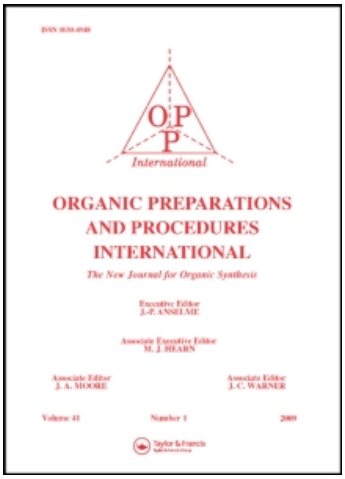

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A FACILE SYNTHESIS OF 2-(2'-SUBSTITUTED VINYL)BENZOXAZOLES

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A FACILE SYNTHESIS OF 2-(2'-SUBSTITUTED VINYL)BENZOXAZOLES

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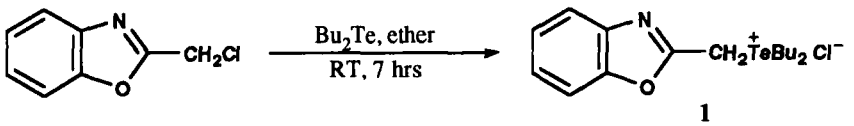
2-(2'-Substituted vinyl)benzoxazoles belong to a versatile class of compounds.[1] The synthesis of these compounds *via* telluronium salt has not been reported. Recently, we described a convenient method for preparing α,β-unsaturated nitriles, ketones, esters, amides and substituted cyclopropanes.[2-5] We now report the facile synthesis of 2-(2'-substituted vinyl)benzoxazoles. 2-Benzoxazolylmethyldibutyltelluronium chloride (**1**), easily prepared (79%) by the reaction of dibutyl telluride with



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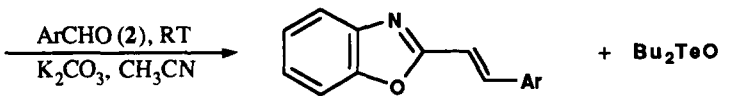

3

a) Ar = C_6H_5 b) Ar = *p*-$CH_3OC_6H_4$ c) Ar = *p*-ClC_6H_4
d) Ar = *p*-FC_6H_4 e) Ar = *p*-$NO_2C_6H_4$ f) Ar = *p*-$CH_3C_6H_4$ g) Ar = 2-furfuryl

2-chloromethylbenzoxazole in ether at room temperature, reacted with aromatic aldehydes **2a-e** in acetonitrile containing trace amounts of formamide in the presence of potassium carbonate to afford 2-(2'-substituted vinyl)benzoxazoles **3**. The IR and ^1H NMR spectra indicated all the products to be the E-isomers. These compounds E-2-(2'-substituted vinyl)benzoxazoles could be obtained with high stereoselectivity in a one-pot reaction directly from 2-chloromethylbenzoxazole, the aldehydes (**2a-g**) and dibutyl telluride at reflux in acetonitrile under neutral conditions.

EXPERIMENTAL SECTION

Melting points are uncorrected and were taken on a Büchi 535 apparatus. Elemental analysis were carried out on a Carlo Erba 1106 apparatus. IR spectra determined on a Nicolet 740 FT-IR spectrophotometer. ^{1}H NMR spectra were recorded on a JNM-FX 90Q spectrometer in DMSO-d using TMS as internal standard.

TABLE. 2-(2'-Substituted vinyl)benzoxazoles

Product	Method A			Method B[a]		Analysis (Found)		
	Time (hrs)	Temp. (°C)	Yield (%)	Time (hrs)	Yield (%)	C	H	N
3a	10	RT	92	8	72	81.43 (81.37)	5.01 (4.87)	6.33 (6.14)
3b	13	RT	52	10	56	76.48 (76.54)	5.21 (5.43)	5.58 (5.35)
3c	6	RT	78	8	71	70.46 (70.31)	3.94 (3.73)	5.48 (5.54)
3d	6	RT	84	8	75	75.30 (75.47)	4.21 (4.36)	5.86 (5.74)
3e	6	RT	71	6	79	67.66 (67.37)	3.79 (3.58)	10.52 (10.67)
3f	–	–	–	10	64	81.68 (81.79)	5.57 (5.30)	5.95 (5.72)
3g	–	–	–	8	71	73.92 (73.99)	4.30 (4.27)	6.63 (6.54)

a) All reactions carried out at reflux.

General Procedure for the Synthesis of 2-(2'-Substituted vinyl)benzoxazoles.

Method A.- A mixture of equimolar amounts of 2-chloromethylbenzoxazole and of dibutyl tellurides in ethyl ether was stirred for 7 hrs at room temperature. The precipitated salt was collected to give the telluronium salt **1** which was washed with ethyl ether and dried, mp. 86-87°; yield 79%. A mixture of **1** (1.1 mmol) potassium carbonate (1.1 mmol) and **2a-e** (1 mmol), in 10 mL of acetonitrile containing 100 µL of formamide was stirred at room temperature. The reaction was monitored with HPLC. After the reaction was completed, water was added and the crystalline product was collected. The products were recrystallized from ethanol-water (see Table).

Method B.- A mixture of 2-chloromethylbenzoxazole (1 mmol), dibutyl telluride (1 mmol) and **2a-g** (1 mmol) in 10 mL of acetonitrile was refluxed with stirring. The reaction was worked up as above. These compounds showed a band at 961-971cm^{-1} for the *trans* double bond.

3a, mp. 78.9-79.3°, lit.[6] 83-84°; IR (KBr): 971 cm^{-1}; ^{1}H NMR: δ 7.18 (1H, d, J = 13.5 Hz), 7.43 (4 H, m), 7.48 (1 H, d, J = 13.5 Hz), 7.76 (5 H, m).

3b, mp. 139.1-139.6°, lit.[6] 136-137°; IR (KBr): 965 cm^{-1} ; ^1H NMR: δ 3.83 (3 H, s), 6.95 (2 H, d, J = 9.0 Hz), 7.05 (1 H, d, J = 13.5 Hz), 7.40 (4 H, m), 7.62 (1 H, d, J = 13.5 Hz), 7.68 (2 H, d, J = 9.0 Hz).

3c, mp. 145.6-146.3°, lit.[6] 144-145°; IR (KBr): 969 cm^{-1}; ^1H NMR: δ 7.14 (1 H, d, J = 12.6 Hz), 7.41 (4 H. m), 7.66 (1 H, d, J = 12.6 Hz), 7.72 (2 H, d, J = 9.0 Hz),, 7.85(2 H, d, J = 9.0 Hz).

3d, mp. 113-113.4°, lit.[6] 116-117°; IR (KBr): 968 cm^{-1}; ^1H NMR: δ 7.15 (1 H. d, J = 12.6 Hz), 7.33 (4 H, m), 7.74 (1 H, d, J = 12.6 Hz), 7.79 (2 H, d, J = 9.0 Hz), 7.95 (2 H, d, J = 9.0 Hz).

3e, mp. 249.8-250.3°, lit.[6] 239-240°; IR (KBr): 961 cm^{-1}; ^1H NMR: δ 7.35 (1 H, d, J = 12.6 Hz), 7.60 (4 H, m), 7.85 (1 H, d, J = 12.6 Hz), 8.00 (2H, d, J = 9.0 Hz), 8.21 (2 H, d, J = 9.0 Hz).

3f, mp. 129.5-130.3°, lit.[6] 131-132°; IR (KBr): 970 cm^{-1}; ^1H NMR: δ 2.35 (3 H, s), 7.10 (2 H, d, J = 9.0 Hz), 7.28 (1 H, d, J = 13.5 Hz), 7.32 (4 H, m), 7.48 (1 H, d, J = 13.5 Hz), 7.70 (2 H, d, J = 9.0 Hz).

3g, mp. 122-122.6°, lit.[7] 123°; IR (KBr) : 962 cm^{-1}; ^1H NMR: δ 6.66 (2 H, m), 6.93 (1 H, d, J = 12.6 Hz), 7.42 (4 H, m), 7.54 (1 H, d, J = 12.6 Hz), 7.73 (3 H, d).

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