Products from the Reaction of Pyrrolimines and Chlordiphenylphosphine

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Abstract

The reaction of pyrrolimines **1** and **4** and chlordiphenylphosphine on exclusion of air and moisture leads to phosphination at the pyrrol nitrogen atom, giving products of type **2**. On admission of air and moisture, however, addition of $OP(C_6H_5)_2$ to the C atom and of H to the N atom of the C=N bond in **1** and **4** takes place, producing **3** and **5**. The carbon atoms of the 3-aminomethylpinane skeleton in **4** and **5** and their diastereotopic splitting are assigned in the ^{13}C NMR spectra. According to an X-ray crystal structure analysis, **6** contains an additional $P(C_6H_5)_2$ substituent at the pyrrol nitrogen atom.

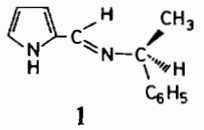
Introduction

The optically-active pyrrolimine **1** can be prepared from 2-pyrrolcarbaldehyde and (S)-(−)-1-phenylethylamine. Rh complexes containing deprotonated **1** as a ligand are efficient catalysts for the enantioselective hydrosilylation of acetophenone with diphenylsilane [1, 2]. The $P(C_6H_5)_2$ derivative **2** of imine **1** has been used as a ligand in Rh catalysts for the same reaction [3]. **2** has been obtained from the reaction of **1** with $ClP(C_6H_5)_2/NEt_3$ with rigorous exclusion of oxygen and moisture [3].

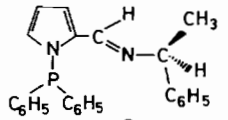
Synthesis and Characterization of 3, 5 and 6

Without these precautions, however, the reaction of **1** with $ClP(C_6H_5)_2/NEt_3$ takes a completely different course. An $OP(C_6H_5)_2$ group adds to the C and an H atom to the N of the C=N double bond in **1** to give **3** [4].

In the formation of **3** a new asymmetric center arises at the C atom in the α-position of the pyrrol ring. Therefore, two diastereomers **a** and **b** are possible for **3**, which differ only in the configuration of the new asymmetric center. After crystallization from ether/petrolether 4:1 the phosphine oxide **3** is obtained as a colorless solid in a diastereomer ratio of **3a**:**3b** = 79:21.



1



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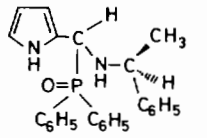
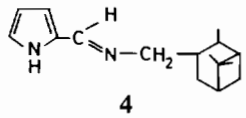


3a, b



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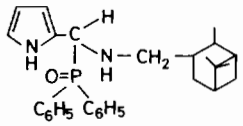
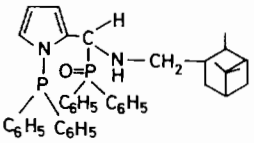


5a, b



6a, b

In the analogous reaction of imine **4** with $ClP(C_6H_5)_2/NEt_3$ a mixture of the corresponding phosphine oxide **5a, b** and compound **6a, b** is obtained, which contains an additional $P(C_6H_5)_2$ substituent at the pyrrol nitrogen [4]. Both compounds form pairs of diastereomers. Recrystallization from ether/petrolether 4:1 gives a product ratio of **5a, b**:**6a, b** = 88:12. After repeated recrystallizations the mixture contains crystals of **6** suitable for an X-ray structure analysis, which established the structure of **6** [5]. The characterization of compounds **3a, b**, **5a, b** and **6a, b** was carried out by ^1H, ^{13}C, ^{31}P NMR spectroscopy, details of which are given below.

The ^1H NMR spectrum of **3a, b** contains characteristic resonances of the two NH protons, the amine–NH at 2.42 and the pyrrol–NH at 9.38 ppm. The ^1H signal of the CH group in α-position of the pyrrol ring, due to the phosphination, is shifted to 4.68 ppm (^{31}P coupling 9.3 Hz). Both the doublet and the quartet of the $CH(CH_3)$ group show diastereotopic splitting (Table I), the quartet being most suitable for the determination of the diastereomer ratio.

In Fig. 1B the ^{13}C NMR spectrum of the pinane carbon atoms of compound **5a, b** is depicted.** For

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**(−)-3-Aminomethylpinane, a product of BASF AG, was used for the synthesis of imine 4.

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TABLE I. ^{13}C-NMR-Parameter of 4 and 5a, b ($CDCl_3$; i-TMS)[b]

	pinane-$\underline{C}H_3$	pinane-$\underline{C}H_2$	pinane-$\underline{C}H$	pinane-$\underline{C}(CH_3)_2$	$N\underline{C}H_2$	pyrrol-$\underline{C}$	other $\underline{C}$
4	21.72(s)	33.70(3)	32.58(s)	32.01(s)	70.04(s)	109.42(s)	$H\underline{C}$=N:
	22.92(s)	40.88(s)	37.54(s)			114.11(s)	151.88(s)
	28.02(s)		41.73(s)			121.78(s)	
			48.09(s)			130.28(s)	
5a, b	21.72(s)	33.34(s)	32.66(s)	38.73(s)	58.29(d)	107.06(s)	$\underline{C}$HP:
	22.09(s)[a]	33.44(s)[a]	33.10(s)[a]		$^3J_{PC}$ 13.5	108.30(s)	57.08(d)
	22.86(s)	40.80(s)	36.29(s)		58.42(d)[a]	108.15(d)	$^1J_{PC}$ 85.7
	22.94(s)[a]	41.37(s)[a]	37.09(s)[a]		$^3J_{PC}$ 13.5	$^3J_{PC}$ 7.5	57.94(d)[a]
	22.97(s)		41.50(s)			108.50(d)[a]	$^1J_{PC}$ 84.5
			41.66(s)[a]			$^3J_{PC}$ 8.5	phenyl-$\underline{C}$:
			47.80(s)			118.54(s)	125.41–133.70
			47.99(s)[a]				

[a] Diastereotopic splitting. [b] δ-values in ppm, coupling constants J in Hz, Bruker WH 90.

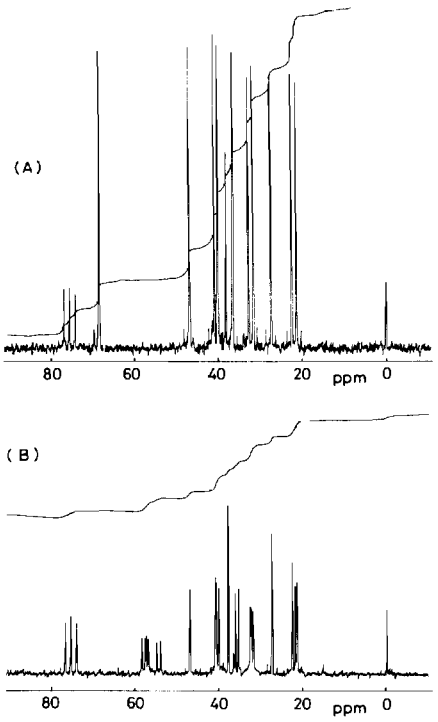

Fig. 1. ^{13}C NMR spectra of 4 (A) and 5a, b (B) (pinane region). $CDCl_3$, i-TMS, Bruker WH 90.

the interpretation of this spectrum a ^{13}C NMR spectrum of the corresponding imine **4** was measured (Fig. 1A). The comparison of these two spectra allows an unequivocal assignment of the 10 carbon atoms of the pinane skeleton (Table I). The spectrum of compound **5a, b** shows diastereotopic splitting for most of the CH_3-, CH_2-, CH-groups of the pinane portion of the molecule, and also for one of the pyrrol C atoms (Table I). The ^{13}C spectra of **4** and **5a, b** exhibit remarkable differences in the chemical shifts of the C-atoms in α-position to the pyrrol ring. In compound **4** the α-C appears at 151.88 ppm, a value normal for an azomethine C atom, whereas in compound **5a, b** it is shifted to high field (57.08 ppm) showing phosphorus coupling and diastereotopic splitting (Table I).

The ^{31}P signal of **3a, b** is a singlet at 33.6 ppm; that of **5a, b**, however, shows the diastereotopic splitting with two singlets at 33.1 and 33.3 ppm. In **6a, b** the two phosphorus atoms cause a P–P-coupling of $^4J_{PP}$ = 2.5 Hz. For one of the ^{31}P signals there is a diastereotopic splitting. On the basis of the differences in the chemical shifts of the ^{31}P signals the diastereomer ratio for both **5a/5b** and **6a/6b** can be roughly estimated to be close to 1:1.

Experimental

3. 2.59 g (12.9 mmol) **1** and 1.30 g (12.9 mmol) NEt_3 were dissolved in 200 ml of ether at −40 °C. 2.84 g (12.9 mmol) $ClP(C_6H_5)_2$ in 50 ml of ether were added slowly during 30 min (admission of air). A white precipitate formed. The reaction mixture was slowly warmed to room temperature and heated to reflux for 2 h. Filtration through 5 cm SiO_2 and evaporation of the solvent gave a yellow, oily product which was purified by SiO_2-chromatography with ether/petrol ether 4:1. After crystallization from ether/petrol ether 4:1 the phosphine oxide **3a, b** was obtained as a colourless solid (diastereomer ratio **a**:**b** = 79:21).

Yield: 2.9 g (57%). M.p.: 157–160 °C. IR: ν(NH) 3230, ν(PO) 1174 cm^{-1} (KBr). ^{1}H NMR ($CDCl_3$, i-TMS, 250 MHz Bruker WM 250): $CH(C\underline{H}_3)$ 1.19(d) $^3J_{HH}$ 7.0; 1.20(d) $^3J_{HH}$ 6.5; $C\underline{H}(CH_3)$ 3.47(q) $^3J_{HH}$ 7.0, 3.69(q) $^3J_{HH}$ 6.3; $C\underline{H}P$ 4.68(t) $^3J_{HH}$ 9.3, $^2J_{PH}$ 10.1; pyrrol–H 5.75(m), 5.98(m), 6.65(m); phenyl–

H 7.12–7.81(m); pyrrol–NH 9.38(m); amine–NH 2.42(m). ^{31}P NMR ($CDCl_3/CHCl_3$ 1:3, ext. 85% H_3PO_4, 101.25 MHz Bruker WM 250): $C\underline{P}O(C_6H_5)_2$ 33.6(s).

5, 6. The analogous reaction of imine **4** with $ClP(C_6H_5)_2/NEt_3$ and work-up gave a mixture of **5a, b** and **6a, b** after crystallization from ether/petrolether in a ratio of 88:12.

5a, b. Yield: 3.5 g (61%). M.p.: 151–153 °C. IR: ν(NH) 3308, 3225, ν(PO) 1187 cm^{-1} (KBr). ^1H NMR ($CDCl_3$, i-TMS, 250 MHz Bruker WM 250): pinane–H 0.59–2.80(m); $C\underline{H}P$ 4.53(t) $^3J_{HH}$ 5.9, $^2J_{PN}$ 9.0; pyrrol–H 5.82(m), 6.02(m), 6.69(m); phenyl–H 7.25–7.87(m); pyrrol–NH 9.51(m). ^{31}P NMR ($CDCl_3/CHCl_3$ 1:3, ext. 85% H_3PO_4, 101.25 MHz Bruker WM 250): 33.1(s), 33.3(s).

6a, b. Yield: 0.5 g (8%). ^{31}P NMR ($CDCl_3/CHCl_3$ 1:3, ext. 85% H_3PO_4, 101.25 MHz Bruker WM 250): 31.1(d), $^4J_{PP}$ 2.5, 31.0(d), $^4J_{PP}$ 2.5, 33.8(s).

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