

A Facile Synthesis of Benzoxazolyl Cyclopropanes

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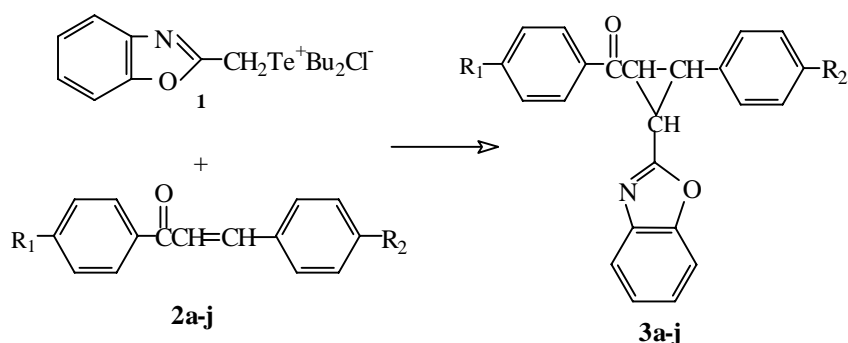
Abstract: 2'-Benzoxazolyl substituted cyclopropane derivatives were synthesized in the yield of 73-89% from the reaction of telluronium ylides with chalcones.

Keywords: Telluronium ylides, telluronium salt, benzoxazolyl cyclopropane.

Benzoxazole derivatives are a versatile class of compounds¹, they can be used as fluorescent bleaches, laser dyes and organic scintillators². Previously we reported the use of telluronium ylides to synthesize 2-(2'-substituted vinyl) benzoxazoles³.

However, the synthesis of 2'-benzoxazolyl substituted cyclopropane derivatives has not been reported yet by the reaction of telluronium ylide with α , β -unsaturated carbonyl compounds.

2-Benzoxazolyl methyldibutyl telluronium chloride **1**, easily prepared by the reaction of dibutyl telluride with 2-chloromethylbenzoxazole in ether at room temperature³, reacted with substituted chalcone **2a-j** in THF in the presence of sodium hydroxide at room temperature to afford 1-(2'-benzoxazolyl) cyclopropanes **3a-j** in 73-89% yields (**Table 1**). All the products were characterized by spectroscopic data and elemental analysis.



Reaction Condition: NaOH (s); THF; RT.

a) $\text{R}_1=\text{H}$, $\text{R}_2=\text{H}$ b) $\text{R}_1=\text{H}$, $\text{R}_2=\text{F}$ c) $\text{R}_1=\text{H}$, $\text{R}_2=\text{Br}$ d) $\text{R}_1=\text{H}$, $\text{R}_2=\text{CH}_3$ e) $\text{R}_1=\text{Cl}$, $\text{R}_2=\text{H}$
f) $\text{R}_1=\text{Cl}$, $\text{R}_2=\text{Cl}$ g) $\text{R}_1=\text{Cl}$, $\text{R}_2=\text{Br}$ h) $\text{R}_1=\text{OCH}_3$, $\text{R}_2=\text{H}$ i) $\text{R}_1=\text{OCH}_3$, $\text{R}_2=\text{F}$ j) $\text{R}_1=\text{OCH}_3$, $\text{R}_2=\text{Br}$

The results summarised in **Table 1** and **Table 2** showed that chalcones substituted with an electron-withdrawing group reacted with telluronium ylide more rapidly than those with an electron-donating group. The preparation of cyclopropanes with telluronium ylides is simpler and more convenient than that with arsenium ylides⁴ and sulfurnium ylides⁵. This reaction also widens the application of telluronium ylides in organic synthesis.

Table 1 Yields, mp and elemental analysis of compounds **3a-j**

Compd.	Reaction Time (h)	Yield (%)	mp (°C)	Elemental Analysis Calcd (Found)		
				C	% H	N
3a	10	74	244-246	81.39 (81.08)	5.05 (5.18)	4.13 (4.36)
3b	8	89	240-242	77.30 (76.98)	4.51 (4.21)	3.92 (3.75)
3c	8	81	266-268	66.04 (65.84)	3.86 (3.74)	3.35 (3.69)
3d	15	82	236-237	81.56 (81.41)	5.42 (5.09)	3.96 (3.82)
3e	8	74	250-252	73.89 (74.17)	4.31 (4.52)	3.75 (3.86)
3f	8	78	205-206	67.66 (67.37)	3.70 (3.47)	3.43 (3.26)
3g	8	82	256-258	61.02 (60.91)	3.34 (3.27)	3.09 (3.31)
3h	15	78	218-220	78.03 (77.74)	5.18 (5.03)	3.79 (3.68)
3i	12	73	210-212	74.40 (74.21)	4.68 (4.59)	3.62 (3.37)
3j	12	84	224-226	64.30 (64.16)	4.05 (4.26)	3.13 (3.12)

Experimental

Melting points were measured on a Buchi 535 apparatus and were uncorrected. Elemental analysis were carried out on a Carlo Erba 1106 apparatus. IR spectra were determined as KBr pellets on Nicolet 740 SX FT-IR spectrometer. ¹H NMR spectra were recorded on a TNMFX 90Q spectrometer in CDCl₃ using TMS as internal standard.

2-Benzoxazolyl methylidibutyl telluronium chloride³ and the substituted chalcones⁶ were synthesized according literature procedure.

A mixture of **1** (1.1 mmol) and sodium hydroxide NaOH (s, 5 mmol) in 5 mL THF was stirred at room temperature. The reaction was monitored by HPLC. After the reaction was completed, water (5 mL) was added, and the mixture was extracted with dichloromethane (5 mL). The product was obtained after evaporation of the solvent and recrystallized from ethanol (95%).

Table 2 IR and ¹HNMR spectra of compounds 3a-j

Product	IR ν (KBr, cm^{-1})	¹ HNMR (δ ppm, CDCl_3)
3a	1640, 1001, 951	3.88~4.16 (m, 3H, H-cyclopropane), 7.00~7.40 (m, 14H, Ar-H)
3b	1640, 1001, 952	4.00~4.18 (m, 3H, H-cyclopropane), 6.98~7.54 (m, 13H, Ar-H)
3c	1640, 1001, 952	3.74~4.02 (m, 3H, H-cyclopropane), 7.02~7.50 (m, 13H, Ar-H)
3d	1642, 1001, 952	2.11 (s, 3H, CH_3), 3.96~4.16 (m, 3H, H-cyclopropane), 6.98~7.44 (m, 13H, Ar-H)
3e	1641, 1001, 953	3.72~4.32 (m, 3H, H-cyclopropane), 7.00~7.62 (m, 13H, Ar-H)
3f	1640, 1009, 947	3.63~4.16 (m, 3H, H-cyclopropane), 6.96~7.46 (m, 12H, Ar-H)
3g	1638, 1010, 951	3.64~4.12 (m, 3H, H-cyclopropane), 6.92~7.42 (m, 12H, Ar-H)
3h	1651, 1012, 952	3.60 (s, 3H, OCH_3), 3.76~4.26 (m, 3H, H-cyclopropane), 7.00~7.40 (m, 13H, Ar-H)
3i	1654, 1010, 951	3.56 (s, 3H, OCH_3), 3.64~4.16 (m, 3H, H-cyclopropane), 7.04~7.44 (m, 12H, Ar-H)
3j	1655, 1009, 951	3.54 (s, 3H, OCH_3), 3.54~4.18 (m, 3H, H-cyclopropane), 7.02~7.36 (m, 12H, Ar-H)

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