193. Synthesis of 1-Bicyclo[3.2.2]nonene and 1(7)-Bicyclo[3.2.2]nonene by Intramolecular *Wittig* Reaction[1])

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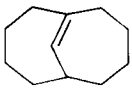
(13.VIII.80)

Summary

The synthesis of 1-bicyclo[3.2.2]nonene (**2**) and of 1(7)-bicyclo[3.2.2]nonene (**3**), two isomeric bridged (*E*)-cycloheptenes, by intramolecular *Wittig* reaction is described. These '*Bredt* olefins' could not be isolated, but dimerized rapidly. In both cases, the main product was shown to be a head-to-tail dimer with a cyclobutane ring. The '*Bredt* olefins' were also trapped *in situ* with furan or 2,5-diphenylbenzo[*c*]furan.

Introduction. – The question of the limits of *Bredt*'s rule is of considerable current interest [1]. In recent years, a number of highly strained bicyclic and polycyclic bridgehead olefins ('*Bredt* olefins'), both stable and unstable, have been synthesized [2]. All the available evidence supports the hypothesis that the strain and stability of a bridgehead olefin may be compared to the strain and stability of the corresponding (*E*)-cycloalkene, from which it can be formally derived by bridging; this concept has been put forward by *Wiseman* thirteen years ago [3], but can be found already in a publication of *Bredt* himself [4].

(*E*)-Cycloheptene has been prepared and trapped *in situ*, but could not be isolated [5]. Several bridgehead olefins related to (*E*)-cycloheptene are known: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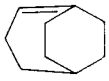
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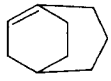
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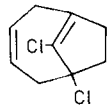

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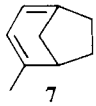
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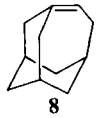
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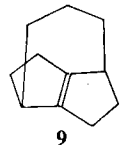
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[1]) Taken in part from the dissertation of *J. L. Chappuis*, Basel 1980.

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0018-019X/80/7/1812-11$01.00/0

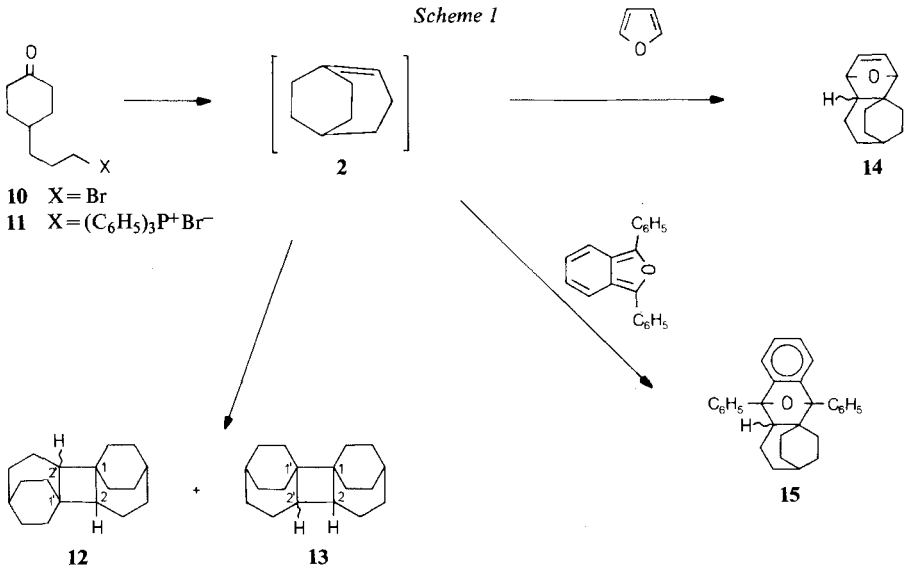
1(11)-Bicyclo[4.4.1]undecene (**1**), formally a tetramethylene-bridged (*E*)-cycloheptene [6], the ethylene-bridged 1-bicyclo[3.2.2]nonene (**2**) and 1(7)-bicyclo-[3.2.2]nonene (**3**; prepared as a mixture [7]), and 6,9-dichloro-1(9),3-bicyclo[4.2.1]-nonadiene (**4**) [8], the methylene-bridged 1-bicyclo[3.2.1]octene (**5**) [9], 1(7)-bicyclo[3.2.1]octene (**6**) [10], and 4-methyl-1,3-bicyclo[3.2.1]octadiene (**7**) [11], and the tricyclic bridgehead olefins homoadamant-3-ene (3-tricyclo[4.3.1.$1^{3,8}$]undecene, **8**) [12], and 2(6)-tricyclo[3.3.3.$0^{2,6}$]undecene (**9**) [13].

(*E*)-Cycloheptene isomerizes to (*Z*)-cycloheptene. Because such an isomerization reaction is not feasible in bridgehead olefins, one would expect that bridged (*E*)-cycloheptenes are kinetically more stable than the reference compound. Indeed, the bicyclo[3.2.2]nonenes **2** and **3** and homoadamant-3-ene (**8**) could be observed at low temperature with ^{1}H-NMR. or IR. spectroscopy [7] [14]; however, all the bridgehead olefins **1**–**9** dimerize rapidly at room temperature or even below. The dimers obtained usually are cyclobutanes formed by a formal [2+2] cycloaddition (see *e.g.* [8] [12]), but notable exceptions are an 'ene' dimer from **9** [13], and a 'homo-ene' dimer from **1** [6].

In order to gain more insight into the stability and dimerization of bridged (*E*)-cycloheptenes, 1-bicyclo[3.2.2]nonene (**2**) and 1(7)-bicyclo[3.2.2]nonene (**3**) have now been prepared separately by the intramolecular *Wittig* reaction [15].

Syntheses. – Starting material for the intramolecular *Wittig* reaction leading to 1-bicyclo[3.2.2]nonene (**2**) was the phosphonium bromide **11** derived from the known 4-(3-bromopropyl)cyclohexanone (**10**) [16] *(Scheme 1)*. The salt **11** was suspended in dry tetraglyme (tetraethylene glycol dimethyl ether) and heated in the presence of potassium *t*-butoxide [17]. The olefin **2** could not be isolated, but a 2.7% yield of a mixture of four dimers in a ratio of 9:1:1.5:4.5 (GLC.) was found besides triphenylphosphine and triphenylphosphine oxide. The main

Scheme 1



hydrocarbon was obtained by repeated crystallization and identified as a head-to-tail dimer **12**.

When the reaction was performed in the presence of excess furan, a 1:1 mixture of the *exo-* and *endo-Diels-Alder* adducts **14** of furan with **2** was found in 2% yield besides 6% of the same mixture of dimers as above. Olefin **2** could be trapped more efficiently with 2,5-diphenylbenzo[*c*]furan, which gave two *Diels-Alder* adducts **15** in 8% yield.

The 1(7)-bicyclo[3.2.2]nonene (**3**) was synthesized starting with ethyl (4-oxocycloheptyl)acetate (**17**) available from ethyl (4-oxocyclohexyl)acetate (**16**) by ring enlargement with diazomethane [18] *(Scheme 2)*. The keto function in **17** was protected with ethylene glycol and a trace of acid, and the ester group in the resulting ethylene acetal **18** reduced with lithium aluminium hydride to yield **19**. This alcohol was transformed into the methanesulfonate **20**, which gave directly 4-(2-bromoethyl)cycloheptanone (**21**) on treatment with excess lithium bromide in boiling acetone.

The intramolecular *Wittig* reaction of phosphonium bromide **22** was performed as with **11**. All attempts to distil 1(7)-bicyclo[3.2.2]nonene (**3**) directly out of the reaction mixture at reduced pressure and to characterize it by NMR. spectroscopy at −80° failed. Conventional work-up followed by column chromatography

Scheme 2

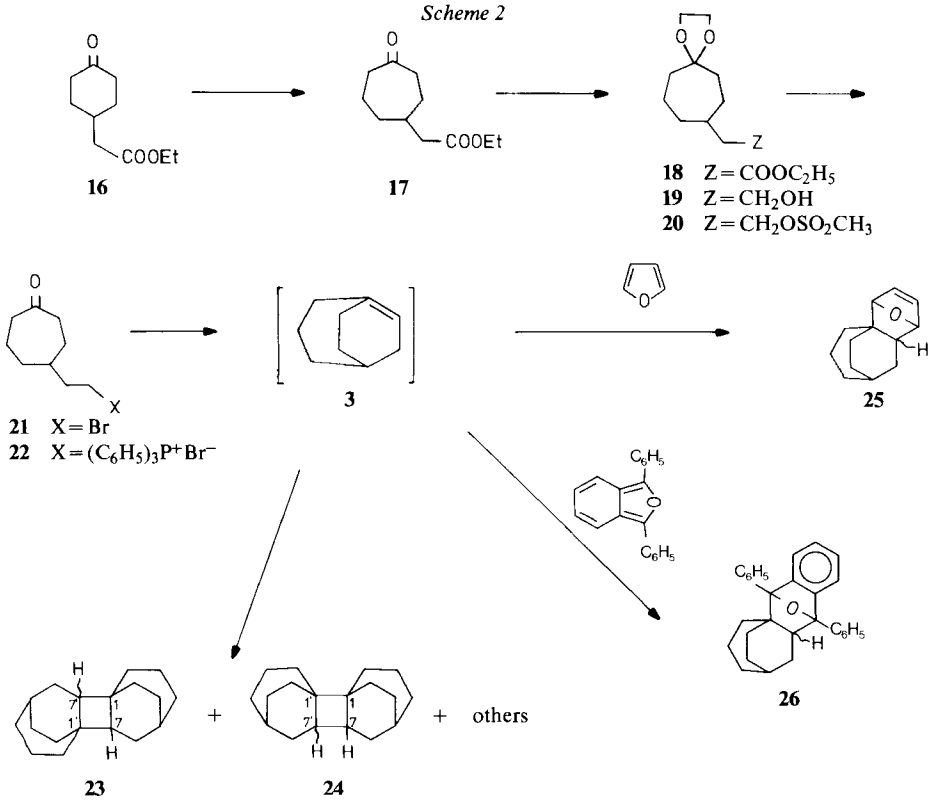


Table 1. *^{13}C-NMR. spectra of adamantene dimers* **27** *and* **28** *[19] and bicyclo[3.2.2]nonene dimers* **12** *and* **23**[a])

	Cyclobutane ring	Other carbon atoms
12	37.4 (*s*); 51.5 (*d*)	30.6 (*d*); 37.9, 35.3, 28.7, 28.7, 25.1, 22.1 (each *t*)
23	37.0 (*s*); 52.4 (*d*)	28.4 (*d*); 38.3, 35.1, 29.4, 25.9, 25.4, 21.8 (each *t*)
27	47.1 (*s*); 47.1 (*d*)	30.7, 30.4, 28.7 (each *d*); 40.7, 39.8, 39.3, 34.2, 32.0 (each *t*)
28	44.3 (*s*); 58.5 (*d*)	31.7, 30.7, 28.6 (each *d*); 50.2, 42.8, 40.0, 35.6, 32.3 (each *t*)

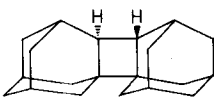
[a]) Solvent $CDCl_3$, δ in ppm (TMS: $\delta = 0$ ppm). Multiplicity determined in off-resonance proton-decoupled spectra: *s* = singlet, *d* = doublet, *t* = triplet.

gave a hydrocarbon fraction, from which a mixture of at least six dimeric compounds was obtained by distillation in 20% yield. The main dimer accounting for *ca.* 60% of the mixture was separated and shown to have the head-to-tail cyclobutane structure **23**. The remaining nonpolar material contained trimers and probably higher oligomers of bridgehead olefin **3**. The composition of the hydrocarbon fraction was shown to be dependent on the reaction conditions: If the *Wittig* reaction was conducted in more dilute solution, the proportion of an unsaturated dimer increased at the expense of others.

Dimerisation and oligomerisation was almost completely suppressed, when the *Wittig* reaction was performed in a mixture of furan and tetraglyme, and *exo*- and *endo-Diels-Alder* adducts with structure **25** were isolated in 41% yield. Olefin **3** was also trapped with 2,5-diphenylbenzo[*c*]furan to give two adducts **26** in 51% yield.

Structure elucidation of the dimers. – The structure proposed for the main dimer **12** (from **2**) and for **23** (from **3**) is based primarily on the ^{13}C-NMR. spectra *(Table 1)* and the assumption that no deep-sited rearrangement of the bicyclo[3.2.2]nonane skeleton had occurred. IR., ^{1}H-NMR., and mass spectra did not yield much information, but are in accord with the structures shown. The symmetrical nature of the dimers is proven by the presence of only nine C-resonances in the broad-band proton-decoupled ^{13}C-NMR. spectrum.

The chemical shift of the fully substituted cyclobutane C-atoms at *ca.* 37 ppm and of the tertiary C-atoms at rather low field (*ca.* 52 ppm) are of special diagnostic value. A comparison with the ^{13}C-NMR. chemical shifts of the related adamantene dimers **27** and **28** [19] demonstrates the head-to-tail structure of both **12** and **23**. The lower value of 52 ppm (for **12** and **23**) compared to 58.5 ppm (in **28**) can be readily accounted for by the differing number of alkyl ring substituents in β-position to the corresponding C-atoms [20].



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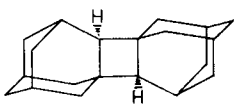

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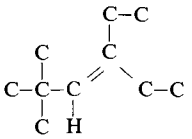
The IR., NMR. and mass spectra of the crude dimer mixture obtained from **2** are in accord with the assumption that the four possible cyclobutane dimers **12** and **13** have been formed. However, it cannot rigorously be excluded that one of the minor components has a different structure.

The dimer mixture obtained from **3** was more complex and contained saturated and unsaturated compounds, as evidenced by the NMR. spectra. Repeated crystallization gave a sample containing **23** and one unsaturated dimer.

This unsaturated dimer shows a one-proton triplet ($J=2$ Hz) at 5.33 ppm in the ^{1}H-NMR. and absorptions at 139.8 (*s*), 131.6 (*d*), and 47–20 ppm (16 C-atoms) in the ^{13}C-NMR. spectra, which demonstrates the presence of a triply substituted C,C double bond. Two features of the ^{13}C-NMR. spectrum are exceptional: The low field absorption of the proton-bearing vinylic C-atom at 131.6 ppm (usual range 115–125 ppm [20]), and a low field methylene C-atom at 46.7 ppm. A reasonable explanation would be a fully substituted C-atom (found at 44.3 ppm) in α-position to the double bond as in structure **29**. This would mean that the proton-proton coupling constant of 2 Hz originates from allylic protons only. The absorption at 46.7 ppm (*t*) points to a methylene C-atom between two bridgeheads, deshielded by a double bond as in bicyclo[2.2.1]heptene or by an additional β-substituent, *i.e.* one fully substituted C-atom in α-position as in partial structure **30** [20].

The available data are not sufficient to propose a structure for this unsaturated dimer at present, but it seems that a rearrangement of the bicyclo[3.2.2]nonane skeleton has taken place.



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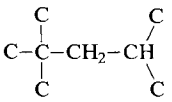

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Characterization of the *Diels-Alder* adducts of '*Bredt* olefins' 2 and 3 with furan and 2,5-diphenylbenzo[*c*]furan. – The reaction of furan and 2,5-diphenylbenzo[*c*]-furan with '*Bredt* olefins' **2** and **3** formed *in situ* gave a mixture of two adducts separable by column chromatography on silica gel in each case. ^{13}C-NMR. and ^{1}H-NMR. data prove that these compounds are *exo*- and *endo*-isomers of the expected *Diels-Alder* adducts (*Tables 2* and *3*).

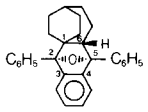
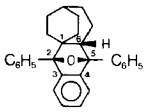
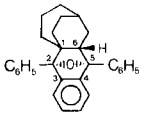
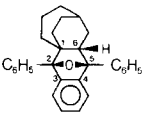
The original vinylic proton of the bridgehead olefin (H–C(6)) appears as a $d\times d$ between 2 and 3 ppm in the diphenylbenzofuran adducts **15** and **26**. The O-atom deshields this proton more strongly if it is *exo*[3]) (*syn* to the O-atom) than *endo*[3]) (*anti* to the O-atom) [21]. The signal of the corresponding proton H–C(6) can also be identified in the *endo*-isomers (*i.e.* *exo*[3])-H-atom) of furan adducts **14** and **25**, respectively, where it is split by an additional coupling ($J_{5,6}=4$ Hz) to the vicinal bridgehead H–C(5). In the *exo*-isomer (*i.e.* *endo*[3])-H-atom) this coupling constant $J_{5,6}$ is less than 1 Hz, because the dihedral angle between the two protons in question is *ca.* 90° [22].

Discussion. – As shown above 1-bicyclo[3.2.2]nonene (**2**) and 1(7)-bicyclo-[3.2.2]nonene (**3**) can be generated by the intramolecular *Wittig* reaction, but their isolation and characterization has not been accomplished. That the '*Bredt* olefins' are indeed formed, is confirmed by the trapping experiments with furan or 2,5-diphenylbenzo[*c*]furan, by the structure of the dimers **12** and **23**, and by the isolation of an equivalent amount of triphenylphosphine oxide generated in the olefin-forming step of the *Wittig* reaction.

Wiseman & Chong [7] were able to observe a mixture of **2** and **3** obtained by pyrolysis of the corresponding bridgehead trimethylammonium hydroxide. Therefore, the *Hofmann* degradation proceeding in the gas phase at 155° seems to be more appropriate for the synthesis of these unstable bridgehead olefins than

[3]) The terms *exo* and *endo* in this context refer to the oxabicyclo[2.2.1]heptane moiety.

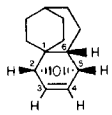
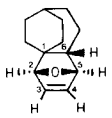
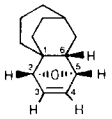
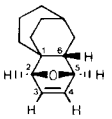
Table 2. *Selected ^1H- and ^{13}C-NMR. data for 2,5-diphenylbenzo[c]furan adducts* **15** *and* **26**[a])

	 *exo*-**15**	 *endo*-**15**	 *exo*-**26**	 *endo*-**26**
Atom	Chemical shifts			
H–C(6)	2.08 (J = 13.0 and 2.9)	2.58 (J = 13.5 and 2.6)	2.30 (J = 12.5 and 7.8)	2.71 (J = 12.8 and 6.6)
C(1)	48.6 (*s*)	49.4 (*s*)	47.4 (*s*)	48.9 (*s*)
C(2)[b])	92.8 (*s*)	91.2 (*s*)	92.1 (*s*)	93.3 (*s*)
C(3)[b])	144.8 (*s*)	145.0 (*s*)	144.2 (*s*)	144.8 (*s*)
C(4)[b])	150.3 (*s*)	147.9 (*s*)	150.1 (*s*)	148.8 (*s*)
C(5)[b])	88.9 (*s*)	89.0 (*s*)	89.1 (*s*)	89.9 (*s*)
C(6)	54.5 (*d*)	53.7 (*d*)	51.9 (*d*)	51.8 (*d*)

[a]) Solvent $CDCl_3$, δ in ppm (TMS: δ = 0 ppm), J in Hz. ^{13}C-NMR. multiplicity determined in off-resonance proton-decoupled spectra: *s* = singlet, *d* = doublet.

[b]) Assignments for C(2)/C(5) and C(3)/C(4) may be interchanged.

Table 3. *Selected ^1H- and ^{13}C-NMR. data for furan adducts* **14** *and* **25**[a])

	 *exo*-**14**	 *endo*-**14**	 *exo*-**25**	 *endo*-**25**
H-Atom	Chemical shifts			
H–C(2)	4.21[b])	4.31	3.94[b])	4.24
H–C(3)/ H–C(4)	6.23/6.45	6.27/6.37	5.89/6.17	6.19/6.27
H–C(5)	4.46[b])	4.67	4.34[b])	4.58
H–C(6)	<2.2	2.35	<2.2	2.35
	^1H-NMR. coupling constants			
$J_{2,3} = J_{4,5}$	1.5	1.5	1.5	1.5
$J_{3,4}$	6	6.5	6	5
$J_{5,6}$	<1	4.5	<1	4
C-Atom	Chemical shifts			
C(1)	42.0 (*s*)	40.7 (*s*)	40.5 (*s*)	43.3 (*s*)
C(2)[c])	88.0 (*d*)	86.0 (*d*)	85.3 (*d*)	86.5 (*d*)
C(3)[c])	131.7 (*d*)	132.4 (*d*)	129.7 (*d*)	131.6 (*d*)
C(4)[c])	138.0 (*d*)	138.1 (*d*)	136.7 (*d*)	139.2 (*d*)
C(5)[c])	83.5 (*d*)	82.8 (*d*)	82.4 (*d*)	82.1 (*d*)
C(6)	47.4 (*d*)	47.6 (*d*)	44.2 (*d*)	44.9 (*d*)

[a]) Solvent $CDCl_3$, except for the ^1H-NMR. of **25** (CCl_4), δ in ppm (TMS: δ = 0 ppm), J in Hz, *s* = singlet, *d* = doublet.

[b]) Assignments for H(2)/H(5) may be interchanged.

[c]) Assignments for C(2)/C(5) and C(3)/C(4) may be interchanged.

the intramolecular *Wittig* reaction performed in solution at 130–140°. However, the *Wittig* reaction allows the formation of the strained double bond at a pre-determined position, and furthermore, the monocyclic starting materials are readily available.

The yield of dimers or trapped products obtained in the synthesis of **2** was very low (8%), whereas up to 50% of products were isolated in the *Wittig* reaction leading to the isomeric olefin **3**. This difference in yield corresponds to the experience gained with the intramolecular *Wittig* reaction leading to annelated [23] or stable bridged olefins [17]: The yield does not depend on the olefin stability, but on the size of the newly formed ring. A sevenmembered ring (olefin **2**) is closed less readily than a sixmembered ring (olefin **3**).

The question of relative strain, stability, and reactivity of bridgehead olefins derived from (*E*)-cycloheptene is still open. Some '*Bredt* olefins' have been observed spectrometrically at low temperature [7] [14], but comparative studies are not available. Force field calculations suggest that there is no simple relation between the size of the individual rings of the bicyclic skeleton and the strain of bridgehead olefins [14] [24]. According to these calculations, 1-bicyclo[3.2.2]nonene (**2**; 19.5 kcal/mol olefin strain) is less strained than 1(7)-bicyclo[3.2.2]nonene (**3**; 20.7 kcal/mol) and less than the tetramethylene-bridged (*E*)-cycloheptene **1** (22.3 kcal/mol) [14]. We note that under identical reaction conditions **3** is trapped by furan more efficiently than **2** and far better than **1**[4]). However, because the competing dimerization reactions of bridgehead olefins **1**–**3** are not comparable with each other, any conclusion as to the relative reactivity of the '*Bredt* olefins' from this observation stands on weak grounds.

The olefin **2** gives a head-to-tail cyclobutane dimer **12** by a [2+2] cycloaddition of the strained double bond. Although a concerted $[\pi^2 s + \pi^2 a]$ cycloaddition according to the *Woodward-Hoffman* rules might be feasible with twisted double bonds present in bridged (*E*)-cycloheptenes, a stepwise mechanism involving diradicals seems to be more probable, because *four* dimers are formed all at the same time. Diradical intermediates rather than a concerted reaction can also account for the formation of *six* dimers, trimers and oligomers from **3**.

Financial support by the *Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung* (project 2.627.0.76 and 2.148.0.78) and the *Ciba-Geigy AG* is greatfully acknowledged.

Experimental Part

General remarks. S. [6]. Moreover, some GLC. analyses were carried out on a *Carlo Erba* Fractovap-GI-450 with capillary columns. Combined GLC./MS. analysis was performed by Mr. *Ch. Quiquerez, Sandoz AG*, Basel, on a *Hewlett-Packard* 59-92 H.

Synthesis of 3-(4'-oxocyclohexyl)propyltriphenylphosphonium bromide (**11**). A mixture of 1.31 g (6.00 mmol) of 4-(3-bromopropyl)cyclohexanone (**10**) [16] and 1.57 g (6.00 mmol) of triphenylphosphine in dry ether (4 ml) was sealed in a pyrex pressure tube and heated at 120° for 60 h. The solid product was washed with several portions of dry ether, dissolved in methylene chloride, evaporated, and dried over P_2O_5 for 48 h at 0.01 Torr, which gave 2.85 g (99%) of **11** as a hygroscopic, glass-like solid. – IR. ($CHCl_3$): 2930, 1710 (C=O), 1440, 1115, 1000. – ^{1}H-NMR. ($CDCl_3$):

[4]) Since our original publication [6], we have been able to trap olefin **1** with furan, albeit with very low efficiency.

1.1–2.0 (*m*, 9 H, CH, CH_2); 2.2–2.7 (*m*, 4 H, 2 H–C(3'), 2 H–C(5')); 3.4–4.0 (*m*, 2 H, 2 H–C(1)); 7.5–8.1 (*m*, 15 arom. H).

From **11** and an equivalent amount of sodium tetraphenylborate in dry methanol the tetraphenylborate was obtained, white crystals, m.p. 130–131°.

$C_{51}H_{50}BOP$ (720.74) Calc. C 84.99 H 6.99 P 4.30% Found C 84.95 H 6.98 P 4.33%

1-Bicyclo[3.2.2]nonene (**2**) *by intramolecular* Wittig *reaction of* **11**. *Dimer* **12**. A suspension of 10.45 g (21.7 mmol) of **11** and 2.68 g (23.9 mmol) of potassium *t*-butoxide in tetraglyme (30 ml) was stirred at 130° for 5 h under nitrogen. The mixture was extracted with several portions of pentane, and the extracts were washed with water and brine. Column chromatography on silica gel with cyclohexane/benzene separated a hydrocarbon fraction (71 mg, 2.7%) from triphenylphosphine, triphenylphosphine oxide, tetraglyme, and more polar material. The hydrocarbon fraction was shown to consist of four dimers (M^+ 244) in a ratio of 9:1:1.5:4.5 (order of increasing retention time) by GLC./MS. (*OV 17*, 70–280°). The main dimer, *pentacyclo[10.2.2.2^{5,8}.0^{1,9}.0^{2,8}]octadecane* (**12**), was obtained pure by repeated crystallization from ether/ethanol, m.p. 143–145°. – IR. (CCl_4): 2925, 2860, 1465, 1445. – ^{1}H-NMR. ($CDCl_3$): 1.0–1.9 (*m*, 28 H, CH, CH_2). – ^{13}C-NMR. ($CDCl_3$): 51.5 (*d*); 37.9 (*t*); 37.4 (*s*); 35.3 (*t*); 30.6 (*d*); 28.7 (*t*, 4 C); 25.1 (*t*); 22.1 (*t*). – MS.: 245 (21), 244 (M^+, 100), 216 (11), 215 (27), 201 (10), 173 (10), 120 (18), 106 (25), 93 (31), 91 (37), 79 (47).

$C_{18}H_{28}$ (244.42) Calc. C 88.45 H 11.55% Found C 88.23 H 11.82%

Adduct **14** *of* **2** *with furan*. A suspension of 4.02 g (8.40 mmol) of **11** and 1.31 g (11.7 mmol) of potassium *t*-butoxide in furan (25 ml, 345 mmol) and tetraglyme (6 ml) was sealed in a pyrex pressure tube and stirred at 130° for 6 h. Extraction with pentane and chromatography on silica gel with cyclohexane/benzene gave 59 mg (6%) of a mixture of dimers as above and 31 mg (2%) of the *Diels-Alder* adduct *14-oxatetracyclo[7.2.2.1^{2,5}.0^{1,6}]tetradec-3-ene* (**14**), partially separated into *exo*- and *endo*-isomers (1:1). *exo*-**14**: IR. (CCl_4): 3080*w*, 2935, 2865, 1460, 1450, 1305, 1010, 900, 890, 700. – ^{1}H-NMR. ($CDCl_3$): 0.8–2.2 (*m*, 14 H, CH, CH_2); 4.21 (*s*, 1 H, H–C(2)); 4.46 (*s*, 1 H, H–C(5)); 6.23 and 6.45 (*AB*×*d*, J_{AB}=6, *J*=1.5, 2 H, H–C(3), H–C(4)). – ^{13}C-NMR. ($CDCl_3$): 138.0; 131.7; 88.0; 83.5; 47.4; 42.0; 37.1; 31.3; 29.8; 29.6; 28.8; 26.6; 24.0; assignments see *Table 3*.

endo-**14**: IR. (CCl_4): 3080*w*, 2935, 2865, 1460, 1450, 1010, 900, 890, 710. – ^{1}H-NMR. ($CDCl_3$): 0.8–2.2 (*m*, 13 H, CH, CH_2); 2.35 (*d*×*d*, *J*=8.5, *J*=4.5, H–C(6)); 4.31 (*s*, 1 H, H–C(2)); 4.67 (*d*, *J*=4.5, 1 H, H–C(5)); 6.27 and 6.37 (*AB*×*d*, J_{AB}=6.5, *J*=1.5, 2 H, H–C(3), H–C(4)). – ^{13}C-NMR. ($CDCl_3$): 138.1, 132.4, 86.0, 82.8, 47.6, 40.7, 36.9, 32.6, 31.4, 30.1, 29.0, 27.5, 23.7; assignments see *Table 3*.

Adducts **15** *of* **2** *with 2,5-diphenylbenzo[c]furan*. To a suspension of 4.65 g (9.7 mmol) of **11**, 19.3 mmol of sodium hydride (washed oil-free with pentane), and 2.05 g (7.6 mmol) of 2,5-diphenylbenzo[*c*]furan in dry tetraglyme (20 ml), 1.26 g (14.3 mmol) of dry 2-methyl-2-butanol were added dropwise under nitrogen. The mixture was heated at 140° for 4 h with stirring. Work-up with benzene and filtration through a short column of silica gel gave a mixture of adduct **15** and unreacted 2,5-diphenylbenzo[*c*]furan. This mixture was stirred with 1.0 g (10 mmol) of maleic anhydride for 4 h at 25° in benzene, evaporated i.V., then heated under reflux in ethanol/4N NaOH 3:1 for 3 h, and again worked up with benzene. Column chromatography on silica gel with cyclohexane/benzene gave 104 mg (3%) of exo-*2,5-diphenyl-3,4-benzo-14-oxatetracyclo[7.2.2.1^{2,5}.0^{1,6}]tetradec-3-ene* (*exo*-**15**) and 202 mg (5%) of *endo*-**15**, which were recrystallized from ether/ethanol. *exo*-**15**: m.p. 204–205°. – IR. (CCl_4): 3070, 3035, 2930, 2860, 1600, 1445, 1345, 1300, 990, 700, 670. – ^{1}H-NMR. ($CDCl_3$): 1.0–2.0 (*m*, 13 H, CH, CH_2); 2.08 (*d*×*d*, *J*=13.0, *J*=2.9, H–C(6)); 7.0–7.8 (*m*, 14 arom. H). – ^{13}C-NMR. ($CDCl_3$): 150.3 (*s*); 144.8 (*s*); 139.2 (*s*); 138.1 (*s*); 128.1 (*d*, 4 C); 126.8 (*d*, 2 C); 126.5 (*d*); 126.1 (*d*, 2 C); 125.8 (*d*, 2 C); 125.7 (*d*); 121.7 (*d*); 116.9 (*d*); 92.8 (*s*); 88.9 (*s*); 54.5 (*d*); 48.6 (*s*); 36.8 (*t*); 29.6 (*t*); 29.1 (*d*); 28.8 (*t*); 27.4 (*t*); 24.9 (*t*); 23.9 (*t*); assignments see *Table 2*.

$C_{29}H_{28}O$ (329.54) Calc. C 88.73 H 7.19% Found C 88.97 H 7.22%

endo-**15**: m.p. 201–202°. – IR. (CCl_4): 3070, 3035, 2940, 2865, 1600, 1500, 1445, 1305, 1005, 990, 700, 660. – ^{1}H-NMR. ($CDCl_3$): 0.9–2.0 (*m*, 13 H, CH, CH_2); 2.58 (*d*×*d*, *J*=13.5, *J*=2.6, H–C(6)); 7.1–7.8 (*m*, 14 arom. H). – ^{13}C-NMR. ($CDCl_3$): 147.9 (*s*); 145.0 (*s*); 139.0 (*s*); 138.0 (*s*); 128.3 (*d*, 2 C); 128.0 (*d*, 2 C); 127.9 (*d*); 127.1 (*d*, 2 C); 127.0 (*d*); 126.0 (*d*, 2 C); 125.9 (*d*, 2 C); 121.5 (*d*);

119.9 (*d*); 91.2 (*s*); 89.0 (*s*); 53.7 (*d*); 49.4 (*s*); 36.3 (*t*); 29.7 (*t*); 29.4 (*d*); 28.4 (*t*); 28.1 (*t*); 24.0 (*t*); 23.3 (*t*); assignments see *Table 2*.

$C_{29}H_{28}O$ (392.54) Calc. C 88.73 H 7.19% Found C 88.89 H 7.24%

Synthesis of ethyl (4-oxocycloheptyl)acetate (**17**) [18]. A solution of diazomethane in ether (prepared from 21.5 g (100 mmol) of *N*-methyl-*N*-nitrosotoluene-4-sulfonamide and KOH) was added to a mixture of 7.35 g (40 mmol) of ethyl (4-oxocyclohexyl)acetate (**16**) and 15 g of ice in methanol (35 ml)[5]) at −10°. After 12 h at 4°, the solution was concentrated i.V., extracted with ether, the extracts washed with brine, dried over $MgSO_4$, and evaporated i.V. to yield 7.90 g (100%) of crude product. Prepared in several small batches 91.8 g of this crude product were distilled through a spinning band column (*Normag* 100 cm, 2500 rpm, 12 h) to give 59.05 g (64%) of **17**, b.p. 101–103°/0.15 Torr ([18]: 41%, distilled at 135° (bath temp.)/0.15 Torr). – IR. (CCl_4): 2930, 2860, 1735 (COOEt); 1705 (C=O); 1280, 1240, 1170 (C–O–C); 1130, 1035. – ^{1}H-NMR. (CCl_4): 1.0–2.6 (*m*, 13 H, CH, CH_2); 1.22 (*t*, *J* = 7, 3 H, CH_3CH_2O); 4.05 (*qa*, *J* = 7, 2 H, CH_3CH_2O).

From earlier fractions, 21.22 g (23%) of the isomeric epoxides *ethyl (1′-oxaspiro[2.5]oct-6′-yl)-acetate* were collected as a 6:1 *cis/trans*-mixture (GLC. *Carbowax* 3%, 150°), b.p. 89–95°/0.15 Torr. – IR. (CCl_4): 3040, 2930, 2860, 1735 (COOEt), 1445, 1280, 1205, 1155 (C–O–C), 1095, 1031, 920. – ^{1}H-NMR. (CCl_4): 1.2–2.3 (*m*, 11 H, CH, CH_2); 1.2 (*t*, *J* = 7, 3 H, CH_3CH_2O); 2.46 (*s*, 2 H, 2 H–C(2′)); 4.05 (*qa*, *J* = 7, 2 H, CH_3CH_2O).

$C_{11}H_{18}O_3$ (198.26) Calc. C 66.64 H 9.15% Found C 66.38 H 9.36%

Later fractions (8.41 g, 9%, b.p. 103–115°/0.15 Torr) contained *ethyl (4- and 5-oxocyclooctyl)acetate* formed by double insertion of diazomethane.

Synthesis of ethyl (4-oxocycloheptyl)acetate ethylene acetal (= ethyl (1,4-dioxaspiro[4.6]undec-8-yl)acetate; **18**). A solution of 57.05 g (288 mmol) of **17**, 76.8 g (1.24 mol) of ethylene glycol, and 0.35 g (1.8 mmol) of *p*-toluenesulfonic acid in benzene (350 ml) was heated under reflux under a water separator for 10 h. The solution was diluted with ether, washed with aqueous $NaHCO_3$ solution and brine, dried over $MgSO_4$, and distilled to give 65.33 g (94%) of **18** as a colourless oil, b.p. 94–102°/0.08 Torr. – IR. (CCl_4): 2980, 2930, 2870, 1735 (COOEt), 1370, 1145, 1120 (C–O–C), 1095. – ^{1}H-NMR. (CCl_4): 1.0–2.2 (*m*, 11 H, CH, CH_2); 1.23 (*t*, *J* = 7, 3 H, CH_3CH_2O); 2.10 (*s*, 2 H, CH_2COO); 3.77 (*s*, 4 H, OCH_2CH_2O); 4.04 (*qa*, *J* = 7, 2 H, CH_3CH_2O).

$C_{13}H_{22}O_4$ (242.31) Calc. C 64.44 H 9.15% Found C 64.21 H 9.39%

Synthesis of 4-(2-hydroxyethyl)cycloheptanone ethylene acetal (= 2-(1,4-dioxaspiro[4.6]undec-8-yl)-ethanol; **19**). A solution of 49.46 g (204 mmol) of **18** in dry tetrahydrofuran (100 ml) and ether (160 ml) was added dropwise to a refluxing suspension of lithium aluminium hydride (9.68 g, 255 mmol) in ether (400 ml). After a further 30 min under reflux, the mixture was hydrolyzed by careful addition of 1N aqueous NaOH (39 ml) with efficient stirring. The precipitate was filtered, and the filtrate distilled to give 36.48 g (89%) of **19** as a colourless oil, b.p. 112–116°/0.15 Torr. – IR. (film): 3420 (OH), 2930, 1450, 1370, 1140, 1105, 1060, 1045, 945. – ^{1}H-NMR. (CCl_4): 1.0–2.0 (*m*, 13 H, CH, CH_2); 2.55 (br., 1 H, HO); 3.52 (*t*, *J* = 6, 2 H, CH_2OH); 3.80 (*s*, 4 H, OCH_2CH_2O).

$C_{11}H_{20}O_3$ (200.28) Calc. C 65.97 H 10.07% Found C 65.91 H 10.29%

Synthesis of 4-(2-mesyloxyethyl)cycloheptanone ethylene acetal (= 2-(1,4-dioxaspiro[4.6]undec-8-yl)-ethyl methanesulfonate; **20**). Freshly distilled methanesulfonyl chloride (15.7 g, 137 mmol) was added dropwise to a solution of 23.91 g (119 mmol) of **19** and 15.7 g (155 mmol) of triethylamine in methylene chloride (100 ml) at −10°. After 30 min at −10°, the solution was diluted with methylene chloride, and worked up as usual: 33.5 g (100%) of crude **20** as a colourless oil. – IR. (film): 2935, 2870, 1350, 1175 (OSO_2), 1110, 975, 945. – ^{1}H-NMR. (CCl_4): 0,9–2.0 (*m*, 13 H, CH, CH_2); 2.87 (*s*, 3 H, CH_3SO_2); 3.74 (*s*, 4 H, OCH_2CH_2O); 4.12 (*t*, *J* = 6, 2 H, CH_2OSO_2):

Synthesis of 4-(2-bromoethyl)cycloheptanone (**21**). A mixture of 33.5 g (119 mmol) of crude **20** and 90 g (1.04 mol) of lithium bromide in dry acetone (550 ml) was heated under reflux for 16 h. The mixture was concentrated i.V. and extracted with ether as usual. Distillation gave 24.6 g (94%) of **21** as a yellowish oil, b.p. 89–90°/0.1 Torr. – IR. (film): 2930, 2860, 1700, 1445, 1340, 1255, 870. –

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[5]) If water or methanol was omitted, the yield of **17** dropped under 10%.

^{1}H-NMR. (CCl_4): 0.8–2.15 (*m*, 9 H, CH, CH_2); 2.15–2.65 (*m*, 4 H, 2 H–C(2), 2 H–C(7)); 3.38 (*t*, J = 6.5, 2 H, CH_2Br).

$C_9H_{15}BrO$ (219.12) Calc. C 49.32 H 6.90 Br 36.46% Found C 49.10 H 7.08 Br 36.20%

Synthesis of 2-(4′-oxocycloheptyl)ethyltriphenylphosphonium bromide (**22**). From **21** and triphenylphosphine in ether as described for **11**: hygroscopic, glass-like solid in 98% yield. – IR. ($CHCl_3$): 2930, 1695 (C=O), 1440, 1115, 1000. – ^{1}H-NMR. ($CDCl_3$): 0.8–2.1 (*m*, 9 H, CH, CH_2); 2.3–2.6 (*m*, 4 H, 2 H–C(3′), 2 H–C(5′)); 3.6–4.1 (*m*, 2 H, CH_2P); 7.5–8.2 (*m*, 15 arom. H).

$C_{27}H_{30}BrOP$ (481.41) Calc. C 67.34 H 6.30 Br 16.60% Found C 67.20 H 6.09 Br 16.80%

Tetraphenylborate: white crystals from methanol, m.p. 125–126°.

$C_{51}H_{50}BOP$ (720.74) Calc. C 84.99 H 6.99 P 4.30% Found C 85.08 H 7.12 P 4.10%

1(7)-Bicyclo[3.2.2]nonene (**3**) *by intramolecular* Wittig *reaction of* **22**. *Identification of dimers.* A flask containing a suspension of 3.22 g (6.7 mmol) of **22** and 0.90 g (8.0 mmol) of freshly sublimed potassium *t*-butoxide in dry hexaglyme (hexaethylene glycol dimethyl ether, 15 ml) was connected to a cold trap (– 196°) with a heated inlet tube (120°), evacuated to 0.2 Torr, and gradually heated to 140° with stirring for 4 h. The content of the cold trap was dissolved in CD_2Cl_2 (– 80°) and transferred to a NMR. tube, rigorously excluding moisture and oxygen. The NMR. spectrum at – 80° showed signals for *t*-butyl alcohol, benzene, formaldehyde di-*t*-butyl acetal (formed from traces of methylene chloride present in the phosphonium bromide and potassium *t*-butoxide), and aliphatic hydrocarbons (saturated dimers), but no signals expected for the vinyl proton of **3**. Distillation of this solution gave 40 mg (5%) of a mixture of dimers. The non-volatile mixture was extracted with pentane, and the pentane solution concentrated i.V. and chromatographed on silica gel with cyclohexane. The hydrocarbon fraction (335 mg, 40%) was shown to consist of at least six dimers (M^+ 244) and trimers (M^+ 366) by GLC./MS. (*OV 17*, 70–280°). Distillation gave 123 mg (15%, total yield 20%) of a mixture of dimers, b.p. 100–120°/0.03 Torr. The main component (*ca.* 60%), *pentacyclo[9.3.2.2^{4,8}.0^{1,9}.0^{2,8}]octadecane* (**23**), was obtained pure by repeated crystallization from ether/ethanol, waxy crystals, m.p. 174–176°. – IR. (CCl_4): 2940, 2860, 1480, 1460, 1450, 1440. – ^{1}H-NMR. ($CDCl_3$): 1.2–2.4 (*m*, CH, CH_2). – ^{13}C-NMR. ($CDCl_3$): 52.4 (*d*); 38.3 (*t*); 37.0 (*s*); 35.1 (*t*); 29.4 (*t*); 28.4 (*d*); 25.9 (*t*); 25.4 (*t*); 21.8 (*t*). – MS.: 245 (12), 244 (M^+, 61), 215 (23), 202 (25), 201 (100), 122 (91), 121 (67), 120 (23), 107 (22), 93 (37), 79 (38), 67 (42).

$C_{18}H_{28}$ (244.42) Calc. C 88.45 H 11.55% Found C 88.64 H 11.75%

In one experiment performed in more dilute solution (10 ml of tetraglyme per 1 g of **22**), the mixture of dimers (9%) contained 32% of an *unsaturated dimer* besides 35% of **23** and minor components (GLC.). This unsaturated dimer was not obtained pure, but could be characterized spectroscopically. – IR. (CCl_4): 2930, 2860, 1450. – ^{1}H-NMR. ($CDCl_3$): 1.2–2.4 (*m*, *ca.* 27 H); 5.33 (*t*, J = 2, 1 H). – ^{13}C-NMR. ($CDCl_3$): 139.8 (*s*); 131.6 (*d*); 46.7 (*t*); 44.3 (*s*); 39.1; 36.2; 36.1; 35.8; 35.3; 34.8; 33.8; 32.0; 30.4; 29.6; 26.5; 26.4; 22.0; 20.2. – MS.: 245 (6), 244 (29), 215 (15), 202 (17), 201 (100), 122 (12), 93 (17), 91 (15), 79 (19), 67 (19).

Adduct **25** *of* **3** *with furan.* The reaction was performed as described for **14**. Chromatography on silica gel with cyclohexane/benzene gave 4.5% of a dimer mixture and 41% of the *Diels-Alder* adduct *14-oxatetracyclo[6.3.2.1^{2,5}.0^{1,6}]tetradec-3-ene* (**25**), partially separated into *exo*- and *endo*-isomers (1:1). *exo*-**25**: b.p. 60–63°/0.1 Torr. – IR. (CCl_4): 3080*w*, 2930, 2860, 1450, 1310, 1000, 905, 900, 885, 695. – ^{1}H-NMR. (CCl_4): 0.7–2.2 (*m*, 14 H, CH, CH_2); 3.94 (*s*, 1 H, H–C(2)); 4.34 (*s*, 1 H, H–C(5)); 5.89 and 6.17 (*AB*×*d*, J_{AB} = 6, J = 1.5, 2 H, H–C(3), H–C(4)). – ^{13}C-NMR. ($CDCl_3$): 136.7 (*d*); 129.7 (*d*); 85.3 (*d*); 82.4 (*d*); 44.2 (*d*); 40.5 (*s*); 37.3 (*t*), 30.2 (*t*); 29.2 (*d*); 28.6 (*t*, 2 C); 24.1 (*t*); 21.6 (*t*); assignments see *Table 3*.

$C_{13}H_{18}O$ (190.28) Calc. C 82.06 H 9.54% Found C 81.84 H 9.66%

endo-**25**: b.p. 59–61°/0.1 Torr. – IR. (CCl_4): 3080*w*, 2925, 2860, 1450, 1000, 900, 880, 730. – ^{1}H-NMR. (CCl_4): 0.4–2.2 (*m*, 13 H, CH, CH_2); 2.35 (*m*, H–C(6)); 4.24 (*s*, 1 H, H–C(2)); 4.58 (*d*, J = 4, 1 H, H–C(5)); 6.19 and 6.27 (*AB*×*d*, J_{AB} = 5, J = 1.5, 2 H, H–C(3), H–C(4)). – ^{13}C-NMR. ($CDCl_3$): 139.2 (*d*); 131.6 (*d*); 86.5 (*d*); 82.1 (*d*); 44.9 (*d*); 43.3 (*s*); 42.2 (*t*); 30.1 (*d*); 29.5 (*t*, 2 C); 27.3 (*t*); 24.8 (*t*); 21.2 (*t*); assignments see *Table 3*.

$C_{13}H_{18}O$ (190.28) Calc. C 82.06 H 9.54% Found C 82.04 H 9.58%

Adduct **26** *of* **3** *with 2,5-diphenylbenzo[c]furan.* The reaction was performed as described for **15**. Chromatography gave 26% exo-*2,5-diphenyl-3,4-benzo-14-oxatetracyclo[6.3.2.1^{2,5}.0^{1,6}]tetradec-3-ene* (*exo*-**26**) and 25% *endo*-**26**, which were recrystallized from ether/ethanol. *exo*-**26**: m.p. 212–213°. – IR. (CCl_4): 3070, 3040, 2930, 2870, 1600, 1495, 1445, 1300, 990, 700, 670. – ^{1}H-NMR. ($CDCl_3$): 0.7–1.8 (*m*, 11 H); 2.0 (*m*, 2 H); 2.30 (*d*×*d*, *J* = 12.5, *J* = 7.8, H–C(6)); 7.0–7.8 (*m*, 14 arom. H). – ^{13}C-NMR. ($CDCl_3$): 150.1 (*s*); 144.2 (*s*); 138.5 (*s*); 137.7 (*s*); 128.1 (*d*, 2 C); 127.9 (*d*, 2 C); 126.9 (*d*, 2 C); 126.5 (*d*); 125.9 (*d*, 3 C); 125.7 (*d*, 2 C); 121.2 (*d*); 116.8 (*d*); 92.1 (*s*); 89.1 (*s*); 51.9 (*d*); 47.4 (*s*); 38.1 (*t*); 29.8 (*t*); 28.9 (*t*); 28.1 (*d*); 26.6 (*t*); 24.0 (*t*); 21.8 (*t*); assignments see *Table 2*.

$C_{29}H_{28}O$ (392.54) Calc. C 88.73 H 7.19% Found C 88.97 H 7.18%

endo-**26**: m.p. 209°. – IR. (CCl_4): 3070, 3030, 2930, 2870, 1600, 1495, 1445, 1305, 1005, 985, 700, 655. – ^{1}H-NMR. ($CDCl_3$): 0.7–1.8 (*m*, 11 H); 2.1 (*m*, 2 H); 2.71 (*d*×*d*, *J* = 12.8, *J* = 6.6, H–C(6)); 7.1–7.7 (*m*, 14 arom. H). – ^{13}C-NMR. ($CDCl_3$): 148.8 (*s*); 144.8 (*s*); 139.6 (*s*); 138.3 (*s*); 128.2 (*d*, 2 C); 128.1 (*d*, 2 C); 127.5 (*d*); 126.9 (*d*); 126.2 (*d*, 2 C); 126.0 (*d*, 2 C); 125.4 (*d*, 2 C); 121.5 (*d*); 120.3 (*d*); 93.3 (*s*); 89.9 (*s*); 51.8 (*d*); 48.9 (*s*); 39.3 (*t*); 29.5 (*t*); 29.3 (*t* and *d*, 2 C); 27.4 (*t*); 24.1 (*t*); 20.9 (*t*); assignments see *Table 2*.

$C_{29}H_{28}O$ (392.54) Calc. C 88.73 H 7.19% Found C 77.55 H 7.20%

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