Preparation and Properties of Substituted Cinnamohydroxamic Acids

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Preparation and properties of eight new para-substituted cinnamohydroxamic acids derived from chloro- and nitro-substituted cinnamic acids are described. These hydroxamic acids were characterized by their melting point, elemental analysis, and ultraviolet and infrared spectra.

Introduction

The hydroxamic acids are varsatile analytical reagents and extensively used as a photometric reagents for metal ions.[1-5,9-13,16] In the present communication the eight new hydroxamic acids derived from cinnamic acid are reported with the idea of finding a more selective reagent for the metal ions.

The physical properties of the substituted cinnamohydroxamic acids are given in Table I. *p*-Chloro-substituted cinnamohydroxamic acids are white crystalline compounds while *p*-nitro-substituted cinnamohydroxamic acids are yellow crystalline. These are readily soluble in organic solvents, viz., chloroform, benzene, and carbon tetrachloride, and sparingly soluble in water.

Chloroform solutions of all the hydroxamic acids gave characteristic violet extracts with vanadium(V) from concentrated hydrochloric acid media.

The ultraviolet and infrared spectra of synthesized hydroxamic acids were determined. In the infrared spectra only those bands which are associated with the hydroxamic acid functional group, N—OH and C=O, have been assigned. The presence of the O—H stretching band is assigned in the region at about 3200 cm^{-1}. The C=O and N—O bands are assigned at about 1630 and 940 cm^{-1}, respectively.

Experimental Section

Materials and Apparatus. The ultraviolet absorption spectral measurements in 95% ethyl alcohol were recorded on a Beckman Model 25 spectrophotometer in the 200–360-nm region.

Infrared spectra were recorded in the 2000–15 000-nm region on a Beckman Model 4220 spectrophotometer as KBr pellets.

All the chemicals used were of B.D.H. or E. Merck quality.

Preparation of Substituted Cinnamic Acids. These were prepared by the reaction of respective benzaldehyde with malonic acid in pyridine medium in the presence of piperidine. A preparation of *p*-chlorocinnamic acid is described in detail.

Preparation of p-Chlorocinnamic Acid. A total of 14.0 g (0.1 mol) of *p*-chlorobenzaldehyde and 20.8 g (0.2 mol) of malonic acid was dissolved in a mixture of 39.5 g (0.5 mol) of pyridine and a few drops of piperidine in a 100-mL round-bottomed flask, and the mixture was heated under reflux for 10–12 h on a water bath. The reaction was completed by boiling the solution for 5 min, cooling, and pouring into an excess of water that contains enough hydrochloric acid to combine with pyridine and filtering off the white granular mass, washing the mass with a little water, and drying. The white mass was crystallized from ethyl alcohol. The yield is 75%, mp 249 °C (lit.[7] mp 249–250 °C).

Preparation of Acid Chlorides. The acid chlorides were prepared by the action of thionyl chloride on the corresponding carboxylic acids and refluxing them on water bath for 3–4 h, the excess thionyl chloride was distilled off under vacuum. The yields and their melting point are in agreement with the literature.[15]

Preparation of N-Phenyl-, m-Tolyl-, p-Tolyl-, and p-Chlorophenylhydroxylamines. These were freshly prepared by the reduction of nitrobenzene, *m*-nitrotoluene, *p*-nitrotoluene, or *p*-chloronitrobenzene, respectively, with zinc dust and ammonium chloride from aqueous solutions and recrystallized from benzene and petroleum ether. The yields and their melting points are in agreement with the literature.[6,8,14]

Preparation of N-Phenyl-p-chlorocinnamohydroxamic Acid. *N*-Phenylhydroxylamine (1.09 g, 0.01 mol) was dissolved in 20 mL of diethyl ether and a fine suspension of 2.12 g (0.02 mol) of sodium carbonate in 15–20 mL of water was added and stirred with a magnetic stirrer with external cooling to lower the temperature to 0 °C or below. Then, 2.01 g (0.01 mol) of the *p*-chlorocinnamoyl chloride dissolved in 20–25 mL of diethyl ether was added dropwise over a period of 30 min. The reaction mixture was then stirred for an additional 15 min and the temperature kept low to prevent possible side reactions. Almost the entire amount of hydroxamic acid was precipitated as a yellowish white granular solid. The precipitated yellowish white product was triturated for about 10 min in a glass mortar with a saturated solution of sodium carbonate to remove the acid impurities, filtered, washed with cold water, and dried under the fold of filter paper. The crude product was crystallized from

Table I. Physical Properties of Para-Substituted Cinnamohydroxamic Acids[a]

cinnamohydroxamic acid	formula	mp, °C	yield, %	IR freq, cm^{-1}			UV spectra	
				ν(O–H)	ν(C=O)	ν(N–O)	λ_{max}, nm	ϵ
N-phenyl-*p*-chloro-	$C_{15}H_{12}NO_2Cl$	164	65	3190	1630	965	288 222	2.2×10^4 1.3×10^4
N-*m*-tolyl-*p*-chloro-	$C_{16}H_{14}NO_2Cl$	168	65	3180	1630	940	288 221	4.2×10^4 2.5×10^4
N-*p*-tolyl-*p*-chloro-	$C_{16}H_{14}NO_2Cl$	170	70	3100	1620	940	278 239	5.0×10^4 2.5×10^4
N-*p*-chlorophenyl-*p*-chloro-	$C_{15}H_{11}NO_2Cl$	187	70	3120	1630	940	295 239	6.3×10^4 2.7×10^4
N-phenyl-*p*-nitro-	$C_{15}H_{12}N_2O_4$	195	65	3240	1625	935	310	1.2×10^4
N-*m*-tolyl-*p*-nitro-	$C_{16}H_{14}N_2O_4$	154	60	3280	1640	950	312	1.1×10^4
N-*p*-tolyl-*p*-nitro-	$C_{16}H_{14}N_2O_4$	180	60	3270	1640	960	315	4.1×10^4
N-*p*-chlorophenyl-*p*-nitro-	$C_{15}H_{11}N_2O_4Cl$	212	60	3140	1620	940	310	1.1×10^4

[a] Elemental analyses in agreement with theoretical values were obtained and submitted for review.

a mixture of benzene and petroleum ether. The white crystals have mp 164 °C and yield 65%.

All the hydroxamic acids could be prepared by following the above procedure.

Acknowledgment

The authors are thankful to Professor S. K. Banerjee, Head, Pharmacy Department, for providing the facilities.

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Received for review January 15, 1979. Accepted March 16, 1979. Financial assistance given by M. S. University of Baroda is gratefully acknowledged.

Synthesis of $CHCl_2I$, CCl_3I, $CHBr_2I$, and CBr_3I

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The synthesis of $CHCl_2I$, CCl_3I, $CHBr_2I$, and CBr_3I has been reinvestigated. $CHCl_2I$ and CCl_3I were synthesized by reacting $CHCl_3$ with NaOI, $CHBr_2I$ was synthesized by reacting $CHBr_3$ with NaOI, and CBr_3I was synthesized by reacting $CHBr_3$ with NaI in acetone. The carbon-13 NMR spectra of $CHCl_2I$, CCl_3I, and $CHBr_2I$ were recorded. The chemical shifts were $CHCl_2I$ 11.2 ppm, CCl_3I 4.2 ppm, and $CHBr_2I$ −45.7 ppm all in reference to Me_4Si.

Introduction

Recently, the trigonal additivity procedure developed by Somayajulu and Zwolinski for correlating and estimating thermodynamic properties of organic substances,[1] such as standard enthalpies of formation, enthalpies of vaporization, and other thermodynamic properties, was found to be equally effective in correlating and estimating carbon-13 chemical shifts[2,3] of halomethanes of the general formula $CH_nF_mCl_pBr_qI_{4-n-m-p-q}$. To complement available literature information on carbon-13 chemical shifts, information was needed on the following key halogen compounds, viz., CCl_pI_u and CBr_qI_u or the corresponding $CH_nCl_pI_u$ and $CH_nBr_qI_u$. Synthetic procedures were sought to prepare these key halomethanes. Particular attention was directed to synthesis of chloroiodomethanes and bromoiodomethanes by using NaOI and NaI as iodating agents.

The original study of NaOI as an iodating agent was conducted by Dehn in 1909.[4] Dehn prepared NaOI in situ by reacting I_2 with aqueous NaOH or by the reaction of KI with NaOCl. When NaOI in aqueous NaOH solution was reacted with $CHCl_3$, CCl_3I was reported as the major product with CCl_2I_2 as a minor product. In turn, when NaOI in aqueous NaOH solution was reacted with $CHBr_3$, CBr_3I was reported as the major product with no evidence of CBr_2I_2.

As a result of these studies Dehn concluded that (1) NaOX reacting with hydrogen containing methanes would replace the hydrogen atom with an X atom and (2) that hypohalites are useful synthetic reagents for the preparation of methane tetrahalides.

Synthesis of $CHCl_2I$ and CCl_3I

(*a*) ***$CHCl_3$ as a Reactant.*** In an attempt to repeat Dehn's synthesis of CCl_3I, 0.4 mol of I_2 was gradually added to a mixture of 300 cm^3 of 6.25 M NaOH and 26 cm^3 of $CHCl_3$ (source: Curtin; purity 99%) in a Morton flask. The reaction was kept in an ice bath and was stirred vigorously for about 15 h. Product analysis for this reaction and the other reactions described in this paper was performed by a Hewlett Packard 5982 A GC/MS data system. Separation was accomplished by a 10 in. × $^1/_8$ in. stainless steel column packed with 3% Apiezon L on 100/120 Suplecoport. The major product was found to be dichloroiodomethane, $CHCl_2I$, with a small amount of trichloroiodomethane, CCl_3I, as a minor product. The ratio between the two products being approximately 10 to 1 with chlorine being displaced preferentially to hydrogen. Some tetrachloroethane (decomposition product) was also observed. The overall yield of $CHCl_2I$ was ca. 10 mol %.

(*b*) ***Carbon Tetrachloride as a Reactant.*** Twenty-five cubic centimeters of carbon tetrachloride (source: Fisher Scientific; purity 99%) was reacted by the same procedure used above for chloroform except that 3 mol excess of I_2 was added and the reaction was allowed to proceed for over 5 days. The yield of CCl_3I was small, less than 5 mol %. Analysis of the products by GC/MS showed the principal products to be trichloroiodomethane and dichlorodiiodomethane with some hexachloroethane. The mole ratio of CCl_3I to CCl_2I_2 was 3.5 to 1.

Synthesis of $CHBr_2I$ and CBr_3I

(*a*) ***Bromoform as a Reactant.*** For the reaction between NaOI and $CHBr_3$, Dehn[4] stated that he obtained higher yields of CBr_3I by reacting KI solution with a mixture of NaOCl or NaOBr solution and bromoform than by reacting bromoform with a NaOI solution prepared by reacting I_2 with NaOH solution. Following Dehn's procedure the NaOI was generated by the gradual addition of 0.21 mol of KI (source: Baker; purity 99.5%) to a mixture of 150 cm^3 of 5.25% NaOCl solution with 23 g of NaOH and 1.8 mol of bromoform (source: Mallinckrodt; purity 99%). The reaction time was 24 h. Product analysis revealed that dibromoiodomethane was the major product (ca. 10 mol %) with trace amounts of bromodiiodomethane and tribromoiodomethane. The mole ratio of $CHBr_2I$ to $CHBrI_2$ to CBr_3I was 100:1:1. Here again our results contradicted Dehn's findings. We found that iodine displaces the halogen preferentially to hydrogen.

(*b*) ***Carbon Tetrabromide as a Reactant.*** Carbon tetra-

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