pound was crystallized from 2-propanol: 176 mg (6%); mp 93–94° of XIII obtained; ir spectrum (Nujol) 1665, 1660 (shoulder), 1650 (shoulder) and 702 cm^{-1}; uv spectrum λ max 222 mμ (ε 21,600), 258 (6000), and 342 (3250); mass spectrum *m/e* (rel intensity) 189 (100), 188 (54), 160 (6), 142 (8.5), 133 (8), 126 (5.4), 97 (8), and 63 (13).

Anal. Calcd for $C_{14}H_6Cl_4O_5$: C, 42.46; H, 1.53; Cl, 35.81. Found: C, 42.72; H, 1.90; Cl, 35.89.

Chlorination of *p*-Dimethylaminobenzaldoxime (XVII) in Methylene Chloride.—XVII (2 g, 0.0122 mol) was dissolved in 300 ml of methylene chloride at 0°. Chlorine gas was passed through this solution for 15 min. After being allowed to stand in an ice–water bath for 2 hr, the reaction mixture was left at room temperature overnight. The excess chlorine was removed by bubbling air through methylene chloride solution. The solvent was removed under reduced pressure and the solid residue was crystallized from 2-propanol. The crystalline material was collected by filtration; 1.04 g was obtained. The crystalline material was recrystallized from 2-propanol; a small amount of methylamine hydrochloride, mp 232–233° (lit.[8] 226–228°), was obtained. When crystalline material was treated with 5% aqueous hydrochloric acid followed by extraction with methylene chloride, XVI was isolated in 6% (150 mg) yield, mp 161.5–162.5°. An analytical sample could be prepared by recrystallization from ethyl acetate: ir spectrum (Nujol) 1600 (>C=N) and 952 cm^{-1}; uv spectrum λ max 323 mμ (ε 1358) and 218 (5633); nmr (acetone-d_6) δ 7.68 (s, 1), 2.9 (s, 2), and 3.0 (s, 4); mass spectrum (rel intensity) *m/e* 460 (28) (parent peak), 444 (19), 400 (100), 230 (61), 213 (90), 204 (78), and 44 (28).

Registry No.—X, 29577-42-2; XIII, 29577-43-3; XVI, 29641-90-5; *o*-chlorobenzaldoxime, 3717-28-0; *p*-chlorobenzaldoxime, 3848-36-0; *p*-methoxybenzaldoxime, 3235-04-9; benzaldoxime, 932-90-1; *o*-nitrobenzaldoxime, 6635-41-2; *m*-nitrobenzaldoxime, 3431-62-7; *p*-nitrobenzaldoxime, 1129-37-9; 6-nitroveratraldoxime, 29577-51-3; 2,4-dinitrobenzaldoxime, 3236-33-7; *o*-methoxybenzaldoxime, 29577-53-5; *o*-chlorobenzhydroxamic chloride, 29568-74-9; 3,5-dichloro-4-methoxybenzhydroxamic chloride, 29568-75-0; 3,5-dichloro-4-methoxybenzal chloride, 29568-76-1; *o*-nitrobenzal chloride, 610-14-0; 6-nitro-3,4-dimethoxybenzal chloride, 29568-78-3; 2,4-dinitrobenzal chloride, 20195-22-6; 3-chloro-2-methoxybenzal chloride, 29568-32-9; 5-chloro-2-methoxybenzal chloride, 29568-33-0; 5-chloro-2-methoxybenzhydroxamic chloride, 29568-34-1; 3,5-dichloro-2-methoxybenzhydroxamic chloride, 29568-35-2; 3,4-diphenylfuroxan, 5585-14-8; *O*-benzoylbenzhydroxamic chloride, 29568-37-4.

Acknowledgments.—The author is grateful to Dr. Victor Hansen for helpful discussion throughout this work. Thanks are also due to Dr. A. K. Bose for the measurements of nmr and mass spectra.

Chlorination of Oximes. II. Pyrolysis of Benzhydroxamic Chloride Derivatives

YUNN HUI CHIANG*

Division of Central Research, Shulton, Inc., Clifton, New Jersey 07015

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The pyrolysis of benzhydroxamic chloride derivatives (XVI) was investigated. It was found that thermolysis of XVI involved two reaction paths depending on the substituents on the aromatic ring. When benzhydroxamic chloride (II) and 3-chloro-4-methoxybenzhydroxamic chloride (IV) were pyrolyzed at 180°, isocyanate derivatives were obtained. On the other hand, nitro- (VIII and XIV) and chloro- (XV) substituted compounds gave *O*-benzoylbenzhydroxamic chloride derivatives as the major product and substituted benzonitriles were isolated as minor components. Based on the fact that rearrangement of II and IV gave isocyanate derivatives in combination with the isolation of nitrile derivatives from the reaction mixture, two reaction mechanisms were proposed for the pyrolytic process. A cyclic mechanism was proposed for the formation of *O*-benzoylbenzhydroxamic chloride (I) and its analogs. It is noted that the iminoxy radical addition mechanism cannot be excluded as an alternate pathway for the formation of I.

The formation of *O*-benzoylbenzhydroxamic chloride (I) as a by-product (12% yield) upon distillation of the chlorination product of benzaldoxime in methylene chloride was observed.[1] When the distillation process was carried out under low temperature (below 100°), no I was isolated from the reaction mixture. It was concluded that I must be the pyrolytic product of benzhydroxamic chloride (II). In order to understand the nature of this pyrolytic process, the pyrolysis of benzhydroxamic chloride derivatives was investigated.

In the thermolysis of II at 180° (8 mm), 70% of phenyl isocyanate and 21% of I was isolated. Similarly, 18% of 3-chloro-4-methoxyphenyl isocyanate (III) was obtained from the pyrolysis of 3-chloro-4-methoxybenzhydroxamic chloride (IV). On the other hand, nitro- and chloro-substituted benzhydroxamic chlorides gave a mixture of substituted benzonitrile and the corresponding *O*-benzoylbenzhydroxamic chloride derivatives. The results are formulated in Scheme I.

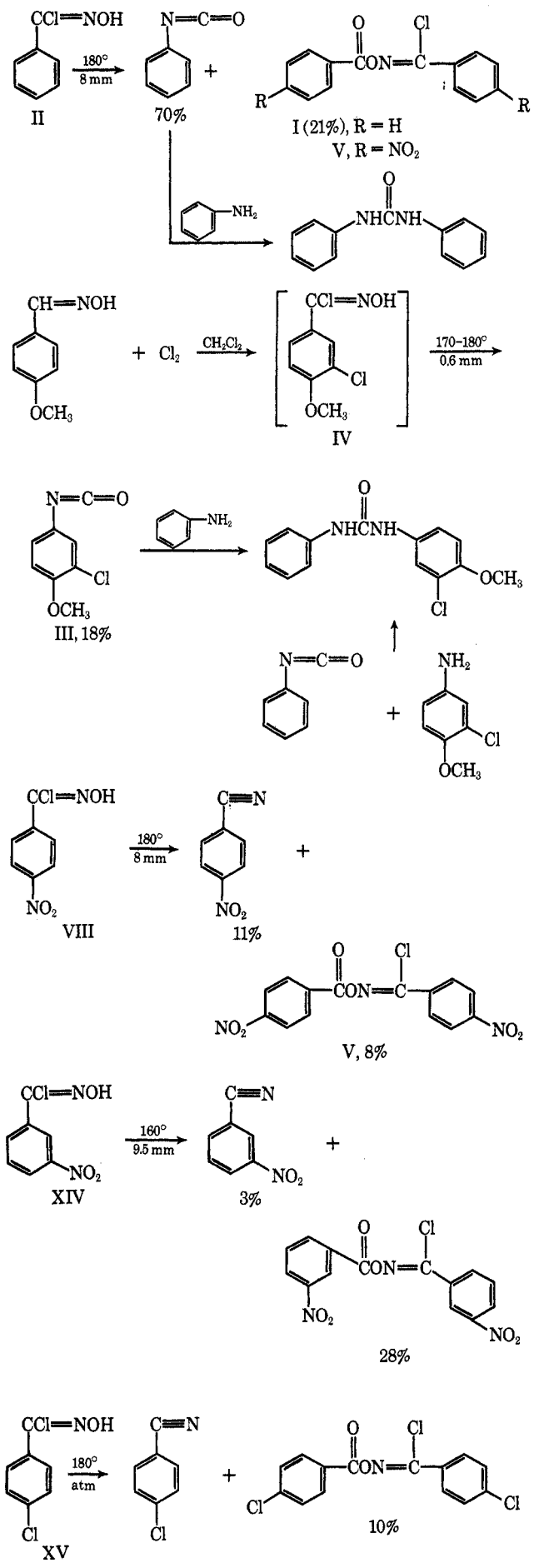
The physical properties of substituted *O*-benzoylbenzhydroxamic chloride derivatives are summarized in Table I.

Phenyl isocyanate was characterized as *N,N*-diphenylurea after reacting with aniline. Compound III was converted to a urea derivative by an unambiguous route (Scheme I). This product proved to be identical with the compound obtained by the reaction of phenylisocyanate with 3-chloro-4-methoxyaniline as shown by mixture melting point and infrared (ir) spectrum. The structure of I was assigned on the basis of its ir, ultraviolet (uv), and mass spectra. The mass spectrum of I exhibited a weak molecular ion peak at *m/e* 259 (2%), two base peaks at *m/e* 105 (rel intensity 100%) and 103 (100%), and other prominent peaks at *m/e* 204 (15%) ($M^+ - Cl$), 138 (30%) ($PhCCl{=}N$), and 119 (10%) ($PhC{\equiv}N{\rightarrow}O$). It is of interest to note that the spectrum also showed a strong peak at *m/e* 122 (27%) ($C_6H_4NO_2$). The exact course of the formation of this ion is not clear. Further evidence that I has the proposed structure was provided by its hydrolysis with aqueous alcoholic sodium hydroxide, which gave benzoic acid and II as final products. The high yield

* Polaroid Corporation, Chemical Development Laboratory, Cambridge, Mass. 02139.

(1) See part I in this series: Y. H. Chiang, *J. Org. Chem.*, **36**, 2146 (1971).

SCHEME I



of benzoic acid (100%) is probably due to the partial hydrolysis of II. Compound II was identified by vpc from the comparison of retention time with an authentic sample. Compound V is identical with that obtained from the reaction of *p*-nitrobenzoyl chloride with *p*-nitrobenzhydroxamic chloride. This fact demonstrated that the pyrolytic product is indeed benzhydroxamic chloride *O*-ester. *p*-Nitro- and *m*-nitrobenzonitrile were isolated in 11 and 3%, respectively, from the reaction mixture. The identity of *p*-chlorobenzonitrile was only detected by ir (2220 cm^{-1}, -C≡N). Compound IV could not be isolated in pure form but its identity was verified by conversion to a urea derivative (Scheme I).

It was reported[2] that aromatic nitrile *N*-oxides sterically hindered by substituents of appropriate size in both ortho positions will not undergo the spontaneous dimerization to furoxans, generally characteristic of nitrile *N*-oxides. At temperatures above 100°, these nitrile oxides rearranged completely to the corresponding isocyanates. The possibility of nitrile *N*-oxide as a reaction intermediate in the formation of isocyanates *via* pyrolysis is excluded since no furoxan was isolated from the pyrolytic product. Furthermore, it is well known that benzonitrile *N*-oxide dimerizes rapidly at elevated temperatures.[2] It is interesting to note that the presence of an electron-withdrawing group or electron-donating group in the benzene ring lead to entirely different reaction products (Scheme I). On the other hand, the unsubstituted phenyl derivative took an intermediate course which yielded both phenyl isocyanate and I as the final products. The mechanism of this pyrolytic reaction was proposed on the basis of products isolated and substituent effects. The reaction pathways are formulated in Scheme II. An imidyl radical, *i.e.*, VI, was proposed as a reaction intermediate for isocyanate formation. Reactions which apparently involve the intermediacy of imidyl radicals are the introduction of cyano groups into hydrocarbons by by reaction with cyanogen chloride,[3,4] thermal cleavage reactions of *N*-chloroketimines,[5] and the photochemical reaction of unsaturated nitrogen-containing compounds.[6] In the cases of II and IV, an imidyl radical was formed upon pyrolysis which either underwent β scission (benzonitrile formation, path a) or rearranged to give phenyl isocyanate (path b).

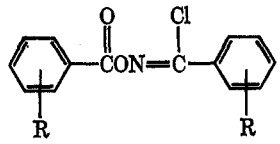
In the cases of nitro- or chloro-substituted benzhydroxamic chloride derivatives, a benzyl radical VII was proposed as an intermediate in the pyrolytic process. The salient facts associated with the postulated radical intermediate VII that eliminated a common imidyl radical intermediate for both reactions (Scheme II) are as follows: (1) the homolysis of VIII should occur in such a way as to provide the more stable transient free radical VII, which stabilized by the presence of the nitro group in the para position;[7] (2) the absence of *p*-nitrophenyl group migration in the course of reaction.

It has been shown that the decomposition of the

(2) (a) C. Grundmann and S, K. Datta, *J. Org. Chem.*, **34**, 2016 (1969); (b) C. Grundmann, H. D. Frommeld, K. Flory, and S. K. Datta, *ibid.*, **33**, 1464 (1968), and references cited therein.
(3) E. Muller and H. Huber, *Chem. Ber.*, **96**, 670, 2319 (1963).
(4) D. D. Tanner and N. J. Bunce, *J. Amer. Chem. Soc.*, **91**, 3028 (1969).
(5) M. L. Poutsma and P. A. Ibarbia, *J. Org. Chem.*, **34**, 2848 (1969).
(6) R. W. Binkley, *ibid.*, **34**, 2072 (1969).
(7) P. D. Bartlett and J. D. Cotman, *J. Amer. Chem. Soc.*, **72**, 3095 (1950).

TABLE I

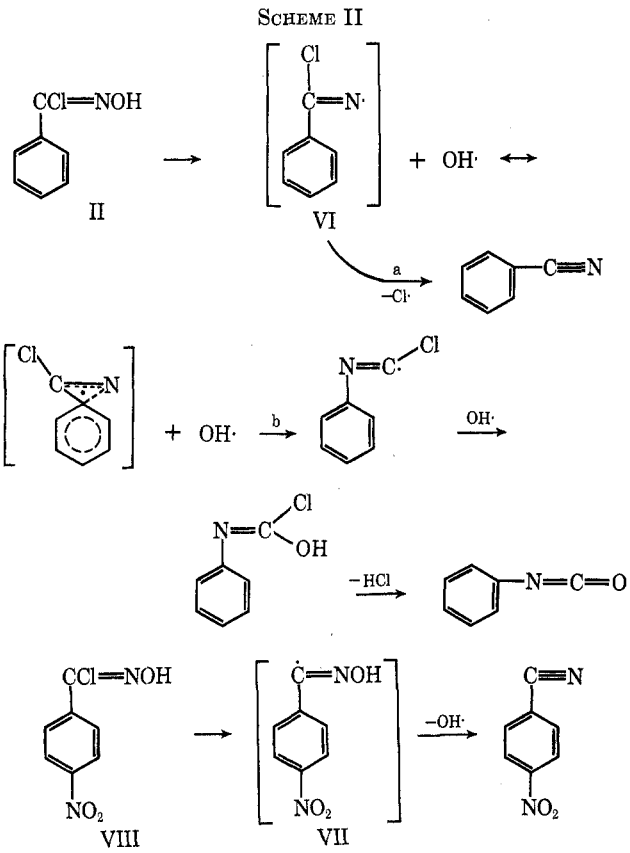
PHYSICAL PROPERTIES OF THE SUBSTITUTED *O*-BENZOYLBENZHYDROXAMIC CHLORIDE DERIVATIVES

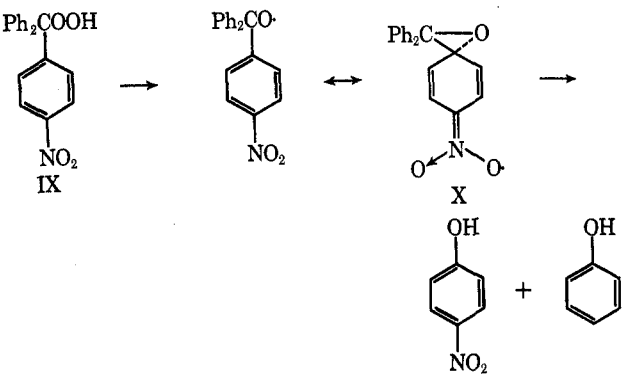


R	Registry no.	% yield	Mp, °C	Formula	Calcd, % C	H	N	Cl	Found, % C	H	N	Cl	λmax, mμ (ε); ν, cm⁻¹
H	29577-09-1	21	108–109[a]	$C_{14}H_{10}ClNO_2$	64.75	3.88	5.39	13.66	64.58	3.88	5.20	13.99	260 (25,700); 1760
m-NO_2	29577-10-4	28	191–192	$C_{14}H_8ClN_3O_6$	48.08	2.30	12.02	10.14	48.44	2.35	12.09	10.50	1775
p-NO_2	29577-11-5	8	202–203	$C_{14}H_8ClN_3O_6$	48.08	2.30	12.02	10.14	48.38	2.38	11.75	11.04	270 (27,900); 1775
p-Cl	29718-39-6	9.4	147–148.5	$C_{14}H_8Cl_3NO_2$	51.17	2.45	4.26	32.37	51.41	2.51	4.18	32.28	1770

[a] See ref 12.

SCHEME II





nitro-substituted peroxide IX in benzene yields over three times as much *p*-nitrophenol (resulting from migration of the *p*-nitrophenyl group) as phenol (resulting from phenyl migration).[7] This suggested that the migratory aptitude of a substituted aryl group is related to the effectiveness of the substituent in stabilizing the bridged transition state (or the bridged intermediate) in the rearrangement. As shown, the *p*-nitro group X would be expected to stabilize such a bridged radical by aiding in the delocalization of the unpaired electron. On the other hand, the apparent absence of *p*-nitrophenyl group migration could possibly be due to much higher rates of β elimination from the imidyl radical or instability of *p*-nitrobenzonitrile under the reaction conditions (*e.g.*, radical addition reactions). Further evidence is required to distinguish the exact nature of this reaction. The presence of nitrile derivatives and pyrolysis at low pressure (*ca.* 8 mm), which eliminated the hydrochloric acid if formed, excluded a Beckman-like ionic mechanism. These facts strongly supported the proposed free-radical mechanism.

The formation of I and its analogs is rationalized in Scheme III. Upon pyrolysis of substituted benzhydroxamic chlorides XVI, a nitrile derivative was obtained which in turn formed an adduct XVII *via* a cyclic mechanism. The formation of isoxazoline derivatives by refluxing II and its derivatives in toluene was reported by several authors.[8] Attention is called to the addition of oximes to α,β-unsaturated ketones.[9] It appears that the oximes, as 1,3 dipoles, react through their nitronic tautomeric form. The cyclic mechanism was proposed on this basis. Hydrolysis of XVII gave the final product. Compound XVII could not be isolated since hydrolysis occurred in the course of recrystallization (aqueous ethanol). The generation of iminoxy radicals from oximes with an oxidizing agent was reported by several authors.[10,11] It was reported[11] that thermal decomposition of *N*-benzhydryl-α,α-diaryl nitrones generated an iminoxy radical and a benzhydryl radical. The possibility that XVI is converted to an iminoxy radical XVIII followed by free-radical addition to the nitrile group cannot be excluded (Scheme III).

In conclusion, it was found that pyrolysis of XVI involved two reaction intermediates depending on the

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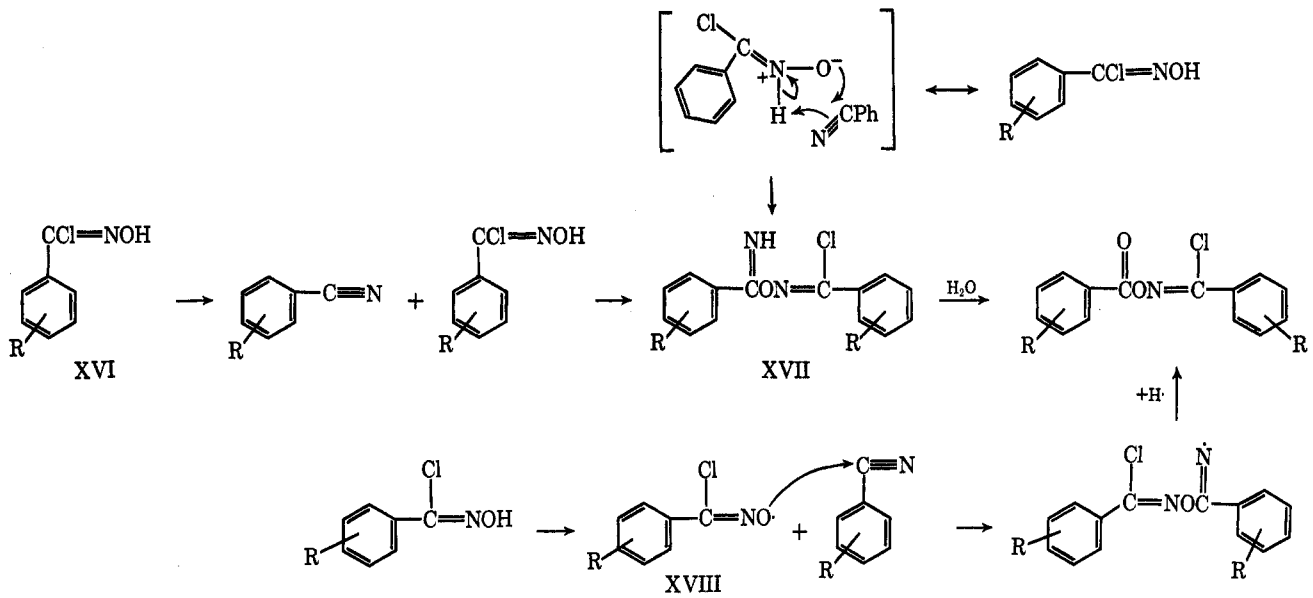
(9) A. Lablache-Combier and M. L. Villaume, *Tetrahedron*, **24**, 695 (1968).

(10) (a) M. Fedtke and H. Mitternacht, *Z. Chem.*, **4**, 389 (1964); *Chem. Abstr.*, **62**, 1533*f* (1965); (b) A. Caragheorgheopol, M. Hartmann, R. Kaehmstedt, and V. E Sahini, *Tetrahedron Lett.*, 4161 (1961).

(11) E. J. Grubbs, J. A. Villarreal, J. D. McCullough, Jr., and J. S. Vincent, *J. Amer. Chem. Soc.*, **89**, 2234 (1967), and references cited therein.

SCHEME III



substituent on a given aromatic ring. The rearrangement of II and IV to give isocyanate derivatives in combination with the isolation of nitrile derivatives from the reaction mixture strongly supported these facts. A four-centered mechanism was proposed for the formation of I and its analogs. It has been pointed out that the iminoxy radical addition mechanism cannot be excluded as an alternate pathway for the formation of I.

Experimental Section

The melting points were obtained on a Fisher-Jones melting point apparatus and are uncorrected, as are the boiling points. Ir spectra were recorded on a Perkin-Elmer Infracord Model 137 sodium chloride spectrophotometer. Uv spectra were obtained on a Coleman-Hitachi 124 double beam spectrophotometer in absolute ethanol. Mass spectra were taken on a Hitachi Perkin-Elmer RMV-7 mass spectrometer using an all-glass inlet. The microanalysis of the compounds were performed by Geller Microanalytical Laboratories, Saddle River, N. J. 07458.

Pyrolysis of Benzhydroxamic Chloride Derivatives XVI.—Typical procedures for the pyrolysis of II and its analogs are described. Most of the pyrolyses could be performed by the method used for II except XV. *When the thermolysis of XV was carried out under low pressure (ca. 10 mm, 180°), a violent explosion occurred.* The pyrolysis of XV must be carried under atmospheric pressure in thick-walled test tube.

Pyrolysis of Benzhydroxamic Chloride (II).—In a 10-ml round-bottomed flask fitted with a vacuum distillation setup is placed 2.57 g of II. After evacuation to a pressure of about 13 mm, the flask was heated in an oil bath (180°) for 30 min. Phenyl isocyanate [bp 104–105° (13 mm), 0.52 g (70%)] distilled off slowly. When the solid residue was crystallized from aqueous ethanol, 0.44 g (21%) of I, mp 108–109°, was obtained.[1] A small amount of the collected phenyl isocyanate was reacted with aniline in anhydrous ether giving *N,N*-diphenylurea. The mixture melting point with an authentic sample was not depressed.

Pyrolysis of 3-Chloro-4-methoxybenzhydroxamic Chloride (IV).—IV (4 g) was dissolved in 400 ml of methylene chloride at 0°. Chlorine gas was passed through this solution at a slow rate for 20 min. After the mixture stood in a cooling bath for 2 hr and then at room temperature overnight, air was bubbled through the reaction mixture until all the excess chlorine was removed. The solvent was removed under reduced pressure and the residue was vacuum distilled to give 0.86 g (18%), bp 140–143° (0.6 mm), of III. When a small amount of III was allowed to react with aniline, a urea derivative, mp 210–211°, was obtained. This compound proved to be identical with the urea obtained by the reaction of phenyl isocyanate with 3-chloro-4-methoxyaniline as shown by mixture melting point and ir spectrum.

Anal. Calcd for $C_{14}H_{13}ClN_2O_2$: C, 60.76; H, 4.73; N, 10.13; Cl, 12.81. Found: C, 60.96; H, 4.82; N, 10.08; Cl, 12.84.

Hydrolysis of I.—I (200 mg) was dissolved in an aqueous alcoholic sodium hydroxide solution (200 mg of sodium hydroxide in 20 ml of methanol and 10 ml of water) and stirred at room temperature overnight (*ca.* 18 hr). The solution was acidified with 5% hydrochloric acid and methanol was removed under reduced pressure. The aqueous solution was extracted with two 50-ml portions of ether and dried over anhydrous magnesium sulfate. After the ether solution was condensed, the residue was analyzed by vpc on an Aerograph Autoprep Model A-700 instrument using 10% Carbowax 20M on Anacrom ABS 70–80 mesh, 10 ft × 1/8 in. column. The ratio of benzoic acid/II is 4.57. When the residue was evaporated to dryness, a solid material was obtained. Upon crystallization of the solid, 97 mg (100%), mp 121–122°, of benzoic acid was collected.

Preparation of V.[12]—To an ether solution (150 ml) which contained 2.01 g (0.01 mol) of VIII and 1.41 g (0.01 mol) of *p*-nitrobenzoyl chloride was added 0.79 g (0.01 mol) of pyridine in 50 ml of ether at 0°. The reaction mixture was stirred at 0° for 1–2 hr and then left at room temperature overnight. After it was washed with 30 ml of water, the ether solution was dried and evaporated. The residue was crystallized from acetone, yielding 0.37 g of V, mp 203–204°. No melting point depression was observed when mixed with the pyrolysis product.

Acknowledgment.—The author is grateful to Dr. Victor Hansen for helpful discussion throughout this work. Thanks are also due to Dr. A. K. Bose for the measurements of nmr and mass spectra.

(12) *Beilstein*, 2nd ed, **9**, 214 (1956).