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**Synthesis of Some Optically Active α -Pyridyl-carbinols and
Determination of Absolute Configuration from the CD of Their
in situ Complexes with $[\text{Mo}_2(\text{OAc})_4]$**

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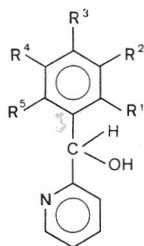
Four new α -pyridyl-aryl-carbinols have been synthesized, and twelve such racemates have been for the first time resolved by standard procedures. From the positive CD-couplet of the complex between (S)-1 and 23 an antiperiplanar arrangement of the H—C(OH, Ph)—C₂(Py)—N-moiety could be derived as the preferred conformation. From the CD-spectra above 300 nm of this and seven other compounds of known absolute configuration in the presence of 23 the following correlation with stereochemistry was derived, which was then applied to determining the absolute configuration of fourteen other α -pyridyl-aryl-carbinols: for (R)-configuration negative CD-bands appear between 500 to 510 (sometimes detectable only as shoulder) and at 408 to 470 nm, between 335 to 380 nm a positive Cotton effect is registered, and another one shows up below 320 nm, which has mostly a positive sign for secondary, but a negative one for tertiary carbinols of the mentioned absolute sense of chirality.

SYNTHESIS

Of the compounds used for these studies 4 racemates have been newly synthesized by known procedures (for details cf. EXPER.). The syntheses followed one of three pathways, *vic.* condensation of a (substituted) benzaldehyde or acetophenone with α -pyridyl lithium, or of α -acetyl-pyridine with an aryl magnesium bromide. By resolution *via* crystallization of diastereomeric salts prepared with different optically active acids, 12 of the 22 compounds have been prepared for the first time in optically active form.

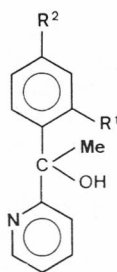
GENERAL REMARKS ON THE CD OF α -PYRIDYL-ARYL-CARBINOLS IN THE PRESENCE OF 23

The CD of α -pyridyl-carbinols depends very much on the solvent used for the measurements. Not only the magnitudes of the Cotton effects, but even their signs are influenced and this restricts direct interpretation to classes of very closely related structures (cf. ref. 1). The obvious reason is the fact that each molecule may adopt several different conformations and, therefore, we investigated also the CD spectra of their complexes with some transition metal clusters. For 1,2-glycols and 1,2-amino alcohols we have shown² that they are bound to the M_2 -cluster in only one single conformation, and in this paper we describe our results with the $[Mo_2(OAc)_4]$ complex (23). This method was applied to 8 compounds of known absolute configuration and the results obtained were then used to determine the absolute configuration of 14 others. Whenever these assignments could be checked by independent interpretations of the CD spectra obtained without addition of the complex, the results were identical. The absolute configuration of one key-compound (16) was determined by X-ray diffraction.³



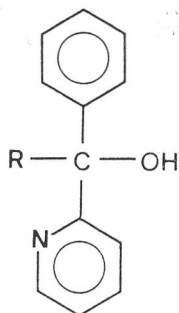
	R ¹	R ²	R ³	R ⁴	R ⁵	
1	H	H	H	H	H	S
2	H	H	Me	H	H	S
3	H	H	F	H	H	R
4	H	H	Cl	H	H	R
5	H	H	OMe	H	H	R
6	H	Me	H	H	H	S
7	Me	H	H	H	H	S
8	Cl	H	H	H	H	S
9	H	-O-CH ₂ -O-	H	H	H	S
10	H	OMe	H	OMe	H	R
11	Cl	H	H	H	Cl	S

As it has been proved,² neither pyridine nor monoalcohol can act as ligand in DMSO solution for the parent complex 23, but glycols or amino alcohols are accepted. This is also the case with α -pyridyl-carbinols 1 through

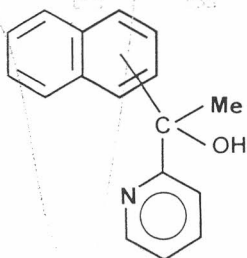


	R ¹	R ²	
12	H	Me	S
13	H	F	S
14	H	Cl	R
15	H	Br	R
16	H	OMe	S
17	H	COMe	S
18	F	H	R

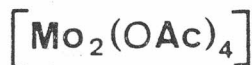
22 since all give several Cotton effects within the absorption bands of the Mo₂-cluster between 530 and 300 nm. For a series of 1,2-glycols we had found that the sign of the 300 nm Cotton effect is in all cases the same as the sign of the torsional angle O—C—C—O in the complex.^{2,4} 1,2-Amino alcohols behave analogously but this most characteristic Cotton effect is slightly shifted. These rules cannot be applied without modification to the α -pyridyl carbinols since the nitrogen and the next C-atom in the pyridine ring are sp²-hybridized. On the basis of the CD-spectra of 8 such compounds with known absolute configuration we are, however, now able to put forward a similar empirical rule for the *in situ* complexes of these α -pyridyl-carbinols in the presence of 23.



19 : R = Et
20 : R = i-Pr



21 : α - | ?
22 : β - | S



23

The distance between nitrogen and oxygen in **1** through **22** allows complexing only if the torsional angle N—C—C—O is appr. $\pm 60^\circ$, similarly to the previously investigated ligands, but the incorporation of the N—C — moiety into the flat pyridine ring does not allow assumptions about the preferred mode of complexing ($+60^\circ$ or -60° for a given absolute configuration). For (+)-**(S)**-**1** we were, however, able to measure the CD of the complex below 300 nm and could, thus, observe the first branch of a strong CD-couplet at 267 nm ($\Delta\epsilon = +15.2$). Such a CD band could not be found for complexes with ligands lacking the pyridine ring. Furthermore **1** in cyclohexane without any complex shows a similar CD-band (Figure 1.). We can, therefore, safely ascribe this strong CD in the complex to the long-wavelength branch of a CD couplet (Figure 2), which has its origin in the interaction between the first $\pi \rightarrow \pi^*$ — transition of the pyridine system (corresponding to the absorption band at 262 nm of α -picoline) and either the B_{1u} - or one of the E_{1u} -transitions of the phenyl. This still leaves some ambiguity for the conformation, and we have therefore prepared the corresponding p-acetyl-phenyl analogue **17**, where we found an analogous CD-couplet.⁵ There is, therefore, no doubt that one of these transitions is involved in polarization along the long axis.

If a negative torsional angle is assumed, then the exciton theory predicts a positive CD-couplet, whereas with the positive torsional angle both transition moments lie (practically) in one single plane, the geometry of which is then achiral and cannot lead to exciton coupling. The strong couplet now proved that the preferred conformation of the ligand in the complexed state is that in which the hydrogen at the centre of chirality is antiperiplanar to the C—N — bond of the pyridine ring.

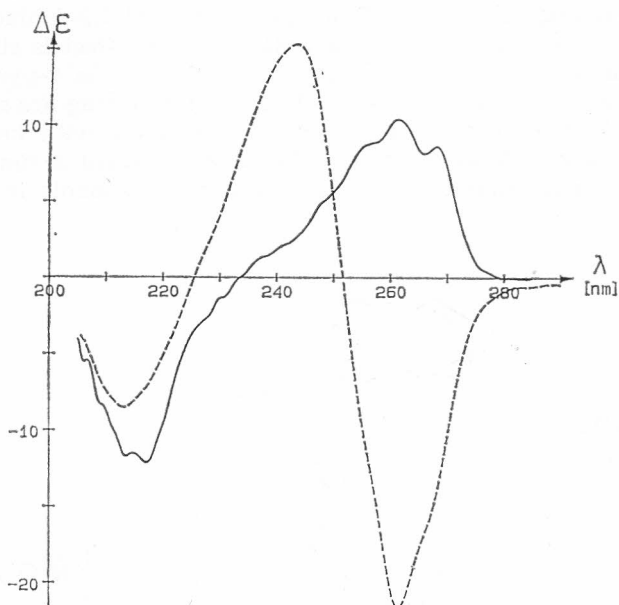


Figure 1. CD of (+)-**(S)**-**1** in cyclohexane (—) and of (-)-**(R)**-**E-17** in iso-octane (---)

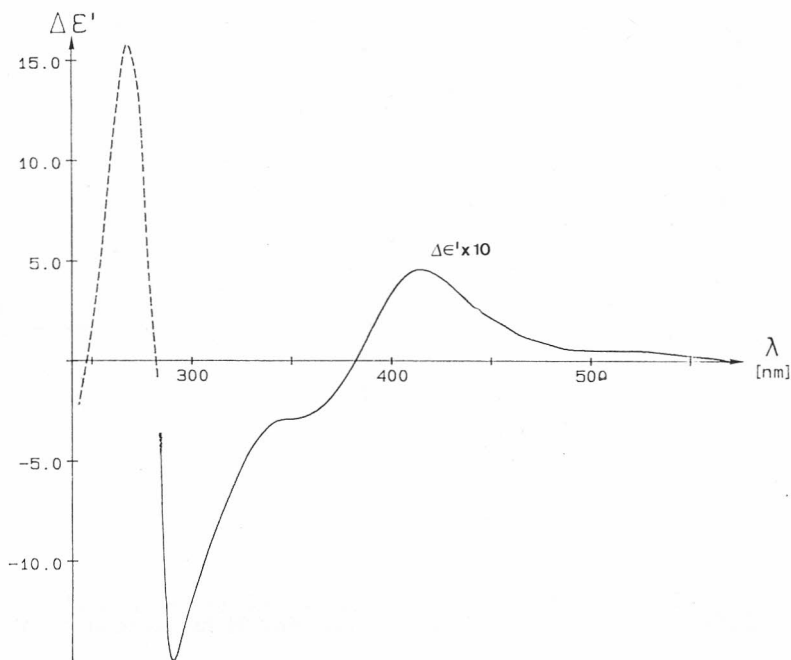


Figure 2. CD of (+)-(S)-1 in DMSO in the presence of 23 after standing 24 hrs at room temperature.

CD OF α -PYRIDYL-CARBINOLS OF KNOWN ABSOLUTE CONFIGURATION IN THE PRESENCE OF 23

Comparison of all these CD-spectra leads to the following generalizations:

1) At the longest wavelengths, a Cotton effect appears between 500 to 510 nm, which is sometimes only seen as a shoulder, and whose sign is opposite to the sign of the torsional angle N—C—C—O in the complex.

2) The second Cotton effect is found between 408—470 nm, its sign being the same as that of the first one.

3) The third Cotton effect has an opposite sign to the first two and appears between 335 to 380 nm.

4) A fourth one below 320 nm, which is not always fully detectable in the CD-spectra, has mostly the same sign as the third for the secondary alcohols, but an opposite sign with tertiary alcohols.

Of the secondary alcohols with known absolute configuration three, *viz.* 1, 8, and 11, have (*S*)-chirality, 4 is an (*R*)-compound. The CD-curve of the latter is thus enantiomorphous to those of the first three mentioned alcohols (Figure 3). Furthermore, 4 develops a more pronounced finestructure below 320 nm after 24 hrs. Whether this (small) change of the shape of the CD-curve with time has to do with a slow change of conformation of the complexed ligand has still to be tested with more *o*-substituted potential ligands. The four tertiary alcohols 14, 15, 16, and 19 follow the same general rules, thus

Table 1: CD of *in situ* complexes of α -pyridyl-carbinols
and 23 in DMSO solution.

Compound	λ [nm] ($\Delta\epsilon'$)
1 ⁸	503 (+0.4), 416 (+1.1), 356 (-0.7), 325 (-0.6), positive below 300 nm.
2	510 (+0.2), 414 (+0.9), 350 sh (-0.3), 298 (-1.1), positive below 290 nm.
3	501 (-0.5), 414 (-1.4), 353 (+0.7), 320 (+0.7), negative below 300 nm.
4 ⁸	506 sh (-0.2), 422 (-0.3), 364 (+0.6), negative below 310 nm.
5	504 (-0.5), 412 (-2.0), 340 (+1.1), negative below 310 nm.
6	505 (+0.2), 408 (+1.2), 352 (-0.2), 318 (-1.0), positive below 295 nm.
7	505 (+0.2), 422 (+0.8), 352 (-1.2), positive below 305 nm. After 24 ^h additional maximum at 294 (-0.9).
8 ⁸	500 sh (+0.3), 435 (+0.5), 351 (-1.0), 305 sh (+0.6), positive at shorter wavelengths. After 24 ^h additional maximum at 290 nm (-0.9) the shoulder at 305 nm becomes maximum at 316 (+0.1).
9	500 sh (+0.5), 421 (+1.0), 362 (-1.0), positive below 333 nm.
10	510 sh (-0.3), 425 (-1.0), 357 (+1.6), negative below 315 nm.
11 ⁸	500 sh (+0.4), 420 (+2.1), 335 (-4.1) after 24 ^h 355 (-0.8), 320 (+0.3), 288 (-1.6), positive below 277 nm.
12	505 sh (+0.2), 439 (+0.3), 357 (-0.8), positive below 325 nm.
13	505 sh (+0.2), 463 (+0.3), 375 (-0.9), positive below 330 nm.
14 ⁹	500 sh (-0.2), 470 (-0.2), 380 (+0.9), negative below 340 nm.
15 ⁹	510 sh (-0.2), 470 (-0.2), 377 (+0.7), negative below 338 nm.
16 ³	505 sh (+0.2), 438 (+0.4), 363 (-0.8), positive below 332 nm.
17	510 sh (+0.1), 442 (+0.2), 373 (-0.7), positive below 340 nm.
18	505 (-0.1), 355 (-2.1), 298 (+0.6), negative below 290 nm.
19 ¹⁰	510 sh (+0.1), 458 (+0.2), 362 (-1.3), positive below 328 nm.
20 ¹⁰	452 (+0.1), 365 (-0.4), positive below 330 nm.
21	490 sh (+0.2), 360 (+1.5), another positive Cotton effect below 300 nm.
22 ⁹	505 sh (+0.3), 444 (+0.4), 360 (-0.8), positive below 330 nm.

sh: shoulder. For definition of $\Delta\epsilon'$ -values cf. lit.⁷.

others, especially since the CD-spectrum of 18 itself looks quite normal⁶ and hence the (*R*)-configuration follows unequivocally.

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EXPERIMENTAL

All m.p.s. (Kofler hot stage apparatus) are uncorrected. Optical rotations were measured with a Perkin-Elmer 241 instrument in chloroform solution if not otherwise stated.

Syntheses of the Racemic Arylpyridyl alkanols and their Optical Resolution General Procedure

To a stirred ethereal solution of 2-pyridyllithium prepared by the halogen-interconversion method (see ref. 11) from 2-bromopyridine (38 g, 240 mmol) in 80 ml dry ether and butyllithium (4.25 g, 600 mmol Li and 41 g, 300 mmol *n*-butylbromide) in 150 ml dry ether at -78°C , the etheric solution (150 ml) of a corresponding (substituted) benzaldehyde or acetophenone (120 mmol) was added dropwise during 45 min. (while the temperature was allowed to rise to -30°C). The mixture was stirred for another 1.5 h at the same temperature, hydrolyzed carefully with 30 ml water and worked-up as usual. The isolated crude reaction product was purified as a base or after conversion into its hydrochloride.

(\pm)-2: Recrystallization (MeOH/Et₂O) of the crude hydrochloride gave 18.4 g (65%) (\pm)-2.HCl of m. p. 192—195 $^{\circ}\text{C}$ (decomp.), (lit.¹² m. p. 178—180 $^{\circ}\text{C}$).

Anal. for C₁₃H₁₄ClNO (235.71) calc'd.: C 66.24; H 5.99; N 5.49%
found: C 66.25; H 6.00; N 5.83%

The free base (\pm)-2 after recrystallization from EtOAc had m. p. 97—98 $^{\circ}\text{C}$ (lit 12 m. p. 96 $^{\circ}\text{C}$).

(+)-(S)-2: After three recrystallizations from acetone (salt (g)/acetone (ml) = 1 : 3) of the diastereomeric salts prepared from 3.98 g (\pm)-2 and 4.64 g (+)-camphor-10-sulfonic acid the resulting crystalline salt (5.13 g) of m. p. 151—152.5 $^{\circ}\text{C}$ and [α]_D = + 38.9 (*c* = 0.3, MeOH) was found to be only partially resolved. Five recrystallizations from EtOAc of the corresponding optically impure base led to the separation of crystals of less soluble racemate (\pm)-2. From the final mother liquor 0.11 g (6%) (+)-2 was obtained of m. p. 88—90 $^{\circ}\text{C}$ and [α]_D = + 105.7 (*c* = 0.5).

(\pm)-3: 14.27 g (50%) pure (\pm)-3.HCl (MeOH/Et₂O).

Anal. for C₁₂H₁₁ClFNO (239.56) calc'd.: C 60.13; H 4.63%
found: C 60.29; H 4.81%

The corresponding free base has m. p. 96—98 $^{\circ}\text{C}$.

(—)-(R)-3: A hot solution of 3.05 g (\pm)-3 and 5.64 g (—)-(2*R*,3*R*)-O,O'-dibenzoyl tartaric acid in 30 ml *i*-PrOH was allowed to cool slowly to room temperature and kept at this temperature for another 24 hrs. The resulting crystalline product (5.44 g, m. p. 144—146 $^{\circ}\text{C}$) was recrystallized five times from 5 ml *i*-PrOH for each gram of salt to give the product of m. p. 153—155 $^{\circ}\text{C}$ and [α]_D = − 92.1 (*c* = 0.8, MeOH). The corresponding pure free base (21% yield) had m. p. 106—107 $^{\circ}\text{C}$ and [α]_D = − 137.9 (*c* = 0.6).

(\pm)-5: 12.94 g (50%, EtOAc) of free base (\pm)-5 of m. p. 132—133 $^{\circ}\text{C}$ (lit. 13 m. p. 133—134 $^{\circ}\text{C}$).

Anal. for C₁₃H₁₃NO₂ (215.12) calc'd.: C 72.54; H 6.09%
found: C 72.37; H 6.06%

(-)-(R)-5: After six recrystallizations of the diastereomeric salts prepared from 4.30 g (\pm)-5 and 4.00 g (+)-camphor-10-sulfonic acid from *i*-PrOH (6 ml for each gram salt) the resulting crystalline product had m. p. 144–147 °C and $[\alpha]_D = -0.1$ ($c = 0.5$, MeOH) and was only partially resolved. The corresponding optically impure base was subjected to several recrystallizations from EtOAc. From the final mother liquor as a dry residue 0.09 g (4% yield) (-)-5 were obtained with m. p. 71–72 °C and $[\alpha]_D = -139.2$ ($c = 0.6$).

(\pm)-6: 18.90 g (79%, EtOAc) of free base (\pm)-6 of m. p. 103–104 °C (lit. 12, 14 m. p. 102–103 °C).

(+)-(S)-6: The diastereomeric salt prepared from 7.96 g (\pm)-6 and 9.28 g (+)-camphor-10-sulfonic acid was subjected to sixfold recrystallization from 9 ml MeOH/acetone (1 : 8) for each gram of salt. The resulting crystalline product (8.13 g, m. p. 153–155 °C, $[\alpha]_D = +38.2$ ($c = 1.1$, MeOH) was only partially resolved. From the hot solution of the corresponding free base **6** (3.58 g, ($[\alpha]_D = +26.0$ ($c = 1.2$)) in 20 ml EtOAc after slowly cooling to room temperature and maintaining for another 24 hrs 2.35 g crystals of (\pm)-6 were isolated. By the fourth partial concentration of the mother liquor the deposited crystals of (+)-6 (0.34 g, (8%), m. p. 61–63 °C) and the dried residue after complete evaporation had the same optical rotation $[\alpha]_D = +137.8$ ($c = 0.5$).

(\pm)-7: 21.10 g (75%, MeOH/Et₂O) of (\pm)-7·HCl of m. p. 182–183 °C (decomp.) (lit. 12 m. p. 179–180 °C).

Anal. for C₁₃H₁₄ClNO (235.71) calc'd.: C 66.24; H 5.99%
found: C 66.59; H 6.00%

The free base (\pm)-7 has m. p. 57–59 °C (lit. 12 m. p. 60 °C).

(+)-(S)-7: A hot solution of 5.97 g (\pm)-7 and 4.50 g (+)-(2R,3R)-tartaric acid in 25 ml *i*-PrOH was allowed to cool slowly to room temperature and kept at this temperature for another 72 hrs (2.79 g, m. p. 79–118 °C). After three more crystallizations from 4 ml *i*-PrOH for each gram of salt, the pure salt had m. p. 119–120 °C and $[\alpha]_D = +32.7$ ($c = 0.7$, MeOH). The pure base **7** (yield 22%) was an oil with $[\alpha]_D = +148.7$ ($c = 0.7$).

(\pm)-9: M. p. 70–71 °C (92%, lit. 15 m. p. 72 °C).

(+)-(S)-9: From the solution of 20.61 g (\pm)-9 and 20.88 g (+)-camphor-10-sulfonic acid in 450 ml acetone after 48 hrs at room temperature the crystalline product obtained was subjected to two recrystallizations from 450 and 270 ml acetone, resp. The isolated diastereomeric salt (8.77 g, m. p. 146–149 °C and $[\alpha]_D = +38.7$ ($c = 0.5$, MeOH)) was only partially resolved. After five recrystallizations from EtOAc, the more soluble racemate was completely removed to give the optically pure base **9** (0.17 g, 2%) with m. p. 93–94 ° and $[\alpha]_D = +117.2$ ($c = 0.6$).

(\pm)-10: The crude base afforded from acetone/pentane 15.73 g (54%) pure (\pm)-10 of m. p. 99–100 °C (lit. 16 m. p. 98–100 °C).

(-)-(R)-10: From 40 ml acetone solution of 5.74 g equimolar mixture of (\pm)-10 and (+)-3-bromocamphor-9-sulfonic acid after 72 hrs 2.30 g crystalline product with m. p. 116–123 °C was separated. After three recrystallizations from 20 ml acetone for each gram of salt the optically pure salt obtained (1.28 g) had m. p. 122–124 °C and $[\alpha]_D = -23.1$ ($c = 0.8$, MeOH). The free base **10** (0.53 g, yield 43%) had m. p. 54–55 °C and $[\alpha]_D = -102.8$ ($c = 0.5$).

(\pm)-12: From EtOAc 20.47 g (80% of m. p. 65–66 °C (lit 17 m. p. 67–68 °C).

(+)-(S)-12: A hot solution of 4.27 g (\pm)-12 and 3.00 g (+)-(2R,3R)-tartaric acid in 20 ml *i*-PrOH was allowed to cool slowly to room temperature and kept there for another 48 hrs. The resulting crystalline product (3.02 g, m. p. 122–131 °C) was recrystallized four times with 3 ml *i*-PrOH for each gram of salt to give enantiomerically pure salt (1.32 g) of m. p. 131–133 °C and $[\alpha]_D = +24.9$ ($c = 0.8$, MeOH). The corresponding free base **12** (0.75 g, 35%) was an oil with $[\alpha]_D = +70.10$ ($c = 0.8$).

(\pm)-13: From MeOH/Et₂O 21.88 g (72%) pure (\pm)-13. HCl, m. p. 189–192 °C (decomp.).

Anal. for $C_{13}H_{13}ClFNO$ (253.57) calc'd.: C 61.54; H 5.17%
found: C 61.74; H 4.99%

(+)-(S)-13: From a solution of 4.34 g (\pm)-13 and 7.72 g (—)-(2R,3R)-O,O'-ditolyl tartaric acid in 20 ml hot *i*-PrOH after slowly cooling and standing for 24 hrs at room temperature 7.79 g salt was collected and subjected to four additional recrystallizations from 0.5 ml *i*-PrOH for each gram of salt. The resulting optically pure salt (4.25 g) of m.p. 164–167 °C and $[\alpha]_D = -77.2$ ($c = 0.9$, MeOH) was converted into the corresponding base 13 (1.62 g, 72%): oil, $[\alpha]_D = +70.60$ ($c = 0.6$).

(\pm)-17: By boiling of a benzene solution (75 ml) of 15.00 g (75 mmol) 4-bromoacetophenone, 4.65 g (75 mmol) dry ethylene glycol and 80 mg *p*-toluenesulfonic acid according to ref. 18 13.30 g (73%) of 2-(4-bromophenyl)-2-methyl-1,3-dioxolan of m.p. 38–40 °C (lit. 18 m.p. 44–45 °C) were obtained. After heating of 10.59 g of the latter with 1.80 g magnesium in 45 ml dry THF for 1 h a solution of 3.63 g 2-acetylpyridine in 15 ml THF was slowly added dropwise at 40 °C. The reaction mixture was refluxed for another hour and allowed to cool to room temperature. Hydrolysis, extraction with 5% HCl, neutralization of the acid layer by diluted ammonia, and extraction with chloroform afforded crude (\pm)-17. It was chromatographed over silicagel with Et_2O /hexane (1:4) and recrystallized from EtOAc/light petroleum: 3.03 g (42%) of m.p. 85–86 °C.

Anal. for $C_{15}H_{15}NO_2$ (241.14) calc'd.: C 74.66; H 6.27; N 5.81%
found: C 74.59; H 6.31; N 5.78%

(+)-(S)-17: From the solution of 3.08 g of an equimolar mixture of (\pm)-17 and (—)-(2S,3S)-tartaric acid in 8 ml *i*-PrOH after standing for four days at room temperature 1.02 g crystalline product of m.p. 104–121 °C was collected. Three recrystallizations from 7 ml *i*-PrOH for each gram of salt afforded 0.53 g optically pure salt of m.p. 130.5–131 °C and $[\alpha]_D = -4.2$ ($c = 0.9$, MeOH). The corresponding free base 17 (0.28 g, 30%) had m.p. 92–94 °C and $[\alpha]_D = +61.8$ ($c = 1.0$).

(\pm)-18: After recrystallization from MeOH/ Et_2O of the crude hydrochloride, prepared according to procedure A, 24.98 g (82%) pure (\pm)-18. HCl of m.p. 215–217 °C (decomp.) was obtained.

Anal. for $C_{13}H_{13}ClFNO$ (253.57) calc'd.: C 61.54; H 5.17%
found: C 61.82; H 5.46%

(—)-(R)-18: 4.60 g of an equimolar mixture of (\pm)-18 and (—)-(2R,3R)-O,O'-di-*p*-tolyl tartaric acid were subjected to six recrystallizations from *i*-PrOH by changing stepwise the relation [solvent (ml)/salt(g)] from 2:1 to 5:1. The optically pure salt obtained (0.36 g) has m.p. 126–128 °C and $[\alpha]_D = -79.1$ ($c = 0.6$, MeOH). The corresponding free base (0.12 g, 14%) has m.p. 68–70 °C and $[\alpha]_D = -25.6$ ($c = 0.5$).

(\pm)-21: The crude reaction product was chromatographed over silicagel with chloroform and recrystallized from chloroform/petroleum ether: 18.86 g (63%) pure (\pm)-21 of m.p. 131–133 °C (lit. 17 m.p. 130–131 °C).

(+)-21: From a hot solution of 7.47 g (\pm)-21 and 4.50 g (+)-(2R,3R)-tartaric acid in 100 ml *i*-PrOH after slowly cooling to room temperature and standing for 48 hrs 8.37 g crystalline product was collected and subjected to seven more recrystallizations from 8 ml *i*-PrOH for each gram of salt to give 1.35 g optically pure salt with m.p. 174–176 °C (decomp.) and $[\alpha]_D = +50.9$ ($c = 0.9$, MeOH). The free base 21 (0.77 g, 21%) had m.p. 160–161 °C and $[\alpha]_D = +93.7$ ($c = 0.9$).

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SAŽETAK

Sinteza optički aktivnih α -piridil-karbinola i određivanje apsolutne konfiguracije pomoću CD spektara njihovih *in situ* kompleksa sa $[\text{Mo}_2(\text{OAc})_4]$

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Sintetizirana su četiri nova α -piridil-aril-karbinola, i po prvi puta je, koristeći standardni postupak, razlučeno dvanaest racemata tog tipa. Iz pozitivnog CD kupleta kompleksa između (*S*)-1 i 23 može se zaključiti da ovaj u preferiranoj konformaciji posjeduje antiperiplanarni raspored strukturne jedinice H—C(OH, Ph)—C₂(Py)—N. Iz CD spektara iznad 230 nm ovog i sedam drugih spojeva poznate apsolutne konfiguracije u prisutnosti 23, izvedena je korelacija s njihovom steričkom građom, koja je zatim primjenjena na određivanje apsolutne konfiguracije drugih četrnaest α -piridil karbinola: za (*R*)-konfiguraciju karakteristične su negativne CD vrpce između 500—510 nm (nekad opazive samo kao »rame«), i između 408—470 nm, dok se između 335—380 nm javlja jedan pozitivni Cottonov efekt. Još jedan Cottonov efekt javlja se ispod 320 nm, koji većinom ima pozitivan predznak za sekundarne, a negativan za tercijarne karbinole spomenutog apsolutnog smjera kiralnosti.