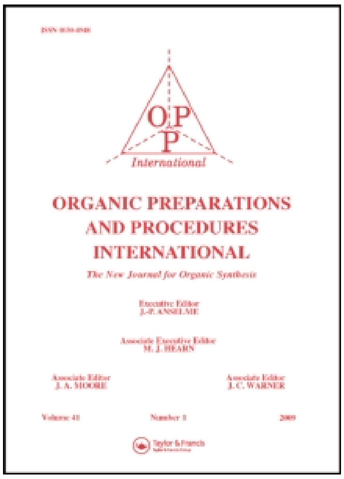

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THE PREPARATION OF 1-ARYL-2-(2-THIENYL)ETHYLENES

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THE PREPARATION OF 1-ARYL-2-(2-THIENYL)ETHYLENES

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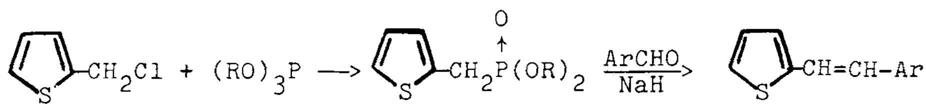
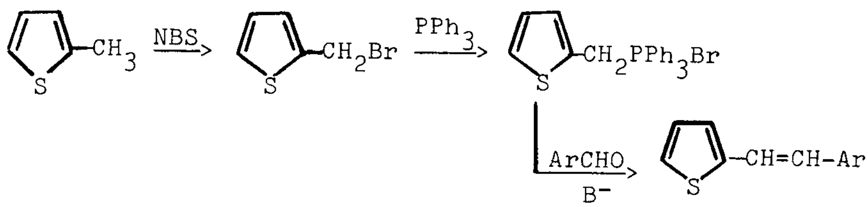
Kellog, Groen and Wynberg[1] have prepared the title compounds by a modified Wittig reaction, as shown below:



This procedure gives fair overall yields but requires several tedious and time-consuming steps.

We now wish to report the very facile and high-yield synthesis of 1-aryl-2-(2-thienyl)ethylene compounds using a direct Wittig reaction, as shown below:



2-Thenyltriphenylphosphonium bromide was prepared quantitatively from 2-thenyl bromide and triphenylphosphine. The unstable 2-thenyl bromide was synthesized by NBS bromination of 2-methylthiophene in 69% yield as determined by NMR integration analysis.

Experimental

Melting points are corrected. Microanalyses by Central Research Department of E. I. du Pont de Nemours & Company, Wilmington, Delaware.

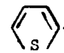
2-Thenyl Bromide. 2-Thenyl bromide was prepared according to the procedure of Dittmer.[2] 2-Methylthiophene (24.0 g.), N-bromosuccinimide (45.5 g.), and benzoyl peroxide (0.23 g.) were brought to reflux in 200 ml. CCl_4. An additional 0.2 g. of benzoyl peroxide was added every ten minutes until 0.93 g. had been added. The total reflux time was 90 minutes. The distillation fraction, b.p. 99-115°/26 mm. (30.0 g.), contained as indicated by NMR integration analysis, 1% of 2-methyl-5-bromothiophene isomer (split singlet at 2.05 δ) and 99% 2-thenyl bromide (singlet at 4.60 δ). Therefore, the overall yield of 2-thenyl bromide from the reaction was 69%. Redistillation gave pure 2-thenyl bromide (b.p. 34-36° at 0.25 mm. Hg).

Analysis:

Calc'd for C_5H_5BrS: C, 33.90; H, 2.82; Br, 45.20; S, 18.08.
Found: C, 33.43; H, 2.73; Br, 45.30; S, 17.89.

2-Thenyltriphenylphosphonium Bromide. The bromomethylthiophene mixture, b.p. 99-115°/26 mm., was refluxed immediately with a molar equivalent of triphenylphosphine in THF. The yield of phosphonium salt precipitate was 71.0 g. (95%), m.p. 320° d. (MeOH).

1-Aryl-2(2-Thienyl)Ethylenes


-CH=CH-Ar

Ar	m.p. °C	Color	M.W.	Formula	Carbon		Hydrogen		Sulfur		N or Cl		Ultraviolet Spectral Data[c]	
					Calc'd	Found	Calc'd	Found	Calc'd	Found	Calc'd	Found	λmax (m)	E x 10^{-4}
Ph	108-9[a]	Straw Yellow	186	$C_{12}H_{10}S$	77.42	77.41	5.38	5.48	17.20	17.13	--	--	323,229,268(S)	2.98,1.12,0.55
3,4-OCH$_2$OPh	112-3	Pale Yellow	230	$C_{13}H_{10}O_2S$	67.83	67.81	4.35	4.41	13.91	13.43	--	--	338,313(S),255(S)	3.14,2.00,0.40
4-iso Pr Ph	78-9	Pale Yellow	228	$C_{15}H_{16}S$	78.94	79.15	7.02	7.40	14.04	13.89	--	--	328,240(S),231	3.34,0.90,1.16
2,4-DiNO$_2$Ph	161-2	Orange Yellow	276	$C_{12}H_8N_2O_4S$	52.17	52.20	2.89	3.13	11.59	11.57	10.14	9.94	385	2.18
3,4-DiClPh	97-8	Dull White	255	$C_{12}H_8Cl_2S$	56.47	56.37	3.14	3.14	12.55	12.52	27.84	28.10	322,248(S),240	2.98,0.65,0.84
2-Thienyl	131-2[b]	Pale Yellow	192	$C_{10}H_8S_2$	62.50	62.65	4.17	4.34	33.33	33.29	--	--	339,325(S),~260(S)	2.83,2.40,0.20
2-Furyl	77-8	Light Yellow	176	$C_{10}H_8OS$	68.18	68.40	4.55	4.66	18.18	18.24	--	--	332,~240(S)	3.02,0.30
4-Pyridyl	146-7	Pale Yellow	187	$C_{11}H_9NS$	70.59	70.57	4.81	4.98	17.11	17.24	7.49	7.40	330,235(S)	2.87,0.65
2-Pyridyl	78-9	Pale Yellow	187	$C_{11}H_9NS$	70.59	70.49	4.81	5.01	17.11	17.13	7.49	7.41	320,272,228	0.88,0.83,0.76
												(d)	354(S),339,305,292	1.08,1.50,1.02,1.04
												(e)	352(S),336,302,288	1.08,1.54,0.96,1.02

(a) m.p. 110-111°, R. Miller and F. Nord, J. Org. Chem. 16, 1386 (1951).
m.p. 111°, Ng Ph. Buu-Hoi et.al., J. Chem. Soc. 2132 (1950).
m.p. 109-110°, G. Van Zyl et.al., J. Am. Chem. Soc. 76, 708 (1954).

(b) m.p. 130.5-131°, R. Miller and F. Nord, J. Org. Chem. 16, 1387 (1951).
m.p. 132.5°, W. Steinkopf and H. Jacob, Ann. 501, 190 (1933).

(c) Absolute MeOH as solvent (d) Carbon Tetrachloride as solvent (e) Cyclohexane as solvent

General Procedure for the Wittig Reaction. To a stirred solution of 0.2 m. 2-thenyltriphenylphosphonium bromide (8.8 g.) and 0.025 m. of the aryl aldehyde in 100 ml. of absolute methanol was added 1 g. of sodium methoxide. The mixture was refluxed for 10 minutes, cooled, washed with water and extracted with ether. The ether was evaporated and the residue was recrystallized from methanol or methanol/H_2O. Yields over 80% of recrystallized thienylethylenes were obtained. The melting points, analyses and principal absorptions in the ultra-violet are reported in the table.

References

1. R. Kellog, M. Groen and H. Wynberg, J. Org. Chem., 32, 3093 (1967).

2. K. Dittmer, R. Martin, W. Herz and S. Cristol, J. Am. Chem. Soc., 71, 1201 (1949).

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