# 10. The Synthesis of Strained Methylene-bridged Bicyclic Olefins by the Intramolecular *Wittig* Reaction[1])

by **Konrad B. Becker**

Institut für Organische Chemie der Universität Basel,
St.-Johanns-Ring 19, CH-4056 Basel

(4. X. 76)

## *Summary*

A convenient synthesis of the strained methylene-bridged *trans*-cyclooctenes bicyclo[3.3.1]-1(2)-nonene (**1**), bicyclo[4.2.1]-1(8)-nonene (**2**), and bicyclo[4.2.1]-1(2)-nonene (**3**) by the intramolecular *Wittig* reaction is described (see *Schemes 1–4*). The (3-oxocycloalkyl)alkyl-phosphonium bromides **20**, **27** and **38** undergoing cyclization to the bridgehead olefins are formed by simple reaction sequences. The spectral properties (IR., $^1$H-NMR., $^{13}$C-NMR., and UV.) of the olefins are discussed with regard to their strain.

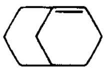
**Introduction.** – Considerable interest has been shown recently in defining the limits of *Bredt*'s rule and in predicting the degree of strain in bridgehead double bonds [2] [3]. *Bredt* himself had limited his qualitative statement, that a double bond at the bridgehead is not possible, to bicyclic olefins of the pinane and camphane series and related compounds [4]. Later *Prelog* demonstrated that larger bicyclic ring systems indeed can accommodate a bridgehead double bond [5]. Based on this research, *Fawcett* drew the conclusion that compounds with a double bond at the bridgehead cannot be isolated if the total number of bridge atoms *S*[2]) is less than nine [6].

In 1967, both *Wiseman* [7] and *Marshall* [8] reported the successful synthesis of bicyclo[3.3.1]-1(2)-nonene (**1**), a reactive but stable bridgehead olefin with seven bridge carbon atoms only. *Wiseman* emphasized that the stability of a bridgehead olefin is related to the stability of the largest *trans*-cycloalkene from which it can be derived formally by bridging. Since *trans*-cyclooctene is a stable, isolable compound [9], the methylene-bridged *trans*-cyclooctenes bicyclo[3.3.1]-1(2)-nonene (**1**), bicyclo[4.2.1]-1-nonene (**2** and **3**), and bicyclo[5.1.1]-1-nonene (**4** and **5**) should be isolable as well. The utility of *Wiseman*'s concept is demonstrated by the successful synthesis and isolation of compounds **2**, **3** [10], **4** and **5** [11], and the increasing number of synthetic approaches to even more strained bridgehead olefins [3].

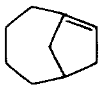
---

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

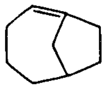
[2]) $S = x + y + z$ in a bicyclo[x.y.z]-1-alkene.



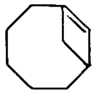
**1**



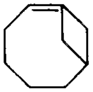
**2**



**3**

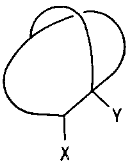


**4**

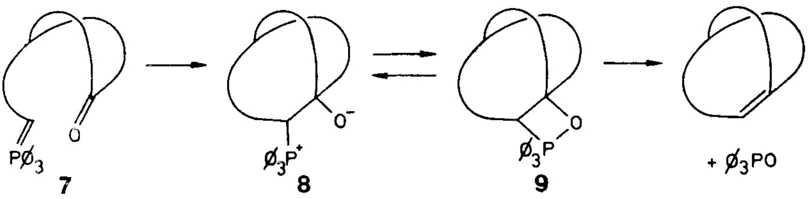


**5**

Strain and reactivity of the double bond in bridgehead olefins such as **1** obviously reduce the number of possible synthetic methods leading to it. These olefins have been prepared mainly by elimination reactions of suitably 1,2-disubstituted bicyclic or polycyclic compounds of type **6**, *e.g.* dihalides, a carboxymethanesulfonate, a diperester, a β-lactone, or cyclic derivatives of vicinal diols [3]. Compounds that bear a substituent only at the bridgehead (**6**, X = H), *e.g.* the trimethylammonium hydroxide, may also yield strained olefins on elimination. The drawback of this method, however, lies in the fact, that the bridge containing the double bond cannot be determined by the mode of synthesis, and therefore mixture of olefins may result.

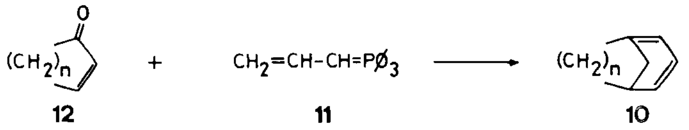


**6**



The results obtained with unstrained, annulated olefins [12] indicate that the intramolecular *Wittig* reaction should be well suited also for the synthesis of strained bridgehead olefins. The ketophosphorane **7**, a simple monocyclic precursor, is expected to yield readily the zwitterion **8**³), a 1,2-disubstituted compound of type **6**. The high tendency of formation of triphenylphosphine oxide then could give rise to the strained double bond *via* the oxaphosphetane **9**.

The intramolecular *Wittig* reaction has been used previously for the synthesis of the bridgehead dienes **10** (n = 2, 3, 4 and 5). The propenylidenephosphorane **11** adds to the double bond of cyclic α,β-unsaturated ketones **12** in a *Michael*-type reaction to give a ketophosphorane capable of cyclization [14].



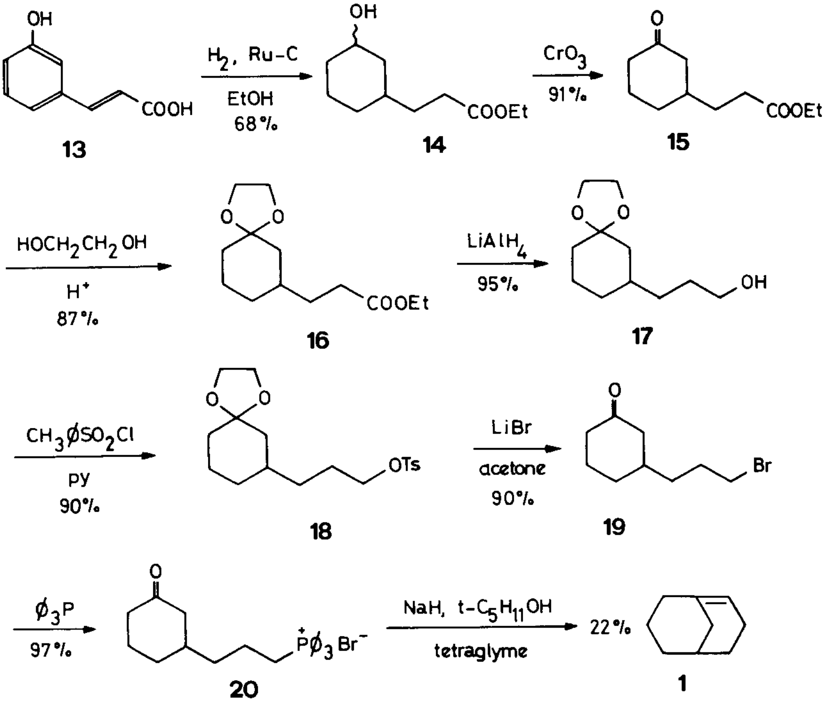
---

³) For a discussion of the intermediacy of compounds **8** and **9** see [13].

The aim of the work presented here was the development of a high-yield synthesis of the methylene-bridged *trans*-cyclooctenes **1**, **2** and **3** by the intramolecular *Wittig* reaction. Whereas bicyclo[3.3.1]-1(2)-nonene (**1**) had been prepared previously by three different routes [7] [8] [15], bicyclo[4.2.1]-1(8)-nonene (**2**) and bicyclo[4.2.1]-1(2)-nonene (**3**) had only been obtained once as a mixture, and had to be separated by preparative gas liquid chromatography [10]. A straightforward synthesis is a prerequisite for a thorough study of the interesting reactivity of such strained bridgehead olefins [16].

**Syntheses.** - Bicyclo[3.3.1]-1(2)-nonene (**1**) was obtained as follows (*Scheme 1*): *m*-Hydroxycinnamic acid (**13**) was hydrogenated in the presence of ruthenium in ethanol [7]. The resulting mixture of stereoisomeric hydroxyesters **14** was oxidized to ketoester **15** with chromium trioxide [17]. Acetalisation with ethylene glycol and a catalytic amount of *p*-toluenesulfonic acid gave acetalester **16**. This was reduced to the hydroxyacetal **17** by lithiumaluminiumhydride in tetrahydrofuran. The reaction with *p*-toluenesulfonyl chloride in pyridine yielded the oily *p*-toluenesulfonate **18**. Lithium bromide in acetone removed the acetal protecting group and substituted the tosyloxy group by bromine, Bromoketone **19** and one equivalent of triphenylphosphine in ether at 120° gave the phosphonium bromide **20** as a highly hygroscopic, non-crystalline solid in pure form. The reaction of **20** with sodium hydride in dry tetraethylene glycol dimethyl ether (tetraglyme) containing one equivalent of 2-methyl-2-butanol yielded, after distillation, 22% of crude, air-sensitive olefin **1**. The

*Scheme 1*

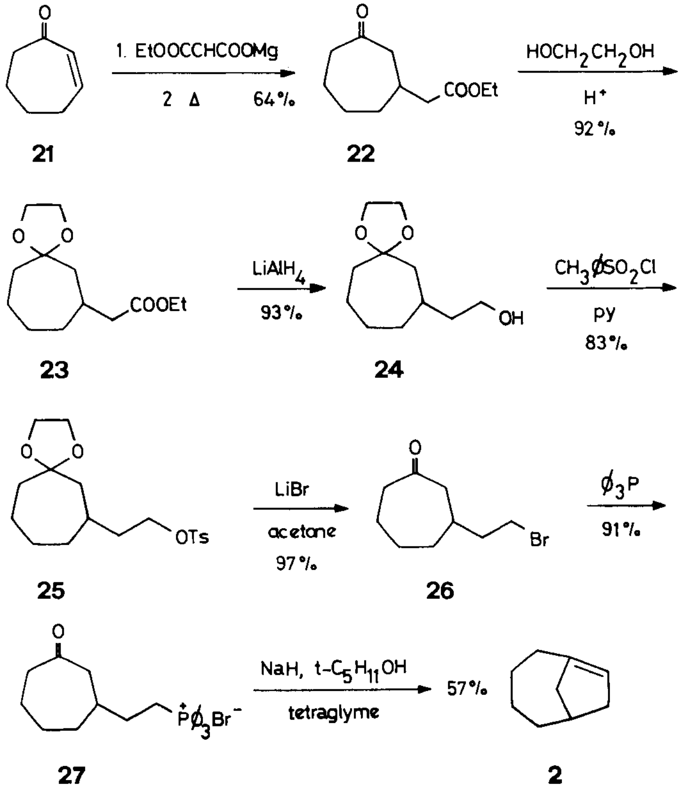


olefin was purified by extraction with water and redistillation, and characterized by its spectral properties and the *Diels-Alder* adduct with 2,5-diphenylbenzo[*c*]furan [7] [8].

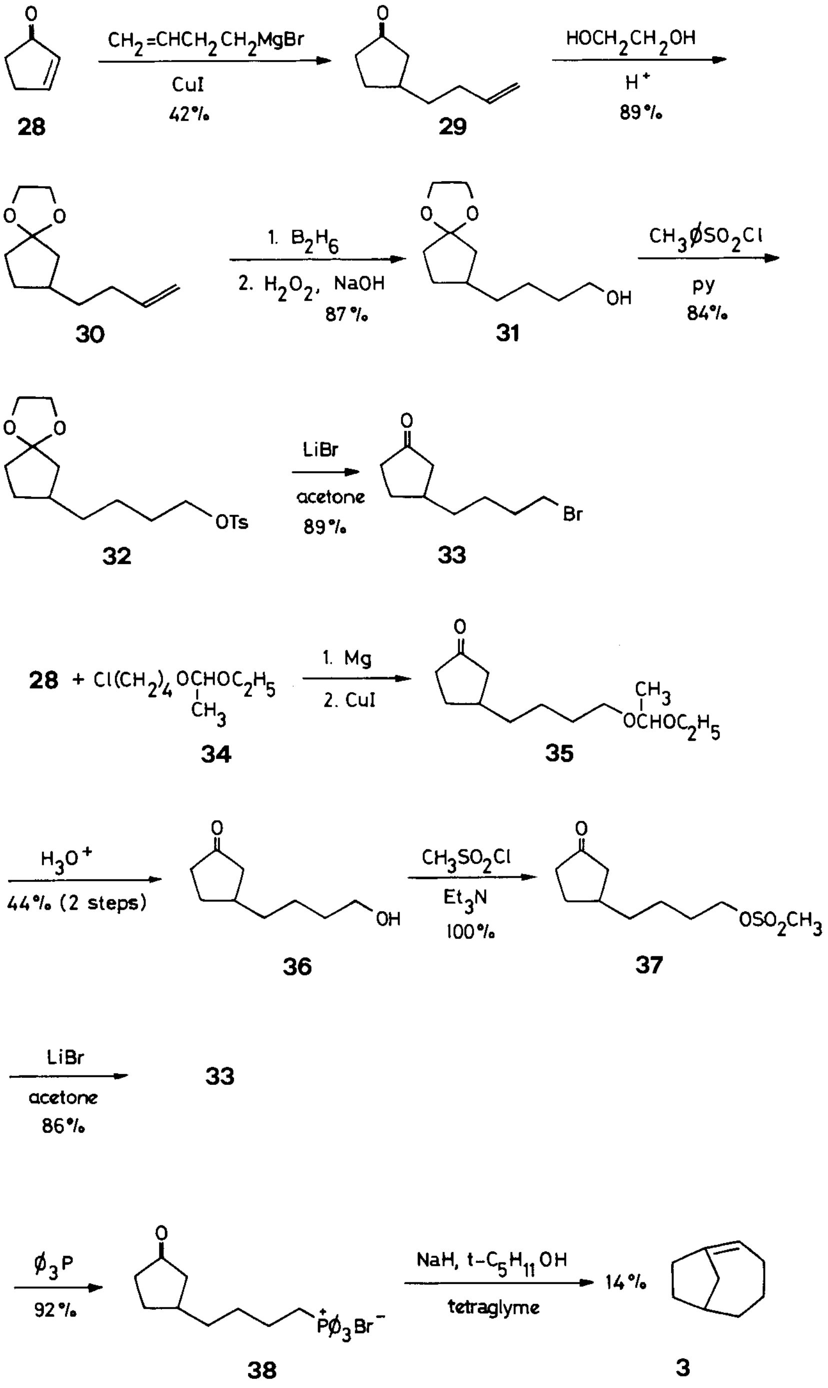
Other combinations of solvent and base were tested in the *Wittig* cyclization, but turned out to be inferior. Tetraglyme was chosen as the solvent, because it allowed distillative isolation of the reactive olefin as it was formed. The phosphonium bromide is only slightly soluble in this polyether. The concentration of the ketophosphorane therefore remains low throughout the reaction, and cyclization is favored. The base necessary to deprotonate the phosphonium bromide is formed *in situ* from the tertiary alcohol and excess sodium hydride.

The synthesis of bicyclo[4.2.1]-1(8)-nonene (**2**) is shown in *Scheme 2*. The known addition of sodium diethyl malonate to 2-cycloheptenone (**21**) [18], followed by hydrolysis, decarboxylation, and re-esterification, gave ketoester **22** in very low yield. The addition of the magnesium salt of monoethyl malonate [19] to **21**, however, proceeded well. Decarboxylation of the crude product gave an acceptable yield of ethyl (3-oxocycloheptyl)acetate (**22**). The transformation of ketoester **22** *via* the ethylene acetal **23**, acetalalcohol **24**, and the crystalline *p*-toluenesulfonate **25** to 3-(2-bromoethyl)cycloheptanone (**26**) was analogous to the synthesis of bromoketone **19** (see above). Cyclization of the phosphonium bromide **27** with sodium hydride and

*Scheme 2*



*Scheme 3*


28
CH2=CHCH2CH2MgBr
CuI
42%
29
HOCH2CH2OH
H+
89%
30
1. B2H6
2. H2O2, NaOH
87%
31
OH
CH3ϕSO2Cl
py
84%
32
OTs
LiBr
acetone
89%
33
Br
28 + Cl(CH2)4OCHOC2H5
CH3
34
1. Mg
2. CuI
35
CH3
OCHOC2H5
H3O+
44% (2 steps)
36
OH
CH3SO2Cl
Et3N
100%
37
OSO2CH3
LiBr
acetone
86%
33
ϕ3P
92%
38
P+ϕ3Br−
NaH, t-C5H11OH
tetraglyme
14%
3

2-methyl-2-butanol in tetraglyme, followed by distillation, extraction with water, and redistillation, gave bicyclo[4.2.1]-1(8)-nonene (**2**) as a waxy solid, m.p. 28–30°, in 57% yield. The latter was identical to the olefin described by *Wiseman et al.* [10] and was characterized by its spectral properties, elemental analysis, and *Diels-Alder* addition products with 2,5-diphenylbenzo[*c*]furan and tetraphenylcyclopentadienone.

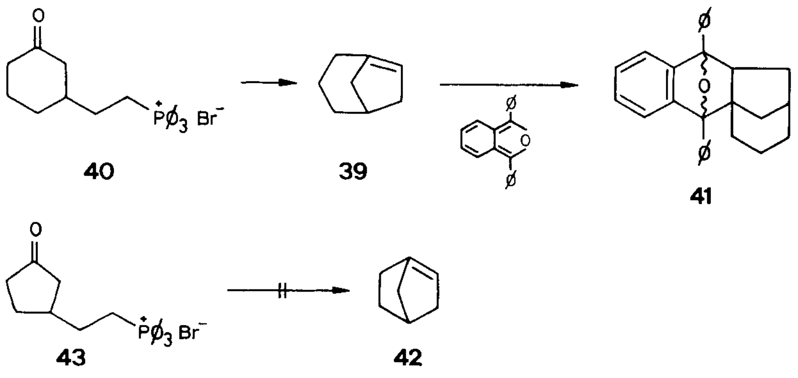
The synthesis of bicyclo[4.2.1]-1(2)-nonene (**3**) required the formation of a seven-membered ring from a cyclopentanone bearing a functionalized butyl side chain in 3-position (*Scheme 3*). The copper-catalysed *Grignard* reaction of 3-butenylmagnesium bromide with 2-cyclopentenone (**28**) gave the olefinic ketone **29** [20]. The keto function was protected as the ethylene acetal, and the resulting alkene **30** hydroborated with diborane [21]. The oxidation of the borane with alkaline hydrogen peroxide gave the expected primary alcohol **31** together with 8% of the isomeric secondary alcohol. Tosylation of **31** yielded the *p*-toluenesulfonate **32**, which was converted to the bromoketone **33** by lithium bromide in acetone.

In an alternative synthesis, a hydroxybutyl side chain was added to 2-cyclopentenone (**28**) by the *Grignard* reaction of acetaldehyde 4-chlorobutyl ethyl acetal (**34**) [22] in the presence of cuprous iodide in tetrahydrofuran (*Scheme 3*). The crude addition product **35** was hydrolysed directly to the hydroxyketone **36**. The methanesulfonate **37** was formed with methanesulfonyl chloride and triethylamine in methylene chloride. The reaction with lithium bromide again gave bromoketone **33**.

The intramolecular *Wittig* reaction of the phosphonium bromide **38** under the usual conditions gave bicyclo[4.2.1]-1(2)-nonene (**3**) in 14% yield after purification. The oily, air-sensitive olefin was characterized by its spectral properties [10], elemental analysis, and the *Diels-Alder* addition product with tetraphenylcyclopentadienone.

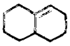
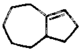
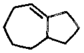
While work on this project was in progress, *Dauben & Robbins* [23] reported the synthesis of bicyclo[3.2.1]-1(7)-octene (**39**) based on the same approach. The phosphonium bromide **40** was cyclized with potassium *t*-butoxide in refluxing tetrahydrofuran, and the unstable bridgehead olefin **39** trapped *in situ* by 2,5-diphenylbenzo[*c*]furan yielding a mixture of *Diels-Alder* adducts **41**. The limits of the intramolecular *Wittig* reaction are demonstrated by the attempted synthesis of norborn-1(2)-ene (bicyclo[2.2.1]-1(2)-heptene; **42**). The same authors found no indication for the formation of **42**, when the phosphonium bromide **43** was treated with base (*Scheme 4*).

*Scheme 4*



**Spectral properties.** – A comparison of the spectroscopic data of the bridgehead olefins **1**, **2** and **3** with those of *trans*-1-methylcyclooctene (**43**) [24] and a series of annulated bicyclic olefins [12] gives little information concerning the strain of the bridgehead double bond (Table 1).

Table 1. *Spectral properties of strained bridgehead olefins*, trans-*1-methylcyclooctene* (**43**) [24], *and representative annulated trisubstituted olefins* [12]

| | | <br>**1** | <br>**2** | <br>**3** | <br>**43**[a] |  |  |  |
|---|---|---|---|---|---|---|---|---|
| IR. spectrum | C=C | 1620 | 1618[b] | 1656 | 1654 | 1666 | 1640 | – |
| (film, cm$^{-1}$) | =C–H | 3022 | 3047 | 3020 | | 3048 | 3042 | 3042 |
| | | 811 | 781 | 838,811 | 880 | 802 | 799,788 | 829 |
| $^1$H-NMR. spectrum | =C–H | 5.65 | 5.40 | 5.30 | 5.29 | 5.22 | 5.27 | 5.59 |
| (CCl$_4$, $\delta$ in ppm) | | | | | | | | |
| $J$ in Hz[c] | | $t$/7 | $s$/(9) | $d \times d$/6,7 | $d \times d$/5.5,10 | $s$/(8) | $s$/(7) | $s$/(14) |
| $^{13}$C-NMR. spectrum | =CH– | 125.1[d] | 127.4[e] | 124.9[e] | 127.4 | 119.1 | 124.2 | 121.1 |
| (CDCl$_3$, $\delta$ in ppm) | =C< | 146.8 | 147.2 | 147.3 | 137.7 | 140.9 | 149.9 | 150.7 |
| | –CH< | 36.6 | 45.4 | 32.3 | – | 37.4 | 48.3 | 44.4 |
| UV. spectrum, $\lambda$(max) | in nm | 206 | 186, 200 | 206 | | | | |
| (Cyclohexan) | log $\varepsilon$ | 3.8 | 3.8, 3.7 | 3.9 | | | | |

[a] Data from [24].

[b] In CCl$_4$.

[c] Multiplicity: $t$ = triplet, $s$ = singlet (halfwidth), $d \times d$ = double doublet.

[d] Pure liquid, external TMS in CDCl$_3$.

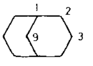
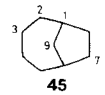
[e] In C$_6$D$_6$.

In the IR. spectrum stretching and out-of-plane bending absorptions of the vinylic proton appear at the usual wavenumber. The weak stretching absorption of the C=C bond lies at somewhat lower wavenumber than expected. This is an indication of some weakening of the double bond character.

In the $^1$H-NMR. spectrum, the vinylic proton resonates in the usual range of $\delta = 5.1$ to 5.7 ppm, however, small differences are found in comparison with the corresponding resonances in annulated olefins. The vinyl proton in bicyclo[3.3.1]-1(2)-nonene (**1**) and bicyclo[4.2.1]-1(8)-nonene (**2**) is slightly deshielded compared to related cyclohexenes and cyclopentenes, respectively, whereas the vinyl proton in bicyclo[4.2.1]-1(2)-nonene (**3**) appears at higher field compared to cycloheptenes. *trans*-1-Methylcyclooctene shows a double doublet with coupling constants of 5.5 and 10 Hz, the bridgehead olefin **3** a double doublet with $J = 6$ and 7 Hz, olefin **1** a triplet with $J = 7$ Hz, and olefin **2** a broadened singlet with a halfwidth of 9 Hz. These differences in the couplings of the vinylic proton reflect the differences in the steric arrangement of the allylic protons.

The $^{13}$C-NMR. chemical shift of the unsaturated carbon atoms in the bridgehead olefins **1**, **2** and **3** gives no indication of strain in these molecules. The only anomaly apparent from a comparison with the $^{13}$C-NMR. spectrum of annulated olefins and the saturated analogues bicyclo[3.3.1]nonane (**44**) and bicyclo[4.2.1]nonane (**45**) is the

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

| |  a)<br>**44** | <br>**45** |
|---|---|---|
| C(1) | 27.9 | 37.4 |
| C(2) | 31.6 | 35.9 b) |
| C(3) | 22.5 | 25.6 |
| C(7) | – | 33.1 b) |
| C(9) | 35.1 | 35.5 |

a) Data from [29]. We thank Dr. *Heumann* for communicating also his assignments for bicyclo-[4.2.1]nonane (**45**).

b) Assignments may be interchanged.

low shift value of 32.3 ppm for the saturated bridgehead in **3** (Table 2)4). The coupling constant $J$(C–H) of 156.2 Hz [7] for the H–C(2) bond of **1** shows no deviation from the usual pattern [25].

A hint to a torsion of the $\pi$-bond is found in the UV. spectrum. The maximum absorption at 206 nm for the bicyclic olefins **1** and **3** lies in the same wavelength range as for *trans*-cyclooctene [26]. Surprisingly, however, bicyclo[4.2.1]-1(8)-nonene (**2**) shows only the end absorption typical of unstrained trisubstituted olefins [27].

*Heilbronner et al.* studied the photoelectron spectra of the isomeric bicyclo[4.2.1]-nonenes **2** and **3**, but found no deviations from spectra of other trisubstituted olefins [28].

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

## Experimental Part

*General remarks*, see [12].

*Ethyl 3-(3-hydroxycyclohexyl)propionate* (**14**). *m*-Hydroxycinnamic acid (**13**) (obtained from *Fluka*) was hydrogenated in ethanol in the presence of Ru/C at 100° and 100 atm. The alcohol obtained (68%, b.p. 110–115°/0.03 Torr) was identical with the product described by *Wiseman et al.* [7], and consisted of a 1:1 mixture of the *cis*- and *trans*-isomer (GLC., Carbowax 20 M).

*Ethyl 3-(3-oxocyclohexyl)propionate* (**15**). **14** was oxidized with *Jones* reagent [17] in acetone: 91% of the ketone **15**, b.p. 85–89°/0.05 Torr, identical with the product described by *Wiseman et al.* [7].

*Ethyl 3-(3,3-ethylenedioxycyclohexyl)propionate* (**16**). 32.1 g (162 mmol) of **15**, 33 g (720 mmol) of ethylene glycol, and 0.2 g of *p*-toluenesulfonic acid in dry benzene (200 ml) were heated under reflux with a water separator for 15 h. The solution was washed with 2N $NaHCO_3$ and water, dried over $MgSO_4$, and evaporated *i.V.* The distillation gave 34.0 g (87%) of the ethylene acetal **16**, b.p. 110–116°/0.01 Torr. – IR. (film): 1735 (COOEt), 1370, 1170, 1097, 1075, 1037, 930. – $^1H$-NMR. ($CCl_4$): 1.0–1.9 (*m*, 11H, 5 $CH_2$ and 1 CH); 1.25 (*t*, 3H, $OCH_2CH_3$); 2.25 (*t*, 2H, $CH_2CO$); 3.86 (*s*, 4H, $OCH_2CH_2O$); 4.10 (*q*, 2H, $OCH_2CH_3$).

$C_{13}H_{22}O_4$ (242.32) Calc. C 64.44 H 9.15% Found C 64.68 H 9.37%

*3-(3,3-Ethylenedioxycyclohexyl)propanol* (**17**). 13.75 g (56.8 mmol) of **16** in dry tetrahydrofuran (25 ml) were added dropwise to a suspension of 1.38 g (36 mmol) of lithiumaluminiumhydride in dry ethyl ether (100 ml). The mixture was heated under reflux for 30 min, then hydrolysed by dropwise addition of 6 ml of 1N NaOH. After stirring for several h, the crystalline precipitate was filtered off and washed with plenty of ether. The distillation of the combined filtrates gave 10.84 g (95%) of

---

4) For a discussion of the $^{13}C$-NMR. chemical shift in annulated olefins see [12].

the ethylene acetal **17**, b.p. 105–108°/0.08 Torr. – IR. (film): 3400 (OH), 2940, 1355, 1152, 1110, 1078, 1014, 948, 846. – $^1$H-NMR. ($CCl_4$): 0.9–1.9 (*m*, 13H, 6 $CH_2$ and 1 CH); 3.05 (br., 1H, OH); 3.52 (*t*, 2H, $CH_2$OH); 3.88 (*s*, 4H, $OCH_2CH_2O$).

$C_{11}H_{20}O_3$ (200.28) Calc. C 65.97 H 10.07% Found C 66.20 H 9.93%

*3-(3,3-Ethylenedioxycyclohexyl)propyl* p-*toluenesulfonate* (**18**). 7.60 g (39.8 mmol) of pure *p*-toluenesulfonyl chloride in dry pyridine (8 ml) were added dropwise to a stirred solution of 7.24 g (36.2 mmol) of **17** in dry pyridine (10 ml) at 0°. The mixture was stirred at 0–5° for 20 h, then diluted with ethyl ether, washed with saturated aqueous $CuSO_4$ (3 × 150 ml) and water, dried over $MgSO_4$, and evaporated *i.V.* The remaining oily *p*-toluenesulfonate **18** (11.54 g, 90%) was used for the next step without purification. White crystals from ethyl ether/hexane (–78°), m.p. *ca.* –20°. – IR. (film): 2940, 1600, 1360, 1190, 1178 ($OSO_2$), 1078, 945, 813, 662. – $^1$H-NMR. ($CDCl_3$): 0.8–1.9 (*m*, 13H, 6 $CH_2$ and 1 CH); 2.45 (*s*, 3H, $CH_3$); 3.90 (*s*, 4H, $OCH_2CH_2O$); 4.00 (*t*, 2H, $CH_2OSO_2$); 7.32 and 7.78 (2*d*, 2H each, ArH).

$C_{18}H_{26}O_5S$ (354.47) Calc. C 61.00 H 7.40 S 9.04% Found C 60.78 H 7.17 S 8.94%

*3-(3-Bromopropyl)cyclohexanone* (**19**). 9.95 g (28.1 mmol) of crude **18** and 48.0 g (553 mmol) of lithium bromide were heated under reflux in acetone (100 ml) for 48 h. The suspension was concentrated *i.V.*, then diluted with ethyl ether, washed with water, dried over $MgSO_4$, and evaporated. The distillation gave 5.54 g (90%) of **19**, b.p. 103–105°/0.10 Torr. – IR. (film): 1712 (C=O), 1345, 1312, 1248, 1225. – $^1$H-NMR. ($CCl_4$): 1.2–2.5 (*m*, 13H, 6 $CH_2$ and 1 CH); 3.39 (*t*, 2H, $CH_2$Br).

$C_9H_{15}BrO$ (219.13) Calc. C 49.33 H 6.90 Br 36.47% Found C 49.46 H 6.89 Br 36.26%

*3-(3-Oxocyclohexyl)propyl-triphenylphosphonium bromide* (**20**). 2.47 g (11.27 mmol) of **19** and 2.96 g (11.27 mmol) of triphenylphosphine in dry ethyl ether (12 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 ethyl ether, dissolved in methylene chloride, evaporated, and dried over $P_2O_5$ for 24 h at 0.01 Torr, which gave 5.29 g (97%) of the phosphonium bromide **20** as a hygroscopic, glass-like solid. – IR. ($CHCl_3$): 2940, 1705 (C=O), 1438, 1111, 992.

$C_{27}H_{30}BrOP$ (481.43) Calc. C 67.36 H 6.28 Br 16.60% Found C 67.21 H 6.32 Br 16.62%

*Bicyclo[3.3.1]-1(2)-nonene* (**1**). 28 mmol of sodium hydride, washed oil-free with pentane, and 5.72 g (11.9 mmol) of **20** were suspended in 40 ml of dry tetraethylene glycol dimethyl ether (tetraglyme) containing 1.05 g (11.9 mmol) of 2-methyl-2-butanol under nitrogen. The mixture was warmed to 70° for 30 min, at which temp. the suspension turned red (formation of the alkylidenephosphorane) and hydrogen evolved. The temp. was raised gradually to 120° during 4 h and the olefin distilled into a cold trap at 12 Torr. In a dry box filled with nitrogen, the crude product (0.32 g, 22%) was diluted with pentane, washed with water, dried over $Na_2SO_4$, and distilled in a bulb tube at 80°/12 Torr. 0.238 g (16%) of **1** were obtained as a colourless oil, identical with the product described by *Wiseman & Pletcher* [7], and *Marshall & Faubl* [8], 98% pure by GLC. (SE-52 or Carbowax 20 M). – IR. (film): 3022, 2940, 2860, 1620 (C=C), 1455, 1318, 1230, 1211, 1098, 1022, 992, 956, 861, 811, 711. – $^1$H-NMR. ($CCl_4$): 0.8–2.6 (*m*, 13H, 6 $CH_2$ and 1 CH); 5.65 (*t*, *J*=7, 1H, =CH). – $^{13}$C-NMR. (pure, with external TMS in $CDCl_3$): 146.8 (C(1)), 125.1 (C(2)), 36.6, 36.3, 34.4, 31.8, 31.6, 30.7, 25.3 (6 $CH_2$ and 1 CH). – UV. (cyclohexane): 206 (3.8). – MS. (*m/e*): 122.

*Addition product of* **1** *with 2,5-diphenylbenzo*[c]*furan*, obtained in benzene or ethyl ether solution at room temp. as a mixture of two isomers, separated by prep. TLC.

(a) *Main isomer*, m.p. 178–179° from 95% ethanol ([7]: 179–180°, [8]: 80.5–81°[5]), [23]: 180–184°).

$C_{29}H_{28}O$ (392.54) Calc. C 88.73 H 7.19% Found C 88.46 H 7.30%

(b) *Minor isomer*, m.p. 201–202° from 95% ethanol ([23]: 199–200°).

$C_{29}H_{28}O$ (392.54) Calc. C 88.73 H 7.19% Found C 88.52 H 7.13%

*Synthesis of bicyclo*[3.3.1]*-1(2)-nonene* (**1**) *by intramolecular* Wittig *reaction using other solvents and bases.* For detailed procedures see [12]. – (a)*Dimethyl sulfoxide anion in dimethyl sulfoxide.* 4 h at 100°. Isolation by steam distillation at 100°/100 Torr, 5% yield. – (b) *Lithium methoxide in dimethylformamide.* 2 h under reflux. The solution was diluted with water and extracted with pentane, yield 3.5%. – (c) *Butyllithium in hexane/ethyl ether or tetrahydrofuran.* No bridgehead olefin was

---

[5]) Verified by Dr. *H. Faubl*, personal communication. This night be another one of the four possible isomers.

formed. – (d)*Potassium* t-*butoxide in tetraglyme*. The distillate (120°/12 Torr) contained 13% of the olefin **1** and *t*-butyl alcohol. The same result was obtained in triglyme (triethylene glycol dimethyl ether), but no olefin was found when the reaction was carried out in tetrahydrofuran. – (e) *Sodium hydride in hexamethylphosphoric acid triamide*. 480 mg (1.0 mmol) of the phosphonium bromide **20** and 1.8 mmol of sodium hydride, washed oil-free with pentane, were suspended in 7 ml of dry hexamethylphosphoric acid triamide. The mixture was heated to 110° and the olefin distilled at 12 Torr. Yield 2.5%. An additional 3% yield was isolated by steam distillation of the residue. – (f) *Sodium hydride and 2-methyl-2-butanol in dimethylformamide*. 4 h under reflux. The solution was diluted with water and extracted with pentane, yield 7%.

*Ethyl (3-oxocycloheptyl)acetate* (**22**). 46.8 g (275 mmol) of potassium monoethyl malonate dissolved in a minimum of water were acidified with 24 ml (280 mmol) of conc. hydrochloric acid. The malonic acid monoester was extracted into ethyl ether, washed with brine, and dried over $MgSO_4$. Evaporation of the solvent *i.V.* gave 34.8 g (96%) of monoethyl malonate. To this acid dissolved in 80 ml of tetrahydrofuran at 0° a *ca.* 1M solution of isopropyl *Grignard* reagent (*ca.* 500 ml, prepared from 18.0 g of magnesium turnings and 78.0 g of isopropyl bromide in 520 ml of tetrahydrofuran) was added dropwise until a weak turbidity appeared. The formation of the magnesium salt was completed by heating under reflux for 30 min. 21.2 g (192.5 mmol) of 2-cycloheptenone (**21**) were added to the solution at 10°. The mixture was stirred at RT. for 2 h, then heated under reflux for 30 min, hydrolysed with 400 ml of 1N sulfuric acid with cooling, concentrated *i.V.*, and extracted with ethyl ether. The extracts were washed with brine, dried over $MgSO_4$, and evaporated. The crude monoethyl (3-oxocycloheptyl)malonate was heated to 190–200° for 30 min with some boiling chips, which effected decarboxylation. The distillation gave 24.6 g (64%) of **22**, b.p. 97–100°/0.1 Torr, as a colourless oil. – IR. (film): 2940, 1735, 1704 (C=O), 1375, 1250, 1180, 1110, 1037. – $^1$H-NMR. ($CCl_4$): 1.0–2.0 (*m*, 7H, 3 $CH_2$ and 1 CH); 1.25 (*t*, 3H, $CH_3CH_2O$); 2.1–2.5 (*m*, 6H, $CH_2CO$); 4.11 (*q*, 2H, $CH_3CH_2O$).

$C_{11}H_{18}O_3$ (198.26) Calc. C 66.64 H 9.15% Found C 66.89 H 9.05%

*Ethyl (3,3-ethylenedioxycycloheptyl)acetate* (**23**) was obtained from **22** and ethylene glycol in benzene as described above for acetal **16**. Yield 92%, b.p. 110–115°/0.1 Torr. – IR. (film): 2940, 1735 (COOEt), 1370, 1180, 1145, 1098, 1032, 948. – $^1$H-NMR. ($CCl_4$): 1.0–1.9 (*m*, 11H, 5 $CH_2$ and 1 CH); 1.25 (*t*, 3H, $CH_3CH_2O$); 2.1 (br., 2H, $CH_2CO$); 3.84 (*s*, 4H, $OCH_2CH_2O$); 4.10 (*q*, 2H, $CH_3CH_2O$).

$C_{11}H_{20}O_3$ (200.28) Calc. C 64.44 H 9.15% Found C 64.48 H 9.22%

*2-(3,3-Ethylenedioxycycloheptyl)ethanol* (**24**). **23** was reduced with lithiumaluminiumhydride in ethyl ether and tetrahydrofuran as described above for alcohol **17**. Yield 93%, b.p. 112–117°/0.2 Torr. – IR. (film): 3420 (OH), 2940, 1369, 1240, 1142, 1100, 1082, 1038, 952, 788. – $^1$H-NMR. ($CCl_4$): 1.2–2.0 (*m*, 13H, 6 $CH_2$ and 1 CH); 2.1 (br., 1H, OH); 3.55 (*t*, 2H, $CH_2OH$); 3.85 (*s*, 4H, $OCH_2H_2CO$).

$C_{11}H_{20}O_3$ (200.28) Calc. C 65.97 H 10.07% Found C 66.00 H 10.21%

*2-(3,3-Ethylenedioxycycloheptyl)ethyl* p-*toluenesulfonate* (**25**) was obtained from **24** and *p*-toluenesulfonyl chloride in pyridine as described above for **18**. 83% yield of **25** as a colourless, viscous oil, which was used in the next step without purification. Colourless needles from hexane (0°), m.p. 55–56°. – IR. ($CCl_4$): 2940, 1602, 1450, 1362, 1191, 1178 ($OSO_2$), 1098, 815, 664. – $^1$H-NMR. ($CCl_4$): 1.0–1.8 (*m*, 13H, 6 $CH_2$ and 1 CH); 2.45 (*s*, 3H, $CH_3$); 3.78 (*s*, 4H, $OCH_2CH_2O$); 4.00 (*t*, 2H, $CH_2OSO_2$); 7.30 and 7.78 (2*d*, 2H each, ArH).

$C_{18}H_{26}O_5S$ (354.47) Calc. C 61.00 H 7.40 S 9.04% Found C 60.95 H 7.34 S 8.83%

*3-(2-Bromoethyl)cycloheptanone* (**26**) was obtained from **25** and lithium bromide in acetone as described above for **19**. 97% yield of **26**, b.p. 83–85°/0.08 Torr, as a yellowish oil. – IR. (film): 2940, 2860, 1700, 1450, 1348, 1322, 1252, 1193, 1168. – $^1$H-NMR. ($CCl_4$): 1.3–2.2 (*m*, 9H, 4 $CH_2$ and 1 CH); 2.2–2.6 (*m*, 4H, 2 $CH_2CO$); 3.34 (*t*, 2H, $CH_2Br$).

$C_9H_{15}BrO$ (219.13) Calc. C 49.33 H 6.90 Br 36.46% Found C 49.68 H 7.02 Br 36.29%

*2-(3-Oxocycloheptyl)ethyl-triphenylphosphonium bromide* (**27**) was obtained from **26** and 1.00 equiv. of triphenylphosphine in dry ether at 120° as a hygroscopic, glass-like solid in 91% yield. – IR. ($CHCl_3$): 2930, 1692 (C=O), 1438, 1110, 992.

$C_{27}H_{30}BrOP$ (481.43) Calc. C 67.36 H 6.28 Br 16.60% Found C 67.58 H 6.30 Br 16.23%

*Bicyclo[4.2.1]-1(8)-nonene* (**2**) was made from **27**, sodium hydride, and 2-methyl-2-butanol in tetraglyme as described above for **1**. The redistillation in a bulb tube at 70°/12 Torr gave 57% of

**2** as a waxy solid, m.p. 28–30°, more than 99% pure by GLC. (SE-52 and Carbowax 20 M). - IR. ($CCl_4$): 3047, 2920, 1618 (C=C), 1329, 951, 781, 675, 651. - $^1$H-NMR. ($CCl_4$): 0.9–2.9 (*m*, 13H, 6 $CH_2$ and 1 CH); 5.40 (*s*, 1H, halfwidth 9 Hz, =CH). - $^{13}$C-NMR. ($C_6D_6$): 147.2 (*s*, C(1)); 127.4 (*d*, C(8)); 45.4 (*d*, C(6)); 38.6 (2C); 34.8; 32.3; 27.1; 23.9 (5*t*, 6 $CH_2$). - UV. (cyclohexane): 186 (3.8), shoulder at 200 (3.7). - MS. (*m/e*): 123 ($M$+1, 2.7), 122 ($M^+$, 24), 80 (100).

$C_9H_{14}$ (122.21) Calc. C 88.45 H 11.55% Found C 88.62 H 11.40%

*Addition product of* **2** *with 2,5-diphenylbenzo*[c]*furan*, obtained in benzene at RT. as a mixture of two isomers, separated by prep. TLC.

(a) *Main isomer*, m.p. 161–162° from ethanol/water.

$C_{29}H_{28}O$ (392.54) Calc. C 88.73 H 7.19% Found C 88.72 H 7.19%

(b) *Minor isomer*, m.p. 144–145° from ethanol/water.

$C_{29}H_{28}O$ (392.54) Calc. C 88.73 H 7.19% Found C 88.48 H 7.35%

*Addition product of* **2** *with tetraphenylcyclopentadienone*, colourless needles from ethanol/water, m.p. 181–182°.

$C_{38}H_{34}O$ (506.69) Calc. C 90.07 H 6.76% Found C 89.90 H 7.04%

*3-(3-Butenyl)cyclopentanone* (**29**). 3-Butenylmagnesium bromide was added to 2-cyclopentenone in tetrahydrofuran in the presence of cuprous iodide. The olefinic ketone obtained in 42% yield was identical with the product described by *Conia et al.* [20]. Colourless oil, b.p. 90–94°/13 Torr.

$C_9H_{14}O$ (138.20) Calc. C 78.21 H 10.21% Found C 78.45 H 10.40%

*4-(3,3-Ethylenedioxycyclopentyl)-1-butene* (**30**) was obtained from **29** and ethylene glycol in benzene as described above for acetal **16**. Yield 89%, b.p. 63–65°/0.3 Torr. - IR. (film): 3080, 2940, 1643 (C=C), 1440, 1337, 1118, 1030, 907. - $^1$H-NMR. ($CCl_4$): 1.0–2.3 (*m*, 11H, 5 $CH_2$ and 1 CH); 3.77 (*s*, 4H, $OCH_2CH_2O$); 4.9 (*m*, 2H, =$CH_2$); 5.6 (*m*, 1H, =CH).

$C_{11}H_{18}O_2$ (182.25) Calc. C 72.49 H 9.96% Found C 72.64 H 9.91%

*4-(3,3-Ethylenedioxycyclopentyl)butanol* (**31**). 8.5 ml (17 mmol) of a *ca.* 2M solution of diborane in tetrahydrofuran were added dropwise at 0° to 6.04 g (33.1 mmol) of **30** in dry tetrahydrofuran (30 ml). The solution was kept at RT. for 2 h. 15 ml of 1.5N NaOH and 6 ml of 30% hydrogen peroxide were added, and the mixture warmed to 45° for 4 h. The product was extracted into ethyl ether, washed with brine, and dried over $MgSO_4$. The distillation gave 5.77 g (87%) of a colourless oil, b.p. 117–118°/0.2 Torr as a 92:8 mixture of **31** and the isomeric secondary alcohol by GLC. (Carbowax 20 M). - IR. (film): 3400 (OH), 2930, 1325, 1120, 1098, 1035, 943. - $^1$H-NMR. ($CCl_4$): 1.1–2.1 (*m*, 13H, 6 $CH_2$ and 1 CH); 2.6 (br., 1H, OH); 3.50 (*t*, 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 65.93 H 10.12%

*4-(3,3-Ethylenedioxycyclopentyl)butyl* p*-toluenesulfonate* (**32**) was obtained from **31** (contaminated with 8% of the secondary alcohol) and *p*-toluenesulfonyl chloride in pyridine as described above for **18**. 84% yield of **32** as a viscous oil, containing some unreacted secondary alcohol. Pure *p*-toluenesulfonate was obtained by chromatography of the crude product on silica gel with methylene chloride. - IR. (film): 2940, 1598, 1357, 1187, 1175 ($OSO_2$), 1095, 928, 814, 660. - $^1$H-NMR. ($CCl_4$): 1.0–2.1 (*m*, 13H, 6 $CH_2$ and 1 CH); 2.47 (*s*, 3H, $CH_3$); 3.78 (*s*, 4H, $OCH_2CH_2O$); 3.95 (*t*, 2H, $CH_2OSO_2$); 7.28 and 7.72 (2*d*, 2H each, ArH).

$C_{18}H_{26}O_5S$ (354.47) Calc. C 61.00 H 7.40 S 9.04% Found C 60.85 H 7.33 S 8.94%

*3-(4-Bromobutyl)cyclopentanone* (**33**) was obtained from crude **32** and lithium bromide in dry acetone as described above for **19**. 89% yield of **33**, b.p. 97–108°/0.15 Torr, as a yellowish oil. - IR. (film): 2930, 1738 (C=O), 1400, 1232, 1153. - $^1$H-NMR. ($CCl_4$): 1.4–2.5 (*m*, 13H, 6 $CH_2$ and 1 CH); 3.37 (*t*, 2H, $CH_2Br$).

$C_9H_{15}BrO$ (219.13) Calc. C 49.33 H 6.90 Br 36.47% Found C 49.58 H 6.82 Br 36.30%

*Acetaldehyde 4-chlorobutyl ethyl acetal* (**34**). Commercial 4-chlorobutanol (*Fluka*) containing HCl was stirred with solid $NaHCO_3$ for 18 h at RT. and filtered. Following a procedure of *Eaton* [22] 94 g (1.30 mol) of ethyl vinyl ether (stabilized with 0.1% KOH) and 2.5 ml of dichloroacetic acid were added simultaneously over a period of 1 h to the 4-chlorobutanol (112 g, 1.03 mol) containing 0.2 ml of dichloroacetic acid. The flask was stoppered and kept at RT. for 16 h. 4 g of solid $Na_2CO_3$ were added and stirring continued for 6 h. The precipitate was filtered off and washed with methylene chloride. Distillation over a trace of $Na_2CO_3$ gave 150 g (80%) of **34**, b.p. 86–89°/13 Torr. The acetal should be stored over $Na_2CO_3$. – IR. (film): 2975, 2938, 2870, 1375, 1128, 1095, 1055. – $^1$H-NMR. ($CCl_4$): 1.15 (*t*, *J*=7, 3H, $CH_3CH_2$); 1.22 (*t*, *J*=5.5, 3H, $CH_3CH$); 1.7 (*m*, 4H, 2 $CH_2$); 3.5 (*m*, 6H, 2 $CH_2O$, 1 $CH_2Cl$); 4.61 (*q*, *J*=5.5, 1H, O–CH–O).

$C_8H_{17}ClO_2$ (180.68) Calc. C 53.18 H 9.48 Cl 19.62% Found C 52.97 H 9.37 Cl 19.87%

*3-(4-Hydroxybutyl)cyclopentanone* (**36**). 5.92 g (31.8 mmol) of **34** in dry tetrahydrofuran (30 ml) were added dropwise to 1.0 g (41 mmol) of magnesium turnings. The *Grignard* reaction was started with a drop of methyl iodide after 1/10 of the chloride had been added. The mixture was heated under reflux for 4 h, filtered under nitrogen through a sintered glass funnel, and cooled to −15°. 0.60 g of finely ground cuprous iodide were added, and the suspension stirred at high speed for 30 min at −15°. 2.10 g (26 mmol) of 2-cyclopentenone in tetrahydrofuran (3 ml) were added from a syringe over 20 min. The suspension was warmed to 0°, stirred for 1 h, and poured into well-stirred saturated aqueous ammonium chloride (500 ml). After 1 h, the mixture was extracted with several portions of ethyl ether. The extracts were washed with saturated aqueous ammonium chloride and brine, dried over $K_2CO_3$, and evaporated *i.V.* Pure *3-(6-methyl-5,7-dioxanonyl)cyclopentanone* (**35**) was isolated by preparative GLC. (SE-52). – IR. (film): 2940, 1740, 1375, 1130, 1095, 1055. – $^1$H-NMR. ($CCl_4$): 1.15 (*t*, 3H, $CH_3CH_2$); 1.22 (*d*, 3H, $CH_3CH$); 1.0–2.5 (*m*, 13H, 6 $CH_2$ and 1 CH); 3.4 (*m*, 4H, 2 $CH_2O$; 4.60 (*q*, 1H, O–CH–O).

$C_{13}H_{24}O_3$ (228.33) Calc. C 68.38 H 10.59% Found C 68.63 H 10.84%

The bulk of the crude acetal **35** was dissolved in 40 ml of tetrahydrofuran/water 3:1 containing 0.4 g of *p*-toluenesulfonic acid, stirred at RT. for 2 h, then diluted with ethyl ether, washed with 2N $NaHCO_3$ and brine, and dried over $MgSO_4$. A flash distillation in a bulb tube at 140°/0.05 Torr and redistillation gave 1.80 g (44%) of pure **36**, b.p. 110–115°/0.08 Torr. – IR. (film): 3450 (OH), 2930, 1738 (C=O), 1155, 1055. – $^1$H-NMR. ($CDCl_3$): 1.2–2.7 (*m*, 13H, CH, $CH_2$); 2.1 (*s*, 1H, OH); 3.68 (br. *t*, 2H, $CH_2O$).

$C_9H_{16}O_2$ (156.23) Calc. C 69.19 H 10.32% Found C 68.99 H 10.52%

*4-(3-Oxocyclopentyl)butyl methanesulfonate* (**37**). 2.90 g (25.1 mmol) of methanesulfonyl chloride in methylene chloride (5 ml) were added dropwise to a solution of 3.64 g (23.3 mmol) of **36** and 3.5 g (35 mmol) of triethylamine in methylene chloride (20 ml) at 0°. After 10 min at 0°, the solution was diluted with methylene chloride, washed with 2N HCl, 2N $NaHCO_3$, and brine, dried over $MgSO_4$, and evaporated *i.V.* The residue, 5.45 g (100%) of methanesulfonate **37**, was used directly for the next step. Pure **37**, a colourless oil, was obtained by chromatography on silica gel with ethyl ether. – IR. (film): 2940, 1740 (C=O), 1348, 1170 ($OSO_2$). – $^1$H-NMR. ($CDCl_3$): 1.0–2.7 (*m*, 13H, 6 $CH_2$ and 1 CH); 3.03 (*s*, 3H, $CH_3$); 4.27 (*t*, 2H, $CH_2O$).

$C_{10}H_{18}O_4S$ (234.31) Calc. C 51.26 H 7.74 S 13.68% Found C 51.14 H 7.90 S 13.60%

*3-(4-Bromobutyl)cyclopentanone* (**33**). 5.21 g (22.2 mmol) of crude **37** and 19.3 g (222 mmol) of lithium bromide were heated under reflux in acetone (100 ml) for 20 h. The solution was concentrated *i.V.*, then diluted with ethyl ether, washed with water, dried over $MgSO_4$, and evaporated. The distillation gave 4.18 g (86%) of **33**, b.p. 107–113°/0.25 Torr, identical with the bromide obtained from **32**.

*4-(3-Oxocyclopentyl)butyl-triphenylphosphonium bromide* (**38**) was obtained from **33** and 1.00 equiv. of triphenylphosphine in dry ethyl ether at 120° for 72 h as a hygroscopic, glass-like solid in 92% yield. – IR. ($CHCl_3$): 2930, 1732 (C=O), 1438, 1110, 994.

*Tetraphenylborate*, white needles from methanol, m. p. 125–127°.

$C_{51}H_{50}BOP$ (720.74 Calc. C 84.99 H 6.99 P 4.30% Found C 84.78 H 7.03 P 4.45%

*Bicyclo[4.2.1]-1(2)-nonene* (**3**) was obtained from **38**, sodium hydride, and 2-methyl-2-butanol in tetraglyme as described above for bicyclo[3.3.1]-1(2)-nonene (**1**). The redistillation in a bulb tube at 80°/12 Torr gave 14% of **3** as a colourless liquid, 99% pure by GLC. (SE-52 and Carbowax 20M). – IR. (film): 3020, 2910, 1656 (C=C), 870, 838, 811, 719. – $^1$H-NMR. (90 MHz, $C_6D_6$): 0.7–2.8 (*m*, 13H, 6 $CH_2$ and 1 CH); 5.40 (*d*×*d*, *J*=6 and 7, 1H, =CH). – $^1$H-NMR. (60 MHz, $CCl_4$): 5.30 (*t*, J=7, 1H, =CH). – $^{13}$C-NMR. ($C_6D_6$): 147.3 (*s*, C(1)); 124.9 (*d*, C(2)); 34.4; 33.8; 32.5; 32.3 (*d*, C(6)); 27.1; 25.6; 23.6 (6*t*, 6 $CH_2$). – UV. (cyclohexane): 206 (3.9). – MS. (*m/e*): 123 ($M^+$+1, 5.2), 122 ($M^+$, 40), 93 (100).

$C_9H_{14}$ (122.21) Calc. C 88.45 H 11.55% Found C 88.22 H 11.43%

*Addition product of* **3** *with tetraphenylcyclopentadienone*, colourless needles from ethanol/water, m.p. 169-170°.

$C_{38}H_{34}O$ (506.69) Calc. C 90.07 H 6.76% Found C 89.86 H 6.98%

*Bicyclo[4.2.1]nonane* (**45**) was obtained upon hydrogenation of bicyclo[4.2.1]-1(8)-nonene (**2**) over 10% Pd/C in methanol or upon *Wolff-Kishner* reduction of bicyclo[4.2.1]-2-nonanone [31]. Waxy solid m.p. 93-95° (sealed tube) after repeated sublimation at 50°/12 Torr ([30]: m.p. 95-96°). - $^{13}$C-NMR. ($CDCl_3$): 37.4 (*d*, 2 *C*H); 35.9; 35.5; 33.1; 25.6 (4*t*, 7 *C*$H_2$).

## REFERENCES

[1] *K. B. Becker*, Chimia *28*, 726 (1974); *K. B. Becker*, Tetrahedron Letters *1975*, 2207.

[2] *G. Köbrich*, Angew. Chem. *85*, 494 (1973), Angew. Chem. Int. Ed. *12*, 464 (1973); *G. L. Buchanan*, Chem. Soc. Rev. *3*, 41 (1974).

[3] *R. Keese*, Angew. Chem. *87*, 568 (1975), Angew. Chem. Int. Ed. *14*, 528 (1975).

[4] *J. Bredt, H. Thouet & J. Schmitz*, Liebigs Ann. Chem. *437*, 1 (1924).

[5] *V. Prelog, L. Ruzicka, P. Barman & L. Frenkiel*, Helv. *31*, 92 (1948); *V. Prelog*, J. chem. Soc. *1950*, 420.

[6] *F. S. Fawcett*, Chem. Rev. *47*, 219 (1950).

[7] *J. R. Wiseman*, J. Amer. chem. Soc. *89*, 5966 (1967); *J. R. Wiseman & W. A. Pletcher*, ibid. *92*, 956 (1970).

[8] *J. A. Marshall & H. Faubl*, J. Amer. chem. Soc. *89*, 5965 (1967); *iidem*, ibid. *92*, 948 (1970).

[9] *K. T. Burgoine, S. G. Davies, M. J. Peagram & G. H. Whitham*, J. chem. Soc. Perkin I *1974*, 2629 and ref. cited there.

[10] *J. R. Wiseman, Hak-Foon Chan & C. J. Ahola*, J. Amer. chem. Soc. *91*, 2812 (1969).

[11] *Fu-Ning Fung*, Diss. Abstracts Int. B *35*, 5328 (1975); *Fu-Ning Fung, Hak-Foon Chan & J. R. Wiseman*, The First Congress of the North American Continent, Mexico 1975, Org. Abstracts No. 69.

[12] *K. B. Becker*, Helv. *60*, 68 (1977).

[13] *M. Schlosser, A. Piskala, C. Tarchini & Huynh Ba Tuong*, Chimia *29*, 341 (1975); compare also *E. Vedejs & K.A.J. Snoble*, J. Amer. chem. Soc. *95*, 5778 (1973).

[14] *W. G. Dauben & J. Ipaktschi*, J. Amer. chem. Soc. *95*, 5088 (1973).

[15] *Moon-geu Kim & J. D. White*, J. Amer. chem. Soc. *97*, 451 (1975).

[16] *K. B. Becker*, Helv. *60*, 94 (1977).

[17] *A. Bowers, T. G. Halsall, E. R. H. Jones & A. J. Lemin*, J. chem. Soc. *1953*, 2548.

[18] *M. Regitz & J. Rüter*, Chem. Ber. *102*, 3877 (1969).

[19] *G. Bram & M. Vilkas*, Bull. Soc. chim. France *1964*, 945; *R. E. Ireland & J. A. Marshall*, J. Amer. chem. Soc. *81*, 2907 (1959).

[20] *P. Beslin, R. Bloch, G. Moinet & J. M. Conia*, Bull. Soc. chim. France *1969*, 508.

[21] *G. Zweifel & H. C. Brown*, Org. Reactions *13*, 1 (1963); *H. C. Brown*, 'Boranes in Organic Chemistry', Cornell University Press, Ithaca (N.Y.) 1972.

[22] Compare *P. E. Eaton, G. F. Cooper, R. C. Johnson & R. H. Mueller*, J. org. Chemistry *37*, 1947 (1972).

[23] *W. G. Dauben & J. D. Robbins*, Tetrahedron Letters *1975*, 151.

[24] *A. J. Bridges & G. H. Whitham*, J. chem. Soc. Perkin I *1975*, 2264.

[25] *J. B. Stothers*, 'Carbon-13 NMR Spectroscopy', Academic Press, New York 1972.

[26] *R. D. Bach*, J. chem. Physics *52*, 6423 (1970); *O. Schnepp, E. F. Pearson & E. Sharman*, J. chem. Physics *52*, 6424 (1970).

[27] *A. I. Scott*, 'Interpretation of the Ultraviolet Spectra of Natural Products', Pergamon, Oxford 1964, p. 20ff.

[28] *Ch. Batich, O. Ermer, E. Heilbronner & J. R. Wiseman*, Angew. Chem. *85*, 302 (1973), Angew. Chem. Int. Ed. *12*, 312 (1973).

[29] *A. Heumann & H. Kolshorn*, Tetrahedron *31*, 1571 (1975).

[30] *M. Hartmann*, Z. Chem. *4*, 457 (1964); *idem*, Liebigs Ann. Chem. *724*, 102 (1969).

[31] *W. Kraus, W. Rothenwöhrer, H. Sadlo & G. Klein*, Angew. Chem. *84*, 643 (1972), Angew. Chem. Int. Ed. *11*, 641 (1972).