

Scheme 1.

TABLE I. YIELDS OF SUBSTITUTED BENZOHYDROXIMOYL CHLORIDES

Substrate		Solvent	Product	Yield ^{a)} %	Mp $\theta_m/^\circ\text{C}$
1	Ar				
1a	C ₆ H ₅	CCl ₄	5a	78	51—52 (lit, ⁵⁾ 48—52)
1a		CH ₂ Cl ₂	5a	66	
1a		CS ₂	5a	78	
1a		C ₆ H ₆ ^{b)}	5a	77	
1a		Hexane	5a	66	
1a		CH ₃ CN	5a	20 ^{c)}	
1b	<i>p</i> -CH ₃ C ₆ H ₄	CCl ₄	5b	66	71—72 (lit, ⁶⁾ 68—69)
1c	<i>p</i> -CH ₃ OC ₆ H ₄	CCl ₄	5c	62	88—89 (lit, ⁶⁾ 88—89)
1d	<i>m</i> -CH ₃ OC ₆ H ₄	CCl ₄	5d	88	66—67
1e	<i>p</i> -CH ₃ SC ₆ H ₄	CCl ₄	5e	73	91.5—92.5
1f	<i>p</i> -ClC ₆ H ₄	CCl ₄	5f	88	91.5—92.5 (lit, ⁷⁾ 88.5—89.5)
1g	<i>m</i> -ClC ₆ H ₄	CCl ₄	5g	74	68—69 (lit, ⁷⁾ 69—70)
1h	<i>p</i> -NO ₂ C ₆ H ₄	CCl ₄ ^{d)}	5h	87	125.5—126.5 (lit, ⁷⁾ 124—125)

a) Isolated yields. b) The reaction was carried out at 5 °C for 5 h and allowed to stand overnight. c) Compounds **7a**, **8a**, and **10a** were obtained in 45, 9, and 27% yields, respectively. d) The reaction was carried out at 25 °C for 15 h.

butylhydroxylamines (**2**), and bis(chlorosulfinyl) compound (**3**). The intermediates **2** and **3** are transformed to **6** and **4** by the subsequent eliminations of *t*-butyl chloride and sulfur dioxide, respectively. In the reaction of **1** with thionyl chloride in acetonitrile, oxadiazole **10** would be formed by cycloaddition of acetonitrile and benzonitrile oxides.

Experimental

Preparation of N-Aroyl-N-*t*-butylhydroxylamines (1). *N*-Aroyl-*N*-*t*-butylhydroxylamines (**1**) were prepared by hydrolysis of the corresponding *N*-aroyl-*O*-benzoyl-*N*-*t*-butylhydroxylamines with sodium hydroxide in methanol, as reported previously.³⁾

Reaction of N-Aroyl-N-*t*-butylhydroxylamines (1) with Thionyl Chloride. A typical run was as follows: Thionyl chloride (10 g, 84 mmol) was added to a stirred mixture of *N*-benzoyl-*N*-*t*-butylhydroxylamine (**1a**) (1.932 g, 10 mmol) and carbon tetrachloride (30 cm³) at −30 °C. The mixture was stirred at −30 °C for 5 h, and allowed to stand overnight at room temperature. The solvent and excess thionyl chloride were evaporated under reduced pressure. Ethanol (10 cm³) was added to the residue, and the mixture was stirred at room temperature for 2 h. After removal of the ethanol, the residue was separated by column chromatography on silica gel, using dichloromethane and ethyl acetate as the eluents. The fractions obtained by dichloromethane as the eluent gave **5a** (1.218 g, 78%) and **8a** (0.062 g, 4%). Benzohydroxamic acid (**7a**) (0.110 g, 8%) was obtained with the chromatography with ethyl acetate as the eluent. Similarly, the reaction of **1b**—**h** with thionyl chloride gave **5b**—**h**. **5d**; Found: C, 51.78; H, 4.24; N, 7.54%. Calcd for C₈H₈ClNO₂: C, 51.77; H, 4.34; N, 7.55%. **5e**; Found: C, 47.64; H, 3.84; N, 6.87%. Calcd for C₈H₈ClNOS: C, 47.64; H, 4.00; N, 6.95%.

Preparation of O-Chlorosulfinylbenzohydroximoyl Chloride (4a). Thionyl chloride (5.0 g, 42 mmol) was added to a solution of benzohydroximoyl chloride (1.555 g, 10 mmol) in dichloromethane (30 cm³) and the mixture was allowed to stand overnight. Removal of the solvent and excess thionyl chloride *in vacuo* gave *O*-chlorosulfinylbenzohydroximoyl chloride (**4a**) (2.303 g, 97%) as a colorless oil. IR (neat) 1590, 1580, 1240, 880, 760, 690, and 600 cm^{−1}.

Preparation of 5-Phenyl-1,3,2,4-dioxathiazole 2-oxide (6a).

A mixture of benzohydroxamic acid (**7a**) (2.742 g, 20 mmol) and thionyl chloride (10 g, 84 mmol) in dichloromethane (30 cm³) was allowed to stand for 6 h at 30 °C. The excess thionyl chloride and the solvent were evaporated under reduced pressure to give (**6a**) (3.554 g, 97%). IR (neat) 1605, 1325, 1240, 1060, 850, and 720 cm^{−1}.

Thermal Decomposition of 4a. A solution of **4a** (0.246 g, 1.03 mmol) in toluene (10 cm³) was refluxed for 4 h. The products were analyzed by GLC.

Hydrolysis of 4a. A solution of **4a** (0.463 g, 1.95 mmol) in acetone (8 cm³) and water (2 cm³) was allowed to stand overnight. After evaporation of acetone, the residue was extracted with diethyl ether. The extract was washed with water and dried over anhydrous calcium chloride. Removal of the ether gave **5a** (0.272 g, 90%).

Alcoholysis of 4a. A solution of **4a** (0.463 g, 1.95 mmol) in ethanol (10 cm³) was allowed to stand for 2 h. The reaction mixture was subjected to GLC analysis, and the remainder was chromatographed on silica gel to isolate the products. Diethyl sulfite (70%, GLC) and **5a** (0.272 g, 90%) were obtained.

References

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