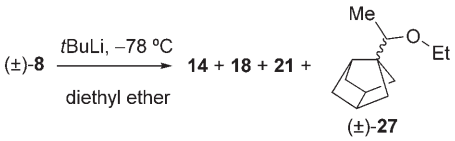


Scheme 5. Preparation of the stereoisomeric mixture of **17** from (±)-**24**.



Scheme 6. Reaction of (±)-**8** with the radical anion from **25** and Li, in THF.

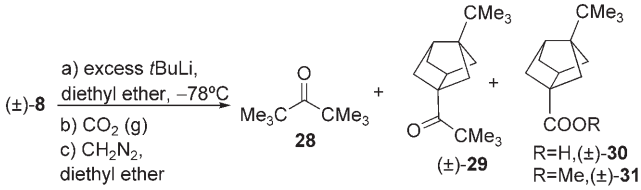
(Scheme 7). GC–MS analysis of the obtained mixture showed the presence, in order of elution, of the following main components (% a.r.): **14** (5.7), **21** (31.2), (±)-**27** (3.1),



Scheme 7. Reaction of (±)-**8** with *t*BuLi in diethyl ether.

and **18** (50.8). The structure of (±)-**27**, which was formed in very low yield, is proposed on the basis of its mass spectrum, taking into account previous results, that is, the formation of (±)-**16** and (±)-**22**. Not unexpectedly, the amount of (±)-**27** formed was much lower than those of the corresponding products (±)-**16** (33.5% a.r.) and (±)-**22** (24.5% a.r.) formed in the similar reactions carried out in 1,4-dioxane and THF, respectively.

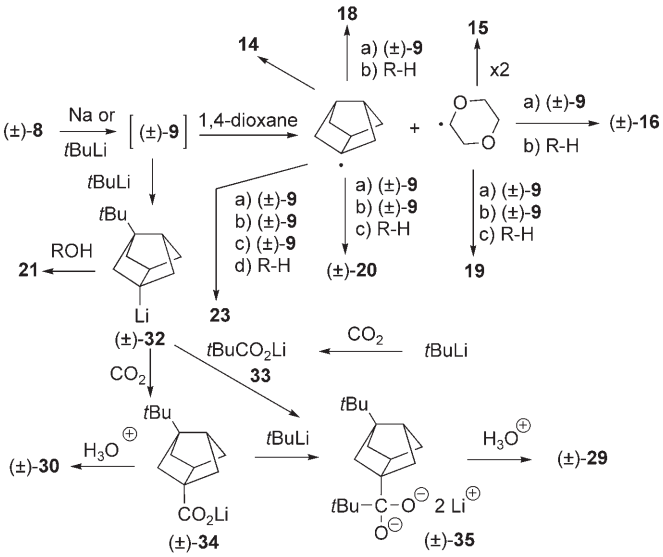
Finally, reaction of (±)-**8** with excess *t*BuLi in anhydrous diethyl ether at −78 °C, followed by quenching of the reaction mixture with trimethylsilyl chloride, gave a very complex mixture from which no defined product could be isolated or identified. However, when the above reaction mixture was quenched by bubbling CO_2 (g),[13a] a very complex mixture of products was obtained as the neutral fraction, which by GC–MS analysis was shown to contain di-*tert*-butyl ketone (**28**)[17] (74.5% a.r.) and a compound whose mass spectrum is compatible for ketone (±)-**29** (7.2% a.r.) as the main components (Scheme 8). Also, an acidic fraction was



Scheme 8. Reaction of (±)-**8** with *t*BuLi in THF and quenching with CO_2.

isolated which, after esterification with a solution of diazomethane in diethyl ether, gave a complex mixture of products. GC–MS analysis of this mixture was shown to contain mainly ester (±)-**31** (43% a.r.) derived from acid (±)-**30**.

According to the known reactivity of small-ring propellanes[2a,b] and, in particular, of [2.2.1]propellane,[2a,3,4] all of the products observed in the reaction of (±)-**8** with sodium in 1,4-dioxane may be explained by assuming the intermediate formation of (±)-**9**. This intermediate could abstract a hydrogen atom from 1,4-dioxane to give the tricyclo[3.3.0.0^{3,7}]oct-1-yl and dioxan-2-yl radicals, from which compounds **14**–**16** and **18**–**20** can be readily derived (Scheme 9). The same is true for the formation of most of the compounds obtained in the reaction of (±)-**8** with



Scheme 9. Possible pathways for the formation of products from the reactions of (±)-**8** with molten sodium or *t*BuLi.

*t*BuLi. However, in this case, the formation of compound **21** reasonably implies 1) nucleophilic addition of *t*BuLi to (±)-**9**, to give (±)-**32**, and 2) protonation. In a similar way, formation of (±)-**30** could be easily explained from (±)-**9** via **32** by 1) reaction with CO_2 to give (±)-**34**, and 2) protonation. Formation of (±)-**29** may be easily explained from (±)-**34** by 1) reaction with *t*BuLi, to give diolate (±)-**35**, and 2) hydrolysis. Alternatively, diolate (±)-**35** could be obtained from (±)-**32** by reaction with lithium pivalate (**33**), itself obtained by reaction of *t*BuLi with CO_2. The formation of (±)-**27** (Scheme 7) could be similar to that of (±)-**16**, while the formation of monoiodide **26** could take place without the intermediate formation of (±)-**9**.

We carried out a density functional theory (DFT) study (UB3LYP/6-31G(d)) of the formation of the stereoisomers of **17** from (±)-**9**, and the results are shown in Figure 2.[9] Reaction of two units of **9** of different absolute configuration (path B) gives diradical *meso*-**38**. Conformational analysis of *meso*-**38** shows the *anti* conformation (*meso*-$\mathbf{38}_{180}$) to be much more stable (10.6 kcal mol^{-1}) than the enantiomeric *gauche* conformations *meso*-$\mathbf{38}_{+60}$ and *meso*-$\mathbf{38}_{-60}$. The formation of *meso*-$\mathbf{38}_{180}$ takes place through a transition state (1.4 kcal mol^{-1}) of lower energy than those leading to *meso*-$\mathbf{38}_{+60}$ or *meso*-$\mathbf{38}_{-60}$ (2.9 kcal mol^{-1}). Fragmentation of this diradical from the more stable *meso*-$\mathbf{38}_{180}$ conformation gives (*E*,*anti*)-**17** in a highly exothermic (−139.9 kcal mol^{-1}) and barrierless process.[18] As the zero-point vibrational energy (ZPVE) correction is larger than the difference in electronic energies, the transition state appears to have a lower energy than the starting minimum. This simply means that the reaction is barrierless and highly exothermic.[22] A path from *meso*-$\mathbf{38}_{-60}$ to the corresponding fragmentation product (*Z*,*syn*)-**17** was not found. In a similar way, reaction of two units of **9** of the same absolute configuration gives diradicals *d*- or *l*-**38** (*dl*-**38**, path A), whose conformational

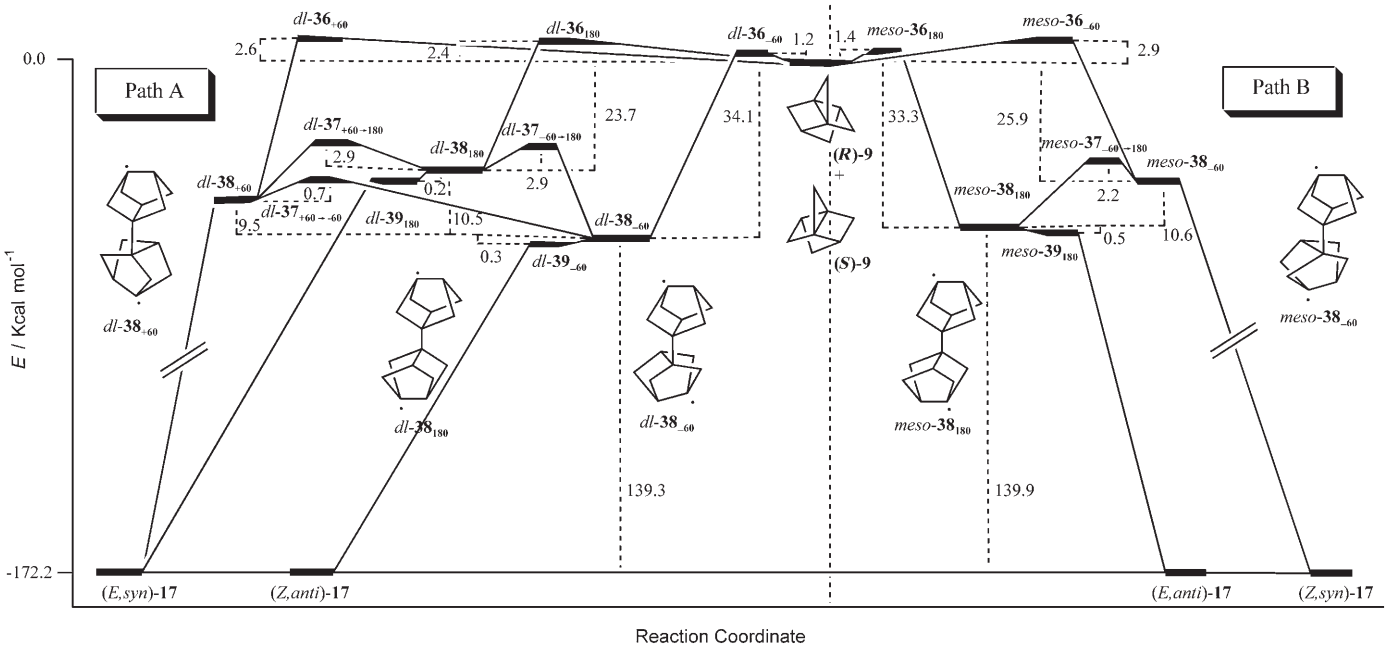


Figure 2. Possible intermediates, rotational interconversion, and transition states from (±)-**9** to the stereoisomers of **17** as calculated by a DFT study at the UB3LYP/6-31G(d) level. Path A corresponds to the coupling of two molecules of **9** of the same absolute configuration, while path B corresponds to the coupling of two molecules of **9** of different absolute configuration. The suffixes 180, +60, and −60 are given to diradicals in approximate *anti* and *gauche* conformations, respectively, around the C−C bond connecting the two tricyclic units. Similarly, these suffixes are applied to transition states for the formation of these diradicals, in this case with reference to the arrangement around the C−C bond which is being formed. Transition states with suffixes −60→180, 60→180, and +60→−60 are rotational transition states which connect the diradical minima indicated by the given suffixes. Relative energies are given in kcal mol^{-1}. Values are taken from corrected enthalpy calculations using UB3LYP/6-31G(d). Transition states connecting *meso*-**38**$_{-60}$ and *dl*-**38**$_{+60}$ with (*Z*,*syn*)-**17** and (*E*,*syn*)-**17**, respectively, were not located. The diradical *meso*-**38**$_{+60}$, the enantiomer of *meso*-**38**$_{-60}$, is not shown.

analysis shows the *gauche* conformation *dl*-**38**$_{-60}$ to be much more stable than the conformations *dl*-**38**$_{+60}$ and *dl*-**38**$_{180}$ by 9.5 and 10.5 kcal mol^{-1}, respectively. In this case, formation of *dl*-**38**$_{-60}$ takes place through a transition state (1.2 kcal mol^{-1}) of lower energy than those leading to *dl*-**38**$_{+60}$ (2.6 kcal mol^{-1}) and *dl*-**38**$_{180}$ (2.4 kcal mol^{-1}), and fragmentation of this diradical from the more stable *dl*-**38**$_{-60}$ conformation gives (±)(*Z*,*anti*)-**17** in a highly exothermic (−139.3 kcal mol^{-1}) and barrierless process. A barrierless path for the conversion of *dl*-**38**$_{180}$ (but not from *dl*-**38**$_{+60}$) to (±)(*E*,*syn*)-**17** was also found. Worthy of note is the stability of the *meso*-**38**$_{180}$ and *dl*-**38**$_{-60}$ conformations. In both cases, the C−C bonds connecting the radical centers and implied in the fragmentation processes show an essentially all-*anti* arrangement. These results are in striking contrast to the conformational analysis of compound **18** (a product formally derived from diradical **38** by hydrogenation), which shows the *anti* conformation to be 0.3 kcal mol^{-1} less stable than the enantiomeric *gauche* ones.[9] In light of these calculations, we propose (±)(*Z*,*anti*)- and (*E*,*anti*)-**17** to be the stereoisomers of **17** formed in the reaction of (±)-**8** with molten sodium or *t*BuLi.

As in the case of [2.2.1]propellane, in trapping experiments with 1,3-diphenylisobenzofuran we did not find evidence for the formation of rearranged products, such as dienes **46** or **47** derived from **9**, via retrocyclopropanation to carbene **45** and rearrangement through transition states **42**, **43**$_{exo}$, **43**$_{endo}$, or **44,** or via [2+2] retrocycloaddition through transition state **41**, as had been observed for [1.1.1]propellanes.[3] In fact, theoretical calculations predicted very high activation energies for these isomerizations (see Figure 3 for details).[9]

Conclusion

We have prepared the diiodo compound (±)-**8** and studied its deiodination by reaction with molten sodium and *t*BuLi. The isolated and/or detected products from the deiodination reactions, in particular the formation of the two stereoisomers of **17**, suggest the intermediate formation of the 1,3-dehydro derivative (±)-**9**, a bridged and highly distorted [2.2.1]propellane with a calculated central C−C bond about 0.15 Å larger than that of the parent propellane. The possible monomolecular rearrangements of **9** have been studied by DFT calculations, which show that they are not kinetically favored processes compared with the dimerization of (±)-**9** to give diradicals **38**. These diradicals can experience a highly exothermic multiple fragmentation reaction through barrierless processes to give two stereoisomers of **17**, probably by fragmentation of the intermediate diradicals in the unexpectedly stable conformations *dl*-**38**$_{-60}$ and *meso*-**38**$_{180}$,

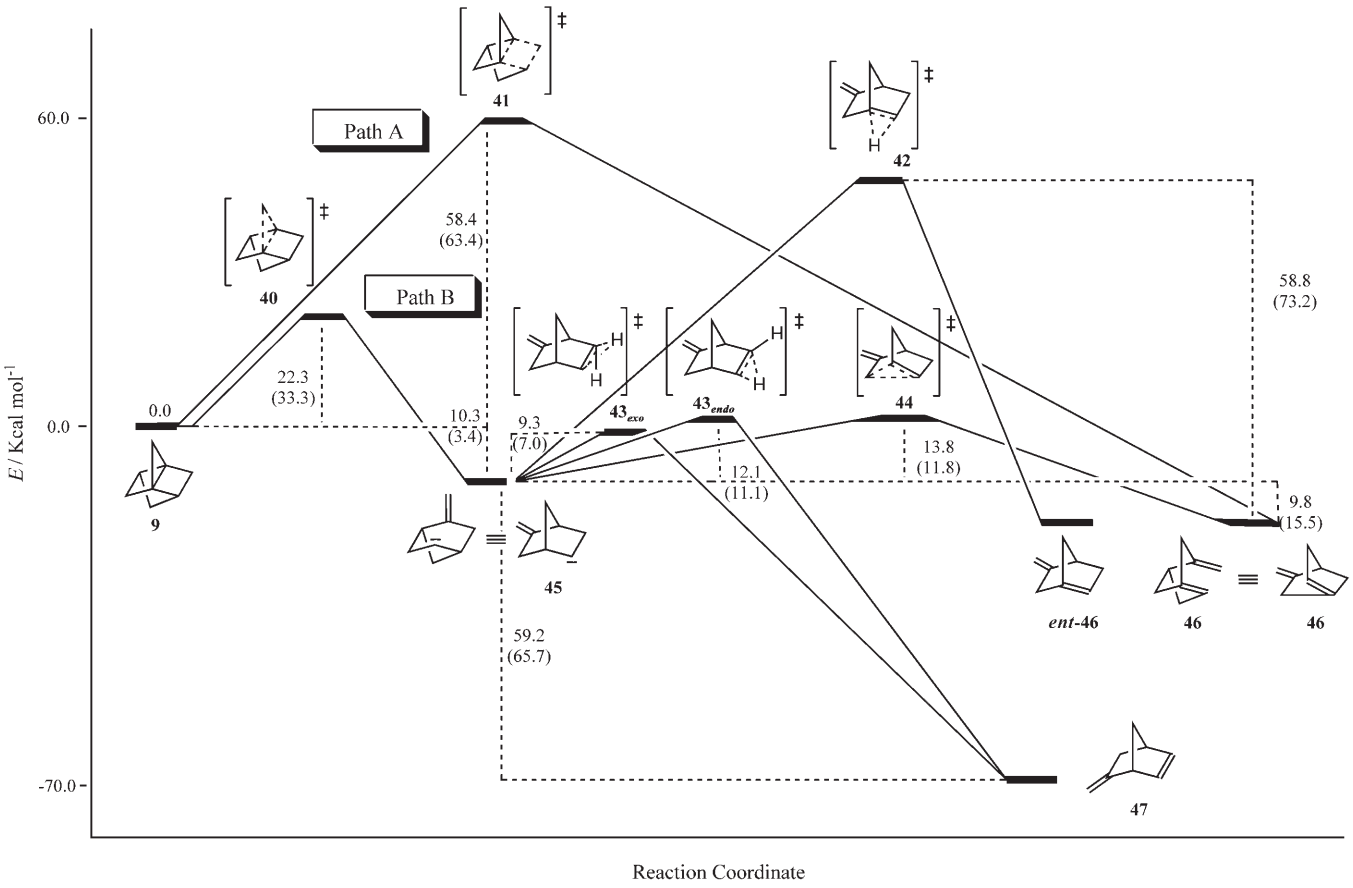


Figure 3. Theoretical study of the unimolecular rearrangements of **9**. Relative energies are given in kcal mol^{-1}. Values correspond to corrected enthalpy calculations using UB3LYP/6-31G(d) or UMP2/6-31G(d) (in parentheses). Path A: thermally forbidden [2+2] retrocycloaddition to **46**. Path B: retrocyclopropanation to carbene **45** and possible rearrangements to **46** or **47**.

which contain an all-*anti* arrangement of the carbon skeleton implied in the fragmentation processes, a situation not found in the corresponding hydrocarbons.

Experimental Section

General methods: Melting points were determined in open capillary tubes with an MFB 595010 M Gallenkamp melting point apparatus. Unless otherwise stated, NMR spectra were recorded at 25 °C in $CDCl_3$ in ^1H (500 MHz) and ^{13}C (75.4 MHz) spectrometers. Chemical shifts (δ) are reported in parts per million in relation to internal tetramethylsilane (TMS). Assignments given for the NMR spectra are based on distortionless enhanced polarization transfer (DEPT), correlation spectroscopy (COSY) $^1H/^1H$, heteronuclear correlation spectroscopy (HETCOR) $^1H/^{13}C$ (heteronuclear single quantum correlation (HSQC) and heteronuclear multiple bond correlation (HMBC) sequences for one-bond and long-range $^1H/^{13}C$ heterocorrelations, respectively), and nuclear Overhauser effect spectroscopy (NOESY) experiments for selected compounds. Diastereotopic methylene protons in tricyclo[3.3.0.0^{3,7}]octane derivatives are referred to as H_α and H_β, as shown in the corresponding structures. MS and GC–MS analyses were carried out on a Hewlett-Packard 5988A spectrometer, the sample being introduced directly or through a gas chromatograph (Hewlett-Packard model 5890 Series II). For achiral GC–MS analyses a 30-m column (HP-5, 5% diphenyl–95% dimethylpolysiloxane) was used; conditions: 10 psi, initial temperature 35 °C (2 min), then heating at a rate of 8 °C min^{-1} to 300 °C, then isothermic at 300 °C. For chiral GC–MS analyses a 30-m (0.25 mm internal diameter) chiral column (Supelco, Beta Dex 120, containing permethylated β-cyclodextrin as the chiral stationary phase) was used; conditions: 10 psi, initial temperature 50 °C (2 min), then heating at a rate of 10 °C min^{-1} to 240 °C, then isothermic at 240 °C. In both cases, the electron impact (EI, 70 eV) or chemical ionization (CI, CH_4) techniques were used. Only significant ions are given: those with higher relative abundance, except for the ions with higher *m*/*z* values. Accurate mass measurements were performed on a Micromass Autospec spectrometer. IR spectra were recorded on Perkin–Elmer Spectrum RXI equipment. Absorption values are given as wavenumbers (cm^{-1}). Column chromatography was performed on silica gel 60 AC.C (35–70 mesh, sodium dodecyl sulfate (SDS), ref. 2000027). Thin-layer chromatography (TLC) was performed on aluminum-backed sheets with silica gel 60 F_{254} (Merck, ref. 1.05554), and spots were visualized with UV light and a 1% aqueous solution of $KMnO_4$. NMR spectroscopy and GC–MS were performed at the "Serveis Científico-Tècnics" of the University of Barcelona, and elemental analyses were carried out at the Microanalysis Service of the IIQAB (CSIC, Barcelona, Spain). Accurate mass measurements were performed on a Micromass Autospec spectrometer at the Mass Spectrometry Laboratory of the University of Santiago de Compostela (Spain).

(±)-Tricyclo[3.3.0.0^{3,7}]octane-1,3-dicarboxylic acid [(±)-13]:[10] Small pieces of lithium (3.59 g, 517 mmol) were added to a boiling solution of (±)-5,7-diiodotricyclo[3.3.0.0^{3,7}]octane-1,3-dicarboxylic acid ((±)-**12**, 3.86 g, 8.62 mmol) in a mixture of *t*BuOH (49 mL, 516 mmol) and THF (170 mL) kept under argon, and the mixture was heated under reflux for

6 h. The mixture was allowed to cool to room temperature and poured onto ice water (300 g). The aqueous solution was washed with diethyl ether (3×100 mL), cooled with an ice-water bath, made acidic (pH 1–2) with aqueous 10% HCl (175 mL), and extracted with AcOEt (5× 200 mL). The combined organic extracts were dried (anhydrous Na_2SO_4) and concentrated under reduced pressure to give a light yellow residue (1.72 g), which was washed with a small amount of cold diethyl ether to give (±)-**13** (1.36 g, 80% yield) as a white solid. M.p. 214–216 °C (diethyl ether), reported[10] 215–215.5 °C (toluene/ethanol); ^{1}H NMR (CD_3OD): δ=1.67 (brs, 2H; 6-H_2), 1.75 (dt, J=9.5 Hz, J'=2.0 Hz, 2H; 4(8)-H_α), 1.91 (dm, J=9.5 Hz, 2H; 4(8)-H_β), 2.00 (t, J=2.0 Hz, 2H; 2-H_2), 2.71 (m, 2H; 5(7)-H), 4.87 ppm (brs; 2 COOH); ^{13}C NMR (CD_3OD): δ=44.0 (CH, C5(7)), 47.4 (CH_2, C6), 51.5 (CH_2, C4(8)), 54.2 (C, C1(3)), 54.8 (CH_2, C2), 178.1 ppm (C, 1(3)-COOH); IR (KBr): $\tilde{\nu}$=3500–2250 (max. at 2996, 2950, 2903, 2706, 2606), 1705, 1482, 1416, 1317, 1286, 1259, 1218, 1202, 1128, 1085, 893, 746 cm^{-1}; MS (EI): m/z (%): 178 ([$M-H_2O$]$^{\cdot+}$, 9), 150 ([$M-H_2O-CO$]$^{\cdot+}$, 53), 133 ([$M+H-2H_2O-CO$]$^+$, 40), 132 (21), 111 (69), 105 ([$M+H-2H_2O-2CO$]$^+$, 100), 104 (21), 93 (56), 91 (36), 79 (73), 77 (60), 67 (77), 65 (82); MS (CI, CH_4): m/z (%): 197 ([$M+H$]$^+$, 18), 179 ([$M+H-H_2O$]$^+$, 45), 151 ([$M+H-H_2O-CO$]$^+$, 100), 133 ([$M+H-2H_2O-CO$]$^+$, 25), 105 ([$M+H-2H_2O-2CO$]$^+$, 14).

(±)-1,3-Diiodotricyclo[3.3.0.0^{3,7}]octane [(±)-8]: A mixture of diacid (±)-**13** (1.78 g, 9.07 mmol), iodine (5.06 g, 19.9 mmol), and IBDA (6.56 g, 98% content, 19.9 mmol) in anhydrous acetonitrile (185 mL) was irradiated under reflux with two 100-W tungsten lamps in an argon atmosphere for 4 h. More iodine (5.06 g, 19.9 mmol) and IBDA (6.56 g, 19.9 mmol) were added and irradiation under reflux was continued for 20 h more. The resulting solution was distilled under atmospheric pressure through a Vigreux column (10 cm). The residue was taken up in diethyl ether (175 mL) and the organic solution was washed with aqueous $Na_2S_2O_3$ solution (10%, 3×165 mL), saturated aqueous $NaHCO_3$ solution (3×165 mL), and brine (2×165 mL). The organic phase was dried (anhydrous Na_2SO_4) and the solvent was distilled under atmospheric pressure through a Vigreux column (10 cm). Most of the iodobenzene formed in the reaction was distilled using rotary microdistillation equipment at 70–80 °C/30 Torr. The light yellow residue (6.60 g) was separated into two fractions (3.35 and 3.25 g), which were independently submitted to column chromatography (silica gel (600 g), *n*-pentane]. The solvent of the chromatographic fractions was distilled off at atmospheric pressure through a Vigreux column (10 cm). After the product isolated from the two chromatographic columns was combined, diiodide (±)-**8** was obtained as a light yellow liquid (2.61 g), which was further purified by distillation on rotary microdistillation equipment at 100–110 °C/30 Torr to give pure (±)-**8** (2.48 g, 76% yield) as a colorless liquid. ^{1}H NMR: δ= 1.64 (quint, J=2.0 Hz, 2H; 6-H_2), 1.77 (dt, J=9.5 Hz, J'=2.0 Hz, 2H; 4(8)-H_α), 2.17 (dq, J=9.5 Hz, J'=2.0 Hz, 2H; 4(8)-H_β), 2.31 (t, J= 2.0 Hz, 2H; 2-H_2), 2.40 ppm (q, J=2.0 Hz, 2H; 5(7)-H); ^{13}C NMR: δ= 24.4 (C, C1(3)), 47.1 (CH_2, C6), 50.6 (CH, C5(7)), 58.9 (CH_2, C4(8)), 69.1 ppm (CH_2, C2); IR (NaCl): $\tilde{\nu}$=2992, 2940, 2892, 1477, 1282, 1252, 1209, 1197, 1132, 1067, 1000, 944, 923, 809 cm^{-1}; MS (EI): m/z (%): 360 ($M^{\cdot+}$, 1), 233 ([$M-I$]$^+$, 28), 106 ([$M-2I$]$^{\cdot+}$, 100), 105 (49), 91 (43), 79 (29), 78 (36), 77 (22); elemental analysis (%) calcd for $C_8H_{10}I_2$: C 26.69, H 2.80, I 70.51; found: C 26.61, H 2.62, I 70.58.

Reaction of (±)-1,3-diiodotricyclo[3.3.0.0^{3,7}]octane [(±)-8] with molten sodium in boiling 1,4-dioxane: isolation of 2-(tricyclo[3.3.0.0^{3,7}]oct-1-yl)-1,4-dioxane [(±)-16], stereoisomeric mixture of (±)(*Z*,*anti*)- and (*E*,*anti*)-bi(5-methylenebicyclo[2.2.1]hept-2-ylidene) [(±)(*Z*,*anti*)- and (*E*,*anti*)-17], bi(tricyclo[3.3.0.0^{3,7}]oct-1-yl) (18), stereoisomeric mixture of 2-[3-(tricyclo[3.3.0.0^{3,7}]oct-1-yl)-tricyclo[3.3.0.0^{3,7}]oct-1-yl]-1,4-dioxane (19), and 1,3-bis(tricyclo[3.3.0.0^{3,7}]oct-1-yl)-tricyclo[3.3.0.0^{3,7}]octane, [(±)-20]; detection of tricyclo[3.3.0.0^{3,7}]octane (14) and stereoisomeric mixture of 2,2′-bi(1,4-dioxan-2-yl) (15): A solution of diiodide (±)-**8** (2.16 g, 6.0 mmol) in anhydrous 1,4-dioxane (5 mL) was added at once to molten sodium (1.38 g, 60 mmol) in boiling 1,4-dioxane (20 mL) and the mixture was heated under reflux for 4 h under an argon atmosphere. The cold mixture was filtered through Celite and the solid was washed with diethyl ether (3×60 mL). The combined filtrate and washings were concentrated at atmospheric pressure using a Vigreux column (10 cm) to give a residue that still contained residual solvent (1.41 g). GC–MS analysis of this mixture showed the presence of the following compounds (retention time (r.t., min); relative a.r.): **14** (4.43; 1.2%), stereoisomers of **15** (11.44 and 11.93; 4.7 and 5.2%), (±)-**16** (14.29; 33.5%), (*E*,*anti*)- and (±)(*Z*,*anti*)-**17** (15.17 and 15.29; 1.5 and 2.4%), **18** (16.48; 32.3%), stereoisomers of **19** (23.35; 13.7%), (±)-**20** (25.12; 5.5%). GC–MS analysis of the above filtrate through Celite showed a much higher content of compound **14** (about 13%). The identity of the stereoisomers of **15** was established by comparison of their mass spectra with those of the described compounds.[12] The identity of compound **14** was established by comparison of its mass spectrum with that of an authentic sample prepared by a modification of a known procedure,[11] as described later on. All of the remaining compounds were isolated as follows. The above residue (1.41 g) was submitted to flash column chromatography on silica gel (210 g, 5 cm internal diameter of the column, hexane/diethyl ether) to obtain, in order of elution: a white solid mixture of **18** and (±)-**20** (263 mg; hexane); a white waxy mixture of (*E*,*anti*)- and (±)(*Z*,*anti*)-**17** (22 mg, 3.5% yield; hexane); and a yellow oily mixture of (±)-**16** and stereoisomers of **19** (455 mg; hexane/diethyl ether from 9:1 to 8:2). The above mixture of **18** and (±)-**20** was sublimed, first at 60–70 °C/30 Torr to give pure **18** (175 mg, 27% yield) as a white solid, and then at 115–125 °C/30 Torr to give (±)-**20** (12 mg, 2% yield) as a white solid. The above mixture of (±)-**16** and stereoisomeric mixture **19** was fractionally distilled using rotary microdistillation equipment, first at 55–65 °C/1 Torr to give (±)-**16** (233 mg, 20% yield) and then at 150–160 °C/1 Torr to give the stereoisomeric mixture **19** (96 mg, 11% yield), both as colorless oils.

(±)-16: ^{1}H NMR: δ=1.30–1.42 (complex absorption, 8H; 2-H_2, 4-H_2, 6-H_2, and 8-H_2), 2.28 (quint, J=2.5 Hz, 1H; 5-H), 2.30 (complex absorption, 2H; 3-H and 7-H), 3.44 (tm, J=11.0 Hz, 1H; 3-H_{ax} dioxane), 3.60 (dt, J=3.0 Hz, J'=11.0 Hz, 1H; 6-H_{ax} dioxane), 3.70 (dd, J=11.5 Hz, J'= 2.5 Hz, 1H; 6-H_{eq} dioxane), 3.76 (dt, J=2.5 Hz, J'=11.5 Hz, 1H; 5-H_{ax} dioxane), 3.77–3.83 ppm (complex absorption, 3H, 2-H_{ax}, 3-H_{eq} and 5-H_{eq} dioxane); ^{13}C NMR: δ=36.4 (CH) and 36.5 (CH) (C3 and C7), 39.2 (CH, C5), 46.8 (CH_2) and 46.9 (CH_2) (C4 and C6), 47.8 (CH_2) and 48.3 (CH_2) (C2 and C8), 50.4 (C, C1), 66.6 (CH_2, C6 dioxane), 67.3 (CH_2, C5 dioxane), 69.4 (CH_2, C3 dioxane), 77.3 ppm (CH, C2 dioxane); IR (NaCl): $\tilde{\nu}$=2962, 2890, 2851, 1481, 1448, 1350, 1270, 1121, 1103, 899, 880 cm^{-1}; GC–MS (EI): m/z (%): 194 ($M^{\cdot+}$, 15), 165 (9), 153 (9), 151 (13), 126 (12), 117 (24), 113 (21), 107 ([$M-C_4H_7O_2$]$^+$, 19), 91 (41), 87 (35), 86 (21), 80 (21), 79 (59), 77 (26), 73 (47), 67 (100), 66 (27); MS (CI, CH_4): m/z (%): 195 ([$M+H$]$^+$, 6), 194 ($M^{\cdot+}$, 9), 193 ([$M+H-H_2$]$^+$, 22), 135 (100), 133 (33), 107 ([$M-C_4H_7O_2$]$^+$, 14), 73 (24); accurate mass measurement calcd for [$C_{12}H_{18}O_2+H$]$^+$: 195.1385; found: 195.1382.

(*E*,*anti*)- and (±)(*Z*,*anti*)-17: IR (KBr): $\tilde{\nu}$=3071, 2968, 2938, 2900, 2888, 2836, 1665, 1460, 1432, 1303, 1292, 874 cm^{-1}; accurate mass measurement calcd for [$C_{16}H_{20}+H$]$^+$: 213.1643; found: 213.1641. NMR data (from the spectra of the mixture) of the main diastereomer (*E*,*anti*)-**17**: ^{1}H NMR: δ=1.43 (s, 4H; 7(7′)-H_2], 1.93 (dd, J=15.5 Hz, J'=2.0 Hz, 2H; 3(3′)-H_{endo}), 1.98 (dd, J=14.5 Hz, J'=2.0 Hz, 2H; 6(6′)-H_{endo}), 2.20–2.24 (complex absorption, 4H; 3(3′)-H_{exo} and 6(6′)-H_{exo}), 2.74 (m, 2H; 1(1′)-H), 2.80 (m, 2H; 4(4′)-H), 4.63 (m, 2H, =CH_{trans}), 4.90 ppm (m, 2H, =CH_{cis}); ^{13}C NMR (100.6 MHz): δ=37.2 (CH_2, C6(6′)), 37.5 (CH_2, C3(3′)), 40.2 (CH_2, C7(7′)), 42.1 (CH, C1(1′)), 46.0 (CH, C4(4′)), 102.8 (CH_2, =CH_2), 131.3 (C, C2(2′)), 154.9 ppm (C, C5(5′)); GC–MS (EI): m/z (%): 212 ($M^{\cdot+}$, 32), 197 (11), 169 (14), 155 (15), 132 (23), 131 (22), 129 (28), 117 (35), 115 (25), 105 (48), 92 (31), 91 (100), 80 (44), 79 (93), 77 (69); NMR data (from the spectra of the mixture) of the minor diastereomer (±)-(*Z*,*anti*)-**17**: ^{1}H NMR: δ=1.40–1.50 (complex absorption, 4H; 7(7′)-H_2), 1.72 (dm, J=13.5 Hz, 2H; 6(6′)-H_{endo}), 1.94–1.98 (m, 2H; 3(3′)-H_{endo}), 2.13 (dm, J=13.5 Hz, 2H; 6(6′)-H_{exo}), 2.23–2.28 (m, 2H; 3(3′)-H_{exo}), 2.80 (m, 2H; 4(4′)-H), 2.93 (m, 2H; 1(1′)-H), 4.63 (m, 2H, =CH_{trans}), 4.90 ppm (m, 2H, =CH_{cis}); ^{13}C NMR (100.6 MHz): δ=37.1 (CH_2, C6(6′)), 38.3 (CH_2, C3(3′)), 40.7 (CH_2, C7(7′)), 42.5 (CH, C1(1′)), 46.0 (CH, C4(4′)), 102.7 (CH_2, =CH_2), 131.7 (C, C2(2′)), 154.9 ppm (C, C5(5′)); GC–MS (EI): m/z (%): 212 ($M^{\cdot+}$, 17), 141 (13), 133 (16), 132 (23), 131 (15), 129 (24), 117 (34), 115 (24), 105 (45), 92 (33), 91 (100), 80 (43), 79 (91), 77 (71).

18: M.p. 93.7–95.1 °C (sublimed); ^{1}H NMR: δ=1.26 (m, 4H; 2(2′,8,8′)-H_α), 1.36–1.38 (complex absorption, 8H; 2(2′,8,8′)-H_β and 4(4′,6,6′)-H_β),

1.43 (m, 4H; 4(4′,6,6′)-H_α), 2.11 (quint, J=2.5 Hz, 2H; 5(5′)-H), 2.27–2.29 ppm (complex absorption, 4H; 3(3′,7,7′)-H); ^{13}C NMR δ=36.8 (CH, C3(3′,7,7′)), 40.2 (CH, C5(5′)), 47.3 (CH_2, C4(4′,6,6′)), 49.4 (CH_2, C2-(2′,8,8′)), 51.5 ppm (C, C1(1′)); IR (KBr): $\tilde{\nu}$=2957, 2934, 2885, 1477, 1293, 1269 cm^{-1}; GC–MS (EI): m/z (%): 214 ($M^{\cdot+}$, 1), 199 (3), 185 (13), 171 (13), 143 (16), 131 (20), 129 (25), 105 (28), 91 (63), 80 (22), 79 (50), 77 (29), 67 (100); MS (CI, CH_4): m/z (%): 215 ($[M+H]^+$, 32), 214 ($M^{\cdot+}$, 25), 213 ($[M+H-H_2]^+$, 100), 185 (37), 135 (48), 133 (42), 121 (35), 107 (31), 93 (58), 81 (63), 79 (56), 67 (68); accurate mass measurement calcd for $[C_{16}H_{22}+H]^+$: 215.1800; found: 215.1799.

Stereoisomeric mixture 19: ^{1}H NMR: δ=1.23–1.53 (complex absorption, 16H; methylenic protons), 2.09 (quint, J=2.5 Hz, 1H; 5′-H), 2.15 (m, 1H; 7-H), 2.28 (complex absorption, 2H; 3′-H and 7′-H), 2.30 (m, 1H; 5-H), 3.45 (ddd, J=12.0 Hz, J'=11.0 Hz, J''=1.5 Hz, 1H; 3-H_{ax} dioxane), 3.60 (complex absorption, 1H; 6-H_{ax} dioxane), 3.70 (dd, J=11.5 Hz, J'=2.5 Hz, 1H; 6-H_{eq} dioxane), 3.73–3.83 ppm (complex absorption, 4H; 2-H_{ax}, 3-H_{eq}, 5-H_{ax} (3.76 ppm, dt, J=2.5 Hz, J'=11.5 Hz) and 5-H_{eq} dioxane); no different signals were observed for both diastereomers; ^{13}C NMR: δ=36.8 (4CH, C3′ and C7′, both diastereomers), 40.06 (2CH, C5′, both diastereomers), 40.12 (CH) and 40.3 (CH) (C5), 40.9 (2CH, C7, both diastereomers), 47.1 (CH_2), 47.2 (CH_2), 47.3 (4 CH_2), 48.1 (CH_2), 48.3 (CH_2), 49.07 (CH_2), 49.14 (CH_2), 49.18 (2CH_2), 49.23 (2CH_2), 50.1 (CH_2), 50.4 (CH_2), (methylene C atoms, both diastereomers), 51.2 (2C), 51.5 (C), 51.6 (C), 52.26 (C) and 52.29 (C) (C1, C1′ and C3, both diastereomers), 66.6 (2CH_2, C6 dioxane, both diastereomers), 67.3 (2CH_2, C5 dioxane, both diastereomers), 69.3 (2CH_2, C3 dioxane, both diastereomers), 77.49 (CH) and 77.50 ppm (CH) (C2); IR (NaCl): $\tilde{\nu}$=2959, 2936, 2886, 2851, 1479, 1448, 1350, 1292, 1268, 1121, 1101, 909, 880 cm^{-1}; GC–MS (EI): m/z (%): 259 ($[M-C_3H_5]^+$, 6), 225 (4), 213 ($[M-C_4H_7O_2]^+$, 24), 171 (14), 143 (16), 131 (35), 129 (29), 119 (15), 117 (24), 107 (17), 105 (31), 93 (28), 91 (76), 87 ($[C_4H_7O_2]^+$, 33), 81 (26), 79 (83), 77 (32), 73 (27), 67 (100); MS (CI, CH_4): m/z (%): 301 ($[M+H]^+$, 21), 300 ($M^{\cdot+}$, 27), 299 ($[M+H-H_2]^+$, 41), 259 ($[M-C_3H_5]^+$, 15), 242 (20), 241 (93), 240 (24), 239 (100), 237 (24), 213 ($[M-C_4H_7O_2]^+$, 72), 171 (22), 159 (25), 135 (23), 131 (25), 121 (22), 107 (22), 105 (27), 93 (20), 91 (22), 87 ($[C_4H_7O_2]^+$, 21), 81 (28), 78 (24), 73 (83), 67 (21); accurate mass measurement calcd for $[C_{20}H_{28}O_2+H]^+$: 301.2168; found: 301.2163.

(±)-20: M.p. 156–158 °C (sublimed); ^{1}H NMR: δ=1.24–1.27 (complex absorption, 4H; 2′(2″)-H_α and 8′(8″)-H_α), 1.30–1.33 (complex absorption, 4H; 2-H_2 and 4(8)-H_α), 1.35–1.39 (complex absorption, 8H; 2′(2″)-H_β, 8′-(8″)-H_β, 4′(4″)-H_β and 6′(6″)-H_β), 1.41–1.45 (complex absorption, 4H; 4′-(4″)-H_α and 6′(6″)-H_α), 1.46–1.50 (complex absorption, 4H; 6-H_2 and 4(8)-H_β), 2.12 (quint, J=2.5 Hz, 2H; 5′(5″)-H), 2.13 (m, 2H; 5(7)-H), 2.28 ppm (complex absorption, 4H; 3′(3″)-H and 7′(7″)-H); ^{13}C NMR: δ=36.8 (CH, C3′(3″) and C7′(7″)), 40.1 (CH, C5′(5″)), 41.2 (CH, C5(7)), 47.3 (CH_2, C4′(4″) and C6′(6″)), 47.6 (CH_2, C6), 49.2 (CH_2) and 49.3 (CH_2) (C2′(2″) and C8′(8″)), 49.5 (CH_2, C4(8)), 51.7 (CH_2, C2), 51.9 (C) and 52.4 ppm (C) (C1(3) and C1′(1″)); IR (KBr): $\tilde{\nu}$=2966, 2933, 2884, 1477, 1291 cm^{-1}; GC–MS (EI): m/z (%): 320 ($M^{\cdot+}$, <1), 305 (1), 279 (4), 277 (5), 213 ($[M-C_8H_{11}]^+$, 5), 211 (5), 185 (6), 171 (14), 143 (18), 131 (24), 129 (34), 117 (22), 105 ($[M-C_8H_{11}-C_8H_{12}]^+$, 31), 93 (23), 91 (68), 81 (25), 79 (75), 77 (33), 67 (100); MS (CI, CH_4): m/z (%): 321 ($[M+H]^+$, 11), 320 ($M^{\cdot+}$, 11), 319 ($[M+H-H_2]^+$, 33), 241 (15), 239 (18), 227 (16), 213 (29), 199 (22), 187 (37), 185 (35), 173 (30), 171 (30), 149 (28), 147 (31), 135 (42), 121 (37), 109 (33), 107 (57), 105 ($[M-C_8H_{11}-C_8H_{12}]^+$, 37), 95 (41), 93 (64), 91 (36), 81 (100), 79 (79), 67 (94); accurate mass measurement calcd for $[C_{24}H_{32}]^{\cdot+}$: 320.2504; found: 320.2510.

Reaction of (±)-8 with *t*BuLi in anhydrous THF: isolation of bi-(tricyclo[3.3.0.0^{3,7}]oct-1-yl) (18), (±)-2-(tricyclo[3.3.0.0^{3,7}]oct-1-yl)-tetrahydrofuran [(±)-22], trimer (±)-20, and stereoisomeric mixture of bi[3-(tricyclo[3.3.0.0^{3,7}]oct-1-yl)-tricyclo[3.3.0.0^{3,7}]oct-1-yl] (23); detection of compounds 14, (±)(*Z*,*anti*)- and (*E*,*anti*)-17, and 21: A solution of *t*BuLi (10 mL, 1.5 M in pentane, 15 mmol) was added dropwise to a cold (−78 °C), magnetically stirred solution of diiodide (±)-**8** (1.08 g, 3.0 mmol) in anhydrous THF (10 mL) under an argon atmosphere, and the mixture was allowed to warm to room temperature. Methanol (5 mL) and water (10 mL) were successively added and the mixture was extracted with diethyl ether (3×20 mL). The combined organic phases were dried (anhydrous Na_2SO_4) and concentrated at atmospheric pressure using a Vigreux column (10 cm) to give a yellowish residue (363 mg). GC–MS analysis of this mixture showed the presence of the following more significant compounds ((r.t., min); relative a.r.): **21** (9.19; 7.2%), (±)-**22** (12.8; 24.5%), (±)(*Z*,*anti*)- and (*E*,*anti*)-**17** (15.17 and 15.29; 0.1 and 0.6%), **18** (16.43; 40.6%), (±)-**20** (25.12; 14.3%), and stereoisomeric mixture **23** (32.81; 2.0%). GC–MS analysis of the combined organic extracts, before evaporation of the solvent, showed the presence of a small amount of **14** (0.4% relative area). This compound, together with minor amounts of compounds **21**, (±)-**22**, **18**, and (±)-**20**, was shown to be present (GC–MS) in the corresponding distillate. The above residue (363 mg) was submitted to flash column chromatography on silica gel (80 g, 5 cm internal diameter of the column, hexane/diethyl ether) to obtain in order of elution: a white solid mixture containing hydrocarbon compounds (171 mg; hexane) and a yellowish oil containing (±)-**22** plus other minor products (102 mg) (hexane/diethyl ether 9:1). The hydrocarbon fraction was submitted to fractional sublimation, first at 60–70 °C/30 Torr to give pure **18** (66 mg, 20% yield) as a white solid, then at 90–100 °C/30 Torr to give a mixture of **18**, (±)-**20**, plus other minor compounds as a white waxy product (26 mg), then at 115–125 °C/30 Torr to give pure (±)-**20**, (20 mg, 6% yield) as a white solid, and finally at 170–180 °C/30 Torr to give the stereoisomeric mixture **23** (9 mg, 3% yield) as a white solid. The above second chromatographic fraction (102 mg) was distilled at 50–60 °C/1 Torr to give pure (±)-**22** (40 mg, 7% yield) as a colorless oil.

(±)-22: ^{1}H NMR: δ=1.26–1.46 (complex absorption, 8H; tricyclic methylenic protons), 1.58–1.65 (m, 1H; 3-H_{trans} tetrahydrofuryl), 1.85–1.96 (complex absorption, 3H; 3-H_{cis}, 4-H_{cis}, 4-H_{trans} tetrahydrofuryl) 2.18 (quint, J=2.5 Hz, 1H; 5-H), 2.30 (complex absorption, 2H; 3-H, 7-H), 3.73–3.77 (m, 1H) and 3.85–3.90 (m, 1H) (5-H_{cis}, 5-H_{trans} tetrahydrofuryl), 4.09 ppm (dd, J=8.5 Hz, J'=6.5 Hz, 1H; 2-H tetrahydrofuryl); ^{13}C NMR: δ=26.3 (CH_2, C4 tetrahydrofuryl), 28.8 (CH_2, C3 tetrahydrofuryl), 36.7 (CH) and 36.8 (CH) (C3 and C7), 39.2 (CH, C5), 47.18 (CH_2) and 47.24 (CH_2) (C4 and C6), 48.5 (CH_2) and 48.7 (CH_2) (C2 and C8), 53.0 (C, C1), 68.2 (CH_2, C5 tetrahydrofuryl), 80.9 ppm (CH, C2 tetrahydrofuryl); IR (NaCl): $\tilde{\nu}$=2963, 2888, 1480, 1315, 1283, 1066, 1041 cm^{-1}; GC–MS (EI): m/z (%): 178 ($M^{\cdot+}$, 6), 149 (24), 137 (21), 135 (35), 119 (21), 110 (24), 97 (71), 93 (20), 80 (21), 79 (45), 77 (23), 71 (100), 67 (44), 55 (45); accurate mass measurement (ES+) calcd for $[C_{12}H_{18}O+H]^+$: 179.1430; found: 179.1437.

Stereoisomeric mixture of *meso*- and (±)-23 (ratio close to 1:1 by ^{13}C NMR spectroscopy): M.p. 202–204 °C (sublimed); ^{1}H NMR (the indicated number of H atoms corresponds to both stereoisomers, while the shown H atoms belong to only half of each compound): δ=1.24–1.28 (complex absorption, 8H; 2′-H_α, 8′-H_α), 1.30–1.34 (complex absorption, 16H; 2-H_α, 2-H_β, 4-H_α, 8-H_β), 1.34–1.39 (complex absorption, 16H; 2′-H_β, 4′-H_β, 6′-H_β, and 8′-H_β), 1.41–1.45 (complex absorption, 8H; 4′-H_α and 6′-H_α), 1.45–1.50 (complex absorption, 16H; 4-H_β, 6-H_α, 6-H_β, 8-H_α), 2.12 (quint, J=2.5 Hz, 4H; 5′-H), 2.12–2.16 (complex absorption, 8H; 5-H, 7-H), 2.26–2.30 ppm (complex absorption, 8H; 3′-H, 7′-H); ^{13}C NMR (100.6 MHz; the indicated number of C atoms corresponds to both stereoisomers, while the shown C atoms belong to only half of each compound): δ=36.8 (8CH, C3′, C7′), 40.1 (4CH, C5′), 41.10 (2CH), 41.11 (2CH) and 41.3 (4CH) (C5, C7), 47.3 (8CH_2, C4′, C6′), 47.6 (4CH_2, C6), 49.2 (4CH_2) and 49.3 (4CH_2) (C2′, C8′), 49.37 (2CH_2), 49.45 (2CH_2) and 49.6 (4CH_2) (C4, C8), 51.5 (2CH_2) and 51.6 (2CH_2) (C2), 51.9 (4C), 52.40 (2C), 52.41 (2C) and 52.8 ppm (4C) (C1, C1′, C3); IR (KBr): $\tilde{\nu}$=2956, 2933, 2883, 1477, 1292 cm^{-1}; GC–MS (EI): m/z (%): 385 ($[M-C_3H_5]^+$, 3), 383 (3), 319 ($[M-C_8H_{11}]^+$, 3), 213 ($[M-C_{16}H_{21}]^+$, 22), 171 (32), 157 (23), 145 (22), 143 (35), 131 (53), 129 (52), 119 (27), 117 (36), 107 (31), 105 (52), 93 (41), 91 (90), 81 (41), 79 (99), 77 (25), 67 (100); MS (CI, CH_4): m/z (%): 427 ($[M+H]^+$, 2), 426 ($M^{\cdot+}$, 2), 425 ($[M+H-H_2]^+$, 4), 319 ($[M-C_8H_{11}]^+$, 2), 213 ($[M-C_{16}H_{21}]^+$, 12), 187 (12), 185 (14), 173 (12), 171 (13), 149 (17), 135 (17), 131 (21), 129 (20), 107 (34), 105 (33), 93 (35), 91 (50), 81 (59), 79 (94), 67 (100); accurate mass measurement calcd for $[C_{32}H_{42}]^{\cdot+}$: 426.3282; found: 426.3287.

21: GC–MS (EI): m/z (%): 149 ($[M-CH_3]^+$, 26), 123 (19), 122 (31), 121 (17), 108 (19), 107 ($[M-C_4H_9]^+$, 100), 93 (35), 91 (25), 81 (26), 80 (35), 79 (53), 67 (24), 57 (60).

Tricyclo[3.3.0.0^{3,7}]octane (14):[13] Lithium (60 mg, 8.4 mmol) was added in small pieces to a solution of (±)-**8** (100 mg, 0.28 mmol) in a mixture of *t*BuOH (0.8 mL, 8.4 mmol) and anhydrous THF (6 mL), heated under reflux and magnetically stirred, and heating under reflux was continued for 6 h with vigorous stirring. The mixture was allowed to cool to room temperature and was poured onto ice water (10 g). The organic phase was separated and analyzed by GC–MS, and was shown to contain mainly compounds **14**, **18**, and (±)-**22** (relative areas by GC–MS: 82.4, 6.7, and 5.9%, respectively). MS of compound **14**: *m*/*z* (%): 109 ([*M*+H]$^+$, 46), 108 ($M^{\cdot+}$, 5), 107 ([*M*+H−H$_2$]$^+$, 42), 79 (64), 67 (100).

Stereoisomeric mixture of (±)(*Z*,*anti*)-, (*E*,*anti*)-, (±)(*E*,*syn*)- and (*Z*,*syn*)-bi(5-methylenebicyclo[2.2.1]hept-2-ylidene) [(±)(*Z*,*anti*)-, (*E*,*anti*)-, (±)(*E*,*syn*)- and (*Z*,*syn*)-17]: HCl (1 N, 1.8 mL) was added to a cold (0 °C) solution of acetal (±)-**24** (298 mg, 1.79 mmol), prepared as described,[14] in THF (31 mL), and the mixture was allowed to warm to room temperature and was stirred at this temperature for 45 h. Saturated aqueous $NaHCO_3$ solution (15 mL) was added to give pH 8. The organic phase was separated and the aqueous phase was extracted with diethyl ether (3×50 mL). The combined organic phases were dried (anhydrous Na_2SO_4) and the solvent was distilled at atmospheric pressure through a Vigreux column (10 cm) to give a yellowish liquid residue (279 mg) containing mainly the expected ketone.

Pyridine (0.9 mL) and powdered Zn (1.65 g, 25.2 mmol) were added to a magnetically stirred mixture of $TiCl_4$ (1.4 mL, 12.8 mmol) in anhydrous 1,4-dioxane (12 mL), kept under argon, and the mixture was heated under reflux for 1 h. Then, a solution of the above ketone (279 mg) in anhydrous 1,4-dioxane (8 mL) was added dropwise and the mixture was heated under reflux for 15 h more. The mixture was allowed to cool to room temperature and was treated with a 10% aqueous solution of K_2CO_3 (40 mL) until a basic pH was achieved. The deep blue mixture was diluted with CH_2Cl_2 (30 mL), filtered through a pad of Celite, and the solid was washed with CH_2Cl_2 (3×10 mL). The organic phase of the combined filtrate and washings was separated, washed with 1 N HCl (3×10 mL) and brine (2×10 mL), dried (anhydrous Na_2SO_4), and concentrated under reduced pressure to give a yellowish oil (107 mg). This product was submitted to column chromatography (15 g, 2 cm internal diameter of the column, hexane) to give a stereoisomeric mixture **17** in the approximate ratio 1:1.2:1.3:1.2 by ^{1}H NMR spectroscopy and GC–MS (27 mg, 14% yield from (±)-**24**) as a colorless oil. Achiral GC–MS analysis of this mixture showed the presence of four components (r.t. (min), relative a.r.): 14.87, 29.45%; 15.03, 22.2%; 15.13, 25.4%; 15.29, 22.95%. The four mass spectra were essentially coincidental among them and comparable with those previously described for (±)(*Z*,*anti*)- and (*E*,*anti*)-**17**. Chiral GC–MS analysis of the mixture showed the presence of six components (r.t. (min), relative a.r.): 18.02, 12.2%; 18.14, 14.8%; 18.24, 10.4%; 18.32, 7.6%; 18.40, 26.7%; 18.54, 28.36%. These results show that two components of the mixture are racemic. Achiral GC–MS analysis of the above stereoisomeric mixture **17**, mixed with product **17** from the reduction of (±)-**8** with molten sodium, showed the main and minor components of the last product to coincide with the third and second components (r.t. 15.13 and 15.03 min) of the present mixture, respectively. Chiral GC–MS analysis of product **17** from the reduction of (±)-**8** with molten sodium, alone and mixed with the stereoisomeric mixture **17** obtained in the present reaction, showed the presence of three components, which coincide with those of r.t. values 18.24, 18.32, and 18.40 min, the main component being the last one. ^{1}H NMR (300 MHz): δ = 1.40–2.40 (complex absorption, 48H; methylenic protons of four stereoisomers), 2.81 (br s, 8H; 4-H of four stereoisomers), 2.70 (br d, J = 2.5 Hz), 2.74 (br d, J = 2.5 Hz), 2.93 (br d, J = 2.5 Hz) and 2.97 (br d, J = 2.5 Hz) (1-H of four stereoisomers), 4.63 (m, 8H, =CH$_{trans}$ of four stereoisomers), 4.89 ppm (m, 8H, =CH$_{cis}$ of four stereoisomers); ^{13}C NMR of (*E*,*syn*)- plus (*Z*,*syn*)-**17**, deduced from the spectrum of the mixture of the four stereoisomers by subtracting the signals of the mixture of (*E*,*anti*)- and (±)(*Z*,*anti*)-**17** (the given C atoms correspond to both stereoisomers, one half of each compound): δ = 36.9 (CH_2), 37.1 (CH_2), 37.5 (CH_2), 38.2 (CH_2), 39.9 (CH_2), 40.6 (CH_2), 41.8 (CH), 42.6 (CH), 45.9 (CH), 46.1 (CH), 102.7 (CH_2), 102.8 (CH_2), 131.3 (C), 131,6 (C), 154.90 (C), 154.91 ppm (C).

Reaction of (±)-8 with the radical anion from 4,4′-di-*tert*-butylbiphenyl and lithium in anhydrous THF: Small pieces of lithium (6 mg, 0.83 mmol) were added to a solution of 4,4′-di-*tert*-butylbiphenyl (**25**, 370 mg, 1.39 mmol) in anhydrous THF (4 mL) placed in a Schlenk tube at room temperature under an argon atmosphere, and the mixture was ultrasound irradiated in a cold (0 °C) bath until consumption of the metal (1 h) with formation of a dark green solution. Then, a cold (0 °C) solution of (±)-**8** (51 mg, 0.14 mmol) in anhydrous THF (1.5 mL) was added dropwise. The solution became red and the color remained for 1 h. Then, the solution was cooled to −78 °C, excess CO_2 (g) was bubbled, and the mixture was allowed to warm to room temperature. A saturated aqueous solution of $NaHCO_3$ (5 mL) was added and the mixture was extracted with diethyl ether (2×10 mL). The combined organic phases were analyzed by GC–MS, which showed the presence of **25** as the main component (87.6% a.r.) and traces of other components, such as the following ones (% a.r.), in order of elution: **26** (0.1), (±)-**22** (0.6), **18** (1.4). The alkaline aqueous phase was acidified to pH 1–2 with 5 N HCl (1.2 mL) at 0 °C and was extracted with AcOEt (5×15 mL). The combined organic phases were dried (anhydrous Na_2SO_4) and concentrated under reduced pressure to give a residue (5 mg) constituted mainly of **25**.

1-Iodotricyclo[3.3.0.0^{3,7}]octane (26): Solid NaOH (67 mg) and 10% Pd on charcoal (44 mg) were added to a solution of (±)-**8** (199 mg, 0.55 mmol) in methanol (6 mL), and the mixture was placed in a hydrogen atmosphere (1 atm) and magnetically stirred at room temperature for 3 h. GC control showed total consumption of the starting compound and the presence of **26** and **14** with an area ratio of 93:7. The mixture was filtered through a pad of Celite and the solid was washed with methanol (2 mL). Water (5 mL) was added to the combined filtrate and washings and the mixture was extracted with CH_2Cl_2 (5×5 mL). The combined organic phases were dried (anhydrous Na_2SO_4) and concentrated under atmospheric pressure using a Vigreux column (10 cm) to give **26** (107 mg, 83% yield) as a colorless oil. The analytical sample was obtained by distillation at 60–70 °C/30 Torr; ^{1}H NMR: δ = 1.32 (dt, J = 9.0 Hz, J' = 2.5 Hz, 2H; 4(6)-H$_\beta$), 1.63 (m, 2H; 4(6)-H$_\alpha$), 1.81 (m, 2H; 2(8)H$_\alpha$), 1.92 (m, 2H; 2(8)H$_\beta$), 2.10 (m, 2H; 3(7)-H), 2.62 ppm (quint, J = 2.5 Hz, 1H; 5-H); ^{13}C NMR: δ = 30.4 (C, C1), 36.5 (CH, C3(7)), 47.0 (CH_2, C4(6)), 49.7 (CH, C5), 59.2 ppm (CH_2, C2(8)); IR (NaCl): $\tilde{\nu}$ = 2972, 2940, 2892, 1479, 1288, 946 cm^{-1}; MS (EI): *m*/*z* (%): 234 ($M^{\cdot+}$, 15), 107 ([*M*−I]$^+$, 29), 91 (28), 79 (100), 77 (24), 67 (62); MS (CI, CH_4): *m*/*z* (%): 235 ([*M*+H]$^+$, 5), 234 ($M^{\cdot+}$, 3), 108 (12), 107 ([*M*−I]$^+$, 100), 79 (93); accurate mass measurement calcd for [$C_8H_{11}I$]$^{\cdot+}$: 233.99055; found: 233.99050.

Reaction of (±)-8 with *t*BuLi in anhydrous diethyl ether: A solution of *t*BuLi (1.4 mL, 0.7 M in pentane, 1 mmol) was added dropwise to a cold (−78 °C) and magnetically stirred solution of diiodide (±)-**8** (73 mg, 0.2 mmol) in anhydrous diethyl ether (1 mL) under an argon atmosphere, and the mixture was stirred at this temperature for 30 min and then allowed to warm to room temperature. Methanol (1 mL) and water (2 mL) were successively added and the mixture was extracted with diethyl ether (3×5 mL). The combined organic phases were dried (anhydrous Na_2SO_4) and concentrated under atmospheric pressure using a Vigreux column (10 cm) to give a white residue (70 mg). GC–MS analysis of this residue showed the presence of the following significant components, in order of elution (% a.r.): **14** (5.7), **21** (31.2), (±)-**27** (3.1), and **18** (50.8). GC–MS (EI) (±)-**27**: *m*/*z* (%): 180 ($M^{\cdot+}$, 5), 165 ([*M*−CH$_3$]$^+$, 18), 137 (23), 134 ([*M*−C$_2$H$_5$OH]$^{\cdot+}$, 17), 119 (30), 105 (22), 99 (63), 95 (31), 93 (84), 92 (32), 91 (57), 80 (36), 79 (66), 77 (42), 73 (100), 71 (63), 67 (58).

Reaction of (±)-8 with *t*BuLi in anhydrous diethyl ether followed by quenching with trimethylsilyl chloride: A solution of diiodide (±)-**8** (261 mg, 0.72 mmol) in anhydrous diethyl ether (5 mL) was added dropwise to a cold (−78 °C) and magnetically stirred solution of *t*BuLi (8.3 mL, 0.7 M in pentane, 5.8 mmol) under an argon atmosphere, and the mixture was stirred at this temperature for 30 min. Then freshly distilled trimethylsilyl chloride (1.9 mL, 14.6 mmol) was added at this temperature and the mixture was allowed to warm to room temperature. Methanol (2 mL) and water (3 mL) were successively added and the mixture was extracted with diethyl ether (3×5 mL). The combined organic phases were dried (anhydrous Na_2SO_4) and analyzed by GC–MS, which indicat-

ed a complex mixture of products from which no single component could be isolated or characterized.

Reaction of (±)-8 with *t*BuLi in anhydrous diethyl ether followed by quenching with CO_2: A solution of diiodide (±)-**8** (100 mg, 0.28 mmol) in anhydrous diethyl ether (2 mL) was added dropwise to a cold (−78 °C) and magnetically stirred solution of *t*BuLi (4 mL, 0.7 M in pentane, 2.8 mmol) under an argon atmosphere, and the mixture was stirred at this temperature for 30 min. Then, excess CO_2 (g) was bubbled at this temperature and the mixture was allowed to warm to room temperature. Methanol (2 mL) and water (5 mL) were successively added and the mixture was extracted with diethyl ether (10 mL). The combined organic phases were dried (anhydrous Na_2SO_4) and concentrated under atmospheric pressure using a Vigreux column (10 cm) to give a yellow oil (25 mg). GC–MS analysis of the organic extracts showed the presence of many components, the two main ones being in order of elution (% a.r.): di-*tert*-butyl ketone, **28** (74.5), and a compound which, on the basis of its mass spectrum, seems to be ketone (±)-**29** (7.2). GC–MS (EI) (±)-**29**: *m*/*z* (%): 248 ($M^{\cdot+}$, 3), 233 ($[M-CH_3]^+$, 3), 207 (15), 191 ($[M-C_4H_9]^+$, 34), 163 ($[M-C_4H_9-CO]^{\cdot+}$, 82), 149 (23), 135 (20), 123 (23), 121 (36), 107 (73), 93 (29), 69 (20), 57 ($C_4H_9^+$, 100). The alkaline aqueous phase was acidified to pH 1–2 with 5 N HCl (3 mL) at 0 °C and was extracted with AcOEt (5×15 mL). The combined organic phases were dried (anhydrous Na_2SO_4) and concentrated under reduced pressure to give a yellow residue (20 mg), which was reacted with an excess of a solution of diazomethane in diethyl ether until the yellow color remained. The excess diazomethane was destroyed by addition of AcOH, the volatile components of the mixture were distilled off in vacuo, and the residue was analyzed by GC–MS, which indicated a complex mixture whose main component seems to be ester (±)-**31** (43 % a.r.) on the basis of its mass spectrum. GC–MS (EI) (±)-**31**: *m*/*z* (%): 207 ($[M-CH_3]^+$, 2), 180 (14), 165 ($[M-C_4H_9]^+$, 33), 163 ($[M-CO_2CH_3]^+$, 53), 123 (37), 122 (42), 121 (37), 107 (100), 57 ($C_4H_9^+$, 81).

Acknowledgements

Financial support from the Ministerio de Ciencia y Tecnología and FEDER (Project CTQ2005-02192) and Comissionat per a Universitats i Recerca (Project 2005-SGR-00180) is gratefully acknowledged. C.A. thanks the Generalitat de Catalunya (Beca predoctoral). We thank the Serveis Cientifico-Tècnics of the University of Barcelona for performing the NMR spectroscopy, the Centre de Supercomputació de Catalunya (CESCA) for computational facilities, and Ms. P. Domènech from the IIQAB (Barcelona, Spain) for carrying out the elemental analyses.

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Received: June 19, 2006
Published online: November 8, 2006

