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STUDIES ON THE PAUSON-KHAND REACTION. EXCLUSIVE FORMATION OF ANGULARLY FUSED TRIQUINANES FROM BICYCLO[3.3.0]OCT-2-ENE AND PROPARGYL DERIVATIVES.

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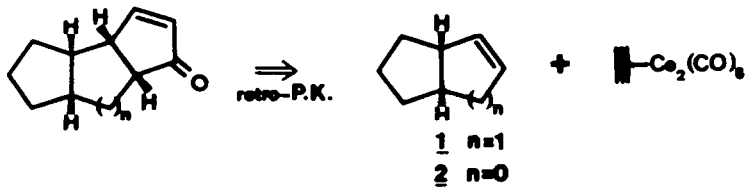
Abstract - Reaction of bicyclo[3.3.0]oct-2-ene with different hexacarbonyl dicobalt complexes of propargyl derivatives leads, under a great variety of experimental conditions, to the exclusive formation of angularly fused triquinanes, the corresponding reduced products being formed if the reaction is run at high temperature. The intermediacy of a π-allyl complex is suggested in order to account for these results, as well as for the presence of minor amounts of Diels-Alder adducts in the reaction mixture.

INTRODUCTION.

Cobalt mediated cyclopentenone annulations (the Pauson-Khand reaction)[1] are presently finding an increasing acceptance as the key step in the synthesis of complex cyclopentanoid compounds, either natural[2] or unnatural.[3] The success of such a reaction relies on the fact that very simple synthetic precursors may be derived by the pertinent retrosynthetic analysis. More work, however, is needed in order to define the scope and limitations of this methodology since it is known that the reaction, either in its intra- or intermolecular version, is strongly dependent -although not clearly understood- on the structure and/or the substitution pattern of the olefinic component.[2a]

In this context, we were interested in evaluating the possibility of entering into the linear cis-anti-cis triquinane skeleton, which is widely distributed among natural sesquiterpenoid compounds, by a cobalt mediated cyclopentenone annulation on cis-bicyclo[3.3.0]oct-2-ene (1)(See scheme 1).



Scheme 1

Since the closely related cis-bicyclo[3.2.0]hept-5-ene (2) reacts smoothly with several alkyne hexacarbonyl dicobalt complexes to afford the corresponding cis-anti-cis tricyclic systems with high regio- and stereoselectivity[4], no significant differences should be expected a priori with the less strained bicyclic olefin 1. In fact, cyclopentene itself has been successfully used in several Pauson-Khand reactions.[5]

For our studies, a series of protected propargyl alcohols 3a-c were selected as the acetylenic components. Although these derivatives have been successfully used in intramolecular processes[2c,3], an evaluation of their ability to participate in intermolecular reactions was still lacking.

RESULTS AND DISCUSSION.

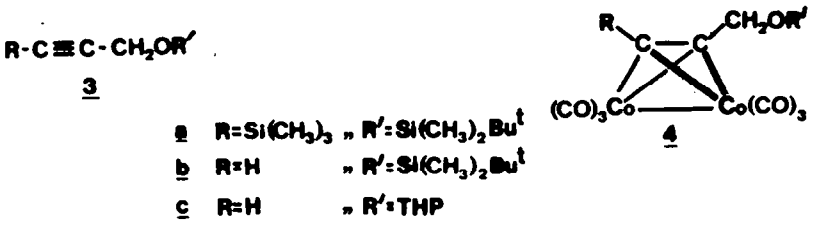
The reactions of the hexacarbonyl dicobalt complexes 4a-c with the bicyclic olefin 1 were studied under a great variety of conditions, the results being summarized in Table 1.

TABLE 1 - Conditions and product distribution for the reaction of bicyclic olefin 1 with dicobalt complexes 4a-c.

Substratum		4a	4b					4c		
Reaction		I	II	III	IV	V	VI	VII	VIII	IX
Molar ratio (1:4)		13/1	9/1	9/1	10/1	15/1	15/1	23/1	28/1	2/1
Solvent		1	a	a	a	1	1	1	b	c
Dilution[d]		3	12	11	10	4	4	5	32	7
Temperature (°C)		134[e]	80[e]	80[f]	80[e]	134[e]	220[g]	220[g]	220[g]	220[h]
Reaction time (h)		21	24	72	1	4	168	120	18	24
Conversion (%)		100	90	20	76	100	100	100	100	100
Products (% yield)	5[i]	0	18	10	16	15				
	6[i]						11	10	10	8
	7a[i]						15	33	40	15
	8[j]						2	3		
	9[j]						2	3		
	10[j]						1	1		
	11[j]						1	1		
	12[j]						0.5	0.5		
	13[j]						0.5	0.5		

[a] In benzene solution; [b] tetralin; [c] iso-octane. [d] Solvent (mL)/4 (g). [e] Under reflux. [f] Schlenk tube. [g] Sealed tube. [h] High pressure reactor. [i] Yield respect to 4. [j] Yield respect to 1.

When the dicobalt complex 4a was used no reaction was observed, apart from some thermal decomposition of the organocobalt complex leading to oligomerization of the acetylenic ligand.



On the other hand, when the corresponding organocobalt complex of acetylene 3b was allowed to react with olefin 1, either in benzene solution or using a large excess of the olefin as the solvent (entries II to V in Table 1), a single cyclopentenone 5 was formed.

Surprisingly enough, careful ^{13}C and ^{1}H NMR analyses showed that cyclopentenone 5 possessed an angularly fused triquinane skeleton (see Figure 1), instead of the expected cis-anti-cis linear one.

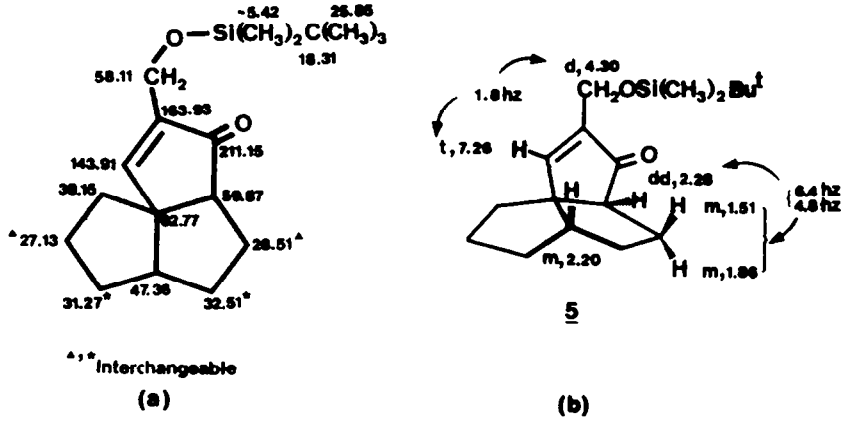
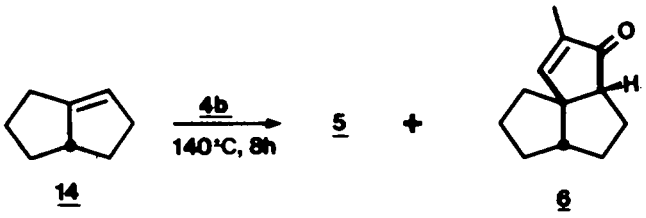


Figure 1. Assignments of δ_C(a) and δ_H(b) in compound 5

Thus, the off-resonance ^{13}C NMR spectrum[6] showed the presence of four distinct quaternary carbon atoms, which are not compatible with the linear triquinane structure. Moreover, although the olefinic proton at 7.26 ppm indicates that the propargylic carbon is α to the carbonyl group, as it would be expected from the normal regioselectivity exhibited by the intermolecular Pauson-Khand reaction, the multiplicity displayed by the signal of this olefinic proton, which appears as a triplet with a J = 1.8Hz, corresponding to the allylic coupling with the propargylic methylene (as confirmed by selective decoupling experiments), is only compatible with the proposed structure having a quaternary allylic carbon. Further structural evidence can be drawn from the fact that the hydrogen atom to the carbonyl group in compound 4a is directly coupled only to two magnetically distinct hydrogen atoms (according to proton-proton bidimensional correlation experiments).

Finally, the structure of triquinane 5 was confirmed by independent synthesis starting from the hardly available bicyclo[3.3.0]oct-1-ene (14), which was prepared from 2-ethoxycarbonylcyclopentanone by a four step sequence, as previously described[7], in 4% overall yield.

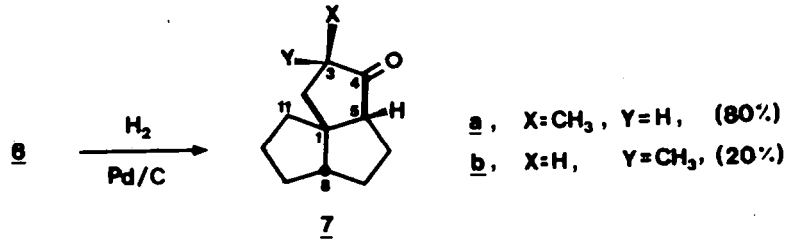
When the olefin 14 was allowed to react with the dicobalt complex 4b at 140°C for 8 h, the angular triquinane 5 was formed in 30% yield, along with a 10% yield of the derivative with the reduced propargyl functionality 6 (Scheme 2). As will be discussed later, the same reduction product is also obtained starting from olefin 1.



Scheme 2

The effects of higher temperature and longer reaction times on the yield of triquinane 5, starting from olefin 1 and complex 4b, was also investigated (entry VI in table 1). Under these conditions, although the yield on triquinane products is somewhat increased, compound 5 is absent from the reaction mixture. Instead, compound 6 (11%) and its hydrogenation product 7a (16%) could be isolated by column chromatography.

It is interesting to note that 7a was isolated as a single diastereomer, probably the one with the methyl group at the endo face, since it was identical with the major product obtained by catalytic hydrogenation of 6 (Scheme 3).

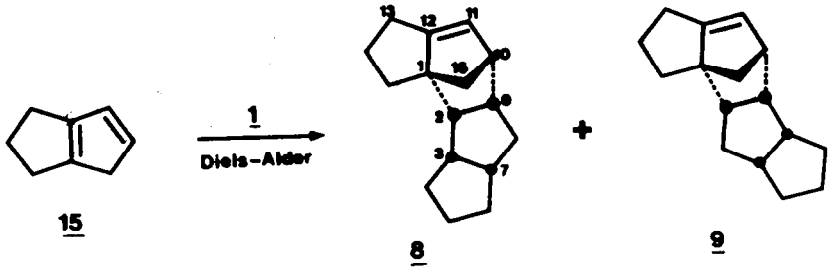


Scheme 3

Along with compounds 6 and 7a, minor amounts of more complex products were also isolated from the reaction mixture. In the first place, a 1:1 mixture of two isomeric hydrocarbons 8 and 9, with a molecular formula $C_{16}H_{22}$ according to high resolution MS, was isolated in 4% yield. The nature of the hydrocarbon skeleton of these diastereomeric dehydrodimers of olefin 1 is clear from their ^{13}C and ^{1}H NMR spectra. On the other hand, their stereochemistry can be inferred from simple steric and thermodynamic considerations. Both pentacyclic hydrocarbons must obviously be formed by a Diels-Alder reaction, indicating that significant amounts of diene 15[8] are present in the reaction medium (see Scheme 4). The intermediacy of 15 will be discussed later in connection with a possible mechanism for the formation of the angularly fused triquinanes 5-7a.

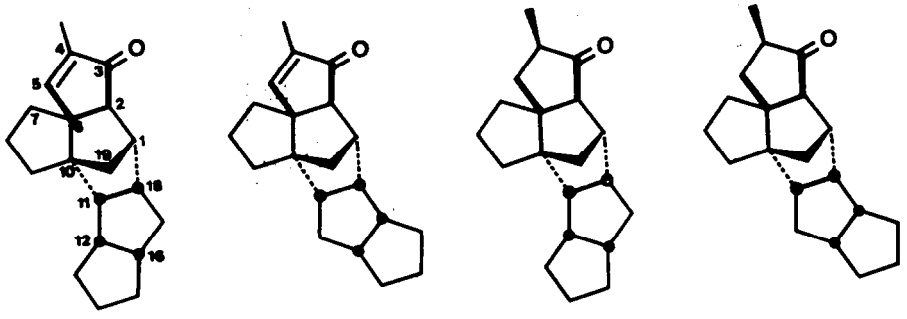
In the second place, 1:1 mixtures of the hexacyclic enones 10 and 11 (2% yield) and the corresponding saturated ketones 12 and 13 (1%) could be isolated too. The structural assignments of compounds 10 and 11 could be easily made from their ^{1}H NMR, MS, IR and UV spectra. Most probably, both compounds arise from a Pauson-Khand reaction of olefins 8 and 9, with concomitant reduction of the propargyl functionality, as already observed in the formation of compound 6. Catalytic hydrogenation with Pd/C of the mixture of 10 and 11 afforded compounds 12 and 13 as the major products, thus giving additional evidence for the structural assignments of these compounds. The formation of 12 and 13 in the reaction mixture exactly parallels that of 7a.

The influence of the hydroxyl protecting group was also studied by using the labile tetrahydropyranyl ether 4c (see entry VII in table 1). Similar results to those just described were obtained, except for a significantly higher yield of the reduced tricyclic ketone 7a. However, a greater excess of olefin 1 was used in this case.



15 8 9

Scheme 4



10 11 12 13

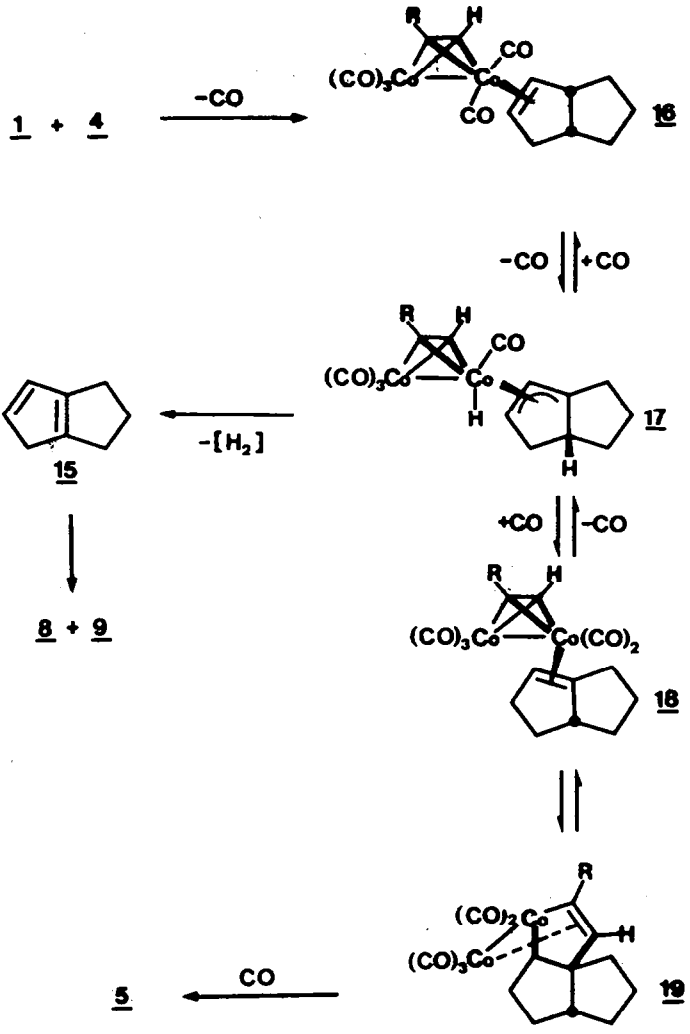
In the course of these studies, we have observed that the "normal" Pauson-Khand reaction, leading to cyclopentenone 5, takes place if relatively low temperatures are used. At higher temperatures (entries VI and VII in table 1), the normal course of the reaction is diverted towards the formation of reduced products 6 and 7a. At the same time, the appearence of products 8 and 13 in the crude reaction mixture suggests that dehydrogenation of olefin 1 to diene 15 has also ocurred. When the reaction was run in the presence of a large excess of tetralin (entry VIII, in table 1), a compound much more prone to dehydrogenation than olefin 1 itself, the yield of compound 7a increased up to 40%, whereas none of the products arising from diene 15 was detected. This fact strongly suggests that the aforementioned oxidative and reductive processes are coupled, so that, in the absence of a better hydrogen donor, olefin 1 is at the origin of both processes.

When only a 2:1 excess of olefin 1 is present in the reaction mixture, the same reductive processes are observed by using iso-octane as the solvent (entry IX, in table 1).

The exclusive formation of the angularly fused triquinane 5 from olefin 1 arises, at least, two fundamental questions on the mechanism of the Pauson-Khand reaction. In the first place, how does the isomerization of olefin 1 to olefin 14 proceed? In the second place, why is olefin 14 much more reactive than the former towards dicobalt hexacarbonyl complexes 4?

The presence of diene 15 in the reaction medium, as evinced by the isolation of the Diels-Alder adducts 8 and 9, may give a clue for a tentative answer to the first question (see Scheme 5).

In fact, the isomerization of an intermediate such as the olefin complex 18 could take place through the π-allyl complex 17 which, in turn, would afford the diene 15 via some formal dehydrogenation process. The intermediacy of such complexes in olefin isomerizations has been proposed in a number of cases.[9] Accordingly, the complex 17 could be the hydrogen-donor species involved in the reductive processes observed when the reaction is run at high temperatures.



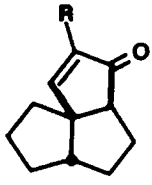
Scheme 5

We have not, at the moment, a satisfactory answer to the second question. Although the greater reactivity of strained olefins is a well established experimental fact in the Pauson-Khand reaction[1a], the fact that cyclopentene itself is a good olefinic component in such a reaction is hardly compatible with the complete lack of reactivity of complex 16 respect to 18. It may well be possible that, due to electronic reasons related to charge defficiency of the olefinic double bond, the more substituted olefin complex 18 is more reactive and/or more stable than 16. In this sense, Pauson[10] suggested, some years ago, the intermediacy of complexes in which the less hindered end of the alkyne was attached to the electrophilic end of the alkene, so that one could expect that the electron-rich olefins should be more reactive than the electron-defficient ones. Although some experiments performed in order to confirm this point gave no conclusive results[10], the enhanced reactivity of vinyl ethers and esters over simple alkenes in intermolecular Pauson-Khand reactions has been emphasized by Schore.[11]

CONCLUSIONS.

In the past few years, the number of isolated natural products with an angularly fused triquinane skeleton -i.e, the tricyclo[6.3.0.0^{1,5}]undecane ring system- has considerably expanded[12], a fact that has led to the parallel development of several synthetic strategies for the construction of these bridged spirane systems.[13,2a,6a] In this context, the results of the present work opens the possibility of entering into the angularly fused triquinane structure by the use of intermolecular Pauson-Khand annulations, and it is worth noting that the alternative strategy of constructing the same system via intramolecular annulations must cope with steric and strain constraints associated to the ring closure process[2a], which could probably be avoided by using the reaction in the intermolecular fashion.

Although the yields of compounds 5 to 7a, starting from olefin 1, are lower than those obtained from olefin 14, the rather difficult preparation of the latter, together with the commercial availability of the former, indicates that the reaction between monosubstituted acetylene dicobalt complexes and cis-bicyclo[3.3.0]oct-2-ene (1) is the more convenient and direct route to compounds of general structure 20. It should be noted that although a large excess of olefin 1 (see Table 1) is usually required in order to attain acceptable yields of triquinanes, the unreacted olefin may be eventually recovered by distillation at the end of the reaction.



20

We have shown that this atypical annulation is compatible with protected propargyl complexes (4), provided that the reaction is run at relatively low temperatures (benzene reflux), in order to avoid the formation of reduction products. These reductive processes could be, however, advantageous if the desired final products are the saturated ketones instead of the usually obtained enones. In this context, the possibility of combining the use of easily dehydrogenable solvents, such as tetralin[14], and high temperatures in the direct synthesis of cyclopentanones through Pauson-Khand annulations will be the subject of further studies in our laboratory.

EXPERIMENTAL

UV, IR and ^{1}H NMR (60 MHz) spectra were recorded on Perkin-Elmer instruments, models Lambda 5, 681 and R-24, respectively, and ^{1}H NMR (200 MHz) and ^{13}C NMR (50 MHz) with a Varian XL-200 apparatus. Mass spectra were run in a Hewlett-Packard 5930A spectrometer and high resolution MS with an updated AEI instrument, model 902 S. All chromatographic purifications were performed on silica gel (Merck, 230-400 mesh-ASTM), using hexane:diethyl ether mixtures of increasing polarity as eluents. Elemental analyses were performed with a 1106 Carlo-Erba microanalyzer instrument.

Highly pure propargyl alcohol and cis-bicyclo[3.3.0]oct-2-ene (1) free of the corresponding isomer 14 are commercially available. Propargyl derivatives 3a-c were prepared according to reference 15. All glass equipment was dried in the oven at 120°C, and solvents were dried and distilled before using.

General procedure (exemplified for reaction II, Table 1).- In a 250 mL reaction flask, equipped with a pressure-equalizing dropping funnel, nitrogen inlet, $CaCl_2$ outlet tube and magnetic stirring, were placed 2.0 g (0.01 mol) of $Co_2(CO)_8$ dissolved in 75 mL of dry benzene. A solution of 0.01 mol of propargyl derivative 3 in 60 mL benzene was added slowly at room temperature, in a 15 min period. After the total addition, the reaction mixture was stirred overnight under the same conditions and the benzene solution was filtered through celite (eventually, the benzene solution was evaporated under vacuum, at room temperature, to give the red complex 4 in 100% yield).

0.09 mol of bicyclo[3.3.0]oct-2-ene (1) were added to the benzene solution of the named complex 4 and the mixture heated under reflux, in a CO atmosphere. The reaction was monitored by TLC and after all the starting complex had disappeared, the reaction mixture was filtered through celite to remove some black solid material (Co) and then concentrated under vacuum. The crude product was purified by flash-chromatography and the isolated product 5 was further purified, if necessary, by additional column chromatographies.

Reaction of 14 with 4b.- 1.0 g (9.3 mmol) of bicyclo[3.3.0]oct-1-ene (14), prepared according to reference 7, was added to a solution of 4.2 g (9.3 mmol) of 4b in 25 mL of tert-butylbenzene. The reaction mixture was heated at 140°C for 8 h, under an atmosphere of CO. The crude product was then treated as above and purified by column chromatography, to afford 0.7 g (30% yield) of 5 and 0.1 g (10% yield) of 6, the conversion respect to the complex 4b being 82%.

Hexacarbonyl-μ-[η^4-1-(tert-butyldimethylsilyloxy)-3-trimethylsilylprop-2-yne]dicobalt-(Co-Co), 4a.- Dark-red oil; IR (CCl_4), 2960, 2940, 2900, 2860, 2085, 2080, 2050, 2030, 1460, 1250, 1100, 840 cm^{-1}; ^1H NMR (60 MHz, CCl_4), 5.90 (br s, 2H), 0.89 (s, 9H), 0.26 (s, 6H); MS, m/e, 528 (M^+, $C_{18}H_{26}O_7Co_2Si_2$), 500, 472, 444, 416, 388, 360 (M^+ - 6CO, 100%), 288, 272, 245, 242, 201, 192.

Hexacarbonyl-μ-[η^4-1-(tert-butyldimethylsilyloxy)prop-2-yne]dicobalt-(Co-Co), 4b.- Dark-red oil; IR (CCl4), 2960, 2940, 2900, 2860, 2095, 2060, 2020, 1985, 1460, 1350, 1250, 1100, 840 cm^{-1}; ^1H NMR (60 MHz, CCl_4), 6.10 (s, 1H, H-C3), 4.95 (br s, 2H, H_2-C1), 1.10 (s, 9H, Bu^t), 0.30 (s, 6H, $SiMe_2$); MS, m/e, 456 (M^+, $C_{15}H_{18}O_7Co_2Si$), 428, 400, 378, 344, 316, 288 (M^+ - 6CO, 100%).

Hexacarbonyl-μ-[η^4-1-(tetrahydropyran-2-yloxy)prop-2-yne]-dicobalt-(Co-Co), 4c.- Dark-red oil; IR (CCl_4), 2950, 2880, 2870, 2100, 2060, 2020, 1200, 1120, 1070, 1040, 1020, 970 cm^{-1}; ^1H NMR (60 MHz, CCl_4), 5.95 (s, 1H, H-C3), 4.90 (s, 2H, H_2-C1), 4.60 (br s, 1H, H-C1'), 3.60 (m, 2H, H_2-C6'), 1.95 (br m, 6H, H_6-C3'4'5'); MS, m/e, 426 (M^+, $C_{14}H_{12}O_8Co_2$), 398, 370, 342, 314, 286, 258 (M^+ - 6CO, 100%).

rac-(1S,5S,8S)-3-(tert-Butyldimethylsilyloxymethyl)tricyclo[6.3.0.0^{1,5}]undec-2-en-4-one, 5.- Colorless oil; IR (film), 3040, 1700, 1635, 1250, 1115, 840 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$), 7.26 (t, J = 1.8Hz, 1H, H-C2), 4.30 (d, J = 1.8Hz, 2H, $-CH_2OSi$), 2.28 (dd, J_1 = 6.4, J_2 = 4.8Hz, 1H, H-C5), 2.20 (m, 1H, H-C8), 1.86 (m, 1H, H -C6), 1.51 (m, 1H, H -C6), 0.92 (s, 9H, Bu^t), 0.07 (s, 6H, $-SiMe_2$); ^{13}C NMR (50.3 MHz, $CDCl_3$), see Fig. 1a; MS, m/e, 306 (M^+), 291 (M^+-CH_3), 249 (M^+ - Bu^t, 100%), 219, 205, 191 (M^+ -$SiMe_2Bu^t$), 175, 131, 105; UV (EtOH), 224 nm (ε = 12840). Elemental analysis, calc. for $C_{18}H_{30}O_2Si$: C, 70.5; H, 9.9. Found: C, 70.4; H, 10.1.

rac-(1S,5S,8S)-3-Methyltricyclo[6.3.0.0^{1,5}]dodec-2-en-4-one, 6.- Colorless oil; IR (film), 3020, 2950, 2860, 1700, 1650, 1460, 1170 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$), inter alia, 7.16 (q, J = 1.5Hz, 1H, H-C2), 2.32 (dd, J_1 = 6.5, J_2 = 4.5Hz, 1H, H-C5), 1.75 (d, J = 1.5Hz, 3H, Me-C3); MS, m/e, 176 (M^+, $C_{12}H_{16}O$), 161, 147, 118, 107 ($C_8H_{11}^+$); UV (EtOH), 220 nm (ε = 10600).

rac-(1R,3R,5S,8S)-3-Methyltricyclo[6.3.0.0^{1,5}]dodecan-4-one, 7a.- Oily product; IR (CCl_4), 2940, 2860, 1735, 1460, 1380, 1260, 1140 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$),inter alia, 2.61 (m, $W_{1/2}$ = 28Hz, 2H, H-C3 and H-C5), 1.01 (d, J = 6.7Hz, 3H, Me-C3); ^{13}C NMR (50.3 MHz, $CDCl_3$), 222.15 (s), 65.21 (s), 59.63 (d), 57.62 (d), 50.8 (d), 34.02 (t), 33.60 (t), 31.42 (t), 29.25 (t), 25.64 (t), 19.66 (t), 15.23 (q); MS, m/e, 178 (M^+), 163 (M^+ - CH_3), 149, 135, 120, 107 ($C_8H_{11}^+$, 100%). Elemental analysis, calc. for $C_{12}H_{18}O$: C, 80.8; H, 10.1. Found: C, 80.7; H, 9.9.

rac-(1R,2R,3S,7S,9R,10S)-Pentacyclo[8.5.1.0^{1,12}.0^{2,9}.0^{3,7}]hexadec-11-ene, 8, and rac-(1S,2S, 4S,8S,9S,10R)-Pentacyclo[8.5.1.0^{1,12}.0^{2,9}.0^{4,8}]hexadec-11-ene, 9.- Oily product; IR (film), 3050, 2940, 2860, 1670, 1650, 1450, 1250, 780 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$), 5.29 (br s, 1H, H-C11), 1.1-2.8 (m, 21H); ^{13}C NMR (50.3 MHz, $CDCl_3$), 151.52 and 159.03 (s, C1), 121.47 and 121.06 (d, C2), 76.69 and 76.66 (d, C3), 64.88 and 63.67 (s, C11), 58.95 and 58.76 (t, C15), 58.63, 55.96, 52.14, 50.25, 50.08, 48.89, 48.32 and 48.02 (d, C4, 6, 10, 11 of 8 and 9), 36.26, 34.47, 34.11, 33.43, 33.02, 32.91, 32.98, 29.33, 29.25, 27.86, 27.71, 27.61, 25.63 and 25.44 (t, C5, 7, 8, 9, 13, 14 and 16, of 8 and 9); MS, m/e, 214 (M^+), 185, 173, 141, 124, 115, 106 ($C_8H_{11}^+$, 100%); high resolution MS, calc. for $C_{16}H_{22}$: 214.17215. Found: 214.17261.

rac-(1S,2S,6S,10R,11R,12S,18R)-4-Methylhexacyclo[8.8.1.0^{2,6}.0^{6,10}.0^{11,18}.0^{12,16}]icos-4-en-3-one,10, and rac-(1R,2R,6R,10S,11S,13S,17S,18S)-4-methylhexacyclo[8.8.1.0^{2,6}.0^{6,10}.0^{11,18}.0^{13,17}]icos-4-en-3-one, 11.- Colorless oily product; IR (film), 3050, 2940, 2850, 1700, 1650, 1450, 1370, 1260 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$), inter alia, 7.16 (q, J = 1.6Hz, 1H, H-C5), 1,72 (d, J = 1.6Hz, 3H, Me-C4); MS, m/e, 282 (M^+, $C_{20}H_{26}O$), 254, 214, 109 ($C_8H_{13}^+$, 100%); UV (EtOH), 220 nm (ε = 13100).

rac-(1S,2S,4R,6S,10R,11R,12S,16S,18R)-4-Methylhexacyclo[8.8.1.0^{2,6}.0^{6,10}.0^{11,18}.0^{12,16}]icosan- 3 -one, 12, and rac-(1R,2R,4S,6R,10S,11S,13S,17S,18S)-4-methylhexacyclo[8.8.1.0^{2,6}.0^{6,10}.0^{11,18}.0^{13,17}]icosan-3-one, 13.- Oily products; IR (CCl_4), 2920, 2850, 1735, 1450, 1130, 920 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$), inter alia, 1.05 (d, J = 6.9Hz, 3H, Me-C4); MS, m/e, 284 (M^+, $C_{20}H_{28}O$), 244, 228, 165, 137, 109 ($C_8H_{13}^+$, 100%). Elemental analysis, calc. for $C_{20}H_{28}O$: C, 84.4; H, 9.9. Found: C, 84.5; H, 9.8.

Preparation of 7a by catalytic hydrogenation of 6.- A solution of 64 mg (0.36 mmol) of 6 in 6 mL of absolute ethanol, containing 82 mg of 10% Pd/C, was hydrogenated under normal conditions (20°C, 1 atm.), until a hydrogen uptake of 8.5 mL. The solution was filtered through celite and then evaporated under vacuum. Analysis of the crude product (60 mg), by IR, NMR, MS and GLC showed that it

was a 8:2 mixture of two isomers. After successive chromatographic purifications on silica gel, 30 mg of the major component were isolated, which physical and spectroscopic properties were identical to those of compound 7a.

Preparation of 12 and 13 by catalytic hydrogenation of 10 and 11.- 85 mg (0.30 mmol) of a 1:1 mixture of 10 and 11 were hydrogenated as indicated above to give 35 mg of a 1:1 mixture of the major isomers, which physical and spectroscopic properties were identical with those of a 1:1 mixture of 12 and 13.

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