Synthesis of 5-Methoxy- and 5-(Dialkylamino)bicyclo[3.2.0]hept-2-en-6-one Derivatives by *cine* Substitution with Methoxide Anions and Dialkylamines

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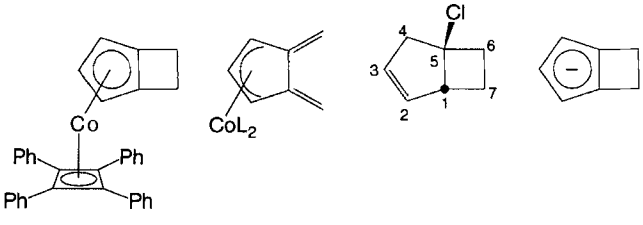
exo-7-Chloro-*endo*-7-phenylbicyclo[3.2.0]hept-2-en-6-one (**5**) undergoes *cine* substitution reactions with methoxide anions and with dialkylamines to give 5-methoxy or 5-dialkylamino derivatives **13**, **14**, **16**–**19** in high yield. While attempts directed to an acetalization have failed, the addition of Grignard reagents to the methoxy derivatives proceeds stereoselectively in high yield. Hydrochlorides **20**/**21** lose amine at 110°C to form 2-phenyltropone (**22**). Thermolysis of diethylamino derivative **24** at 170°C (temperature determined by DSC) results in the formation of the dienaminone **25**.

Transition metal complexes with substituted cyclopentadienyl ligands are of current interest with regard to the influence of the substituents on the reactivity of the metallic center of these complexes, e.g. alkyne trimerization, formation of pyridines from alkynes and nitriles, the synthesis of cyclohexadienes and, of course, tacticity in Ziegler Natta polymerizations[1]. Such complexes are usually prepared by synthesis and subsequent complexation of the cyclopentadiene derivative at a metal. Another possibility is the manipulation of an already coordinated cyclopentadienyl ligand. This seems more promising in some cases because of stereochemical reasons: Whereas the complexation of a somehow substituted cyclopentadienyl anion can principally take place at either face of the ligand more or less selectively, the faces are effectively differentiated in a cyclopentadienyl complex. This differentiation should allow the selective formation of functionalized cyclopentadienyl complexes by appropriate reactions of the complexed ligand. This line of thought increasingly applies to reactions forming more than just one new bond, e.g. cycloaddition reactions.

We have previously reported on the synthesis of some η^5-(bicyclo[3.2.0]hepta-1,3-dienyl)cobalt(I) complexes and shown that a ring opening reaction followed by a [4 + 2] cycloaddition takes place on heating, provided the activation barrier of the ring-opening reaction is smaller than that of the decomplexation reaction of the other ligands at the metal[2,3]. This condition is fulfilled by the tetraphenylcyclobutadiene complex **1**; at 200°C the reaction of **1** with dienophiles like *N*-methylmaleinimide results in the formation of [4 + 2] cycloadducts in good yield. More recently, a ferrocene example has been published by Trahanovsky and Ferguson[4], the reaction temperature being also 200°C. Bearing in mind the wide applicability of *ortho*-quinodimethanes in organic synthesis the corresponding reactions with the lower homologue bear considerable potentials in organic syntheses. This is especially true in the light of the facial discrimination of the ligand by complexation to a metal: Substituents at the anellated ring would render the *ortho*-quinodimethane analogue **2** (L = 2e ligand) chiral.



1 **2** **3** **4**

There are some points which have up to now prevented a broader application of the reaction: The reaction temperature of 200°C is too high for most organic substrates, and methods to liberate the organic ligand from the metal are limited for (cyclobutadiene)(cyclopentadienyl)cobalt and ferrocene systems. However, the choice of these systems is necessary to allow reaction temperatures as high as 200°C to be used. To overcome these problems it is mandatory to decrease the activation energy of the ring opening reaction. From the chemistry of benzocyclobutenes[5–7] it is known that the activation energy of the ring opening reaction can be tuned by the choice of substituents at the anellated ring.

For these reasons we have felt a need for bicyclo[3.2.0]-hepta-1,3-dienyl anions with substituents at the four-membered ring. So far, only the synthesis of the unsubstituted anion **4** via chloride **3** has been described by Oda and Breslow[8], the synthesis of **3** being unsuitable for most substituted systems. A dehydrobromination of the more easily ac-

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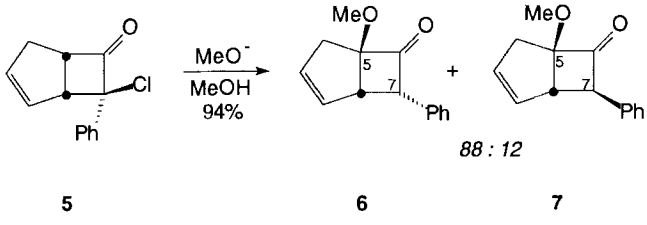
cessible 4-bromobicyclo[3.2.0]hept-2-ene causes an immediate rearrangement to spiro[2.4]hepta-4,6-diene[9]. This has been the reason for us to prepare bicyclo[3.2.0]hept-2-ene derivatives with potential leaving groups at C-5. In this paper we report on the synthesis of some methoxy and dialkylamino derivatives and reactions of these compounds. Some of the material presented has been published in preliminary form[10].

Substituted bicyclo[3.2.0]hept-2-en-6-one derivatives are easily obtained by [2 + 2] cycloaddition of appropriately substituted ketenes with cyclopentadienes[11]. Dreiding has found that the [2 + 2] cycloaddition reaction of cyclopentadiene to chlorophenylketene selectively yields *exo*-7-chloro-*endo*-7-phenylbicyclo[3.2.0]hept-2-en-6-one (**5**)[12]. This is important because the product already contains a phenyl substituent at the four-membered ring which is known to facilitate the envisaged ring opening reaction[5–7]. Even more important is that **5** is formed stereoselectively with an *exo*-7-chloro substituent: This is the ideal precondition for a subsequent *cine* substitution reaction[13], which allows the introduction of a nucleophile into the 5-position.

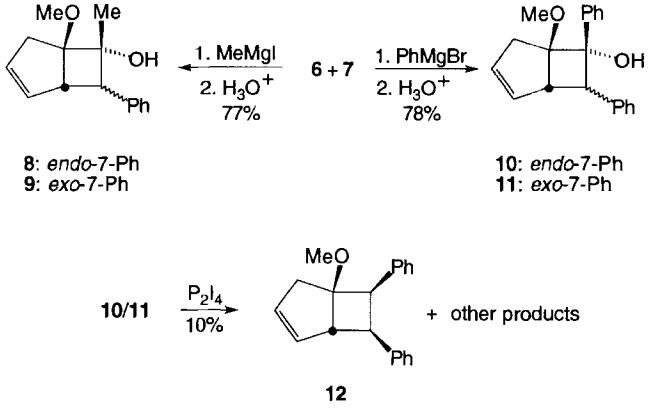


So far there is only one report of a *cine* substitution with a bicyclo[3.2.0]heptane derivative. Garin and Cammack have shown that the reaction of 7-chloro-7-methylbicyclo-[3.2.0]hept-2-en-6-ones with methoxide gives 5-methoxy-7-methylbicyclo[3.2.0]hept-2-en-6-one products only with the *exo*-7-chloro isomer, whereas the *endo*-7-chloro compound undergoes a Favorsky rearrangement[14]. This observation can be understood by regarding the *cine* substitution as a kind of *syn*-stereospecific S_N2' reaction[15,16] of the strained enol of the starting ketone. The reaction is driven by loss of strain and finally leads to a mixture of diastereomers (C-7). Because of the exclusive *exo*-7-chloro configuration reactions of **5** with nucleophiles should result in *cine* substitution products; no Favorski rearrangement product is to be expected. Indeed, treatment of **5** with an excess of sodium methoxide followed by aqueous acidic workup yields a 88:12 mixture of *cine* substitution products **6** and **7** in 94% overall yield. The preference for **6** is explained by preferred protonation of the enolate formed from the *exo* face. The formation of **6** and **7** is remarkable, because Hassner[17] has recently reported that the cycloadduct of cyclopentadiene and chlorophenylketene is unreactive toward methoxide ions. Brady[18] has noted earlier that *cine* substitution reactions with cycloadducts of cyclopentadiene and chloroketenes are less favored due to the strain of their enolates.

Compounds **6** and **7** are characterized by an inspection of their spectroscopic data. The ^{1}H-NMR signal of *exo*-7-H in **6** is a characteristic feature and appears at $\delta = 4.89$ as a doublet with $^3J_{1,exo\text{-}7} = 10.4$ Hz. In the EI mass spectrum the molecular ion peak ($m/z = 214$) is not observed, a peak at $m/z = 186$ is registered instead, indicating a loss of CO. It has later been shown that this is a typical property of this class of compounds. Chemical ionization (NH_3) allows the observation of signals at $m/z = 215$ $[M + H]^{+\cdot}$ and 232 $[M + NH_4]^{+\cdot}$. Compounds **6** and **7** are obtained as a viscous oil with more than 95% purity, which can be evaporated at 80°C/0.001 mbar and condensed in a cold flask. Attempts to purify the material by crystallization, column chromatography, or preparative HPLC have failed because of partial decomposition. Compound **6** is thermally more labile than **7**.

All attempts to protect the keto groups in **6** and **7** by the formation of an acetal or a thioacetal have failed. Reactions with phenyl- and methylmagnesium bromide give the *endo*-6-hydroxy derivatives in 77 and 78% yield, respectively, as mixtures of diastereomers (**8**:**9** = 86:14, **10**:**11** = 65:35).

The configuration at C-6 has been established for **8** and **9** by a NO effect between the two methyl groups. The similarly of all spectroscopic data of **10/11** to those of **8/9** indicates the same configuration in the phenylated products.

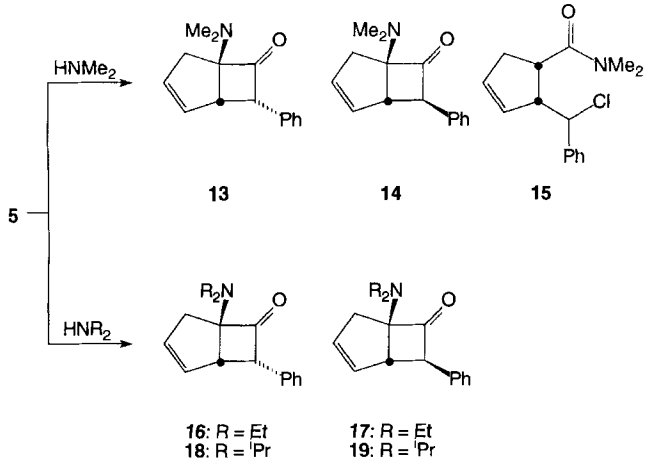


Numerous attempts to reduce the hydroxy functionality in **8**–**11** have failed. Only the treatment of **10/11** with diphosphorus tetraiodide[19] gives 5-methoxy-*exo*-6,*exo*-7-diphenylbicyclo[3.2.0]hept-2-ene (**12**), albeit in poor yield (10%) besides other products. Compound **12** is interesting, because it should facilitate the preparation of the *cis*-6,7-diphenylbicyclo[3.2.0]hepta-1,3-dienyl anion by replacing the methoxy group by chlorine using BCl_3 and subsequent treatment with lithium diisopropylamide[8]. The *cis*-6,7-diphenylbicyclo[3.2.0]hepta-1,3-dienyl anion is a potential ligand with a presumably drastically reduced activation energy of the ring opening reaction leading to the corresponding 4,5-dimethylenecyclopentenyl system. However, so far the low yield of **12** precludes its synthesis on a preparative scale.

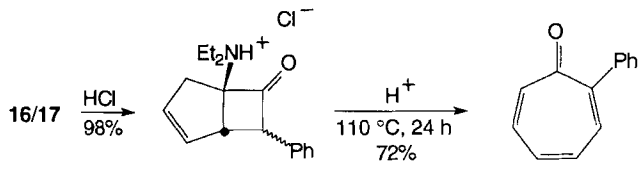
In order to avoid the problems connected with the presence of two oxygen-containing substituents in the system

the use of nucleophiles other than methoxide in the *cine* substitution has been envisaged. With a projected subsequent elimination reaction in mind, the use of a chloride as a nucleophile would be especially attractive. However, all attempts to perform a *cine* isomerization from **5** to a 5-chloro-7-phenylbicyclo[3.2.0]hept-2-en-6-one have failed. Therefore, secondary amines have been tested. It has been found that the *cine* substitution takes place; however, the yields and the product composition are highly dependent on the choice of the amine.

Treatment of **5** with dimethylamine gives a mixture of the distereomeric *cine* substitution products **13** and **14** (58:42) and ring-opened amide **15**, which is isolated as a single diastereomer (overall yield 71%). Treatment of **5** with diethylamine exclusively yields *cine* substitution products **16** and **17** (61:39) in 85% yield. While the reaction with diethylamine is complete within 14–17 hours, the corresponding reaction with diisopropylamine needs a period of 11 days for 50% conversion. However, unchanged **5** is easily recovered, and the yield (referred to consumed **5**) is 75% of **18** and **19** (90:10). These observations are easily explained by the bulkiness of the diisopropylamino substituent as compared to the diethylamino group. The reaction products are characterized spectroscopically; for **19** only incomplete data have been obtained because of the small fraction of **19** in the diastereomeric mixture with **18**. Like the methoxy derivative **6** the corresponding amino derivatives show a ^{1}H-NMR doublet for *exo*-7-H of $\delta \approx 5$ due to coupling with 1-H. In the EI mass spectra of the amino ketones the signal corresponding to a molecular ion is not observed; however, as for the methoxy compounds, a peak [M − 28] appears. Because of the high yield diethylamino derivatives **16** and **17** have been selected for further investigations.

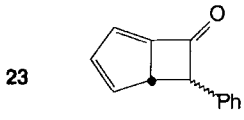


In order to prepare the important 6-oxobicyclo-[3.2.0]hepta-1,3-dienyl complexes, protection of the keto group in **16/17** as an acetal appeared advantageous. To perform an acid-catalyzed acetalization it is necessary to first transform the amino substituent into an ammonium group. Compounds **20/21** are obtained in 98% yield by treatment of **16/17** with HCl-saturated diethyl ether or better with aqueous hydrochloric acid followed by complete evaporation of the water and excess HCl. The following reaction with 1,2-ethanediol in boiling benzene with azeotropic removal of water does, however, not result in the formation of the acetal. Instead, 2-phenyltropone (**22**) is isolated. Further experiments show that **20/21** react in the presence of a catalytic amount of *p*-toluenesulfonic acid in boiling toluene to give **22** in 72% yield.



20: *endo*-7-Ph
21: *exo*-7-Ph

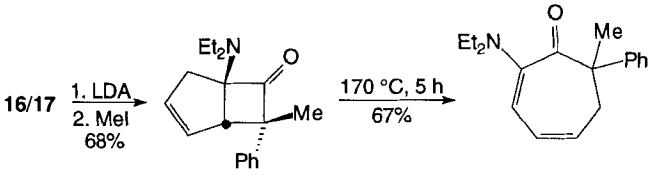
22



23

Brady[18,20] and Bartlett[21] have reported on transformations of certain 7-chlorobicyclo[3.2.0]hept-2-en-6-one derivatives yielding tropone or tropolone derivatives. However, their mechanistic proposals cannot be applied to the reaction of **20/21** to afford **22**. We believe that the ammonium group is liberated from the molecule in a process similar to a Hofmann elimination. This process would generate the highly strained α,β,γ,δ-bisunsaturated ketone **23** as an intermediate which could open the four-membered ring with intra- or intermolecular hydrogen transfer to give **22**. Alternatively, a system with a bond between C-5 and C-7 may be discussed. However, this system appears even more strained. Another possibility is a conrotatory ring expansion of the enol of **20/21** to a cycloheptane derivative and a subsequent elimination of amine[22].

The formation of **22** involves a removal of 7-H. To prevent this, **16/17** was metallated by treatment with lithium diisopropylamide and the resulting enolate subsequently methylated with methyl iodide. Exclusive attack of the electrophile at the *exo* face of the enolate results in the formation of diastereomerically pure **24** in 68% yield; the configuration at C-7 has been established by NOE experiments.The DSC (*D*ifferential *S*canning *C*alorimetry) analysis of **24** indicates a thermal reaction at 170°C. Heating of **24** in a kugelrohr oven at 170°C indeed results in an isomerization to enamine **25** in 67% yield.



24

25

This reaction contrasts with that of **20/21** giving 2-phenyltropone (**22**) where the amino group remains unaffected. Compound **25** is an interesting, highly functionalized cycloheptane derivative whose chemistry will be investigated in the future.

In summary, we have described the synthesis and some reactions of bicyclohept-2-en-6-one derivatives with methoxy and dialkylamino substituents at the bridgehead C-5. Most of the compounds reported can easily be obtained in multigram quantities. Further investigations finally directed to substituted bicyclo[3.2.0]hepta-1,3-dienyl anions are under way.

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Experimental

General: See ref.[23].

5-Methoxy-7-phenylbicyclo[3.2.0]hept-2-en-6-one (**6/7**): In a 4-l three-necked round-bottom flask equipped with a magnetic stirring bar, a reflux condenser, an argon inlet, and a 100-ml dropping funnel is placed 1000 ml of methanol. 15.75 g (685 mmol) of sodium is cut to small pieces and given into the flask in small portions with cooling (ice bath). After complete dissolution of the sodium a solution of 50 g (229 mmol) of **5**[12] in 80 ml of methanol is added dropwise. After complete addition the mixture is stirred for 2 h at 25°C. Then 3000 ml of water is added, and the mixture is acidified with concd. hydrochloric acid. The mixture is extracted three times with 2000 ml of diethyl ether each, the combined organic layers are washed with 500 ml of a saturated aqueous solution of sodium hydrogen carbonate and 500 ml of water, dried with magnesium sulfate, filtered, and the solvent is evaporated from the filtrate in a rotary evaporator under reduced pressure. The residual syrup is dried at 0.001 mbar for 8 h to yield 46.23 g [216 mmol, 94%, purity >95% (NMR)] of **6/7** (*endo:exo* = 88:12). For further purification the compounds are evaporated at 80°C/0.001 mbar and condensed in cold flask which proceeds with partial decomposition of the *endo* isomer **6**. – IR (film): $\tilde{\nu}$ = 3085 cm^{-1} (w), 3059 (m), 2937 (m, OCH_3), 1774 (s, C=O), 1602 (m, Ph), 1497 (m), 1451 (m), 1306 (m), 1133 (m, C–O). – ^1H NMR (400 MHz, $CDCl_3$) of **6**: δ = 2.53 [m, 1H, *exo*-4-H, $^4J_{2,exo\text{-}4} \approx 2.2$, $^3J_{3,exo\text{-}4} \approx 2.2$, $^2J_{endo\text{-}4,exo\text{-}4} = -17.6$, $^5J_{exo\text{-}4,exo\text{-}7} \approx 0.7$ (?), $^4J_{1,exo\text{-}4} \approx 1.1$ Hz], 2.83 (dt, 1H, *endo*-4-H, $^4J_{2,endo\text{-}4} \approx 2.4$, $^3J_{3,endo\text{-}4} \approx 2.4$, $^4J_{1,endo\text{-}4} \approx 2.4$ Hz), 3.47 (s, 3H, OCH_3), 3.85 (m, 1H, 1-H, $^3J_{1,2} \approx 2.4$, $^4J_{1,3} \approx 1.3$, $^3J_{1,exo\text{-}7} = 10.4$ Hz), 4.89 (d, 1H, *exo*-7-H), 5.43 (m, 1H, 2-H, $^3J_{2,3} = 6.1$ Hz), 5.78 (m, 1H, 3-H), 7.13 (m, 2H, *o*-H), 7.2–7.3 (m, 3H, *m*-, *p*-H); **7**: δ = 2.67 (m, 1H, *exo*-4-H, $^4J_{2,exo\text{-}4} = 1.6$, $^3J_{3,exo\text{-}4} = 2.4$, $^2J_{endo\text{-}4,exo\text{-}4} = -18.7$, $^4J_{1,exo\text{-}4} > 0$ Hz), 2.97 (m, 1H, *endo*-4-H, $^4J_{2,endo\text{-}4} = 2.8$, $^3J_{3,endo\text{-}4} = 2.2$, $^4J_{1,endo\text{-}4} = 1.8$ Hz), 3.41 (s, 3H, OCH_3), 3.59 (m, 1H, 1-H, $^3J_{1,2} = 2.8$, $^4J_{1,3} > 0$, $^3J_{1,endo\text{-}7} = 6.1$ Hz), 3.74 (m, 1H, *endo*-7-H), 5.91 (m, 1H, 3-H or 2-H, $^3J_{2,3} = 5.7$ Hz), 6.14 (m, 1H, 2-H or 3-H). – ^{13}C NMR (50 MHz, $CDCl_3$) of **6**: δ = 37.2 (t, C-4, $^1J_{C,H} = 130.8$ Hz), 48.6 (d, C-1, $^1J_{C,H} = 145.6$ Hz), 54.0 (q, OCH_3, $^1J_{C,H} = 142.1$ Hz), 66.5 (d, C-7, $^1J_{C,H} = 136.0$ Hz), 102.1 (s, C-5), 127.0 (d, C-2, -3, or -11, $^1J_{C,H} = 165.7$ Hz), 127.7 (d, C-9 or -10, $^1J_{C,H} = 158.7$ Hz), 127.9 (d, C-9 or -10, $^1J_{C,H} = 159.6$ Hz), 129.2 (d, C-2, -3 or -11, $^1J_{C,H} = 163.1$ Hz), 131.8 (d, C-2, -3, or -11, $^1J_{C,H} = 167.4$ Hz), 134.0 (s, C-8), 209.6 (s, C-6); **7**: δ = 39.8 (t, C-4, $^1J_{C,H} = 130.8$ Hz), 48.3 (d, C-1, $^1J_{C,H} = 145.6$ Hz), 53.2 (q, OCH_3, $^1J_{C,H} = 136.0$ Hz), 66.5 (d, C-7, $^1J_{C,H} \approx 130$ Hz), 101.5 (s, C-5), 126.7 (d, C-2, -3 or -11, $^1J_{C,H} = 160.4$ Hz), 127.0 (d, C-9 or -10, $^1J_{C,H} = 163.9$ Hz), 128.4 (d, C-9 or -10, $^1J_{C,H} = 159.6$ Hz), 130.3 (d, C-2, -3, or -11, $^1J_{C,H} = 168.3$ Hz), 132.9 (d, C-2, -3 or -11), 135.5 (s, C-8), 207.5 (s, C-6). – MS (70 eV), *m/z* (%): 187 (1), 186 (9), 155 (6), 128 (6), 96 (100), 95 (6), 91 (4), 81 (12), 39 (9). – $C_{14}H_{14}O_2$ (214.3): calcd. C 78.48, H 6.59; found C 77.48, H 6.56.

5-Methoxy-exo-6-methyl-7-phenylbicyclo[3.2.0]hept-2-en-endo-6-ol (**8/9**): A solution of methylmagnesium iodide is prepared from 2.84 g (116.1 mmol) of magnesium filings and a solution of 16.58 g (7.3 ml, 116.1 mmol) of iodomethane in 50 ml of diethyl ether. Then a solution of 20.0 g (93.5 mmol) of **6/7** in 100 ml of diethyl ether is added dropwise causing an immediate precipitation. After complete addition the mixture is heated at reflux for 2 h, cooled to room temp. and acidified with 5 N HCl. The mixture is extracted five times with 200 ml of diethyl ether each, the combined organic layers are washed with 300 ml of a satd. aq. sodium hydrogen carbonate solution and 300 ml of water, dried with $MgSO_4$, filtered, and the solvent is removed from the filtrate in a rotary evaporator under reduced pressure. 20.2 g of a red-yellow oil is obtained as the residue, which is chromatographed on silica gel (column 40 × 3 cm, pentane/diethyl ether, 1:1) to afford 16.66 g (72.4 mmol, 77%) of **8/9** [*endo:exo* = 86:14, purity ca. 95% (NMR)]. An analytical sample is further purified by preparative GC (8 m, diameter 20 mm, 20% SE-30 on Volaspher A4, 100–120 mesh, column 260°C, injector 320°C, outlet 190°C). – IR (film): $\tilde{\nu}$ = 3454 cm^{-1} (s, OH), 3055 (m), 1767 (m, C=O, impurity?), 1496 (s), 1453 (s), 1090 (s, C–O), 702 (s). – ^1H NMR (200 MHz, $CDCl_3$) of **8**: δ = 1.43 (s, 3H, *exo*-6-CH_3), 1.97 (br. s, 1H, *endo*-6-OH), 2.47 (br. d, 1H, *exo*-4-H, $^2J_{endo\text{-}4,exo\text{-}4} = -17.8$ Hz), 2.92 (br. d, 1H, *endo*-4-H), 3.22 (s, 3H, OCH_3), 3.46 (m, 1H, 1-H), 3.64 (d, 1H, *exo*-7-H, $^3J_{1,exo\text{-}7} = 9.6$ Hz), 5.71 (m, 1H, 2-H, $^3J_{2,3} = 6.0$ Hz), 5.85 (m, 1H, 3-H), 7.2 (m, 5H, Ph); configurational assignment at C-6 by NOE measurement; due to signal overlap and low intensity the signals of **9** could not be assigned. – ^{13}C NMR (50 MHz, $CDCl_3$) of **8**: δ = 24.1 (q, CCH_3, $^1J_{C,H} = 125.6$ Hz), 33.2 (t, C-4, $^1J_{C,H} = 127.3$ Hz), 47.7 (d, C-1, $^1J_{C,H} = 142.1$ Hz), 50.7 (d, C-7, $^1J_{C,H} = 129.9$ Hz), 51.2 (q, OCH_3, $^1J_{C,H} = 141.3$ Hz), 78.9 (s, C-6), 91.3 (s, C-5), 126.1 (d, *p*-C, $^1J_{C,H} = 156.1$ Hz), 127.7 (d, *o*- or *m*-C, $^1J_{C,H} = 159.6$ Hz), 129.2 (d, *m* or *o*-C, $^1J_{C,H} = 157.0$ Hz), 131.3 (d, C-2 or -3, $^1J_{C,H} \approx 168$ Hz), 133.5 (d, C-2 or -3, $^1J_{C,H} = 162.2$ Hz), 137.0 (s, *i*-C); **9**: δ = 24.2 (q, CCH_3, $^1J_{C,H} \approx 125$ Hz), 35.8 (t, C-4, $^1J_{C,H} \approx 129$ Hz), 49.2 (d, C-1, $^1J_{C,H} = 141.3$ Hz), 51.7 (q, OCH_3, $^1J_{C,H} = 142.1$ Hz), 56.1 (d, C-7, $^1J_{C,H} = 136.9$ Hz), 75.5 (s, C-6), 87.4 (s, C-5), 124.6 (d, *p*-C, $^1J_{C,H} \approx 156$ Hz), 128.1 (d, *m*- or *o*-C, $^1J_{C,H} = 160.4$ Hz), 128.6 (d, *m*- or *o*-C, $^1J_{C,H} = 157.8$ Hz), 131.2 (d, C-2 or -3, $^1J_{C,H} \approx 168$ Hz), 133.4 (d, C-2 or -3, $^1J_{C,H} = 163.1$ Hz), 138.4 (s, *i*-C). – MS (70 eV), *m/z* (%): 230 (2) [M^+], 187 (26), 155 (53), 134 (17), 131 (13), 130 (100), 129 (32), 115 (20), 97 (10), 96 (92), 91 (27), 53 (12), 43 (35). – $C_{15}H_{18}O_2$ (230.3): calcd. C 78.23, H 7.88; found C 77.92, H 7.84.

5-Methoxy-exo-6,7-diphenylbicyclo[3.2.0]hept-2-en-endo-6-ol (**10/11**): A solution of phenylmagnesium bromide is prepared from 2.84 g (116.1 mmol) of magnesium filings and a solution of 18.34 g (116.8 mmol) of bromobenzene in 50 ml of diethyl ether. Then a solution of 20.0 g (93.5 mmol) of **6/7** in 100 ml of diethyl ether is added dropwise causing an immediate precipitation. After completed addition the mixture is heated at reflux for 2 h, cooled to room temp. and acidified with 5 N HCl. The mixture is extracted five times with 200 ml of diethyl ether each, the combined organic layers are washed with 300 ml of a satd. aq. sodium hydrogen car-

bonate solution and 300 ml of water, dried with $MgSO_4$, filtered, and the solvent is removed from the filtrate in a rotary evaporator under reduced pressure. 25.79 g of a red-yellow oil is obtained as the residue, which is chromatographed on silica gel (column 40 × 3 cm). Impurities are removed by elution with pentane, then pentane/diethyl ether (4:1). The following elution with diethyl ether yields 21.36 g (73.2 mmol, 78%) of **10/11** (*endo:exo* = 65:35) as a viscous syrup. Upon standing in the refrigerator partial crystallization occurs. An analytical sample of **10** is recrystallised from diethyl ether (bright yellow crystals, m.p. 84.6−85.2°C). − IR (KBr): $\tilde{\nu}$ = 3539 (m, OH), 3059 (m), 1495 (s, Ph), 1445 (s, Ph), 1205 (m, C−OH), 1098 (s, C−O), 737 (s). − ^{1}H NMR (400 MHz, $CDCl_3$) of **10**: δ = 2.58 (d, 1H, *exo*-4-H, $^2J_{endo\text{-}4,exo\text{-}4}$ = −17.2 Hz), 2.88 (s, 3H, OCH_3), 3.05 (d, 1H, *endo*-4-H), 3.69 (m, 1H, 1-H, $^3J_{1,2} \approx 2.3$, $^3J_{1,exo\text{-}7}$ = 9.4 Hz), 4.64 (d, 1H, *exo*-7-H), 5.99 (m, 1H, 2- or 3-H, $^3J_{2,3}$ = 6.1 Hz), 6.05 (m, 1H, 2- or 3-H), 7.2−7.6 (m, 10H, Ph); **11**: δ = 2.44 (br. s, 2H, *endo*-4-H, *exo*-4-H), 3.28 (s, 3H, OCH_3), 3.42 (m, 1H, *endo*-7-H, $^3J_{1,endo\text{-}7}$ = 7.4 Hz), 3.50 (m, 1H, 1-H, $^3J_{1,2}$ = 2.7 Hz), 5.88 (m, 3-H, $^3J_{2,3}$ = 5.9 Hz), 6.07 (m, 1H, 2-H), 7.2−7.6 (m, 10H, Ph). − ^{13}C NMR (50 MHz, $CDCl_3$) of **10**: δ = 34.0 (t, C-4, $^1J_{C,H}$ = 126.4 Hz), 49.3 (d, C-1 or -7, $^1J_{C,H} \approx 142$ Hz), 49.4 (d, C-1 or -7, $^1J_{C,H} \approx 142$ Hz), 52.2 (q, OCH_3, $^1J_{C,H}$ = 141.3 Hz), 81.5 (s, C-6), 92.8 (s, C-5), 126.5 (d, *p*-C, $^1J_{C,H} \approx 162$ Hz), 126.7 (d, *m*- or *o*-C, $^1J_{C,H}$ = 159.6 Hz), 127.0 (d, *p*-C, $^1J_{C,H}$ = 160.4 Hz), 127.7 (d, *m*- or *o*-C, $^1J_{C,H}$ = 159.6 Hz), 128.1 (d, *m*- or *o*-C, $^1J_{C,H}$ = 159.6 Hz), 129.1 (d, *m*- or *o*-C, $^1J_{C,H}$ = 157.8 Hz), 131.6 (d, C-2 or -3, $^1J_{C,H}$ = 168.3 Hz), 134.1 (d, C-2 or -3, $^1J_{C,H}$ = 163.1 Hz), 136.6 (s, *i*-C), 142.1 (s, *i*-C); **11**: δ = 37.9 (t, C-4, $^1J_{C,H}$ = 129.0 Hz), 50.8 (d, C-1 or -7, $^1J_{C,H}$ = 142.1 Hz), 51.20 (d, C-1 or -7, $^1J_{C,H}$ = 142.1 Hz), 51.25 (q, OCH_3, $^1J_{C,H}$ = 143.0 Hz), 79.2 (s, C-6), 81.5 (s, C-5), 126.3 (d, *p*-C), 127.2 (d, *p*-C), 127.84 (d, *m*- or *o*-C), 127.87 (d, *m*- or *o*-C), 127.92 (d, *m*- or *o*-C), 128.1 (d, *m*- or *o*-C), 132.3 (d, C-2 or -3, $^1J_{C,H} \approx 170$ Hz), 133.5 (d, C-2 or -3, $^1J_{C,H}$ = 162.2 Hz), 138.1 (s, *i*-C), 142.6 (s, *i*-C). − MS (70 eV), *m/z* (%): 292 (3) [M^+], 197 (14), 196 (100), 130 (63), 105 (34), 97 (20), 96 (95), 81 (10), 77 (21). − $C_{20}H_{20}O_2$ (292.4): calcd. C 82.16, H 6.89; found C 82.35, H 6.90.

Treatment of **10/11** *with Diphosphorus Tetraiodide:* 9.86 g (17.0 mmol) of diphosphorus tetraiodide in 100 ml of toluene in a 250-ml round-bottom flask equipped with a magnetic stirring bar, a reflux condenser, and an argon inlet is heated for 30 min at 100°C. A solution of 2.5 g (8.5 mmol) of **10/11** in 30 ml of toluene is added, and the mixture is stirred at 100°C for 14 h. After cooling to room temp. 50 ml of a 10% aqueous solution of $Na_2S_2O_5$ is added, and the mixture is extracted three times with 120 ml of diethyl ether each. The combined organic layers are washed three times with 100 ml of water each, dried with $MgSO_4$, filtered, and the solvent is removed from the filtrate in a rotary evaporator under reduced pressure. Column chromatography of the residue on silica gel (50 × 1 cm) with pentane and then with pentane/diethyl ether (10:1) gives 120 mg of **12** and 390 mg of unidentified side products. Subsequently, elution with pentane/diethyl ether (10:1) furnishes 590 mg of a product mixture which is again chromatographed on silica gel (50 × 1 cm). Elution with pentane/diethyl ether (4:1) gives 230 mg of a yellow oil. GC (Packard, 40 m PS 240, 80−280 cm^{-1}, 8°C/min): I (50.5%, rel. retention time = 1) *5-methoxy-exo-6,exo-7-diphenylbicyclo[3.2.0]hept-2-ene* (**12**). − IR (film): $\tilde{\nu}$ = 3085 cm^{-1} (m), 3057 (s), 3026 (s), 1602 (s), 1495 (s), 1088 (s, C−O), 750 (s, Ph), 730 (s), 699 (s). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.64 (m, 1H, *endo*-4-H, $^4J_{2,endo\text{-}4} \approx 2.4$, $^3J_{3,endo\text{-}4} \approx 2.4$, $^2J_{endo\text{-}4,exo\text{-}4}$ = −17.7, $^4J_{1,endo\text{-}4} \approx 2.4$ Hz), 2.97 (s, 3H, OCH_3), 2.98 (m, 1H, *exo*-4-H, $^4J_{2,exo\text{-}4} \approx 2.2$, $^3J_{3,exo\text{-}4} \approx 2.2$ Hz), 3.46 (m, 1H, *endo*-7-H, $^3J_{1,endo\text{-}7}$ = 6.0, $^3J_{endo\text{-}6,endo\text{-}7}$ = 9.6 Hz), 3.66 (m, 1H, 1-H, $^3J_{1,2}$ = 2.3, $^4J_{1,3} > 0$ Hz), 4.00 (d, 1H, *endo*-6-H), 5.97 (m, 1H, 3-H, $^3J_{2,3}$ = 6.1 Hz), 6.13 (m, 1H, 2-H), 6.9−7.4 (m, 10H, Ph). − ^{13}C NMR (50 MHz, $CDCl_3$): δ = 43.5 (t, C-4), 48.6 (d, C-1, -6, or -7), 51.0 (q, OCH_3), 52.7 (d, C-1, -6, or -7), 54.1 (d, C-1, -6, or -7), 85.7 (s, C-5), 125.8 (d, *p*-C), 125.9 (d, *p*-C), 128.0 (d, *m*- or *o*-C), 128.3 (d, *m*- or *o*-C), 128.4 (d, *m*- or *o*-C), 130.6 (d, *m*- or *o*-C), 131.8 (d, C-2 or -3), 134.1 (d, C-2 or -3), 137.7 (s, *i*-C), 140.8 (s, *i*-C). − GC-MS (70 eV), *m/z* (%): 276 (2) [M^+], 159 (11), 96 (100), 91 (14), 53 (9). − II (4.8%, 1.01) *1,1,2-Triphenylethane*, identified by a comparison of the mass spectrum with that of an authentical sample. − III (8.4%, 1.03) *5-Methoxy-6,7-diphenylbicyclo[3.2.0]hept-2-ene;* GC-MS (70 eV): Like fract. I (**12**). − IV (8.8%, 1.36) *1,6-Diphenylhexa-1,3,5-triene* (?); GC-MS (70 eV), *m/z*: 232 [M^+].

Treatment of exo-7-Chloro-endo-7-phenylbicyclo[3.2.0]hept-2-en-6-one (**5**) *with Dimethylamine*

a) In a 25-ml thick-walled screw-capped bottle 1.04 g (4.77 mmol) of **5**[12] is dissolved in 5 ml of dimethylamine. The bottle is immediately tightly closed and allowed to stand at 25°C for 14 h. Then ist is carefully opened, and excess dimethylamine is allowed to evaporate. The residue is taken up in 50 ml of diethyl ether and the resulting solution extracted with 50 ml of a saturated aqueous sodium hydrogencarbonate solution and then with 50 ml of water. The organic layer is subsequently extracted twice with 50 ml each of 2 N HCl, and the organic layer (layer A) is washed twice with 100 ml of water. Potassium hydroxide is added to the collected acidic layers until they are basic. They are extracted three times with 50 ml of diethyl ether each, and the collected organic layers (layer B) are washed twice with 50 ml of water each, and dried with $MgSO_4$. After removal of the solvent from the filtrate in a rotary evaporator under reduced pressure and drying of the residue at 0.001 mbar 0.53 g (2.33 mmol, 49%) of *5-(dimethylamino)-7-phenylbicyclo[3.2.0]hept-2-en-6-one* (**13/14**, *endo:exo* = 58:42) is obtained as a yellow-brown oil which soon becomes red on standing in the air. − IR (film): $\tilde{\nu}$ = 3057 cm^{-1} (m), 2784 (s, NMe_2), 1776 (s, C=O), 700 (s). − ^{1}H NMR (200 MHz, $CDCl_3$) of **13**: δ = 2.35 [s, 6H, $N(CH_3)_2$], 2.45−2.65 (m, 2H, *endo*-4-H, *exo*-4-H), 3.72 (m, 1H, 1-H, $^3J_{1,2}$ = 6.2, $^3J_{1,exo\text{-}7}$ = 10.1 Hz), 4.92 (d, 1H, *exo*-7-H), 5.40 (m, 1H, 2-H), 5.76 (m, 1H, 3-H), 6.9−7.3 (m, 5H, Ph); **14**: δ = 2.27 [s, 6H, $N(CH_3)_2$], 2.45−2.65 (m, 2H, *endo*-4-H, *exo*-4-H), 3.41 (m, 1H, 1-H, $^3J_{1,2}$ = 5.8, $^3J_{1,endo\text{-}7}$ = 5.3 Hz), 3.82 (d, 1H, *endo*-7-H), 5.80 (m, 1H, 3-H), 6.03 (m, 1H, 2-H), 6.9−7.3 (m, 5H, Ph). − ^{13}C NMR (50 MHz, $CDCl_3$) of **13**: δ = 30.2 (t, C-4, $^1J_{C,H}$ = 130.8 Hz), 40.3 [q, $N(CH_3)_2$, $^1J_{C,H}$ = 134.3 Hz], 46.9 (d, C-1, $^1J_{C,H}$ = 146.5 Hz), 66.3 (d, C-7, $^1J_{C,H}$ = 130.5 Hz), 90.6 (s, C-5), 126.8 (d, *p*-C, $^1J_{C,H}$ = 160.4 Hz), 127.9 (d, *o*- or *m*-C, $^1J_{C,H}$ = 159.6 Hz), 128.0 (d, *o*- or *m*-C, $^1J_{C,H}$ = 158.7 Hz), 129.7 (d, C-2, $^1J_{C,H} \approx 160$ Hz), 132.8 (d, C-3, $^1J_{C,H}$ = 165.2 Hz), 134.4 (s, *i*-C), 209.5 (s, C-6); **14**: δ = 32.6 (t, C-4, $^1J_{C,H}$ = 131.7 Hz), 39.4 [q, $N(CH_3)_2$, $^1J_{C,H}$ = 134.3 Hz], 47.5 (d, C-1, $^1J_{C,H}$ = 143.9 Hz), 68.2 (d, C-7, $^1J_{C,H}$ = 134.3 Hz), 89.9 (s, C-5), 126.6 (d, *p*-C, $^1J_{C,H} \approx 157$ Hz), 127.2 (d, *o*- or *m*-C, $^1J_{C,H}$ = 156.1 Hz), 128.4 (d, *o*- or *m*-C, $^1J_{C,H}$ = 160.4 Hz), 130.9 (d, C-3, $^1J_{C,H}$ = 164.3 Hz), 133.1 (d, C-2, $^1J_{C,H} \approx 165$ Hz), 136.2 (s, *i*-C), 208.8 (s, C-6); the signal assignment is based on a C,H COSY spectrum. − MS (70 eV), *m/z* (%): 200 (14), 199 (100), 198 (40), 155 (29), 154 (19), 122 (56), 109 (37), 108 (90), 94 (25). − $C_{15}H_{17}NO$ (227.3): calcd. C 78.56, H 8.35, N 6.12; found C 78.76, H 7.73, N 6.36.

Layer A is dried with $MgSO_4$. After removal of the solvent from the filtrate in a rotary evaporator under reduced pressure and drying of the residue at 0.001 mbar 0.27 g (1.02 mmol, 22%) of *cis-2-(α-chlorobenzyl)-N,N-dimethylcyclopent-3-ene-1-carboxamide* (**15**) is obtained as *one* diastereomer, which is recrystallized from diethyl

ether (colorless, hygroscopic needles, m.p. 94°C). – IR (KBr): $\tilde{\nu}$ = 1700 cm^{-1} (s, C=O), 776 (s), 712 (s), 678 (s). – ^1H NMR (400 MHz, $CDCl_3$): δ = 2.76 (m, 1H, α5-H, $^4J_{3,\alpha5} \approx 2.2$, $^3J_{4,\alpha5} \approx 2.2$, $^2J_{\alpha5,\beta5} = -17.3$, $^3J_{1,\alpha5} \approx 2.3$, $^4J_{2,\alpha5} \approx 2.3$ Hz), 3.17 (m, 1H, β5-H, $^4J_{3,\beta5} \approx 2.2$, $^3J_{4,\beta5} \approx 2.2$, $^4J_{2,\beta5} \approx 2.3$, $^3J_{1,\beta5} = 10.1$ Hz), 3.45 (s, 3H, NCH_3), 3.64 (s, 3H, NCH_3), 4.34 (m, 1H, 2-H, $^3J_{2,3} \approx 2.2$, $^4J_{2,4} \approx 2.2$, $^3J_{1,2} = 8.6$, $^3J_{2,9} = 7.5$ Hz), 5.04 (m, 1H, 3-H, $^3J_{3,4}$ = 5.8 Hz), 5.09 (m, 1H, 1-H, $^4J_{1,9} = 0.9$ Hz), 5.74 (m, 1H, 4-H), 6.61 (dd, 1H, 9-H), 7.21 (m, 2H, *o*-H), 7.2–7.4 (m, 3H, *m*-, *p*-H). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 37.0 (t, C-5, $^1J_{C,H} = 134.5$ Hz), 39.7 (q, NCH_3, $^1J_{C,H} = 143.6$ Hz), 41.5 (q, NCH_3, $^1J_{C,H} = 143.0$ Hz), 46.4 (d, C-2, $^1J_{C,H} = 144.8$ Hz), 53.1 (d, C-1, $^1J_{C,H} = 143.4$ Hz), 93.1 (d, C-7, $^1J_{C,H} = 158.0$ Hz), 125.4 (d, C-9 or -10, $^1J_{C,H}$ = 160.7 Hz), 127.5 (d, C-3, -4, or -11, $^1J_{C,H} = 167.7$ Hz), 128.0 (d, C-9 or -10, $^1J_{C,H} = 167.4$ Hz), 128.4 (d, C-3, -4, or -11, $^1J_{C,H}$ = 168 Hz), 130.3 (d, C-3, -4, or -11, $^1J_{C,H} = 166.0$ Hz), 133.2 (s, C-8), 182.8 (s, C-6). – MS (70 eV), *m/z* (%): 265 (4) [M^+ (^{37}Cl)], 263 (12) [M^+ (^{35}Cl)], 228 (15), 227 (10), 155 (33), 154 (19), 138 (22). – MS (NH_3-CI), *m/z* (%): 455 (7) [M_2^+ + H], 228 (100) [M^+ + H]. – $C_{15}H_{18}ClNO$ (263.8): calcd. C 68.30, H 6.88, Cl 13.44, N 5.31; found C 68.25, H 6.79, Cl 13.38, N 5.25.

b) 10.0 g (47.7 mmol) of **5**[12] is dissolved in 15 ml of dimethylamine in a thick-walled screw-capped flask, which is immediately tightly closed. The flask is allowed to stand at −20°C for 12 h, then at 4°C for 4 h. The contents become solid. The flask is carefully opened, and excess dimethylamine is allowed to evaporate. Workup performed as under a) furnishes 1.90 g (8.4 mmol, 18%) of **13/14** (*endo:exo* = 60:40) and 7.31 g (27.2 mmol, 58%) of **15**.

5-(Diethylamino)-7-phenylbicyclo[3.2.0]hept-2-en-6-one (**16/17**): A solution of 20.0 g (91.53 mmol) of **5**[12] in 200 ml of diethylamine in a 500-ml three-necked round-bottom flask equipped with a magnetic stirring bar and an argon inlet is stirred at 25°C for 17 h. The diethylamine is removed in a rotary evaporator under reduced pressure, and the residue is taken up in 200 ml of diethyl ether. The ethereal solution is washed twice with 200 ml of water each and then extracted with 2 N HCl until the aqueous layer remains colorless. The aqueous layers are collected, and sodium hydroxide is added until basicity. The mixture is extracted three times with 200 ml of diethyl ether each. The combined organic layers are washed with 200 ml of a saturated aqueous solution of sodium hydrogencarbonate and 200 ml of water, then dried with $MgSO_4$. The solvent is evaporated from the filtrate in a rotary evaporator under reduced pressure to afford a brown syrup which is dried at 0.001 mbar; yield 19.83 g (77.8 mmol, 85%) of **16/17** (*endo:exo* = 61:39). – IR (film): $\tilde{\nu}$ = 1774 cm^{-1} (s, C=O), 699 (s). – ^1H NMR (200 MHz, $CDCl_3$) of **16**: δ = 1.10 [t, 6H, $N(CH_2CH_3)_2$, ^3J = 7.1 Hz], 2.5–3.0 [m, 6H, $N(CH_2CH_3)_2$, *endo*-4-H, *exo*-4-H], 3.66 (m, 1H, 1-H, $^3J_{1,exo\text{-}7}$ = 10.1 Hz), 5.04 (d, 1H, *exo*-7-H), 5.41 (m, 1H, 2-H, $^3J_{2,3} = 6.3$, $^3J_{1,2} = 4.6$, $^4J_{2,endo\text{-}4} \approx {}^4J_{2,exo\text{-}4} \approx 2.2$ Hz), 5.80 (m, 1H, 3-H), 7.1–7.4 (m, 5H, Ph); **17**: δ = 1.05 [t, 6H, $N(CH_2CH_3)_2$, ^3J = 7.1 Hz], 2.5–3.0 [m, 6H, $N(CH_2CH_3)_2$, *endo*-4-H, *exo*-4-H], 3.38 (m, 1H, 1-H, $^3J_{1,endo\text{-}7}$ = 4.9 Hz), 3.81 (d, 1H, *endo*-7-H), 5.85 (m, 1H, 3-H, $^3J_{2,3}$ = 5.9 Hz), 6.02 (m, 1H, 2-H, $^3J_{1,2} = 4.7$, $^4J_{2,endo\text{-}4} \approx {}^4J_{2,exo\text{-}4} \approx 2.5$ Hz), 7.1–7.4 (m, 5H, Ph). – ^{13}C NMR (50 MHz, $CDCl_3$) of **16**: δ = 14.6 [q, $N(CH_2CH_3)_2$, $^1J_{C,H} = 125.6$ Hz], 32.5 [t, $N(CH_2CH_3)_2$, $^1J_{C,H} = 131.7$ Hz], 44.3 (t, C-4, $^1J_{C,H} = 136.9$ Hz), 48.1 (d, C-1, $^1J_{C,H} = 141.3$ Hz), 65.4 (d, C-7, $^1J_{C,H} = 132.5$ Hz), 90.7 (s, C-5), 126.4 (d, *p*-C, $^1J_{C,H} = 160.4$ Hz), 127.66 (d, *o*- or *m*-C, $^1J_{C,H} = 160.4$ Hz), 127.71 (d, *o*- or *m*-C, $^1J_{C,H} = 160.4$ Hz), 129.4 (d, C-2, $^1J_{C,H} = 158.0$ Hz), 132.7 (d, C-3, $^1J_{C,H} = 161.3$ Hz), 134.3 (s, *i*-C), 208.8 (s, C-6); **17**: δ = 14.4 [q, $N(CH_2CH_3)_2$, $^1J_{C,H} = 125.6$ Hz], 34.7 [t, $N(CH_2CH_3)_2$, $^1J_{C,H} = 131.6$ Hz], 43.8 (t, C-4, $^1J_{C,H} = 137.8$ Hz), 49.6 (d, C-1, $^1J_{C,H} = 141.3$ Hz), 68.4 (d, C-7, $^1J_{C,H} = 134.3$ Hz), 90.4 (s, C-5), 126.3 (d, *p*-C), 127.2 (d, *o*- or *m*-C, $^1J_{C,H} = 159.1$ Hz), 128.1 (d, *o*- or *m*-C, $^1J_{C,H} = 159.1$ Hz), 131.0 (d, C-3, $^1J_{C,H} \approx 166$ Hz), 133.0 (d, C-2, $^1J_{C,H} = 157.8$ Hz), 136.6 (s, *i*-C), 208.4 (s, C-6). – MS (70 eV), *m/z* (%): 228 (13), 227 (66), 226 (13), 212 (10), 198 (20), 155 (21), 150 (24), 137 (19), 136 (100), 128 (18), 105 (36), 100 (25), 94 (14), 91 (22). – MS (NH_3-CI), *m/z* (%): 256 (38) [M + H^+], 192 (16), 178 (8), 138 (6), 91 (8), 75 (6), 74 (100) [$H_2N(C_2H_5)_2$], 72 (6). – $C_{17}H_{21}NO$ (255.4): calcd. C 79.96, H 8.29, N 5.49; found C 79.91, H 8.21, N 5.54.

5-(Diisopropylamino)-7-phenylbicyclo[3.2.0]hept-2-en-6-one (**18/19**): A solution of 1020 mg (4.7 mmol) of **5**[12] in 10 ml of diisopropylamine in a 50-ml two-necked round-bottom flask equipped with an argon inlet and a magnetic stirring bar is stirred at 25°C for 11 d. The diisopropylamine is removed in a rotary evaporator under reduced pressure, and the residue is taken up in 50 ml of diethyl ether. The ethereal solution is washed twice with 50 ml of water each and then extracted with 2 N HCl until the aqueous layer remains colorless. The organic layer is dried with $MgSO_4$. After removal of the solvent in a rotary evaporator under reduced pressure 510 mg (2.33 mmol, 50%) of **5** is obtained. The combined aqueous layers are treated with sodium hydroxide until basicity and then extracted three times with diethyl ether. The combined organic layers are washed with 50 ml of a saturated aqueous solution of sodium hydrogen carbonate, then with 50 ml of water, and dried with $MgSO_4$. After removal of the solvent from the filtrate in a rotary evaporator under reduced pressure and drying of the resulting brown syrup at 0.001 mbar 500 mg (1.77 mmol, 75% relative to consumed **5**) of **18/19** (*endo:exo* = 90:10) is obtained. An analytical sample is purified by column chromatography (silica gel, 50 × 2 cm, pentane/diethyl ether, 6:1) and obtained as a bright yellow oil. – IR (film): $\tilde{\nu}$ = 1772 cm^{-1} (s, C=O), 699 (s, =CH, Ph). – ^1H NMR (200 MHz, $CDCl_3$) of **18**: δ = 1.02 {d, 6H, $N[CH(CH_3)_2]$, ^3J = 6.9 Hz}, 1.09 {d, 6H, $N[CH(CH_3)_2]$, ^3J = 6.9 Hz}, 2.13 (md, 1H, *endo*-4-H or *exo*-4-H, $^2J_{endo\text{-}4,exo\text{-}4} = -17.4$ Hz), 2.68 (md, 1H, *endo*-4-H or *exo*-4-H), 3.15 {sept., 2H, $N[CH(CH_3)_2]$}, 3.63 (dm, 1H, 1-H, $^3J_{1,7} = 10.3$, $^3J_{1,2} = 4.4$ Hz), 5.10 (d, 1H, 7-H), 5.35 (m, 1H, 2-H, $^3J_{2,3} = 6.4$, $^4J_{2,endo\text{-}4} \approx {}^4J_{2,exo\text{-}4} \approx 2.2$ Hz), 5.75 (m, 1H, 3-H, $^3J_{3,4} = 3.9, 4.7$ Hz), 7.0–7.2 (m, 5H, Ph); **19**: Signals partially obscured by overlap. – ^{13}C NMR (50 MHz, $CDCl_3$) of **18**: δ = 22.2 {q, $N[CH(CH_3)_2]$, $^1J_{C,H} = 124.7$ Hz}, 23.7 {q, $N[CH(CH_3)_2]$, $^1J_{C,H} = 124.7$ Hz}, 37.1 (t, C-4, $^1J_{C,H} = 137.8$ Hz), 47.4 {d, $N[CH(CH_3)_2]$, $^1J_{C,H} = 124.7$ Hz}, 48.9 (d, C-1, $^1J_{C,H} = 148.2$ Hz), 65.6 (d, C-7, $^1J_{C,H} = 130.8$ Hz), 89.4 (s, C-5), 126.8 (d, *p*-C, $^1J_{C,H} = 160.4$ Hz), 128.3 (d, *o*-,*m*-C, $^1J_{C,H}$ = 159.7, 158.7 Hz), 129.0 (d, C-2, $^1J_{C,H} = 165.7$ Hz), 134.2 (d, C-3, $^1J_{C,H} = 166.6$ Hz), 134.7 (s, *i*-C), 207.6 (s, C-6); **19**: Signals partially obscured by overlap. – MS (70 eV), *m/z* (%): 283 (1.3) [M^+], 256 (15), 255 (79), 240 (25), 213 (15), 212 (72), 170 (24), 165 (21), 164 (100), 155 (51), 143 (26), 129 (16), 128 (25), 122 (43), 108 (25), 91 (23), 80 (27), 65 (15), 58 (40), 43 (34). – $C_{19}H_{25}NO$ (183.4): calcd. C 80.52, H 8.89, N 4.94; found C 80.49, H 8.87, N 4.99.

5-(Diethylamino)-7-phenylbicyclo[3.2.0]hept-2-en-6-one Hydrochloride (**20/21**): A solution of 3.22 g (12.63 mmol) of **16/17** in 100 ml of diethyl ether is extracted with 2 N HCl until the aqueous layer remains colorless. The combined aqueous layers are washed twice with 100 ml of diethyl ether, and the layers are separated. The water and excess HCl are removed at 0.1 mbar without heating, and the residue is dried for 3 d at 0.001 mbar to furnish 3.61 g (12.38 mmol, 98%) of **20/21** (*endo:exo* = 83:17) as orange crystals (melting interval 55–62°C). – IR (KBr): $\tilde{\nu}$ = 3426 cm^{-1} (m, H_2O), 2578 (s), 2431 (s), 1781 (s, C=O), 702 (s). – ^1H NMR (200 MHz, $CDCl_3$) of **20**: δ = 1.5 (m, 6H, CH_3), 2.8–3.8 (m, 6H, *endo*-4-H, *exo*-4-H, NCH_2), 4.43 (d, 1H, 1-H, $^3J_{1,exo\text{-}7}$ = 10.7 Hz),

5.42 (d, 1H, 2-H, $^3J_{2,3}$ = 6.0 Hz), 5.80 (d, 1H, 3-H), 6.14 (d, 1H, *exo*-7-H), 7.0–7.5 (m, 5H, Ph), 12.52 (br. s, 1H, NH); **21**: δ = 1.5 (m, 6H, CH_3), 2.8–3.8 (m, *endo*-4-H, *exo*-4-H, NCH_2), 4.07 (d, 1H, *endo*-7-H, $^3J_{1,endo\text{-}7}$ = 7.2 Hz), 4.23 (d, 1H, 1-H), 6.00 (d, 1H, 3-H, $^3J_{2,3}$ = 5.5 Hz), 6.26 (d, 1H, 2-H), 7.0–7.5 (m, 5H, Ph), 12.30 (br. s, 1H, NH). – ^{13}C NMR (50 MHz, $CDCl_3$) of **20**: δ = 9.7 (q, NCH_2CH_3), 10.5 (q, NCH_2CH_3), 34.1 (t, C-4), 46.0 (t, NCH_2CH_3), 47.9 (t, NCH_2CH_3), 48.7 (d, C-1), 67.6 (d, C-7), 86.7 (s, C-5), 126.7 (d, *p*-C), 127.1 (d, *o*- or *m*-C), 127.7 (d, *o*- or *m*-C), 128.8 (d, C-2 or -3), 131.0 (d, C-2 or -3), 132.2 (s, *i*-C), 203.0 (s, C-6); **21**: Signals only incompletely visible. – $C_{17}H_{22}ClNO$ (291.8): calcd. C 69.97, H 7.60, Cl 12.15, N 4.80; found C 68.41, H 7.43, Cl 12.21, N 4.89.

Attempted Quaternization of **16/17** *Followed by Acetal Formation:* A solution of 1.0 g (3.9 mmol) of **16/17** in 10 ml of benzene is flushed with hydrogen chloride for 30 min. Then 0.46 g (7.4 mmol) of 1,2-ethanediol and 0.60 g (3.5 mmol) of *p*-toluenesulfonic acid are added. The mixture is heated at reflux in a water separation apparatus for 24 h. The solvent is condensed into a cold trap, and the residue is taken up in 100 ml of diethyl ether. The ethereal solution is washed with a saturated aqueous solution of sodium hydrogen carbonate and twice with 100 ml of water each. After drying with $MgSO_4$ and removal of the solvent from the filtrate in a rotary evaporator under reduced pressure an oil is obtained which is dried at 0.001 mbar. 650 mg (3.6 mmol, 92%) of *2-phenyltropone* (**22**) is crystallized from hexane (m.p. 82°C, ref.[24] 83–84°C), identified by a comparison of the IR spectrum with that reported in ref.[24]

Thermolysis of **20/21** *in the Presence of p-Toluenesulfonic Acid in Toluene:* 300 mg (1.03 mmol) of **20/21** and 200 mg (1.16 mmol) of *p*-toluenesulfonic acid in 25 ml of toluene are heated at reflux for 24 h. The mixture is washed twice with 50 ml of a saturated aqueous solution of sodium hydrogen carbonate each and with 50 ml of water, filtered, and dried with $MgSO_4$. After removal of the solvent from the filtrate in a rotary evaporator at reduced pressure 150 mg [purity 90% (NMR), 0.74 mmol, 72%] of **22** is obtained. The product is identified by a comparison of the ^{1}H- and ^{13}C-NMR spectra with those of an authentic sample.

5-(Diethylamino)-exo-7-methyl-endo-7-phenylbicyclo[3.2.0]-hept-2-en-6-one (**24**): In a flame-dried 250-ml Schlenk flash equipped with a magnetic stirring bar 5.5 ml (39 mmol) of diisopropylamine is added dropwise at 0°C to 20 ml of a 1.5 M solution of butyllithium in hexane. The mixture is stirred for 15 min at 0°C and then for another 15 min at 25°C. Then the hexane and excess diisopropylamine are evaporated into a cold trap at 0.1 mbar. The solid, colorless residue (lithium diisopropylamide[25]) is dried for 30 min at 45°C/0.001 mbar. Then at −78°C 100 ml of THF is slowly added followed by dropwise addition of a solution of 5.66 g (22.2 mmol) of **16/17**. The mixture is stirred at −78°C for 1 h and then at −25°C for 1 h. Subsequently, at −78°C 19 ml (160.6 mmol) of iodomethane is added during 5 min to the mixture which is allowed to warm to room temp. over a period of 14 h. The solvent and excess iodomethane are removed into a cold trap at 0.1 mbar. The residue is taken up in 100 ml of diethyl ether, and the solution obtained is extracted three times with 100 ml of water each. The organic layer is extracted with 2 N HCl until aqueous layer remains colorless. The organic layer is discarded, and potassium hydroxide is carefully added to the combined aqueous layers until basicity. Then these layers are extracted four times with 100 ml of diethyl ether each, and the combined organic layers are dried with $MgSO_4$. The solvent is removed from the filtrate in a rotary evaporator under reduced pressure, and the remaining brown syrup is dried at 0.001 mbar to furnish 4.09 g (15.2 mmol, 68%) of **24**. 2.5 g is further purified by column chromatography on silica gel (50 × 2 cm, pentane/diethyl ether, 50:1) to afford 1.9 g of **24** as a bright yellow oil. – IR (film): $\tilde{\nu}$ = 3058 cm^{-1} (m), 1772 (s, C=O), 702 (s, Ph). – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.09 (t, 6H, CH_2CH_3, $^3J_{9',10}$ = 7.1, $^3J_{9,10}$ = 7.3 Hz), 1.85 (s, 3H, 7-CH_3), 2.43 (m, 2H, *endo*-4-H, *exo*-4-H, $^4J_{2,endo\text{-}4} \approx 2.4$, $^4J_{2,exo\text{-}4} \approx 2.4$, $^3J_{3,endo\text{-}4}$ = 2.3, $^3J_{3,exo\text{-}4}$ = 2.3 Hz), 2.59 (m, 2H, 9'-H, $^2J_{9,9'}$ = −13.3 Hz), 2.76 (m, 2H, 9-H), 3.08 (m, 1H, 1-H, $^3J_{1,2}$ = 2.4, $^4J_{1,3}$ = 1.2 Hz), 5.44 (m, 1H, 2-H, $^3J_{2,3}$ = 6.1 Hz), 5.60 (m, 1H, 3-H), 7.0–7.4 (m, 5H, Ph). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 15.1 (q, NCH_2CH_3, $^1J_{C,H}$ = 125.6 Hz), 27.3 (q, 7-CH_3, $^1J_{C,H}$ = 129.9 Hz), 32.6 (t, C-4, $^1J_{C,H}$ = 131.7 Hz), 44.7 (t, NCH_2CH_3, $^1J_{C,H}$ = 131.7 Hz), 55.0 (d, C-1, $^1J_{C,H}$ = 144.7 Hz), 68.4 (s, C-7), 88.5 (s, C-5), 126.1 (d, C-10, $^1J_{C,H}$ = 157.8 Hz), 126.1 (d, C-12, $^1J_{C,H} \approx$ 158 Hz), 128.0 (d, C-11, $^1J_{C,H}$ = 159.6 Hz), 131.1 (d, C-3, $^1J_{C,H}$ = 164.8 Hz), 132.2 (d, C-2, $^1J_{C,H}$ = 163.9 Hz), 141.2 (s, C-9), 213.1 (s, C-6). – MS (70 eV), *m/z* (%): 242 (8), 241 (38), 226 (100), 164 (26), 136 (70). – $C_{18}H_{23}NO$ (269.4): calcd. C 80.26, H 8.61, N 5.20; found C 80.36, H 8.73, N 5.34.

Thermolysis of **24**: 420 mg (1.56 mmol) of **24** is thermolyzed in a kugelrohr apparatus under argon under atmospheric pressure at 170°C for 5 h. Then the product is distilled at 170°C/0.001 into the first bulb during 4 h and then into the second bulb over 3 h. In this way 280 mg (1.04 mmol, 67%) of *2-(diethylamino)-7-methyl-7-phenylcyclohepta-2,4-dien-1-one* (**25**) is obtained as a dark red-yellow oil. – IR (film): $\tilde{\nu}$ = 1566 cm^{-1} (s, C=O), 700 (s). – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.89 [t, 6H, $N(CH_2CH_3)_2$, ^3J = 7.1 Hz], 1.50 (s, 3H, 7-CH_3), 2.46 (dd, 1H, 6b-H, $^2J_{6a,6b}$ = −14.5, $^3J_{5,6b}$ = 6.2 Hz), 2.80 [q, 4H, $N(CH_2CH_3)_2$], 3.16 (dd, 1H, 6a-H, $^3J_{5,6a}$ = 6.2, $^4J_{4,6a}$ = 1.2 Hz), 4.89 (d, 3-H, $^3J_{3,4}$ = 6.4 Hz), 5.73 (dt, 1H, 5-H, $^3J_{4,5}$ = 10.6 Hz), 5.98 (ddd, 1H, 4-H), 7.1–7.4 (m, 5H, Ph). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 12.0 [q, $N(CH_2CH_3)_2$, $^1J_{C,H}$ = 126.4 Hz], 23.8 (q, 7-CH_3, $^1J_{C,H}$ = 129.1 Hz), 36.4 (t, C-6, $^1J_{C,H}$ = 127.7 Hz), 43.6 [t, $N(CH_2CH_3)_2$, $^1J_{C,H}$ = 135.2 Hz], 62.7 (s, C-7), 99.9 (d, C-3, $^1J_{C,H}$ = 154.3 Hz), 123.4 (d, C-4, -5, or -12, $^1J_{C,H}$ = 156.9 Hz), 126.7 (d, C-10 or -11, $^1J_{C,H}$ = 157.8 Hz), 126.8 (d, C-4, -5, or -12, $^1J_{C,H}$ = 157.8 Hz), 127.6 (d, C-4, -5, or -12, $^1J_{C,H}$ = 166.5 Hz), 128.1 (d, C-10 or -11, $^1J_{C,H}$ = 160.4 Hz), 141.5 (s, C-9), 150.6 (s, C-2), 204.9 (s, C-1). – MS (70 eV), *m/z* (%): 269 (100) [M^+], 254 (42), 240 (29), 226 (38), 151 (60), 136 (61), 108 (32), 94 (19), 80 (41), 53 (24). – $C_{18}H_{23}NO$ (269.4): calcd. C 80.26, H 8.61, N 5.20; found C 80.19, H 8.71, N 5.25.

Quaternization of **24** *with Iodomethane:* A solution of 780 mg (2.9 mmol) of **24** in 5 ml (11.4 g, 80.3 mmol) of iodomethane is heated at reflux for 16 h. After cooling to room temp. (25°C) excess iodomethane is evaporated at 0.1 mbar and condensed in a cold trap. 1200 mg (2.9 mmol, 100%) of *diethylmethyl(exo-7-methyl-6-oxo-endo-7-phenylbicyclo[3.2.0]hept-2-en-5-yl)ammonium iodide* is obtained as a pink powder (dec. at 165°C). – IR (KBr): $\tilde{\nu}$ = 1779 cm^{-1} (s, C=O), 1447 (s), 1006 (s), 764 (s), 707 (s), 670 (s). – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.51 (2 t, 6H, CH_2CH_3, $^3J_{9,10} \approx$ 7.2, $^3J_{11,12} \approx$ 7.2 Hz), 1.81 (s, 3H, 7-CH_3), 2.75 (m, 1H, *exo*-4-H, $^4J_{2,exo\text{-}4}$ = 2.8, $^3J_{3,exo\text{-}4}$ = 2.0, $J_{1,exo\text{-}4}$ = 1.0 Hz), 3.36 (s, 3H, NCH_3), 3.62 (m, 1H, *endo*-4-H, $^4J_{2,endo\text{-}4} > 0$, $^3J_{3,endo\text{-}4}$ = 2.2 Hz), 3.8–4.3 (*m*, 4H, 9-, 9'-, 11-, 11'-H), 4.80 (*m*, 1H, 1-H, $^4J_{1,3} > 0$, $^3J_{1,2}$ = 3.0 Hz), 5.65 (m, 1H, 3-H, $^3J_{2,3}$ = 5.8 Hz), 5.86 (m, 1H, 2-H), 7.01 (m, 2H, *o*-H?), 7.2 (m, 3H, *m*-, *p*-H). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 9.7 + 10.1 (2 q, NCH_2CH_3), 25.7 (q, 7-CH_3), 37.8 (t, C-4), 45.9 (q, NCH_3), 55.5 (d, C-1), 55.8 (t, NCH_2CH_3), 56.1 (t, NCH_2CH_3), 68.1 (s, C-7), 94.4 (s, C-5), 125.9 (d, *o*- or *m*-C), 127.3 (d, *p*-C), 128.5 (d, *o*- or *m*-C), 130.8 (d, C-2 or -3), 132.1 (d, C-2 or -3), 138.3 (s, *i*-C), 204.6 (s, C-6). – MS (glycerine-FAB),

m/z (pos. ion, %) = 538.3 (62) [(M + I)$^+$]; *m/z* (neg. ion, %) = 284.2 (64) [(M − I)$^-$]. − $C_{19}H_{26}INO$ (411.3): calcd. C 55.48, H 6.37, I 30.85, N 3.41; found C 55.89, H 6.38, I 31.22, N 3.42.

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[212/93]