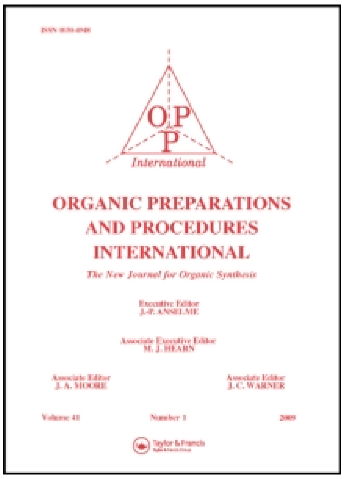

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FACILE SYNTHESIS OF 2-ARYL-4H-3,1-BENZOXAZIN-4-ONES

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FACILE SYNTHESIS OF 2-ARYL-4H-3,1-BENZOXAZIN-4-ONES

Submitted by
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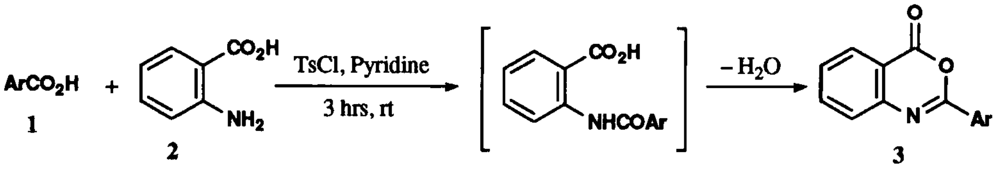
Substituted 4H-3,1-benzoxazin-4-ones are potential intermediates in the synthesis of 2,3-disubstituted-4-(3H)quinazolinones,[1] pharmaceutical agents[2] and linking-units in thermally stable polymers.[3] A wide variety of procedures leading to benzoxazin-4-ones are available in literature. The most common approach consists of the reaction of N-acylanthranilic acid with acetic anhydride[1a] or treatment of anthranilic acid with carboxylic acid chlorides.[4] In recent years, the synthesis of title compounds has been achieved by heating aromatic carboxylic acid with anthranilic acid in the presence of reagents like triphenylphosphite and pyridine[5] or phosphorus pentoxide-methanesulfonic acid[3c] (PPMA) or phosphorus oxychloride.[6] All the above mentioned methods involve drastic conditions in addition to the complex work-up procedures. This report describes a simple method for the synthesis of 2-aryl-4H-3,1-benzoxazin-4-ones in reasonable yields under mild conditions.

The synthesis involves the initial reaction of substituted benzoic acid (1) with tosyl chloride (TsCl) in pyridine at room temperature for 5 minutes followed by the addition of anthranilic acid (2) All the benzoxazin-4-ones synthesized show characteristic carbonyl absorption around 1760 cm^{-1} in their IR spectra [Table].

TABLE. Yield and Characterization Data of 2-Aryl-4H-3,1-benzoxazin-4-ones[a]

Entry	Ar	Yield (%)	mp. (lit.[b]) (°C)	IR ($CHCl_3$) (C=O cm^{-1})	Mass Spectra M$^{+\bullet}$(relative intensity)
1	C_6H_5-	61	123 (122)	1761	223 (100)
2	*o*-$CH_3C_6H_4$-	52	114 (114)	1760	237 (100)
3	*p*-$CH_3C_6H_4$-	62	155 (156)	1756	237 (100)
4	*o*-ClC_6H_4-	42	138 (138)	1763	257 (100)
5	*p*-ClC_6H_4-	37	190 (190)	1760	257 (100)
6	*o*-$OCH_3C_6H_4$-	50	189 (—)[c]	1766	253 (50)
7	*p*-$OCH_3C_6H_4$-	54	160 (158)	1760	253 (85)
8	*o*-$NO_2C_6H_4$-	33	192 (192)	1769	268 (70)
9	*p*-$NO_2C_6H_4$-	41	202 (203)	1760	268 (100)

a) All the compounds have also been characterized by ^{1}H NMR spectra. b) See references. c) *Anal.* Calcd. for $C_{15}H_{11}NO_3$: C, 71.14; H, 4.38; N, 5.53; Found: C, 71.21; H, 4.58; N, 5.30



The mechanism probably involves initial formation of the mixed anhydride of the carboxylic acid (**1**), which then acylates anthranilic acid (**2**) to yield N-aroylanthranilic acid. Cyclization with the loss of H_2O from N-aroylanthranilic acid yields 2-aryl-4H-3,1-benzoxazin-4-ones (**3**). N-phenylanthranilic acid, prepared independently, yields 2-phenyl-4H-3,1-benzoxazin-4-one in the presence of pyridine under identical conditions.

Mild conditions, shorter reaction times coupled with moderate yields make this present method an attractive alternative to literature methods.

EXPERIMENTAL SECTION

Mps were determined in open capillary tubes using a Toshniwal capillary melting point apparatus and are uncorrected. Tosyl chloride was recrystallized from petroleum ether (60-80°). Infrared spectra were recorded using Shimadzu 470 infrared spectrophotometer. ^{1}H NMR a spectra were recorded in a Hitachi R-600-60 MHz nmr instrument using TMS as internal standard. Mass spectra were recorded using Finnigan MAT 8230 mass spectrometer. Elemental analysis were carried out using Heraeus-CHN-rapid analyser.

Typical Procedure.- The carboxylic acid (**1**) (20 mmol) was dissolved in pyridine (15 mL) and tosyl chloride (TsCl) (1.89 g, 10 mmol) was added with stirring at room temperature. After 5 minutes, anthranilic acid (1.37 g, 10 mmol) was added with vigorous stirring at room temperature. The stirring was continued for 3 hours at room temperature. The resulting mixture was poured into a saturated aqueous sodium bicarbonate solution (100 m L) with stirring. The resulting solution was extracted with dichloromethane (3 x 50 mL). The combined extracts were washed with distilled water, and the organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed through rotary evaporator to yield the solid product. Purification was effected by recrystallization from petroleum ether (60-80°) for all the compounds except for **8** and **9**, for which absolute ethanol-petroleum ether (1:1) mixture was used. All the benzoxazin-4-ones synthesized were characterized thoroughly by their mps and spectral data [Table].

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PREPARATION OF bis(2,2,2-TRIFLUOROETHYL)SELENIDE AND TELLURIDE AND OF bis(2,2,2-TRIFLUOROETHYL)DISELENIDE AND DITELLURIDE

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Organoselenium and organotellurium compounds are useful synthons in organic synthesis.[1] Dialkyl tellurides find applications as precursors for the growth of the semiconductor cadmium mercury telluride (CMT) by MOCVD, useful in infrared detectors and related devices.[2] Diorganyl sulphides and selenides containing 2,2,2-trifluoroethyl group have successfully been used for the synthesis of thioynamines and selenoynamines respectively.[3] We therefore sought to develop a convenient method for the preparation of new organoselenium and organotellurium compounds containing 2,2,2-trifluoroethyl groups.

bis(2,2,2-Trifluoroethyl)selenide (**1**), telluride (**2**), diselenide (**3**) and ditelluride (**4**) have been prepared for the first time by reaction of 1-iodo-2,2,2-trifluoroethane with sodium selenide or telluride

$$\mathrm{nE} + 2\mathrm{Na} \xrightarrow{\text{liq. } NH_3} \mathrm{Na_2E_n}$$

$$\mathrm{Na_2E_n} + 2\mathrm{CF_3CH_2I} \longrightarrow \mathrm{(CF_3CH_2)_2E_n} + 2\mathrm{NaI}$$

(E = Se or Te; n = 1 or 2)