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ANHYDROUS FERRIC CHLORIDE DISPERSED ON SILICA GEL INDUCED RING ENLARGEMENT OF TERTIARY CYCLOALKANOLS. II [1] : A CONVENIENT HOMOLOGATION OF CYCLOALKANONES, PREPARATION OF SPIRO SYSTEMS AND PROPELLA - γ-LACTONES

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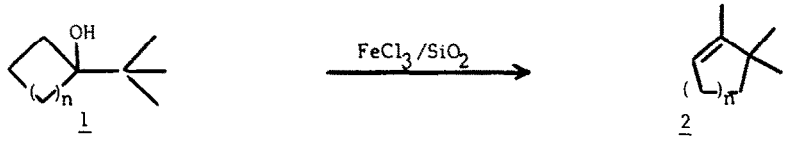
Abstract - The reagent obtained by mixing anhydrous $FeCl_3$ and silica gel induced, in the lack of any solvent, dehydration of tertiary cycloalkanols, specific $C_4 \longrightarrow C_5$ and $C_5 \longrightarrow C_6$ ring enlargement, formation of spiro compounds and propella-γ- lactones and cleavage of tetrahydropyranyl ethers.

We have recently reported that the pale yellowish green powder simply obtained by stirring anhydrous ferric chloride (8%) and silica gel, without solvent at room temperature for 24 hr is effective for dehydration of tertiary alcohols [1] as well as the MAZUR' reagent, a yellowish brown powder obtained by mixing a solution of hydrated ferric chloride ($FeCl_3$, $6H_2O$) and silica gel and removal of the solvent (ether, methanol, acetone ...) at 60° under vacuum (0.1 torr) [2]. Furthermore, we have found that tertiary cyclobutanols 1 (n = 1) underwent dehydration and specific $C_4 \longrightarrow C_5$ ring enlargement into cyclopentene derivatives 2.



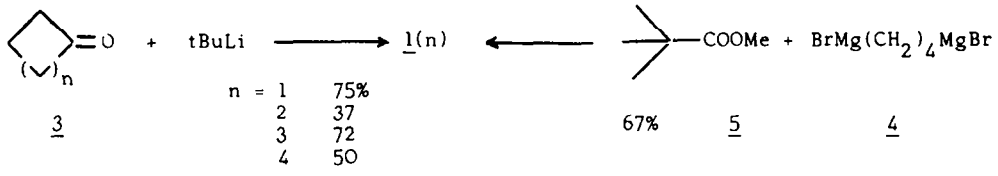
1 2

The synthetic applications of the rearrangement which occurs at room temperature, in dry medium, was illustrated by the ready preparation of isolaurolene and derivatives, campholenic ether and (±)-cuparene [1].

We report in this paper the behaviour of three, five, six and seven-membered 1-t-butylcycloalkanols with the anhydrous $FeCl_3$-SiO_2 reagent and the formation of spiro compounds and propella-γ-lactones.

Preparation and ring enlargement of 1-t-butylcycloalkanols 1

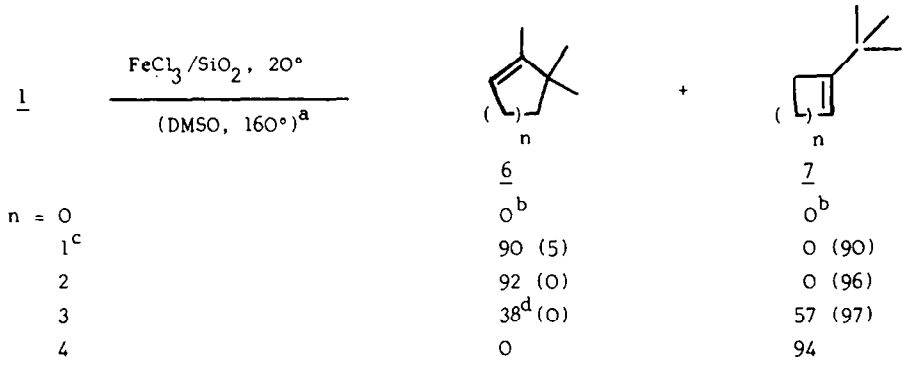
The required tertiary cycloalkanols 1 (n = 1 - 4) were readily prepared by addition of t-butyllithium, at low temperature, to the corresponding cycloalkanones. Addition of t-BuLi to the cyclopropanone hemiacetal magnesium salt [3] provided the 1-t-butylcyclopropanol 1 (n = 0) in 47% yield.



3 5 4

However, the addition of the two nucleophilic centres of 1,4-di(bromomagnesio) butane (4) to methyl privalate (5), following a Grignard reaction [4] recently renewed by Canonne and coworkers [5] gave a better yield [6] of 1-t-butylcyclopentanol 1 (n = 2). Unfortunately, this alternative route to 1 was not convenient to prepare 1-t-butylcyclobutanol, cyclohexanol and -cycloheptanol (1, n = 1, 3, 4).

As previously reported for 1-t-butylcyclobutanol (1, n = 1), when neat 1-t-butylcyclopentanol (1, n = 2) was added to the pale yellow green anhydrous $FeCl_3$-SiO_2 powder in dry medium, the color of the stirred mixture turned to yellow-orange and after few hours to yellowish-brown. As monitored by thin layer chromatography, the reaction was complete within 3 hours. Then the product of the reaction was either distilled directly into a cold trap or eluted from silica gel with ether. As expected, a specific $C_5 \longrightarrow C_6$ ring enlargement induced by anhydrous $FeCl_3/SiO_2$ was observed, leading exclusively to 1,6,6-trimethylcyclohexene (6, n = 2) in 92% yield; while, in the presence of iodine as reported by [7] the cycloalkanol (1, n = 2) underwent dehydration into a mixture of (6, n = 2) and 1-t-butylcyclopentene (7, n = 2), in 16 and 82% yield, respectively.

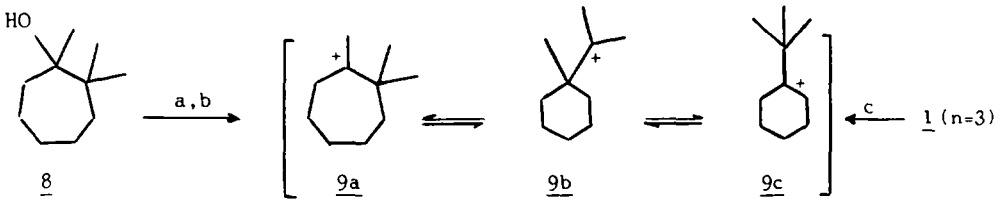


	6	7
n = 0	0[b]	0[b]
1[c]	90 (5)	0 (90)
2	92 (0)	0 (96)
3	38[d] (0)	57 (97)
4	0	94

Scheme I. - Dehydration and ring enlargement of tertiary cycloalkanols.

a) The yields of the reaction in DMSO at 160° are noted in parentheses. b) When n = 0 the product of the reaction was a ring-opened compound. c) See ref. 1. d) Formation of a reduction product (M, wt = M + 2).

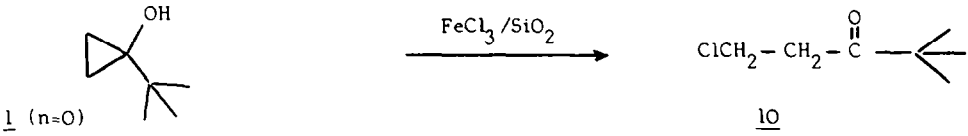
On the other hand, upon treatment with anhydrous $FeCl_3$-SiO_2 under the same conditions, 1-t-butylcyclohexanol (1, n = 3) underwent either dehydration to 1-t-butylcyclohexene (7, n = 3) (57%) or ring enlargement and reduction to 1,1,2-trimethylcycloheptane. It was known that 1,2,2-trimethylcycloheptanol 8 led by action of iodine at 80-100° [8] or by action of thionyl chloride-pyridine at -45° [9] to the olefins (6, n = 3) (and its exo isomer) and (7, n = 3) derived from the tautomeric carbocations 9a and 9c, respectively. So, the formation of (7 n = 3) from the 1-t-butylcyclohexanol (1, n = 3) and the anhydrous $FeCl_3$-SiO_2 reagent was not surprising.



8 9a 9b 9c

a) I_2, 80-100°; b) $SOCl_2$-pyridine-45°C; c) Anh. $FeCl_3$-SiO_2, 20°.

Nevertheless, the formation of 1,1,2-trimethylcycloheptane confirmed by its ^{13}C NMR and mass spectra was unexpected. Thus in these conditions 9a, if such a species is really involved, prefers to take a hydride from the silica gel medium, rather than to undergo proton elimination to give a cycloheptene. Upon treatment with anhydrous $FeCl_3$-SiO_2 reagent 1-t-butylcycloheptanol (1, n = 4) underwent exclusively dehydration leading to 1-t-butylcycloheptene (7, n = 4), no product involving a $C_7 \longrightarrow C_8$ ring enlargement being obtained. Finally, the 1-t-butylcyclopropanol (1, n = 0) gave with $FeCl_3$-SiO_2 only the t-butyl (2-chloroethyl) ketone 10.



1 (n=0) 10

Like cyclopropanols in acidic medium or in the presence of metallic halides, (1, n = 0) underwent also in these conditions a $FeCl_3$ induced ring-opening.[10]

As shown in Scheme 1, on heating for instance in DMSO at 160°[11], the tertiary cycloalkanols (1, n = 1-4) led to the corresponding 1-t-butylcycloalkenes 7 in excellent yields as noted in parentheses; only 5% of ring enlargement product (6, n = 1) being formed from the strained 1-t-butylcyclobutanol (1, n = 1).[1] Among the numerous methods developed to prepare cycloalkane derivatives, the $C_4 \longrightarrow C_5$[12], $C_5 \longrightarrow C_6$[13] and $C_6 \longrightarrow C_7$[14] ring expansions have only quite recently been taken into account, so this specific rearrangement which occurs in mild conditions opens a new and convenient route to these systems.

Preparation and ring-enlargement of 1-cycloalkylcycloalkanols into spiro-compounds

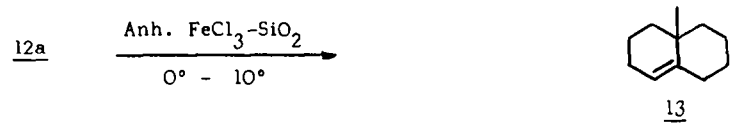
The discovery of a growing number of naturally occuring spiro-compounds has recently stimulated considerable effort to achieve spiro-annelation of cycloalkanes.[15] So it was interesting to test the ability of the anhydrous ferric chloride dispersed on silica gel to induce ring enlargement of 1-cycloalkylcycloalkanols such as 12 to provide the spiro system under mild conditions.

11 a n = 1
b = 2

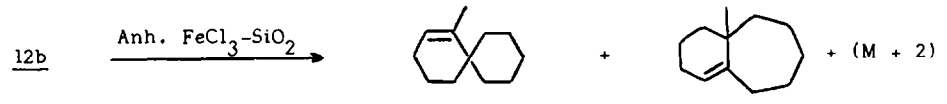
12a,b

Addition of 1,4-di(bromomagnesio)butane 4 in THF at -65° to the methyl 1-methylcycloalkylcarboxylates 11[16], readily available by methylation (LDA, ICH_3) of the cycloalkylcarboxylates, led after liquid chromatography to the expected tertiary cycloalkanols 12 in 80% yields. Upon addition to the anhydrous $FeCl_3$-SiO_2 reagent at 0°, 12a underwent dehydration and double ring enlargement to provide, after stirring for 4 h at 10°, the

6-methylbicyclo[4.4.0]dec-1-ene 13, in 93% yield.

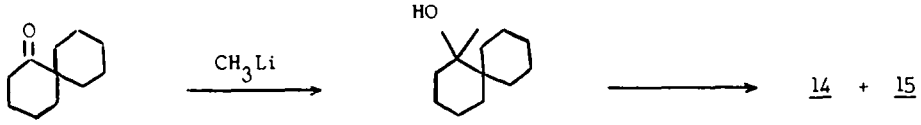


On the other hand, upon addition to $FeCl_3$-SiO_2 at 0° and stirring for 4 hr at 10°, 12b underwent dehydration and ring enlargement to provide the 1-methylspiro[5.5]undec-1-ene 14 and the 7-methylbicyclo[5.4.0]undec-1(11)-ene 15 in 74 and 12% yields, respectively. The same treatment at 20° for 4 hr led to a mixture of 14 and 15 in 58 and 7% yields, respectively. The reactions produced also 6 and 19% of saturated compounds.



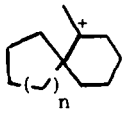
	14	15	
0 - 10°	74	12	6
20°	58	7	19

The spirocyclic olefin 14 was unequivocally synthesized from the 1-methylspiro[5.5]undecan-1-ol 17, obtained by addition of methyllithium to the spiroketone 16.[17] On heating in DMSO at 160°, 16 underwent dehydration to give 14 and 15 in 76 and 12% yields, respectively.



DMSO, 160°	76	12
$FeCl_3$-SiO_2, 20°	73	19

It is interesting to note that, by the action of $FeCl_3$-SiO_2, 17 underwent dehydration and rearrangement leading to 14 and 15 in roughly comparable yields to those obtained from 12b. After 45 mn at 0°, 70% of dehydration occured, and the reaction was complete within 4 hr at 20°.

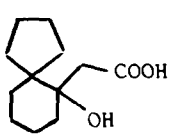


18a n = 1
b = 2

In both cases, the same species, likely 18, was formed after ionisation of the hydroxyl group, methyl transfer and $C_5 \longrightarrow C_6$ ring enlargement of cycloalkanols 12. When n = 1, 18a underwent a second favored $C_5 \longrightarrow C_6$ ring expansion (see Scheme I) leading to 13, exclusively. However, when n = 2, the carbocation 18b prefers to undergo a proton elimination leading to 14 rather than a less favorable $C_6 \longrightarrow C_7$ ring enlargement (see Scheme I) leading to 15.

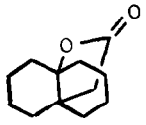
Preparation of propella-γ-lactones from spiro-ketones

Propellalactones have been prepared from the Baeyer-Villiger oxidation of the corresponding propellane ketones [18] and have been transformed into other important polycarbocyclic ring systems, such as dispirolactones [19]. Recently, the acid-catalyzed reaction of the 3-hydroxy acid 19 obtained by addition of acetate dianion to the spiro[5.4.]decan-2-one has been described.[20]



19

97% H_2SO_4, C_6H_6 reflux 98%
$SnCl_4$, $5H_2O$, C_6H_6 reflux 63
$ZnCl_2$, C_6H_6 reflux 39
$FeCl_3$-SiO_2, RT 88



20

From the reaction of 19 with 97% sulfuric acid in boiling benzene for 8 hr the propella-γ-lactone 20 was obtained in 98% yield; with a Lewis acid such as $SnCl_4$, $5H_2O$ or $ZnCl_2$ 20 was formed in 63 and 39% yields, respectively.[20] We have found that upon treatment with $FeCl_3$-SiO_2 reagent at 40° for 3 hr (or at r.t. for 60 hr) 19 underwent dehydration and lactonisation to give 20 in 88% yield. We have obtained, under the same conditions, the formation of an oxacamphane, viz. the campholenic ether, from the $FeCl_3$-SiO_2 induced dehydration and cyclisation of a 2(-2-hydroxyethyl)cycloalkanol.[1]

Cleavage of tetrahydropyranyl ethers

The anhydrous $FeCl_3$-SiO_2 reagent was also effective in cleaving tetrahydropyranyl ethers, in dry medium. For instance, upon treatment at 20° for 45 h the neat ethers 21a gave the corresponding alcohol 22a in 98.5% yield; while at 40° for 90 min. 22a was obtained in 95% yield. In the same way, 2-pentyn-1-ol 22b was obtained from 21b in 92% yield.

$$R - CH_2OTHP \xrightarrow{FeCl_3\text{-}SiO_2} R - CH_2OH$$

21a R = C_5H_{11} 22a,b
b C_2H_5 C≡C

For another example of ether cleavage see reference 1. Further synthetic applications of this anhydrous $FeCl_3$-SiO_2 reagent are currently under investigation and will be reported in due course.

EXPERIMENTAL

Preparation of the anhydrous $FeCl_3$-SiO_2 reagent, see reference 1.

General dehydration procedure, see reference 1.

Syntheses of cycloalkanols 1 :

1-t-butylcyclopropanol (1, n = 0) from cyclopropanone hemiacetal. To an oven-dried, nitrogen-flushed, 250 ml, three-necked flask fitted with a mechanical stirrer, a pressure-equalizing dropping funnel, and a reflux condenser topped with a connecting tube leading to a bubbler, were added magnesium (0.48 g, 20 mmol) and diethyl ether (40 ml). To this stirred suspension methyl iodide (2.85 g, 20 mmol) in ether (40 ml) was added dropwise. After all the magnesium was dissolved, the flask was cooled in an ice bath. Then, a solution of 2.04 g (20 mmol) of 1-ethoxycyclopropanol[3,21] in 40 ml of anhydrous ether was added dropwise. A gas, presumably methane, evolved, while a white suspension was formed. To the stirred suspension cooled at -60°, 14 ml of a 1.6 N solution of t-BuLi (22 mmol) was added dropwise over 2 h. The reaction mixture was stirred at -50° for 1 h and at room temperature overnight. Then, 40 ml of a cold saturated solution of NH_4Cl was added. The organic layer was decanted and the aqueous layer extracted three times with 75 ml of ether. The combined organic layers were washed quickly with a 0.2 N solution of HCl and then with 2 ml of saturated brine, dried over $MgSO_4$, filtered, concentrated on a rotary evaporator (room temperature) to give 1.6 g of a crude product. Purification by chromatography on 50 g of silica gel; elution with pentane-ether (90:10) gave 7.07 g (47%) of 1-t-butylcyclopropanol (1, n = 0) : NMR (CCl_4) : δ 2.3 (s, OH) ; 0.9 (s, 9H) ; 0.52 (s, 4H). IR (CCl_4) : 3620 and 3500 cm^{-1} (ν OH), 1235 and 1002 cm^{-1}. M.S. m/e (rel. intensity) : 114 (M^+, 3.71) 57 (100), 41 (67).

1-t-butylcyclopentanol (1, n = 1) from cyclopentanone: the preparation has been reported by Buhler in 27% yield.[6] We improved the yield (37%) by adding dropwise t-BuLi and cyclopentanone, simultaneously.

1-t-butylcyclohexanol (1, n = 2) from cyclohexanone: the preparation has been reported in 53% yield.[6] We improved the yield to 72%, as for (1, n = 1).

1-t-butylcyclopentanol (1, n = 1) from methyl pivalate: a 250 ml three-necked, round-bottomed flask, equipped with a nitrogen inlet, a reflux condenser, a magnetical stirrer, and a pressure-equalizing dropping funnel was charged with 3.6 g (150 mg.at.) of magnesium and 60 ml of anhydrous THF. Under rapid stirring, a solution of 11.9 g (50 mmol) of 1,4-dibromobutane in THF (60 ml) was added dropwise for 3 h. Then, the reaction mixture was stirred at room temperature for an additional 3 h and cooled to -35 - -40°. A solution of 5.8 g (50 mmol)of methyl pivalate 5 in 50 ml of THF was added, dropwise, within 3 h. The mixture was stirred at -15° for 1 h and at room temperature overnight. After hydrolysis with saturated aqueous ammonium chloride, the organic layer was separated, the aqueous layer was extracted three times with ether (80 ml) and the combined layers were dried on $MgSO_4$. After removal of the solvents, the residue was distilled (b.p. 93-97° (12 mm); lit.[6] 95-18° (15 mm) to give 4.75 (67%) of 1-t-butylcyclopentanol .

N.B. Upon the same treatment, the reaction of methyl pivalate (5) with 1.1 equivalent of 1,3-di(bromomagnesio)propane [23], and 1,5-di(bromomagnesio)pentane [5] gave very poor yields (~2%) of the expected 1-t-butylcycloalkanols (1, n = 1 or 3).

Ring-opening of 1-t-butylcyclopropanol (1, n = 0): a mixture of 170 mg (1.5 mmol) of (1, n = 0) and 1.8 g of anhydrous $FeCl_3$-SiO_2 was stirred at 20° for 6 h, while the color of the medium turned from yellow to white. Elution with ether and chromatography on 6 g of silica gel yielded 197 mg (88.5%) of t-butyl (2-chloroethyl) ketone 10 : NMR (CCl_4): δ 3.69 (t, J = 6 Hz, 2H) ; 2.9 (t, J = 6 Hz, 2H) ; 1.15 (s, 9H). IR (CCl_4) : 1715 ($\nu_{C=O}$) 1478 cm^{-1}. M.S. : m/e (rel. intensity) : 150 (M^+, 5.6), 57 (100), 41 (43.7).
Anal. calc. for $C_7H_{13}OCl$: C, 56.6 ; H, 8.8 ; Cl, 23.85. Found: C, 55.4 ; H, 8.8 ; Cl, 23.7%

Dehydration and ring enlargement of 1-t-butylcyclopentanol (1, n = 2): to 2.4 g of anhydrous $FeCl_3$-SiO_2 in a 10 ml flask was added 0.3 g of 1 (n = 2) and the mixture was stirred at room temperature for 3 h. The product was then distilled directly under vacuum (15 mm) into a trap cooled by liquid nitrogen to yield 230 mg (92.7%) of 1,6,6-trimethylcyclohexane (6, n = 2), with spectral data identical with those reported [7] for this compound.

Dehydration and ring enlargement of 1-t-butylcyclohexanol (1, n = 3): a mixture of 468 mg (3 mmol) of (1, n = 3) and 3.6 g of $FeCl_3$-SiO_2 was stirred at room temperature for 12 h, while the color turned from light yellow to brownish yellow. Elution with ether gave 400 mg (94% yield) of a mixture of 1-t-butylcyclohexene (7, n = 3) and a compound which was not (6, n = 3). Purification by gas chromatography (D.C. 710, 3 m, 110°) gave 200 mg (57% yield) of (7, n = 3) and 130 mg of 1,1,2-trimethylcycloheptane as determined from spectral data (^{13}C NMR in CS_2 [8]). The spectral data of (7, n = 3) were also identical with those reported.[7]

Dehydration of 1-t-butylcycloheptanol (1, n = 4): a mixture of 340 mg (2 mmol) of (1, n = 4) and 3 g of anhydrous $FeCl_3$-SiO_2 was stirred at room temperature for 1 h. Elution with ether gave 286 mg (94% yield) of 1-t-butylcycloheptene (7, n = 4) with spectral data identical with those reported [24]. NMR ^{13}C ($CDCl_3$) δ : 153.41 (s), 122.26 (d), 36.54 (s), 33.44 (t), 29.07 (t), 28.77 (q), 28.40 (t), 27.67 (t), 27.37 (t).

Dehydration in DMSO at 160°: 4 mmol of 1-t-butylcycloalkanol (1) in 6 ml of anhydrous DMSO was heated at 160-170° [11] for 3 h. Then the reaction mixture was extracted with pentane and the organic layer was washed with 3 x 1 ml of water. Removal of the solvent on a rotary evaporator yielded the expected olefins 7 in high yields: from (1, n = 2) the 1-t-butylcyclopentene (7, n = 1) was obtained in 96% yield, with spectroscopic data identical with those reported [7] ; from (1, n = 3) the 1-t-butylcycloheptene (7, n = 2) was obtained in 97% yield : NMR (CCl_4) δ 5.40 (m, 1H), 1.98 (m, 4H), 1.55 (m, 4H), 1.0 (s, 9H) ; IR (CCl_4) : 1653 cm^{-1} ($\nu_{C=C}$) ; M.S. m/e (rel. intensity) : 138 (M^+, 25), 123 (80), 81 (100, M-t-C_4H_9), 67 (58), 57 (97), 41 (64).

Methyl 1-(1-methylcyclopentane) carboxylate (11a): to a solution of lithium diisopropylamide, prepared by addition of a solution of 17.7 ml of 1.5 N (26.5 mmol) n-BuLi in hexane to 2.65 g (26.5 mmol) of diisopropylamine in 20 ml of THF was added dropwise at 0°, a solution of 3.2 g (25 mmol) of methyl cyclopentanecarboxylate in 10 ml of THF. After stirring for 15 mn, was added a solution of 4.26 g (30 mmol) of methyl iodide in 10 ml of THF. The mixture was stirred at room temperature for 2 h, cooled to 0° and treated with a NH_4Cl solution to neutrality. The mixture was extracted with ether (3 x 50 ml), washed with water (2 x 3 ml) and dried over $MgSO_4$. After removal of the solvent, distillation of the residue gave 3.42 g (90% yield) of methyl 1-(1-methylcyclopentane) carboxylate (11a) (b.p. 77° (50 mm). NMR (CCl_4) : δ 3.63 (s, 3H), 2.35 - 1.93 (m, 2H), 1.93 - 1.23 (m, 6H), 1.23 (s, 3H). IR (neat) : 1723 cm^{-1} ($\nu_{C=O}$).

1-(1-Methylcyclopentyl) cyclopentanol (12a): to a solution of 1,4-di(bromomagnesio)butane prepared from 3.33 g (15.4 mmol) of 1,4-dibromobutane and 1.2 g (50 mg.at.) of magnesium in 50 ml of anhydrous THF was added dropwise over 3 h a solution of 1.42 g (10 mmol) of 11a in 30 ml of THF. The mixture was stirred at -10° for 1 h and at room temperature overnight. After hydrolysis with 10 ml of saturated aqueous NH_4Cl and extraction with ether (3 x 50 ml) the solution was dried on Na_2SO_4 and concentrated in vacuum. Chromatography on 40 g of silica gel and elution with pentane-ether (92/8) gave 1.38 g (82%) of 1-(1-methylcyclopentyl)cyclopentanol (12a). NMR (CCl_4) : δ 0.98 (s, 3H), 1.16 (s, OH), 1.1 - 2.3 ppm (m, 16H). IR (neat): 3620 and 3480 cm^{-1} (ν OH). Anal. calc. for $C_{11}H_{20}O$: C, 78.5 ; H, 12.0. Found: C, 77.4 ; H, 12.0%.

Methyl 1-(1-methylcyclohexane)carboxylate (11b) was prepared in 75% yield from the methyl 1-cyclohexanecarboxylate following the reported procedure.[16]

1-(1-Methylcyclohexyl) cyclopentanol (12b): to a solution of 1,4-di(bromomagnesio)butane prepared from 6.48 g (30 mmol) of 1,4-dibromobutane and excess of magnesium 2.4 g (0.1 mg.at.) in 80 ml of anhydrous THF was added dropwise over 3 h a solution of 3.12 g (20 mmol) of methyl 1-methylcyclohexanecarboxylate (11b) in 40 ml of THF. The mixture was stirred a -12° for 1 h then a room temperature overnight. Hydrolysis as described for 12a and purification by chromatography on 125 g of silica gel (elution with pentane-ether (92:8) gave 2.91 g (80%) of 1-(1-methylcyclohexyl) cyclopentanol (12b). NMR (CCl_4) δ: 2.2 - 1.5 (m, 9 CH), 1.13 (s, OH) and 0.93 ppm (s, 3H). IR (neat): 3625 and 3480 cm^{-1} (ν OH). M.S. m/e (rel. intensity): 182 (M^+, 0.2), 164 ($M^+ - H_2O$, 8), 85 (100), 84 (46), 67 (67), 55 (65), 41 (58). Anal. calc. for $C_{12}H_{22}O$: C, 79.0 ; H, 12.2. Found: C, 88.2 ; H, 12.0%.

Dehydration and ring enlargement of 1-(1-methylcyclopentyl)cyclopentanol (12a): a mixture of 336 mg (2 mmol) of 12a and 2.4 g of anhydrous $FeCl_3$-SiO_2 reagent was stirred at 0° and then at 10° for 4 h. After filtration on Florisil 280 mg (93%) of 6-methylbicyclo[4.4.0] dec-1-ene (13) were obtained. NMR (CCl_4) δ : 5.35 (m, H), 2.5 - 1.0 (m, 14H) and 1.08 ppm (s, 3H). IR (neat) : 1662 ($\nu_{C=C}$). M.S. m/e,(rel. intensity): 150 (49.5), 135 (91.5), 121 (43), 108 (49), 107 (43), 91 (53.5), 79 (89), 77 (48), 67 (93), 55 (37), 41 (100). Analysis for $C_{11}H_{18}$: C, 87.9 ; H, 12.1. Found: C, 88.2 ; H, 12.0%.

Dehydration and ring enlargement of 1-(1-methylcyclohexyl) cyclopentanol (12b): to 364 mg (2 mmol) of 12b was added at 0° 2.4 g of anhydrous $FeCl_3$-SiO_2. Then the mixture was stirred at 0 - 10°C for 10 minutes, while the color turned deep green. Then the mixture was filtered through 6 g of Florisil eluted with 50 ml of pentane. The solvent was distilled to yield 308 mg of a mixture of 1-methyl spiro[5.5]undec-1-ene 14 and 7-methyl bicyclo[5.4.0]undec-1(11)-ene 15 and a third compound in 74, 12 and 6% yields respectively as shown by gas chromatography. The products were separated by preparative G.C. (D.C. 710, (3 m) at 155°. The spectral data of 14 were : NMR (CCl_4) δ : 5.31 (m, H), 2.3 - 0.8 (m, 16H) and 1.58 ppm (d, J = 2 Hz, 3H). IR (neat): 1660 ($\nu_{C=C}$). M.S.: m/e (rel. intensity): 164 M^+, 73.7), 121 (75), 107 (100), 93 (84.5), 79 (46). Anal. calc. for $C_{12}H_{20}$:C, 87.8 ; H, 12.3. Found: C, 87.8 ; H, 12.2. The spectral data of 15 were: NMR (CCl_4) δ : 5.30 (m, H), 2.8 - 1.0 (m, 16H) and 1.10 ppm (s, 3H). IR (neat) 1640 cm^{-1} ($\nu_{C=C}$). M.S. m/e (rel. intensity) 164 (M^+, 35), 149 (38), 121 (53), 108 (76), 93 (82), 81 (62), 79 (64), 67 (100), 55 (69), 43 (53). Anal. calc. for $C_{12}H_{20}$: C, 87.7 ; H, 12.3. Found: C, 87.7 ; H, 12.0%.

The mixture of 12b and $FeCl_3$-SiO_2, stirred at room temperature for 4 h led to 14 and 15 in 57 and 7% yield, respectively; 19% of a saturated compound (M = 166) being formed.

Unequivocal synthesis of 14 from 1-methylspiro[5.5]undecan-1-ol (17): to a solution of 4.98 g (30 mmol) of spiro[5.5]decan-1-one 16 17 in 40 ml of anhydrous ether cooled at -60° was added dropwise within 3 h, under an argon atmosphere, 27 ml of a 1.2 N solution of MeLi (33 mmol). The reaction mixture was stirred at -50° for 1 h and at room temperature overnight. After usual work up the residue was chromatographied on 220 g of silica gel; elution with hexane-ether (92:8) gave 4.48 g (82%) of 1-methylspiro[5.5]undecan-1-ol (17). NMR (CCl_4) δ: 2.2 - 0.8 (m, 18H), 1.2 (s, OH), 1.11 (s, 3H). IR (neat): 3620 and 3475 cm^{-1} (ν_{OH}). M.S. : m/e (rel. intensity): 182 (M^+, 19), 164 (M^+-H_2O, 65), 135 (85), 122 (85), 82 (64), 71 (92), 67 (67.8), 43 (100), 41 (84). Anal. calc. for $C_{12}H_{22}O$: C, 79.1 ; H, 12.2. Found: C, 78.3 ; H, 12.2%.

A solution of 364 mg (2 mmol) of 17 in 2ml of anhydrous DMSO [11] was heated at 160° for 3 h. Then the reaction product was extracted with ether and washed with 3 x 1 ml of water. The organic phase was dried over Na_2SO_4 and concentrated in vacuum to give 300 mg (91.5% yield) of a mixture of 4 and 15 in 85 and 13% ratio, with spectral data identical this those of the compounds 14 and 15 obtained from 12b.

A mixture of 364 mg (2 mmol) of 17 and 2.4 g of anhydrous $FeCl_3$-SiO_2 was stirred at 0° for 45 mn (as monitored by g.c. 70% of dehydration was obtained), then at room temperature for 4 h. After work-up was obtained a mixture of 14 and 15 in 73 and 19% yield, respectively, and 7% of saturated compounds (M^+ = 166).

Rearrangement of the (6-hydroxy spiro [4.5] decane)-acetic acid 19 and lactonisation to 20. A mixture of 414 mg (2 mmol) of 19 [20] and 2.4 g of anhydrous $FeCl_3$-SiO_2 reagent (containing 10% of $FeCl_3$ to improve the rate of the reaction) was stirred at room temperature for 60 h. Then, the product was filtered on 2 g of Florisil and eluted with ether to give 340 mg (88% yield) of the γ-propellalactone 20, with spectral data identical with those reported [20]. On heating 333 mg of 19 with 2 g of anh. $FeCl_3$-SiO_2 (10-90), at 40° for 3 hr, 265 mg of 20 (87% yield) were obtained.

Cleavage of the tetrahydropyranyl ethers 21. A mixture of 372 mg (2 mmol) of ether 21a and 2.4 g of $FeCl_3$-SiO_2 was stirred at room temperature. As monitored by tlc the reaction was completed within 45 h. Then, the solid was pourred into a column containing 2 g of florisil and the product eluted with 20 ml of ether to give, after solvant removal in vacuum, 240 mg (98.5% yield) of 1-hexanol 22a. On heating the mixture 21a+$FeCl_3$-SiO_2 at 40° for 90 min., 22a was obtained in 95% yield.

A mixture of 10 g (0.06 mole) of ether 21b and 72 g of anhydrous $FeCl_3$-SiO_2 was stirred in a flask for 4 days. The solid mixture was then poured into a column containing 20 g of florisil and the product was eluted with 200 ml of ether to give 4.6g (92% yield) of pratically pure 2-pentyn-1-ol 22b.

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