130. Heterocyclic Spiro-naphthalenones. Part III. Synthesis and Reactions of Some Spiro [naphthalene-1, 2'-pyrrolidin]-2-ones and Spiro [naphthalene-2, 2'-pyrrolidin]-1-ones

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Summary

The spironaphthalen-2-ones **2**, **10** and **18** were prepared by *N*-bromosuccinimide (NBS) oxidation of **1**, **9** and **17** respectively, whereas spironaphthalen-1-ones **24** and **25** were obtained by treating **23** with NBS.

The stereoisomeric reduction products **29**, **30** and **32** obtained from **24** and **25**, gave the pentacyclic compound **33** on treatment with polyphosphoric acid.

Introduction. – In part I [1] of this study we reported the synthesis of spiro-[naphthalene-piperidin]ones where the N-atom was linked to the spiro C-atom by a methylene group. This junction was performed by an intramolecular *Mannich* condensation. In part II [2] we presented the synthesis of spiro[furan-naphthalen]-ones where the furan oxygen was directly linked to the spiro C-atom by oxidative cyclization.

We now report oxidative cyclizations leading to the formation of some spiro-[naphthalene-pyrrolidin]ones where the N-atom is directly bonded to the spiro C-atom. The stereochemical course of their reduction by hydrides and a few typical dehydrations in polyphosphoric acid (PPA) are discussed.

Results. – The hydroxynaphthylpropylamine **1** was oxidized with NBS to the spironaphthalenone **2**. With $NaBH_4$, **2** gave the allylic alcohol **3** as the sole product, whereas $LiAlH_4$ afforded the alcohols **3** and **4** in a 2:1 ratio. The *cis*-compound **3** forms an intramolecular hydrogen bridge in contrast to compound **4**; on silica gel TLC. **3** has a much higher Rf value than the more polar **4**. Moreover CH_2Cl_2 solutions of **3** show a broad absorption in their IR. spectrum centered at 3300 cm^{-1} and not affected by dilution.

Both allylic alcohols **3** and **4** gave on hydrogenation the stereoisomeric alcohols **5** and **6**. On heating in PPA, **3** was rearranged to the known tetrahydrobenzo-quinoline **7** [3], whereas **5** gave the naphthylpropylamine **8** by 2 successive eliminations. The NMR. spectrum of **8** showed the typical pattern of 1-alkylated naphthalenes.

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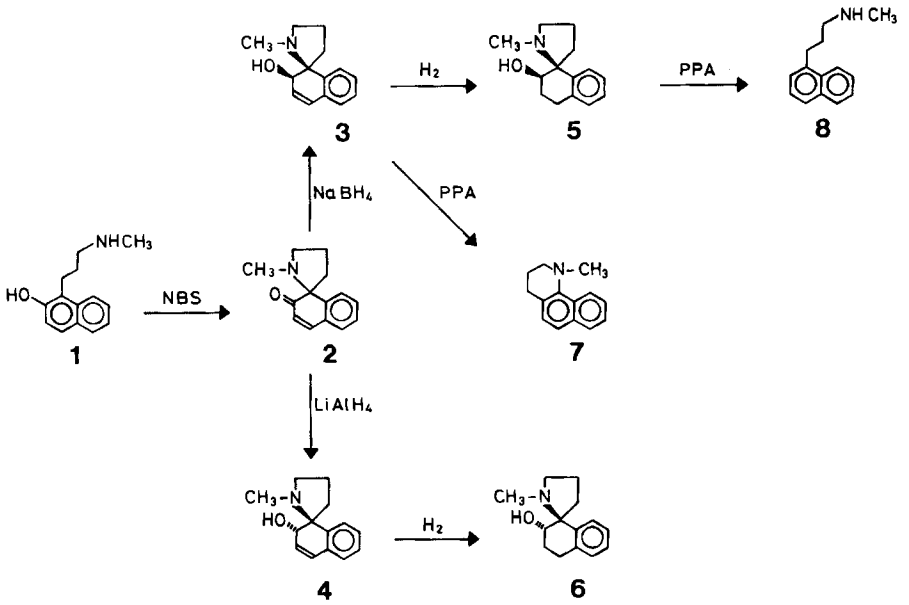


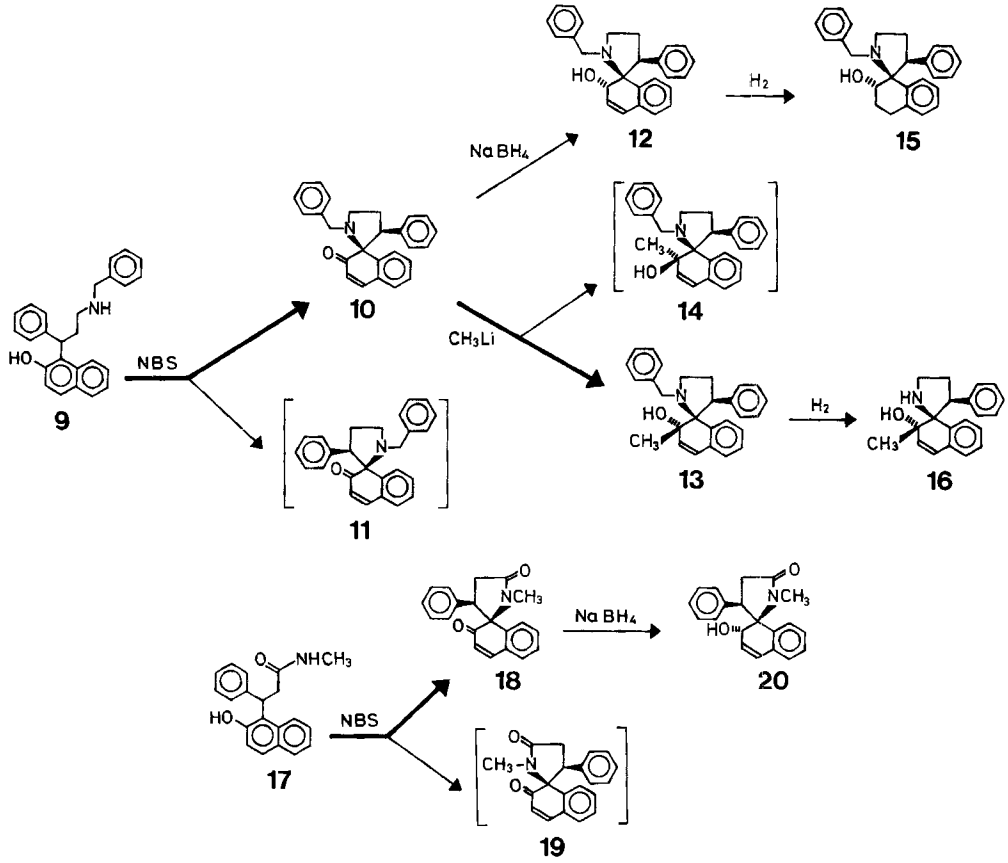
The *N*-benzylnaphthylpropylamine **9** with NBS gave mainly the *trans*-spironaphthalenone **10** and about 10% of the *cis* isomer **11**; they were not separated. The NMR. spectrum of this mixture showed 2 doublets at 6.1 and 5.55 ppm ($J = 10$ Hz) which account for H–C(3) in compounds **10** and **11** respectively. The lower δ-value for this signal is attributed to **11** and may be explained by the plane of the phenyl ring in this isomer being approximately parallel and above the plane of the double bond.

Crude **10** treated with $NaBH_4$ gave the allylic alcohol **12**[1]). When **10** was treated with CH_3Li at $-20°$ the tertiary allylic alcohol **13** was the sole product. At higher temperatures, substantial amounts of the stereoisomer **14** were also produced but not isolated. The configurations shown for **13** and **14** were based on their Rf values in the same way as for the isomers **3** and **4**. The alcohol **12** absorbed 1 equiv. of H_2 to give **15**. Hydrogenation of **13**, however, under identical conditions, resulted in debenzylation to **16**, the double bond remaining intact.

With NBS the propionamide **17** gave the spirolactam **18** containing about 20% of the stereoisomer **19**. Compound **18** was purified by crystallization. The NMR. spectrum of the mixture showed 2 sets of doublets: one small centered at 6.3 and one larger at 5.6 ppm, attributed to H–C(3) in **19** and **18** respectively. The lower δ-value observed for the doublet corresponding to **18** is explained as previously for the spiropyrrolidine **11**. Compound **18** was reduced with $NaBH_4$ to yield the alcohol **20**. It was assumed that $NaBH_4$ attacked the carbonyl group from the less hindered side to give the configuration shown.

With methylamine the benzochromanone **21** [1] [5] gave the amide **22** which was reduced with $LiAlH_4$ to the hydroxynaphthylpropylamine **23**. Compound **23** was

[1]) The debenzylation product of **12** has a configuration identical with that proposed for **12** (X-ray analysis) [4].



treated with 2 equiv. of NBS to yield the 2 stereoisomeric bromo-spironaphthalenones **24** and **25** (1:1) separated by crystallization of their salts. NMR. spectroscopy showed the olefinic proton of **24** to have a lower δ-value than that of **25**. The reasons for this higher field signal of **24** are those already discussed for compound **11**.

The aromatic ketone **24** on reduction with $NaBH_4$ gave the stereoisomeric benzyl alcohols **26** and **27** (1:2) separated by crystallization. It was again assumed that **26**, with the lower Rf value, was the *trans* isomer. The more strongly hindered aromatic ketone **25** gave only **28** with $NaBH_4$ which is assumed to attack from the less hindered side.

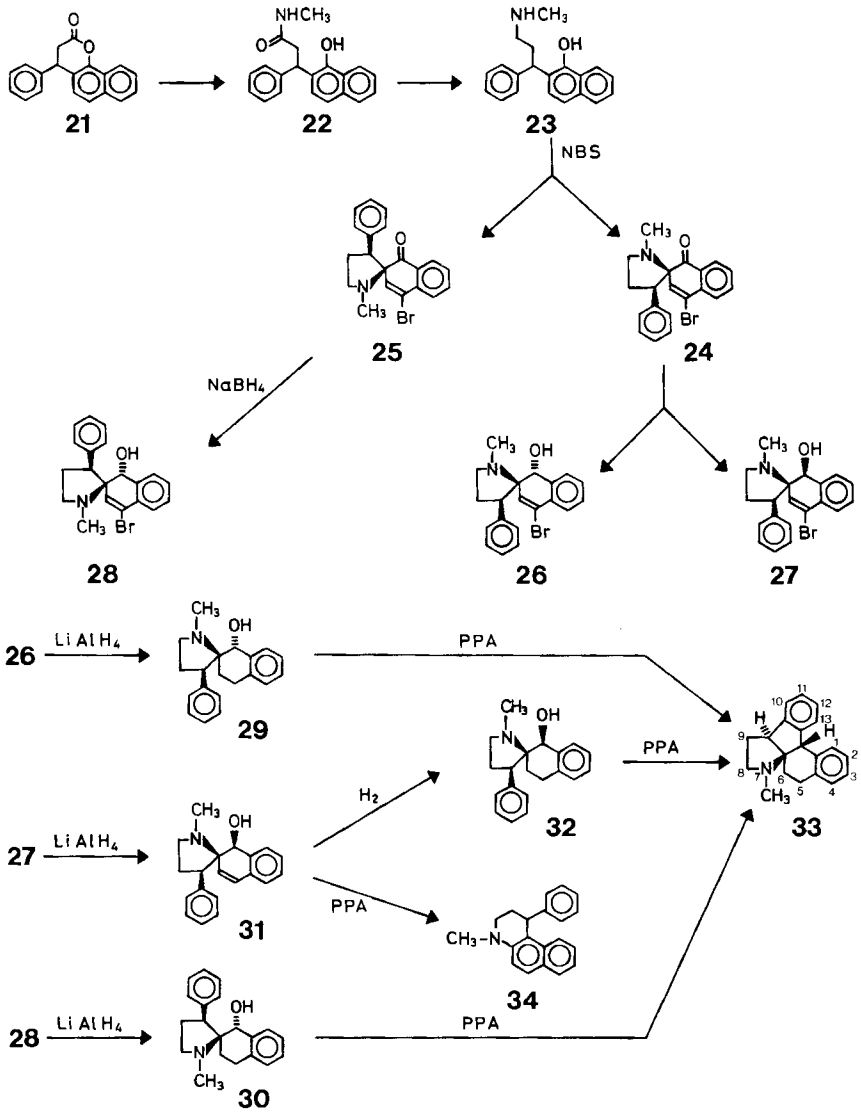
When the *N, O-trans* bromo-compounds **26** or **28** were treated with $LiAlH_4$ both the bromine and the olefin were attacked to give the tetrahydronaphthol **29** or **30** respectively. The $LiAlH_4$ reduction of the *N, O-cis* bromo-compound **27** under similar conditions gave the dihydronaphthol **31** which was hydrogenated to **32**.

Surprisingly, all 3 stereoisomers **29**, **30** and **32** when heated in PPA, gave the pentacyclic compound **33**. The NMR. spectrum of **33** showed a singlet at 4.35 ppm accounting for H–C(13b); the integration for 8 aromatic protons was in accord with the assumption of an intramolecular alkylation of the phenyl group. Molecular

models showed that the configuration indicated for **33** was the only one geometrically possible[2]).

As the configuration of **29** and **32** is different from that of **33**, the yield of **33** was somewhat lower when prepared from **29** or **32** than from **30** which has the same configuration as **33**. When heated in PPA the olefinic compound **31** gave the known benzoquinoline **34** [6].

We thank *Th. Jauner* and *A. Horisberger* for their excellent experimental assistance.



[2]) X-Ray structure analysis of compound **33** confirmed the correctness of the proposed configuration [4].

Experimental Part

General. – For general remarks on NMR. spectra and microanalysis see [1].

1-(3-Methylaminopropyl)-2-naphthol (**1**) *naphthalene-1,5-disulfonate.* Compound **1** was synthetized by a 4-step route, starting from *benzo*[d]*chroman-3-one* [7], analogous to that used for the previously reported preparation of *1-(3-methylamino-1-phenylpropyl)-2-naphthol* [1]. Compound **1** was obtained in 27% yield over 4 steps; m.p. of the naphthalene-1,5-disulfonate (NDS) 257–258°.

1'-Methyl-spiro[naphthalene-1,2'-pyrrolidin]-2-one (**2**) *naphthalene-1,5-disulfonate.* The amine **1** (21.5 g, 0.1 mol) was dissolved in methanol (250 ml) and solid NBS (17.8 g, 0.1 mol) was added portionwise with stirring at RT. After standing at RT. for 1 h, the mixture was treated with a solution of NDS (14.4 g, 0.05 mol) in methanol. The product crystallized to give 22.2 g of **2** · NDS (62%): m.p. 239–244° (from H_2O/ethanol). – NMR.: 6.0 (*d*, H–C(3)). – $C_{19}H_{19}NO_4S$: C,H,N.

cis-*1'-Methyl-1,2-dihydro-spiro[naphthalene-1,2'-pyrrolidin]-2-ol* (**3**) *naphthalene-1,5-disulfonate.* The base of ketone **2** (19.8 g, 0.093 mol) was dissolved in methanol (1000 ml) and $NaBH_4$ (7.6 g, 0.185 mol) was added portionwise between 0 and 5°. After standing for 30 min the mixture was poured into water and extracted with $CHCl_3$. The extract was dried and evaporated and the residue treated with NDS and ethanol to give 23.5 g (71.3%) of **3** as NDS salt; m.p. 206–209° (from dimethylformamide/ethanol/ether). – IR.: 3300 cm^{-1} br. – NMR.: 6.3 and 6.0 (2 $d \times d$, $J \approx 2$, 10 and 1.5, 10, H–C(3) and H–C(4)); 4.4 (narrow *m*, H–C(2)). – $C_{19}H_{21}NO_4S$: C,H,N.

trans-*1'-Methyl-1,2-dihydro-spiro[naphthalene-1,2'-pyrrolidin]-2-ol* (**4**) *naphthalene-1,5-disulfonate.* A solution of base made from **2** NDS salt (30 g, 0.084 mol) in tetrahydrofuran (THF) (500 ml) was added slowly to a suspension of $LiAlH_4$ (6.4 g, 0.168 mol) in THF (500 ml), keeping the mixture below 15°. The excess $LiAlH_4$ was destroyed by adding dropwise a 10% solution of H_2O in THF. The solution was filtered and the filtrate was concentrated and poured into water. The product was extracted with $CHCl_3$, dried and evaporated. The oily base was treated with NDS (12.1 g, 0.42 mol) and ethanol and ether was added to slight turbidity to give 7.75 g (25.7%) of crude **3** NDS salt. The mother liquor was concentrated, ether was added to turbidity, and the desired stereoisomeric alcohol was allowed slowly to crystallize, yielding 8.2 g (27%) of **4** · NDS. The product was recrystallized from H_2O/alcohol/ether, m.p. 199–203°. – IR.: 3450 br., 3600 cm^{-1} sharp. – NMR.: 6.35 and 6.05 (2 $d \times d$, $J = 2$, 10 and 1.5, 10, H–C(3) and H–C(4)); 4.8 (narrow *m*, H–C(2)). – $C_{19}H_{21}NO_4S$: C,H,N.

cis-*1'-Methyl-1,2,3,4-tetrahydro-spiro[naphthalene-1,2'-pyrrolidin]-2-ol* (**5**) *naphthalene-1,5-disulfonate.* The base of **3** liberated from its NDS salt (5.85 g, 0.0163 mol), was dissolved in methanol and Pd/C (5.4%, 800 mg) was added. The mixture was hydrogenated under normal conditions. After the usual work-up the oily residue was treated with NDS in ethanol to give 2.8 g (47%) of **5** · NDS, m.p. 185–190°. – $C_{19}H_{23}NO_4S$: C,H,N.

trans-*1'-Methyl-1,2,3,4-tetrahydro-spiro[naphthalene-1,2'-pyrrolidin]-2-ol* (**6**) *naphthalene-1,5-disulfonate.* As for the preparation of **5** from **3**. Yield 63% of **6** NDS salt, m.p. 163–166°. – $C_{19}H_{23}NO_4S$: C,H,N.

1-Methyl-1,2,3,4-tetrahydro-benzo[h]*quinoline* (**7**) *hydrochloride.* The base **3** made from the NDS salt (3.6 g, 0.01 mol) was heated in PPA (640 g) at 80° for 15 min. The hot solution was poured into cold water and made alkaline with 30% NaOH solution. The product was extracted with $CHCl_3$, then dried and evaporated. The oily residue was treated with HCl/ether/ethanol, giving 520 mg of **7** · HCl (22%), m.p. 174–179° ([3]: only b.p. of base given). – $C_{14}H_{16}ClN$: C,H,N.

N-*Methyl-3-(1-naphthyl)-propylamine* (**8**). The base prepared from **5** NDS salt (360 mg, 1 mmol) was heated at 170° in PPA (10 g) for 20 min. The mixture was poured into ice/water, made alkaline with 30% NaOH and extracted with $CHCl_3$, then dried and evaporated. The main product was separated from by-products by TLC. (Al_2O_3, heptane/$CHCl_3$/ethanol 65:35:10) to give 55 mg of an oil which was assumed to be **8** from its NMR. spectrum. – NMR.: 7.6 (br. *m*, 7 ar. H); 2.45 (*s*, CH_3N).

trans-*1'-Benzyl-3'-phenylspiro[naphthalene-1,2'-pyrrolidin]-2-one* (**10**). The naphthylpropylamine **9** [1] (100 g, 0.272 mol) was suspended in 800 ml methanol/water 2:1 and cooled to 5°. A solution of NBS (48.5 g, 0.272 mol) in methanol/water 1:1 was added dropwise and with stirring over a period of 30 min. The reaction mixture was then poured into H_2O, made alkaline with 30% NaOH-solution, and extracted with $CHCl_3$, dried and evaporated. The yellow residue (75 g) which did not crystallize contained the *trans*-isomer **10** and the *cis*-isomer **11** 9:1 (NMR.). The mixture was used for the next steps. – NMR. (mixture of **10** and **11**): 6.1 (*d*, $J = 10$, 0.9 H, H–C(3) of **10**); 5.55 (*d*, $J = 10$, 0.1 H, H–C(3) of **11**).

(1RS,2RS,3'RS)1'-Benzyl-3'-phenyl-1,2-dihydro-spiro[naphthalene-1,2'-pyrrolidin]-2-ol (**12**) *naphthalene-1,5-disulfonate.* To a solution of the crude ketone **10** (75 g, ~0.2 mol) in methanol and cooled with ice/water, $NaBH_4$ (12 g, 0.32 mol) was added portionwise over a period of 45 min. After the usual work-up the residue was dissolved in ethanol (150 ml) and a solution of NDS (29 g, 0.1 mol) in ethanol was added. The **12**·NDS was allowed to crystallize to give 55 g (57%); m.p. 180–184°. – $C_{31}H_{29}NO_4S$: C,H,N.

(1RS,2RS,3'RS)1'-Benzyl-3'-phenyl-1,2,3,4-tetrahydro-spiro[naphthalene-1,2'-pyrrolidin]-2-ol (**15**) *naphthalene-1,5-disulfonate.* The base of **12** (18.5 g, 0.05 mol) dissolved in ethanol (200 ml) containing 5N HCl (80 ml) was hydrogenated at normal pressure and temperature in the presence of Pd/C 5.4%. When 1 equiv. of H_2 had been absorbed the mixture was worked up in the usual way. The crude oily product **15** was converted to its NDS giving 18.8 g (74%); m.p. 223–225°. – $C_{31}H_{31}NO_4S$: C,H,N.

(1RS,2RS,3'RS)1'-Benzyl-2-methyl-3'-phenyl-1,2-dihydrospiro[naphthalene-1,2'-pyrrolidin]-2-ol (**13**). A stirred solution of crude **10** (11 g, ~0.03 mol) in ether (110 ml) at −20°, was treated dropwise with CH_3Li (22.5 ml of 2M CH_3Li solution in ether, 0.045 mol) and was then allowed to regain RT. Water (75 ml) was added dropwise and the organic layer separated, dried and evaporated. The residue was recrystallized from cold ether giving 3.5 g (31%) of pure **13**; m.p. 167–170°. – NMR.: 5.9 and 5.6 (2*d*, *J* = 10, H–C(3) and H–C(4)); 2.2 (*s*, H_3C–C(2)). – $C_{27}H_{27}NO$: C,H,N.

When the reaction was carried out at RT. a crude product **13** was obtained, containing about 20% of a by-product thought to be the (*1RS,2SR,3'SR*) isomer (**14**); this was not isolated. – NMR.: 5.5 and 5.2 (2*d*, *J* = 10, H–C(3) and H–C(4)); 2.5 (*s*, H_3C–C(2)).

(1RS,2RS,3'RS)2-Methyl-3'-phenyl-1,2-dihydro-spiro[naphthalene-1,2'-pyrrolidin]-2-ol (**16**) *hydrochloride.* Compound **13** (9 g, 0.0236 mol) was dissolved in methanol (475 ml). A saturated solution of HCl in methanol (10 ml) and Pd/C (5.4%, 0.9 g) were added. The mixture was hydrogenated under standard conditions until 1 equiv. of H_2 was absorbed. After filtration and evaporation the residue was recrystallized in methanol/ether to give 4.55 g (58.8%) of **16** as hydrochloride; m.p. 267–270°. – $C_{20}H_{22}ClNO$: C,H,N.

cis-*1'-Methyl-3'-phenyl-spiro[naphthalene-1,2'-pyrrolidine]-2,5'-dione* (**18**). To a suspension of the amide **17** [1] (48 g, 0.154 mol) in methanol (480 mol) containing 2N NaOH (79 ml, 0.158 mol) NBS (28 g, 0.157 mol) was added portionwise. The mixture was then heated to 30–40°. After a further 30 min at RT. the mixture was poured into water and extracted with $CHCl_3$.

The organic extract was dried and evaporated almost to dryness, ether was added, and the solution was filtered through charcoal. The product was allowed to crystallize giving 5.9 g (12.3%) of a mixture containing 80% of **18** and 20% of **19**. After recrystallization, pure **18** was obtained; m.p. 147–149°, yellow crystals which slowly decompose on standing. – NMR. (mixture of **18** and **19**): 6.3 (*d*, *J* = 10, 0.2 H, H–C(3) *trans* isomer **19**); 5.6 (*d*, *J* = 10, 0.8 H, H–C(3) *cis* isomer **18**). $C_{20}H_{17}NO_2$: C,H,N.

(1RS,2RS,3'SR)2-Hydroxy-1'-methyl-3'-phenyl-1,2-dihydro-spiro[naphthalene-1,2'-pyrrolidin]-5'-one (**20**). A solution of the lactam **18** (12.1 g, 0.04 mol) in methanol (400 ml), cooled to 0–5°, was treated with $NaBH_4$ (760 mg, 18.5 mmol). The usual work-up yielded 9.3 g (76%) of **20**; m.p. 144–147° (methanol). – $C_{20}H_{19}NO_2$: C,H,N.

N-*Methyl-3-(1-hydroxy-2-naphthyl)-3-phenylpropionamide* (**22**). The benzochromanone **21** [1] [5] (2.74 g, 0.01 mol) was dissolved in 33% CH_3NH_2/abs. ethanol (10 ml) (exothermic reaction). After 30 min, H_2O (100 ml) was added and the mixture was extracted with $CHCl_3$. The organic layer was dried and evaporated to give crude **22** which was recrystallized from ether/toluene to give 3.0 g (98.5%); m.p. 77–80°. – $C_{20}H_{19}NO_2$: C,H,N.

N-*Methyl-[3-(1-hydroxy-2-naphthyl-2)-3-phenyl]propylamine* (**23**). $LiAlH_4$ (15.2 g, 0.4 mol) was suspended in THF (400 ml) under N_2. A solution of the amide **22** (61.1 g, 0.2 mol) in THF (400 ml) was added dropwise and the mixture was allowed to reflux for 4 h. After ice-cooling, excess $LiAlH_4$ was cautiously destroyed with 10% H_2O/THF. The usual work-up gave 7.3 g (62%) of **23**, m.p. 168–173° ($CHCl_3$/ether). – $C_{20}H_{21}NO$: C,H,N.

trans-*4-Bromo-1'-methyl-3'-phenylspiro[naphthalene-2,2'-pyrrolidin]-1-one* (**24**) *hydrochloride and its* cis *isomer* **25** *naphthalene-1,5-disulfonate.* A solution of the amine **23** (99.5 g, 0.34 mol) in methanol (2.5 l) containing 1N NaOH (340 ml) was cooled to −20° and NBS (121 g, 0.68 mol) was added portionwise. After completion of the addition the mixture was brought slowly to RT. and then poured into water (15 l), extracted with $CHCl_3$, dried and evaporated. The oily residue was extracted several times with hot hexane, and the extract was treated with charcoal, filtered and evaporated. The oily

mixture of bases was dissolved in ethanol and HCl/ether was added to give 34.5 g (25%) of the isomer **24**·HCl; m.p. 194–197°. –NMR.: 6.6(*s*, H–C(3)). – $C_{20}H_{19}BrClNO$: C,H,N.

NDS (15 g) dissolved in ethanol was added to the mother liquor, ether was also added and the second isomer (**25**) crystallized as NDS salt (23 g, 11.2%); m.p. 204–208° (ethanol/ether). – NMR.: 6.2 (*s*, H–C(3)). – $C_{25}H_{22}BrNO_4S$: C,H,N.

*(1*RS,2SR,3'RS*)4-Bromo-1'-methyl-3'-phenyl-1,2-dihydro-spiro[naphthalene-2,2'-pyrrolidin]-1-ol* (**26**) *hydrochloride and its (1*RS,2RS,3'SR*) isomer* **27** *naphthalene-1,5-disulfonate.* A solution of **24** made from its hydrochloride (49 g, 0.121 mol) in methanol (1 l) was cooled to 0–5° and treated with $NaBH_4$ (5 g, 0.132 mol), added in small portions. Two products were detected on TLC. (Polygram Sil G UV_{254}; heptane/$CHCl_3$/ethanol 65:35:10), the faster-running compound being the isomer **27** and the slower-running being **26**. After the usual work-up the oily residue was dissolved in ethanol, treated with HCl/ethanol and was allowed to crystallize to give 10.5 g (21%) of pure **26**·HCl; m.p. 228–229°. – NMR.: 6.2 (*s*, H–C(3)); 5.1 (*s*, H–C(1)). – $C_{20}H_{21}BrClNO$: C,H,N.

The mother liquor was treated with NDS (14.4 g, 0.1 mol) in ethanol and the second isomer (**27**·NDS) was allowed to crystallize giving 30 g (48.2%) of product; m.p. 225–226° (ethanol/H_2O/ether). – NMR.: 6.2 (*s*, H–C(3)); 4.75 (*s*, H–C(1)). – $C_{25}H_{24}BrNO_4S$: C,H,N.

*(1*RS,2SR,3'SR*)4-Bromo-1'-methyl-3'-phenyl-1,2-dihydro-spiro[naphthalene-2,2'-pyrrolidin]-1-ol* (**28**) *hydrochloride.* As for the reduction of **3** to **5**. Yield 84% of the alcohol **28** from **25**. Isolated as HCl salt; m.p. 220–221°. – NMR.: 6.4 (*s*, H–C(3)); 4.8 (*s*, H–C(1)). – $C_{20}H_{21}BrClNO$: C,H,N.

*(1*RS,2SR,3'RS*)1'-Methyl-3'-phenyl-1,2,3,4-tetrahydro-spiro[naphthalene-2,2'-pyrrolidin]-1-ol* (**29**) *hydrochloride.* A solution of the base **26**, made from its hydrochloride (1.11 g, 2.72 mmol), in THF (10 ml) was added dropwise to a suspension of $LiAlH_4$ (207 mg, 5.45 mmol) in THF (10 ml). After the usual work-up, **29** (450 mg) isolated as hydrochloride was obtained (50.5%); m.p. 151–152° (ethanol/ether). – NMR.: 4.65 (*s*, H–C(1)). – $C_{20}H_{24}ClNO$: C,H,N.

*(1*RS,2SR,3'SR*)1'-Methyl-3'-phenyl-1,2,3,4-tetrahydro-spiro[naphthalene-2,2'-pyrrolidin]-1-ol* (**30**) *hydrochloride.* As for the reduction of **26** to **29**, compound **30** was obtained in 61% yield from the bromo-compound **28**; isolated as hydrochloride, m.p. 226–228° (ethanol/ether). – NMR.: 4.6 (*s*, H–C(1)). – $C_{20}H_{24}ClNO$: C,H,N.

*(1*RS,2RS,3'SR*)1'-Methyl-3'-phenyl-1,2-dihydro-spiro[naphthalene-2,2'-pyrrolidin]-1-ol* (**31**). As for the reduction of **26** to **29**, compound **31** was obtained from **27** (53%); m.p. 120–122° (ether). – NMR.: 6.4 and 5.6 (2*d*, J = 12, H–C(3) and H–C(4)); 4.7 (*s*, H–C(1)). – $C_{20}H_{21}NO$: C,H,N.

*(1*RS,2RS,3'SR*)1'-Methyl-3'-phenyl-1,2,3,4-tetrahydro-spiro[naphthalene-2,2'-pyrrolidin]-1-ol* (**32**) *hydrochloride.* As for the hydrogenation of **3** to **5**, but using PtO_2 as catalyst. From the olefinic compound **31** product **32** isolated as hydrochloride was obtained in 50.7% yield; m.p. 224–227°. – NMR.: 4.5 (*s*, H–C(1)). – $C_{20}H_{24}ClNO$: C,H,N.

*(6a*RS,*9a*RS,*13b*RS*)7-Methyl-5,6,8,9,9a,13b-hexahydro-7*H*-benzo[5,6]fluoreno[8a,9-b]pyrrole* (**33**) *hydrochloride.* Compound **29** hydrochloride (2.5 g) was stirred in PPA (50 g) and heated 15 min at 100°. The solution was poured into H_2O and made alkaline with 10% NaOH. The product was extracted with $CHCl_3$, dried and evaporated. The crude base **33** was converted to its hydrochloride, 1.0 g (43%); m.p. 261–262° dec. (ethanol/ether). – NMR.: 4.35 (*s*, H–C(13b)); 3.7 (*d*×*d*, J = 3 and 10, H–C(9a)). – $C_{20}H_{22}ClN$: C,H,N.

Compound **33** was also obtained under similar conditions from **30** (58%) or from compound **32** (25%). All 3 products had identical m.p. and NMR. spectra.

4-Methyl-1-phenyl-1,2,3,4-tetrahydro-benzo[f]*quinoline* (**34**). Compound **31** (290 mg) was heated in PPA (6 g) at 100° for 5 min. The solution was poured into H_2O, made alkaline with 10% NaOH and extracted with $CHCl_3$. After drying and evaporating the extract the oily residue was crystallized from hexane to give 100 mg of the benzoquinoline **34**; m.p. 98–100° ([6] 90–92°). – $C_{20}H_{19}N$: C,H,N.

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