20. [2+2]-Cycloadditions to Strained Bridgehead Olefins. II. Diphenylketene[1])

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Summary

The strained bridgehead olefins bicyclo[3.3.1]non-1-ene (**1**), bicyclo[4.2.1]non-1(8)-ene (**2**), and bicyclo[4.2.1]non-1-ene (**3**), and the comparable monocyclic (*E*)-1-methylcyclooctene (**4**) react with diphenylketene (**6**) to give a single cycloadduct **7**, **8**, **9** and **10**, respectively, in which the diphenyl-substituted C-atom is bound to the bridgehead. The structure of the cyclobutanone **8** has been determined by X-ray analysis of a twin crystal obtained by crystallization with spontaneous enrichment of enantiomers.

Introduction. – Strained bridgehead olefins (*Bredt* olefins [1]) such as bicyclo[3.3.1]non-1-ene (**1**), bicyclo[4.2.1]non-1(8)-ene (**2**), and bicyclo[4.2.1]non-1-ene (**3**) undergo a variety of additions uncommon to unstrained trialkyl-substituted olefins [2] [3]. The [2+2]-cycloaddition is of special interest, because the strained (and twisted [4]) double bond of the bridgehead olefin might prefer to react antarafacially in a concerted [π2s+π2a]-mode, which is thermally allowed according to the *Woodward-Hofmann* rules [5]. Highly strained *Bredt* olefins dimerize by a [2+2]-cycloaddition, however, this reaction is believed to be a stepwise process *via* diradicals rather than a concerted reaction [6]. Bridged (*E*)-cyclooctenes such as **1**, **2** and **3** do not dimerize to cyclobutanes [7] on heating for extended periods of time, but react readily with 1,1-dichloro-2,2-difluoroethene (**5**) [8], a reagent which gives cyclobutanes by a diradical intermediate.

Ketenes react with olefins to give cyclobutanones. This reaction is considered to occur *via* a concerted [π2s+π2a]-cycloaddition, in which the ketene double bond constitutes the antarafacial reaction partner [9]. The frontier orbital approach has been applied successfully to the problem of regioselectivity of this cycloaddition [10]. The regioselectivity of the addition of ketenes to strained bridgehead olefins might

[1]) Taken in part from the dissertation of *M.K. Hohermuth*, Basel 1980. Presented at the meeting of the Swiss Chemical Society, Berne, 17.10.1980.

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therefore give some insight into the effect of strain on the frontier orbitals of C,C-double bonds.

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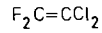

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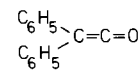

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Results. – The *Bredt* olefins **1**, **2** and **3**, and (*E*)-1-methylcyclooctene (**4**) react with an equimolar amount of diphenylketene (**6**) in benzene at RT. within minutes to a single[3]) cycloadduct **7**, **8**, **9** and **10**, respectively. The addition of **6** to the unstrained (*Z*)-1-methylcyclooctene (**11**) occurs only at 120° (3 h), which demonstrates the accelerating effect of strain on the cycloaddition. The cyclobutanones were isolated simply by evaporation of the solvent and recrystallization.

In the ^{1}H-NMR. spectra of the adducts, a $d \times d$ or a *m* corresponding to one proton is found at lower field than the other aliphatic protons. On the basis of the chemical shift or the coupling mode, it is not yet possible to decide whether this proton (the original vinylic proton) is located α to the carbonyl group or α to the diphenyl-substituted C-atom. In the ^{13}C-NMR. spectra, the four C-atoms of the cyclobutanone ring are readily identified *(Table 1)*. The chemical-shift data again do not allow to assign the structure of the adducts with certainty.

A proof for the structure of the adducts **7**–**10** and **12** was obtained by reduction to the corresponding cyclobutanols. In all cases, reduction with lithium aluminium hydride gave a single alcohol, to which we assign structure **13**–**17**. In the ^{1}H-NMR. spectra of these compounds, the proton α to the hydroxyl group appears at δ 4.4–5.2 ppm as a doublet with a coupling constant of 7.5–11 Hz to a vicinal proton. The alternative orientation in the cycloaddition of **6** to the bridgehead olefins would have led finally to a cyclobutanol with protons separated by four bonds and hence a coupling constant of less than 2 Hz. The configuration depicted in **13**–**17** is based on the assumption that the hydride ion attacks the carbonyl group from the less hindered side[4]).

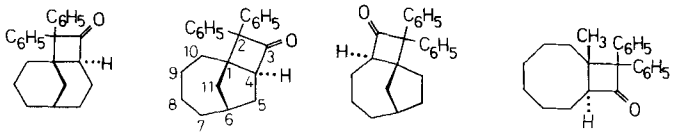
Table 1. *^{13}C-NMR. chemical-shift data for cyclobutanones* **7**–**10** *and* **12**[a])

					Other aliphatic C-atoms
7	39.1 (*s*)	78.9 (*s*)	210.4 (*s*)	58.4 (*d*)	27.9 (*d*), 36.4, 36.0, 31.3, 25.5, 21.8, 17.3 (each *t*)
8	50.6 (*s*)	78.8 (*s*)	213.5 (*s*)	69.5 (*d*)	41.3 (*d*), 40.9, 36.7, 36.4, 31.4, 26.1, 22.8 (each *t*)
9	51.2 (*s*)	73.7 (*s*)	210.7 (*s*)	66.9 (*d*)	36.2 (*d*), 39.4, 38.6, 34.9, 25.5, 24.4, 22.9 (each *t*)
10	41.0 (*s*)	79.1 (*s*)	209.4 (*s*)	63.7 (*d*)	42.4, 29.8, 29.0, 28.7, 26.4, 22.4 (each *t*), 21.3 (*qa*)
12	41.9 (*s*)	78.7 (*s*)	214.8 (*s*)	68.3 (*d*)	32.1, 30.6, 28.4, 25.7, 25.4, 24.8 (each *t*), 26.4 (*qa*)

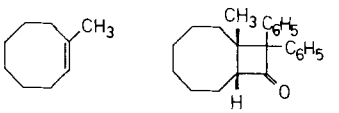
[a]) Solvent $CDCl_3$, δ in ppm, *s* = singlet, *d* = doublet, *t* = triplet, *qa* = quadruplet.

[3]) The selectivity is > 99%, according to GC.

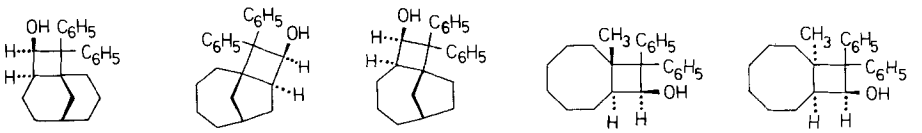
[4]) For compound **8**, it can be readily seen in the projection shown below *(Fig. 2)* that the *syn*-H-atom of the methylene bridge C(11) hinders addition to the carbonyl group from the *exo*-side. This statement is true only if the conformation in solution resembles the conformation in the crystal.



7 **8** **9** **10**



11 **12**



13 **14** **15** **16** **17**

X-Ray analysis. The structure of the cycloadduct **8** was additionally secured by X-ray analysis. Slow crystallization from methanol gave a crystal suitable for structure determination. This crystal turned out to be a twin with relative amounts of the two enantiomers in the ratio 3:2. Obviously a spontaneous enantiomer separation had occurred on crystallization [11]. This unexpected behavior was proved also by optical rotatory dispersion spectra of solutions prepared from different crystals, which were either dextrarotatory, laevorotatory, or neutral. *Figures 1* and *2* show two different projections of the molecule. Bond lengths and bond angles are within the expected range. The phenyl rings bisect under an angle

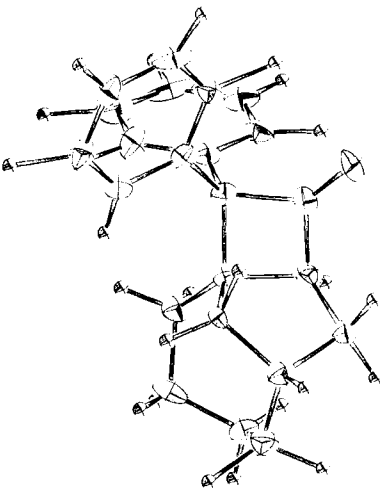


Fig. 1. ORTEP *drawing of* **8** *showing 20% probability thermal ellipsoids for the C- and O-atoms*

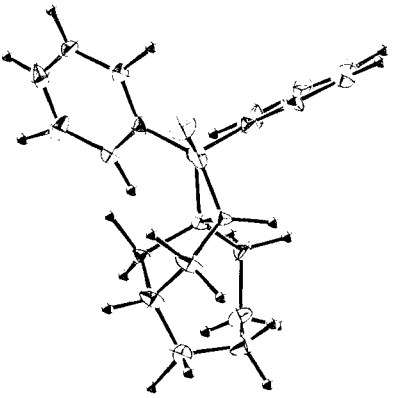


Fig. 2. ORTEP *drawing of* **8** *showing 20% probability thermal ellipsoids for the C- and O-atoms*

of 81°. The cyclobutanone ring is puckered. The dihedral angle between the plane containing the carbonyl group (C(2), C(3), C(4)) and the plane containing the fully substituted bridgehead (C(1), C(2), C(4)) is 32°. The carbonyl group is not exactly planar. The displacement of the O-atom from the (C(2), C(3), C(4))-plane is 0.132 Å and the O-atom lies on the same side of the plane as C(1). Such *endo*-deviations of O-atoms in carbonyl groups were observed in several cyclobutanone derivatives [12]. The fractional atomic coordinates of **8** are collected in *Table 2.* The structure of the diphenylketene adduct **8** shows some striking similarities to the X-ray structure of the bis(triphenylphosphine)platinum(0) complex **18** of bicyclo[4.2.1]non-1(8)-ene [13] and the calculated structure of **2** itself, as revealed by a comparison of the torsion angles *(Table 3).* This means that the conformation of the bicyclo[4.2.1]nonane skeleton is not much influenced whether the bond between the bridgehead C(1) and the two-carbon bridge is a (strained) free C,C-double bond, a complexed C,C-double bond, or a single bond but part of an annulated cyclobutanone ring.

Discussion. – The *Bredt* olefins **1–3** and the 1-methylcyclooctenes **4** and **11** react with diphenylketene (**6**) to give a single cycloadduct. This result fits nicely into the great number of experimental observations collected for the [2+2]-cycloaddition reaction of ketenes to olefins [9]. The complete *syn*-stereoselectivity[5]) reveals that, although the olefinic double bond is distorted, it still undergoes clean suprafacial addition to ketenes.

Frontier orbital theory indicates that the structure of the (ketene/olefin)-cycloaddition reaction is dictated by the interaction of the HOMO(olefin) and the LUMO(ketene) [10]. Normal trialkyl-substituted olefins are therefore expected to form a bond between the less substituted olefinic C-atom (larger HOMO coefficient) and the carbonyl group C-atom of the ketene (larger LUMO coefficient). This regioselectivity is also observed for the strained olefins under study.

When 1,3-dipolar cycloadditions [3] and ketene cycloadditions to strained bridgehead olefins are compared, some important differences must be noted.

[5]) *syn*-Stereospecificity for the *E*/*Z*-pair of 1-methylcyclooctenes.

Table 2. *Fractional atomic coordinates of* **8**

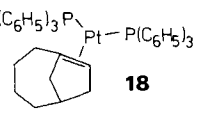
C(1)	0.3605(7)	0.8917(5)	0.3069(9)
C(2)	0.4099(7)	0.9782(5)	0.4215(10)
C(3)	0.3462(7)	0.9346(5)	0.5957(10)
C(4)	0.3491(8)	0.8440(5)	0.5085(11)
C(5)	0.1940(9)	0.7920(6)	0.4891(11)
C(6)	0.1213(9)	0.7991(6)	0.2688(11)
C(7)	0.1639(10)	0.7217(6)	0.1446(12)
C(8)	0.3422(11)	0.7047(5)	0.1568(13)
C(9)	0.4240(10)	0.7760(6)	0.0437(12)
C(10)	0.4808(9)	0.8559(5)	0.1758(12)
C(11)	0.1877(7)	0.8883(5)	0.2013(9)
O(12)	0.2923(6)	0.9601(4)	0.7392(7)
C(13)	0.5863(8)	0.9931(5)	0.4653(11)
C(14)	0.6712(9)	0.9659(6)	0.6435(11)
C(15)	0.8349(8)	0.9763(6)	0.6793(12)
C(16)	0.9121(10)	1.0157(5)	0.5348(16)
C(17)	0.8276(10)	1.0451(6)	0.3590(13)
C(18)	0.6667(9)	1.0327(6)	0.3220(13)
C(19)	0.3306(7)	1.0653(5)	0.3511(10)
C(20)	0.3048(8)	1.1312(5)	0.4886(10)
C(21)	0.2329(9)	1.2085(5)	0.4266(14)
C(22)	0.1891(9)	1.2217(6)	0.2223(11)
C(23)	0.2158(10)	1.1578(5)	0.0810(12)
C(24)	0.2892(8)	1.0793(5)	0.1460(11)
H(4)	0.458(8)	0.800(5)	0.565(9)
H(5A)	0.100(8)	0.834(5)	0.580(9)
H(5B)	0.216(8)	0.715(5)	0.514(9)
H(6)	-0.019(8)	0.802(4)	0.276(9)
H(7A)	0.106(7)	0.723(4)	-0.046(9)
H(7B)	0.114(8)	0.666(5)	0.249(9)
H(8A)	0.378(8)	0.647(5)	0.080(9)
H(8B)	0.402(8)	0.697(4)	0.292(9)
H(9A)	0.350(8)	0.792(4)	-0.067(9)
H(9B)	0.523(8)	0.751(5)	0.020(9)
H(10A)	0.517(7)	0.906(4)	0.077(8)
H(10B)	0.596(8)	0.838(5)	0.255(9)
H(11A)	0.173(7)	0.898(5)	0.044(9)
H(11B)	0.129(7)	0.945(4)	0.297(9)
H(14)	0.619(7)	0.941(4)	0.783(9)
H(15)	0.907(7)	0.955(5)	0.816(9)
H(16)	1.035(8)	1.028(5)	0.560(9)
H(17)	0.875(8)	1.072(4)	0.189(9)
H(18)	0.599(8)	1.059(4)	0.158(9)
H(20)	0.351(8)	1.111(5)	0.697(9)
H(21)	0.198(8)	1.250(5)	0.546(9)
H(22)	0.151(7)	1.278(5)	0.174(9)
H(23)	0.174(7)	1.199(5)	-0.117(9)
H(24)	0.322(8)	1.027(5)	0.064(9)

Addition of diazomethane, phenyl azide, or 2,4,6-trimethylbenzonitrile oxide to **1**, **2** and **3** give mixtures of two regioisomers, whereas a single cycloadduct is formed with diphenylketene. According to frontier orbital theory, the regioselectivity of both cycloaddition-reaction types should be similar because both reactions are controlled by the HOMO of the strained olefin. The simple frontier orbital picture obviously does not account for the differences observed. As pointed out earlier [3], secondary orbital interactions may be rather important in cycloaddition of *Bredt* olefins as a consequence of the twist and out-of-plane deformations of the strained double

Table 3. *Torsional angles for the diphenylketene adduct* **8**, *the platinum complex* **18**, *and the Bredt olefin* **2**.

	a	b	c	d	e	f	g	h	i	j	k	l[a])
8	−94	+37	+46	−89	+72	−62	+83	−38	+34	−17	−7	−62
18[b])	−102	+46	+38	−84	+59	−41	+66	−45	+40	−16	−10	−85
2[c])	−113	+54	+37	−80	+62	−54	+77	−43	+34	−10	−18	−78

[a]) Meaning of the letters: 



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[b]) X-Ray analysis, data from [13].

[c]) Calculated values, from [4].

bond. It is not surprising that such secondary interactions are different for 1,3-dipolar cycloadditions, a $[\pi 2s + \pi 4s]$-reaction, and the ketene cycloaddition, a $[\pi 2s + \pi 2a]$-process.

The concerted thermal dimerization of highly strained, unstable *Bredt* olefins or related (*E*)-cycloalkenes constitutes another $[\pi 2s + \pi 2a]$-process. In analogy to the ketene cycloaddition to bridged (*E*)-cyclooctenes, a single cyclobutane dimer would be expected. Experimentally, always mixtures of dimers are formed, and this points to a stepwise diradical process rather than a concerted cycloaddition. Mixtures of regioisomers are also found in the cycloaddition of 1,1-dichloro-2,2-difluoroethene (**5**) to strained bridgehead olefins [8], a typical diradical process.

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Experimental Part

General remarks see [6]. The optical rotatory dispersion (ORD.) was measured on a *JASCO* J-20 spectropolarimeter in the laboratory of Dr. *P. Moser, Ciba-Geigy AG.*

2,2-Diphenyltricyclo[5.3.1.0^{1,4}]undecan-3-one (**7**). Bicyclo[3.3.1]non-1-ene (**1**, 250 mg, 2.05 mmol) in dry benzene was treated with diphenylketene (**6**, 388 mg, 2.00 mmol). After 2 min at RT., the solution was colorless. Evaporation and crystallization from $CH_3OH/CHCl_3$ gave 490 mg (77%) **7**; m.p. 194–195°. – IR. (KBr): 3080, 2930, 1760, 1490, 1447, 1140, 1080, 710. – ^{1}H-NMR. ($CDCl_3$): 7.60 (*d*, 1H, arom. H); 7.51 (*d*, 1H, arom. H); 7.3–7.0 (*m*, 8H, arom. H); 3.15 (*m*, 1H, H–C(4)); 2.1–1.0 (*m*, 13H, H–C(7) and 6 CH_2). – ^{13}C-NMR. ($CDCl_3$): see *Table 1.*

$C_{23}H_{24}O$ (316.45) Calc. C 87.30 H 7.65% Found C 87.04 H 7.55%

2,2-Diphenyltricyclo[4.4.1.0^{1,4}]undecan-3-one (**8**). Bicyclo[4.2.1]non-1(8)-ene (**2**, 559 mg, 4.57 mmol) in dry benzene was treated with **6** (756 mg, 3.89 mmol). After 10 min at RT., the solution was colourless. Chromatography over silica gel with CH_2Cl_2 gave 1.20 g (97%) **8**; m.p. 138–140°. Crystals for X-ray analysis were obtained by slow evaporation of a methanolic solution. – ORD. (dioxane): $[\phi]_{322} = \pm 350°$, enantiomeric excess unknown. – IR. (KBr): 3060, 2930, 1765, 1490, 1448, 1260, 1115, 710. – ^{1}H-NMR. ($CDCl_3$): 7.5–7.0 (*m*, 10H, arom. H); 3.52 (*d* × *d* × *d*, *J* = 10, 4 and 1, H–C(4)); 2.48 (*m*, 1H, H–C(6)); 2.3–1.1 (*m*, 12H, 6 CH_2). – ^{13}C-NMR. ($CDCl_3$): see *Table 1.*

$C_{23}H_{24}O$ (316.45) Calc. C 87.30 H 7.65% Found C 87.55 H 7.79%

Crystal data. Monoclinic, space group $P2_1$ (No.4), $a = 8.628(2)$, $b = 15.293(4)$, $c = 6.808(2)$, $\beta = 97.39(2)°$, $V = 891$ Å^3, $Z = 2$, $D_x = 1.180$ g/cm^3. On a *PICKER* FACS-1 diffractometer the intensities of 2483 reflections were measured, of which 1514 were treated as observed ($I > 2(I)$). A twin

correction according to *Britton* [14] was applied, and then the structure could be solved by direct methods (program MULTAN 77). Block diagonal least squares refinements with anisotropic temperature factors for the C- and O-atoms converged at $R = 0.103$. All H-atoms could be localized in a difference *Fourier* synthesis. The inclusion of the H-atoms in the calculations lowered the R-factor to 0.077. Final atomic coordinates are given in *Table 2*. The estimated standard errors derived from least squares refinements are comparatively large because of the twin nature of the crystal.

2,2-Diphenyltricyclo[6.2.1.0^{1,4}]undecan-3-one (**9**). Bicyclo[4.2.1]non-1(2)-ene (**3**, 135 mg, 1.10 mmol) in dry benzene was treated with **6** (230 mg, 1.18 mmol). After 5 min at RT., the solution was colourless. Evaporation and crystallization from methanol gave 290 mg (83%) **9**; m.p. 182–184°. – IR. (KBr): 3080, 2910, 1760, 1490, 1445, 1160, 1075, 712. – ^{1}H-NMR. (CCl_4): 7.6–7.0 (*m*, 10 H, arom. H); 3.19 (*d*×*d*, $J = 10.5$ and 6, H–C(4)); 2.6–2.2 (*m*, 2 H, CH_2); 2.1–1.2 (*m*, 11 H, H–C(8) and 5 CH_2). – ^{13}C-NMR. ($CDCl_3$): see *Table 1*.

$C_{23}H_{24}O$ (316.45) Calc. C 87.30 H 7.65% Found C 87.25 H 7.77%

1-Methyl-10,10-diphenyl-trans-*bicyclo[6.2.0]decan-9-one* (**10**). (*E*)-1-Methylcyclooctene (**4**, 476 mg, 3.83 mmol) in dry benzene was treated with **6** (740 mg, 3.81 mmol). After 10 min at RT., the solution was colourless. Evaporation and crystallization from methanol gave 1.05 g (87%) **10**, m.p. 125–126°. – IR. (KBr): 3060, 2910, 1765, 1490, 1445, 1142, 715. – ^{1}H-NMR. ($CDCl_3$): 7.7–7.6 (*m*, 2 H, arom. H); 7.3–7.1 (*m*, 8 H, arom. H); 3.26 (*d*×*d*, $J = 10$ and 2, H–C(8)); 2.2–1.1 (*m*, 12 H, 6 CH_2); 1.09 (*s*, H_3C–C(1)). – ^{13}C-NMR. ($CDCl_3$): see *Table 1*.

$C_{23}H_{26}O$ (318.46) Calc. C 86.74 H 8.23% Found C 86.58 H 8.43%

1-Methyl-10,10-diphenyl-cis-*bicyclo[6.2.0]decan-9-one* (**12**). (*Z*)-1-Methylcyclooctene (**11**, 550 mg, 4.43 mmol) and **6** (1.33 g, 6.85 mmol) were dissolved in benzene, sealed in a *Pyrex* pressure tube, and kept at 120° for 72 h. Crystallization from methanol gave 1.10 g (78%) **12**; m.p. 141–142°. – IR. (KBr): 3060, 2910, 1765, 1490, 1445, 1142, 715. – ^{1}H-NMR. ($CDCl_3$): 7.7–7.6 (*m*, 2 H, arom. H); 7.4–7.1 (*m*, 8 H, arom. H); 2.53 (*d*×*d*, $J = 10$ and 1.5, H–C(8)); 2.1–1.0 (*m*, 12 H, 6 CH_2); 1.21 (*s*, H_3C–C(1)). – ^{13}C-NMR. ($CDCl_3$): see *Table 1*.

$C_{23}H_{26}O$ (318.46) Calc. C 86.74 H 8.23% Found C 86.54 H 8.29%

2,2-Diphenyltricyclo[5.3.1.0^{1,4}]undecan-3-ol (**13**). Ketone 7 (0.20 g, 0.63 mmol) in dry ether was added dropwise to a suspension of $LiAlH_4$ (0.10 g, 2.6 mmol) in dry ether, and boiled under reflux for 2 h. The mixture was hydrolyzed with 0.4 ml of 1N NaOH, and filtered. The alcohol **13** (195 mg, 94%) was obtained from the filtrate by evaporation and crystallization from $CHCl_3$; m.p. 185–187°. – IR. (KBr): 3450 (br., OH), 2930, 1500, 1450, 1092, 710. – ^{1}H-NMR. ($CDCl_3$): 7.4–7.1 (*m*, 10 H, arom. H); 4.63 (*d*, $J = 8.8$, H–C(3)); 2.63 (*m*, H–C(4)); 2.37 (*s*, OH); 2.1–1.0 (*m*, 13 H, H–C(7) and 6 CH_2). – ^{13}C-NMR. ($CDCl_3$): 146.0 (*s*); 140.6 (*s*); 130.7, 128.5, 127.8, 126.0, 125.9 (each *d*); 79.3 (*d*, C(3)); 64.5 (*s*, C(2)); 45.8 (*d*, C(4)); 40.7 (*s*, C(1)); 37.8, 34.8, 31.5 (each *t*); 28.1 (*d*, C(7)); 25.8, 23.6, 20.8 (each *t*).

2,2-Diphenyltricyclo[4.4.1.0^{1,4}]undecan-3-ol (**14**). From ketone **8** as above, there was obtained 83% alcohol **14**; m.p. 60–62°. – IR. (KBr): 3400 (br., OH), 2920, 1495, 1445, 1128, 705. – ^{1}H-NMR. ($CDCl_3$): 7.3–7.1 (*m*, 10 H, arom. H); 4.40 (*d*, $J = 7.6$, H–C(3)); 2.83 (*t*×*d*, $J_t = 7.6$, $J_d = 3.5$, H–C(4)); 2.6–2.4 (*m*, 2 H, CH_2); 2.1–0.7 (*m*, 12 H, OH, H–C(6) and 5 CH_2). – ^{13}C-NMR. ($CDCl_3$): 147.9 (*s*); 141.0 (*s*); 131.0, 128.2, 128.1, 127.8, 127.7, 126.1, 126.0 (each *d*); 83.1 (*d*, C(3)); 62.4 (*s*, C(2)); 58.0 (*d*, C(4)); 52.0 (*s*, C(1)); 42.6 (*t*); 40.8 (*d*, C(6)); 38.3, 36.9, 36.4, 25.9, 23.6 (each *t*).

2,2-Diphenyltricyclo[6.2.1.0^{1,4}]undecan-3-ol (**15**). From ketone **9** as above, there was obtained 99% alcohol **15** as a colorless oil. – IR. (film): 3400 (br., OH), 2920, 1495, 1442, 1135, 1095, 705. – ^{1}H-NMR. ($CDCl_3$): 7.3–7.1 (*m*, 10 H, arom. H); 4.40 (*d*×*d*, $J = 10$ and 8.5, H–C(3)); 2.5–1.0 (*m*, 14 H, H–C(4,8) and 6 CH_2); 1.40 (*d*, $J = 10$, OH). – ^{13}C-NMR. ($CDCl_3$): 146.1 (*s*); 141.6 (*s*); 131.0, 128.1, 127.9, 127.8, 126.2, 126.0 (each *d*); 75.7 (*d*, C(3)); 63.4 (*s*, C(2)); 54.7 (*d*, C(4)); 51.4 (*s*, C(1)); 40.0 (*t*); 37.4 (*t*); 36.7 (*d*, C(8)); 36.0, 30.7, 27.2, 23.3 (each *t*).

1-Methyl-10,10-diphenyl-trans-*bicyclo[6.2.0]decan-9-ol* (**16**). From ketone **10** as above, there was obtained 87% alcohol **16**; m.p. 74–75.5°. – IR. (KBr): 3460 (br., OH), 2920, 1495, 1445, 1095, 700. – ^{1}H-NMR. ($CDCl_3$): 7.5–7.4 (*m*, 2 H, arom. H); 7.3–7.1 (*m*, 8 H, arom. H); 4.36 (*d*, $J = 10$, H–C(9)); 2.73 (*t*, $J = 10$, H–C(8)); 2.45 (*s*, OH); 1.9–1.0 (*m*, 12 H, 6 CH_2); 0.97 (*s*, H_3C–C(1)). – ^{13}C-NMR. ($CDCl_3$): 146.7 (*s*); 140.7 (*s*); 131.0, 128.4, 127.8, 127.7, 125.9, 125.8 (each *d*); 77.4 (*d*, C(9));

64.4 (*s*, C(10)); 51.0 (*d*, C(8)); 42.6 (*s*, C(1)); 40.3, 30.7, 29.1, 28.8, 28.0, 25.8 (each *t*); 23.1 (*qa*, CH_3–C(1)).

1-Methyl-10,10-diphenyl-cis-*bicyclo[6.2.0]decan-9-ol* (**17**). From ketone **12** as above, there was obtained 99% alcohol **17**; m.p. 116–117°. – IR. (KBr): 3430 (br., OH), 2920, 1490, 1445, 1115, 705. – ^{1}H-NMR. ($CDCl_3$): 7.81 (*d*, 1 H, arom. H); 7.73 (*d*, 1 H, arom. H); 7.4–7.0 (*m*, 8 H, arom. H); 5.18 (*d*×*d*, *J* = 9 and 6.8, H–C(9)); 2.26 (*d*, *J* = 6.8, OH); 2.08 (*d*×*d*, *J* = 11 and 9, H–C(8)); 2.0–1.0 (*m*, 12 H, 6 CH_2); 1.17 (*s*, H_3C–C(1)). – ^{13}C-NMR. ($CDCl_3$): 150.1 (*s*); 143.2 (*s*); 130.7, 127.7, 127.3, 127.2, 125.2 (each *d*); 74.6 (*d*, C(9)); 63.8 (*s*, C(10)); 52.6 (*d*, C(8)); 42.8 (*s*, C(1)); 32.7 (*t*); 31.3 (*t*); 26.9 (*qa*, CH_3–C(1)); 26.2, 25.1 (2 C); 24.4 (each *t*).

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