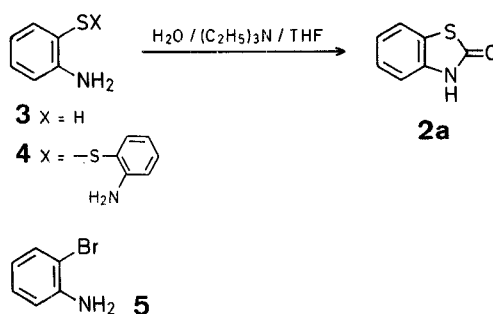


In general, the reaction is carried out in tetrahydrofuran in an autoclave at 80°C for 10 hours. The initial pressure of carbon monoxide is 10 kg/cm² at 20°C and ~13 kg/cm² at 80°C; the pressure gradually decreases as the reaction proceeds. Under these conditions, a variety of benzothiazolones (**2a-h**) were obtained in satisfactory yields directly from the corresponding 2-halonitrobenzenes (**1a-i**).

Treatment of 2-aminobenzenethiol (**3**) or 2,2'-diaminodiphenyl disulfide (**4**) under similar conditions gave product **2a** in high yield whereas the use of 2-bromoaniline (**5**) as starting compound in this reaction resulted in quantitative recovery of **5**.



A Facile One-Pot Synthesis of Benzothiazolones from 2-Halonitrobenzenes

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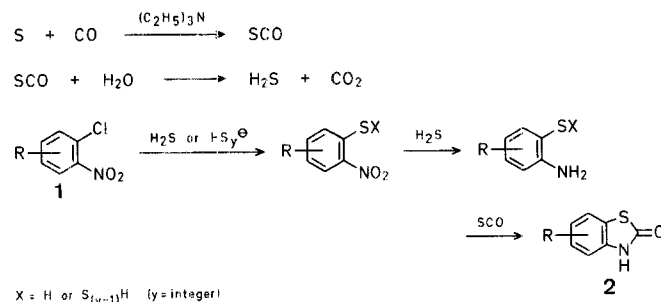
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The skeleton of benzothiazolones is a structural constituent of several useful pesticides, medicines, and dyestuffs. As regards the synthesis of benzothiazolones, the carbonylation of 2,2'-diaminodiphenyl or 2,2'-dinitrodiphenyl disulfide (or 2-amino- or 2-nitrophenylmercaptan) with phosgene^{1,2,3} or with carbon monoxide in the presence of a transition metal⁴ has been reported as a preparative method. However, the utility of these carbonylation reactions is considerably limited by the unsatisfactory availability of the starting compounds, toxicity of reagents, low yields, and troublesome procedures.

We report here a facile one-pot synthesis of benzothiazolones (**2**) by the reaction of 2-halonitrobenzenes (**1**) with carbon monoxide and elemental sulfur in the presence of water and triethylamine. This procedure involves three consecutive reactions, namely, nucleophilic displacement, reduction, and carbonylation.

These facts may indicate that nucleophilic displacement of the halogen atom activated by the nitro group in **1** by a sulfur nucleophile (possibly H₂S or HS_y[⊖]; y is an integer) takes place prior to reduction of the nitro group to an amino group by hydrogen sulfide generated *in situ*. It may be assumed⁹ that in this reaction carbon oxide sulfide is initially generated from sulfur and carbon monoxide in the presence of triethylamine; hydrolysis of carbon oxide sulfide with water then gives hydrogen sulfide and carbon dioxide. Subsequent carbonyl insertion between the N- and S-atoms of **3** or its analogs affords the cyclized product **2**.



In view of the availability of starting substrates and reagents, the simple procedures, the good yields, and the considerably wide applicability, the present reaction may possess practical importance both as a laboratory method and an industrial process for the synthesis of benzothiazolones.

Table. Benzothiazolones (**2**) from 2-Halonitrobenzenes (**1**)^a

Substrate	R	X	Product	Yield [%] of 2		m.p. [°C]	m.p. [°C] reported or Molecular Formula	M.S. <i>m/e</i>
				G.L.C. ^b	Isolated			
1a	H	Cl	2a	82	78	138–139°	138 ^{o1}	151 (M ⁺), 123, 96
1b	5-Cl	Cl	2b	77	72	237–239°	235–237 ^{o5}	187, 185 (M ⁺), 159, 157, 130, 122, 95
1c	3-Cl	Cl	2c	71		216–218°	203–205 ^{o6}	187, 185 (M ⁺), 159, 157, 130, 122, 95
1d	5-CH ₃	Cl	2d	53		168–170°	168–169 ^{o7}	165 (M ⁺), 137, 110
1e	3-CH ₃	Cl	2e	67	65	171–172°	169–170 ^{o8}	165 (M ⁺), 137, 110
1f	5-CF ₃	Cl	2f	89	84	211–213°	214–218 ^{o3}	219 (M ⁺), 200, 191, 164
1g	5-OCH ₃	Cl	2g	60		167–169°	168–170 ^{o7}	182 (M ⁺), 150, 122
1h	5-COOCH ₃	Cl	2h	66	60	219–220°	C ₉ H ₇ NO ₅ S ^c (209.2)	209 (M ⁺), 178, 150, 122
1i	H	Br	2a	91		138–139°	138 ^{o1}	151 (M ⁺), 123, 96

^a Initial CO pressure at 20°C: 10 kg/cm²; conditions: 80°C, 10 h.

^b Column: silicon OV-17, phenanthrene as internal standard.

^c calc. C 51.66 H 3.38 N 6.70 S 15.32
found 51.52 3.37 6.74 15.40

2-Oxo-2,3-dihydro-1,3-benzothiazoles (Benzothiazolones, **2**); General Procedure:

In a 100 ml stainless-steel autoclave are placed the 2-halonitrobenzene **1** (5.0 mmol), powdered sulfur (0.80 g, 25 mmol), water (0.54 g, 30 mmol), triethylamine (2.8 ml, 20 mmol), and freshly distilled tetrahydrofuran (20 ml). Then, carbon monoxide is introduced up to a pressure of 10 kg/cm² at 20°C (~40 mmol CO). The mixture is stirred and heated at 80°C (maximum pressure 13 kg/cm²) for 10 h. The pressure gradually decreases as the reaction proceeds and is finally 7–8 kg/cm². The mixture is allowed to cool, carbon monoxide is carefully removed from the system, and the solvent is evaporated under reduced pressure. The residual oil is analyzed (G.L.C. and T.L.C.) and crystallized from ethanol.

Products **2a–g** thus obtained were identified by comparison of their G.L.C. behavior and spectroscopic properties with those of authentic samples^{1,3,5–8}. The yields of products **2a–h** were determined by G.L.C. analysis (silicon OV-17, 2 m) using phenanthrene as internal standard. Microanalysis and spectroscopic data of compound **2h** were in accord with the assigned structure.

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