Acid-Induced Dimerization Reactions of *N*-(Diphenylphosphinyl)-2-propenimines Leading to Pyridine Derivatives

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(Received April 6, 1991)

Synopsis. Treatment of *N*-(diphenylphosphinyl)-3-aryl-1-phenyl-2-propenimines with *p*-toluenesulfonic acid in heated xylene provided 4-aryl-2,6-diphenylpyridines and 4-aryl-3-arylmethyl-2,6-diphenylpyridines via an unprecedented dimerization reaction of the 2-propenimine.

Previously, we described on the reactions of the *N*-phosphinyl-1-azaallyl anions, generated from the corresponding *N*-phosphinyl imine and enamine, with α,β-unsaturated carbonyl compounds[1] or aromatic aldehydes[2] to afford pyridine derivatives. We also reported on the synthesis of *N*-(diphenylphosphinyl)-1,3-diphenyl-2-propenimine (**1a**) and its chemical behavior under basic conditions.[2] In contrast to simple *N*-phosphinyl imines,[3] little is known on the chemical properties of the *N*-phosphinyl-2-propenimines which are supposed to be rather electron-deficient 1-azadienes, except for the aza-Diels–Alder reaction under high pressure.[4] In this note, we describe on the acid-induced reaction of the *N*-phosphinyl-2-propenimines **1a—d** giving pyridine derivatives.

Results and Discussion

The imine **1a** was treated with a catalytic amount of anhydrous *p*-toluenesulfonic acid in refluxing xylene to give 2,4,6-triphenylpyridine (**2a**) and 3-benzyl-2,4,6-triphenylpyridine (**3a**). Similar reactions with the imines **1b** and **1c** provided 3-aryl-2,6-diphenylpyridines (**2b** and **2c**) and 4-aryl-3-arylmethyl-2,6-diphenylpyridines (**3b** and **3c**). In these reactions, the presence

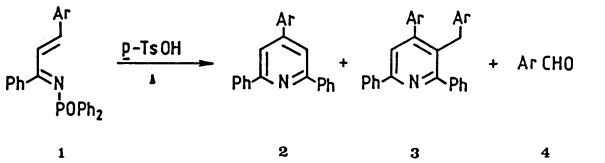

Fig. 1.

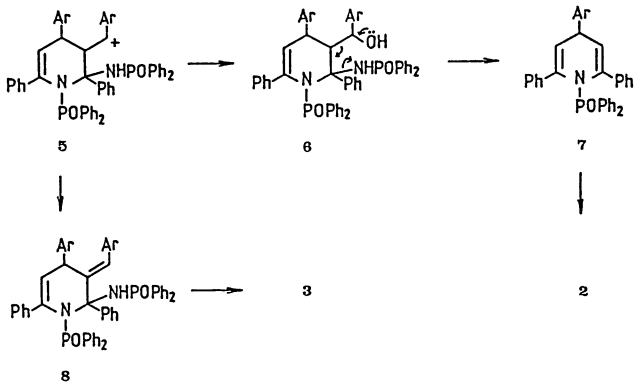

Fig. 2.

Table 1. Yields of the Products by the Acid-Induced Reaction of the 2-Propenimines **1a—d**

Imine	Ar	Yield/%			
		2	(mp; °C)[a]	**3**	**4**
1a	C_6H_5	30	(140—141)	20	GLC[b]
1b	*p*-MeC_6H_4	30	(124—125)	25	GLC[b]
1c	*p*-$MeOC_6H_4$	28	(103—104)	20	GLC[b]
1d	*p*-$Me_2NC_6H_4$	27	(133—134)	0	16[c]

a) Undepressed on admixture with authentic specimens.[2] b) Detected by GLC analyses. c) Isolated as the corresponding 2,4-dinitrophenylhydrazone.

of aromatic aldehydes **4a—c** originating from the 3-aryl substituents of the imines **1a—c** was observed by GLC analysis. The reaction with the *p*-dimethylamino derivative **1d** afforded the pyridine **2d** and *p*-(dimethylamino)benzaldehyde (**4d**), identified as the corresponding 2,4-dinitrophenylhydrazone, but the (arylmethyl)pyridine **3d** was not isolated. The yields of the products are summarized in Table 1.

Some control experiments were conducted to clarify the mechanistic aspect of the present reaction. The use of an acid is essential for the present transformation, because the imine **1a** was quantitatively recovered when heated in xylene in the absence of *p*-toluenesulfonic acid. In the presence of water, the reaction of **1a** with *p*-toluenesulfonic acid gave the pyridine **2a** and the 1,3-diphenyl-2-propenone in 26 and 34% yield, respectively, and the benzylpyridne **3a** was not obtained. Thus, the present transformation can be best explained by the mechanism as shown in Fig. 2. The initial step would be an acid-catalyzed dimerization of the imine **1** giving an intermediate **5**, which would react with a trace amount of water to afford **6**. Elimination of the aldehydes **4** and diphenylphosphinic amide from **6** leads to the pyridines **2** via the dihydropyridines **7**. On the other hand, the formation of the (arylmethyl)pyridines **3** can be ascribed to a sequence of deprotonation, elimination of the phosphorus moieties, and isomerization. Although the reason why the (arylmethyl)pyridine **3d** was not formed in the reaction of **1d** is ambiguous, the *p*-dimethylamino group may stabilize the cationic intermediate **5** and facilitate its reaction with water prior to its deprotonation.

Although two examples of dimerization reactions of 2-propenimines giving pyridines and pyrimidines have been reported,[5,6] the reaction described above seems to be an unprecedented type of dimerization reaction of the 2-propenimines.

Experimental[7]

***N*-(Diphenylphosphinyl)-3-(*p*-methylphenyl)-1-phenyl-2-propenimine (1b):** 60%; mp 139—140 °C (Et_2O); IR (KBr)

1612 (C=N), 1190 (P=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.20 (3H, s), 6.90 (1H, d, J=16.2 Hz), 7.10—7.50 (13H, m), 7.64—7.80 (2H, m), 7.82—8.20 (4H, m), 8.29 (1H, dd, J=16.2, 1.1 Hz); ^{13}C NMR ($CDCl_3$) δ=20.5, 127.5—145.0, 180.2 (d, J_{P-C}=8.5 Hz); ^{31}P NMR ($CDCl_3$) δ=18.8; MS m/z (rel intensity) 421 (M^+, 31), 220 (100). Found: C, 79.72; H, 5.84; N, 3.21%. Calcd for $C_{28}H_{24}NOP$: C, 79.79; H, 5.74; N, 3.32%.

***N*-(Diphenylphosphinyl)-3-(*p*-methoxylphenyl)-1-phenyl-2-propenimine (1c):** 69%; mp 140—141 °C (Et_2O); IR (KBr) 1614 (C=N), 1190 (P=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.81 (3H, s), 6.76—7.08 (3H, m), 7.24—7.58 (11H, m), 7.64—7.80 (2H, m), 7.82—8.10 (4H, m), 8.12 (1H, dd, J=16.0, 1.0 Hz); ^{13}C NMR ($CDCl_3$) δ=54.9, 114.0—148.5, 180.4 (d, J_{P-C}=8.6 Hz); ^{31}P NMR ($CDCl_3$) δ=18.6; MS m/z (rel intensity) 437 (M^+, 19), 249 (100, M^+-POPh_2), 201 (85). Found: C, 76.73; H, 5.40; N, 3.21%. Calcd for $C_{28}H_{24}NO_2P$: C, 76.87; H, 5.53; N, 3.20%.

***N*-(Diphenylphosphinyl)-3-[*p*-(dimethylamino)phenyl]-1-phenyl-2-propenimine (1d):** 61%; mp 186—187 °C (benzene); IR (KBr) 1629 (C=N), 1181 (P=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.88 (6H, s), 6.56 (2H, d, J=8.6 Hz), 6.88 (1H, d, J=15.2 Hz), 7.10—7.48 (11H, m), 7.56—7.73 (2H, m), 7.74—8.18 (5H, m); ^{13}C NMR ($CDCl_3$) δ=39.8, 111.7—151.8, 181.1 (d, J_{P-C} =8.5 Hz); ^{31}P NMR ($CDCl_3$) δ=18.2; MS m/z (rel intensity) 450 (M^+, 19), 249 (100, M^+-POPh_2), 201 (46). Found: C, 76.97; H, 6.12; N, 6.02%. Calcd for $C_{29}H_{27}N_2OP$: C, 77.31; H, 6.04; N, 6.22%.

Acid-Induced Reaction of the 2-Propenimines 1a—d. Hydrated *p*-toluenesulfonic acid (9 mg, 0.05 mmol) was added in xylene (20ml) and water was removed by azeotropic distillation. To the resultant solution was added the imine **1** (0.5 mmol) and the mixture was refluxed for 48 h under nitrogen. The presence of aromatic aldehydes **4a—c** was detected by GLC analysis on 10%-SE30 (90 °C) and 10%-Carbowax (130 °C) columns. The solution was washed with aq $NaHCO_3$ and dried over $MgSO_4$. After removal of the solvent in vacuo, the residue was separated on TLC (silica gel, benzene) to give 4-aryl-2,6-diphenylpyridines **2a—d** and 4-aryl-3-arylmethyl-2,6-diphenylpyridines **3a—c**. In the reaction with **1d**, *p*-(dimethylamino)benzaldehyde **4d** was isolated as the 2,4-dinitrophenylhydrazone. The yields of the products are summarized in Table 1.

3-Benzyl-2,4,6-triphenylpyridine (3a): Mp 142—143 °C (pentane) (lit,[8] 137—138 °C); IR (KBr) 1582, 1536 cm^{-1}; ^1H NMR ($CDCl_3$) δ=4.08 (2H, s), 6.48—6.72 (2H, m), 6.90—7.09 (3H, m), 7.12—7.60 (13H, m), 7.62 (1H, s), 8.02—8.18 (2H, m); MS m/z (rel intensity) 397 (M^+, 100). Found: C, 90.62; H, 6.00; N, 3.35%. Calcd for $C_{30}H_{23}N$: C, 90.64; H, 5.83; N, 3.52%.

4-(*p*-Methylphenyl)-3-[(*p*-methylphenyl)methyl]-2,6-diphenylpyridine (3b): Mp 157—158 °C (pentane); IR (KBr) 1580, 1512 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.21 (3H, s), 2.34 (3H, s), 4.03 (2H, s), 6.55 (2H, d, J=8.1 Hz), 6.90 (2H, d, J=8.1 Hz), 7.13—7.57 (12H, m), 7.61 (1H, s), 7.96—8.20 (2H, m); ^{13}C NMR ($CDCl_3$) δ=21.0, 21.2 34.6, 120.8—152.4, 154.5, 160.4; MS m/z (rel intensity) 425 (M^+, 70), 424 (100), 334 (6), 105 (4). Found: C, 89.97; H, 6.46; N, 3.25%. Calcd for $C_{32}H_{27}N$: C, 90.31.; H, 6.39; N, 3.29%.

4-(*p*-Methoxyphenyl)-3-[(*p*-methoxyphenyl)methyl]-2,6-diphenylpyridine (3c): Mp 168—169 °C (pentane); IR (KBr) 1601, 1512 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.70 (3H, s), 3.80 (3H, s), 4.01 (2H, s), 6.58 (4H, s), 6.87 (2H, d, J=8.9 Hz), 7.17 (2H, d, J=8.9 Hz), 7.18—7.56 (8H, m), 7.61 (1H, s), 8.02—8.16 (2H, m); ^{13}C NMR ($CDCl_3$) δ=34.3, 55.2, 113.6—157.8, 159.4, 160.4; MS m/z (rel intensity) 457 (M^+, 31), 455 (100), 121 (16). Found: C, 83.92; H, 6.07; N, 3.27%. Calcd for $C_{32}H_{27}NO_2$: C, 84.00; H, 5.95; N, 3.06%.

***p*-(Dimethylamino)benzaldehyde 2,4-Dinitrophenylhydrazone:**[9] Mp and mixed mp 230 °C (decomp); IR (KBr) 3287, 1620, 1603, 1507, 1425, 1141, 1125 cm^{-1}.

Acid-Induced Reaction of the Imine 1a in the Presence of Water. Water (36 mg, 2 mmol) was added to a solution of the imine **1a** (203 mg, 0.5 mmol) and *p*-toluenesulfonic acid (10 mg, 0.05 mmol) in xylene (5 ml) and the mixture was refluxed for 22 h. After removal of the solvent, the residue was separated on TLC (silica gel, benzene) to give 2,4,6-triphenylpyridine **2a** (20 mg, 26%) and 1,3-diphenyl-2-propenone identified as the 2,4-dinitrophenylhydrazone[9] (66 mg, 34%): Mp and mixed mp 248 °C.

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7) The *N*-phosphinyl-2-propenimines **1b—d** were prepared by a similar procedure previously described for **1a** in Ref. 2. Spectra of the pyridines **2a—d**, and general conditions and instruments used in this work have been described in Ref. 1. The ^{31}P NMR spectra were taken by use of 85%-H_3PO_4 as an external standard.

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