A Facile Synthesis of *trans*-β-Trifluoromethylstyrene, *trans*-2,3,4,5,6-Pentafluorostilbene and their Derivatives

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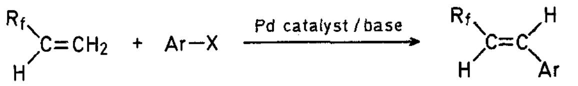
Although β-trifluoromethylstyrene[1,2,3,4], 2,3,4,5,6-pentafluorostilbene[5,6] and their derivatives are important intermediates for the synthesis of fluorine-containing organic compounds, there have been only a few reports on their preparations. Moreover, the reported methods have a limitation with regard to the position and sort of substituent groups which can be introduced to the aromatic ring.

We report here a convenient, one-step synthesis of a variety of substituted β-trifluoromethyl- and β-pentafluorophenylstyrenes via arylation of trifluoropropene (**1**) and pentafluorostyrene (**2**) promoted by palladium catalysts[7]. The phenylation of 3,3,3-trifluoropropene (**1**) or pentafluorostyrene (**2**) proceeded smoothly by heating the mixture of the olefin (**1** or **2**), iodobenzene (**3a**), a palladium catalyst (1 mol%) and a base such as triethylamine or potassium acetate to give *trans*-β-trifluoromethylstyrene (**4a**) or *trans*-pentafluorostilbene (**5a**) in high yield.



1 $R_f = CF_3$ **3** **4** $R_f = CF_3$
2 $R_f = C_6F_5$ **5** $R_f = C_6F_5$

Similarly, a variety of substituted iodobenzenes **3** readily reacted with **1** and **2** to give the corresponding *trans*-products, **4** and **5**, respectively, in good yield. Substituted bromobenzenes **3** (X = Br) can be also employed, but in this case the addition of triphenylphosphine (2 mol%) is found to be indispensable to promote the reaction. Bromonaphthalene, bromothiophene, and bromopyridine showed enough reactivity and the desired products were obtained in moderate yield. *trans*-β-Bromostyrene reacted with **1** in the presence of palladium chloride to give *trans,trans*-1-trifluoromethyl-4-phenyl-1,3-butadiene in 59% yield. Typical results are summarized in Tables 1 and 2, and the physical properties and the spectral data are listed in Tables 3 and 4. As Tables 1 and 2 show, the present reaction is not sensitive to the electronic nature of the substituents on the aryl halides **3** but is rather sensitive to the steric congestion. Aryl chlorides such as chlorobenzene and chlorotoluene were found to be unreactive under the present conditions.

***trans*-β-Trifluoromethylstyrene (4a):**

To a mixture of palladium chloride (17.7 mg, 0.1 mmol), iodobenzene (2.04 g, 10 mmol), and potassium acetate (1.37 g, 14.0 mmol) in methanol (5 ml) in a 50 ml autoclave is added 3,3,3-trifluoropropene (1.92 g, 20 mmol). The mixture is stirred for 20 h at 125 °C. The reaction mixture is poured into water (20 ml), and extracted with ether (3 × 10 ml). The combined extracts are dried with anhydrous sodium sulfate and concentrated. The residue is distilled under reduced pressure to give **4a**; yield: 1.63 g (95%).

Table 1. Arylation of 3,3,3-Trifluoropropene (**1**)

Halide No.	Ar	X	Catalyst	Base (mmol)/ solvent (ml)	Conditions temp./time	Conversion [%][a]	Product	Yield [%][a]	Selectivity [%][b]
3a	C_6H_5	J	$PdCl_2$	KOAc (14)/CH_3OH (5)	125 °C/20 h	100	**4a**	95	95
	C_6H_5	J	$PdCl_2$	$(C_2H_5)_3N$ (10)/C_6H_6 (4)	125 °C/20 h	97	**4a**	69	71
	C_6H_5	J	$PdCl_2$	$(C_4H_9)_3N$ (10)/—	125 °C/ 2 h	95	**4a**	50	53
	C_6H_5	J	$PdCl_2$	K_2CO_3 (10)/CH_3OH (5)	125 °C/20 h	78	**4a**	39	50
	C_6H_5	J	$Pd(OAc)_2$	KOAc (14)/CH_3OH (5)	125 °C/20 h	100	**4a**	94	94
	C_6H_5	J	$Pd[P(C_6H_5)_3]_4$	KOAc (14)/CH_3OH (5)	125 °C/20 h	100	**4a**	90	90
	C_6H_5	J	Pd-black	KOAc (14)/CH_3OH (5)	125 °C/20 h	93	**4a**	88	94
	C_6H_5	J	Pd/C	KOAc (14)/CH_3OH (5)	125 °C/20 h	87	**4a**	75	86
	C_6H_5	Br	$Pd(OAc)_2/2P(C_6H_5)_3$	—/$(C_2H_5)_3N$ (3)	125 °C/44 h	92	**4a**	68	74
3b	4-H_3CO—C_6H_4	J	$PdCl_2$	KOAc (14)/CH_3OH (5)	125 °C/20 h	83	**4b**	78	94
3c	4-H_3C—C_6H_4	J	$PdCl_2$	KOAc (14)/CH_3OH (5)	125 °C/20 h	96	**4c**	93	97
3d	4-HOOC—C_6H_4	J	$Pd(OAc)_2$	$(C_2H_5)_3N$ (3.5 ml)/CH_3CN (4)	125 °C/14 h	100	**4d**	80[c]	80
3e	4-O_2N—C_6H_4	J	$Pd(OAc)_2$	$(C_2H_5)_3N$ (3.5 ml)/CH_3CN (4)	125 °C/14 h	100	**4e**	62	62
3f	4-H_3COOC—C_6H_4	J	$Pd(OAc)_2$	$(C_2H_5)_3N$ (3.5 ml)/CH_3CN (4)	125 °C/14 h	100	**4f**	77	77
3g	3-F—C_6H_4	Br	$Pd(OAc)_2/2P(C_6H_5)_3$	—/$(C_2H_5)_3N$ (3)	125 °C/40 h	100	**4g**	79	79
3h	3-F_3C—C_6H_4	Br	$Pd(OAc)_2/2P(C_6H_5)_3$	—/$(C_2H_5)_3N$ (3)	125 °C/40 h	100	**4h**	80	80
3i	2-Cl—C_6H_4	Br	$Pd(OAc)_2/2P(C_6H_5)_3$	—/$(C_2H_5)_3N$ (3)	125 °C/97 h	35	**4i**	12	35
3j	2-naphthyl	Br	$Pd(OAc)_2/2P(C_6H_5)_3$	—/$(C_2H_5)_3N$ (3)	160 °C/28 h	100	**4j**	42	42
3k	1-naphthyl	Br	$Pd(OAc)_2/2P(C_6H_5)_3$	—/$(C_2H_5)_3N$ (3)	160 °C/30 h	100	**4k**	22	22
3l	2-thienyl	Br	$Pd[P(C_6H_5)_3]_2Cl_2$	KOAc (14)/CH_3OH (5)	125 °C/72 h	100	**4l**	39	39
3m	3-pyridyl	Br	$Pd(OAc)_2/2P(C_6H_5)_3$	—/$(C_2H_5)_3N$ (3)	160 °C/51 h	100	**4m**	65	65
3n	C_6H_5—CH=CH—	Br	$PdCl_2$	KOAc (14)/CH_3OH (5)	125 °C/63 h	100	**4n**	59	59

[a] Determined by G.L.C. analysis (conditions: 3 mm × 1.2 m glass column packed with 30% silicone DC 550 on Uniport B at 100–200 °C using *n*-dodecane as internal standard).
[b] Based on consumed halide.
[c] Yield of isolated product.

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Table 2. Arylation of Pentafluorostyrene (**2**)

Halide No.	Ar	X	Catalyst	Base (mmol)/ solvent (ml)	Conditions temp./time	Product	Yield [%][a]
3a	C_6H_5	J	$PdCl_2$	KOAc (3.5)/CH_3OH (2)	100 °C/18 h	**5a**	80
	C_6H_5	J	$Pd(OAc)_2$	—/$(C_2H_5)_3N$ (1)	100 °C/18 h	**5a**	91
3b	4-H_3CO—C_6H_4	J	$Pd(OAc)_2$	—/$(C_2H_5)_3N$ (1)	100 °C/18 h	**5b**	84
3e	4-O_2N—C_6H_4	J	$Pd(OAc)_2$	$(C_2H_5)_3N$ (1 ml)/CH_3CN (1.5 ml)	100 °C/18 h	**5c**	80
3n	C_6H_5	Br	$PdCl_2$	KOAc (3.5)/CH_3OH (2)	100 °C/60 h	**5d**	81

[a] Yield of isolated product.

Table 3. Characterization of *trans*-β-Trifluoromethylstyrene Derivatives (**4**)

Product	m.p. [°C] or b.p. [°C]/torr	Molecular formula[a] or Lit. m.p. [°C] or b.p. [°C]/torr		I.R. [cm⁻¹] $\nu_{C=C}$	$\delta_{=CH}$	¹H-N.M.R. (CDCl₃) $\delta_{=CH}$ [ppm]	J_{trans} [Hz]	¹⁹F-N.M.R. ($CDCl_3$/$CFCl_3$) δ_{CF_3} [ppm]	M.S. m/e (M⁺)
4a	64°/18	61–62°/20[1]		1670	970	6.2, 7.2	16.2	−63.8	172
4b	37–37.5°	$C_{10}H_9F_3O$	(202.2)	1665	970	6.0, 7.0	16.2	−63.3	202
4c	59°	$C_{10}H_9F_3$	(186.2)	1665	970	6.1, 7.0	16.1	−63.6	186
4d	214° (dec.)	247–248°[2]		1690	980	(6.5, 7.3)[b]	(16.2)[b]	(−63.7)[b]	216
4e	96–98°	97–99°[3]		1670	975	6.3, 7.2	16.2	−64.6	217
4f	74.5–77.5°	$C_{11}H_9F_3O_2$	(230.2)	1675	980	6.3, 7.1	16.1	−64.2	230
4g	68°/18	119–120°/170[4]		1670	965	6.2, 7.1	16.3	−64.1	190
4h	55°/2	$C_{10}H_6F_6$	(240.1)	1675	970	6.3, 7.2	16.2	−64.3, −63.6	240
4i	oil	$C_9H_6ClF_3$	(206.6)	1670	970	6.2, 7.6	16.2	−64.2	206, 208
4j	108–108.5°	$C_{13}H_9F_3$	(222.2)	1665	965	6.3, 7.3	16.2	−63.8	222
4k	oil	$C_{13}H_9F_3$	(222.2)	1665	970	6.2, 7.9	16.1	−64.0	222
4l	oil	$C_7H_5F_3S$	(178.2)	1660	960	6.0, 7.2	16.0	−63.8	178
4m	oil	$C_8H_6F_3N$	(173.1)	1670	975	6.3, 7.1	16.2	−64.5	173
4n	34–35°	$C_{11}H_9F_3$	(198.2)	1650	990	5.4, 6.6[c] 6.2, 6.3	15.0[c] 15.7	(−63.7)[c]	198

[a] Satisfactory microanalyses obtained: C ±0.20, H ±0.22, N ±0.05.
[b] Methanol-d_4.
[c] Benzene-d_6.

Table 4. Characterization of *trans*-2,3,4,5,6-Pentafluorostilbene Derivatives (**5**)

Product	m.p. [°C] (from C_2H_5OH)	Molecular formula[a] or Lit. m.p. [°C]		I.R. [cm⁻¹] $\delta_{=CH}$	¹H-N.M.R. (CDCl₃) J_{trans} [Hz]	¹⁹F-N.M.R. ($CDCl_3$/$CFCl_3$) [ppm] $\delta_{2,6\text{-}F}$	$\delta_{3,5\text{-}F}$	$\delta_{4\text{-}F}$	M.S. m/e (M⁺)
5a	139.5–140°	139–140°[5]		960	17.0,	−143.3	−163.5	−157.1	270
5b	130.5–133°	$C_{15}H_9F_5O$	(300.2)	955	17.0	−143.9	−164.0	−158.2	300
5c	128–129.5°	$C_{14}H_6F_5NO_2$	(315.2)	960	17.0	−142.4	−162.8	−154.7	315
5d	144.5–146.5°	$C_{16}H_9F_5$	(296.2)	980, 960	17.0 17.0	−143.5	−163.8	−157.5	296

[a] Satisfactory microanalyses obtained: C ±0.11, H ±0.14, N ±0.04.

***trans*-2,3,4,5,6-Pentafluorostilbene (5a):**

A mixture of palladium acetate (6.72 mg, 3×10^{-2} mmol), pentafluorostyrene (585 mg, 3 mmol), and iodobenzene (612 mg, 3 mmol) in triethylamine (1 ml) is heated in a sealed tube at 100 °C for 18 h. The reaction mixture is poured into water (10 ml), and extracted with ether (3 × 10 ml). The extracts are dried with anhydrous sodium sulfate and concentrated under reduced pressure. The residue is purified by column chromatography on silica gel using benzene as eluent to give colorless solid **5a**; yield: 737 mg (91%).

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