A Novel Formation of Phenyl-Substituted Pyridines by the Reaction of *N*-(Diphenylphosphinyl)-1-azaallyl Anions with α,β-Unsaturated Carbonyl Compounds. A New Synthetic Equivalent of Primary Vinylamines

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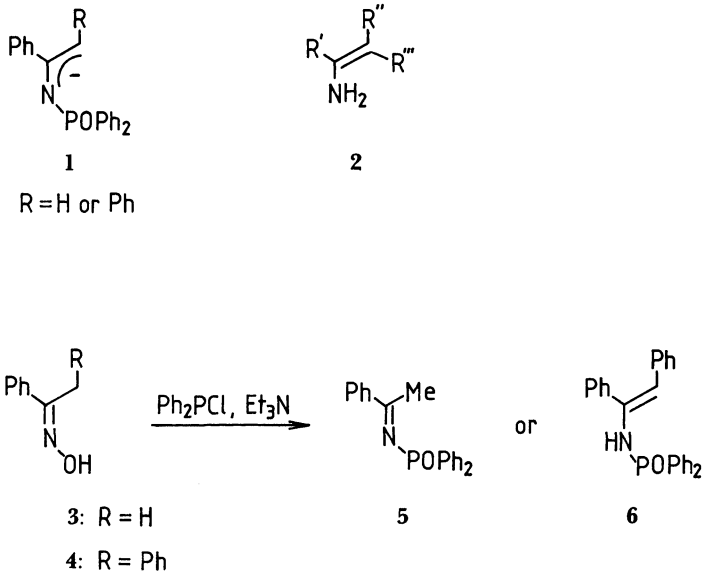
The *N*-phosphinyl-1-azaallyl anions, which were derived from the corresponding imine or enamine, reacted with α,β-unsaturated carbonyl compounds to afford phenyl-substituted pyridines along with 1-propanone and 1,5-pentanedione derivatives. A plausible mechanism involving a sequence of Michael addition and intramolecular aza-Horner-Wittig reaction is described, and the 1-azaallyl anions were found to behave as a synthetic equivalent of primary vinylamines.

Although much attention has been received on the chemistry of 1-azaallyl anions,[1] most of the anions have been utilized for selective carbon–carbon bond formations and the reactivity on the nitrogen atom has been unexplored.[1] It is of interest to investigate the chemical behavior of 1-azaallyl anions bearing a phosphinyl group on the nitrogen atom such as **1**, because they can be regarded as Horner-Wittig type variations of *N*-vinyliminophosphoranes which have been useful for the preparations of pyridines,[2] pyrroles,[3] and 1-azaazulenes.[4] The *N*-vinyliminophosphoranes, consequently, have proved useful as a synthetic equivalent of primary vinylamines **2**, which are labile even at low temperature.[5] Recently, an *N*,*N*-bis(trimethylsilyl)enamine[6] and 1-amino-2-hydroxyalkylsilanes[7] have also been recognized as synthetic equivalents of **2** and they have afforded a pyridine derivative and/or 2-azadienes. We wish to describe here on the reactions of the *N*-phosphinyl-1-azaallyl anions **1** with α,β-unsaturated carbonyl compounds to yield mainly phenyl-substituted pyridines along with 1-propanone and 1,5-pentanedione derivatives.

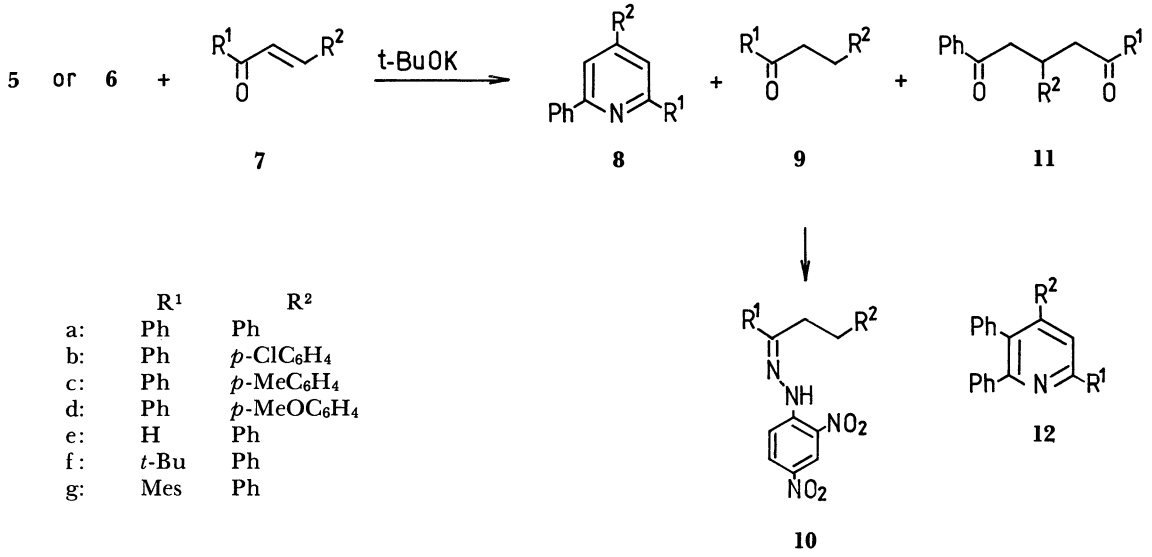
Results and Discussion

N-(Diphenylphosphinyl)-1-phenylethanimine (**5**) was prepared by the reaction of acetophenone oxime (**3**) with chlorodiphenylphosphine in the presence of triethylamine at −40 °C.[8] A similar reaction with deoxybenzoin oxime (**4**), however, resulted in the formation of *N*-(1,2-diphenylethenyl)-*P*,*P*-diphenylphosphinic amide (**6**) in a 42% yield. In the ^{1}H NMR spectra of **6**, a singlet peak at δ=6.53 can be assigned to the β-proton of **6**. A peak of the β-carbon of **6** at 113.3 ppm in the ^{13}C NMR spectra and an absorption of N–H stretching (3356 cm^{-1}) in the IR spectra also support the structure of **6**, although the stereochemistry of the double bond is ambiguous.

The *N*-phosphinyl-1-azaallyl anion **1** (R=H) was generated by the treatment of **5** with potassium *t*-butoxide in benzene at ambient temperature. To this



Scheme 1.



Scheme 2.

Table 1. Yields of the Products by the Reaction of **5** or **6** with **7**

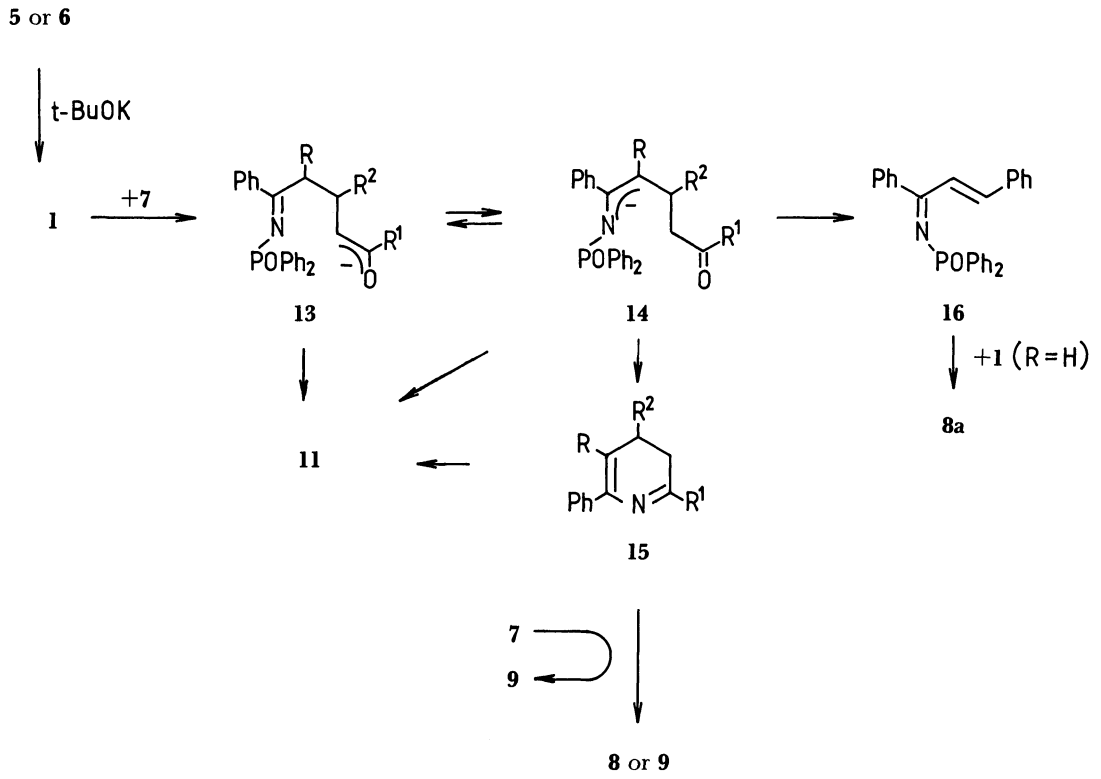
Entry	Substrates		Yield/% 8	10	11	12
1	**5**	**7a**	49	12	7	—
2		**7b**	48	9	6	—
3		**7c**	32	4	13	—
4		**7d**	27	5	20	—
5		**7e**	14[a)]	—	—	—
6		**7f**	9	—	7	—
7		**7g**	b)	—	28	—
8	**6**	**7a**	—	—	—	17
9		**7e**	—	—	—	21

a) Isolated as picrate. b) The pyridine **8a** was obtained in a 2% yield.

mixture, 1,3-diphenyl-2-propen-1-one (**7a**) was added in one portion and stirring was continued for 24 h. Separation on TLC afforded 2,4,6-triphenylpyridine (**8a**), 1,3-diphenyl-1-propanone (**9a**) which was identified by conversion to the corresponding 2,4-dinitrophenylhydrazone (**10a**), and 1,3,5-triphenyl-1,5-pentanedione (**11a**). The yields of the products are summarized in the Table 1 (Entry 1). Similar reactions of **5** with 3-aryl-1-phenyl-2-propen-1-ones (**7b—d**) provided the pyridine derivative (**8b—d**) bearing the aryl group at the 4-position of the pyridine ring, along with propanones **9b—d** and pentanediones **11b—d** (Entries 2—4). In the reaction of **5** with **7b**, diphenylphosphinic acid was also isolated (70% yield). Upon treatment with cinnamaldehyde (**7e**), the imine **5** provided 6-unsubstituted pyridine **8e** which was isolated as the picrate in a 14% yield (Entry 5). The presence of a bulky group adjacent to the carbonyl group of **7** appears to decrease the yields of the pyridine derivatives by steric effects: the reaction of **5** and **7f** gave pyridine **8f** in a 9% yield along with **11f** in a 7% yield (Entry 6). Further, the reaction with **5g** provided **11g** in a 28% yield, accompanied by the formation of a small amount of the pyridine **8a** instead of **8g** (Entry 7). In similar reactions of **6** with **7a** and **7e**, 2,3,4,6-tetraphenylpyridine (**12a**) and 2,3,4-triphenylpyridine (**12e**) were obtained in 17 and 21% yields, respectively (Entries 8 and 9). The best yield of the pyridine **8a** was attained by use of potassium *t*-butoxide–benzene system, which was chosen by a survey of various bases and solvents such as *t*-BuOK, NaH, DBU, KOH (with a phase-transfer catalyst), and benzene, THF, or DMSO.

All the pyridines except **12e** have been previously reported and their structures were unequivocally characterized by comparison of physical data with those described in the literatures. The structures of **9**, **10**, and **11a—d** were confirmed by comparison with authentic specimens independently prepared (see Experimental).

The present reaction can be best explained by the mechanism shown in Scheme 3. The *N*-phosphinyl-1-azallyl anions **1**, generated from the corresponding imine **5** or enamine **6**, would initially undergo the Michael addition to **7** giving the intermediate **13**. Isomerization of **13** could give **14**, and its intramolecular aza-Horner-Wittig reaction and the subsequent dehydrogenation would lead to the pyridine derivatives **8** or **12**. At the stage of dehydrogenation, **7** could act as a hydrogen acceptor to yield **9**.[9)] Further, the 1,5-pentanedione derivatives **11a—d** could arise from hydrolysis of the intermediates **13**, **14**, and/or **15** with a trace amount of water in the solvent or under the work-up conditions. The difficulty of the pyridine formations for **7f** and **7g** could be ascribed to the steric effects at the stage of the intramolecular cyclization



Scheme 3.

from **14** to **15**. In the reaction with **7g**, the retro-Michael-type degradation of **14** giving **16** and the subsequent reaction of **16** with **1** could result in the formation of a small amount of **8a**.

In conclusion, the *N*-phosphinyl-1-azaallyl anions **1**, derived from the corresponding imine **5** or enamine **6**, reacted with α,β-unsaturated carbonyl compounds **7** to give mainly the pyridine derivatives via Michael addition, followed by the intramolecular aza-Horner-Wittig reaction. The present study demonstrates that the anion **1** has shown bidentate reactivities on the β-carbon and the nitrogen atoms, and the anion **1** was found to behave as a synthetic equivalent of primary vinylamines **2**. The *N*-phosphinyl imines have recently been reported to be useful for preparations of amines by reduction[8),10)] and of oxaziridines by oxidation reactions,[11)] and the reactions described above may open up another usefulness of the *N*-phosphinyl imine.

Experimental

General. All the melting points were measured with a Yanagimoto hot-stage apparatus and uncorrected. The IR spectra were obtained with a Hitachi 345 spectrometer. The ^{1}H-(90 MHz) and ^{13}C NMR (22.5 MHz) spectra were recorded with a JEOL-FX-90Q spectrometer with tetramethylsilane as an internal standard. The ^{31}P NMR (36.2MHz) were measured with the same spectrometer by use of 85%-H_3PO_4 as an external standard. The mass spectra were obtained with a Shimadzu QP-1000 spectrometer. Elemental analyses were performed with a Perkin-Elmer Model 240 apparatus. All reactions were carried out under nitrogen atmosphere. Benzene and tetrahydrofuran were dried and purified by standard methods. The 3-aryl-1-phenyl-2-propen-1-one derivatives **7a—d**,[12)] **7f**,[13)] and **7g**[14)] were prepared according to the methods described in the literatures.

***N*-(Diphenylphosphinyl)-1-phenylethanimine (5)**[8)]: To a cooled (−40 °C) solution of acetophenone oxime (**3**) (4.06 g, 30 mmol) and Et_3N (3.03 g, 30 mmol) in dichloromethane–petroleum ether (100 ml, 1/1) was added a solution of chlorodiphenylphosphine (6.63 g, 30 mmol) in dichloromethane (4 ml) over 2 min. The mixture was stirred at −40 °C for 60 min and then warmed up to ambient temperature over 60 min. Insoluble material ($Et_3N \cdot HCl$) was removed by filtration and the filtrate was concentrated in vacuo. Ether was added to the residue and the resulted crystals were filtered to give colorless powder of **5** (5.32 g, 56%): mp 128—130 °C (lit,[8)] mp 135—137 °C); IR (KBr) 3077, 1641, 1591, 1576, 1438, 1279, 1199, 1180, 1121, 1108 cm^{-1}; ^{1}H NMR δ=2.95 (3H, d, $^2J_{P-H}$=2.2Hz), 7.24—8.18 (15H, m); ^{31}P NMR ($CDCl_3$) δ=18.7.

***N*-(1,2-Diphenylethenyl)-*P,P*-diphenylphosphinic Amide (6)**; According to the same procedure for **5**, deoxybenzoin oxime (**4**) (6.52 g, 31 mmol) was treated with chlorodiphenylphosphine (6.84 g, 31 mmol) and Et_3N (3.14 g, 31 mmol) to provide colorless needles of **6** (4.48 g, 42%): mp 150—153 °C (benzene–ether); IR (KBr) 3356, 3036, 1627, 1436, 1410, 1330, 1235, 1195, 1120, 1104 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=4.80 (1H, d, $^2J_{P-H}$=10.3 Hz, NH), 6.53 (1H, s), 6.69—7,00 (5H, m), 7.23—7.53 (11H, m), 7.85—8.10 (4H, m); ^{13}C NMR ($CDCl_3$) δ=113.3 (d, $^3J_{P-C}$=3.7 Hz), 125.5—138.2; ^{31}P NMR ($CDCl_3$)

δ=17.6; MS *m/z* (rel intensity) 395 (M^+, 84), 201 (100). HR-MS Found: 395.1442, Calcd for $C_{26}H_{22}NOP$: 395.1439. Found: C, 78.82; H, 5.57; N, 3.54%. Calcd for $C_{26}H_{22}NOP$: C, 78.97; H, 5.61; N, 3.54%.

General Procedure for the Reaction of 5 or 6 with α,β-Unsaturated Carbonyl Compounds 7. To a solution of the imine **5** (160 mg, 0.5 mmol) or the enamine **6** (198 mg, 0.5 mmol) in benzene (10 ml) was added potassium *t*-butoxide (67 mg, 0.6 mmol) and the mixture was stirred at ambient temperature for 5 min. To this mixture was added **7** (0.5 mmol) in one portion and stirring was continued for 24 h. The products were extracted with benzene. The organic phase was successively washed with aqueous sodium hydrogencarbonate and water, and dried over Na_2SO_4. Concentration afforded the mixture of the products, which were separated on TLC (silica gel, benzene) to give the pyridine **8** or **12**, the 1-propanone derivatives **9**, and the 1,5-pentanedione derivatives **11**. The 1-propanones **9** were transformed to the corresponding 2,4-dinitrophenylhydrazones **10** upon treatment with an acidic methanol solution of 2,4-dinitrophenylhydrazine. The yields of the products are summarized in the Table 1. In the reaction of the imine **5** and **7b**, the aqueous phase was acidified with hydrochloric acid and the resulted precipitate was filtered to give diphenylphosphinic acid (76 mg, 70%).

2,4,6-Triphenylpyridine (8a): mp 141—142 °C (hexane) (lit,[15] mp 137 °C); IR ($CHCl_3$) 2928, 1592, 1542, 1494, 1451, 1392, 1074, 1028 cm^{-1}; ^1H NMR ($CDCl_3$) δ=7.43—7.84 (11H, m), 7.90 (2H, s), 8.16—8.27 (4H, m); MS *m/z* (rel intensity) 307 (M^+, 100), 306 (49).

4-(*p*-Chlorophenyl)-2,6-diphenylpyridine (8b): mp 127—131.5 °C (hexane) (lit,[16] mp 128.5—130 °C); IR ($CHCl_3$) 3003, 1604, 1581, 1547, 1406, 1387, 1095, 1034 cm^{-1}; ^1H NMR ($CDCl_3$) δ=7.20—7.72 (10H, m), 7.79 (2H, s), 8.06—8.28 (4H, m); MS *m/z* (rel intensity) 343 (M^++2, 37), 341 (M^+, 100), 306 (42).

2,6-Diphenyl-4-(*p*-methylphenyl)pyridine (8c): mp 119—122.5 °C (hexane) (lit,[17] mp 118—118.5 °C); IR ($CHCl_3$) 3007, 1598, 1583, 1544, 1389, 1116, 1022; ^1H NMR ($CDCl_3$) δ=2.43 (3H, s), 7.08—7.72 (10H, m), 7.86 (2H, s) 8.10—8.30 (4H, m); MS *m/z* (rel intensity) 321 (M^+, 100), 306, (32).

2,6-Diphenyl-4-(*p*-methoxyphenyl)pyridine (8d): mp 99—100 °C (hexane) (lit,[17] mp 99—100 °C); IR ($CHCl_3$) 2999, 2928, 1598, 1549, 1512, 1464, 1397, 1297, 1190, 1117, 1035 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.84 (3H, s), 7.02 (2H, d, *J*=8.8 Hz), 7.30—7.60 (6H, m), 7.66 (2H, d, *J*=8.8 Hz), 7.82 (2H, s), 8.10—8.30 (4H, m); MS *m/z* (rel intensity) 337 (M^+, 100), 322 (21), 306 (10).

2,4-Diphenylpyridine (8e): oil, picrate: mp 197—199 °C (methanol) (lit,[18] picrate: mp 190.5—192.5 °C); IR ($CHCl_3$) 2954, 1599, 1545, 1473, 1447, 1397, 1072 cm^{-1}; ^1H NMR ($CDCl_3$) δ=7.20—8.14 (12H, m), 8.73 (1H, dd, *J*=5.0, 0.9 Hz).

6-*t*-Butyl-2,4-diphenylpyridine (8f): mp 94—94.5 °C (methanol) (lit,[19] mp 87—88 °C); IR (KBr)1612, 1605, 1575, 1505, 1413, 770 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.48 (9H, s), 7.20—7.80 (10H, m), 8.00—8.25 (2H, m); MS *m/z* (rel intensity) 287 (M^+, 60), 272 (100), 245 (40), 230 (8). Found: C, 87.99; H, 7.44; N, 4.51%. Calcd for $C_{21}H_{21}N$: C, 87.76; H, 7.37; N, 4.87%.

1,3-Diphenyl-1-propanone (9a): mp 72 °C (hexane) (lit,[20] mp 72 °C); IR ($CHCl_3$) 2887, 1687, 1600, 1453, 1293, 1106 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.94—3.42 (4H, m), 7.04—7.60 (8H, m), 7.80—8.04 (2H, m).

3-(*p*-Chlorophenyl)-1-phenyl-1-propanone (9b): mp 56—57 °C (hexane) (lit,[20] mp 58 °C); IR ($CHCl_3$) 3007, 2927, 1682, 1601, 1492, 1452, 1403, 1367, 1297, 1178, 1096, 1019 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.90—3.38 (4H, m), 7.14—7.76 (7H, m), 7.88—8.04 (2H, m).

3-(*p*-Methylphenyl)-1-phenyl-1-propanone (9c): colorless oil; IR ($CHCl_3$) 3008, 2927, 1687, 1604, 1582, 1519, 1457, 1371, 1301, 1180, 1110, 1004, 982 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.30 (3H, s), 2.84—3.38 (4H, m), 7.11 (4H, s), 7.28—7.56 (3H, m), 7.84—8.00 (2H, m).

3-(*p*-Methoxyphenyl)-1-phenyl-1-propane (9d): mp 64—66 °C (hexane) (lit,[20] mp 66 °C); IR ($CHCl_3$) 2998, 2935, 2835, 1681, 1611, 1599, 1582, 1541, 1451, 1364, 1304, 1242, 1174, 1109, 1037 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.88—3.98 (4H, m), 3.75 (3H, s), 6.84 (2H, d, *J*=8.8 Hz), 7.14 (2H, d, *J*=8.8 Hz), 7.38—7.60 (3H, m), 7.84—8.02 (2H, m).

1,3-Diphenyl-1-propanone 2,4-Dinitrophenylhydrazone (10a): mp 188.5—192.5 °C (chloroform–methanol); IR (KBr) 3329, 1605, 1590, 1504, 1414, 1335, 1307, 1120, 1105 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.82—3.34 (4H, m), 7.10—7.50 (8H, m), 7.78—7.94 (2H, m), 8.07 (1H, d, *J*=9.4 Hz), 8.29 (1H, dd, *J*=9.4, 2.4 Hz), 9.12 (1H, d, *J*=2.4 Hz), 11.36 (1H, br); MS *m/z* (rel intensity) 390 (M^+, 11), 389 (48), 372 (11), 196 (12), 119 (37), 105 (25), 104 (62), 103 (49), 91 (100), 77 (38). Found: C, 64.60; H, 4.61; N, 14.25%. Calcd for $C_{21}H_{18}N_4O_4$: C, 64.61; H, 4.65; N, 14.35%.

3-(*p*-Chlorophenyl)-1-phenyl-1-propanone 2,4-Dinitrophenylhydrazone (10b): mp 201.5—203 °C (chloroform–methanol); IR (KBr) 3311, 1616, 1592, 1511, 1492, 1422, 1332, 1309, 1261, 1239, 1104 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.76—3.28 (4H, m), 7.02—7.56 (7H, m), 7.72—7.92 (2H, m), 8.08 (1H, d, *J*=9.4 Hz), 8.35 (1H, dd, *J*=9.4, 2.4 Hz), 9.14 (1H, d, *J*=2.4 Hz), 11.40 (1H, br); MS *m/z* (rel intensity) 425 (M^++2, 5), 423 (M^+, 12), 196 (11), 138 (17), 127 (26), 125 (86), 103 (97), 77 (100). Found: C, 59.53; H, 4.03; N, 12.98%. Calcd for $C_{21}H_{17}N_4O_4Cl$: C, 59.37; H, 4.03; N, 13.19%.

3-(*p*-Methylphenyl)-1-phenyl-1-propanone 2,4-Dinitrophenylhydrazone (10c): mp 162—165 °C (chloroform–methanol); IR (KBr) 3298, 1622, 1601, 1519, 1426, 1340, 1319, 1131, 1114 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.25 (3H, s), 2.80—3.28 (4H, m), 7.06—7.60 (7H, m), 7.80—7.96 (2H, m), 8.06 (1H, d, *J*=9.5 Hz), 8.31 (1H, dd, *J*=9.5, 2.6 Hz), 9.12 (1H, d, *J*=2.6 Hz), 11.35 (1H, br); MS *m/z* (rel intensity) 403 (M^+−1, 8), 119 (17), 118 (14), 105 (100), 77 (58). Found: C, 65.33; H, 4.67; N, 13.83%. Calcd for $C_{22}H_{20}N_4O_4$: C, 65.34; H, 4.98; N, 13.85%.

3-(*p*-Methoxyphenyl)-1-phenyl-1-propanone 2,4-Dinitrophenylhydrazone (10d): mp 172—174 °C (chloroform–methanol); IR (KBr) 3309, 1622, 1606, 1519, 1431, 1342, 1318, 1256, 1118 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.75—3.27 (4H, m), 3.73 (3H, s), 6.80 (2H, d, *J*=8.8 Hz), 7.15 (2H, d, *J*=8.8, Hz), 7.20—7.60 (3H, m), 7.80—7,95 (2H, m), 8.06 (1H, d, *J*=9.6 Hz), 8.32 (1H, dd, *J*=9.6, 2.2 Hz), 9.11 (1H, d, *J*=2.2 Hz), 11.34 (1H, br); MS *m/z* (rel intensity) 420 (M^+, 8), 373 (5), 134 (5), 122 (9), 121 (100), 103 (26), 91 (24), 77 (47). Found: C, 63.19; H, 4.80; N, 13.58%. Calcd for $C_{22}H_{20}N_4O_5$: C, 62.85; H, 4.80; N, 13.33%.

1,3,5-Triphenyl-1,5-pentanedione (11a): mp 85.5—86.5 °C (ethanol) (lit, [21] mp 85 °C); IR (KBr) 3009, 2885, 1692, 1675, 1596, 1493, 1450, 1357, 1274, 1203, 1071, 985 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.38 (2H, dd, *J*=16.7, 6.8 Hz), 3.46 (2H, dd, *J*=16.7, 6.8 Hz), 4.06 (1H, quint., *J*=6.8 Hz), 7.12—7.66 (11H,

m), 7.84—8.06 (4H, m); MS *m/z* (rel intensity) 328 (M^+, 3), 209 (39), 105 (100), 77 (86).

3-(*p*-Chlorophenyl)-1,5-diphenyl-1,5-pentanedione (11b): mp 113—113.5 °C (ethanol) (lit,[16] 109.5—110.5 °C); IR (KBr) 3023, 2805, 1696, 1680, 1606, 1500, 1459, 1371, 1235, 1213, 1090, 1005 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.35 (2H, dd, J=16.8, 6.9 Hz), 3.45 (2H, dd, J=16.8, 6.9 Hz), 4.03 (1H, quint., J=6.9 Hz), 7.18—7.66 (10H, m), 7.84—8.04 (4H, m); MS *m/z* (rel intensity) 364 (M^++2, 2), 362 (M^+, 6), 245 (23), 243 (70), 105 (100), 77 (88).

1,5-Diphenyl-3-(*p*-methylphenyl)-1,5-pentanedione (11c): mp 121—122 °C (ethanol); IR (KBr) 3016, 2885, 1673, 1591, 1570, 1510, 1447, 1361, 1291, 1238, 1201, 1194, 1180, 1005 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.27 (3H, s), 3.35 (2H, dd, J=16.6, 6.8 Hz), 3.45 (2H, dd, J=16.6, 6.8 Hz), 4.02 (1H, quint., J=6.8 Hz), 6.96—7.66 (10H, m), 7.80—8.04 (4H, m); MS *m/z* (rel intensity) 342 (M^+, 11), 224 (18), 223 (100), 105 (95), 77 (63). Found: C, 84.19; H, 6.50%. Calcd for $C_{24}H_{22}O_2$: C, 84.18; H, 6.48%.

1,5-Diphenyl-3-(*p*-methoxyphenyl)-1,5-pentanedione (11d): mp 96.0—96.5 °C (ethanol) (lit, [21] mp 94 °C); IR (KBr) 2999, 2827, 1683, 1596, 1515, 1447, 1356, 1240, 1204, 1192, 1183, 1117, 1037 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.34 (2H, dd, J=16.6, 6.9 Hz), 3.44 (2H, dd, J=16.6, 6.9 Hz), 3.74 (3H, s), 4.01 (1H, quint., J=6.9 Hz), 6.80 (2H, d, J=8.9 Hz), 7.19 (2H, d, J=8.9 Hz), 7.30—7.66 (6H, m), 7.84—8.04 (4H, m); MS *m/z* (rel intensity) 358 (M^+, 7), 240 (11), 239 (62), 238 (10), 105 (100), 77 (72).

6,6-Dimethyl -1,3-diphenyl-1,5-heptanedione (11f):[22] mp 133—134 °C (hexane); IR ($CHCl_3$) 2955, 1710, 1686, 1600, 1445, 1363 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.03 (9H, s), 2.93 (2H, d, J=6.9 Hz), 3.20—3.40 (2H, m), 3.88 (1H, quint., J=6.9 Hz), 7.12—7.52 (8H, m), 7.80—7.98 (2H, m); ^{13}C NMR ($CDCl_3$) δ=26.1 (q), 36.8 (d), 42.9 (t), 44.1 (s), 44.5 (t), 126.5, 127.5, 128.1, 128.4, 132.8, 137.1, 144.1, 198.6, 213.6; MS *m/z* (rel intensity) 308 (M^+, 23), 307 (100), 306 (46), 230 (20), 202 (13). Found: C, 81.99; H, 7.86%. Calcd for $C_{21}H_{24}O_2$: C, 81.78; H, 7.84%.

1,3-Diphenyl-5-(2,4,6-trimethylphenyl)-1,5-pentanedione (11g):[22] colorless oil, bp 260 °C (bath temp, 533 Pa); IR ($CHCl_3$)1680, 1620, 1598, 1455, 982 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.99 (6H, s), 2.22 (3H, s), 3.17 (2H, dd, J=7.0, 1.9 Hz), 3.38 (2H, dd, J=7.0, 1.9 Hz), 4.06 (1H, quint., J=7.0 Hz), 6.75 (2H, s), 7.10—8.02 (10H, m); MS *m/z* (rel intensity) 370 (M^+, 3), 251 (40), 209 (21), 147 (100), 105 (30). HR-MS Found: 370.1945. Calcd for $C_{26}H_{21}O_2$: 370.1933.

2,3,4,6-Tetraphenylpyridine (12a): mp 189.5—190 °C (hexane) (lit,[23] mp 178—181 °C); IR ($CHCl_3$) 3054, 1580, 1534, 1493, 1446, 1417, 1377, 1073, 1027, 1004 cm^{-1}; ^1H NMR ($CDCl_3$) δ=6.86—7.82 (18H, m), 7.77 (1H, s), 8.10—8.26 (2H, m); MS *m/z* (rel intensity) 383 (M^+, 57), 382 (100). Found: C, 90.77; H, 5.55; N, 3.66%. Calcd for $C_{29}H_{21}N$: C, 90.83; H, 5.52; N, 3.65%.

2,3,4-Triphenylpyridine (12e): mp 189—190 °C (methanol); IR ($CHCl_3$) 2958, 1577, 1490, 1437, 1395, 1073, 1009 cm^{-1}; ^1H NMR ($CDCl_3$) δ=6.80—7.42 (15H, m), 7.33 (1H, d, J=5.0 Hz), 8.71 (1H, d, J=5.0 Hz); MS *m/z* (rel intensity) 307 (M^+, 48), 306 (100). Found: C, 89.67; H, 5.56; N, 4.37%. Calcd for $C_{23}H_{17}N$: C, 89.87; H, 5.57; N, 4.56%.

Diphenylphosphinic Acid: mp and mixed mp 198—198.5 °C (benzene) (lit,[24] mp 190—192 °C); IR (KBr) 3075, 3050, 1660, 1437, 1180, 1130, 965 cm^{-1}.

Independent Synthesis of the 3-Aryl-1-phenyl-1-propanone Derivatives (9a—d).[25] To a cooled (−15 °C) suspension of copper(I) iodide (3.04 g, 16 mmol) in anhydrous THF (15 ml) was added $LiAlH_4$ (152 mg, 4 mmol) and the mixture was stirred for 3 min. To the solution was added **7a—d** (2 mmol) and stirring was continued for 60 min. Ethanol and aqueous sodium hydroxide was added to the reaction mixture and the products were extracted with CH_2Cl_2 (10 ml×3). The organic phase was dried over Na_2SO_4. Concentration and purification on TLC afforded **9a** (21%), **9b** (47%), **9c** (36%), and **9d** (35%), along with recovery of **7a—d**. The yields of **9** were not optimized.

Independent Synthesis of the 3-Aryl-1,5-diphenyl-1,5-pentanedione Derivatives (11a—d).[16] To a solution of acetophenone (5.41 g, 45 mmol) and an aromatic aldehyde (15 mmol) in ethanol (35 ml) was added a solution of NaOH (4 g, 100 mmol) in water (40 ml), and the mixture was stirred for 24 h. The resulted precipitate was collected by suction and washed with ethanol. Recrystallization from ethanol gave **11a** (52%), **11b** (47%), **11c** (66%), and **11d** (46%).

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References

1) J. K. Whitesell and M. A. Whitesell, *Synthesis,* **1983**, 517; for earlier works, see: D. A. Evans, *J. Am. Chem. Soc.*, **92**, 7593 (1970); G. Wittig, R. Roderer, and S. Fischer, *Tetrahedron Lett.*, **1973**, 3517.

2) T. Kobayashi and M. Nitta, *Chem. Lett.*, **1986**, 1549; T. Kobayashi, Y. Iino, and M. Nitta, *Nippon Kagaku Kaishi,* **1987**, 1237; Y. Iino and M. Nitta, *Bull. Chem. Soc. Jpn.*, **61**, 2235 (1988).

3) Y. Iino, T. Kobayashi, and M. Nitta, *Heterocycles,* **24**, 2437 (1986).

4) M. Nitta, Y. Iino, E. Hara, and T. Kobayashi, *J. Chem. Soc., Perkin Trans. 1,* **1989**, 51; M. Nitta, Y. Iino, and K. Kamata, *Heterocycles,* **29**, 1655 (1989).

5) J. L. Ripoll, H. Lebrun, and A. Thuillier, *Tetrahedron,* **36**, 2497 (1980).

6) R. J. P. Corriu, V. Huynh, J. J. E. Moreau, and M. Pataud-Sat, *Tetrahedron Lett.*, **23**, 3257 (1982).

7) S. Tomoda, Y. Matsumoto, Y. Takeuchi, and Y. Nomura, *Chem. Lett.*, **1986**, 1193.

8) B. Krzyzanowska and W. J. Stec, *Synthesis,* **1982**, 270.

9) 1,3-Diphenyl-2-propen-1-one is known to act as a hydrogen acceptor: A. T. Balaban, *C. R. Acad. Sci., Ser. C,* **256**, 4239 (1963). The presence of oxidants such as Cu $(OAc)_2$ [T. W. Bell and S. D. Rothenberger, *Tetrahedron Lett.*, **28**, 4817 (1987)] or Pd/C was without effect for the present reaction.

10) B. Krzyzanowska and W. J. Stec, *Synthesis,* **1978**, 521; R. O. Hutchins, A. Abdel-Magid, Y. P. Stercho, and A. Wambsgans, *J. Org. Chem.*, **52**, 702 (1987); R. O. Hutchins and M. C. Rutledge, *Tetrahedron Lett.*, **28**, 5619 (1987).

11) D. R. Boyd, J. F. Malone, M. R. McGuckin, W. B. Jennings, M. Rutherford, and B. M. Saket, *J. Chem. Soc., Perkin Trans. 2,* **1988**, 1145; W. B. Jennings, S. P. Watson, and D. R. Boyd, *Tetrahedron Lett.*, **30**, 235 (1989).

12) E. P. Kohler and H. M. Chadwell, *Org. Synth.*, Coll. Vol. 1, 78 (1941).
13) D. Vorländer and F. Kalkow, *Ber.*, **30**, 2269 (1897).
14) A. N. Nesmeyanov and V. A. Sanova, *Izvest. Akad. Nauk S. S. S. R., Otdel. Khim. Nauk*, **1949**, 422; *Chem. Abstr.*, **44**, 1402i (1950).
15) A. R. Katritzky, D. E. Leaby, A. Maguestiau, and R. Hamming, *J. Chem. Soc., Perkin Trans. 1*, **1983**, 45.
16) R. L. Frank and R. P. Seven, *J. Am. Chem. Soc.*, **71**, 2629 (1941).
17) R. Lombard and J.-P. Stephan, *Bull. Soc. Chim. Fr.*, **1958**, 1458.
18) T. Kobayashi, Y. Iino, and M. Nitta, *Nippon Kagaku Kaishi*, **1986**, 785.
19) A. R. Katritzky and S. S. Thind, *J. Chem. Soc., Perkin Trans. 1*, **1980**, 1895.
20) Y. Sasson, M. Cohen, and J. Blum, *Synthesis*, **1973**, 359.
21) Z. S. Ariyan and H. Suschitzky, *J. Chem. Soc.*, **1961**, 2242.
22) J. Bertrand, L. Gorrichon, and P. Maroni, *Tetrahedron*, **40**, 4127 (1984).
23) Y. Suzuki, *Nippon Kagaku Kaishi*, **1980**, 604.
24) W. A. Higgins, P. W. Vogel, and W. G. Craig, *J. Am. Chem. Soc.*, **77**, 1864 (1955).
25) E. C. Ashby and J. J. Lin, *Tetrahedron Lett.*, **1975**, 4453.