

*Journal of Organometallic Chemistry*, 71 (1974) 153–158  
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## ADDUCTS OF 4-SUBSTITUTED PYRIDINES WITH GRIGNARD REAGENTS

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(Received November 1st, 1973)

### Summary

Various adducts of the formula (4-substituted pyridine)<sub>2</sub> MgBr<sub>2</sub> have been synthesized by treatment of a 4-substituted pyridine with organomagnesium bromides. The properties of the adducts have been studied through their NMR and IR spectra.

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### Introduction

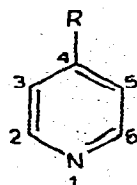
In an earlier paper [1] we described adducts of the formula (4-ROPy)<sub>2</sub> MgBr<sub>2</sub>. Subsequently [2], we discussed the vibrational spectra of  $\gamma$ -picoline, ( $\gamma$ -picoline)<sub>2</sub> MgBr<sub>2</sub>, ( $\gamma$ -picoline)<sub>4</sub> MgBr<sub>2</sub> and ( $\gamma$ -picoline)<sub>4</sub> MgI<sub>2</sub>. In the present paper the adducts formed by the reaction of organomagnesium bromides and 4-alkyl- and -thioalkyl-pyridines are described. Some previously reported data are included for comparison.

### Results and discussion

Mixing equimolecular amounts of a 4-substituted pyridine (I–VIII) and a Grignard reagent gave white amorphous precipitates of the formula (4-substituted pyridine)<sub>2</sub> MgBr<sub>2</sub>. Although we used three different Grignard reagents: ethyl-, allyl- and phenyl-magnesium bromide, we always obtained the same adduct, the structure of which depended only on the pyridine derivative, as shown by the analytical data and by NMR and IR spectroscopy. (The analytical data are given in Table 1.) It is noteworthy that the adduct (4-BzPy)<sub>2</sub> MgBr<sub>2</sub> could not be prepared. All attempts resulted in impure coloured products with analytical data corresponding to a formula between (4-BzPy)<sub>3</sub> MgBr<sub>2</sub> and (4-BzPy)<sub>4</sub> MgBr<sub>2</sub>.

TABLE 1  
ANALYTICAL DATA FOR THE ADDUCTS

Adduct	Analysis found (calcd.) (%)	
	Mg	Br
(4-MePy) <sub>2</sub> MgBr <sub>2</sub>	6.72 (6.563)	42.86 (43.147)
(4-EtPy) <sub>2</sub> MgBr <sub>2</sub>	6.15 (6.101)	39.99 (40.108)
(4-PhPy) <sub>2</sub> MgBr <sub>2</sub>	5.04 (4.916)	32.25 (32.316)
(4-MeSPy) <sub>2</sub> MgBr <sub>2</sub>	5.80 (5.595)	36.25 (36.780)
(4-EtSPy) <sub>2</sub> MgBr <sub>2</sub>	5.41 (5.255)	34.11 (34.549)
(4-BzSPy) <sub>2</sub> MgBr <sub>2</sub>	4.29 (4.143)	27.61 (27.239)
(4-PhSPy) <sub>2</sub> MgBr <sub>2</sub>	4.50 (4.351)	28.60 (28.607)



- (I): R = CH<sub>3</sub>;                      (V): R = SCH<sub>3</sub>;  
 (II): R = CH<sub>2</sub>CH<sub>3</sub>;               (VI): R = SCH<sub>2</sub>CH<sub>3</sub>;  
 (III): R = CH<sub>2</sub>Ph;               (VII): R = SCH<sub>2</sub>Ph;  
 (IV): R = Ph;                       (VIII): R = SPh.

### NMR spectra

The NMR resonances of the pyridines (I–VIII) and the corresponding adducts are listed in Table 2. Although the fine structure of the spectrum of a pyridine derivative does not differ from that of its adduct, the positions of the peaks do, especially the resonance patterns of the ring protons. These appear as two slightly perturbed doublets, as expected for the appropriate A<sub>2</sub>B<sub>2</sub> system.

TABLE 2  
COMPARISON OF CHARACTERISTIC NMR RESONANCES FOR SOME 4-SUBSTITUTED PYRIDINES AND THE CORRESPONDING ADDUCTS<sup>a</sup>

Compound	H <sub>2</sub> , H <sub>6</sub> <sup>b</sup>	H <sub>3</sub> , H <sub>5</sub> <sup>b</sup>	R
4-MePy	1.61 d	2.86 d	—CH <sub>3</sub> : 7.68 s
Adduct	1.39 d	2.68 d	7.60 s
4-EtPy	1.58 d	2.83 d	—CH <sub>2</sub> —: 7.38 q —CH <sub>3</sub> : 8.83 t
Adduct	1.34 d	2.68 d	7.32 q 8.83 t
4-PhPy	1.41 d	2.43 d	—Ph: too broad to assign
Adduct	1.20 d	2.27 d	
4-MeSPy	1.67 d	2.86 d	—CH <sub>3</sub> : 7.55 s
Adduct	1.48 d	2.73 d	7.48 s
4-EtSPy	1.68 d	2.85 d	—CH <sub>2</sub> —: 6.99 q —CH <sub>3</sub> : 8.70 t
Adduct	1.47 d	2.72 d	6.94 q 8.68 t
4-BzSPy	1.68 d	2.81 d	—CH <sub>2</sub> —: 5.74 s —Ph: 2.66 m
Adduct	(?) 1.55 d	2.66 d	5.68 s 2.64 m
4-PhSPy	1.71 d	3.06 d	—Ph: 2.49 m
Adduct	1.51 d	2.93 d	2.44 m

<sup>a</sup> The data are in  $\tau$ -values; s, singlet, d, doublet, t, triplet, q, quadruplet, m, multiplet. <sup>b</sup>  $J_{2,3}$  and  $J_{5,6}$  have the value of 5.3 Hz for all pyridines and adducts.

The doublet of the  $H_2-H_6$  resonance shows, for a pyridine derivative relative to its adduct, a mean deshielding of 21 Hz, and the  $H_3-H_5$  resonance one of 14 Hz. For the protons of the R groups the deshielding is very small. The unexpected shifts of  $(4\text{-BzSPy})_2\text{MgBr}_2$  may be due to the extremely low solubility of this adduct in acetonitrile.

### IR spectra

Various systems of numbering are in use for describing the fundamental modes of monosubstituted benzenes and pyridines; the lettering proposed by Spinner [3] and already used by Cook [4] has also been applied to describe the various modes of vibration.

The characteristic bands for the  $1650-600\text{ cm}^{-1}$  region are given in Table 3. Table 4 gives the bands in the low frequency region ( $600-200\text{ cm}^{-1}$ ). The shifts and intensity variations of the four characteristic ring vibrations ( $\nu_{8a}$ ,  $\nu_{8b}$ ,  $\nu_{19a}$ ,  $\nu_{19b}$ ) are in good agreement with the results obtained for the 4-alkoxy pyridines [1]. The shift of about  $20\text{ cm}^{-1}$  for the  $\nu_{8a}$  band, indicates that strong complexes have been formed [4]; the strength of the formation is comparable for the 4-RO-pyridines, 4-RS-pyridines and the 4-R-pyridines.

The  $\nu_{12}$  unsymmetric and the totally symmetric  $\nu_1$  ring breathing modes are situated in the region of  $1000\text{ cm}^{-1}$ . The band in the  $980\text{ cm}^{-1}$  region appears as very strong in the Raman spectrum, and is assigned to the  $\nu_1$  mode [2, 5]. Wong [6] stated that the intensity of the  $\nu_{12}$  mode is affected by the substituents on the 4-position of the pyridine ring. From the data of Table 3, we can conclude that this band appears as very weak in the region  $1070-1020\text{ cm}^{-1}$ .

The  $\nu_{12}$  vibration shifts considerably and becomes more intense on complex formation. The strong back-donation of the  $d$ -electrons of the  $\text{Cu}^{\text{II}}$  and  $\text{Zn}^{\text{II}}$  complexes to the ring system causes an increased  $\nu_{12}$  frequency compared with that in the original pyridine derivative.

The frequency of  $\nu_{12}$  of the hydrochlorides decreases, since no back-bonding is possible [6].  $\text{Mg}^{\text{II}}$  is a hard acid and has no  $d$ -electrons and thus the shift of the  $\nu_{12}$  band is expected to decrease.

The  $\nu_1$  band increases on complex formation [3] so the strong band arising in the  $1020\text{ cm}^{-1}$  region for the complexes can be regarded as composed of the  $\nu_{12}$  and  $\nu_1$  vibrations. The  $\nu_{11}$  and  $\nu_4$  modes hardly shift on complex formation. In the region of the  $\nu_4$  mode a band of medium intensity has been observed for the 4-RS-pyridines and possibly involves some  $\nu(\text{C-S})$  mode.

The splitting of the bands appearing in the  $700\text{ cm}^{-1}$  region can be due to the geometry of the complex. The two low-frequency ring modes are situated in the  $500\text{ cm}^{-1}$  range and are in agreement with the literature data found at higher frequency for the complexes [8]. The data observed for the  $500\text{ cm}^{-1}$  region are given in Table 4.  $\nu(\text{Mg-N})$  can be unambiguously assigned to the strong and medium-strong bands appearing at  $290$  and  $240\text{ cm}^{-1}$ . The position of these bands suggests a strong complex, since the metal-nitrogen stretching frequency gives a measure of the coordination strength for the complexes of pyridine derivatives [7].

The Mg-Br frequencies could not be assigned, and probably occur around and below  $200\text{ cm}^{-1}$ .

TABLE 3  
CHARACTERISTIC IR FREQUENCIES (in  $\text{cm}^{-1}$ ) OF SOME 4-SUBSTITUTED PYRIDINES AND THE CORRESPONDING ADDUCTS IN THE REGION  
1650-600  $\text{cm}^{-1}$

Description <sup>a</sup>	$\nu_{8a}$	$\nu_{8b}$	$\nu_{19a}$	$\nu_{19b}$	$\nu_{12}$	$\nu_1$	$\nu_{11}$	$\nu_4$	$\nu_{(R-S-X)}$
4-MePy	1602 vs	1556 s	1494 s	1409 s	1042 ms	991 s	800 s	724 m	
Adduct	1628 vs	1557 mw	1506 s	1427 s	1018 s		308 s	722 s	
4-EtPy	1602 vs	1560 ms	1495 m	1414 s	1069 w	990 m	815 s	721 m	
Adduct	1617 vs	1554 m	1500 ms	1423 vs	1018 m		820 s	723 m	
4-PhPy	1592 vs	1548 ms	1484 s	1409 vs	1069 w		823 s	732 s	
Adduct	1613 vs	1548 m	1488 vs	{ 1424 s 1417 s }	1011 s		824 s	{ 728 s 754 s }	
4-MeSPy	1578 s	1542 m	1483 s	1409 s	1073 w	986 w	794 s	728 s	694 s
Adduct	1598 s	1539 m	1491 s	1422 s	1014 m		798 s	720 s, 735 s	709 s
4-EtSPy	1576 s	1542 m	1483 s	1408 ms	{ 1063 w 1049 w }	970 m	795 s	719 m	707 s
Adduct	1599 s	1536 m	1491 s	1424 s	1012 m		798 s	727 s	719 (sh)
4-BzSPy	1575 s	1535 m	1481 m	1401 m	{ 1063 w 1022 m }	874 m	793 s	712 s	692 m
Adduct	1599 s	1540 m	1488 s	1421 s	1017 s		798 s	718 s, 708 s	683 s
4-PhSPy	1573 s	1543 m	1477 s	1408 s	{ 1065 m 1024 m }	{ 997 w 984 w }	798 s	708 (sh), 702 m	687 s
Adduct	1602 s	{ 1558 (sh) 1536 mw }	1486 s	1421 s	1012 s		789 s	749 s, 716 s	689 s

<sup>a</sup> Ref. 3.

TABLE 4

CHARACTERISTIC IR FREQUENCIES (IN  $\text{cm}^{-1}$ ) OF SOME 4-SUBSTITUTED PYRIDINES AND THE CORRESPONDING ADDUCTS IN THE LOW-FREQUENCY REGION

4-MePy	514 s, 485 vs, 401 vvw, 385 vw, 347 vw
Adduct	540 s, 494 vs, 362 w, 300 (sh), 285 vs, 243 mw
4-EtPy	563 s, 490 ms
Adduct	557 ms, 482 vs, 407 mw, 282 s, 240 (sh)
4-PhPy	556 m, 487 mw, 368 vw, 260 vw
Adduct	556 s, 486 s, 381 m, 366 m, 294 m, 287 ms, 259 s
4-MeSPy	493 s, 276 vw
Adduct	491 vs, 444 w, 361 mw, 286 s, 229 m
4-EtSPy	494 s, 300 vw
Adduct	490 vs, 472 w, 345 mw, 318 m, 269 s, 224 m
4-BzSPy	493 s, 475 m, 370 vvw, 352 vvw, 298 vw, 242 vw
Adduct	489 vs, 473 m, 355 w, 330 mw, 300 m, 285 m, 275 (sh), 224 ms
4-PhSPy	515 s, 433 s, 439 vw, 280 vvw
Adduct	513 s, 487 vs, 450 m, 303 ms, 286 vvw, 272 ms, 243 vw, 219 ms

## Conclusion

The shifts in the NMR and IR spectra and the IR intensity variations of some characteristic fundamentals of the aromatic ring and the position of the magnesium—nitrogen stretching frequency indicate strong bonding in the complex. Some shifts in the IR are not in agreement with the literature data obtained for other complexes, but they can be explained by the absence of back-donation in magnesium complexes.

## Experimental

### Synthesis of the pyridines

The compounds 4-MeSPy (V) [9] and 4-EtSPy (VI) [10] were made from 4-thiopyridone and methyl and ethyl iodide respectively. 4-PhSPy (VIII) was synthesized by reaction of *N*-pyridyl-4-pyridinium chloride hydrochloride with thiophenol [11]. Saturation with  $\text{H}_2\text{S}$  of a solution of *N*-pyridyl-4-pyridinium chloride hydrochloride in pyridine, and subsequent reaction with benzyl chloride gave 4-BzSPy (VII) [12].

*N*-Pyridyl-4-pyridinium chloride hydrochloride, 4-thiopyridone and pyridines (I), (II), (III) and (IV) were all purchased from Aldrich Europe Co. Pyridines (I), (II) and (III) were distilled over  $\text{CaH}_2$  while pyridine (IV) was recrystallized from diethyl ether before use.

### Synthesis of the adducts

The adducts were prepared as previously described [1]. However, we should emphasize that use of an excess of the pyridine derivative led to adducts of the formula  $(4\text{-RPy})_4\text{MgBr}_2$  [2]. The analyses and measurements of spectra were carried out as previously described [1].

## Acknowledgements

We thank the Fonds voor Kollektief Fundamenteel Onderzoek for financial help, and J. Aerts, A. De Beleyr, Y. Luyten and J. Schrooten for technical assistance.

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