Palladium-Catalyzed Condensation of Aryl Halides with Phenylsulfonylacetonitrile and Diethyl Cyanomethylphosphonate[1)]

Takao Sakamoto, Eisaku Katoh, Yoshinori Kondo, and Hiroshi Yamanaka*

Pharmaceutical Institute, Tohoku University, Aobayama, Aoba-ku, Sendai 980, Japan. *Received November 30, 1989*

The palladium(0)-catalyzed condensation of aryl halides with the sodium salts of phenylsulfonylacetonitrile and diethyl cyanomethylphosphonate in dimethoxyethane gave the corresponding α-phenylsulfonylareneacetonitriles and diethyl arylcyanomethylphosphonates in good yields.

The α-phenylsulfonylareneacetonitriles were easily desulfonylated with zinc to give the areneacetonitriles, and the arylcyanomethylphosphonates were converted to the alkylideneareneacetonitriles by means of the Horner–Emmons reaction.

Keywords palladium-catalyzed reaction; aryl halide; phenylsulfonylacetonitrile; diethyl cyanomethylphosphonate; desulfonylation; zinc dust; Horner–Emmons reaction

Previously, we reported that the condensation of aryl halides with malononitrile was effectively promoted by the catalytic action of tetrakis(triphenylphosphine)palladium to give arylated malononitriles in satisfactory yields.[2)] The catalytic action of the palladium complex was similarly observed in the reaction of aryl halides with ethyl cyanoacetate,[2)] but the reaction with acetylacetone, ethyl acetoacetate, and diethyl malonate gave unsatisfactory results over the same catalyst.[3)]

As an extension of the palladium-catalyzed condensation of aryl halides with active methylene compounds, we investigated the palladium(0)-catalyzed condensation of 4-substituted iodobenzenes, bromopyridines, and some other heteroaryl bromides with phenylsulfonylacetonitrile and diethyl cyanomethylphosphonate over the same catalyst. This is the main subject of the present paper. Additionally, some chemical conversions of the functional group of the condensation products thus obtained were examined.

When iodobenzene (**1a**) was heated with the sodium salt of phenylsulfonylacetonitrile in the presence of tetrakis(triphenylphosphine)palladium in dimethoxyethane (DME), α-phenylsulfonylbenzeneacetonitrile (**3a**) was obtained in almost quantitative yield. As well as phenylsulfonylacetonitrile, the reaction of **1a** with the sodium salt of diethyl cyanomethylphosphonate under the same conditions proceeded smoothly, and diethyl [cyano(phenyl)methyl]phosphonate (**4a**) was isolated in 85% yield.

In order to compare the substituent effect in these reactions, several 4-substituted iodobenzenes (**1b**—**e**) were allowed to react with phenylsulfonylacetonitrile and diethyl cyanomethylphosphonate. As shown in Tables I and II, no significant effect of the 4-substituents on the yields was observed, and the corresponding arylated acetonitriles were obtained in 69—90% yields. Exceptionally, the condensation of 4-nitroiodobenzene (**1e**) with diethyl cyanomethylphosphonate gave **4e** in low yield; it seems **4e** decomposes under the reaction conditions.

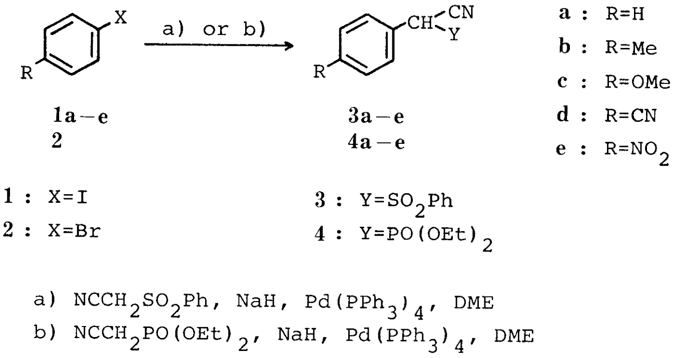


Chart 1

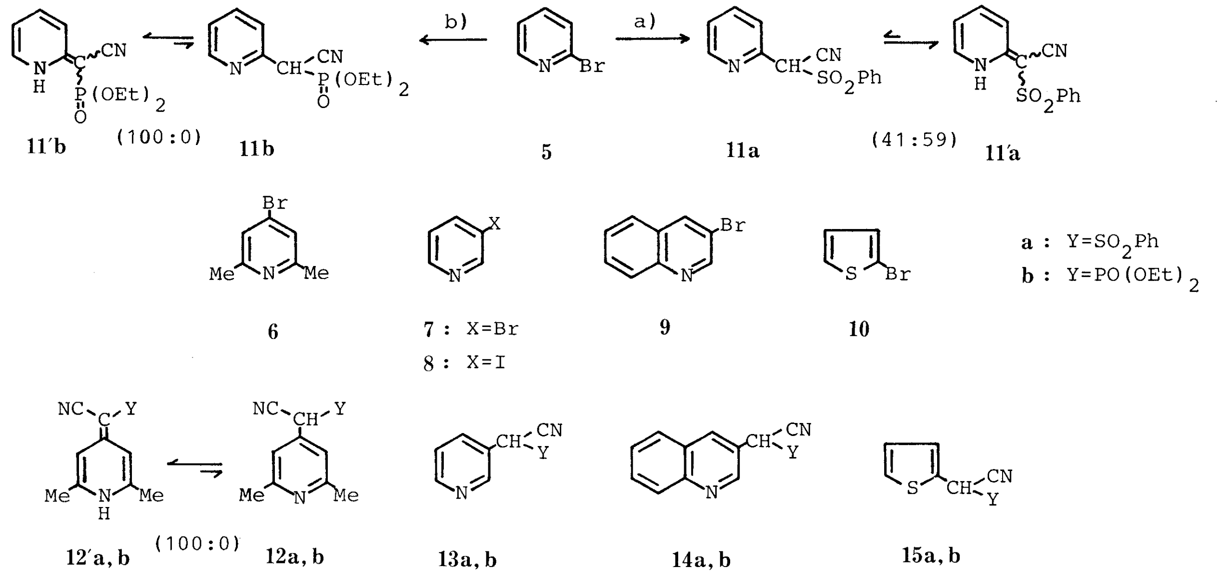
Then, the application of this condensation to the synthesis of heteroaromatics with certain functional groups was investigated. Namely, bromopyridines such as 2-bromopyridine (**5**), 4-bromo-2,6-dimethylpyridine (**6**),[4)] and 3-bromopyridine (**7**) were allowed to react with phenylsulfonylacetonitrile and diethyl cyanomethylphosphonate in the same manner. As illustrated in Chart 2, all the reactions

Table I. Palladium-Catalyzed Condensation of Aryl Halides with Phenylsulfonylacetonitrile

Substrate	Reaction time (h)	Product	Yield (%)
1a	2	**3a**	96
2	5	**3a**	82
1b	2	**3b**	80
1c	1	**3c**	90
1d	1	**3d**	78
1e	2	**3e**	78
5	2	**11a**	85
6	1	**12a**	66
7	3	**13a**	89
8	2	**13a**	97
9	1	**14a**	80
10	2	**15a**	84

Table II. Palladium-Catalyzed Condensation of Aryl Halides with Diethyl Cyanomethylphosphonate

Substrate	Reaction time (h)	Product	Yield (%)
1a	3	**4a**	85
2	5	**4a**	80
1b	1	**4b**	82
1c	2.5	**4c**	69
1d	1	**4d**	86
1e	1/6	**4e**	17
5	1	**11b**	72
6	1.5	**12b**	71
7	3	**13b**	79
8	1	**13b**	80
9	1	**14b**	74
10	3	**15b**	59



a) $NCCH_2SO_2Ph$, NaH, $Pd(PPh_3)_4$, DME; b) $NCCH_2PO(OEt)_2$, NaH, $Pd(PPh_3)_4$, DME

Chart 2

TABLE III. Spectral Data for α-Phenylsulfonylareneacetonitriles

No.	IR ($CHCl_3$) cm^{-1}	^{1}H-NMR ($CDCl_3$) δ (ppm)
3a	2260, 1335, 1165	5.15 (1H, s), 7.1—7.6 (5H, m), 7.6—8.0 (5H, m)
3b	2250, 1335, 1165	2.35 (3H, s), 5.10 (1H, s), 7.1—7.4 (4H, m), 7.4—8.0 (5H, m)
3c	2255, 1335, 1160	3.77 (3H, s), 5.02 (2H, m), 7.3—8.0 (7H, m)
3d	2240, 1350, 1165	5.22 (1H, s), 7.2—7.3 (2H, m), 7.3—8.0 (7H, m)
3e	1350, 1165	5.26 (1H, s), 7.2—7.5 (3H, m), 7.5—8.0 (4H, m), 8.1—8.4 (2H, m)
11a	2190, 1300	5.49 (0.41H, s), 6.5—6.8 (0.41H, m), 7.1—8.2 (8H, m), 8.52 (0.59H, dd, *J*=4.0, 2.0 Hz), 11.9—12.8 (0.59 H, br)
12a	2170, 1365, 1145[a]	2.39 (6H, s), 6.8—7.3 (2H, br s), 7.5—8.1 (5H, m), 11.7—12.6 (1H, br)[b]
13a	2250, 1350, 1165	5.26 (1H, s), 7.2—7.5 (1H, m), 7.5—8.0 (5H, m), 8.49 (1H, d, *J*=2.0 Hz), 8.71 (1H, dd, *J*=5.0, 2.0 Hz)
14a	2260, 1350, 1165	5.53 (1H, s), 7.3—8.1 (8H, m), 8.1—8.3 (2H, m), 8.84 (1H, d, *J*=2.0 Hz)
15a	2250, 1365, 1145	5.31 (1H, s), 6.9—7.2 (2H, m), 7.2—8.0 (6H, m)
17	2245, 1335, 1155	1.03 (3H, t, *J*=7.0 Hz), 2.3—3.3 (2H, m), 7.2—8.0 (8H, m), 8.5—8.7 (1H, m)
19	2240, 1335, 1160	1.03 (3H, t, *J*=7.0 Hz), 2.48 (6H, s), 2.59 (2H, q, *J*=7.0 Hz), 6.96 (2H, s), 7.3—7.9 (5H, m)
20	2240, 1335, 1160	1.06 (3H, t, *J*=7.0 Hz), 2.72 (2H, q, *J*=7.0 Hz), 7.2—7.8 (7H, m), 8.5—8.8 (2H, m)

a) In KBr. *b*) In dimethylsufoxide-d_6 (DMSO-d_6).

TABLE IV. Spectral Data for Diethyl α-Arylcyanomethylphosphonates

No.	IR ($CHCl_3$) cm^{-1}	^{1}H-NMR ($CDCl_3$) δ (ppm)
4a	2265, 1265, 1025,	1.20 (6H, dt, *J*=7.0, 2.0 Hz), 3.1—4.0 (4H, m), 4.45 (1H, d, *J*=29 Hz), 7.2—7.7 (5H, m)
4b	2250, 1265, 1025	1.28 (6H, t, *J*=7.0 Hz), 2.33 (3H, d, *J*=2.0 Hz), 3.8—4.6 (5H, m), 7.1—7.6 (4H, m)
4c	2250, 1260, 1025	1.27 (6H, t, *J*=7.0 Hz), 3.77 (3H, s), 3.9—4.6 (5H, m), 7.3—7.6 (2H, m)
4d	2250, 2240, 1270, 1025	1.31 (6H, dt, *J*=7.0, 3.0 Hz), 3.9—4.7 (5H, m), 7.5—7.9 (4H, m)
4e	2250, 1270, 1020	1.33 (6H, dt, *J*=7.0, 3.0 Hz), 3.9—4.8 (5H, m), 7.6—7.9 (2H, m), 8.2—8.6 (2H, m)
11b	2180, 2190, 1030	1.38 (6H, t, *J*=7.0 Hz), 3.9—4.4 (4H, m), 6.3—6.7 (1H, m), 7.1—7.7 (3H, m), 13.0—14.0 (1H, br)
12b	2170, 1025[a]	1.25 (6H, t, *J*=7.0 Hz), 2.32 (6H, s), 3.7—4.3 (4H, m), 6.4—6.7 (1H, br s), 11.7—12.6 (1H, br)[b]
13b	2260, 1265, 1025	1.32 (6H, t, *J*=7.0 Hz), 3.9—4.8 (5H, m), 7.3—7.6 (1H, m), 7.7—8.2 (1H, m), 8.6—9.0 (2H, m)
14b	2260, 1270, 1025	1.31 (6H, dt, *J*=7.0, 2.0 Hz), 3.7—4.9 (5H, m), 7.3—8.0 (3H, m), 8.0—8..5 (2H, m), 8.9—9.0 (1H, m)
15b	2250, 1265, 1025	1.33 (6H, dt, *J*=7.0, 2.0 Hz), 3.9—4.8 (5H, m), 6.9—7.5 (3H, m)

a) In KBr. *b*) In DMSO-d_6.

tested gave the desired products (**11a**, **b**, **12a**, **b**, and **13a**, **b**) in 59—97% yields, suggesting the wide generality of our method.

In many palladium-catalyzed reactions, 3-iodopyridines are known to be better starting materials than 3-bromopyridines in terms of the yields of products, but in our present investigation, no significant difference was found in the yields of **13a, b** from 3-bromopyridine (**7**) and 3-iodopyridine (**8**), or in the yields of **3a** and **4a** from iodobenzene (**1**) and bromobenzene (**2**).

Similarly, 3-bromoquinoline (**9**) and 2-bromothiophene (**10**) were allowed to react with phenylsulfonylacetonitrile and diethyl cyanomethylphosphonate, and the corresponding derivatives (**14a, b** and **15a, b**) were obtained, as expected.

Among the heteroarylated acetonitriles **11a, b** and **12a, b** were found to exist as the tautomers (**11'a, b** and **12'a, b**) or as a mixture of the tautomers by proton nuclear magnetic resonance (^{1}H-NMR) spectrometry. The relative contents of the tautomers under the conditions of ^{1}H-NMR spectrometric measurement are shown in Chart 2.

In relation to our reaction, the condensation of iodobenzene with the sodium salts of phenylsulfonylacetonitrile[5)] and diethyl cyanomethylphosphonate[6)] in the presence of a stoichiometric amount of cuprous iodide has been reported. As these reactions were carried out at higher temperature, the condensation product of iodobenzene with diethyl cyanomethylphosphonate is not the primary product (**4a**) but the rearranged product, 2-phenylbutyronitrile.

Accordingly, the palladium(0)-catalyzed condensation of aryl halides with active methylene compounds seems to be a more favorable reaction in general to introduce the active methylene moiety containing a cyano group into aromatic ring systems.

Next, desulfonylation of the α-phenylsulfonylpyridineacetonitriles (**11a**, **12a**, and **13a**) was examined. When **11a**, **12a**, and **13a** were treated with zinc dust[7)] in acetic acid and ethanol at room temperature, the respective pyridineacetonitriles (**16**, **21**, and **23**) were isolated in satisfactory yields. In connection with these results, the desulfonylation of **11a**, **12a**, and **13a** with Raney nickel resulted in the formation of resinous products, although Raney nickel has been reported to be useful for the desulfonylation of the corresponding benzene derivatives.[5)]

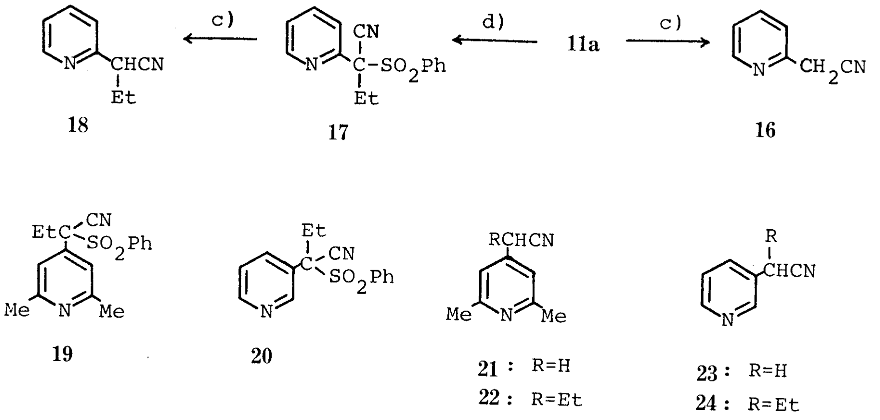
Monoalkylation of pyridineacetonitriles, particularly 2-pyridineacetonitriles and 4-pyridineacetonitriles, is difficult due to the concomitant formation of dialkylated products.[8)] Thus, the ethylation with ethyl iodide under basic conditions followed by the desulfonylation with zinc dust was examined with **11a**, **12a**, and **13a**, and successful results were obtained in each case, as shown in Chart 3 and

Table V. Desulfonylation of α-Phenylsulfonylpyridineacetonitrile

Substrate	Reaction time (h)	Product	Yield (%)
11a	1	**16**	94
12a	3	**21**	72
13a	1	**23**	97
17	2	**18**	89
19	0.5	**22**	99
20	1	**24**	89

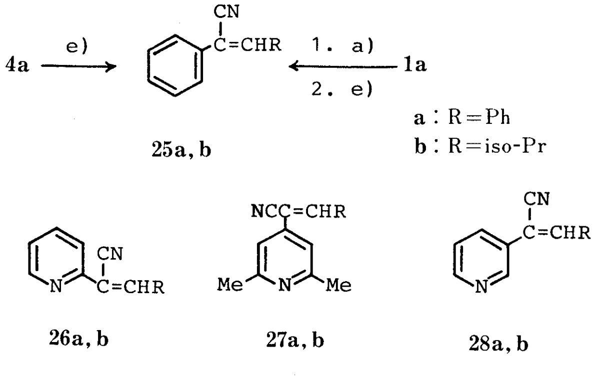
Table VI. One-Pot Synthesis of Alkylideneareneacetonitriles

Substrate	Reaction time (h)	Product	Yield (%)
1a	1	**25a**	78
1a	6	**25b**	77
5	2	**26a**	59
5	15	**26b**	73
6	5	**27a**	78
6	8	**27b**	69
8	1	**28a**	74
8	9	**28b**	73



c) Zn, AcOH, EtOH; d) NaH, EtI, DMF

Chart 3



a) $NCCH_2SO_2Ph$, NaH, $Pd(PPh_3)_4$, DME; e) NaH, RCHO, DMF

Chart 4

TABLE VII. Physical Constants and Spectral Data for Pyridineacetonitriles

No.	mp (°C) or bp (°C)/mmHg	Appearance (Recryst. solvent)	IR ($CHCl_3$) cm^{-1}	^1H-NMR ($CDCl_3$) δ (ppm)
16	95 / 40[a]	Colorless liquid	2250	3.87 (2H, s), 7.1—7.9 (3H, m), 8.52 (1H, dd, $J=4.0$, 1.0 Hz)[b]
21	64—65[c]	Colorless prisms (Hexane)	2255	2.50 (6H, s), 3.68 (2H, s), 6.94 (2H, s)
23	100 / 26[d]	Colorless liquid	2255	3.78 (2H, s), 7.2—7.6 (1H, m), 7.6—7.9 (1H, m), 8.5—8.8 (2H, m)[b]
18	80 / 5[e]	Colorless liquid	2250	1.07 (3H, t, $J=7.0$ Hz), 2.06 (2H, dq, $J=7.0$, 7.0 Hz), 3.59 (1H, t, $J=7.0$ Hz), 7.1—8.0 (3H, m), 8.5—8.8 (1H, m)
22	90 / 5[f]	Colorless liquid	2250	1.06 (3H, t, $J=7.0$ Hz), 1.88 (2H, dq, $J=7.0$, 7.0 Hz), 3.59 (1H, t, $J=7.0$ Hz), 7.1—8.0 (3H, m), 8.5—8.8 (1H, m)[b]
24	80 / 5[g]	Colorless liquid	2250	1.09 (3H, t, $J=7.0$ Hz), 1.93 (2H, dq, $J=7.0$, 7.0 Hz), 3.79 (1H, t, $J=7.0$ Hz), 7.1—7.4 (1H, m), 7.4—7.8 (1H, m), 8.4—8.7 (2H, m)

a) Lit.[9] bp 96—101 °C/2 mmHg. b) In CCl_4. c) *Anal.* Calcd for $C_9H_{10}N_2$: C, 73.94; H, 6.89; N, 19.16. Found: C, 73.78; H, 6.77; N, 19.16. d) Lit.[10] bp 91 °C/2 mmHg. e) Lit.[11] bp 124—127 °C/15 mmHg. f) *Anal.* Calcd for $C_{11}H_{14}N_2$: C, 75.82; H, 8.10; N, 16.08. Found: C, 75.58; H, 8.16; N, 15.85. g) Lit.[12] bp 73—75 °C/0.1 mmHg.

TABLE VIII. Physical Constants and Spectral Data for Alkylideneareneacetonitriles

No.	mp (°C) or bp (°C)/mmHg	Appearance (Recryst. solvent)	IR ($CHCl_3$) cm^{-1}	^1H-NMR (CCl_4) (ppm)
25a	83.5—84.5[a]	Colorless scales (Et_2O–hexane)	2225	7.4—8.0 (11H, m)
25b	100 / 26[b]	Colorless liquid	2225	1.17 (6H, d, $J=7.0$ Hz), 2.6—3.4 (1H, m), 6.55 (1H, d, $J=10.0$ Hz), 7.2—7.7 (5H, m)
26a	57—59[d]	Colorless pillars (EtOH)	2220	7.0—7.7 (4H, m), 7.7—8.3 (4H, m), 8.5—8.8 (2H, m)[c]
26b	100 / 26[e]	Colorless liquid	2230	1.21 (6H, d, $J=7.0$ Hz), 2.9—3.4 (1H, m), 7.0—7.3 (1H, m), 7.4—7.9 (3H, m), 8.4—8.6 (1H, m)
27a	148—150[f]	Colorless scales (C_6H_6–hexane)	2225	2.59 (6H, s), 7.23 (2H, s), 7.3—7.6 (3H, m), 7.62 (1H, d, $J=10.0$ Hz), 7.8—8.1 (2H, m)[c]
27b	127—130[g]	Colorless prisms (Acetone–hexane)	2220	1.19 (6H, d, $J=7.0$ Hz), 2.46 (6H, s), 2.6—3.4 (1H, m), 6.71 (1H, d, $J=9.0$ Hz), 6.96 (2H, s)
28a	103—105[h]	Yellow needles (Et_2O–hexane)	2220	7.2—7.6 (6H, m), 7.8—8.2 (3H, m), 8.97 (1H, dd, $J=5.0$, 2.0 Hz), 8.94 (1H, d, $J=2.0$ Hz)
28b	75 / 4[i]	Colorless liquid	2220	1.20 (6H, d, $J=7.0$ Hz), 2.6—3.4 (1H, m), 6.64 (1H, d, $J=10.0$ Hz), 7.1—7.4 (1H, m), 7.6—7.9 (1H, m), 8.48 (1H, dd, $J=4.0$, 2.0 Hz), 8.72 (1H, d, $J=2.0$ Hz)

a) Lit.[13] mp 84 °C. b) Lit.[14] bp 94.5—95 °C/1 mmHg. c) In $CDCl_3$. d) Lit.[8] mp 59.5—60.5 °C. e) Lit.[15] bp 103—104 °C/1.5 mmHg. f) *Anal.* Calcd for $C_{16}H_{14}N_2$: C, 82.02; H, 6.02; N, 11.96. Found: C, 82.25; H, 5.92; N, 12.01. g) *Anal.* Calcd for $C_{19}H_{19}N_5O_7$ (picrate, mp 165—166 °C): C, 53.14; H, 4.46; N, 16.31. Found: C, 52.92; H, 4.38; N, 16.23. h) Lit.[16] mp 107—109 °C. i) Lit.[15] bp 80—85 °C/0.5 mmHg.

Tables V and VI.

Further, diethyl [cyano(phenyl)methyl]phosphonate (**4a**) smoothly underwent the Horner–Emmons condensation with benzaldehyde to give α-(phenylmethylene)benzeneacetonitrile (**25a**) in 88% yield. Since the reaction conditions of palladium-catalyzed condensation and the Horner–Emmons reaction are both basic, the palladium(0)-catalyzed condensation of iodobenzene (**1a**) with diethyl cyanomethylphosphonate followed by the Horner–Emmons condensation with benzaldehyde was carried out in one-pot, and **25a** was isolated in 72% yield. Based on these results, **25b**, **26a**, **b**—**28a**, **b** were all prepared by the one-pot process.

Based on the present investigation, the palladium(0)-catalyzed condensation of aryl (or heteroaryl) halides with active methylene compounds containing a cyano group may be concluded to have wide utility for the synthesis of heteroaromatic side-chain derivatives.

Experimental

All melting points and boiling points are uncorrected. Infrared (IR) spectra were measured with a JASCO IR-810 spectrometer. ^1H-NMR spectra were taken at 60 MHz with a JEOL JMN-PMX 60 spectrometer. Chemical shifts are expressed in δ (ppm) values, and coupling constants are expressed in hertz (Hz). The following abbreviations are used: s = singlet, d = doublet, *t* = triplet, q = quartet, dd = double doublet, dt = double triplet, dq = double quartet, m = multiplet, and br = broad.

General Procedure for the Palladium-Catalyzed Condensation of Aryl Halides with Phenylsulfonylacetonitrile Anhydrous DME (20 ml), NaH (10.5 mmol), and phenylsulfonylacetonitrile (1.00 g, 5.5 mmol) were added to a solution of $Pd(PPh_3)_4$ (0.2 mmol) in anhydrous DME prepared *in situ*[2] under an N_2 atmosphere, and the mixture was stirred for *ca.* 10 min at room temperature. After addition of an aryl halide (5 mmol), the mixture was refluxed for an appropriate time, as shown in Table I. After removal of the solvent *in vacuo*, the residue was diluted with water, neutralized with concentrated HCl, and extracted with $CHCl_3$. The residue obtained from the $CHCl_3$ extract was purified by silica gel column chromatography, and the product was recrystallized from an appropriate solvent, as shown in Table IX.

General Procedure for the Palladium-Catalyzed Condensation of Aryl Halides with Diethyl Cyanomethylphosphonate The reaction was carried out basically according to the general procedure described above except for the use of an aryl halide (5 mmol), diethyl cyanomethylphosphonate (6 mmol), and NaH (11 mmol). The reaction time and the recrystallization solvent are listed in Table X.

General Procedure for the Ethylation of α-Phenylsulfonylpyridineacetonitriles A mixture of an α-phenylsulfonylpyridineacetonitrile (5 mmol) and NaH (5 mmol) in dimethylformamide (DMF) (10 ml) was stirred at room temperature until the evolution of H_2 stopped, then ethyl iodide (1.29 g, 6 mmol) was added. The whole mixture was stirred at room temperature for the time described in each case. The reaction mixture was diluted with water and extracted with benzene. The crude product obtained from the benzene extract was purified by recrystallization.

α-Ethyl-α-phenylsulfonyl-2-pyridineacetonitrile (17) According to the general procedure, α-phenylsulfonyl-2-pyridineacetonitrile (**11a**) was allowed to react for 5 h to give **17** in 80% yield.

TABLE IX. Physical Constants and Analytical Data for α-Phenylsulfonylareneacetonitriles

No.	mp (°C)	Appearance (Recryst. solvent)	Formula	Analysis (%)							
				Calcd				Found			
				C	H	N	S	C	H	N	S
3a	148—150[a]	Colorless needles (Et_2O–hexane)									
3b	114—115	Colorless needles (C_6H_6–hexane)	$C_{15}H_{13}NO_2S$	66.40	4.83	5.16	11.82	66.61	4.71	5.10	11.78
3c	115—116	Colorless needles (C_6H_6–hexane)	$C_{15}H_{13}NO_3S$	62.70	4.56	4.87	11.16	62.95	4.53	4.91	11.29
3d	180—181	Colorless prisms (C_6H_6–hexane)	$C_{15}H_{10}N_2O_2S$	63.82	3.57	9.92	11.36	64.07	3.60	9.99	11.58
3e	177—178	Yellow needles (C_6H_6)	$C_{14}H_{10}N_2O_4S$	55.62	3.33	9.27	10.61	55.91	3.23	9.26	10.39
11a	125—127	Colorless prisms (AcOEt–hexane)	$C_{13}H_{10}N_2O_2S$	60.45	3.90	10.85	12.41	60.67	3.94	10.61	12.51
12a	275 (dec.)	Colorless prisms (AcOEt–hexane)	$C_{15}H_{14}N_2O_2S$	62.92	4.93	9.78	11.20	63.03	5.06	9.80	11.23
13a	159—160	Colorless prisms (AcOEt–hexane)	$C_{13}H_{10}N_2O_2S$	60.45	3.90	10.85	12.41	60.37	3.99	10.72	12.57
14a	145—146	Colorless prisms (EtOH)	$C_{23}H_{15}N_5O_9S$[b]	51.40	2.81	13.23	5.97	51.58	3.05	13.03	6.38
15a	119—121	Colorless needles (Et_2O–hexane)	$C_{12}H_9NO_2S_2$	54.73	3.44	5.32	24.35	54.52	3.64	5.22	24.39
17	109—110	Yellow prisms (Et_2O–hexane)	$C_{15}H_{14}N_2O_2S$	62.92	4.93	9.78	11.20	62.78	4.97	9.70	11.18
19	124—126	Yellow prisms (C_6H_6–hexane)	$C_{17}H_{18}N_2O_2S$	64.94	5.79	8.91	10.20	65.16	5.84	8.84	10.43
20	84—85	Colorless prisms (Et_2O–hexane)	$C_{15}H_{14}N_2O_2S$	62.92	4.93	9.78	11.20	63.07	4.93	9.77	11.03

a) Lit.[17] mp 149.5—150 °C. *b*) Picrate: mp 193—194 °C.

TABLE X. Physical Constants and Analytical Data for Diethyl α-Arylcyanomethylphosphonates

No.	mp (°C) or bp (°C)/mmHg	Appearance (Recryst. solvent)	Formula	Analysis (%)					
				Calcd			Found		
				C	H	N	C	H	N
4a	100 / 1.0[a]	Colorless liquid	$C_{12}H_{16}NO_3P$	56.92	6.53	5.43	56.63	6.58	5.49
4b	140 / 0.8	Colorless liquid	$C_{13}H_{18}NO_3P$	58.42	6.79	5.24	58.26	6.73	5.20
4c	140 / 0.8	Colorless liquid	$C_{13}H_{18}NO_4P$	55.12	6.40	4.94	55.04	6.48	4.89
4d	130.5—131.5	Colorless needles (C_6H_6)	$C_{13}H_{15}N_2O_3P$	56.12	5.43	10.07	56.14	5.40	9.84
4e	89—90	Colorless needles (Hexane)	$C_{12}H_{15}N_2O_5P$	48.33	5.07	12.37	48.62	4.96	12.31
11b	80—81	Yellow needles (Et_2O–hexane)	$C_{11}H_{15}N_2O_3P$	51.97	5.95	11.02	51.80	5.88	11.13
12b	194—195	Colorless needles (Acetone)	$C_{13}H_{19}N_2O_3P$	55.31	6.78	9.92	55.49	6.70	9.74
13b	159—160	Yellow liquid	$C_{21}H_{23}N_6O_8P$[b]	48.65	4.74	16.21	48.48	4.66	16.22
14b	104—106	Colorless prisms (C_6H_6)	$C_{15}H_{17}N_2O_3P$	59.21	5.63	9.21	59.47	5.86	9.20
15b	140 / 0.8	Colorless liquid	$C_{10}H_{14}NO_3PS$	48.33	5.07	9.37	48.62	4.96	9.28

a) Lit.[18] bp 120—124 °C/0.03 mmHg. *b*) Picrolonate: mp 159—160 °C.

α-Ethyl-2,6-dimethyl-α-phenylsulfonyl-4-pyridineacetonitrile (19) According to the general procedure, 2,6-dimethyl-α-phenylsulfonyl-4-pyridineacetonitrile (**12a**) was allowed to react for 20 h to give **19** in 83% yield.

α-Ethyl-α-phenylsulfonyl-3-pyridineacetonitrile (20) α-Phenylsulfonyl-3-pyridineacetonitrile (**13a**) was allowed to react for 2 h to give **20** in 94% yield.

General Procedure for the Desulfonylation of α-Phenylsulfonylpyridineacetonitriles A mixture of an α-phenylsulfonylpyridineacetonitrile (2 mmol), AcOH (2 ml), anhydrous EtOH (3 ml), and zinc dust (0.65 g, 10 mmol) was stirred at room temperature for an appropriate time, as shown in Table V. After removal of the solvent, the residue was neutralized with 3 N Na_2CO_3 and extracted with $CHCl_3$. The crude product obtained from the $CHCl_3$ extract was purified by distillation and/or recrystallization.

α-(Phenylmethylene)benzeneacetonitrile (25a) A mixture of diethyl [cyano(phenyl)methyl]phosphonate (**4a**) (1.27 g, 5 mmol), 60% NaH (220 mg, 5.5 mmol), and anhydrous DME was stirred until the evolution of H_2 stopped. Then, benzaldehyde (0.64 g, 6 mmol) was added, and the whole mixture was refluxed for 2 h. After removal of the solvent, the residue was diluted with water and extracted with $CHCl_3$. The crude product obtained from the $CHCl_3$ extract was purified by silica gel column chromatography using hexane–benzene (3 : 1, v/v). Yield 0.90 g (88%).

General Procedure for the One-Pot Synthesis of Alkylideneareneacetonitrile An aldehyde (6 mmol) was added to the reaction mixture obtained according to the general procedure for the palladium-catalyzed condensation of aryl halides with diethyl cyanomethylphosphonate. Then, the mixture was heated for an appropriate time, as shown in Table VI. After removal of the solvent, the residue was diluted with water and extracted with $CHCl_3$. The crude product obtained from the $CHCl_3$ extract was purified by silica gel column chromatography followed by recrystallization or distillation.

References and Notes

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