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THE SYNTHESIS AND BASE INDUCED HOMOKETONIZATION OF 5-SUBSTITUTED HOMOCUNEYL 4-ACETATES

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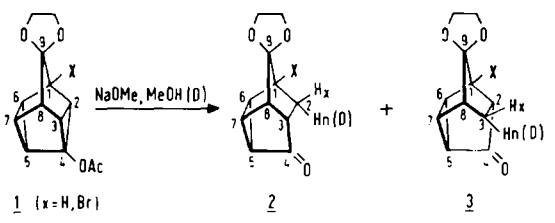
Abstract—The synthesis of two 5-substituted homocuneyl 4-acetates *viz* 4 - acetoxy - 5 - carbomethoxypentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane (**8**) and 4 - acetoxy - 5 - benzoylpentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane (**9**) is described starting from dicarboxylic acid (**10**). The base induced cage opening of these acetates has been studied. It was found for **9** that the regiochemistry of this process is not affected by the carbonyl containing functionality at C_5. Exclusive opening of the cyclopropanol ring is observed.

Bridgehead substituted homocuneyl acetates **1** are reactive structures which both under basic and acidic conditions give rise to a stereospecific cyclopropanol ring opening leading to half cage ketones **2** and **3** (Scheme 1).[1] As reported earlier, the stereochemical course of the homoketonization in these highly strained molecules is exclusively retention of configuration at the carbon of substitution. Under basic conditions homoketonization of **1** (X = Br) produces ketones **2** and **3** in a 4 : 1 ratio, whereas under acidic conditions **2** and **3** are obtained in a ratio of about 1 : 1. These experimental results clearly demonstrate that in homocuneyl acetate **1** these cyclopropanol ring opening reactions proceed through different mechanisms. The base-induced homoketonization goes through a carbanion type intermediate followed by rapid protonation (SE_i-type process)[2]. The observed preference of the C_4–C_2 bond cleavage can be attributed to the more pronounced carbanion-stabilizing effect of the electron-withdrawing 1-bromo substituent on C_2 as compared with C_3.

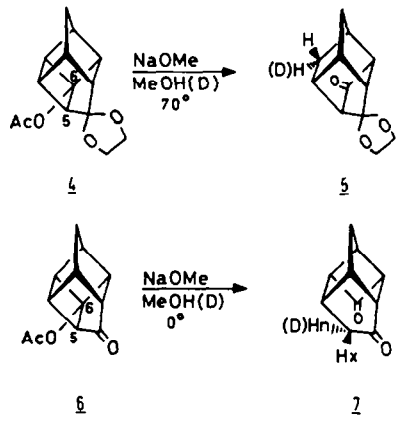
The acid initiated cage opening involves probably initial sigma protonation of the cyclopropane ring and subsequent C–C cleavage[3]. Apparently, the 1-bromo substituent hardly affects the regiochemistry of this SE_2-type process.

The observation that the regiochemistry of the base-induced homoketonization in strained polycyclic alcohols is influenced by electronic features, gave us reasons to investigate the directive effect of carbonyl containing substituents, present at the position β to the bridgehead alcohol function, on the cage opening process. We were particularly interested to learn whether a conjugative stabilization of one of the possible carbanionic intermediates would be sufficient to overrule the thermodynamic factors that in non-β-functionalized cage alcohols control the cage opening. These thermodynamic factors are determined by the relative strain energies of the conceivable cage opened products.[4]



1 (x=H,Br) 2 3

Scheme 1.



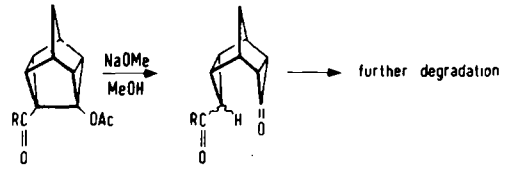
4 5 6 7

Scheme 2.

Recently, we showed that in the 1,3-bishomocubane cage system this directive effect indeed can be demonstrated.[5] While ketal acetate **4** yields exclusively the thermodynamically controlled homoketonization product **5**, cage fisssion of the β-keto-substituted analogue **6** leads regiospecifically to **7** by scission of the central C_5–C_6 bond (Scheme 2).

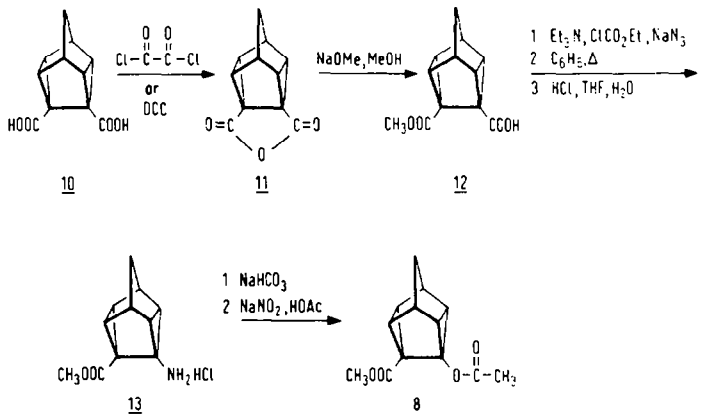
In analogy, cleavage of the central C_4–C_5 bond in the homocuneane cage system may be anticipated when a β-ketofunction is being introduced at C_5. This would then lead to a highly strained tetracyclonanone system still containing two cyclopropane rings (Scheme 3). Under the nucleophilic conditions used, this cyclopropanone derivative will certainly undergo further degradation with the concomitant relief of strain energy.

It is quite clear that the homocuneane structure represents a more subtile case than the aforementioned bishomocubane system as here strain features particularly disfavor fission of the C_4–C_5 central bond (cyclopropanol vs cyclopentanol ring opening). This



8 R=OCH$_3$
9 R=C$_6$H$_5$

Scheme 3.



Scheme 4.

paper deals with the synthesis of such β-keto-functionalized homocuneyl-4-acetates **8** and **9** and their base-induced homoketonization.

The homocuneane cage system is readily accessible from homocubane by the Ag(I)-catalyzed cage transformation reaction.[6] The synthesis of homocuneyl acetate **1** has been realized using this method[1]. Although a variety of monosubstituted 4-homocubane derivatives are easily prepared, no convenient routes to 4,5-disubstituted homocubanes are available. Hence, this approach for the synthesis of 4,5-disubstituted homocuneane derivatives cannot be used.

Alternative routes to acetates **8** and **9** are depicted in the Schemes 4 and 5, respectively. The synthesis starts off with 4,5-homocuneane dicarboxylic acid **10** which is prepared from norbornadiene and dimethyl acetylene dicarboxylate according to the method of Wenkert *et al.*[7] The anhydride **11** was obtained in quantitative yield using either oxalylic chloride or N,N'-dicyclohexylcarbodimide as the dehydrating agent. Half ester **12** could be prepared from **11** in 80% yield by carefully monotoring the basic methanolysis reaction. Transformation of half ester **12** into amine hydrochloride **13** was achieved by conversion of **12** into the corresponding carbonylazide and subsequent Curtius rearrangement (yield: 69%). Deamination of **13** with $NaNO_2$ in AcOH gave a complex mixture of at least seven products (GLC) among which the desired acetate **8** was present in 10% yield only. Doubling of the yield could be achieved by applying the free amine of **13** in this diazotation reaction. The isolation of acetate **8** from the mixture using TLC met with difficulties as the acetate decomposes rapidly on silica gel. Despite extensive experimentation, **8** could not be obtained in an analytically pure state. However, according to the spectral data and a GLC analysis, this acetate **8** was pure enough (~95%) for further experimentation.

The benzoyl carboxylic acid **14** was obtained in 70% yield by treatment of anhydride **11** with diphenyl cadmium (Scheme 5). In a similar way as described for the synthesis of amine **13**, carboxylic acid **14** was converted into amine **15** in an overall yield of 35%.

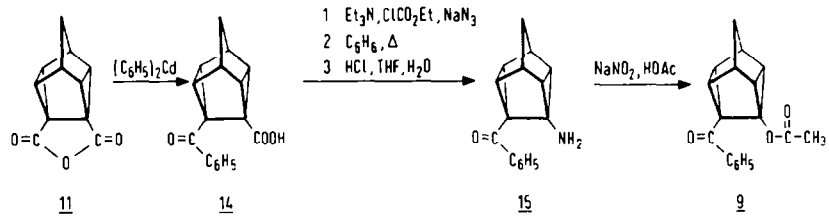
The rather low overall yield is mainly due to the poor formation of the carbonylazide from **14** applying the mixed anhydride method. Besides the azide only starting carboxylic acid **14** was isolated. Molecular models suggest that nucleophilic attack of the azide anion according to route *a* in **16** leading to the desired azide, is severely hindered by the benzoyl function at C_5.

Consequently, the alternative carbonyl attack, route *b*, producing starting material **14**, is favored. Efforts to supress this undesired pathway by using the pivaloic derived anhydride **17**, failed.

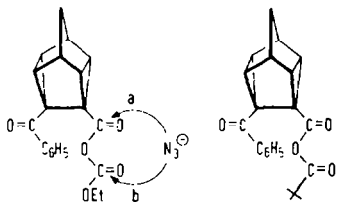
The deamination of benzoyl amine **15** in AcOH proceeded without problems affording acetate **9** as a single compound in almost quantitative yield. An analytically pure product could readily be obtained by sublimation.

The homoketonization experiments with acetates **8** and **9** were performed by treating them with NaOMe in MeOH at room temperature. Acetate **8** gave, after stirring for 5 hr and subsequent work-up, a yellow oil which, as shown by GLC, constituted of a mixture of four products. Unfortunately, due to the instability of the products, separation of this mixture by chromatographic methods could not be accomplished. From a spectral analysis it was concluded that starting material was no longer present and that probably cage-opening had taken place in view of the occurrence of a strong carbonyl absorption at 1730 cm^{-1} in the IR spectrum (*cf* spectrum of **18**, *vide infra*).

The benzoyl acetate **9** reacted rapidly to afford a single crystalline product in 76% yield. An analytically pure sample could readily be obtained by TLC on silica, m.p. 126–128°. Based on the spectral and analytical data half cage structure **18** was assigned to this product. The IR spectrum exhibits phenyl and cyclopropane absorp-



Scheme 5.



16 17

tions at 3080, 3060 and 3030 cm^{-1}, CO absorptions at 1730 (cyclopentanone) and 1670 (COC_6H_5) cm^{-1}, and aromatic C=C absorptions at 1595 and 1575 cm^{-1}. The ^{1}H NMR spectrum of **18** in $CDCl_3$ (Fig. 1) displays a rather complicated resonance pattern which, however, could be completely resolved by applying NMR-shift reagents combined with spin-spin decoupling techniques. The aromatic phenyl protons at *a*, *b* and *c* appear as multiplets at δ 7.91 and δ 7.51 ppm, respectively. A doublet (one half of an AB pattern) is observed at δ 1.64 ($J \sim 9$ Hz). Irradiation at this doublet caused the doublet at δ 2.11 ($J \sim 9$ Hz) to collapse to a singlet. Based on this decoupling experiment and the very small shift gradients which were observed when Eu(fod)$_3$ was added (*vide infra*), these doublets were ascribed to the C_9-methylene protons. Upon the addition of the downfield shift reagent Eu(fod)$_3$ as many as six protons were strongly affected, indicating that the lanthanide reagent complexes at both carbonyl centers. The aromatic two proton-absorption at δ 7.91, the doublet of doublet (1 H) at δ 3.31, the multiplet (2 H) at δ 2.58 and a doublet that emerged from the complex multiplet at δ 1.98 ppm showed all large shift gradients. These resonances were attributed to the aromatic ortho protons *a*, and the cage protons H_7, H_6, H_3 and H_n as these protons are spatially close to the complexing carbonyl groups. Unequivocal assignment of all signals was accomplished with the aid of spin-spin decoupling experiments of the complexed compound **18** as shown in Fig. 2. Irradiation at the doublet assigned to H_n led only to simplification of the multiplet at δ 2.48 thus establishing the position of H_x. Irradiation at this latter position (2 H) caused the doublet for H_n at δ 3.15 to collapse to a singlet while the doublet at δ 2.04 changed into a singlet and the major coupling in the absorption at δ 4.02 ppm disappeared. As the doublet at δ 2.04 had already been assigned to one of the C_9-methylene protons, this experiment revealed the position of the second C_9-methylene proton, which coincides with H_x, and that of proton H_3 ($J_{H_x H_3} \sim 8$ Hz). The multiplet at δ 3.58 was attributed to H_8. Irradiation of this absorption which exhibited only a small downfield shift gradient, caused the signal for H_3 at δ 4.02 to change into a doublet and the doublet of doublets at δ 5.13 to collapse to a doublet. Consequently, this latter absorption must be attributed to proton H_7. Based on its large shift gradient ($\Delta\delta$ 1.75) and coupling with H_7, the multiplet at δ 4.33 was assigned to H_6. Finally, proton H_1 is observed at δ 3.33 ppm. Careful analysis of the reaction mixture excluded the presence of any products which would be indicative of scission of the central C_4–C_5 bond in **9**.

We studied also the stereochemistry of the homoketonization of **9**. This cyclopropanol ring-opening proceeded with complete *retention* of configuration. Upon treatment with NaOMe in MeOH exclusive formation of *endo*-mono-deuterated ketone **18** was observed (Experimental).

In conclusion, the base induced homoketonization of homocuneyl-4-acetates appears not to be affected by a carbanion stabilizing substituent such as a benzoyl group. Apparently, the decrease in activation energy for C_4–C_5 fission which would be the ultimate result of stabilization of a C_5–carbanionic species is not sufficient to compete with the thermodynamic control which

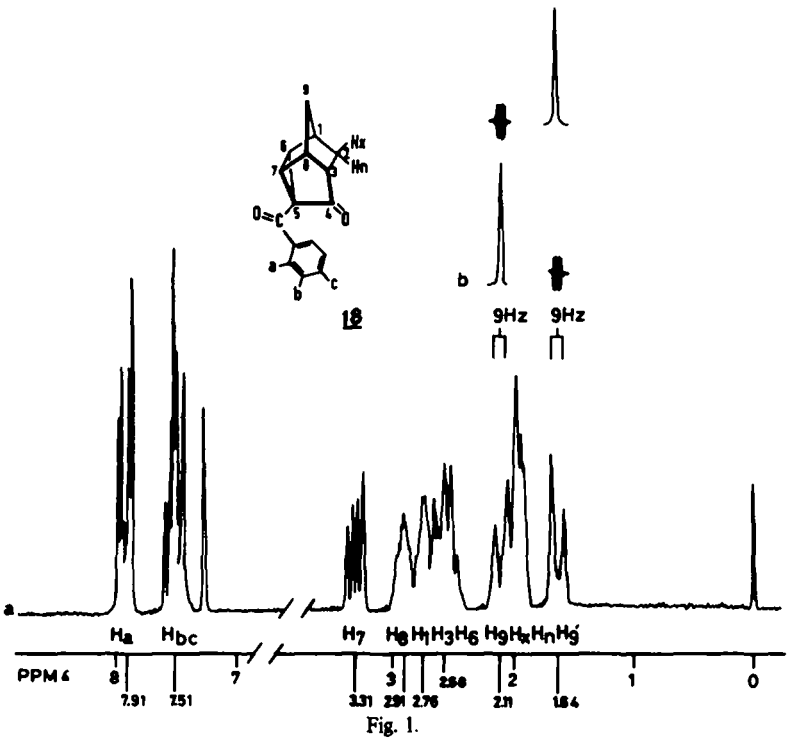


Fig. 1.

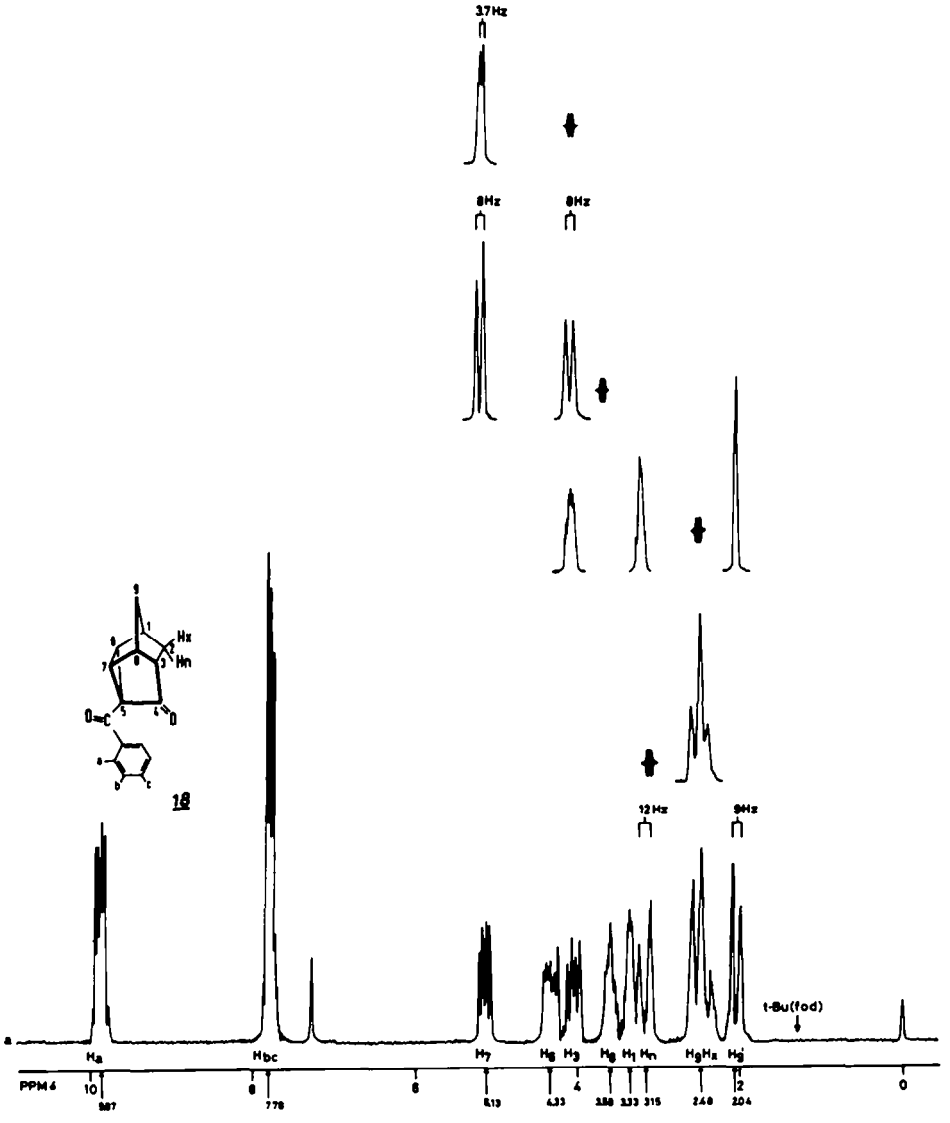


Fig. 2.

evidently is in favor of the cyclopropanol ring opening. Possibly, the anticipated conjugative stabilization of such a cyclopropyl carbanion is not very efficient due to I-strain.[8] In the bishomocubane system, however, such strain effects hardly play a role and cage opening is governed by the β-CO function.

It should be emphasized that this cage opening of benzoyl acetate **9** represents the first example of a base induced ketonization reaction of a β-hydroxyketone in which the regiochemistry of C–C bond cleavage is *not* directed by the CO function. This result is an illustration of a diversion of a normal reaction pattern through cage strain.

EXPERIMENTAL

IR spectra were taken on a Perkin–Elmer 257 grating spectrometer. NMR spectra were recorded on a Varian HA-100, Varian EM-390 or Bruker WH-90, using TMS as internal standard. Mass spectra were recorded on a Varian SM-1B spectrometer. All m.ps are uncorrected. Elemental analyses were carried out in the micro analytical department of the University of Nijmegen.

Pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]*nonane* 4,5 - *dicarboxylic acid* (**10**) was prepared in 39% yield as described by Wenkert *et al.*[7], m.p. 231–233° decomp (lit[7]: 245–249°).

Pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]*nonane* 4,5-*dicarboxylic anhydride* (**11**). (a) To a suspension of **10** (5.0 g, 24.3 mmole) in benzene (50 ml) was added dropwise a soln of oxalylic chloride (7.5 g, 59.1 mmole) in benzene (10 ml). After refluxing for 3 hr, water was added, the benzene layer separated, washed with 5% $NaHCO_3$ aq and water, and finally treated with charcoal. After drying ($MgSO_4$), solvent was removed to give anhydride **11** as a yellow oil which slowly crystallized (4.5 g, 98%). Recrystallization from cyclohexane gave an analytically pure sample, m.p. 106.5–107.5° (lit. 104–106°[7]).

(b) Treatment of **10** (1.0 g, 4.85 mmole) with N,N'-dicyclohexylcarbodiimide (DCC) (0.98 g, 4.76 mmole) in THF (25 ml) gave **11** in quantitative yield. After stirring the mixture for 1 hr, DCU was filtered off, the filtrate washed with 5% $NaHCO_3$ aq and water. After drying ($MgSO_4$), the solvent was removed to afford the pure anhydride.

IR ν_{max}^{KBr} 3060 (cyclopropyl C–H), 1840, 1780 (C=O) cm^{-1}; NMR ($CDCl_3$) δ 3.10 (s, 6H), 1.84 (s, 2H, H_9H_9); *m/e* 188 (M^+). (Found: C, 70.01; H, 4.30. Calc. For $C_{11}H_8O_3$: C, 70.21; H, 4.29%.)

5 - *Carbomethoxypentacyclo*[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]*nonane* 4 - *carboxylic acid* (12)

A catalytic amount of NaOMe was added to a stirred soln of **11** (1.5 g, 8.0 mmole) in MeOH (50 ml). After stirring at room temp for 2 hr, water was added and the mixture extracted with $CHCl_3$. The organic layer was dried ($MgSO_4$) and the solvent evaporated to give halfester **12** as a crystalline material (1.4 g, 80%), m.p. 85–86°.

IR ν_{max}^{KBr} (cyclopropyl C–H), 2600–2800 (OH···O=C), 1720 (C=O, ester), 1645 (C=O, acid) cm^{-1}; NMR ($CDCl_3$) δ 12.78 (broad s, 1 H, OH), 3.70 (s, 3 H, CO_2CH_3), 2.84–3.04 (m, 4 H, $H_2H_3H_6H_7$), 2.70–2.84 (m, 2 H, H_1H_8), 1.96 (s, 2 H, H_9H_9); *m/e* 220 (M^+). (Found: C, 65.51; H, 5.52. Calc. for $C_{12}H_{12}O_4$: C, 65.46; H, 5.49%.) Prolonged reaction times led to mixtures of monoester **12** and the corresponding diester. These esters could be separated by chromatography over silicagel ($CHCl_3$).

5-*Carbomethoxypentacyclo*[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]*nonane* 4-*amino hydrochloride* (13)

To a stirred ice-cooled soln of **12** (1.0 g, 4.7 mmole) in acetone (10 ml) and water (0.4 ml) was added dropwise Et_3N (0.48 g, 4.7 mmole) in acetone (10 ml). After addition, a soln of ethyl chloroformate (0.66 g, 6.1 mmole) in acetone (2.2 ml) was added during 15 min, then the mixture stirred for 30 min at 0° and a soln of NaN_3 (0.46 g, 7.1 mmole) in water (1.6 ml) added. After being stirred for 2 hr at 0°, the mixture was poured onto crushed ice and extracted with benzene. The benzene layer was dried ($MgSO_4$) and evaporated to give the carbonylazide. The azide was dissolved in anhyd benzene and refluxed for 6 hr. Solvent was removed *in vacuo* affording the isocyanate. The crude isocyanate was dissolved in THF (10 ml), conc HCl (2.4 ml) was added and the mixture heated under reflux for 2 hrs. The THF was removed *in vacuo*, the residu diluted with distilled water and ether extracted. The aqueous layer evaporated to dryness giving the crude **13** (0.74 g, 69%), m.p. 148–152°. IR ν_{max}^{KBr} 3520, 3420, 3300–2600 (NH_3^+), 1720 (C=O) cm^{-1}; NMR (D_2O) δ 4.02 (s, 3 H, CO_2CH_3), 3.22 (s, 4H), 2.96 (s, 2H), 2.16 (AB quartet, J ~ 9 Hz, 2H, H_9H_9); *m/e* 227, 229 (M^+, 1 Cl), 191 (M^+–HCl); *m/e* (M^+–HCl): 191.0940; calc. for $C_{11}H_{13}O_2N$: 191.0946. The free amino could be obtained by treating **13** with 5% $NaHCO_3$ aq and subsequent extraction with $CHCl_3$. After drying ($MgSO_4$) and removal of the solvent, the amine was obtained in 40% yield. IR ν 3370 (NH_2) 3040 (cyclopropyl C–H), 1710 (C=O) cm^{-1}.

4 - *Acetoxy* - 5 - *carbomethoxypentacyclo*[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]*nonane* (8)

$NaNO_2$ (2.5 g, 36 mmole) was added in small portions during 2 hr of **13** (0.48 g, 2.1 mmole) in AcOH (13 ml). After stirring at room temp for 5½ hr, the soln was neutralized with 5% $NaHCO_3$ aq. The mixture was $CHCl_3$ extracted and the organic phase washed with 5% $NaHCO_3$ aq and water. After drying ($MgSO_4$), solvent was removed yielding a yellow oil (0.43 g). GLC (SE 30 1/8 in) showed the presence of 7 products. The oil was dissolved in $CHCl_3$ and chromatographed over silica (TLC, 60 F 254, 0.25 mm, MERCK). Acetate **8**, slightly contaminated with 4 minor byproducts, was obtained in 10% yield as determined by NMR. Deamination of the free amine of **13** under identical conditions yielded a mixture of products from which **8** could be isolated (slightly contaminated; purity ~ 95% according to GLC) in 27% yield. Attempts to obtain **8** analytically pure by extended chromatography or sublimation failed due to instability of the acetate.

Methanolysis of acetate **8**

NaOMe (0.043 g, 0.8 mmol) was added to a stirred soln of **8** (0.069 g, 0.2 mmol) in MeOH (5 ml). After stirring at room temp for 5 hr, solvent was removed, water was added and the mixture extracted with ether. After drying ($MgSO_4$), the solvent was removed to give a yellow oil (0.023 g), which according to GLC-analysis (SE 30, 6', 1/8") consisted of 4 products. The NMR spectrum ($CDCl_3$) showed a complex pattern between δ 0.7 and 4.2 ppm. No starting material was present in the mixture as shown by the absence of the signal of the acetate methyl protons. The IR spectrum (neat) showed a C=O absorption at 1730 cm^{-1} (in this region no other absorptions were present). Attempts to separate the mixture by column or TLC on silica gel failed.

5-*Benzoylpentacyclo*[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]*nonane* 4-*carboxylic acid* (14)

$CdCl_2$ (5.85 g, 31.9 mmole), dried at 110° *in vacuo*, was slowly added to a cold soln (−10°) of PhMgBr (prepared from Mg (56 mmole) and phenyl bromide (75 mmole)) in ether (50 ml).[10] After stirring for 1 hr at −10°, a soln of **11** (5.64 g, 30 mmol) in ether (150 ml) was slowly added to this suspension and the mixture subsequently refluxed for 14 hr. A white gummy ppt was obtained which was hydrolyzed with 10% H_2SO_4 aq. The mixture was ether extracted and the organic phase washed with water. The ether layer was then extracted with 5% Na_2CO_3 aq. The water soln was separated, filtered and added to 10% H_2SO_4 aq. The so-obtained yellow ppt was dissolved in ether, the ether layer washed with water and treated with charcoal. After drying ($MgSO_4$), solvent was removed yielding a yellow oil (5.57 g, 70%). Crystallization from cyclohexane gave pure **14**, m.p. 145–160° (dec).

IR ν_{max}^{KBr} 1675 (C=O, broad), 1595, 1575 (C=C) cm^{-1}; NMR (CD_2Cl_2) δ 7.91 (m, 2H), 7.44 (m, 3H), 2.93 (s, 4H, $H_2H_3H_6H_7$), 2.67 (m, 2H, H_1H_8), 1.98 (AB quartet, J ~ 9 Hz, 2H, H_9H_9); *m/e* 266 (M^+). (Found: C, 76.77; H, 5.44. Calc. for $C_{17}H_{14}O_3$: C, 76.68; H, 5.30%.)

4-(5-*Benzoylpentacyclo*[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]*nonyl*)*amine* (15)

The same procedure as for the preparation of amine **13** was used. Starting from **14**, the azide was obtained in 45% yield together with unchanged **14**. The azide was isolated in only 14% when pivaloyl chloride was used instead of ethyl chloroformate. Amine **15** was obtained as crystalline material in 35% yield; m.p. (HCl-salt) 162–165° (dec) IR ν_{max}^{KBr} 3370, 3310 (NH_2), 3040, 3020 (cyclopropyl C–H and phenyl C–H), 1655 (COC_6H_5), 1595, 1575 (C=C) cm^{-1}; NMR (CCl_4) δ 7.93 (m, 2H), 7.43 (m, 3H), 2.70 (m, 2H), 2.53 (m, 2H), 2.20 (m, 2H), 1.96 (broad s, 2H, NH_2), 1.76 (s, 2H); *m/e* (M^+): 237.1155; Calc. for $C_{16}H_{15}ON$: 237.1154. This amine was pure enough for further transformations.

4-*Acetoxy*-5-*benzoylpentacyclo*[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]*nonane* (9)

The same procedure as for the preparation of **8** was used. Starting from **15**, the acetate **9** was obtained as a yellow oil (90%) which was purified by sublimation (105°/13 mm), m.p. 60–65°.

IR (CCl_4) ν 3050 (cyclopropyl C–H), 1750 ($OCOCH_3$), 1665 (COC_6H_5), 1595 (C=C) cm^{-1}; NMR ($CDCl_3$) δ 7.86 (m, 2H), 7.46 (m, 3H), 2.83 (m, 4H, $H_2H_3H_6H_7$), 2.50 (m, 2H, H_1H_8), 1.76 (AB quartet, J ~ 9 Hz, 2H, H_9H_9), 1.33 (s, 3H, $OCOCH_3$); *m/e*: 280.1094; calc. for $C_{18}H_{16}O_3$: 280.1099.

4-*Benzoyltetracyclo*[4.3.0.0^{2,4}.0^{3,8}]*nonane*-5-*one* (18)

NaOMe (0.054 g, 1 mmole) was added to a stirred soln of **9** (0.090 g, 0.32 mmole) in MeOH (15 ml). After stirring at room temp for 2 hr, solvent was removed, water was added and the mixture extracted with ether (3 ×).

The organic phase was washed with water, dried ($MgSO_4$) and the solvent evaporated to give **18** as a yellow oil (0.06 g, 76%). Purification by prep. TLC (0.25 mm SiO_2, CH_2Cl_2) gave a pure sample, m.p. 126–128°, IR ν (CCl_4) 3080, 3060, 3030 (cyclopropyl C–H and phenyl C–H), 1730 (C=O), 1670 (COC_6H_5), 1595, 1575 (C=C) cm^{-1}; NMR ($CDCl_3$) δ 7.91 (m, 2H), 7.51 (m, 3H), 3.31 (d of d, 1H, H_2), 2.91 (m, 1H, H_1), 2.76 (m, 1H, H_8), 2.58 (m, 2H, H_3H_6), 2.11 (d, J ~ 9 Hz, half of an AB pattern, 1H, H_9), 1.98 (m, 2H, H_xH_n), 1.64 (d, J ~ 9 Hz, half of an AB pattern, 1H, H_9); *m/e*: 238.0987; calc. for $C_{16}H_{14}O_2$: 238.0994.

4 - *Benzoyl* - 7 - *endo* - *deuteriotetracyclo*[4.3.0.0^{2,4}.0^{3,8}]*nonan*-5-*one* (18a)

This was prepared as described above using MeOD instead of MeOH. Purification by prep TLC (0.25 mm SiO_2, CH_2Cl_2) gave a pure sample, m.p. 127.5–129°. IR ν (CCl_4) 3080, 3060, 3030 (cyclopropyl C–H and phenyl C–H), 1730 (C=O), 1670 (COC_6H_5), 1595 (C=C) cm^{-1}; NMR ($CDCl_3$) δ 7.91 (m, 2H), 7.51 (m, 3H), 3.31 (d of d, 1H, H_2), 2.91 (m, 1H, H_1), 2.76 (m, 1H, H_8), 2.58 (m, 2H, H_3H_6), 2.11 (d, J ~ 9 Hz, half of an AB pattern, 1H, H_9), 1.96 (m, 1H, H_x), 1.62 (d, J ~ 9 Hz, half of an AB pattern, 1H, H_9); *m/e*: 239.1072; calc. for $C_{16}H_{13}DO_2$: 239.1077.

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