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Iodine-Catalyzed Efficient Hydrophosphonylation of *N*-Tosyl Aldimines†

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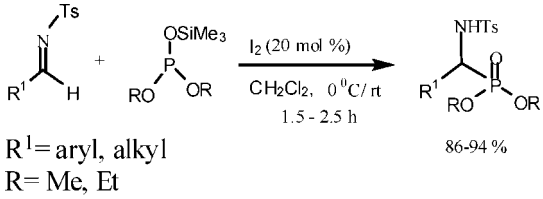

Treatment of *N*-tosyl aldimines with dialkyl trimethylsilyl phosphites at 0 °C in the presence of iodine as a catalyst afforded the corresponding sulfonamide phosphonates in excellent yields within 1.5 to 2.5 h.

α-Aminophosphonates and their derivatives possess various important biological properties including antifungal, antibacterial, and herbicidal activities.[1] They are also inhibitors of a variety of enzymes.[2] Additionally they are useful as fire retardants for cotton.[1a] A few methods have been developed for the synthesis of these compounds at high temperatures or by using some catalysts.[1a,3] Recently some research groups have accomplished the synthesis of these compounds in optically active forms.[1b,2,4]

In continuation of our work[5] on the development of useful synthetic methodologies we have observed that sulfonamide phosphonates can efficiently be synthesized by treatment of *N*-sulfonyl aldimines with dialkyl trimethylsilyl phosphites in the presence of iodine as a catalyst at 0 °C (Scheme 1).

SCHEME 1. Synthesis of α-Aminophosphonates from *N*-Tosyl Aldimines

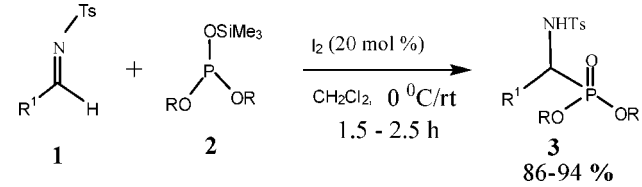

TABLE 1. Reaction of *N*-Tosyl Benzaldimine with Various Phosphites in the Presence of Different Lewis Acid Catalysts[a]

entry	phosphite	catalyst	time (h)	yield (%)[b]
1	$Me_3SiOP(OMe)_2$	I_2	1.5	93
		$FeCl_3$	2.5	83
		$ZrCl_4$	3.0	81
2	$Me_3SiOP(OEt)_2$	I_2	1.5	94
		$FeCl_3$	2.5	85
		$ZrCl_4$	3.0	80
3	$HP(O)(OMe)_2$	I_2	2.0	NR[c]
		$FeCl_3$	3.0	NR[c]
		$ZrCl_4$	3.5	NR[c]
4	$HP(O)(OEt)_2$	I_2	2.0	NR[c]
		$FeCl_3$	2.5	NR[c]
		$ZrCl_4$	3.0	NR[c]
5	$P(OMe)_3$	I_2	2.0	NR[c]
		$FeCl_3$	2.5	NR[c]
		$ZrCl_4$	3.5	NR[c]
6	$P(OEt)_3$	I_2	2.0	NR[c]
		$FeCl_3$	2.5	NR[c]
		$ZrCl_4$	3.0	NR[c]

[a] Reaction conditions: *N*-tosyl aldimine (1.0 mmol), phosphite (1.3 mmol), catalyst (20 mol %), DCM (2 mL), 0 °C, N_2 atmosphere. [b] Isolated yield. [c] No reaction.

Initially the reaction of *N*-tosyl benzaldimine with different phosphites in the presence of various catalysts was thoroughly studied. Alkyl phosphites (e.g., $(MeO)_3P$, $(EtO)_3P$, $(MeO)_2P(O)H$, $(EtO)_2P(O)H$) afforded no products in the presence of iodine after 2 h. The reaction was conducted at 0 °C to room temperature. However, the reaction with dialkyl trimethylsilyl phosphites underwent smoothly at 0 °C within 1.5 h to furnish the corresponding sulfonamide phosphonates in excellent yields (Table 1). These silyl phosphites are commercially available and have been used here for the first time for hydrophosphonylation of aldimines.

Besides iodine various other catalysts were also utilized to carry out the reaction. However, considering the reaction time and yield iodine was preferred (Table 1).

Finally a series of sulfonamide phosphonates were prepared (Table 2) from different *N*-tosyl aldimines[6] derived from various aromatic, heteroaromatic, and aliphatic aldehydes, using dialkyl

† Part 186 in the series Studies on Novel Synthetic Methodologies.

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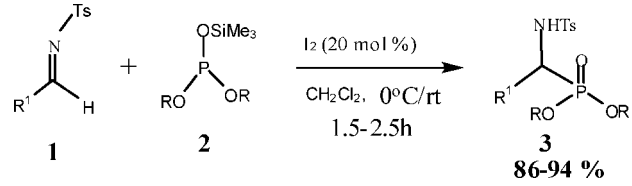
TABLE 2. Synthesis of α-Aminophosphonates by the Reaction of Various *N*-Tosyl Aldimines and Dialkyl Trimethylsilyl Phosphites in the Presence of Iodine[a]



1 2 3 86-94 %

entry	R′	R	time (h)	product	yield (%)[b]
1	C_6H_5	Me	1.5	**3a**	93
2	3-ClC_6H_4	Me	1.5	**3b**	90
3	4-ClC_6H_4	Me	1.5	**3c**	92
4	3-F,4-ClC_6H_3	Me	1.75	**3d**	89
5	4-$NO_2C_6H_4$	Me	1.5	**3e**	91
6	4-$MeOC_6H_4$	Me	2.0	**3f**	87
7	4-$PhCH_2OC_6H_4$	Me	2.0	**3g**	90
8	4-MeC_6H_4	Me	1.75	**3h**	92
9	2-furyl	Me	2.5	**3i**	86
10	2-thienyl	Me	2.0	**3j**	88
11	C_6H_5	Et	1.5	**3k**	94
12	4-ClC_6H_4	Et	1.5	***3l***	92
13	CH_3CH_2	Me	1.5	**3m**	90
14	$CH_3CH_2CH_2$	Me	1.5	**3n**	89

[a] Reaction conditions: *N*-tosyl aldimine (1.0 mmol), dialkyl trimethylsilyl phosphite (1.3 mmol), I_2 (20 mol %), DCM (2 mL), 0 °C, N_2 atmosphere. [b] Isolated yield.

trimethylsilyl phosphites in the presence of iodine. The aromatic aldehydes contained both electron-donating as well as electron-withdrawing groups. The aliphatic aldimine derivatives also afforded the desired phosphonates conveniently. The reaction was conducted at 0 °C. The conversion was completed within 1.5 to 2.5 h and the sulfonamide phosphonates were formed in excellent yields (86−94%). Both dimethyl trimethylsilyl phosphite and diethyl trimethylsilyl phosphite underwent the conversion smoothly. With the latter reagent the reaction can also be carried out at room temperature. The structures of the products were settled from their spectral (IR, ^{1}H and ^{13}C NMR, and HRMS) data.

The *N*-tosyl group of the products can easily be deprotected[7] to furnish the corresponding α-amino phosphonates which can be used to explore their biological properties. It can be mentioned here that there have been only a few methods reported[1a,3a,4e] for the preparation of *N*-tosyl α-aminophosphonates. The catalyst, iodine, is inexpensive, easily available, and nontoxic. It efficiently conducts the hydrophosphonylation of *N*-sulfonylimines by polarizing the −CH=N− bond of the compounds.

In conclusion, we have developed a facile method for the synthesis of sulfonamide phosphonates from *N*-tosyl aldimines and dialkyl trimethylsilyl phosphites with iodine as a catalyst. The simple experimental procedure, mild reaction conditions, application of an easily available catalyst, impressive yields, and short reaction times are the notable advantages of the method.

Experimental Section

General Experimental Procedure. Tosylimine (1 mmol) was taken in CH_2Cl_2 (2 mL) under N_2 and I_2 (20 mol %) was added. The mixture was kept at 0 °C. Dialkyl trimethylsilyl phosphite (1.3 mmol) was subsequently added and the mixture was stirred. The reaction was monitored by TLC. After completion the reaction was quenched with hypo solution (10 mL) and the mixture was extracted with CH_2Cl_2 (3 × 10 mL). The extract was dried and concentrated and the residue was subjected to column chromatography (silica gel, hexane−EtOAc) to obtain pure sulfonamide phosphonate.

The spectral (IR, ^{1}H and ^{13}C NMR, and HRMS) data of the products are given below.

3a: mp 167−169 °C; IR 3134, 1598, 1456, 1332, 1241, 1165 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.46 (2H, d, J = 8.0 Hz), 7.29−7.20 (3H, m), 7.16−7.05 (3H, m), 6.97 (2H, d, J = 8.0 Hz), 4.84 (1H, dd, J = 24.0, 10.0 Hz), 3.89 (3H, d, J = 10.0 Hz), 3.41 (3H, d, J = 10.0 Hz), 2.24 (3H, s); ^{13}C NMR (50 MHz, $CDCl_3$) δ 142.8, 138.0, 133.4, 129.0, 128.3, 128.0, 127.1, 55.2 (d, J = 156.2 Hz), 54.4 (d, J = 6.5 Hz), 54.1 (d, J = 6.0 Hz), 21.2; HRMS (ESI) calcd for $C_{16}H_{21}NO_5PS$ (MH^+) 370.0873, found 370.0874.

3b: mp 145−147 °C; IR 3125, 1458, 1336, 1238, 1162 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.49 (2H, d, J = 8.0 Hz), 7.18−7.06 (4H, m), 7.02 (2H, d, J = 8.0 Hz), 6.90 (1H, dd, J = 10.0, 4.0 Hz), 4.80 (1H, dd, J = 24.0, 10.0 Hz), 3.92 (3H, d, J = 10.0 Hz), 3.49 (3H, d, J = 10.0 Hz), 2.31 (3H, s); ^{13}C NMR (50 MHz, $CDCl_3$) δ 143.2, 137.8, 135.1, 134.2, 129.6, 129.2, 128.0, 127.1, 126.5, 55.1 (d, J = 6.7 Hz), 54.5 (d, J = 150.2 Hz), 54.2 (d, J = 6.7 Hz), 21.2; HRMS (ESI) calcd for $C_{16}H_{19}ClNO_5PSNa$ (MNa^+) 426.0307, found 426.0325.

3c: mp 203−205 °C; IR 3146, 1598, 1523, 1463, 1306, 1241 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.52 (1H, m), 7.46 (2H, d, J = 8.0 Hz), 7.24 (2H, d, J = 8.0 Hz), 7.02 (2H, d, J = 8.0 Hz), 6.96 (2H, d, J = 8.0 Hz), 4.81 (1H, dd, J = 24.0, 10.0 Hz), 3.92 (3H, d, J = 10.0 Hz), 3.48 (3H, d, J = 10.0 Hz), 2.30 (3H, s); ^{13}C NMR (50 MHz, $CDCl_3$) δ 143.4, 138.0, 134.1, 132.2, 129.7, 129.1, 128.6, 127.4, 55.2 (d, J = 6.8 Hz), 54.5 (d, J = 150.4 Hz), 54.0 (d, J = 6.0 Hz), 21.2; HRMS (ESI) calcd $C_{16}H_{20}ClNO_5PS$ (MH^+) 404.0483, found 404.0492.

3d: mp 164−166 °C; IR 3126, 1600, 1502, 1338, 1238, 1165 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.89 (1H, br dd, J = 8.0, 2.0 Hz), 7.48 (2H, br d, J = 8.0 Hz), 7.27 (1H, d, J = 8.0 Hz), 7.11 (1H, m), 7.01 (2H, d, J = 8.0 Hz), 6.87 (1H, dd, J = 10.0, 8.0 Hz), 4.81 (1H, dd, J = 24.0, 10.0 Hz), 4.01 (3H, d, J = 10.0 Hz), 3.52 (3H, d, J = 10.0 Hz), 2.29 (3H, s); ^{13}C NMR (50 MHz, $CDCl_3$) δ 155.9, 143.2, 138.0, 130.9, 130.2 (d, J = 8.0 Hz), 129.0, 128.1 (d, J = 8.0 Hz), 126.9, 121.1 (d, J = 15.0 Hz), 116.2 (d, J = 15.0 Hz), 55.3 (d, J = 6.0 Hz), 54.2 (d, J = 150.0 Hz), 54.1 (d, J = 6.0 Hz), 21.2; HRMS (ESI) calcd for $C_{16}H_{19}ClFNO_5PS$ (MH^+) 422.0389, found 422.0398.

3e: mp 226−228 °C; IR 3133, 1597, 1494, 1337, 1240, 1161 cm^{-1}; ^{1}H NMR (200 MHz, DMSO-d_6) δ 9.01 (1H, dd, J = 10.0, 3.0 Hz), 7.95 (2H, d, J = 8.0 Hz), 7.51 (2H, d, J = 8.0 Hz), 7.46 (2H, d, J = 8.0 Hz), 7.08 (2H, d, J = 8.0 Hz), 5.10 (1H, dd, J = 24.0, 10.0 Hz), 3.70 (3H, d, J = 10.0 Hz), 3.49 (3H, d, J = 10.0 Hz), 2.19 (3H, s); ^{13}C NMR (50 MHz, DMSO-d_6) δ 146.6, 142.7, 142.2, 138.0, 129.6, 129.0, 126.8, 122.9, 54.2 (d, J = 7.2 Hz), 53.3 (d, J = 6.2 Hz), 52.4 (d, J = 150.0 Hz), 20.4; HRMS (ESI) calcd for $C_{16}H_{20}N_2O_7PS$ (MH^+) 415.0723, found 415.0729.

3f: mp 166−168 °C; IR 3128, 1611, 1514, 1334, 1246, 1160 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.49 (2H, d, J = 8.0 Hz), 7.22−7.11 (3H, m), 6.99 (2H, d, J = 8.0 Hz), 6.62 (2H, d, J = 8.0 Hz), 4.70 (1H, dd, J = 24.0, 10.0 Hz), 3.89 (3H, d, J = 10.0 Hz), 3.72 (3H, s), 3.41 (3H, d, J = 10.0 Hz), 2.29 (3H, s); ^{13}C NMR (50 MHz, $CDCl_3$) δ 159.8, 143.0, 138.1, 129.6, 129.0, 126.9, 125.4, 114.0, 55.1, 54.8 (d, J = 6.0 Hz), 54.0 (d, J = 155.5 Hz), 53.9 (d, J = 6.0 Hz), 21.2; HRMS (ESI) calcd for $C_{17}H_{22}NO_6PSNa$ (MNa^+) 422.0798, found 422.0813.

3g: mp 214−216 °C; IR 3141, 1609, 1512, 1335, 1241, 1161 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.50 (2H, d, J = 8.0 Hz), 7.45−7.31 (6H, m), 7.18 (2H, d, J = 8.0 Hz), 6.99 (2H, d, J = 8.0 Hz), 6.71 (2H, d, J = 8.0 Hz), 4.98 (2H, s), 4.81 (1H, dd, J = 24.0, 10.0 Hz), 3.89 (3H, d, J = 10.0 Hz), 3.41 (3H, d, J = 10.0

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Hz), 2.29 (3H, s); ^{13}C NMR (50 MHz, $CDCl_3$) δ 157.7, 142.8, 138.2, 136.9, 129.8, 129.7, 128.9, 128.7, 128.2, 127.8, 127.1, 125.8, 114.6, 70.0, 54.6 (d, J = 6.0 Hz), 54.2 (d, J = 150.4 Hz), 54.0 (d, J = 6.0 Hz), 21.2; HRMS (ESI) calcd for $C_{23}H_{27}NO_6PS$ (MH^+) 476.1291, found 476.1300.

3h: mp 202−204 °C; IR 3136, 1459, 1337, 1248, 1160 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.48 (2H, d, J = 8.0 Hz), 7.09 (2H, d, J = 8.0 Hz), 6.99 (2H, d, J = 8.0 Hz), 6.91 (2H, d, J = 8.0 Hz), 6.72 (1H, m), 4.78 (1H, dd, J = 24.0, 10.0 Hz), 3.82 (3H, d, J = 10.0 Hz), 3.40 (3H, d, J = 10.0 Hz), 2.30 (3H, s), 2.24 (3H, s); ^{13}C NMR (50 MHz, $CDCl_3$) δ 143.0, 138.1, 130.2, 129.0, 128.1, 127.2, 54.3 (d, J = 156.4 Hz), 54.2 (d, J = 6.2 Hz), 54.0 (d, J = 6.0 Hz), 21.2, 21.0; HRMS (ESI) calcd for $C_{17}H_{22}NO_5PSNa$ (MNa^+) 406.0849, found 406.0858.

3i: mp 159−161 °C; IR 3126, 1458, 1340, 1249, 1166 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.58 (2H, d, J = 8.0 Hz), 7.20−7.711 (3H, m), 6.23 (1H, dd, J = 10.0, 4.0 Hz), 6.21−6.10 (2H, m), 4.92 (1H, dd, J = 24.0, 10.0 Hz), 3.85 (3H, d, J = 10.0 Hz), 3.56 (3H, d, J = 10.0 Hz), 2.32 (3H, s); ^{13}C NMR (50 MHz, $CDCl_3$) δ 146.3, 142.8, 142.6, 137.1, 129.0, 127.0, 110.5, 109.9, 54.8 (d, J = 6.0 Hz), 54.1 (d, J = 6.0 Hz), 46.8 (d, J = 156.1 Hz), 21.1; HRMS (ESI) calcd for $C_{14}H_{18}NO_6PSNa$ (MNa^+) 382.0485, found 382.0501.

3j: mp 150−152 °C; IR 3131, 1465, 1330, 1241, 1161 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.58 (2H, d, J = 8.0 Hz), 7.20−6.96 (5H, m), 6.75 (1H, m), 5.10 (1H, dd, J = 24.0, 10.0 Hz), 3.89 (3H, d, J = 10.0 Hz), 3.51 (3H, d, J = 10.0 Hz), 2.32 (3H, s); ^{13}C NMR (50 MHz, $CDCl_3$) δ 143.1, 138.4, 135.5, 129.2, 127.7, 126.9, 126.7, 126.1, 54.8 (d, J = 6.2 Hz), 54.1 (d, J = 6.0 Hz), 50.2 (d, J = 156.2 Hz), 21.2; HRMS (ESI) calcd for $C_{14}H_{18}NO_5PS_2Na$ (MNa^+) 398.0256, found 398.0267.

3k: mp 124−126 °C; IR 3109, 1460, 1336, 1239, 1165 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.99 (1H, m), 7.43 (2H, d, J = 8.0 Hz), 7.28−7.17 (2H, m), 7.12−6.93 (3H, m), 6.85 (2H, d, J = 8.0 Hz), 4.79 (1H, dd, J = 24.0, 10.0 Hz), 4.42−4.28 (2H, m), 3.88 (1H, m), 3.60 (1H, m), 2.21 (3H, s), 1.42 (3H, t, J = 7.0 Hz), 1.02 (3H, t, J = 7.0 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 143.2, 138.4, 134.5, 129.1, 128.7, 128.0, 126.8, 64.6 (d, J = 6.0 Hz), 64.4 (d, J = 6.2 Hz), 54.9 (d, J = 151.2 Hz), 20.4, 15.3 (d, J = 6.0 Hz), 15.1 (d, J = 6.2 Hz); HRMS (ESI) calcd for $C_{18}H_{24}NO_5PSNa$ (MNa^+) 420.1010, found 420.1022.

3l: mp 163−165 °C; IR 3122, 1597, 1492, 1339, 1239, 1161 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.82 (1H, dd, J = 10.0, 4.0 Hz), 7.40 (2H, d, J = 8.0 Hz), 7.12 (2H, d, J = 8.0 Hz), 6.98 (2H, d, J = 8.0 Hz), 6.95 (2H, d, J = 8.0 Hz), 4.72 (1H, dd, J = 24.0, 10.0 Hz), 4.45−4.28 (2H, m), 3.92 (1H, m), 3.71 (1H, m), 2.29 (3H, s), 1.42 (3H, t, J = 7.0 Hz), 1.12 (3H, t, J = 7.0 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 143.4, 138.0, 133.7, 132.2, 129.9, 129.1, 128.1, 126.6, 64.2 (d, J = 6.5 Hz), 64.0 (d, J = 6.5 Hz), 54.9 (d, J = 153.7 Hz), 21.2, 16.2 (d, J = 6.5 Hz), 15.9 (d, J = 6.5 Hz); HRMS (ESI) calcd for $C_{18}H_{23}ClNO_5PSNa$ (MNa^+) 454.0620, found 454.0605.

3m: mp 105−107 °C; IR 3125, 1599, 1468, 1326, 1233, 1162 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.81 (2H, d, J = 8.0 Hz), 7.29 (2H, d, J = 8.0 Hz), 6.37 (1H, dd, J = 10.0, 3.0 Hz), 3.69 (6H, d, J = 10.0 Hz), 3.61 (1H, m), 2.42 (3H, s), 1.75 (1H, m), 1.59 (1H, m), 0.82 (3H, t, J = 7.0 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 143.0, 138.8, 129.5, 127.0, 54.0 (d, J = 6.2 Hz), 53.2 (d, J = 6.2 Hz), 51.3 (d, J = 156.6 Hz), 23.5, 21.3, 10.6 (d, J = 6.5 Hz); HRMS (ESI) calcd for $C_{12}H_{20}NO_5PSNa$ (MNa^+) 344.0697, found 344.0687.

3n: mp 116−118 °C; IR 3110, 1599, 1471, 1330, 1228, 1162 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.79 (2H, d, J = 8.0 Hz), 7.30 (2H, d, J = 8.0 Hz), 6.09 (1H, dd, J = 10.0, 3.0 Hz), 3.72 (1H, m), 3.68 (6H, d, J = 10.0 Hz), 2.42 (3H, s), 1.67 (1H, m), 1.52 (1H, m), 1.42−1.28 (2H, m), 0.79 (3H, t, J = 7.0 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 143.1, 138.6, 129.2, 127.1, 53.9 (d, J = 6.2 Hz), 53.0 (d, J = 6.2 Hz), 49.9 (d, J = 155.5 Hz), 32.2, 21.1, 18.2 (d, J = 6.5 Hz), 13.4; HRMS (ESI) calcd for $C_{13}H_{22}NO_5PSNa$ (MNa^+) 358.0854, found 358.0854.

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Supporting Information Available: Spectra (^{1}H and ^{13}C NMR and HRMS) of the products **3a**−**n**. This material is available free of charge via the Internet at http://pubs.acs.org.

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