209. A Simple Alkylative 1,2-Carbonyl Transposition of Cyclohexenones

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Dedicated to Professor *H. H. Inhoffen* on his 70th anniversary

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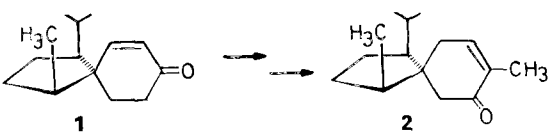
Summary. Acid catalysed dehydration of the diols **5**, derived from the cyclohexenone **3** affords mixtures of **8** and **11**. The product ratio **8**/**11**, although strongly dependent on both the reaction conditions and the substituent R, is independent of the diol configuration; this indicates a cationic intermediate **6**. Conditions were found, which allow the sequence **A** → **B** → **C** → **D** (*Scheme 2*) to be applied to the syntheses of the enones **8**, **21** and **25** in fair to good yields from the corresponding cyclohexenones **3**, **18** and **22**.

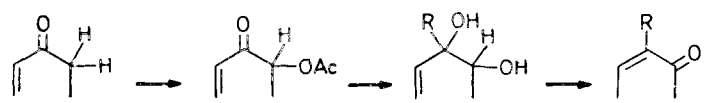
Recently we have reported a simple conversion of the cyclohexenone **1** to the spirosesquiterpene acorenone-B (**2**; *Scheme 1*) [1] using the sequence outlined in *Scheme 2* (**A** → **B** → **C** → **D**). The efficiency of the 1,2-enone transposition **1** → **2** compares favorably with an alternative approach requiring $Hg(OAc)_2$ promoted hydrolysis of a dienol thioether [2]. In view of the apparent potential of cyclohexenone transpositions in the synthesis and modification of terpenes and steroids[1]) it was decided to study the scope and limitations of this sequence.

Scheme 1



1 **2**

Scheme 2



A **B** **C** **D**

A first series of experiments investigates the conversion of 4,4-diphenyl-2-cyclohexenone (**3**) to the rearranged cyclohexenones **8** systematically introducing different substituents (R = CH_3, C_2H_5, *n*-C_4H_9, C_6H_5 and H) at the former site of the carbonyl

[1]) 6-Acetoxy-2-cyclohexenones have also been used to convert substituted 2-cyclohexenones to 5-cyclohexenones [3].

group (*Scheme 3*, Table 1). Acetoxylation of **3** with lead tetraacetate in boiling toluene afforded the acetate **4** (56%), which was converted to the diols **5** (94–98%) with the appropriate organometallic reagents. For example, reaction of **4** with methyllithium furnished a crystalline diol **5** (R = CH_3), which was dehydrated under various

Scheme 3

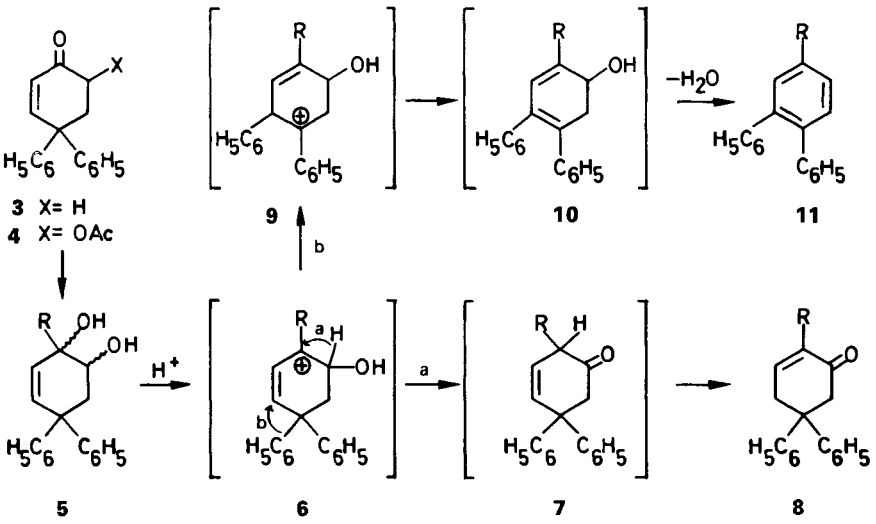


Table 1. *Acid catalysed dehydration of the diols* **5**

R	Configuration of **5**	Reaction conditions	Product ratio **8**/**11**	Isolated yield of **8**
CH_3	–	oxalic acid, 145°, 2 h	67:33 [a]	42%
CH_3	–	TsOH/C_6H_6, reflux, 2 h	97:3 [b]	90%
CH_3	–	MsOH/TFE, 25°, 15 min	70:30 [b]	–
CH_3	–	TsOH/sulfolane, 65°, 1 h	97:3 [b]	92%
C_2H_5	–	MsOH/TFE, –20 to –5°, 3 h	62:38 [b]	47%
C_2H_5	–	TsOH/C_6H_6, reflux, 0.5 h	20:80 [a]	18%
C_2H_5	–	TsOH/sulfolane, 25°, 12 h, then 60°, 0.5 h	93:7 [b]	52%
n-C_4H_9	–	TsOH/C_6H_6, reflux, 1.5 h	14:86 [a]	10%
n-C_4H_9	–	MsOH/TFE, –30 to –5°, 3 h	60:40 [b]	43%
n-C_4H_9	–	TsOH/sulfolane, 65°, 0.5 h	89:11 [b]	58%
C_6H_5	–	TsOH/C_6H_6, reflux, 2 h	–	48%
H	*cis* (73%)	TsOH/sulfolane, 70°, 2.5 h	53:47 [a] [b]	28%
H	*cis* (73%)	TsOH/C_6H_6, reflux, 1 h	58:42 [a]	38%
H	*trans* (90%)	TsOH/C_6H_6, reflux, 1 h	60:40 [a] [b]	46%

[a] Based on yields of isolated **8** and **11**.
[b] Determined by GC. analysis of crude reaction mixture.

acidic conditions (Table 1) to give the rearranged enone **8** (R = CH_3) together with variable amounts of the aromatic byproduct **11** (R = CH_3)[2]).

This acid catalysed dehydration presumably involves initial formation of an allylic carbenium ion **6** which undergoes a pinacol-type hydrogen shift (path a) (**6** → **7**), followed by migration of the olefinic bond (**7** → **8**). Evidently the carbenium ion **6** may also undergo a 1,2-phenyl shift (**6** → **9**) (path b) with subsequent deprotonation and dehydration (**9** → **10** → **11**)[3]).

Similarly, the diols **5** obtained by reaction of **4** with ethylmagnesium iodide, *n*-butyllithium, phenyllithium or sodium borohydride gave mixtures of **8** and **11**, whose ratio depends critically on the individual reaction conditions (Table 1). The diol **5** (R = CH_3) afforded with *p*-toluenesulfonic acid in boiling benzene or in sulfolane (= tetrahydrothiophen-1,1-dioxid) at 65° almost exclusively the enone **8** (90 to 92%). Sulfolane (at 65°) proved to be the solvent of choice for the *p*-toluenesulfonic acid catalysed reaction **5** → **8** when R = C_2H_5 (52%) and **5** → **8** when R = *n*-C_4H_9 (58%); however, the highest yields of the enones **8** (R = C_6H_5) (48%) and **8** (R = H) (46%) were obtained in refluxing benzene.

In order to investigate the possibility of stereochemical effects on the reaction **5** → **8** + **11** the *cis*- and *trans*-diols **5a** and **5b** (*Scheme 5*) were prepared selectively (in 73% and 90% configurational purity, respectively) by reduction of the acetate **4** with either lithium tri-*s*.-butylborohydride (L-selectride) or sodium borohydride. The configurational assignment of **5a** and **5b** is based on ^{1}H-NMR. spectral comparison of the corresponding disilylethers **16** and **17**. In analogy with shikimic acid [6] the coupling constants J_{BC} = 4.5 Hz and J_{CD} = 4.5 Hz indicate the *cis*-relationship of H_C and H_D in **16**, whereas the smaller coupling constant J_{BC} = 1.7 Hz and the larger one (J_{CD} = 7.5 Hz) correspond to the *trans* position of H_C and H_D in **17**. Under identical conditions, the *cis*- and *trans*-diol **5a** and **5b** both afforded the same 3:2 mixture of **8** and **11** (R = H)[4]) which was easily separated by chromatography (*cf.* Table 1). Hence it appears that the product ratio **8**/**11** is independent of the diol configuration, a fact which supports the postulated intermediacy of the carbenium ion **6**.

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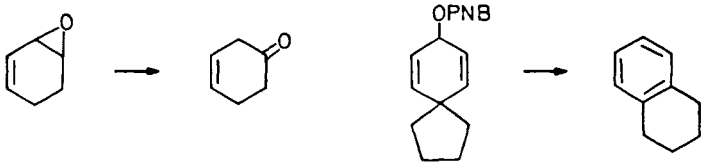
[2]) The assignment of structure **11** (R = CH_3) is based on IR., UV., ^{1}H-NMR. and mass spectra as well as on the analogous formation of **11** (R = H) from **5** under similiar acidic conditions (see footnote [4])).

[3]) The two reactions **6** → **7** and **6** → **11** resemble the previously described transformations **12** → **13** [4] and **14** → **15** [5], respectively.

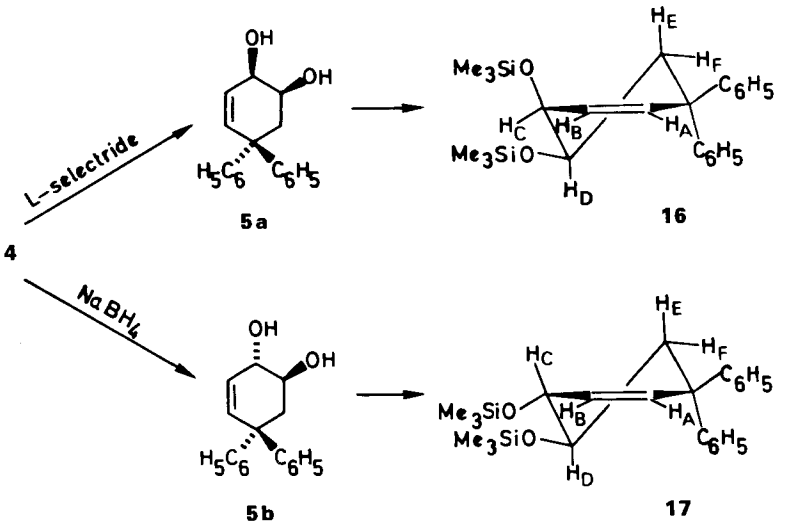
Scheme 4



12 **13** **14** **15**

[4]) The less polar aromatic product **11** (R = H) is identical with an authentic sample of *o*-terphenyl.

Scheme 5



In a second series of experiments, analogous transpositions were carried out on other cyclohexenone systems as described in *Scheme 6* and Table 2.

Scheme 6

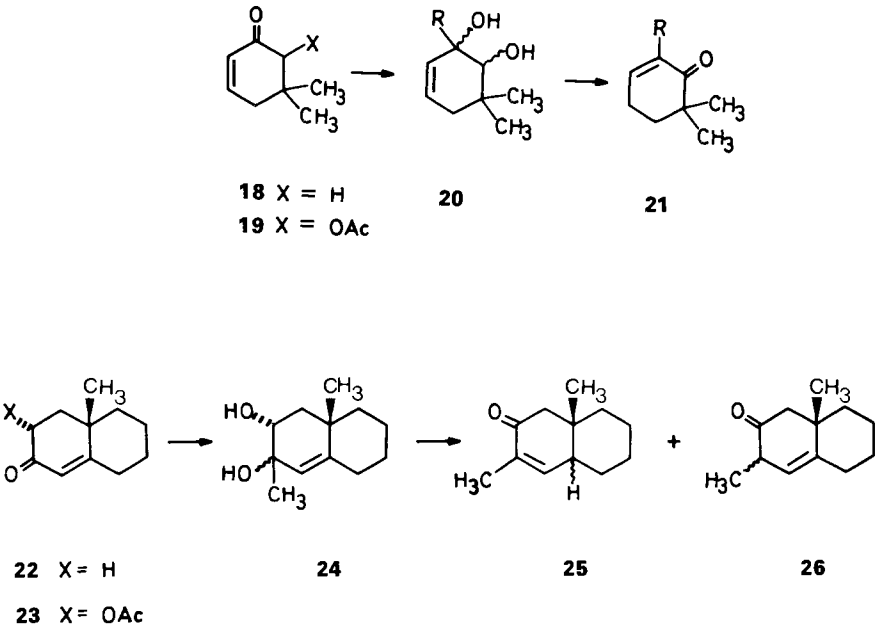


Table 2. *Acid catalysed dehydration of the diols* **20** *and* **24**

Diol		Reaction conditions	Product(s)		Yield[a]
20	(R = CH_3)	TsOH/C_6H_6, reflux, 15 min	**21**	(R = CH_3)	80%
20	(R = H)	TsOH/C_6H_6, reflux, 15 min	**21**	(R = H)	32%
24		MsOH/TFE, 25°, 1 h	**25**/**26** 9:1		31%
24		TsOH/C_6H_6, reflux, 2 h	**25**/**26** 3:1		54%

[a] Based on isolated product(s).

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Experimental Part

General remarks. The usual work-up of reaction mixtures involved addition of water, extraction with ether, washing of the organic layer with aqueous sodium hydrogencarbonate and H_2O, drying over anhydrous sodium sulfate and removal of the solvent *in vacuo*. Gaschromatograms (GC.): steel column (2 mm/2 m), 5% SE 30 on Chromosorb W, 220°, 2.5 atm N_2 unless specified otherwise; retention time in min. Preparative chromatography was carried out on silical gel (*Merck*, 0.05–0.20 nm). Melting points (m.p.) are not corrected. – UV. spectra: in ethanol; λ_{max} in nm, ε in parentheses. – IR. spectra: in CH_2Cl_2 unless specified otherwise; $\tilde{\nu}_{max}$ in cm^{-1}. – ^{1}H-NMR. spectra: in $CDCl_3$, internal standard tetramethylsilane (δ = 0 ppm); abbreviations: *s* = singlet, *d* = doublet, *t* = triplet, *q* = quartet, *m* = multiplet, *J* = spin-spin coupling constant (Hz). Mass spectra (MS.): *m/e*, relative peak intensity in % in parentheses.

6-Acetoxy-4,4-diphenyl-2-cyclohexenone (**4**). A mixture of 4,4-diphenyl-2-cyclohexenone (**3**) [7] (1.0 g, 4.03 mmol) and lead tetraacetate (5.0 g, 11.3 mmol) in dry toluene (25 ml) was heated under reflux for 14 h. The filtered solution was washed with aqueous sodium hydrogencarbonate, dried (Na_2SO_4) and evaporated. The viscous residue (1.5 g) afforded after chromatography (benzene/ethyl acetate 24:1) the crystalline acetate **4** (0.70 g, 56%) of m.p. 106–107° (ether/pentane). – IR.: 1750, 1705. – ^{1}H-NMR. (100 MHz): 2.16 (*s*, 3H); 2.6–3.2 (*m*, 2H); 5.45 (*d* × *d*, *J* = 5.5 and 12.5, 1H); 6.3 (*d*, *J* = 10, 1H); 7.1–7.6 (11H). – MS.: 306 (M^+, 2.3), 263 (9), 246 (100), 220 (25), 218 (27), 191 (25).

2-Methyl-5,5-diphenylcyclohex-3-ene-1,2-diol (**5**); *R* = CH_3. A solution of the acetate **4** (0.15 g, 0.49 mmol) in ether (15 ml) was added to a stirred 2.1 M solution of methyllithium in ether (3 ml, 6.3 mmol) under argon at – 78° during 0.5 h. The mixture was allowed to warm up to 0°, stirred for 0.5 h at 0°, for 12 h at 25°, refluxed for 2 h and quenched with aqueous ammonium chloride at 0°. Usual work-up and crystallization of the residue (ether/pentane) afforded the diol **5** (R = CH_3; 0.13 g, 95%), m.p. 135–140°. – IR.: 3595, 3450 br., no C=O. – ^{1}H-NMR. (90 MHz): 1.35 (*s*, 3H); 1.7–2.3 (OH, 2H); 2.3–2.5 (2H); 3.52 (*d* × *d*, *J* = 5 and 9, 1H); 5.87 (*d*, *J* = 10, 1H); 6.18 (*d*, *J* = 10, 1H); 6.9–7.5 (10H).

Acid catalysed dehydration of the diol **5** (*R* = CH_3). a) Molten oxalic acid dihydrate (2.5 g, 19.8 mmol) was added to the diol **5** (R = CH_3; 118 mg, 0.42 mmol). The mixture was heated to 140°–150° for 2 h. Usual work-up gave a viscous residue, which was chromatographed on silica gel (8 g). Elution with benzene afforded 3,4-diphenyltoluene **11**, R = CH_3; 23 mg, 22% as an oil, b.p. 100° (bath)/0.1 Torr. – GC.: single peak, retention time 3.53. – IR.: no OH, no C=O. – UV.: 235 (23980). – ^{1}H-NMR. (90 MHz): 2.42*s*, 3H; 6.9–7.3 (13H). – MS.: 244 (M^+, 100), 229 (50).

Further elution with benzene/ethyl acetate 19:1 afforded 2-methyl-5,5-diphenyl-2-cyclohexenone (**8**; R = CH_3; 47 mg, 42%): m.p. 82° (ether/pentane). – IR.: 1672. – GC.: single peak, retention time 6.12. – UV.: shoulder 234 (7420). – ^{1}H-NMR. (100 MHz): 1.72 (*s*, br. 3H); 3.17 (*m*, 2H); 3.24 (*s*, 2H); 6.74 (*m*, 1H); 7.0–7.4 (10H); irrad. at 1.72 → observation of *d* (*J* = 4) at 3.17, and *t* (*J* = 4) at 6.74; irrad. at 3.2 → observation of sharp *s* at 1.72, and broad *s* at 6.74. – MS.: 262 (M^+, 91), 180 (67), 165 (21), 82 (100).

b) A solution of the diol **5** (R = CH_3; 44 mg, 0,16 mmol) and *p*-toluenesulfonic acid monohydrate (30 mg) in benzene (5 ml) was heated under reflux for 2 h. Usual work-up gave a viscous residue which, after distillation at 120° (bath)/0.05 Torr afforded crystalline **8** (R = CH_3; 37 mg, 90%). – GC.: 97% pure.

c) Methanesulfonic acid (3 drops) was added to a solution of the diol **5** (R = CH_3; 10 mg) in trifluoro-ethanol (1 ml) at 25° and the mixture was stirred at 25° for 15 min. Usual work-up gave a pale yellow viscous residue (6 mg) which was shown, by GC. analysis, to contain **8** (R = CH_3) and **11** (R = CH_3) in the ratio of 7:3.

d) A solution of the diol **5** (R = CH_3; 50 mg, 0.18 mmol) and *p*-toluenesulfonic acid (25 mg) in sulfolane (5 ml) was heated at 65° for 1 h. Usual work-up and distillation of the residue at 140° (bath)/0.2 Torr afforded **8** (R = CH_3; 43 mg, 92%). – GC.: 97% **8** (R = CH_3), 3% **11** (R = CH_3).

2-Ethyl-5,5-diphenyl-2-cyclohexenenone (**8**; *R* = C_2H_5) *and 4-ethyl-1,2-diphenylbenzene* (**11**; *R* = C_2H_5). A solution of the acetate **4** (100 mg, 0.33 mmol) in dry ether (10 ml) was added to a stirred solution of ethyl magnesium iodide (0.4 ml, 5.0 mmol; prepared from ethyl iodide) at – 78°. The mixture was allowed to warm up to 25°, stirred for 12 h at 25°, heated under reflux for 1 h and quenched with aqueous ammonium chloride at 0°. Usual work-up afforded the diol **5** (R = C_2H_5) as a viscous oil (90 mg, 94%). – IR.: 3590, 3410 br.

a) Methanesulfonic acid (10 drops) was added to a stirred solution of the diol **5** (R = C_2H_5; 90 mg, 0.3 mmol) in trifluoro-ethanol (10 ml) at – 20°. The mixture was allowed to warm up to – 5° during 3 h. Usual work-up gave a viscous residue (90 mg) which was chromatographed on silica gel (10 g). Elution with toluene afforded 4-ethyl-1,2-diphenyl-benzene (**11**, R = C_2H_5; 15 mg, 19%) as a colourless oil, b.p. 135° (bath)/0.1 Torr. – GC.: single peak, retention time 4.54. – IR.: no OH, no C=O. – UV.: 235 (25800). – ^{1}H-NMR. (100 MHz): 1.33 (*t*, *J* = 7, 3H); 2.76 (*q*, *J* = 7, 2H); 7.0–7.5 (13H). – MS.: 258 (M^+, 100), 243 (38), 229 (45).

Further elution with toluene/ethyl acetate 19:1 furnished 2-ethyl-5,5-diphenyl-2-cyclohexenone (**8**; R = C_2H_5) as a pale yellow oil (40 mg, 47%), b.p. 135° (bath)/0.1 Torr. – GC.: single peak, retention time 7.65. – IR.: 1680. – UV.: shoulder 234 (6930). – ^{1}H-NMR. (100 MHz): 0.88 (*t*, *J* = 7, 3H); 2.15 (*q*, br., *J* = 7, 2H); 3.15 (*m*, 2H); 3.20 (*s*, 2H); 6.66 (*m*, 1H); 7.0–7.4 (10H). – MS.: 276 (M^+, 21), 180 (10), 165 (4), 96 (57), 58 (42), 43 (100).

b) A solution of the diol **5** (R = C_2H_5; 100 mg, 0.34 mmol) and *p*-toluenesulfonic acid monohydrate (30 mg) in benzene (10 ml) was heated under reflux for 0.5 h. Usual work-up afforded an oily residue which was chromatographed. Elution with benzene gave the less polar **11** (R = C_2H_5; 70 mg, 80%) and the more polar **8** (R = C_2H_5; 17 mg, 18%).

c) A solution of the diol **5** (R = C_2H_5; 115 mg, 0.39 mmol) and *p*-toluenesulfonic acid mono hydrate (60 mg) in sulfolane (5 ml) was stirred at 25° for 12 h and then at 60° for 0.5 h. Usual work-up afforded an oil (100 mg) which contained **8** (R = C_2H_5) and **11** (R = C_2H_5) in the ratio 93:7 (GC.). Chromatography (benzene/ethyl acetate 9:1) furnished pure enone **8** (R = C_2H_5; 56 mg, 52%).

*2-*n*-Butyl-5,5-diphenyl-2-cyclohexenone* (**8**; *R* = n-C_4H_9) *and 4-*n*-butyl-1,2-diphenylbenzene* (**11**; *R* = n-C_4H_9). A solution of the acetate **4** (100 mg, 0.33 mmol) in ether (10 ml) was added to a stirred 1.6M solution of *n*-butyllithium in hexane (0.84 ml, 1,34 mmol) at – 78°. The mixture was allowed to warm up to 25°, stirred for 12 h at 25° and quenched with aqueous ammonium chloride at 0°. Usual work-up afforded the diol **5** (R = *n*-C_4H_9) as a viscous oil. – IR.: 3595, 3450 br.

a) A solution of the diol **5** (R = *n*-C_4H_9; 100 mg, 0.31 mmol) and *p*-toluenesulfonic acid monohydrate (30 mg) in benzene (8 ml) was heated under reflux for 1 h. Usual work-up yielded an oil (100 mg) which was chromatographed. Elution with benzene and distillation at 140° (bath)/0.1 Torr afforded 4-*n*-butyl-1,2-diphenylbenzene (**11**; R = *n*-C_4H_9) as an oil (60 mg, 67%). – GC.: single peak, retention time 5.33. – IR.: no OH, no C=O. – UV.: 235 (27470). – ^{1}H-NMR. (100 MHz): 0.96 (*t*, *J* = 7, 3H); 1.2–1.9 (4H); 2.72 (*t*, *J* = 7, 2H); 7.0–7.5 (13H). – MS.: 286 (M^+, 54), 272 (11), 257 (8), 243 (69), 230 (100), 215 (28), 205 (15), 202 (13), 79 (92).

Further elution with benzene, followed by crystallization (pentane) yielded the 2-*n*-butyl-5,5-diphenyl-2-cyclohexenone (**8**, R = *n*-C_4H_9; 9 mg, 10%), m.p. 71–72°. – GC.: single peak, retention time 12.6. – IR.: 1675. – UV.: shoulder 232 (8470). – ^{1}H-NMR. (100 MHz): 0.80 (*t*,

J = 6, 3H); 0.9–1.4 (4H); 2.13 (t, J = 7, 2H); 3.17 (m, 2H); 3.22 (s, 2H); 6.67 (t, J = 4, 1H); 7.0–7.5 (10H). – MS.: 304 (M^+, 74), 226 (20), 180 (45), 165 (21), 124 (100), 109 (28).

b) A solution of the diol **5** (R = n-C_4H_9; 110 mg, 0.34 mmol) and of p-toluenesulfonic acid monohydrate (30 mg) in sulfolane (6 ml) was stirred at 65° for 0.5 h. Usual work-up afforded a yellow oil (100 mg) which was chromatographed. Elution with benzene gave an oil (10 mg), which was shown by GC. analysis to contain **11** (R = n-C_4H_9) and another nonidentified compound (retention time 8.49) in the ratio of 2:1. Further elution with benzene/ethylacetate 9:1 and distillation at 140°/0.1 Torr gave the enone **8** (R = n-C_4H_9; 60 mg, 58%; GC.: 99% pure).

c) Methanesulfonic acid (10 drops) was added to a solution of the diol **5** (R = n-C_4H_9; 110 mg, 0.34 mmol) in trifluoro-ethanol (8 ml) at – 30°. The mixture was stirred at – 30° for 2 h and then allowed to warm up to – 5°. Usual work-up afforded a pale yellow oil (90 mg), which was shown by GC. analysis to contain **8** (R = n-C_4H_9) and **11** (R = n-C_4H_9) in the ratio 3:2. Chromatography furnished the aromatic product **11** (R = n-C_4H_9; 22 mg, 25%) and the enone **8** (R = n-C_4H_9; 45 mg, 43%).

2,5,5-Triphenyl-2-cyclohexenone (**8**; $R = C_6H_5$). A solution of the acetate **4** (0.10 g, 0.33 mmol) in dry ether (10 ml) was added to a stirred 2.3 M solution of phenyllithium in benzene/ether 7:3 (0.55 ml, 1.26 mmol) at – 78° under argon. The mixture was allowed to warm up to 25°, stirred for 1 h at 25° and then refluxed for 1 h. Usual work-up furnished the crude diol **5** (R = C_6H_5; 0.195 g; IR.: 3600, 3350 br.) which was heated in refluxing benzene (10 ml) in the presence of p-toluenesulfonic acid monohydrate (0.30 g) for 2 h. Usual work-up furnished an oil (0.148 g), which on chromatography (benzene) afforded the enone **8** (R = C_6H_5; 0.051 g, 48%), m.p. 150–151° (ether/pentane). – IR.: 1680. – UV.: 265 (5150). – ^{1}H-NMR. (100 MHz): 3.3–3.5 (4H); 7.03 (t, J = 4.5, 1H); 7.26 (s, 15H). – MS.: 324 (M^+, 16), 178 (5), 165 (4), 144 (100), 116 (21).

cis-*5,5-Diphenylcyclohex-3-ene-1,2-diol* (**5a**). A solution of the acetate **4** (100 mg, 0.33 mmol) in dry THF (5 ml) was added to a stirred 1 M solution of L-selectride in THF (1 ml, 1.0 mmol) at – 78° during 10 min. The mixture was stirred at – 78° for 3 h and then allowed to warm up to 0°. Subsequent addition of 3 M aqueous sodium hydroxide (4 ml), 30% aqueous hydrogen peroxide (4 ml) and water (20 ml), extraction with water and evaporation of the washed (sat. Na_2CO_3 aqueous sodium carbonate) and dried ($MgSO_4$) extracts furnished a 73:27 mixture of the *cis*-diol **5a** and the *trans*-diol **5b** (GC. analysis after silylation) as a colourless oil (85 mg, 98%). – IR.: 3590, 3410 br.

cis-*3,3-Diphenyl-5,6-bis(trimethylsilyloxy)cyclohexene* (**16**). The 73:27 mixture of **5a** and **5b** (80 mg, 0.3 mmol), trimethylsilyl-acetamide (100 mg, 0.76 mmol) and hexane (8 ml) were heated under reflux for 1 h. Evaporation of the filtered mixture and distillation of the residue at 150° (bath)/0.1 Torr afforded an oil (90 mg, 71%), which by GC. and ^{1}H-NMR. analysis was shown to be the *cis*-silylether **16** (retention time 9.99), contaminated with 27% of its *trans*-isomer **17** (retention time 10.95). – ^{1}H-NMR. (100 MHz): – 0.04 (s, 9H, $3H_3C$—Si); 0.18 (s, 9H, $3H_3C$—Si); 2.14 (d, J = 12, 1H, H_F); 2.88 (t, J = 12, 1H, H_E); 3.72 (m, 1H, H_D); 4.1 ($d \times t$, J = 1.7 and 4.5, 1H, H_C); 5.9 ($d \times d$, J = 10 and 4.5, 1H, H_B); 6.18 ($d \times d$, J = 10 and 1.7, 1H, H_A); 7.1–7.5 (10H); irrad. at 2.88 → observation of $d \times d$ (J = 4.5 and 3.5) at 3.72. – MS.: no M^+, 395 ($M^+ - 15$, 6), 294 (72), 230 (100).

trans-*5,5-Diphenylcyclohex-3-ene-1,2-diol* (**5b**). Sodium borohydride (35 mg, 0.93 mmol) was added portionwise to a solution of the acetate **4** (100 mg, 0.33 mmol) in methanol (8 ml) at 25°. The mixture was stirred at 25° for 12 h, acidified with acetic acid at 0°, diluted with water and extracted with ether. Evaporation of the washed (sat. aqueous sodium carbonate) and dried extracts furnished a 9:1 mixture of the *trans*-diol **5b** and the *cis*-diol **5a** (GC. analysis after silylation) as a colourless oil. – IR.: 3595 and 3410 br.

trans-*3,3-Diphenyl-5,6-bis(trimethylsilyloxy)cyclohexene* (**17**). The 9:1 mixture of **5b** and **5a** (75 mg, 0.28 mmol), trimethylsilylacetamide (100 mg, 0.76 mmol) and hexane (8 ml) were treated as the 73:23 mixture (*cf.* above): 80 mg (74%) of an oil which was composed of 90% **17** (retention time 11.07) and 10% **16** (retention time 10.00). – ^{1}H-NMR. (100 MHz): 0.0 (s, 9H, $3H_3C$—Si); 0.2 (s, 9H, $3H_3C$—Si); 2.45 (m, 2H, H_E and H_F); 3.65 (q, J = 7.5, 1H, H_D); 4.23 ($d \times t$, J = 7.5 and 1.7, 1H, H_C); 5.72 ($d \times d$, J = 10 and 1.7, 1H, H_B); 6.06 ($d \times d$, J = 10 and 1.7, 1H, H_A); 7.0–7.5 (10H); irrad. at 2.45 → observation of d, (J = 7.5) at 3.65; irrad. at 3.65 → observation

of *s* at 2.45 and broad *s* at 4.23; irrad. at 4.23 → observation of *d*, (J = 10) at 5.72, and *d*, (J = 10) at 6.06. – MS.: no M^+, 395 (M^+ – 15, 4), 294 (46), 230 (100).

Acid catalysed dehydration of the diol **5b**. A solution of the *trans*-diol **5b** (90% pure, 100 mg, 0.38 mmol) and of *p*-toluenesulfonic acid monohydrate (60 mg) in benzene (10 ml) was heated under reflux for 1 h. Usual work-up gave a pale yellow oil, (100 mg) which was shown by GC. analysis to contain **8** (R = H) and **11** (R = H) in the ratio of 3:2. Chromatography with toluene afforded pure *o*-terphenyl **11**, R = H; (35 mg, 40%), m.p. 51–55° (pentane – 30°). Its identity with authentic material was confirmed by mixed m.p., GC., and UV. comparison. – GC.: single peak, retention time 2.58. – UV.: 233 (25990). – ^{1}H-NMR. (90 MHz): 7.18 (*s*, 10H); 7.40 (*s*, 4H). – MS.: 230 (M^+, 100).

Further elution with benzene/ethylacetate 9:1 furnished the pure 5,5-diphenyl-2-cyclohexenone **8**, R = H; (43 mg, 46%), m.p. 106–108° (ether/pentane). – GC.: single peak, retention time 5.47. – IR.: 1680. – ^{1}H-NMR. (100 MHz): 3.2 (*m*, 2H); 3.25 (*s*, 2H); 6.10 (*d* × *t*, J = 10 and 3, 1H); 7.02 (*d* × *t*, J = 10 and 4, 1H); 7.15–7.5 (10H); irrad. at 3.20 → observation of *d* (J = 10) at 6.10, and *d* (J = 10) at 7.02. – MS.: 248 (M^+, 52), 220 (4), 180 (100), 165 (20).

Acid catalysed dehydration of the diol **5a**. a) A solution of the diol **5a** (73% pure, 90 mg, 0.34 mmol) and *p*-toluenesulfonic acid monohydrate (60 mg) in benzene (10 ml) was heated under reflux for 1 h. Usual work-up afforded an oil (80 mg), which was chromatographed. Elution with benzene gave **11** (R = H; 23 mg, 28%). Further elution with benzene/ethylacetate 9:1 afforded the enone **8** (R = H; 32 mg, 38%).

b) A solution of the diol **5a** (73% pure, 60 mg, 0.23 mmol) and *p*-toluenesulfonic acid monohydrate (40 mg) in sulfolane (5 ml) was stirred at 70° for 2.5 h. Usual work-up gave an oil, which by GC. analysis was shown to contain **8** (R = H) and **11** (R = H) in the ratio of 53:47. Chromatography of the mixture afforded pure **11** (R = H; 15 mg, 27%) and pure **8** (R = H; 16 mg, 29%).

6-Acetoxy-5,5-dimethyl-2-cyclohexenone (**19**). A mixture of 5,5-dimethyl-2-cyclohexenone (**18**) [8] (0.70 g, 5.0 mmol) and 90% lead tetraacetate (4.5 g, 10.0 mmol) in dry benzene (10 ml) was refluxed under N_2 for 12 h. Usual work-up of the filtered solution afforded the acetate **19** (0.70 g, 77%), m.p. 92–93° (ether/pentane 1:1). – GC. (3 mm/3 m glass column, 5% OV 225, 160°): single peak, retention time 10.77. – IR. ($CHCl_3$): 1750, 1690. – ^{1}H-NMR. (100 MHz): 1.02 (*s*, 3H); 1.13 (*s*, 3H); 2.23 (*s*, 3H); 2.35–2.6 (2H); 5.3 (*s*, 1H); 6.10 (*d* × *d*, J = 10 and 2.7, 1H); 6.86 (*d* × *d* × *d*, J = 10, 5.5 and 2.7, 1H); irrad. at 2.45 → observation of *d* (J = 10) at 6.10 and *d* (J = 10) at 6.86. – MS.: 182 (M^+, 17), 140 (19), 122 (23), 114 (80), 72 (100).

2,6,6-Trimethyl-cyclohex-3-ene-1,2-diol (**20**; $R = CH_3$). A solution of the acetate **19** (0.182 g, 1.0 mmol) in ether (10 ml) was added to a stirred 1.5 M solution of methyllithium in ether (4 ml, 6 mmol) under argon at – 70° during 10 min. The mixture was allowed to warm up to 25° and quenched with aqueous ammonium chloride at 0°. Usual work-up afforded the diol **20** (R = CH_3) as a colourless amorphous solid (0.16 g, 100%). – IR. ($CHCl_3$): 3650–3590 br.

2,6,6-Trimethyl-2-cyclohexenone (**21**; $R = CH_3$). A solution of the diol **20** (R = CH_3; 0.312 g, 2.0 mmol) and *p*-toluenesulfonic acid monohydrate (0.10 g) in benzene (10 ml) was heated under reflux for 15 min. Usual work-up gave a mobile oil (0.240 g, GC.: 96% pure) which was chromatographed (pentane/ether 19:1) to give the pure enone **21** (R = CH_3; 0.220 g, 80%), b.p. 60–65° (bath)/10 Torr. – GC. (3 mm/3 m glass column, 5%/OV 225, 120°): single peak, retention time 6.44. – IR. ($CHCl_3$): 1675, 1630. – UV.: 236 (6000). – ^{1}H-NMR. (100 MHz): 1.1 (*s*, 6H); 1.7–2.0 (5H); 2.2–2.5 (2H); 6.65 (*m*, 1H); irrad. at 2.34 → observation of *s* at 6.65. – MS.: 138 (M^+, 20), 82 (100), 54 (20).

6,6-Dimethyl-cyclohex-3-ene-1,2-diol (**20**; $R = H$). A solution of $AlCl_3$ (1.1 g, 8.0 mmol) in dry ether (15 ml) was added dropwise to a stirred solution of $LiAlH_4$ (0.80 g, 21 mmol) in ether (20 ml) at 0° during 10 min. The solution was stirred at 25° for 0.5 h and then added (using a hypodermic syringe) to a stirred solution of the acetate **19** (1.0 g, 6.0 mmol) in ether (15 ml) at – 20° during 10 min. The mixture was allowed to warm up (during 40 min) to 25°, was stirred at 25° for 1 h and quenched by subsequent addition of water/ether 3:1 (4 ml), 2 N aqueous sodium hydroxide (1 ml) and water (2 ml). The filtered solution was washed (sat. aqueous sodium chloride), dried and evaporated to give the diol **20** (R = H) as an oil, (0.80 g, 100%). – IR. (film): 3500–3440 br.

Reduction of **19** with either $LiAlH_4$ or L-selectride gave the saturated diol.

6,6-Dimethyl-2-cyclohexenone (**21**; *R* = *H*). A solution of the diol **20** (R = H; 0.60 g, 4.2 mmol) and *p*-toluenesulfonic acid monohydrate (0.20 g) in benzene (15 ml) was heated under reflux for 15 min. Usual work-up followed by distillation at 70–75° (bath)/10 Torr afforded the crude enone **21** (R = H) as a colourless oil (0.160 g, 32%). – GC. (OV 225/120°): retention time 4.41 (89%) and 5.39 (10%). An analytical sample was isolated from prep. GC. (10%, OV 225/120°). – IR. (film): 1675, 1630. – UV.: 228 (10000). – ^{1}H-NMR. (100 MHz): 1.13 (*s*, 6H); 1.85 (*t*, *J* = 6, 2H); 2.3–2.5 (2H); 5.97 (*d* × *t*, *J* = 10 and 2, 1H); 6.88 (*d* × *t*, *J* = 10 and 4, 1H); irrad. at 2.4 → observation of *s* at 1.85, *d* (*J* = 10) and *d* (*J* = 10) at 6.88. – MS.: 124 (M^+, 13), 68 (100).

4-Acetoxy-6-methyl-bicyclo[4.4.0]dec-1(2)-en-3-one (**23**). A mixture of 6-methyl-bicyclo[4.4.0]-dec-1(2)-en-3-one (**22**) [9] (5.0 g, 30 mmol) and lead tetraacetate (26.8 g, 60 mmol) in dry toluene (50 ml) was heated under reflux for 7 h. Usual work-up of the filtered solution followed by distillation afforded the acetate **23** (4.3 g, 64%), b.p. 108–109°/0.2 Torr, m.p. 105–106° (ether/petroleum ether). – GC. (2 mm/4 m steel column, 5% FFAP, 230°): single peak, retention time 10.76. – IR.: 1740, 1690, 1625. – ^{1}H-NMR. (100 MHz): 1.40 (*s*, 3H); 2.08 (*s*, 3H); 1.2–2.4 (10H); 5.35 (*d* × *d*, *J* = 11.5 and 7.5, 1H); 5.64 (*s*, 1H). – MS.: 222 (M^+, 6), 180 (9), 162 (2), 136 (100), 121 (30).

1,4-Dimethyl-bicyclo[4.4.0]dec-4-en-3-one (**25**) *and 1,4-dimethyl-bicyclo[4.4.0]dec-5-en-3-one* (**26**). A solution of the acetate **23** (100 mg, 0.45 mmol) in ether (10 ml) was added to a stirred 2.1 M solution of methyllithium in ether (3.5 ml, 7.35 mmol) under argon at – 78° during 10 min. The mixture was allowed to warm up to 25°, stirred at 25° for 1 h, refluxed for 2 h and quenched with aqueous ammonium chloride at 0°. Usual work-up afforded the diol **24** (85 mg, 96%). – IR.: 3600–3400 br.

a) Methanesulfonic acid (4 drops) was added to a solution of the diol **24** (35 mg, 0.18 mmol) in trifluoro-ethanol (1 ml) at 25° and the mixture was stirred at 25° for 1 h. Usual work-up and distillation at 100° (bath)/0.2 Torr afforded a nonseparable 7:1 mixture of **25** and **26** (10 mg, 32%). – GC. (5% OV 225, 190°): 2 peaks, retention time 5.74 (86%) and 6.66 (12%). – ^{1}H-NMR. (100 MHz) of *cis*-(**25**): 1.04 (*s*, 3H); 1.8 (*s*, br. 3H); 1.0–2.7 (11H); 6.5 (*m*, 1H); irrad. at 1.8 → observation of *d* (*J* = 4) at 6.5. – ^{1}H-NMR. (100 MHz) of *trans*-(**25**): 0.9 (*s*, 3H); 1.8 (*s*, br. 3H); 1.0–2.7 (11H); 6.34 (*m*, 1H); irrad. at 1.8 → observation of *d* (*J* = 2) at 6.34. A weak *m* at 5.9 which collapsed to a *s* on irradiation at 2.3 was assigned to the olefinic proton of **26**. Integration indicated a product ratio *cis*-**25**/*trans*-**25**/**26** of 6:3:1. For the configurational assignment of **25** see [10].

b) A solution of the diol **24** (45 mg, 0.23 mmol) and *p*-toluenesulfonic acid monohydrate (30 mg) in benzene (8 ml) was heated under reflux for 2 h. Usual work-up followed by distillation at 100°/0.2 Torr furnished a 3:1 mixture of **25** and **26** (22 mg, 54%). – GC. (5% OV 225, 190°): 2 peaks, retention time 5.74 (63%) and 6.66 (23%).

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