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9,9-Dimethyl-8,10-dioxapentacyclo[5.3.0.0^{2,5}.0^{3,5}.0^{3,6}]decane and naphthotetracyclo[5.1.0.0^{1,6}.0^{2,7}]oct-3-ene: new substituted [1.1.1]propellanes as precursors to 1,2,3,4-tetrafunctionalized bicyclo[1.1.1]pentanes

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Abstract—Two new substituted [1.1.1]propellanes have been generated from the corresponding bicyclo[1.1.0]butanes in either single-step (**1a**) or four-step procedures (**1b**). The observed degree of double lithiation of the bicyclo[1.1.0]butanes is discussed in the context of DFT computational results. Addition reactions across the central C(1)–C(3) bonds of the propellanes were studied. Only the propellane **1b** gave the biacetyl addition product.

1. Introduction

Polyfunctionalized bicyclo[1.1.1]pentanes (BCPs)[1] bearing functional substituents in addition to the two bridgehead ones are rare and sought-after as potential structural elements for molecular electronics and architecture.[2–4] Among a handful of such derivatives are 2,2-dichloro-[5] and polyfluoro derivatives,[6,7] which were obtained by direct halogenation of bicyclo[1.1.1]pentane-1,3-dicarboxylic acid or its esters.[8] Further transformations of the halogens to other groups have not been successful. In contrast, transformations of the carboxyl groups proceeded smoothly,[7,9] which enable the generation of 2,2-dichloro[1.1.1]propellane.[9] Recently, chlorination of the 2,4-dimethylene derivative of bicyclo[1.1.1]pentane-1,3-dicarboxylic acid and subsequent transformations of the halogenated products led to bicyclo[1.1.1]pentane-1,2,3,4-tetracarboxylic acid, the first example of tetrafunctionalized BCP **A**.[10]

A more versatile and general approach to polyfunctionalized BCPs **A** may, in principle, involve appropriately substituted [1.1.1]propellanes **B** (Fig. 1). Subsequent addition of biacetyl across the central bond of the propellane[11] introduces a carbonyl group amenable to further functional group manipulation.[12–14]

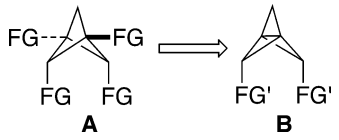
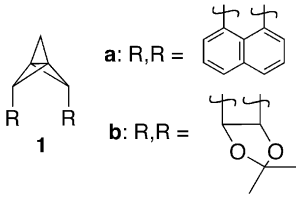


Figure 1. Retrosynthetic analysis for preparation of 1,2,3,4-tetrafunctionalized bicyclo[1.1.1]pentanes **A** through propellanes **B**.

Most [1.1.1]propellanes prepared to date are mono or geminally disubstituted derivatives of the parent [1.1.1]propellane or its 2,4-dimethylene or 2,4-trimethylene derivatives.[1,15] Only a handful of [1.1.1]propellanes are substituted with aryl,[16–18] vinyl[18] or alkoxymethyl[19,20] groups which are inert to propellane generation conditions and can be converted to the versatile carboxyl group. To our knowledge there is only one propellane with a benzyl group bridging the 2 and 4 positions,[16] which is a potential precursor to 1,2,3,4-tetrafuctionalized BCPs **A**. Unfortunately, the chemistry of this propellane has not been investigated.



Keywords: Substituted bicyclo[1.1.0]butanes and [1.1.1]propellanes; Theoretical models; Radical reactions.
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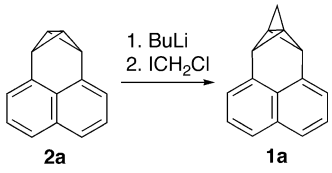
In order to develop synthetic access to tetrafunctionalized BCPs **A**, we focused on two new propellanes **1a** and **1b**. Here, we report the generation of the two substituted propellanes and some reactions at the central C–C bond with the emphases on the addition of biacetyl.

2. Results and discussion

2.1. Preparation of propellanes

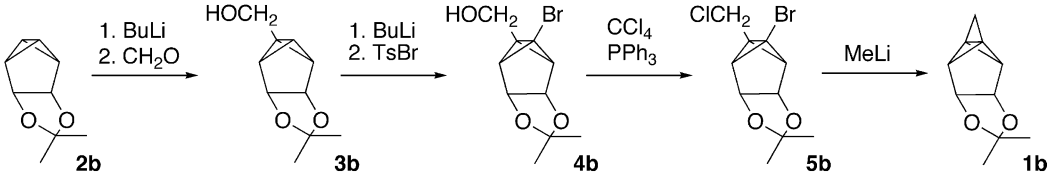
Propellanes **1a** and **1b** were prepared from appropriate bicyclo[1.1.0]butanes **2a** and **2b** using the methodology developed by Szeimies.[16] The former propellane was prepared in a single annelation step with $ClCH_2I$ taking advantage of the almost quantitative double deprotonation of **2a** (Scheme 1). The propellane **1a** was prepared in yields estimated at 30–40% and used as crude solutions in subsequent reactions.



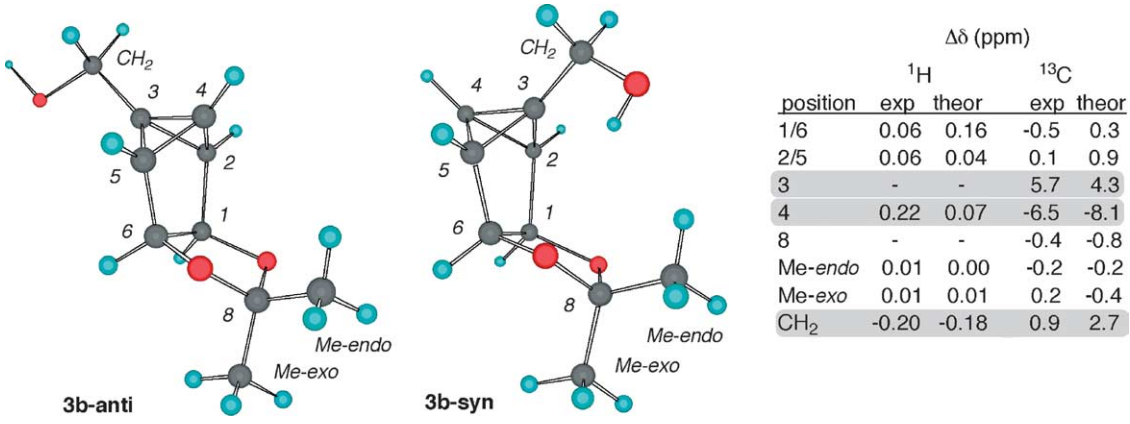
Scheme 1.

In contrast, propellane **1b** could not be prepared in the single-step procedure since the double deprotonation of **2b** was inefficient. Using *n*-BuLi, *sec*-BuLi or *tert*-BuLi at different temperatures, the double deprotonation occurred to less than 20%, as determined by quenching with D_2O and GCMS analysis.[21] Also prolonged reaction times led to decomposition of the precursor **2b**. This necessitated the use of the four-step route[16] shown in Scheme 2. Thus, hydroxymethylation of **2b** gave alcohol **3b** as a mixture of two isomers in about 2:1 ratio contaminated with a more polar compound presumably the corresponding bis(hydroxymethyl) derivative. After purification on alumina, the isomeric mixture of alcohols **3b** was brominated and the resulting **4b** was subsequently converted to the dihalide **5b** using the general literature conditions.[16] To improve the separation of the pure **5b**, small amounts of EtOH were added in the end of the reaction to convert the residual Ph_3P to the oxide. The overall average yield for the three steps was about 25%.

To assign stereochemistry of the two isomers formed during hydroxymethylation of **2b**, the minor isomer of **3b** was isolated chromatographically and the solid alcohol was purified by sublimation. NOESY experiments were inconclusive and the stereochemistry of the isomers was assigned based on a comparison of computational and experimental NMR data (Fig. 2). The analysis shows that the differences in theoretical chemical shifts $\Delta\delta$ (theor) for the *anti* and *syn* isomers follows the trend in the differences in experimental chemical shifts $\Delta\delta$ (exp) between the minor and major isomers. Perhaps the most diagnostic are the bridgehead positions of the bicyclo[1.1.0]butane ring and the hydroxymethyl group, which are most affected by the structural variation in the two isomers. Thus, the bridgehead carbon atom C(3) is significantly shielded, while C(4) is deshielded in the major and *syn* isomers relative to the minor and *anti*. Also, the CH_2 protons are significantly deshielded and the ^{13}C nucleus is shielded in the major and *syn* isomers relative to the minor and *anti*. This is consistent with general trends in exo/endo stereoisomers of bicycloalkanes.



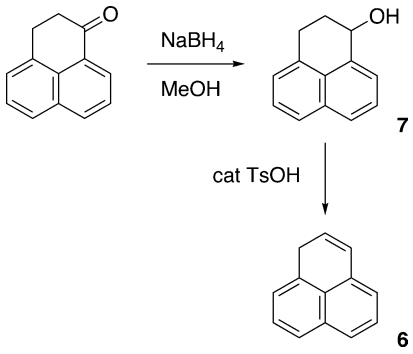
Scheme 2.



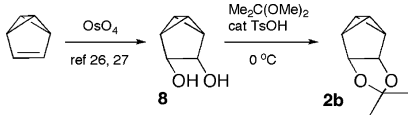
Δδ (ppm)

	^1H		^{13}C	
position	exp	theor	exp	theor
1/6	0.06	0.16	-0.5	0.3
2/5	0.06	0.04	0.1	0.9
3	-	-	5.7	4.3
4	0.22	0.07	-6.5	-8.1
8	-	-	-0.4	-0.8
Me-*endo*	0.01	0.00	-0.2	-0.2
Me-*exo*	0.01	0.01	0.2	-0.4
CH_2	-0.20	-0.18	0.9	2.7

Figure 2. Optimized gas phase geometries for **3b**-anti and **3b**-syn isomers and comparison of the difference in experimental and computed NMR chemical shifts: $\Delta\delta$ (exp)=δ (**3b**-minor)−δ (**3b**-major); $\Delta\delta$ (theor)=δ (**3b**-anti)−δ (**3b**-syn). Theoretical results obtained at the B3LYP/6-31G(d,p) level of theory.



Scheme 3.



Scheme 4.

Thus, the comparison indicates that the major isomer of **3b** has *syn* stereochemistry. This conclusion, however, is in contrast with previous reports on regioselectivity of methylation of a related carbocyclic system, where configuration of the major product was established to be *anti* based on independent synthesis.[22] Perhaps the dominance of the *syn* isomer in the present case results from the complexing ability of the 1,3-dioxolane ring oxygen atoms and preferential deprotonation of the pro-*syn* position.

Propellane **1b** was generated by treatment of a mixture of stereoisomers **5b** with MeLi and used as crude Et_2O/pentane solutions without further purification. ^{1}H NMR of **1b** shows that the propellane CH_2 group is deshielded by about 0.6 ppm relative to that in the parent [1.1.1]propellane.[16] For comparison, the CH_2 group in **1a** is shielded by about 0.25 ppm.

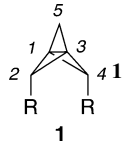
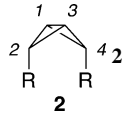
The bicyclo[1.1.0]butane **2a** was prepared from *1H*-phenalene (**6**), obtained by dehydration of 2,3-dihydro-*1H*-phenalen-1-ol[23] (**7**), following closely the literature procedure.[24] The alcohol **7** was conveniently prepared from 2,3-dihydro-*1H*-phenalen-1-one by substituting $NaBH_4$ for $LiAlH_4$ used in the original procedure[25] (Scheme 3).

Bicyclo[1.1.0]butane **2b** was prepared from benzvalene in two steps and 35% average overall yield (Scheme 4). Thus, **2b** was obtained by the reaction of glycol[26,27] **8** with 2,2-dimethoxypropane in the presence of TsOH for 30 min at 0 °C. Benzoic acid in benzene used in a similar procedure[26] was found to be ineffective in the present case. The preparation of benzvalene followed a literature procedure[28] except that a larger than recommended amount of MeLi was used in the third part of the reaction. When the second portion of MeLi was stoichiometric relative to CH_2Cl_2, the yields of benzvalene established by NMR[29] were 36–57% and similar to those reported in the literature.[28]

2.2. Molecular geometry and strain of 1 and 2

Structural effects on molecular geometry and strain energy of the parent [1.1.1]propellane (**1c**) and bicyclo[1.1.0]butane (**2c**) rings in **1** and **2** were assessed at the B3LYP/6-31G(d,p) level of theory and results are collected in Table 1. Analysis shows that the central C(1)–C(3) bond has virtually the same length in all three propellanes **1**, while in bicyclo[1.1.0]butanes **2a** and **2b** is shorter by about 0.02 Å than in the parent **2c**. The latter is consistent with experimental results for **2a**[30] and **2c**.[31] A comparison of the angles α indicates a modest contraction of

Table 1. Selected structural parameters and strain energies of propellanes **1** and bicyclo[1.1.0]butanes **2**

	d_{C1-C3} (Å)	α[a] (deg)	β[b] (deg)	SE[c] (kcal/mol)
 **1**				
a	1.576	118.6	124.3	94
b	1.576	112.4	112.2	92.5
c, R=H	1.578	120.0	122.6	98
	1.596(5)[d]			98[e]
 **2**				
a	1.471	118.0	124.6	62
	1.47(3)[f]	120(2)[f]	124(2)[f]	
b	1.472	110.9	113.0	60
c, R=H	1.491	121.9	124.7	66
	1.497(3)[g]	122.7(5)[g]	121.6(9)[g]	64[e]

[a] Angle between the two cyclopropane rings defined as C(2)-*-C(4), where * is the C(1)–C(3) midpoint.
[b] Angle defined as R-C(2)-*, where * is the C(1)–C(3) midpoint.
[c] Homodesmotic strain energies (SE) calculated according to Figure 3.
[d] Electron diffraction data; Hedberg, L.; Hedberg, K. *J. Am. Chem. Soc.* **1985**, *107*, 7257–7260.
[e] Ref 31.
[f] Solid state data; Ref. 30.
[g] Infrared data; Ref. 31.

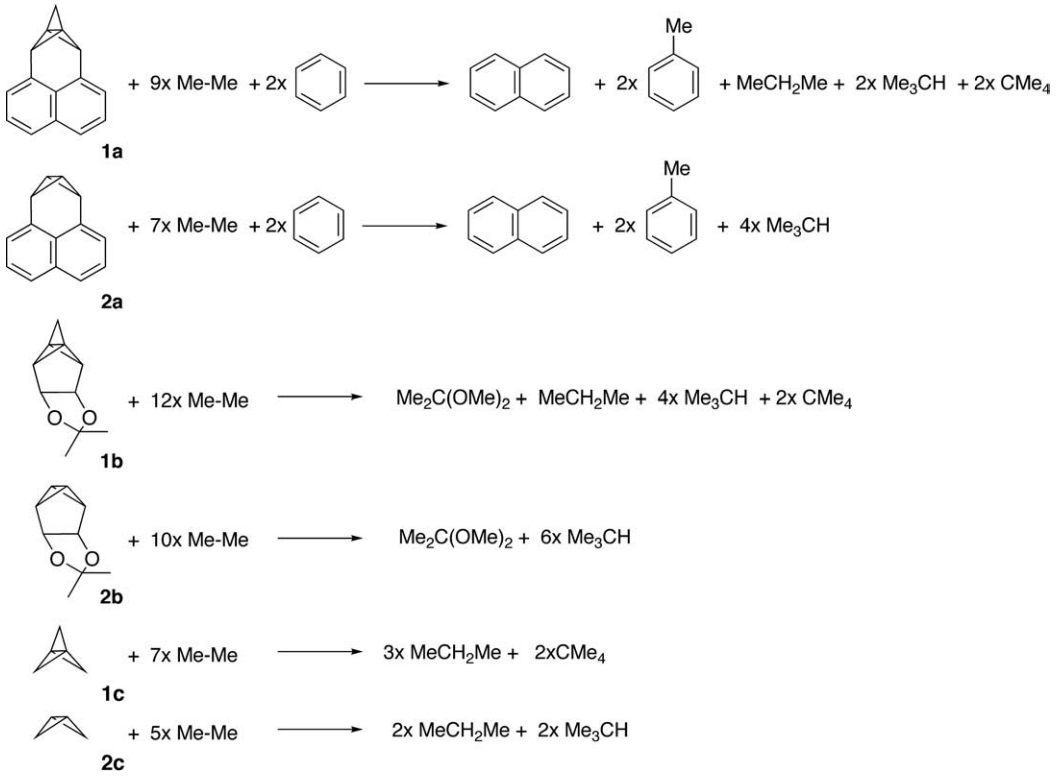


Figure 3. Homodesmotic reactions. Strain energies are listed in Table 1.

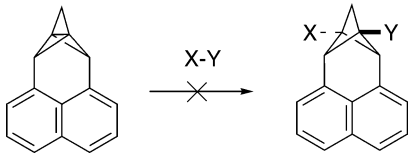
the angle between the cyclopropyl faces in the naphthalene derivatives **1a** and **2a** relative to the parent systems **1c** and **2c**. In contrast, the angle α in the dioxolane derivatives is smaller by about 7° for **1b** and 11° for **2b**, relative to the parent hydrocarbons. Similar results are obtained for the exocyclic bond angle β, which indicates a generally larger distortion of the propellane and bicyclobutane rings in the dioxolane (**b**) than in the naphthalene (**a**) derivatives.

In spite of significant deformation of the parent rings in the ketal derivatives **1b** and **2b**, the strain energies (SE) calculated using homodesmotic reactions[32] shown in Figure 3 are similar (within 6 kcal/mol) to those calculated in this work and previously reported[33] for the parent hydrocarbons.

The theoretical models for **1** and **2** provide an opportunity to analyze factors that may affect the efficiency of the double deprotonation of **2a** and **2b**. Previous studies concluded that a high degree of lithiation occurs for bicyclo[1.1.0]butanes carrying an sp^2 substituent, such as a phenyl ring, or those having a small angle between the cyclopropane faces.[21] Thus, the ease of double deprotonation of **2a** is in agreement with these empirical observations. In contrast, the low efficiency of complete deprotonation of **2b** is inconsistent with the previous conclusions and the 95% of double deprotonation observed[21] for 2,4-dimethylenebicyclo-[1.1.0]butane (tricyclo[3.1.0.0^{2,6}]hexane), a close analog of **2b**; both compounds have very similar small angle α of about 111°. Also, the computational analysis of the electronic structure of the bicyclobutanes is inconsistent with the deprotonation results. The NBO population analysis shows that the hybridization of the C(1/3) exocyclic hybrid is $sp^{1.81}$ in **2b** which has more s-character than the analogous orbital found in **2a** ($sp^{1.90}$). This would suggest enhanced C–H acidity of the bridgehead positions in the former and a more facile double deprotonation than in **2a**. For comparison, in the parent BCB the exocyclic orbital is $sp^{1.93}$ hybridized. Thus, the origin of the problem with the double deprotonation of **2b** is not clear.

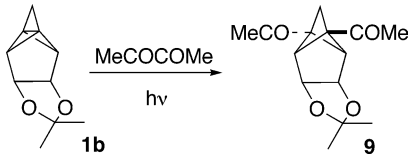
2.3. Reaction of propellanes 1

Initially, we investigated addition reactions to **1a**. Unfortunately, no radical or photochemical addition to this propellane gave a characterizable product (Scheme 5). Thus, the photochemically-induced addition of biacetyl[11] to **1a** in cyclohexane gave only highly colored decomposition products, even when a uranium glass filter was used to limit excitation of the naphthalene ring.[34] The colored products presumably resulted from the light-induced rearrangement of **1a** and subsequent polymerization of the olefins.[35] Addition of I_2 to **1a** in ether[36] resulted only in a black tar. Similarly, radical addition of PhSH or PhSSPh[36] to **1a** in ether at ambient temperature led to a brown complex mixture of unidentified products. Finally, attempts to introduce a carboxyl group at the bridgehead positions in **1a** first by lithiation either with *t*-BuLi[37] or lithium 4,4′-di-*t*-butylbiphenyl[13] followed by carboxylation with CO_2 was unsuccessful, and only a complex mixture of products was obtained.



Scheme 5.

In contrast, propellane **1b** underwent a smooth addition of biacetyl to form the diketone **9** in good yield (Scheme 6). The pure diketone **9** was separated from other by-products using column chromatography. The formation of polar by-products is promoted by large amounts of ether used as solvent, presumably due to light-induced radical reactions between biacetyl, ether and propellane.



Scheme 6.

3. Summary and conclusions

The preparation of both propellanes **1a** and **1b** was accomplished in about 5% overall yield starting from commercial 1-chloromethylnaphthalene (for **1a**) and cyclopentadiene (for **1b**) and using demanding seven-step procedures. Of the two propellanes, only **1b** proved useful for the formation of tetrasubstituted bicyclo[1.1.1]pentanes, and the diketone **9** was obtained in high yield from **1b**. In contrast, neither the photochemically- or thermally-induced radical additions to the central C(1)–C(3) bond in **1a**, nor a reaction with organometallic reagents led to isolable bicyclo[1.1.1]pentane derivatives.

The stereochemistry of the main isomer formed in hydroxymethylation of bicyclobutane **2b** was assigned as *syn* based on the comparison of experimental and theoretical chemical shifts for the *syn* and *anti* isomers. Simple analyses of molecular geometry and the hybridization of the C(1/3) exocyclic bond orbital in bicyclo[1.1.0]butanes **2a** and **2b** could not explain the observed marked difference in their ability to form dianions.

Thus, propellane **1b** is a promising precursor to 1,2,3,4-tetrafunctionalized bicyclo[1.1.1]pentanes. The functional group transformations of diketone **9** will be reported elsewhere.

4. Computational details

All quantum-mechanical calculations were carried out at the B3LYP/6-31G(d,p) level of theory[38,39] using the Linda–Gaussian 98 package[40] on a Beowulf cluster of 16 processors. Geometry optimizations were undertaken using appropriate symmetry constraints and default convergence limits. The isotropic shielding factors were obtained by using the GIAO algorithm.

5. Experimental

5.1. General

Melting points are uncorrected. ^{1}H and ^{13}C NMR spectra were obtained at 300 and 75 MHz, respectively, in $CDCl_3$, unless specified otherwise. Chemical shifts were referenced to TMS (^{1}H) or solvent (^{13}C). IR spectra were recorded for neat samples on NaCl plates. Mass spectrometry data were acquired using a GCMS instrument. FAB/HRMS spectrometry was performed at Notre Dame University, IN. Elemental Analysis was provided by Atlantic Microlabs, GA. All reactions with organometallic reagents were performed under nitrogen and strictly anhydrous conditions. In these cases the glassware used was heated in vacuo to remove all residual moisture. All workup operations with propellanes **1a** and **1b** were performed in an inert atmosphere.

5.1.1. Naphthotetracyclo[5.1.0.0^{1,6}.0^{2,7}]oct-3-ene (1a). To a solution of the bicyclobutane[24] **2a** (145 mg, 0.814 mmol) in Et_2O (10 mL), *n*-BuLi solution in hexane (0.74 mL, 1.79 mmol, 2.44 M) was added at ambient temp and stirred for 6 h. The reaction mixture was cooled to −30 °C and chloroiodomethane (174 mg, 0.984 mmol) was added dropwise and stirred for 2 h at ambient temp. Then a 2 N aqueous NH_3 (5 mL) was added at 0 °C and stirred for 25 min. The aqueous layer was extracted with benzene (2×8 mL), the combined organic layers were dried (Na_2SO_4), and concentrated at reduced pressure. In case of visible precipitation, the solution can be filtered through a microfilter to remove polymeric materials. The resulting solid **1a** was about 90% pure by NMR: ^{1}H NMR (C_6D_6) major signals δ 1.81 (s, 2H), 3.57 (s, 2H), 6.86 (d, J=6.8 Hz, 2H), 7.06 (dd, J_1=8.4 Hz, J_2=6.8 Hz, 2H), 7.37 (d, J=8.4 Hz, 2H). The crude solid propellane was dissolved in an appropriate solvent and used in subsequent reactions.

5.1.2. 9,9-Dimethyl-8,10-dioxapentacyclo[5.3.0.0^{2,5}.0^{3,5}.0^{3,6}]decane (1b). To a solution of dihalide **5b** (231 mg, 0.83 mmol) in Et_2O/pentane (15 mL, 2:1), MeLi in Et_2O (1.6 M, 0.62 mL, 0.99 mmol) was added at −30 °C and stirred for 2 h at ambient temp. Then a 2 N aqueous NH_3 (10 mL) was added at 0 °C and stirred for 20 min. The aqueous layer was extracted with Et_2O (2×10 mL) and the combined organic layers were dried (Na_2SO_4). The resulting solution of propellane **1b** was used directly for the next transformation to form **9**: ^{1}H NMR (ether/pentane/$CDCl_3$) δ 2.64 (s, 2H), 2.66 (s, 2H), 4.64 (s, 2H), the Me groups are obscured by the solvent peaks; MS, *m*/*z* (%) 163 (1) $[M-H]^+$, 149 (100) $[M-CH_3]^+$.

5.1.3. 8,8-Dimethyl-7,9-dioxatetracyclo[4.3.0.0^{2,4}.0^{3,5}]nonane (2b). To a solution of the diol **8** (16.2 g, 145 mmol) and 2,2-dimethoxypropane (500 mL) in $CHCl_3$ (500 mL), *p*-TsOH·H_2O (350 mg, 1.84 mmol) was added at −5 to 0 °C and the mixture was stirred for 30 min at the temperature below 0 °C. The reaction mixture was diluted with $CHCl_3$ (500 mL), washed with $NaHCO_3$ (2×300 mL) and brine (300 mL), dried (Na_2SO_4) and volatiles were removed under reduced pressure. Kugelrohr distillation (bp 40–44 °C/0.4–0.5 Torr) gave 19.9 g (90% yield) of the acetonide **2b** as a colorless low melting solid. For other four runs in 4–150 mmol scale the yields were 70–89%. Mp 19–21 °C; ^{1}H NMR δ 1.28 (s, 3H), 1.47 (s, 3H), 2.02 (dt, J_1=8.4 Hz, J_2=2.0 Hz, 1H), 2.29 (br s, 2H), 2.33–2.38 (m, 1H), 4.49 (br s, 2H); ^{13}C NMR δ 2.9, 8.6, 25.4, 26.9, 37.6, 82.4, 114.1; MS, *m*/*z* (%) 152 (2) $[M]^+$, 137 (100); HRMS, calcd

for $C_9H_{11}O_2$: 151.0759, found 151.0763. Anal. Calcd for $C_9H_{12}O_2$: C, 71.03; H, 7.95. Found: C, 70.51: H, 7.62.

5.1.4. 8,8-Dimethyl-7,9-dioxatetracyclo[4.3.0.0^{2,4}.0^{3,5}]nonan-3-ylmethanol (3b). To a solution of the bicyclobutane **2b** (6.00 g, 39.4 mmol) in Et_2O (50 mL), *n*-BuLi solution in hexane (18.5 mL, 43.4 mmol, 2.35 M) was added at ambient temperature and stirred for 4 h. Gaseous formaldehyde, prepared by depolymerization of paraformaldehyde (6.00 g) at 170 °C, was introduced into the reaction mixture. After additional stirring for 1 h, water (25 mL) was added at ice bath cooling. The organic layer was washed with water (3× 10 mL) and the combined aqueous phases were extracted with ether (2×10 mL). The organic layer was dried (Na_2SO_4) and concentrated in vacuo. Column chromatography (Al_2O_3, Grade IV; CH_2Cl_2/MeOH 19:1 ratio containing 1% Et_3N, R_f=0.35) gave 4.09 g (57% yield) of alcohol **3b** as a 2:1 mixture of regio-isomers. For other four runs in 2–50 mmol scale the yields were 40–60%. The minor isomer was isolated as a slightly less polar fraction in the chromatographic purification of the mixture.

Minor isomer (**3b**-anti): mp 60.5–62 °C; ^{1}H NMR δ 1.26 (s, 3H), 1.45 (s, 3H), 2.42 (br s, 1H), 2.43 (s, 2H), 4.04 (s, 2H), 4.54 (s, 2H); ^{13}C NMR δ 7.0, 24.7, 25.3, 26.8, 40.7, 59.5, 82.1, 113.9; IR 3400 (br, OH), 1212 (C–O) cm^{-1}; GC/MS, rt 11.6 min, *m/z* (%) 182 (2) $[M]^+$, 167 (23) $[M-CH_3]^+$, 107 (55), 95 (100). Anal. Calcd for $C_{10}H_{14}O_3$: C, 65.91; H 7.74. Found: C, 65.79; H, 7.79.

Major isomer (**3b**-syn) assigned from the mixture: ^{1}H NMR δ 1.25 (s, 3H), 1.44 (s, 3H), 2.19 (br s, 1H), 2.37 (s, 2H), 4.24 (s, 2H), 4.48 (s, 2H); ^{13}C NMR δ 13.5, 18.9, 25.1, 27.0, 40.6, 58.6, 82.6, 114.3; GC/MS, rt 10.9 min, *m/z* (%) 182 (1) $[M]^+$, 167 (100) $[M-CH_3]^+$, 95 (55).

5.1.5. 4-Bromo-8,8-dimethyl-7,9-dioxatetracyclo[4.3.0.0^{2,4}.0^{3,5}]nonan-3-ylmethanol (4b). To a solution of the isomeric mixture of alcohols **3b** (1.79 g, 9.83 mmol) in Et_2O (10 mL), *n*-BuLi solution in hexane (10 mL, 23.0 mmol, 2.3 M) was added and the mixture was stirred for 5 h. Solid *p*-toluenesulfonyl bromide[41] (2.70 g, 11.6 mmol) was added at 0 °C and the mixture was stirred for 1 h at ambient temperature. Then 10% NaOH (5 mL) was added dropwise. The aqueous layer was washed with Et_2O (3×20 mL), the combined organic layers were dried (Na_2SO_4) and concentrated in vacuo to give 2.23 g (87% yield) of 85% pure (GCMS) **4b** as a yellowish oil, which was used without further purification for the next transformation. For other four runs in 1–15 mmol scale the yields were 60–82%. ^{1}H NMR δ (major signals) 1.26 (s, 3H), 1.44 (s, 3H), 2.67 (br s, 2H), 4.36 (br s, 2H), 4.62 (br s, 2H); MS, *m/z* (%) 260/262 (10/8) $[M]^+$, 187/185 (38/42), 67 (100); HRMS, calcd for $C_{10}H_{13}BrO_3$: 260.0048, found 260.0051.

5.1.6. 3-Bromo-4-(chloromethyl)-8,8-dimethyl-7,9-dioxatetracyclo[4.3.0.0^{2,4}.0^{3,5}]nonane (5b). A solution of crude bromo alcohol **4b** (1.69 g, 6.47 mmol) and Ph_3P (3.54 g, 13.5 mmol) in CCl_4 (35 mL) was stirred for 10 h at 80 °C. EtOH (2 mL) was added and stirring was continued for additional 3 h. After cooling, Celite (~5 g) was added and the mixture concentrated in vacuo. The solid residue was washed with petroleum ether containing CH_2Cl_2 (10%), the resulting solution was concentrated and the residue sublimed to give 1.19 g (66% yield) of **5b** as a white solid. For other four runs in 1–14 mmol scale the yields were 58–67%. Mp 55–65 °C; ^{1}H NMR δ major/minor 1.27/1.25 (s, 3H), 1.49/1.45 (s, 3H), 2.72/2.73 (s, 2H), 4.05/4.30 (s, 2H), 4.58/4.62 (s, 2H); ^{13}C NMR δ major/minor 22.7/22.9, 25.5/24.9, 27.0/26.7, 29.6/25.3, 40.0/39.4, 47.2, 82.2/81.7, 115.0/114.5; MS, *m/z* (%) 280/278 (3/2) $[M]^+$, 265/263 (10/8) $[M-CH_3]^+$, 77 (100). Anal. Calcd for $C_{10}H_{12}BrClO_2$: C, 42.96; H 4.33. Found: C, 43.19; H, 4.39.

5.1.7. 2,3-Dihydro-*1H*-phenalen-1-ol.[25] (7) 2,3-Dihydro-*1H*-phenalen-1-one[42] (3.64 g, 20.0 mmol) was added in one portion to a solution of $NaBH_4$ (984 mg, 26.0 mmol) in MeOH (50 mL) at 0 °C. The reaction mixture was stirred for 24 h at ambient temperature and quenched with 5% aq HCl (5 mL) and H_2O (200 mL). The precipitate was filtered and dissolved in Et_2O (80 mL). The organic phase was washed with H_2O (10 mL), dried (Na_2SO_4) and concentrated to yield the crude product. Flash column chromatography (SiO_2 3.5×30 cm, CH_2Cl_2, R_f=0.35) gave 3.17 g (86% yield) of alcohol **7** as an off-white light-sensitive solid: mp 81–83 °C (lit.[25] 85–86 °C); ^{1}H NMR δ 1.89 (br s, 1H), 2.09–2.26 (m, 2H), 3.07 (dt, J_1=16.4 Hz, J_2=5.9 Hz, 1H), 3.31 (ddd, J_1=16.4 Hz, J_2=8.2 Hz, J_3=5.4 Hz, 1H), 7.29 (dd, J_1=6.8 Hz, J_2=0.7 Hz, 1H), 7.39 (dd, J_1=7.7 Hz, J_2=6.8 Hz, 1H), 7.45 (dd, J_1=7.7 Hz, J_2=7.1 Hz, 1H), 7.54 (d, J=7.1 Hz, 1H), 7.69 (d, J=7.7 Hz, 1H), 7.78 (d, J=7.1 Hz, J_2=0.9 Hz, 1H).

5.1.8. 3,5-Diacetyl-9,9-dimethyl-8,10-dioxatetracyclo-[5.3.0.0^{2,5}.0^{3,6}]decane (9). Freshly distilled 2,3-butanedione (2 mL) was added to a solution of propellane **1b** in Et_2O/pentane prepared from 231 mg (0.83 mmol) of dihalide **5b**. The mixture was stirred at about 5 °C and irradiated with a 450 W medium-pressure Hanovia mercury lamp for 5 h. Volatiles were removed and the residue was short-path distilled (110 °C/0.01 Torr) giving 175 mg (85% based on **5b**) of hygroscopic diketone **9**. Alternatively, diketone was purified by column chromatography (neutral Alumina, Grade 1, hexane/CH_2Cl_2 9:1). For other three runs in 0.5–3 mmol scale the yields were 50–68% based on **5b**. ^{1}H NMR δ 1.28 (s, 6H), 2.08 (s, 3H), 2.21 (s, 3H), 2.42 (s, 2H), 3.33 (t, J=0.8 Hz, 2H), 4.85 (t, J=0.8 Hz, 2H); ^{13}C NMR δ 24.1, 24.3, 27.0, 27.4, 43.1, 47.7, 55.2, 65.0, 81.1, 114.7, 204.4; MS, *m/z* (%) 235 (100) $[M-CH_3]^+$; HRMS, calcd for $C_{14}H_{19}O_4$: 251.1283, found 251.1286.

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