9. The Synthesis of Cycloalkenes by the Intramolecular *Wittig* Reaction[1])

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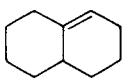
(4. X. 76)

Summary

A simple synthesis of a series of bicyclo[m.n.0]-1-alkenes (m, n = 3, 4, 5) from 2-oxocycloalkanecarboxylates by the intramolecular *Wittig* reaction is reported (see p. 70–72). The spectral properties (IR., ^{1}H-NMR. and ^{13}C-NMR.) of these annulated trisubstituted olefins are discussed.

Introduction. – Isomerically pure samples of the bicyclic olefins **1**, **2** and **3** were required to identify the solvolysis products of bridgehead chlorides [1]. Bicyclo-[4.4.0]-1(2)-decene(= $\Delta^{1,9}$-octalin; **1**) containing variable amounts of the 2- and 1(6)-isomer was synthesized previously by elimination of water from 2-bicyclo[4.4.0] decanol [2]. The hydrindenes **2** and **3** were minor components of a product mixture obtained upon *Wolff-Kishner* reduction of the hydrindenone **4**. The olefins **2** and **3** had to be separated by column chromatography, and their identification rested on rather insecure spectroscopic evidence [3].



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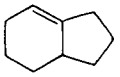

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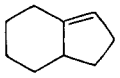

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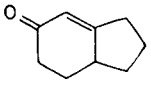


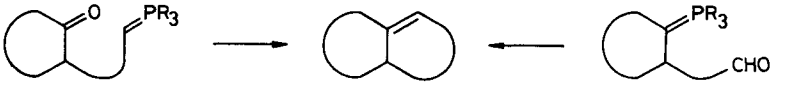
4

Therefore, a general synthetic approach was sought that would produce these trisubstituted annulated olefins in isomerically pure form and in good yield. In the past few years, many new methods have been developed for the stereospecific and regiospecific synthesis of the olefinic double bond [4]. Whereas elimination reactions with compounds bearing one functional group at the bridgehead or in α to the bridgehead yield mixtures of isomers, such reactions of vicinal difunctional compounds **5**, *e.g.* diols [5], dihalides [6], halohydrins [7], or hydroxycarboxylic acids [8], should give the olefin **6** in isomerically pure form. These difunctional compounds **5**, however, are not generally accessible by simple routes.

[1]) Taken in part from the 'Habilitationsschrift' of *K. B. Becker*, Basel 1976.

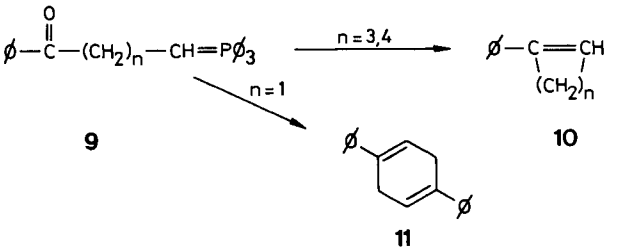
5 **6**

An intramolecular *Wittig* reaction of a ketophosphorane **7** or an aldehydephosphorane **8** is expected to yield the olefin **6** *via* an intermediate zwitterion of type **5** (X, Y = R_3P^+, O^-). The *Wittig* reaction is known to give olefins in high purity under conditions where no isomerization is observed [9]. In the intramolecular version complications could arise due to enolization or other base-catalysed side reactions of the carbonyl function; however, these turned out to be unimportant under appropriate reaction conditions. The ketophosphoranes **7** can easily be prepared from the corresponding ω-bromoalkylketones which are readily available by classical synthetic procedures.



7 **6** **8**

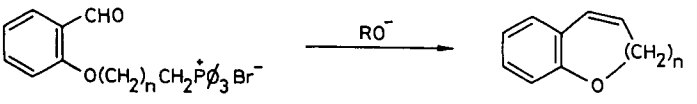
The intramolecular *Wittig* reaction. – The first example of an intramolecular *Wittig* reaction was reported in 1962 [10] [11]. The phosphoranes **9** (n = 3,4), obtained from the corresponding phosphonium bromides with sodium ethoxide or butyllithium, gave 1-phenylcyclopentene (**10**, n = 3) and 1-phenylcyclohexene (**10**, n = 4), albeit in low yield. 1-Phenylcyclobutene (**10**, n = 2) was not formed, and with n = 1, an *inter*molecular *Wittig* reaction yielding 1,4-diphenylcyclohexadiene (**11**) occurred.



9 **10**

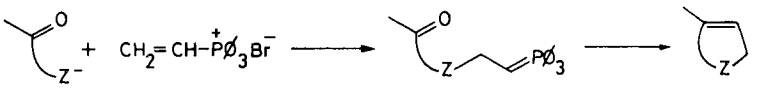
11

A great number of examples of intramolecular *Wittig* reactions have been reported by *Schweizer et al.* The *o*-hydroxybenzaldehyde derivatives **12** were cyclized to benzopyran (**13**, n = 1), dihydrobenzoxepin (**13**, n = 2), and dihydrobenzoxocin (**13**, n = 3) with an eight-membered ring [12].

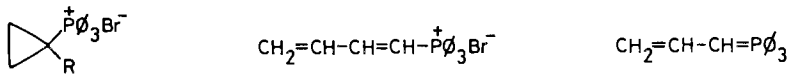


12 **13**

A ketophosphorane **16** suitable for cyclization can also be formed *in situ* by nucleophilic addition of substituted ketones **14** to vinyltriphenylphosphonium bromide (**15**). This reaction has been applied to the synthesis of dihydrofurans (Z = O) [13], dihydrothiophenes and dihydrothiopyrans (Z = S) [14], cyclic unsaturated malonic esters (Z = C(COOEt)$_2$) [15], dihydroquinolines (Z = NR) [16], and other heterocycles [17]. Similar reactions are observed on nucleophilic additions of keto-enolates to the cyclopropylphosphonium bromide **17** [18], or to the vinylogue of **15**, butadienyltriphenylphosphonium bromide (**18**) [19].



14 **15** **16**



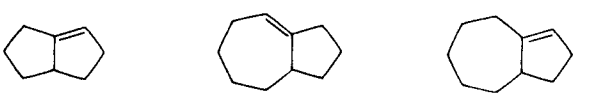
17 **18** **19**

(R = H, COOEt)

Cyclohexadienes are formed on addition of propenylidenephosphorane **19** to α,β-unsaturated ketones [20]. The intramolecular *Wittig* reaction has also been applied to the synthesis of an unsaturated *meta*-cyclophane [21], the construction of the thiazine ring in a cephemic acid derivative [22], and the formation of cyclopentenones and cyclohexenones from enollactones [23]. Intramolecular applications of the related *Horner-Wadsworth-Emmons* reaction using phosphonates in place of phosphoranes are also known [24].

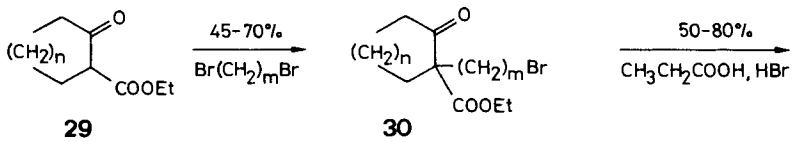
From the above examples one can conclude that the intramolecular *Wittig* reaction should give an easy and direct access to annulated trisubstituted olefins of type **6**. The aim of this work was to find optimum conditions, and overcome limitations of the reaction in view of its application to the synthesis of strained bridgehead olefins [25].

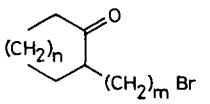
Syntheses. – The intramolecular *Wittig* reaction was applied to the synthesis of bicyclo[4.4.0]-1(2)-decene(=$\Delta^{1,9}$-octalin; **1**) [2], the hydrindenes bicyclo[4.3.0]-1(2)-nonene (**2**) and bicyclo[4.3.0]-1(9)-nonene (**3**) [3], bicyclo[3.3.0]-1(2)-octene (**20**) [26], and the two new octahydroazulenes bicyclo[5.3.0]-1(2)-decene (**21**) and bicyclo[5.3.0]-1(10)-decene (**22**).



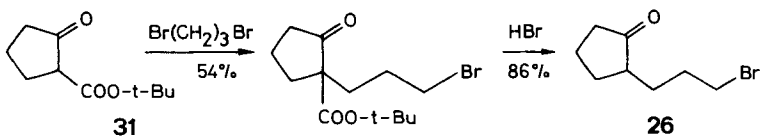
20 **21** **22**

The prerequisite ω-bromoalkylketones **23–28** were prepared following a general method of *Mayer* [27] and *Christol* [28]. Ethyl 2-oxocyclopentanecarboxylate (**29**, n = 1), ethyl 2-oxocyclohexanecarboxylate (**29**, n = 2), and ethyl 2-oxocycloheptanecarboxylate (**29**, n = 3) were alkylated as their potassium salts with an excess of α,ω-dibromoalkanes in toluene. The bromoalkyl-β-ketoesters **30** were hydrolysed and decarboxylated with concentrated hydrobromic acid in propionic acid at reflux temperature. The yields for the alkylation, hydrolysis and decarboxylation are only moderate and could not be raised by other reaction conditions [29]. *t*-Butyl 2-oxocyclopentanecarboxylate (**31**) [30] was alkylated as well as the ethyl ester **29** (n = 1), but was hydrolysed under milder conditions and with better yields.



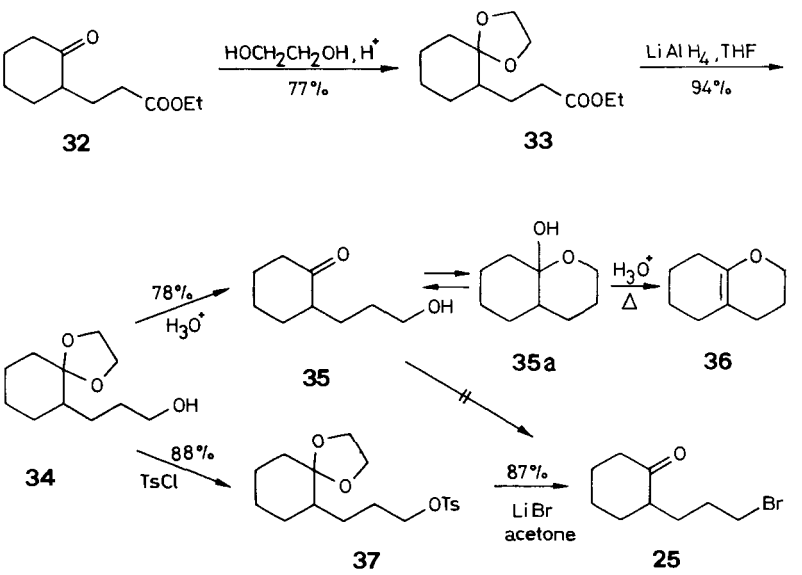


23 n = 2, m = 4 **26** n = 1, m = 3
24 n = 1, m = 4 **27** n = 1, m = 5
25 n = 2, m = 3 **28** n = 3, m = 3

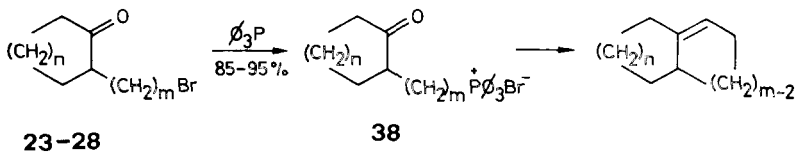


An alternative synthesis was developed for the ketobromide **25**. Ethyl 3-(2-oxocyclohexyl)propionate (**32**) [31] was transformed into the acetal **33** with ethylene glycol, and then reduced to the hydroxyacetal **34** with lithiumaluminiumhydride in tetrahydrofuran. Careful hydrolysis gave the hydroxyketone **35**, which in solution is in equilibrium with its hemiacetal **35a**, the isomer obtained upon crystallization. Prolonged treatment with acid or heat yielded the cyclic enol ether **36** [32]. Attempts to convert the alcohol **35** directly to the bromide **25** met with limited success. If, however, hydroxyacetal **34** was transformed into the *p*-toluenesulfonate **37**, and the latter treated with a large excess of lithium bromide in acetone [33], a bromine atom was introduced and the acetal protecting group cleaved in one step with formation of 2-(3-bromopropyl)cyclohexanone (**25**) in good yield.

The reaction of the bromoalkylcycloalkanones **23–28** with triphenylphosphine in ethyl ether or without solvent at 100–120° gave the corresponding extremly hygroscopic phosphonium bromides **38**, usually as non-crystalline solids. The crude ketophosphonium bromides **38** were added to a solution of dimethyl sulfoxide anion in dimethyl sulfoxide [34], and the deep-red solution of the resulting ketophosphoranes



warmed to 80°. The olefins **1–3**, **20** and **22** were isolated in yields of 50–65% by steam distillation at reduced pressure. The formation of the seven-membered ring of bicyclo-[5.3.0]-1(2)-decene (**21**) was accomplished in 19% yield under identical conditions. Cyclization was also realized with lithium ethoxide in dimethylformamide [35], sodium 2-methyl-2-butoxide in tetraethylene glycol dimethyl ether [25], butyllithium in a mixture of ethyl ether and tetrahydrofuran, or with potassium in hexamethyl-phosphoric acid triamide [36]. The reaction with sodium amide in ammonia gave little olefin. Moderate yields could be obtained in the two-phase system methylene chloride and aqueous sodium hydroxide [37].



The olefins were obtained analytically pure after redistillation, and no traces of isomeric olefins could be detected. Yields of 50–65% would seem moderate, however, they lie well within the range of the yields obtained in *inter*molecular *Wittig* reactions between phosphoranes and ketones [9].

Spectral properties of the olefins. – With the aim of assessing strain in bridgehead olefins from spectral properties [25] the IR., ^{1}H-NMR. and ^{13}C-NMR. spectra of the annulated olefins **1–3**, **20–22**, and the corresponding 1-methylcycloalkenes **39–41** were measured (Table 1).

Table 1. *Spectral properties of annulated bridgehead olefins and 1-methylcycloalkenes*

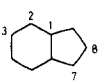
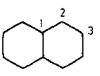
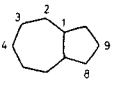
		 **1**	 **2**	 **3**	 **20**	 **21**	 **22**	 **39**	 **40**	 **41**
IR. spectrum	C=C	1666	1675	1660	1663	a)	1640	1659	1672	a)
(film, $\tilde{\nu}_{(max)}$ in cm^{-1})	=C–H	3048	3050	3042	3052	3042	3042	3047	3043	3048
		802	787, 858	793	790	829	799, 788	786	791	841
^{1}H-NMR. spectrum	=C–*H*	5.22	5.28	5.15	5.17	5.59	5.27	5.25	5.31	5.46
(CCl_4, δ in ppm)										
Halfwidth (in Hz)		8	7	4	7	14	7	7	8	b)
^{13}C-NMR. spectrum	=*C*H–	119.1	116.8	119.9	117.6	121.1	124.2	124.2	121.4	125.7
($CDCl_3$, δ in ppm)	=*C*<	140.9	144.8	145.9	154.5	150.7	149.9	140.1	133.9	140.3
	–*C*H<	37.4	40.9	45.7	52.5	44.4	48.3	–	–	–

a) Not observed.
b) Broad triplet J = 6 Hz.

The IR. spectrum shows a very weak C=C stretching absorption in the expected range of 1660–1675 cm^{-1} [38]. Neither the =C–H stretching absorption (3040–3050 cm^{-1}) nor the =C–H out-of-plane deformation (around 800 cm^{-1}) points to a dependence of the wavelength on ring size.

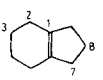
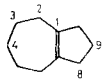
In the ^{1}H-NMR. spectrum the vinylic proton of a cyclopentene derivative resonates at higher field than that of a cyclohexene or a cycloheptene. This sequence is found in the bicyclic olefins as well as in the simple methylcycloalkenes. The peak width, however, does not follow a uniform pattern. It is the result of subtle changes in geometry around the adjacent bonds, and is not simply rationalized [39].

Table 2. *^{13}C-NMR. spectra of saturated bicyclic hydrocarbons*

	 *cis*-**42**	 *cis*-**43**	*trans*-**44**	 *cis*-**45**[a]	*trans*-**46**[a]	 *cis*-**47**	*trans*-**48**
C(1)	43.3	39.6	47.0	36.9	44.2	43.6	46.5
C(2)	34.3	29.7[b]	32.3[b]	29.8	34.8	35.9[b]	35.3[b]
C(3)	26.4	23.7	27.0	24.6	27.2	29.8	28.1
C(4)						31.8[c]	26.8[c]
C(7)		27.9[b]	31.6[b]				
C(8)		22.4	22.0			33.1[b]	34.5[b]
C(9)						26.6[c]	24.1[c]

a) Data from ref. [42].
b)c) Assignments may be interchanged.

Table 3. *^{13}C-NMR. spectra of tetrasubstituted annulated olefins*

				
	49	**50**	**51**	**52**
C(1)	146.0	133.9	127.6	137.2
C(2)	29.2	36.0	30.6	40.0
C(3)	28.4	23.2[a])	23.5	30.1[a])
C(4)				30.7
C(7)		25.8[a])		
C(8)		21.7		27.7[a])
C(9)				22.4

[a]) These assignments may be interchanged.

Inspection of the ^{13}C-NMR. spectra yields no clear-cut picture. The unsaturated bridgehead carbon atom resonates in the range of 140–151 ppm (downfield from tetramethylsilane) except in the case of bicyclo[3.3.0]-1(2)-octene (**20**). The high value of 154.5 ppm for C(1) in **20** possibly reflects the strain in this compound [40]. The chemical shift of the saturated bridgehead carbon atom lies between 37 and 48 ppm, except for **20** (52.5 ppm). No anomaly is found with the vinylic carbon atom, which resonates in the range of 116 to 124 ppm. A comparison with calculated chemical shifts derived from acyclic olefins, alkylcyclopentenes, alkylcyclohexenes [41], the saturated hydrocarbons *cis*-bicyclo[3.3.0]octane (**42**), *cis*- and *trans*-hydrindane (**43** and **44**), *cis*- and *trans*-decalin (**45** and **46**), and *cis*- and *trans*-bicyclo[5.3.0]decane (**47** and **48**) shows no good correlation (Table 2).

At the present time the influence of the ring geometry on the ^{13}C shieldings in bicyclic unsaturated systems is not well understood, and additional evidence on the effect of stereochemical changes is needed. Generally, a bridgehead carbon atom incorporated in a six-membered ring resonates at higher field than a bridgehead carbon atom which is part of a five-membered or a seven-membered ring. This statement is also true for the tetrasubstituted annulated olefins **49–52** (Table 3).

Financial support from *Ciba-Geigy AG* is greatfully acknowledged. I thank Prof. *C. A. Grob* for his encouragement and continuous interest in this work.

Experimental Part

General remarks. – Melting points (m.p.) are corrected, boiling points (b.p.) are not corrected. IR. spectra were recorded on a *Perkin-Elmer* 177, and are given in cm^{-1}. The ^{1}H-NMR. spectra at 60 MHz were measured on a *Varian* EM 360, the ^{1}H-NMR. spectra at 90 MHz and the ^{13}C-NMR. spectra at 22.63 MHz on a *Bruker* WH-90 *Fourier* transform spectrometer by Mr. *K. Aegerter*. The chemical shift values are in ppm relative to tetramethylsilane (TMS) as an internal standard ($\delta = 0$), and the coupling constants J in Hz. The multiplicity is abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Gas liquid chromatography (GLC.) analyses were carried out on a *Perkin-Elmer* F 11 or 3920, separations on the *Perkin-Elmer* 3920. UV. spectra were measured on a *Beckmann* DK 2, the wave length λ(max) is given in nm, followed by the extinction

coefficient log ε in brackets. Mass spectra were recorded by Mr. *A. Raas* on a *AEI*-MS 30 at 70 eV. Elemental analyses were carried out by Mr. *E. Thommen*. Abbreviations: *i. V.* = *in vacuo*, RT. = room temperature.

General procedure for the alkylation of ethyl or t-butyl 2-oxocyclopentanecarboxylate, ethyl 2-oxocyclohexanecarboxylate, and ethyl 2-oxocycloheptanecarboxylate with α,ω-dibromoalkanes exemplified by *ethyl 1-(3-bromopropyl)-2-oxocyclohexanecarboxylate* (**30**, n = 2, m = 3). 25.5 g (0.15 mol) of ethyl 2-oxocyclohexanecarboxylate were slowly added to a suspension of 5.50 g (0.141 mol) of finely divided potassium in toluene, then stirred for 2 h. 87.5 g (0.433 mol) of 1,3-dibromopropane were added and the solution heated under reflux for 20 h. The solid potassium bromide was filtered off, the filtrate washed with water, and dried over $MgSO_4$. The distillation gave 23.1 g (56%) of **30** as a colourless liquid, b.p. 102–108°/0.1 Torr. – IR. (film): 2940, 1715 (C=O), 1297, 1240, 1092, 1025. – ^{1}H-NMR. (CCl_4): 1.2–2.6 (*m*, 12H, 6 CH_2); 1.30 (*t*, 3H, CH_3); 3.38 (*m*, 2H, CH_2Br); 4.20 (*q*, 2H, OCH_2).

$C_{12}H_{19}BrO_3$ (291.19) Calc. C 49.49 H 6.58 Br 27.44% Found C 49.67 H 6.38 Br 27.11%

Ethyl 1-(4-bromobutyl)-2-oxocyclohexanecarboxylate. Yield 72%, b.p. 120–122°/0.08 Torr. – IR. (film): 2950, 1718 (C=O), 1215, 1100, 1032. – ^{1}H-NMR. (CCl_4): 1.2–2.5 (*m*, 14H, 7 CH_2); 1.28 (*t*, 3H, CH_3); 3.40 (*t*, 2H, CH_2Br); 4.20 (*q*, 2H, CH_2O).

$C_{13}H_{21}BrO_3$ (305.22) Calc. C 51.15 H 6.94 Br 26.18% Found C 51.13 H 6.88 Br 26.42%

Ethyl 1-(4-bromobutyl)-2-oxocyclopentanecarboxylate. Yield 61%, b.p. 117–118°/0.06 Torr ([27]: 144–147°/2 Torr). – IR. (film): 2960, 1752, 1725 (C=O), 1262, 1228, 1030. – ^{1}H-NMR. (CCl_4): 1.2–2.6 (*m*, 12H, 6 CH_2); 1.25 (*t*, 3H, CH_3); 3.38 (*t*, 2H, CH_2Br); 4.13 (*q*, 2H, CH_2O).

Ethyl 1-(3-bromopropyl)-2-oxocyclopentanecarboxylate. Yield 47%, b.p. 85–88°/0.03 Torr. – IR. (film): 2980, 1752, 1728 (C=O), 1232, 1028. – ^{1}H-NMR. (CCl_4): 1.4–2.6 (*m*, 10H, 5 CH_2); 1.25 (*t*, 3H, CH_3); 3.36 (*t*, 2H, CH_2Br); 4.13 (*q*, 2H, CH_2O).

$C_{11}H_{17}BrO_3$ (277.17) Calc. C 47.67 H 6.18 Br 28.83% Found C 47.88 H 6.21 Br 28.78%

Ethyl 1-(5-bromopentyl)-2-oxocyclopentanecarboxylate. Yield 50%, b.p. 109–110°/0.18 Torr. – IR. (film): 2940, 1753, 1728 (C=O), 1224, 1030. – ^{1}H-NMR. (CCl_4): 1.0–2.6 (*m*, 14H, 7 CH_2); 1.25 (*t*, 3H, CH_3); 3.35 (*t*, 2H, CH_2Br); 4.13 (*q*, 2H, CH_2O).

$C_{13}H_{21}BrO_3$ (305.22) Calc. C 51.15 H 6.94 Br 26.18% Found C 51.40 H 6.94 Br 26.25%

Ethyl 1-(3-bromopropyl)-2-oxocycloheptanecarboxylate. Yield 68%, containing *ca.* 15% of *O*-alkylated product. Fractional distillation gave 37% of the *C*-alkylated β-ketoester in 97% purity, b.p. 120–123°/0.04 Torr. – IR. (film): 2935, 1710 (br., C=O), 1222, 1145, 1018. – ^{1}H-NMR. (CCl_4): 1.2–2.5 (*m*, 14H, 7 CH_2); 1.27 (*t*, 3H, CH_3); 3.38 (br.*s*, 2H, CH_2Br); 4.19 (*q*, 2H, OCH_2).

$C_{13}H_{21}BrO_3$ (305.22) Calc. C 51.15 H 6.94 Br 26.18% Found C 51.40 H 7.18 Br 25.98%

t-*Butyl 1-(3-bromopropyl)-2-oxocyclopentanecarboxylate*. Yield 54%, b.p. 110–113°/0.10 Torr. – IR. (film): 2975, 1750, 1726 (C=O), 1370, 1248, 1145, 845. – ^{1}H-NMR. (CCl_4): 1.2–2.5 (*m*, 10H, 5 CH_2); 1.42 (*s*, 9H, 3 CH_3); 3.35 (*t*, 2H, CH_2Br).

$C_{13}H_{21}BrO_3$ (305.22) Calc. C 51.15 H 6.94 Br 26.18% Found C 51.42 H 7.19 Br 26.03%

General procedure for the hydrolysis and decarboxylation of ethyl 1-(ω-bromoalkyl)-2-oxocycloalkanecarboxylate (30) exemplified by *2-(3-bromopropyl)cyclohexanone* (**25**). 33.7 g (0.116 mol) of ethyl 1-(3-bromopropyl)-2-oxocyclohexanecarboxylate (**30**, n = 2, m = 3) in propionic acid (100 g) and 48% aqueous hydrobromic acid (35 g) were heated under reflux for 6 h, while a slow flow of hydrogen bromide was bubbled into the solution. The cooled solution was poured on ice, neutralized with solid sodium carbonate, and extracted with ether. The ether solutions were washed with 2N $NaHCO_3$ and brine, dried over $MgSO_4$, and evaporated *i. V.* The distillation gave 14.7 g (58%) of 2-(3-bromopropyl)cyclohexanone (**25**), b.p. 74–76°/0.05 Torr. – IR. (film): 2940, 1705 (C=O), 1445, 1310, 1254, 1128. – ^{1}H-NMR. (CCl_4): 1.2–2.4 (*m*, 13H, 6 CH_2 and 1 CH); 3.36 (*t*, J = 7, 2H, CH_2Br).

$C_9H_{15}BrO$ (219.12) Calc. C 49.33 H 6.90 Br 36.47% Found C 49.30 H 6.99 Br 36.24%

2-(4-Bromobutyl)cyclohexanone (**23**). Yield 64%, b.p. 100–103°/0.08 Torr. – IR. (film): 2940, 1710 (C=O), 1318, 1250, 1130. – ^{1}H-NMR. (CCl_4): 1.1–2.6 (*m*, 15H, 7 CH_2 and 1 CH); 3.50 (*t*, 2H, CH_2Br).

$C_{10}H_{17}BrO$ (233.15) Calc. C 51.51 H 7.35 Br 34.28% Found C 51.80 H 7.54 Br 34.35%

2-(4-Bromobutyl)cyclopentanone (**24**). Yield 65%, b.p. 100–101°/0.2 Torr. – IR. (film): 2940, 1730 (C=O), 1452, 1268, 1154. – ^{1}H-NMR. (CCl_4): 1.0–2.5 (*m*, 13H, 6 CH_2 and 1 CH); 3.50 (t, J=7, 2H, CH_2Br).

$C_9H_{15}BrO$ (219.12) Calc. C 49.33 H 6.90 Br 36.47% Found C 49.15 H 7.07 Br 35.89%

2-(3-Bromopropyl)cyclopentanone (**26**). Yield 61%, b.p. 83–84°/0.3 Torr. – IR. (film): 2965, 1740 (C=O), 1408, 1247, 1155. – ^{1}H-NMR. (CCl_4): 1.2–2.4 (*m*, 11 H, 5 CH_2 and 1 CH); 3.40 (*t*, 2H, CH_2Br).

$C_8H_{13}BrO$ (205.10) Calc. C 46.85 H 6.39 Br 38.96% Found C 46.73 H 6.11 Br 38.79%

2-(5-Bromopentyl)cyclopentanone (**27**). Yield 81%, b.p. 97–98°/0.2 Torr. – IR. (film): 2940, 1740 (C=O), 1408, 1270, 1158. – ^{1}H-NMR. (CCl_4): 1.2–2.4 (*m*, 15H, 7 CH_2 and 1 CH); 3.38 (*t*, 2H, CH_2Br).

$C_{10}H_{17}BrO$ (233.15) Calc. C 51.51 H 7.35 Br 34.28% Found C 51.75 H 7.55 Br 34.12%

2-(3-Bromopropyl)cycloheptanone (**28**). Yield 83%, b.p. 104–105°/0.3 Torr. – IR. (film): 2930, 1702 (C=O), 1455, 1250, 932. – ^{1}H-NMR. (CCl_4): 1.2–2.5 (*m*, 15H, 7 CH_2 and 1 CH); 3.42 (*t*, 2H, CH_2Br).

$C_{10}H_{17}BrO$ (233.15) Calc. C 51.51 H 7.35 Br 34.28% Found C 52.11 H 7.44 Br 34.09%

Hydrolysis and decarboxylation of t-butyl 1-(3-bromopropyl)-2-oxocyclopentanecarboxylate. A solution of 1.35 g (4.43 mmol) of the *t*-butyl β-ketoester in acetic acid (7 ml) and 48% hydrobromic acid (7 ml) was heated under reflux for 15 min, then worked-up as above. Distillation gave 0.78 g (86%) of 2-(3-bromopropyl)cyclopentanone (**26**), identical with the product from the hydrolysis and decarboxylation of the ethyl ester.

Alternative synthesis of 2-(3-bromopropyl)cyclohexanone (25). – *Ethyl 3-(2,2-Ethylenedioxycyclohexyl)propionate* (**33**). 82.3 g (0.416 mol) of ethyl 3-(2-oxocyclohexyl)propionate (**32**) [31], 246.3 g (3.97 mol) of ethylene glycol and 3.0 g (0.016 mol) of *p*-toluenesulfonic acid in dry toluene (2.5 l) were heated under reflux with a water separator for 5 h. The solution was washed with 2N $NaHCO_3$ and water, dried over $MgSO_4$, and evaporated i.V. The distillation gave 77.57 g (77%) of the ethylene acetal **33**, b.p. 104–108°/0.1 Torr. – IR. (film): 2940, 1728 (COOEt), 1175, 1090. – ^{1}H-NMR. (CCl_4): 1.0–2.3 (*m*, 13H, 6 CH_2 and 1 CH); 1.2 (*t*, 3H, CH_3); 3.8 (*s*, 4H, OCH_2CH_2O); 3.96 (*q*, 2H, OCH_2CH_3).

$C_{13}H_{22}O_4$ (242.32) Calc. C 64.44 H 9.15% Found C 64.69 H 9.23%

3-(2,2-Ethylenedioxycyclohexyl)propanol (**34**). 65.0 g (0.268 mol) of **33** in dry tetrahydrofuran (40 ml) were added dropwise to a suspension of 5.60 g (0.147 mol, 10% excess) of lithiumaluminiumhydride in tetrahydrofuran (260 ml). The mixture was heated under reflux for 30 min, then hydrolysed by dropwise addition of 50 ml of saturated aqueous potassium sodium tartrate. After stirring for several h, the crystalline precipitate was filtered off and washed with plenty of ether. The combined filtrates were dried and evaporated. The distillation yielded 50.3 g (94%) of the alcohol **34**, b.p. 95°/0.08 Torr. – IR. (film): 3400 (OH), 2940, 2880, 1445, 1162, 1092, 928. – ^{1}H-NMR. (CCl_4): 1.0–1.9 (*m*, 13H, 6 CH_2 and 1 CH); 2.4 (*s*, 1H, OH); 3.45 (*m*, 2H, CH_2OH); 3.80 (*s*, 4H, OCH_2CH_2O).

$C_{11}H_{20}O_3$ (200.28) Calc. C 65.97 H 10.07% Found C 65.80 H 9.99%

2-(3-Hydroxypropyl)cyclohexanone (**35**). 15.1 g (75.3 mmol) of **34** in 0.6N hydrochloric acid (50 ml) and dioxane (100 ml) were stirred at 50° for 5 h. Dioxane was distilled off at reduced pressure, and the product extracted with ether. The ether solutions were washed with 2N $NaHCO_3$ and water, dried over $MgSO_4$, and evaporated. The distillation at 75–76°/0.08 Torr gave 9.18 g (78%) of the hydroxyketone **35** as its hemiacetal 2-oxabicyclo[4.4.0]-1-decanol (**35a**), m.p. 64–66°. From pentane (–20°): white needles of m.p. 67–68° ([32]: 67–69°). – IR. ($CHCl_3$): 3600, 3400, 2940, 1708 *w* (C=O), 1445, 1185, 1135, 1080, 950, 870. – IR. (KBr): 3400, 2940, 1455, 1260, 1192, 1135, 1080, 1062, 995, 950, 868, 845. – ^{1}H-NMR. ($CDCl_3$): 1.1–2.5 (*m*, 13H, 6 CH_2 and 1 CH); 2.04 (*s*, 1H, OH); 3.3–4.1 (*m*, 2H, CH_2OH).

$C_9H_{16}O_2$ (156.23) Calc. C 69.19 H 10.32% Found C 69.20 H 10.40%

2-Oxabicyclo[4.4.0]-1(6)-decene (**36**). 1.0 g (6.4 mmol) of **35a** were heated under reflux in 2N hydrochloric acid (2 ml) and dioxane (10 ml) for 10 h. The mixture was worked up as above. Flash distillation in a bulb tube at 80–90°/14 Torr gave 710 mg (80%) of the enol ether **36**. – IR. (film): 2935, 1694 (C=C–O), 1238, 1152. – ^{1}H-NMR. (CCl_4): 1.6–2.1 (*m*, 12H); 3.83 (*t*, J=5, 2H, CH_2O).

$C_9H_{14}O$ (138.21) Calc. C 78.21 H 10.21% Found C 78.11 H 10.03%

3-(2,2-Ethylenedioxycyclohexyl)propyl p-*toluenesulfonate* (**37**). 10.5 g (55.1 mmol) of *p*-toluenesulfonyl chloride in dry pyridine (20 ml) were added dropwise to a stirred solution of 10.8 g (54.0 mmol) of 3-(2,2-ethylenedioxycyclohexyl)propanol (**34**) in pyridine (20 ml) at −5°. The mixture was kept at 0–5° for 20 h, then diluted with ethyl ether and poured on a mixture of 27 ml of conc. hydrochloric acid and 80 g of ice. The ether solution was separated, washed with saturated aqueous $CuSO_4$ and water, dried over $MgSO_4$, and evaporated. The remaining semi-solid *p*-toluenesulfonate **37** (16.9 g, 88%) was used for the next step without purification. White prisms from ethyl ether/pentane at −20°, m.p. 38–39°. – IR. (CCl_4): 3040, 2930, 2875, 1350, 1170 (OSO_2), 1090, 920, 812. – ^{1}H-NMR. (CCl_4): 1.0–1.8 (*m*, 13H, 6 CH_2 and 1 CH); 2.40 (*s*, 3H, CH_3); 3.75 (*s*, 4H, OCH_2CH_2O); 3.87 (*t*, 2H, CH_2OSO_2); 7.13 and 7.58 (2*d*, 2H each, ArH).

$C_{18}H_{26}O_5S$ (354.47) Calc. C 61.00 H 7.40% Found C 60.78 H 7.35%

2-(3-Bromopropyl)cyclohexanone (**25**). 8.88 g (25.1 mmol) of crude **37** and 43.5 g (500 mmol) of lithium bromide in dry acetone (150 ml) were heated under reflux for 40 h. The solution was concentrated *i.V.*, then diluted with ethyl ether, washed with water, dried over $MgSO_4$, and evaporated. The distillation gave 4.76 g (87%) of **25**, b.p. 83–86°/0.1 Torr, identical with the product obtained on hydrolysis and decarboxylation of the corresponding β-ketoester **30** (see above).

General method for the synthesis of oxoalkyl-triphenylphosphonium bromides (38) exemplified by *3-(2-oxocyclohexyl)propyl-triphenylphosphonium bromide*. 11.40 g (52.0 mmol) of 2-(3-bromopropyl)cyclohexanone (**25**) and 13.64 g (52.0 mmol) of triphenylphosphine in dry ethyl ether (40 ml) were sealed in a pyrex pressure tube, and heated to 120° for 70 h. The solid product was washed with several portions of dry ether, dissolved in methylene chloride, evaporated, and dried over P_2O_5 for 24 h at 0.02 Torr: 24.2 g (97%) of the corresponding phosphonium bromide, an extremly hygroscopic, glass-like solid, which was used directly in the next step. *Tetraphenylborate*, obtained from the phosphonium bromide and sodium tetraphenylborate in methanol, white needles from acetone/methanol, m.p. 163–163.5°.

$C_{51}H_{50}BOP$ (720.74) Calc. C 84.99 H 6.99 P 4.30% Found C 85.25 H 6.90 P 4.29%

4-(2-Oxocyclohexyl)butyl-triphenylphosphonium bromide. Yield 99%, glass-like solid. *Tetraphenylborate*, white needles from methanol (0°), m.p. 85–87°.

$C_{52}H_{52}BOP$ (734.77) Calc. C 85.00 H 7.13 P 4.22% Found C 84.72 H 7.00 P 4.35%

4-(2-Oxocyclopentyl)butyl-triphenylphosphonium bromide. Yield 98%, glass-like solid. – IR. ($CHCl_3$): 2940, 1730, 1440, 1113, 995.

$C_{27}H_{30}BrOP$ (481.43) Calc. C 67.36 H 6.28 Br 16.60% Found C 67.58 H 6.28 Br 16.82%

3-(2-Oxocyclopentyl)propyl-triphenylphosphonium bromide. Yield 92%, yellowish needles, m.p. 208–209°. – IR. ($CHCl_3$): 2940, 1730, 1440, 1115, 998. – ^{1}H-NMR. ($CDCl_3$): 1.3–2.5 (*m*, 11H, CH, CH_2); 3.8 (br., 2H, CH_2P); 7.8 (*m*, 15H, ArH).

$C_{26}H_{28}BrOP$ (467.40) Calc. C 66.81 H 6.04 Br 17.10% Found C 66.57 H 6.07 Br 17.32%

5-(2-Oxocyclopentyl)pentyl-triphenylphosphonium bromide. Yield 92%, glass-like solid. *Tetraphenylborate*, white crystals from methanol, m.p. 65–68°.

$C_{52}H_{52}BOP$ (734.77) Calc. C 85.00 H 7.13 P 4.22% Found C 84.73 H 7.20 P 4.17%

3-(2-Oxocycloheptyl)propyl-triphenylphosphonium bromide. Yield 91%, glass-like solid. *Tetraphenylborate*, white needles from acetone/methanol, m.p. 161–162°.

$C_{52}H_{52}BOP$ (734.77) Calc. C 85.00 H 7.13 P 4.22% Found C 85.48 H 7.08 P 4.21%

General procedure for the intramolecular *Wittig* reaction, exemplified by the synthesis of *bicyclo[4.3.0]-1(2)-nonene* (=$\Delta^{7,8}$-*hydrindene*; **2**). 20.7 g (43.1 mmol) of 4-(2-oxocyclopentyl)butyl-triphenylphosphonium bromide in dimethyl sulfoxide (50 ml) were added dropwise to a stirred solution of *ca.* 45 mmol of dimethyl sulfoxide anion [34] in dimethyl sulfoxide (20 ml) under nitrogen. The red suspension was warmed to 80° for 10 min, when a clear solution was obtained. The olefin was distilled at 35–45°/12 Torr into a cold trap, diluted with pentane, washed with water, and dried over $MgSO_4$. Redistillation gave 2.98 g (57%) of **2**, b.p. 166–167°. No isomeric hydrindenes were found with GLC. – IR. (film): 3050, 2920, 2860, 1675 (C=C), 1450, 858, 787 (=CH). – ^{1}H-NMR. (CCl_4):

0.8–2.4 (*m*, 13H, CH_2, CH); 5.28 (br.*s*, 1H, =CH). – ^{13}C-NMR. ($CDCl_3$): 144.8 (*s*, C(1)); 116.8 (*d*, C(2)); 40.9 (*d*, C(6)); 33.4, 30.2, 29.1, 25.2, 23.1, 22.6 (6*t*, 6CH_2).

C_9H_{14} (122.21) Calc. C 88.45 H 11.55% Found C 88.26 H 11.68%

Bicyclo[4.4.0]-1(2)-decene (=*$\Delta^{1,9}$-octalin*; **1**). Yield 51%, isolated by steam distillation, b.p. 80–81°/17 Torr. – IR. (film): 3048, 2920, 2850, 1666 (C=C), 1448, 1310, 925, 802 (=CH), 674. – ^{1}H-NMR. (CCl_4): 1.3–2.4 (*m*, 15H, CH_2, CH); 5.22 (br.*s*, 1H, =CH). – ^{13}C-NMR. ($CDCl_3$): 140.9 (*s*, C(1)); 119.1 (*d*, C(2)); 37.4 (*d*, C(6)); 35.6, 35.3, 31.2, 27.9, 26.9, 25.5, 21.6 (7*t*, 7CH_2).

$C_{10}H_{16}$ (136.24) Calc. C 88.16 H 11.84% Found C 88.38 H 12.02%

Bicyclo[4.3.0]-1(9)-nonene (=*$\Delta^{1,8}$-hydrindene*; **3**). Yield 59%, b.p. 137–138°. – IR. (film): 3042, 2920, 2860, 1660 (C=C), 1440, 905, 793 (=CH). – ^{1}H-NMR. (CCl_4): 0.8–2.7 (*m*, 13H, CH_2, CH); 5.15 (br.*s*, 1H, =CH). – ^{13}C-NMR. ($CDCl_3$): 145.9 (*s*, C(1)); 119.9 (*d*, C(9)); 45.7 (*d*, C(6)); 36.1, 31.2, 30.9, 29.1, 27.6, 26.4 (6*t*, 6CH_2).

C_9H_{14} (122.21) Calc. C 88.45 H 11.55% Found C 88.29 H 11.50%

Bicyclo[3.3.0]-1(2)-octene (**20**). Yield 64%, b.p. 124–129°. – IR. (film): 3052, 2955, 2845, 1663 (C=C), 1450, 1322, 903, 790 (=CH). – ^{1}H-NMR. (CCl_4): 0.8–3.1 (*m*, 11H, CH, CH_2); 5.17 (br.*s*, 1H, =CH). – ^{13}C-NMR.[1] ($CDCl_3$): 154.5 (*s*, C(1)); 117.6 (*d*, C(2)); 52.5 (*d*, C(5)); 38.0, 32.4 (2C); 28.9, 23.8 (4*t*, 5CH_2).

C_8H_{12} (108.18) Calc. C 88.82 H 11.18% Found C 88.84 H 11.20%

Bicyclo[5.3.0]-1(2)-decene (**21**). Yield 19%, b.p. 182–184°, isolated by steam distillation. – IR. (film): 3042, 2918, 2845, 1440, 967, 829 (=CH). No absorption in the range 1600–1700 (C=C). – ^{1}H-NMR. (CCl_4): 0.7–2.6 (*m*, 15H, CH, CH_2); 5.59 (br.*s*, 1H, =CH). – ^{13}C-NMR. ($CDCl_3$): 150.7 (*s*, C(1)); 121.1 (*d*, C(2)); 44.4 (*d*, C(7)); 36.1, 35.1, 34.2, 31.8, 29.2, 27.9, 25.7 (7*t*, 7CH_2).

$C_{10}H_{16}$ (136.24) Calc. C 88.16 H 11.84% Found C 87.90 H 12.12%

Bicyclo[5.3.0]-1(10)-decene (**22**). Yield 66%, b.p. 116–120°/90 Torr, isolated by steam distillation. – IR. (film): 3042, 2925, 2850, 1640 (C=C), 1450, 951, 799, 788. – ^{1}H-NMR. (CCl_4): 1.1–2.8 (*m*, 15H, CH, CH_2); 5.27 (br.*s*, 1H, =CH). – ^{13}C-NMR. ($CDCl_3$): 149.9 (*s*, C(1)); 124.2 (*d*, C(10)); 48.3 (*d*, C(7)); 34.8, 33.5, 31.1 (2C); 30.7, 28.6, 28.2 (6*t*, 7CH_2).

$C_{10}H_{16}$ (136.24) Calc. C 88.16 H 11.84% Found C 88.28 H 11.82%

Synthesis of Bicyclo[4.3.0]-1(9)-nonene (3) by intramolecular *Wittig* reaction using other solvents and bases (yields were determined by GLC. using an internal standard). – *Lithium methoxide in methanol/dimethylformamide* [35]. 1.64 g (3.41 mmol) of 3-(2-oxocyclohexyl)propyl-triphenylphosphonium bromide in 5 ml of methanol were added to a solution of lithium methoxide prepared from 26 mg (3.7 mmol) of lithium wire in methanol (5 ml) and dimethylformamide (5 ml). The mixture was heated under reflux for 4 h, and all volatile compounds distilled at 140°. The remaining solution was kept at 140° for 20 h, cooled, diluted with water, and extracted with pentane. Yield: 38% in the distillate, 19% in pentane solution, total 57%.

Sodium 2-methyl-2-butoxide in tetraethylene glycol dimethyl ether. For exper. conditions see [25]. Yield 48%.

Butyllithium in ethyl ether/tetrahydrofuran. 0.86 g (1.79 mmol) of the phosphonium bromide were suspended in a mixture of dry ethyl ether (15 ml) and tetrahydrofuran (5 ml), and treated with 1.9 mmol of butyllithium in hexane (2 ml). The ether was distilled off and the remaining solution heated under reflux for 60 h. Yield 43%.

Potassium in hexamethylphosphoric acid triamide [36]. 1.28 g (2.66 mmol) of the phosphonium bromide in methylene chloride (2 ml) were added dropwise to a solution of 104 mg (2.66 mmol) of potassium in 10 ml of dry hexamethylphosphoric acid triamide. Methylene chloride and dimethylamine were distilled off at reduced pressure. The remaining solution was kept at RT. for 20 h, diluted with water, and extracted with pentane. Yield: 4% in the distillate, 38% in pentane solution, total 42%.

Sodium amide in ammonia. A solution of sodium amide was prepared from 110 mg (4.78 mmol) of sodium, 30 ml of dry, distilled ammonia and a trace of ferric nitrate. 1.77 g (3.68 mmol) of the

solid phosphonium bromide in a dropping funnel were washed continuously into the mixture by ammonia dropping from a dry ice condenser over 6 h. After additional 2 h, cold pentane was added, the ammonia distilled off, and the remaining suspension hydrolysed carefully with water. Yield 14%.

Aqueous sodium hydroxide and methylene chloride. 0.36 g (0.747 mmol) of the phosphonium bromide in 3 ml of methylene chloride and 2 ml of 50% aqueous sodium hydroxide were stirred under nitrogen for 2 h. Yield 42%.

Compounds used for comparison of their spectral properties. – 1-Methylcyclopentene (**39**), 1-methylcyclohexene (**40**), and hydrindane (mixture of 90% *cis*-**43** and 10% *trans*-**44**) were obtained from *Fluka* and purified by distillation. Bicyclo[3.3.0]-1(5)-octene (**49**) [43], $\Delta^{8,9}$-hydrindene (**50**) [1], $\Delta^{9,10}$-octalin (**51**) [1], and 1-methylcycloheptene (**41**) [44] were prepared according to literature procedures. Bicyclo[5.3.0]-1(7)-decene (**52**) was formed on isomerization of bicyclo[5.3.0]-1(2)-decene (**21**) with *p*-toluenesulfonic acid, and was isolated from the mixture of isomers by chromatography with cyclohexane on silica gel impregnated with 10% of silver nitrate. *cis*-Bicyclo[3.3.0]octane (**42**) was obtained upon hydrogenation of *cis*-bicyclo[3.3.0]-2-octene [45]. A mixture of *ca.* 75% *cis*-bicyclo[5.3.0]decane (**47**) and 25% *trans*-bicyclo[5.3.0]decane (**48**) was formed upon hydrogenation of azulene.

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