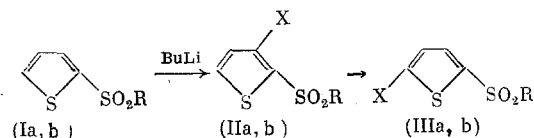


REGIOSELECTIVE LITHIATION OF 2-SULFONYLTHIOPHENES IN THE 3-POSITION

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According to the data of [1], lithiation of phenyl 2-thienylsulfone (Ia) by *n*-BuLi in ether occurs in the 5 position of the thiophene ring. We found the conditions (ether 2 N solution of *n*-BuLi, toluene:ether = 7,5-10:1, -30 to -40°C) under which (Ia) and also *tert*-butyl 2-thienylsulfone (Ib) are lithiated almost exclusively in the 3 position of the thiophene ring. This apparently occurs because of coordination of the metallating agent at the SO₂ group. The 3-Li derivatives (IIa, b) (X = Li) are kinetically controlled products undergoing conversion to 5-Li derivatives (IIIa, b) (X = Li) in a more polar medium or at a higher temperature (Table 1).



The following 3-X-2-RSO₂ thiophenes (R, X, yield, %, and mp, °C, are given) were obtained under the above mentioned conditions by reaction with an appropriate electrophile (CO₂, Me₂SO₄, DMFA): Ph, COOH, 58, 165,5-166,5; Ph, Me, 89 (67% was isolated with a 95,2% content of the main substance), 91,5-92,5; CMe₃, COOH, 75, 137-138; CMe₃, CHO, 64, 118-119,5.

TABLE 1

Metallation conditions			X	Yield, %			
				R=Ph		R=CMe ₃	
solvent	T., °C	time, min		(II)	(III)	(II)	(III)
Toluene-ether, 8:1	-30 ÷ -40	360	COOH	58	0	75	0
»	-30 ÷ -40	360	Me	89	5	73	3
»	-30 ÷ -40	360	CHO	—	—	74	0
Ether	0	7	COOH	—	—	58	17
»	0	240	COOH	3	57	25	34
»	0	240	Me	2,5	86,5	—	—

LITERATURE CITED

1. W. Truce and M. Amos, *J. Am. Chem. Soc.*, **73**, 3013 (1951).

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