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ADDUCTS OF 4-SUBSTITUTED PYRIDINES WITH GRIGNARD REAGENTS

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Summary

Various adducts of the formula (4-substituted pyridine)$_2$ MgBr$_2$ 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.

Introduction

In an earlier paper [1] we described adducts of the formula $(4\text{-ROPy})_2\text{-}$ $MgBr_2$. Subsequently [2], we discussed the vibrational spectra of γ-picoline, (γ-picoline)$_2$ MgBr$_2$, (γ-picoline)$_4$ MgBr$_2$ and (γ-picoline)$_4$ MgI$_2$. 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.

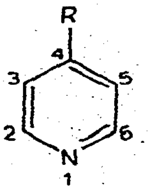
Results and discussion

Mixing equimolecular amounts of a 4-substituted pyridine (I—VIII) and a Grignard reagent gave white amorphous precipitates of the formula (4-substituted pyridine)$_2$ MgBr$_2$. 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)$_2$ MgBr$_2$ could not be prepared. All attempts resulted in impure coloured products with analytical data corresponding to a formula between (4-BzPy)$_3$ MgBr$_2$ and (4-BzPy)$_4$ MgBr$_2$.

TABLE 1

ANALYTICAL DATA FOR THE ADDUCTS

Adduct	Analysis found (calcd.) (%)	
	Mg	Br
$(4\text{-MePy})_2MgBr_2$	6.72	42.86
	(6.563)	(43.147)
$(4\text{-EtPy})_2MgBr_2$	6.15	39.99
	(6.101)	(40.108)
$(4\text{-PhPy})_2MgBr_2$	5.04	32.25
	(4.916)	(32.316)
$(4\text{-MeSPy})_2MgBr_2$	5.80	36.25
	(5.595)	(36.780)
$(4\text{-EtSPy})_2MgBr_2$	5.41	34.11
	(5.255)	(34.549)
$(4\text{-BzSPy})_2MgBr_2$	4.29	27.61
	(4.143)	(27.239)
$(4\text{-PhSPy})_2MgBr_2$	4.50	28.60
	(4.351)	(28.607)



(I): $R = CH_3$;
(II): $R = CH_2CH_3$;
(III): $R = CH_2Ph$;
(IV): $R = Ph$;
(V): $R = SCH_3$;
(VI): $R = SCH_2CH_3$;
(VII): $R = SCH_2Ph$;
(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_2B_2 system.

TABLE 2

COMPARISON OF CHARACTERISTIC NMR RESONANCES FOR SOME 4-SUBSTITUTED PYRIDINES AND THE CORRESPONDING ADDUCTS [a]

Compound	H_2, H_6 [b]	H_3, H_5 [b]	R	
4-MePy	1.61 d	2.86 d	$-CH_3$: 7.68 s	
Adduct	1.39 d	2.68 d	7.60 s	
4-EtPy	1.58 d	2.83 d	$-CH_2-$: 7.38 q	$-CH_3$: 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	$-CH_3$: 7.55 s	
Adduct	1.48 d	2.73 d	7.48 s	
4-EtSPy	1.68 d	2.85 d	$-CH_2-$: 6.99 q	$-CH_3$: 8.70 t
Adduct	1.47 d	2.72 d	6.94 q	8.68 t
4-BzSPy	1.68 d	2.81 d	$-CH_2-$: 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	

[a] The data are in τ-values; s, singlet, d, doublet, t, triplet, q, quadruplet, m, multiplet. [b] $J_{2,3}$ 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 $(4\text{-BzSPy})_2MgBr_2$ 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 cm^{-1} region are given in Table 3. Table 4 gives the bands in the low frequency region (600—200 cm^{-1}). The shifts and intensity variations of the four characteristic ring vibrations (ν_{8a}, ν_{8b}, ν_{19a}, ν_{19b}) are in good agreement with the results obtained for the 4-alkoxypyridines [1]. The shift of about 20 cm^{-1} for the ν_{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 ν_{12} unsymmetric and the totally symmetric ν_1 ring breathing modes are situated in the region of 1000 cm^{-1}. The band in the 980 cm^{-1} region appears as very strong in the Raman spectrum, and is assigned to the ν_1 mode [2, 5]. Wong [6] stated that the intensity of the ν_{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 cm^{-1}.

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

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

The ν_1 band increases on complex formation [3] so the strong band arising in the 1020 cm^{-1} region for the complexes can be regarded as composed of the ν_{12} and ν_1 vibrations. The ν_{11} and ν_4 modes hardly shift on complex formation. In the region of the ν_4 mode a band of medium intensity has been observed for the 4-RS-pyridines and possibly involves some ν(C—S) mode.

The splitting of the bands appearing in the 700 cm^{-1} region can be due to the geometry of the complex. The two low-frequency ring modes are situated in the 500 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 cm^{-1} region are given in Table 4. ν(Mg—N) can be unambigously assigned to the strong and medium-strong bands appearing at 290 and 240 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 cm^{-1}.

TABLE 3

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

Description [a]	ν_{8a}	ν_{8b}	ν_{19a}	ν_{19b}	ν_{12}	ν_1	ν_{11}	ν_4	$\nu_{(R-S-X)}$
4-MePy	1602 vs	1556 s	1494 s	1409 s	1042 ms	991 s	800 s	724 m	
Adduct	1623 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 m	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	1068 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	974 m	793 s	712 s	692 m
Adduct	1599 s	1540 m	1488 s	1421 s	1017 s		798 s	718 s, 708 s	693 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

[a] Ref. 3.

TABLE 4

CHARACTERISTIC IR FREQUENCIES (IN 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, 483 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 H_2S 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 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 $(4\text{-RPy})_4MgBr_2$ [2]. The analyses and measurements of spectra were carried out as previously described [1].

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