10, 29478-09-9; 11, 29478-10-2; 12, 29478-11-3; 1-(2-chloroethyl)-3-phenyl-2,2-dichloroimidazolidine-4,5-dione, 29478-12-4; 1-(2-chloroethyl)-3-(*p*-chlorophenyl)-2,2-dichloroimidazolidine-4,5-dione, 29576-46-3; 1-(2-chloroethyl)-3-(*m*-nitrophenyl)-2,2-dichloroimidazoline-4,5-dione, 29478-13-5; 1-(2-chloro-2-methylpropyl)-3-(*m*-nitrophenyl)-2,2-dichloroimidazolidine-4,5-dione, 29641-82-5.

Chlorination of Oximes. I. Reaction and Mechanism of the Chlorination of Oximes in Commercial Chloroform and Methylene Chloride

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The chlorination of benzaldoximes in commercial chloroform and methylene chloride was undertaken. It was found that substituted oximes which possess electron-wtihdrawing groups gave benzal chloride derivatives upon chlorination in methylene chloride and pure chloroform. On the other hand, benzhydroxamic chloride derivatives were obtained when chlorination was performed in commercial chloroform and methylene chloride containing 0.75% ethanol. In the presence of an electron-donating group, a mixture of benzal chloride and benzhydroxamic chloride derivatives was isolated irrespective of the solvent used. Benzhydroxamic chloride (I) was the sole product when chlorination was catalyzed by triethylamine. It appears that triethylamine and ethanol catalyzed the benzhydroxamic chloride formation. The abnormal chlorination reaction of benzaldoxime, *o*-hydroxybenzaldoxime (XI), and *p*-dimethylaminobenzaldoxime (XVII) in methylene chloride solution is particularly interesting. The mechanism of benzal chloride formation in the chlorination of oximes was examined. It is assumed that *p*-nitro-α-nitrosobenzyl chloride (XXa) emerged in the course of reaction; this was demonstrated by chemical evidence and spectroscopic studies. Two reaction mechanisms are proposed for the formation of benzal chloride. In the first of the mechanisms it is suggested that the chloronitroso intermediate decomposed unimolecularly to give a carbanion and a nitrosyl ion. In the second one, it can be considered as a nucleophilic displacement on the nitroso group, perhaps by chloride ion, and that the carbanion and nitrosyl chloride are thereby produced. The mechanism of isomerization of aromatic α-chloro-α-nitroso compounds was proposed according to the experimental results. Generally, it is assumed that the isomerization process could be separated into three categories. (1) One way is amine-catalyzed isomerization through a carbanion intermediate. (2) Ethanol-catalyzed isomerization gave a cyclic intermediate through intermolecular H bonding with electron-withdrawing substituted α-chloro-α-nitroso compound. (3) When electron-donating substituent is present, intramolecular isomerization *via* H bonding is operative.

The halogenation of oximes has been applied to the preparation of nitro compounds,[1] halonitro paraffins,[2] and, in particular, hydroxamic halide derivatives. The conversion of oximes to hydroxamic chlorides *via* chlorination was studied in some detail[3] since this is the first step in the synthetic route to nitrile oxides for sterically unhindered compounds.[4] Grundman and Richter[4] reported that nitrile oxides could be prepared by dehydrogenation of the corresponding aldoximes with *N*-bromosuccinimide in *N*,*N*-dimethylformamide solution. The reaction apparently proceeded first to the hydroxamic bromide which was subsequently dehydrobrominated by the base to the nitrile oxide. Solvents such as chloroform,[3c,d,g,9] ether,[3a,5] or 8.3 *N* aqueous hydrochloric acid solution[3a,e] have been employed in the chlorination of oximes. It was found that aromatic aldoximes bearing bulky ortho substituents could not be chlorinated to hydroxamic chlorides without a considerable additional uptake of chlorine by the molecule, presumably by substitution in the aromatic ring.[6] Furthermore, strong electron-donating substituents in the aromatic nucleus facilitated chlorination of the ring with the result that a mixture of chlorinated products was formed.[3a]

I wish to report some interesting results which were discovered in the course of investigating the chlorination of oximes. It was found that substituted aromatic oximes, especially in the presence of a nitro group in the ring, gave the corresponding benzal chloride derivatives upon treatment with chlorine in methylene chloride or pure chloroform solution at -20 to $0°$. However, when commercial (comm) chloroform[7] or methylene chloride which contained 0.75% ethanol was used as the solvent (at -15 to $20°$), substituted benzhydroxamic chlorides were obtained. For the purpose of mechanistic study of benzal chloride formation, a systematic investigation of the chlorination of oximes in commercial chloroform and methylene chloride was undertaken. The results were summarized in Table I.[8-10]

The use of benzhydroxamic chloride and its derivatives as precursors for 1,3-dipolar addition reactions has been studied extensively for the past 10 years. In spite of the wide application of benzhydroxamic chlo-

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(1) D. C. Iffland, G. X. Criner, M. Koral, F. J. Lotspeich, Z. B. Papanastassiou, and S. M. White, Jr., *J. Amer. Chem. Soc.*, **75**, 4044 (1953).

(2) E. M. Cherkasova and N. N. Mel'nikov, *Zh. Obshch. Khim.*, **19**, 321 (1949); *Chem. Abstr.*, **43**, 6569*a* (1949).

(3) See, for example (a) R. H. Wiley and B. J. Wakefield, *J. Org. Chem.*, **25**, 546 (1960); (b) B. G. Bowenlock and W. Luttke, *Quart. Rev., Chem. Soc.*, **12**, 321 (1958); (c) J. T. Hackmann and P. A. Harthoorn, British Patent 949,371 (1964); (d) T. Farley, F. H. Rathmann, and D. Tangen, *Proc. N. D. Acad. Sci.*, **13**, 61 (1959); (e) G. W. Perold, A. P. Steyn, and F. V. K. von Reiche, *J. Amer. Chem. Soc.*, **79**, 462 (1957); (f) M. H. Benn, *Can. J. Chem.*, **42**, 2393 (1963).

(4) C. Grundmann and R. Richter, *J. Org. Chem.*, **33**, 476 (1968), and other papers in this series.

(5) G. Casnati and A. Ricca, *Tetrahedron Lett.*, No. 4, 327 (1967).

(6) C. Grundmann and J. M. Dean, *J. Org. Chem.*, **30**, 2809 (1965).

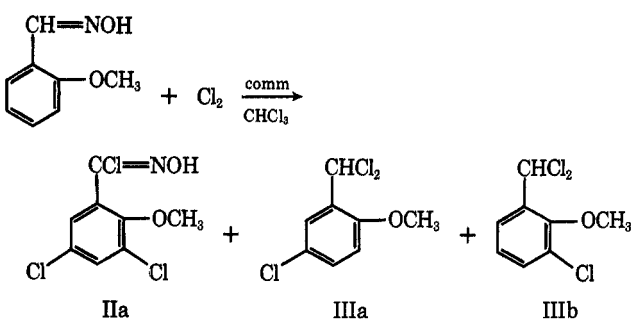
(7) Commercial chloroform (reagent grade) contains 0.75% ethanol as stabilizer (purchased from Matheson Coleman and Bell, East Rutherford, N. J.). It is purified by the method of L. F. Fieser, "Experiments in Organic Chemistry," 3rd ed, D. C. Heath, Boston, Mass., 1955, p 283.

(8) J. Heilbron, "Dictionary of Organic Compounds," Oxford University Press, New York, N. Y., 1965.

(9) G. Bianchetti, D. Pocar, and P. D. Croce, *Gazz. Chim. Ital.*, **93**, 1714 (1963); *Chem. Abstr.*, **60**, 14500*h* (1964).

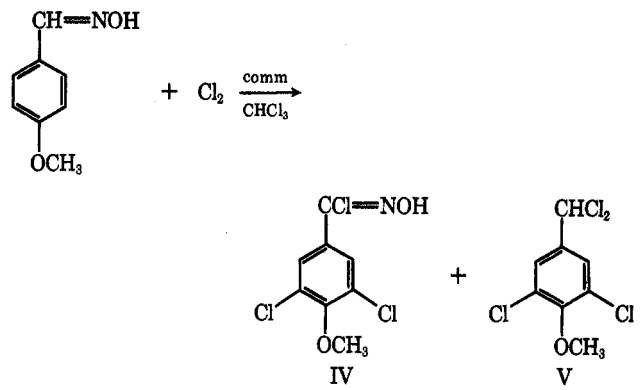
(10) E. H. Hunteress, "Organic Chlorine Compounds," Wiley, New York, N. Y., 1948, pp 889, 895.

ride (I) and its derivatives, the basic methods for preparation of these compounds are limited only to two variations, *i.e.*, (1) chlorination of oximes in *ca.* 8.3 *N* hydrochloric acid at 0°[11] and (2) chlorination of oximes in chloroform.[3g,12,13] Both methods were used for the preparation of I. It was found that I could best be prepared by using commercial chloroform as solvent and the pure compound was obtained by vacuum distillation (below 100°) instead of recrystallization from petroleum ether.[14] This compound decomposed upon standing in the atmosphere within several days. Identification was achieved by converting I to 3,4-diphenylfuroxan upon treatment with 10% aqueous sodium hydroxide solution.[3a] The use of a number of substituted benzhydroxamic chlorides as precursors for the preparation of nitrile oxides without describing a method of preparation has been disclosed.[3a,15,16] In general, chloro- and nitro-substituted benzaldoximes gave benzhydroxamic chloride derivatives in 27–59% yield when commercial chloroform was employed as solvent for the chlorination process. *o*-Nitrobenzaldoxime failed to give the hydroxamic chloride derivative upon chlorination. Instead, a yellow oily residue was collected after work-up. A violent explosion occurred in the course of vacuum distillation (pot temperature 130°). When *o*-methoxybenzaldoxime was chlorinated in commercial chloroform, a mixture of substituted benzhydroxamic chloride IIa (11%) and benzal chloride IIIa and IIIb (58%) was obtained. The isomeric



IIa IIIa IIIb

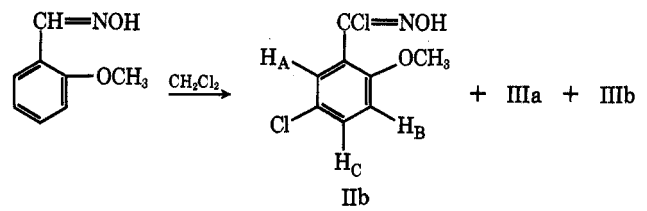
3-chloro- (IIIb) or 5-chloro-2-methoxybenzal chloride (IIIa) could not be separated into its components. The isomeric mixture was collected from vacuum distillation and gave satisfactory elemental analysis. The nmr spectrum showed a ratio of 1:1.16, which was calculated from the methoxy signal (δ 4.10, 4.18) for these two isomeric products. Similarly, chlorination of *p*-methoxybenzaldoxime resulted in 11% of 3,5-dichloro-4-methoxybenzhydroxamic chloride (IV) and 22% of 3,5-dichloro-4-methoxybenzal chloride (V) in commercial chloroform. The structure of V was assigned on the basis of the infrared (ir) and nmr spectra. It decomposed rapidly in the sealed tube under nitrogen atmosphere and did not give correct elemental analysis. The aromatic and methoxy protons appeared as singlets at δ 7.88 and 4.26, respectively. The benzal proton gave a sharp singlet at δ 6.94. Hence, the nmr spectrum was completely consistent with the assigned



IV V

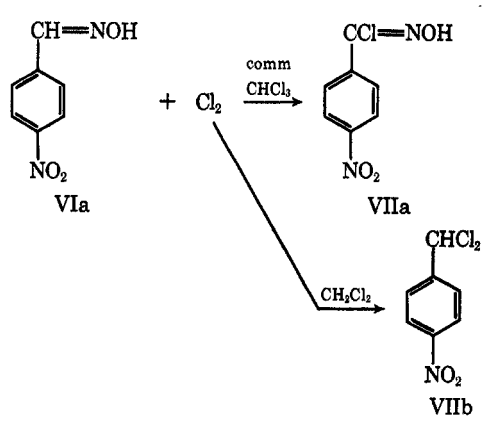
structure. The lack of hydroxy absorption in the ir spectrum further supported this fact.

The chlorination of oximes in methylene chloride is particularly interesting. The nitro-substituted benzaldoximes gave benzal chloride derivatives as the final product in 37–80% yield. On the other hand, chloro- and methoxy-substituted benzaldoximes yielded mixtures of benzhydroxamic chloride and benzal chloride derivatives. The chlorination of *o*-methoxybenzaldoxime in methylene chloride gave 5-chloro-2-methoxybenzhydroxamic chloride (IIb) together with



IIb

a mixture of IIIa and IIIb. In contrast to the chlorination in chloroform, monosubstituted benzhydroxamic chloride was obtained. It is interesting to note that chlorination of *p*-methoxybenzaldoxime in methylene chloride also gave a monosubstituted derivative, *i.e.*, 3-chloro-4-methoxybenzhydroxamic chloride. The structure has been proven by the chemical evidence (see part II in this series). The structure of IIb was assigned on the basis of elemental analysis and ir and nmr spectra. The nmr spectrum gave a methoxyl signal at δ 3.90 (s) and a hydroxy peak at δ 2.96. Proton signals in the aromatic region were at δ 7.17 (d, J = 9 cps, H_B) and δ 7.46 (m, H_A and H_C). It was noted that the yield for *o*- and *p*-methoxybenzhydroxamic chloride derivatives markedly increased from 5 to 22% and 11 to 53%, respectively, in the presence of triethylamine. Furthermore, *p*-nitrobenzhydroxamic chloride (VIIa) was the sole product (52% yield) upon



VIa VIIa VIIb

(11) O. Piloty and H. Steinbock, *Ber.*, **35**, 3112 (1902).
(12) N. Singh, J. S. Dandhu, and S. Mahon, *Tetrahedron Lett.*, 4453 (1968), and references cited therein.
(13) A. Dondoni, A. Mangini, and S. Ghersetti, *ibid.*, 4789 (1966).
(14) M. H. Benn, *Can. J. Chem.*, **42**, 2393 (1964).
(15) P. Rajagonalan and C. N. Talaty, *Tetrahedron Lett.*, 2101 (1966).
(16) A. Dondone, *ibid.*, 2397 (1967).

TABLE I

PRODUCTS FROM THE CHLORINATION OF OXIMES

Oximes	Solvent–catalyst	Reaction temp, °C	Products	Mp or bp (mm), °C, $n^{T}D$	Yield, %	C, % Obsd	C, % Calcd	H, % Obsd	H, % Calcd	N, % Obsd	N, % Calcd	Cl, % Obsd	Cl, % Calcd
Benzaldoxime	Comm $CHCl_3$	−15 to −20	Benzhydroxamic chloride	50–51 (*ca.* 45%[3a] 49[3e])	54								
o-Nitrobenzaldoxime	CH_2Cl_2	0	*o*-Nitrobenzal chloride	113 (2.5) [143–144 (12)[8]], $n^{19}D$ 1.5773	80								34.31 34.42
m-Nitrobenzaldoxime	CH_2Cl_2	0	*m*-Nitrobenzal chloride	66–67 (65)[8]	33								34.56 34.42
	Comm $CHCl_3$	−15 to −20	*m*-Nitrobenzhydroxamic chloride	101–102 (96–97)[6a]	58								17.82 17.68
p-Nitrobenzaldoxime	CH_2Cl_2	0	*p*-Nitrobenzal chloride	43–44 (46)[8]	20–66								34.38 34.42
	CH_2Cl_2–dark	0	*p*-Nitrobenzal chloride		44								
	Pure $CHCl_3$	−15 to −20	*p*-Nitrobenzal chloride		50								
	Comm $CHCl_3$	−15 to −20	*p*-Nitrobenzhydroxamic chloride	126–127 (116)[9]	59	42.09	41.91	2.39	2.51	13.96	13.97	17.71	17.68
	CH_2Cl_2–Et_3N	0	*p*-Nitrobenzhydroxamic chloride		52								
	CH_2Cl_2–0.75% EtOH	0	*p*-Nitrobenzhydroxamic chloride		77								
	CH_2Cl_2–0.75% EtOH	−15 to −20	*p*-Nitrobenzhydroxamic chloride		52–59								
6-Nitroveratraldoxime	CH_2Cl_2	0	6-Nitro-3,4-dimethoxybenzal chloride	109–110	37	40.72	40.62	3.41	3.41	5.20	5.27	26.15	26.65
2,4-Dinitrobenzaldoxime	CH_2Cl_2	0	2,4-Dinitrobenzal chloride	121 (0.03), $n^{19}D$ 1.6010	50	34.69	33.49	1.74	1.61	11.39	11.16	28.20	28.25
o-Chlorobenzaldoxime	CH_2Cl_2	0	*o*-Chlorobenzal chloride	53 (0.12), $n^{16}D$ 1.5661 [100 (10), $n^{16}D$ 1.5670][10]	61	43.33	43.52	2.52	2.02			52.81	54.46
	Comm $CHCl_3$	−15 to −20	*o*-Chlorobenzhydroxamic chloride	57–58	27	44.34	44.24	2.55	2.65	7.46	7.37	37.39	37.32
p-Chlorobenzaldoxime	CH_2Cl_2	0	*p*-Chlorobenzal chloride	93–94 (4), $n^{19}D$ 1.5672 [108 (10)][3a]	3–45	43.23	43.01	2.47	2.58			54.55	54.41
			p-Chlorobenzhydroxamic chloride	88–90 (82–86)[3a]	23–69							37.32	37.32
	Comm $CHCl_3$	−15 to −20	*p*-Chlorobenzhydroxamic chloride		51								

p-Methoxybenzaldoxime	CH_2Cl_2	0	3-Chloro-4-methoxybenzhydroxamic chloride		22									
			3,5-Dichloro-4-methoxybenzal chloride		40									
	CH_2Cl_2–Et_3N	−15 to −20	3,5-Dichloro-4-methoxybenzhydroxamic chloride	151–152	53	37.99	37.75	2.45	2.38	5.60	5.50	41.57	41.79
	Comm $CHCl_3$	−15 to −20	3,5-Dichloro-4-methoxybenzal chloride	97 (0.03), $n^{22}D$ 1.6728	22									
			3,5-Dichloro-4-methoxybenzhydroxamic chloride		11									
o-Methoxybenzaldoxime	CH_2Cl_2	0	3-Chloro- and 5-chloro-2-methoxybenzal chloride	79–82 (0.03), $n^{24}D$ 1.5658	26	42.29	42.61	2.91	3.13			47.32	47.17
			5-Chloro-2-methoxybenzhydroxamic chloride	143–145	5	43.82	43.66	3.19	3.21	6.26	6.37	32.10	32.22
	CH_2Cl_2–Et_3N	−15 to −20	5-Chloro-2-methoxybenzhydroxamic chloride		22									
	Comm $CHCl_3$	−15 to −20	3,5-Dichloro-2-methoxybenzhydroxamic chloride	130–132	11	37.98	37.75	2.39	2.38	5.53	5.50	42.28	41.79
			3-Chloro- and 5-chloro-2-methoxybenzal chloride		58									

chlorination when triethylamine was added to a methylene chloride solution of *p*-nitrobenzaldoxime (VIa). Thus, in the presence of an equivalent amount of triethylamine, benzhydroxamic chloride derivatives became the only isolable chlorination product. When VIa was chlorinated in pure chloroform or methylene chloride, *p*-nitrobenzal chloride (VIIb) was obtained in 50 and 66% yield, respectively; no VIIa was isolated from the reaction mixture. It is concluded that the presence of 0.75% ethanol had altered the reaction pathway. This fact was further proved by using methylene chloride which contained 0.75% ethanol as reaction solvent. A 77% yield of VIIa was obtained when VIa was chlorinated under these conditions. The chlorination of *p*-chlorobenzaldoxime (VIb) was studied by varying reaction time at 0° with methylene chloride as solvent. The results were listed in Table II.

TABLE II

PRODUCT DISTRIBUTION FROM THE CHLORINATION OF VIb

Reaction time, hr, at 0°	VIIIa, %	VIIIb, %	VIIIa/VIIIb
0	23	34	0.68
1	63	8	7.88
2	41	18	2.28
3	57	32	1.78
5	38	45	0.84

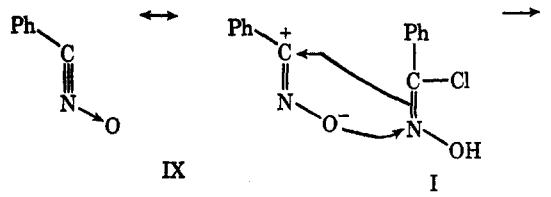
When the reaction mixture was warmed to *ca.* 50° in a water bath immediately after addition of chlorine (*i.e.*, 0-hr reaction time), the yield of *p*-chlorobenzhydroxamic chloride (VIIIa) was reduced to a minimum. It is obvious that the optimal condition for the formation of VIIIa is 1 hr at 0° of cooling.

I have examined the chlorination of benzaldoxime and *o*-hydroxy- (XI) and *p*-dimethylaminobenzaldoxime (XVII) in methylene chloride solution. The reaction products from chlorination of benzaldoxime were formulated as follows.

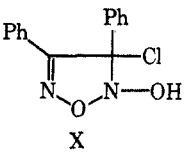
X

The formation of *O*-benzoylbenzhydroxamic chloride will be explained in detail in a subsequent paper. Benzonitrile, which formed as a result of dehydration, was obtained in 23% yield upon vacuum distillation as the low-boiling fraction. A crystalline material was collected from the high-boiling fraction by filtration. After several recrystallizations from ethyl acetate, 2-hydroxy-3,4-diphenyl-3-chloro-1,2,5-Δ^4-oxadiazoline (X) was obtained. On the basis of ir, ultraviolet (uv), and mass spectra, the structure of X was proposed. The mass spectrum of X showed, in addition to the weak molecular ion at *m/e* 274 (2%), an ion at *m/e* 103 (intensity 100%) corresponding to the benzonitrile ion. Fragments were also present corresponding to the benzonitrile *N*-oxide (IX) (*m/e* 119, 55%) and benzhydrox-

amic chloride (*m/e* 155, 9%) ions. In view of the uv spectrum of 3,4-diphenylfuroxan [λ_{max}^{EtOH} 237 mμ (ε 27,223), 280 (8831)], the absorption of λ_{max}^{EtOH} 258 mμ (ε 19,900) for X indicates the presence of a $C_6H_5CH{=}N$ chromophore.[3e,17,18] Barnes, Pinkeny, and Phillips[19] examined the ir absorption of isoxazolines and attributed strong absorption found at 1710 cm^{-1} (in dioxane solution) to the C=N-grouping, though the summary given by Bellamy[20] leads one to expect specific absorption for the -C=N-grouping around 1660 cm^{-1}. Thus, the strong ir band at 1735 cm^{-1} for X is ascribed as C=NO- absorption.[21] Compound X probably resulted from the reversed addition of IX to I, *i.e.*,

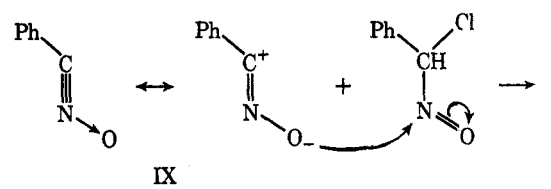


IX I

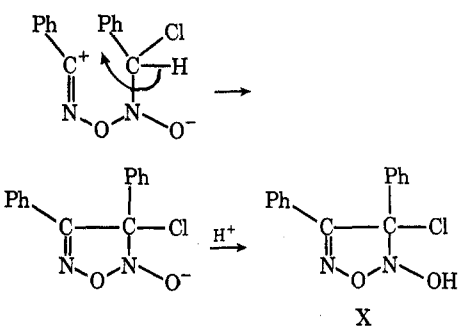


X

It is reported that the addition of IX to I[22] and to benzaldoxime in the presence of boron trifloride[23] occurred in conventional fashion. The exact nature of this reversed addition is unknown. A plausible explanation is the addition of IX to the nitroso tautomer, *i.e.*,



IX



X

It is noted that the positive character of the nitrogen atom in the nitroso compound is greatly enchanced by the oxygen atom in comparison to I.

(17) E. Borelli, *Proc. Int. Meet. Mol. Spectrosc., 4th Bologna*, **2**, 522 (1959); *Chem. Abstr.*, **58**, 4689 (1963).

(18) G. E. McCasland and E. C. Horswill, *J. Amer. Chem. Soc.*, **73**, 3923 (1951).

(19) R. P. Barnes, G. E. Pinkney, and G. M. Phillips, *ibid.*, **76**, 276 (1954).

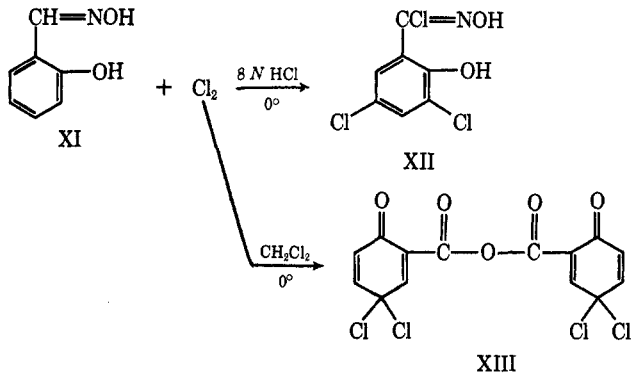
(20) L. J. Bellamy, "The Infrared Absorption of Complex Molecules," Methuen and Co. Ltd., London, 1954, p 223.

(21) G. Bianchi and E. Frati, *Gazz. Chim. Ital.*, **96**, 559 (1966); *Chem. Abstr.*, **65**, 7160*g* (1966).

(22) R. Huisgen, *Angew. Chem.*, **75**, 751 (1963).

(23) S. Morrocchi and A. Ricca, *Chim. Ind. (Milan)*, **49**, 629 (1967); *Chem. Abstr.*, **67**, 907374 (1967).

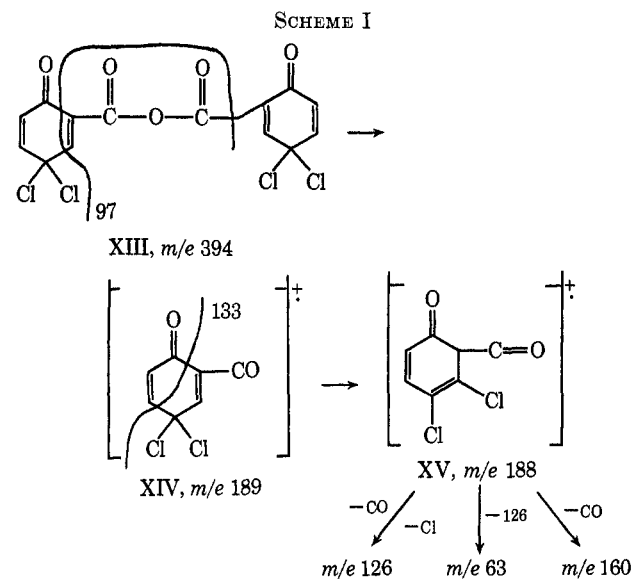
Wiley and Wakefield[3a] reported that 3,5-dichloro-2-hydroxybenzhydroxyamic chloride (XII) was obtained upon chlorination of *o*-hydroxybenzaldoxime (XI) in 8 *N* hydrochloric acid at 0°. When XI was chlorinated in methylene chloride, XIII was collected as the reaction product. No hydroxamic chloride derivative was isolated from the reaction mixture. The assign-



XI XII XIII

ment of structure XIII is made by examination of the ir, uv, and mass spectra. The uv spectrum showed an absorption at λ_{max}^{EtOH} 222 mμ (ε 21,600) and 342 (3250) which represent the presence of an α,β-unsaturated ketone.[24] The absorption at λ_{max}^{EtOH} 258 mμ (ε 6000) is indicative of the presence of a disubstituted α,β-unsaturated ketone [HC(C=O)=C—C=O]. The ir absorption at 1665 cm^{-1} is also attributed to the α,β-unsaturated ketone.[20] In addition, the cis-disubstituted ethylene (HC=CH) absorbs at 702 cm^{-1}. Scheme I presents what appears to be the most rea-

SCHEME I

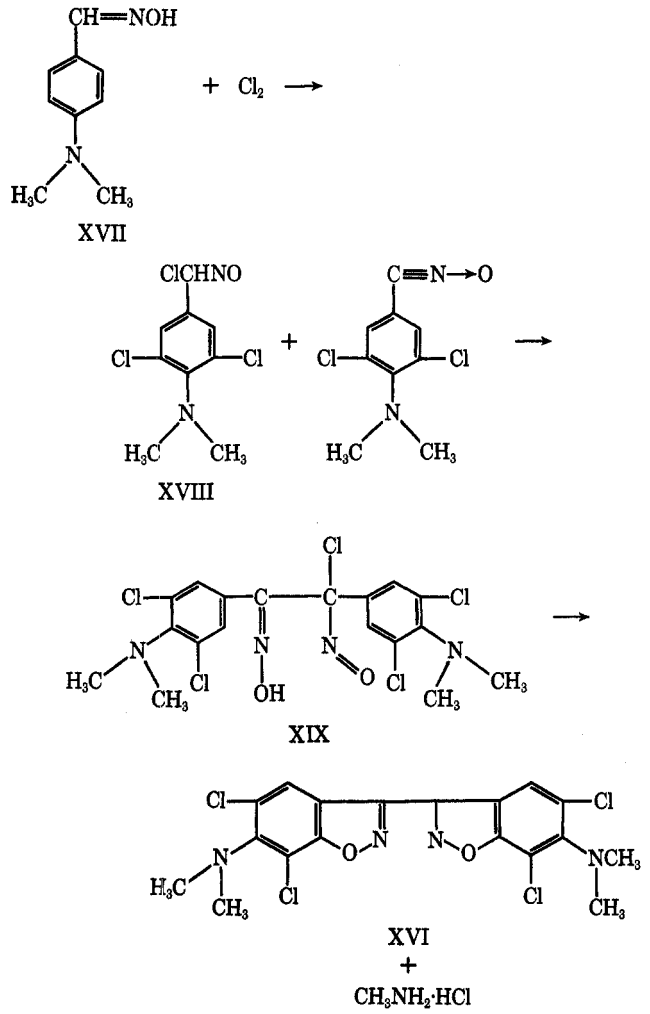


XIII, *m/e* 394 XIV, *m/e* 189 XV, *m/e* 188 *m/e* 126 *m/e* 63 *m/e* 160

sonable fragmentations which account for the mass spectrum. The ir spectrum has no hydroxyl absorption and the carbonyl group absorbed at 1665 cm^{-1} with two shoulders at 1660 and 1650 cm^{-1}. Fragments of *m/e* 133 (8%) and 97 (8%) further supported the proposed structure. The mechanism of formation of XIII is unknown. Similarly, the chlorination of *p*-dimethylaminobenzaldoxime (XVII) in methylene chloride gave an interesting product instead of the expected benzhydroxamic chloride derivative. A small amount

(24) R. B. Woodward, *J. Amer. Chem. Soc.*, **63**, 1123 (1941).

of methylamine hydrochloride was also isolated. Compound XVI was obtained in 6% yield and its structure



was assigned with the aid of uv, ir, nmr, and mass spectra. The spectrum of XVI consists of a singlet at δ 7.68 (aromatic proton) and two singlets centered at δ 2.95 (*N*-methyl proton). The mass spectrum of XVI showed a parent peak at *m/e* 460 (28%) and a base peak at *m/e* 400 ($M^+ - 2NO$) (intensity 100%). Cleavage of the central carbon–carbon bond gave a molecular ion *m/e* 230 (54%) corresponding to the monomer of XVI. The presence of the dimethylamino group is suggested by the occurrence of *m/e* 44 (28%) ion. The only other fragments of significant intensity corresponded to M^+ – oxygen (19%), $^1/_2M^+$ – OH (90%), and $^1/_2M^+$ – CN (78%). These facts eliminated the possibility that XVI was a 3,4-diarylfuroxan derivative. The ir spectrum showed an absorption at 1600 cm^{-1} for the >C=N– group in contrast to 3,4-diphenylfuroxan which absorbs at 1575 and 1590 cm^{-1}. The presence of a substituted isoxazole system in XVI was indicated by its absorption at 952 cm^{-1}.[25] The uv spectrum also displayed marked differences between XVI and 3,4-diphenylfuroxan. It is surprising to find that the uv spectrum of XVI is quite different from those of the benzisoxazole derivatives reported by Casini *et al.*[26] The formation of XVI is visualized as the addition of nitrile *N*-oxide to the C–H bond of the chloronitroso intermediate XVIII. The final product was obtained by the ring closure of the chloronitroso intermediate XIX. The origin of the isolated methylamine hydrochloride is unknown.

In the hope of better defining the intricacy and complexity involved in the chlorination of oximes, I have reported the chlorination of benzaldoxime, XI, and XVII in methylene chloride solution. It is emphasized that the author made no attempt to clarify the exact nature of this reaction but to call attention to the paucity of mechanistic study on this complicated chlorination process. The solvent effect of this chlorination reaction is remarkable. The change from a polar solvent to a nonpolar one could alter the entire reaction pathway.[3a,c,d,e,g,5,9] This new reaction evidently provides a highly convenient route to benzal chlorides which are not readily accessible by conventional methods. For example, 2,4-dinitrobenzal chloride, which could not be prepared by the reaction of phosphorus pentachloride and the corresponding aldehyde,[27] is readily prepared by this method in 50% yield.

In 1958 Gowenlock and Lüttke[28] called attention to the paucity of kinetic data on the isomerization (to oxime) of primary and secondary aliphatic nitroso compounds. The amine-catalyzed isomerization of nitrosocyclohexane to oxime was reported by DiGiacomo.[29] Two possible mechanism consistent with the kinetic data were proposed by the author. The intermediacy of the amine–nitroso monomer complex is suggested. It has been shown that the rate constant increased with decreasing solvent polarity. The mechanistic study of the isomerization of aromatic nitroso compounds to oximes was largely limited to the qualitative observation that blue or green solutions of nitroso compounds gave, on standing, colorless solutions of the corresponding oximes. The mechanism of benzhydroxamic chloride formation has been demonstrated to be a two-stage process consisting of halogenation and subsequent isomerization of the secondary nitroso compound formed.[28] The addition of chlorine to oxime proceeding to the chloronitroso compound in the absence of light was reported by Muller and Metzger.[30] While the isomerization of primary and secondary *C*-nitroso compounds to the benzhydroxamic chloride is well known, the mechanism of benzal chloride formation is relatively obscure. Based on the following chemical evidence in combination with the spectroscopic study of VIa and VIb, it is concluded that the formation of benzal chloride derivatives also proceeds through a *C*-nitroso intermediate XX.

(1) An aliquot of mixture of VIa or VIb and chlorine in methylene chloride gave a positive Liebermann test for nitroso compounds.[31]

(2) Compound VIIa was the sole product (52% yield) upon chlorination when triethylamine was added to a methylene chloride solution of VIa. It is obvious that the base-catalyzed isomerization had altered the reaction pathway.

(25) W. B. Renfrow, J. F. Witte, R A. Wolf, and N. R. Bohl, *J. Org. Chem.*, **33**, 150 (1968).

(26) G. Casini, F. Gualtieri, and M. L. Stein, *J. Heterocycl. Chem.*, **6**, 279 (1969).

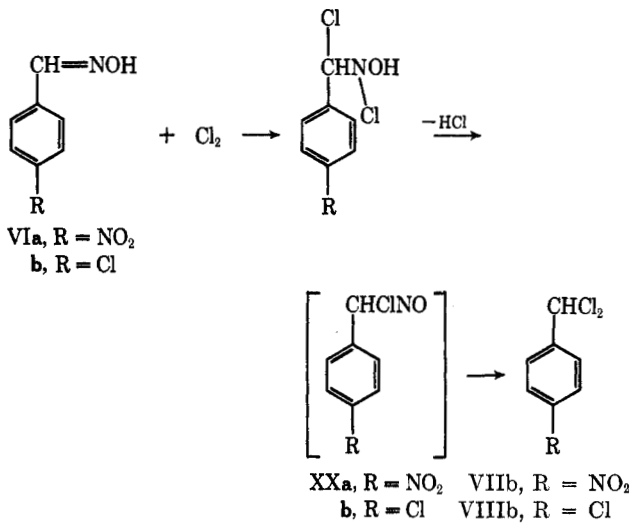
(27) The preparation of this compound has been claimed without describing any physical constants: *Beilstein*, 2nd ed **5**, 265 (1956).

(28) (a) R. H. Wiley and B. J. Wakefield, *J. Org. Chem.*, **25**, 546 (1960); (b) B. G. Gowenlock and W. Lüttke, *Quart. Rev., Chem. Soc.*, **12**, 321 (1958).

(29) A. DiGiacomo, *ibid.*, **30**, 2614 (1965).

(30) E. Muller and H. Metzger, *Chem. Ber.*, **88**, 165 (1955).

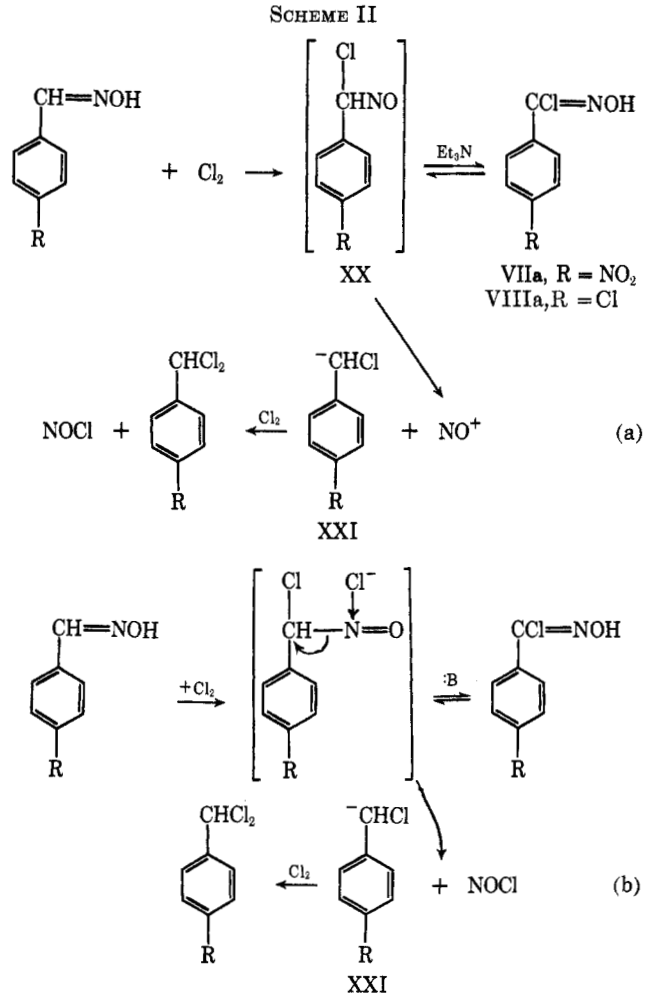
(31) N. D. Cheronis and J. B. Entrikin, "Semimicro Qualitative Organic Analysis," 2nd ed, Interscience, New York, N. Y., 1957.



(3) The visible spectra of the mixture of VIa or VIb and chlorine showed an absorption at $\lambda_{max}^{CH_2Cl_2}$ 635 mμ and 640, respectively. This fact is indicative of the presence of a *C*-nitroso intermediate.[28] The infrared of the mixture showed the –N=O stretching frequency at 1525 cm^{-1} and the –CN– frequency at 1015, 824, and 770 cm^{-1}.[28,32] A crude estimation of the concentration of intermediate XXb in the reaction mixture was attempted. The relatively stable XXb was chosen for this purpose. Since it was observed qualitatively, *i.e.*, the blue solution, which was assumed to be due to this *C*-nitrosocompound, does not discolor at 0° for at least 3 hr. In the case of XXa, the blue color disappeared within 0.5 hr. The extinction coefficient of the closely related *p*-chloronitrosobenzene [λ_{max} 750 mμ (ϵ 45.5)][33] was taken as standard. The extinction coefficient of XXb is expected to be smaller than *p*-chloronitrosobenzene. It is found that a minimum of 38.6% of XXb is formed immediately after addition of chlorine.

(4) Upon treatment with chlorine in methylene chloride solution, VIIIa could not be converted to VIIa. Furthermore, when chlorination of VIa in methylene chloride solution was carried out in darkness, 44% of VIIIa was obtained showing that the loss of NO is not a free-radical reaction. In view of the evidence listed above, the reaction mechanisms shown in Scheme II are proposed for the formation of benzal chloride. The mechanism described in eq a suggested that the intermediate XX decomposed unimolecularly to give carbanion XXI and a nitrosyl ion. The carbanion XXI and nitrosyl ion in turn reacted with 1 mol of chlorine to give the final products. The second proposed mechanism, formulated in eq b, has been considered as a nucleophilic displacement on the nitroso group, perhaps by chloride ion, and that carbanion XXI and nitrosyl chloride are thereby produced. The presence of nitrosyl chloride was demonstrated by trapping with an aqueous aniline hydrochloride–hydrochloric acid solution. The resulting benzenediazonium chloride coupled with phenol in alkaline solution very rapidly at ice bath temperature to form an orange-colored solution which is indicative of the presence of *p*-hydroxyazobenzene.[34] The proposed nitrosyl ion formation was further supported by the fact that an absorption maximum of 440 mμ, which is indicative of nitrosyl ion absorption, was observed from an aliquot of the reaction mixture between VIa and chlorine in methylene chloride.[35]

SCHEME II



Invariably in methylene chloride solution, nitro-substituted oximes gave the benzal chloride as the final product. The carbanion XXI is probably stabilized by nitro substituents through inductive and/or conjugative effects.[36]

The chloro derivatives resulted in a mixture of VIIb and VIIIb and the ratio of these two products was determined by the cooling period after addition of chlorine (see Table II). However, when methoxy-substituted oximes were chlorinated under these conditions, benzal chloride derivatives became the predominant product irrespective of the solvent used (commercial chloroform or methylene chloride). The stabilization of a carbanion by nitro groups in the ortho or para positions is known while a carbanion stabilized by a chloro group through an inductive effect is also reported.[36] It is well known that the methoxy group destabilizes carbanions. The evidence cited clearly indicates that α-chloro-α-nitroso intermediate XX is

(32) W. Lüttke, *J. Phys. Radium*, **15**, 633 (1954); *Chem. Abstr.*, **52**, 17960e (1958).

(33) K. Nakamoto and R E. Rundle, *J. Amer. Chem. Soc.*, **78**, 1113 (1956).

(34) L. F. Fieser and M. Fieser, "Organic Chemistry," 3rd ed, Reinhold, New York, N. Y., 1956, p 618.

(35) L. J. Beckham, W. A. Fessler, and M. A. Kise, *Chem. Rev.*, **48**, 334 (1951).

(36) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965, p 60.

the precursor for benzal chloride derivative formation. Thus, the variation in final product between nitro- and methoxy-substituted oximes must depend on the isomerization state. It is interesting to note that there is competition between elimination of a proton (see below) or nitrosyl ion from XX. Attention is called to the product distribution from the chlorination of VIb (see Table II). The ratio of VIIIa/VIIIb reached a maximum at 1 hr of the reaction time and decreases progressively as the reaction time increases. There is little difference between product ratio and reaction time when nitro- or methoxy-substituted oximes were chlorinated at various different reaction times. The balance of inductive and conjugative effects of the chloro-substituent in VIa enables one to speculate about the conditions favorable for the elimination of nitrosyl ion. It is conceivable that the presence of XX for extended periods, *i.e.*, by depressing the rate of isomerization by cooling, favors the elimination of nitrosyl ion.

The data presented in Table II concerning the products observed upon chlorinating VIb as a function of time reveals that (disregarding the 0-hr point) the formation of VIIIb is a linear function of time which can be described by the following equation (see Figure 1).

$$\% \text{ VIIIb} = 9.17 \times \text{time (in hours)}$$

The linear correlation between the per cent yield of VIIIb and time indicated that the formation of benzal chloride is a zero-order reaction. It is difficult to reconcile this fact with either of the mechanisms proposed previously. It is conceivable that the linear correlation is accidentally coincided with the formation of VIIIb. In order to verify the kinetic implication of data presented in Table II, a detailed study along this line is required.

Although the formation of nitrosyl ion from the electron impact of nitro compounds is well defined,[37] it is believed that this is the first example of the elimination of nitrosyl ion formation through the C–N heterolysis of a *C*-nitro compound.

The difference existing in final product between nitro-substituted and chloro- and methoxy-substituted oximes upon chlorination in methylene chloride and commercial chloroform deserves some explanation. Previously, the difference was attributed to the effect of ethanol on the isomerization process. The mechanism of isomerication of aromatic oximes is scarcely known. The amine-catalyzed isomerization of nitroso cyclohexane to oximes[29] is the only work of this kind reported to date. It is significant to note that benzal chloride derivatives were isolated as the major product upon chlorination of methoxy-substituted oximes in commercial chloroform. In contrast, benzhydroxamic chloride derivatives were the sole product when nitro- or chloro-substituted oximes were chlorinated in commercial chloroform. Obviously, the ethanol-catalyzed isomerization is only effective in the presence of electron-withdrawing groups. Ethanol-catalyzed isomerization of XX to oxime was demonstrated by the fact that no hydroxamic chloride derivative was isolated upon removal of ethanol from commercial chloroform. Compound VIIb was isolated in 59% yield when the

(37) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Interpretation of Mass Spectra of Organic Compounds," Holden-Day, San Francisco, Calif., 1964, p 206.

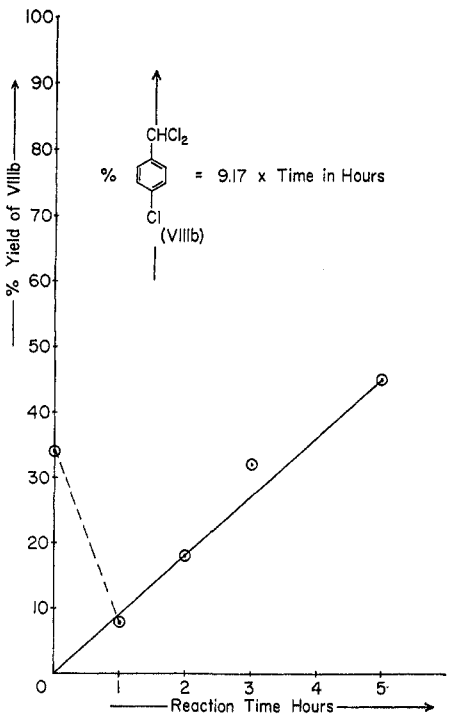


Figure 1.

chlorination of VIa was carried out in pure chloroform. On the basis of experimental results in hand, it is concluded that the isomerization process proceeds through three different pathways depending upon the catalyst and substituent in the benzene ring.

(1) Carbanion mechanism with triethylamine as catalyst follows.

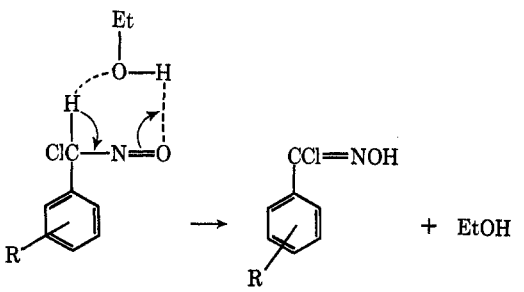
$$\text{ArCClNO} \xrightarrow{\text{Et}_3\text{N}} \text{ArC}^-\text{ClNO} + \text{Et}_3\text{NH}^+ \quad (1)$$

$$\text{ArC}^-\text{ClN=O} \longleftrightarrow \underset{\text{XXII}}{\text{ArCCl=NO}^-} \quad (2)$$

$$\text{ArCCl=NO}^- + \text{Et}_3\text{NH}^+ \longrightarrow \text{ArCCl=NOH} + \text{Et}_3\text{N}$$

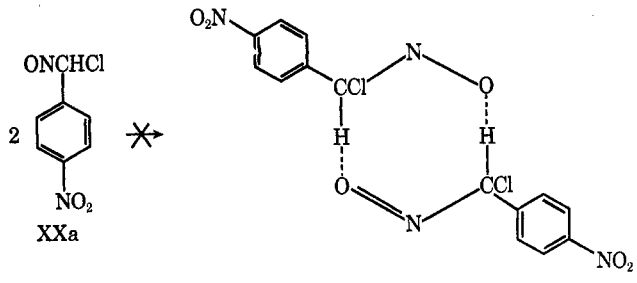
The fact that benzhydroxamic chloride derivatives were obtained after amine-catalyzed chlorination in all cases strongly supports the proposed mechanism. The abstraction of a proton from the chloronitroso compound resulted in a resonance stabilized anion (eq 2). The final product was obtained by protonation of anion XXII.

(2) Intermolecular H bonding mechanism with ethanol as catalyst follows.



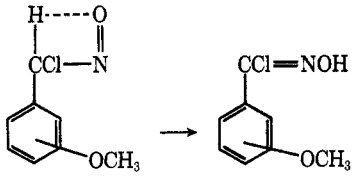
In the mechanism outlined, a cyclic intermediate was suggested for ethanol-catalyzed isomerization. It is expected that electron-withdrawing substituents such

as the nitro group would increase markedly the acidity of benzylic proton which becomes more susceptible to H bonding with ethanol. The absence of VII as the final chlorination product (in methylene chloride) of VIa is indicative of the lack of intermolecular H bonding between two molecules of XXa resembling the amine complex described by Giacomo.[29]



The lack of ethanol-catalyzed isomerization suggested that the methoxy-substituted α-chloro-α-nitroso compound is incapable of H bonding with ethanol due to an intramolecular H bonding (see below). Furthermore, the possibility of intermolecular H-bonding formation could also be excluded on this basis.

(3) The fact that chlorination of *o*- or *p*-methoxybenzaldoxime gave predominatly benzal chloride derivatives both in commerical chloroform and methylene chloride leads one to postulate the intramolecular isomerization mechanism for these compounds, *i.e.*,



The absence of intramolecular isomerization for XX is assumed to be due to the electron-withdrawing effect of the nitro group which reduces the electron density around nitrosyl oxygen.

Thus, the absence of benzhydroxamic chloride formation upon chlorination of VIa in methylene chloride is attributed to the incapability of intramolecular H bonding of XXa. Similarly, predominant benzal chloride formation as chlorination product for methoxy-substituted oximes could be explained on the basis of a slow intramolecular isomerization process.

The mechanisms cited above were based solely on product analysis. Further kinetic and stereochemical studies of oximes in relation to products will probably shed more light on the exact nature of the elimination and isomerization processes.

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. The nmr spectra were obtained with a Varian A-60A spectrometer using tetramethylsilane as internal standard. 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.

Oximes.—Benzaldoxime was purchased from K & K Laboratories, Inc., Plainview, N. Y., as a mixture of α and β isomers. The other oximes were prepared by the hydroxylamine hydrochloride–sodium acetate method.[38]

Chlorination of Oximes. General Procedure.—Substituted benzaldoxime (5 g) was dissolved in 400 ml of methylene chloride at −20 to 0°. Chlorine gas was passed through this solution at a slow rate for 20 min. After standing 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 crystallized from the proper solvent or vacuum distilled if appropriate. Substituted benzal chlorides were isolated as the final product. When commercial chloroform was used as solvent, the same procedure was applied except that the reaction temperature was maintained at −15 to −20°. The product under these conditions was the benzhydroxamic chloride derivative. The individual oximes chlorinated by the above methods are listed in Table I. *Extra caution must be taken when liquid products are distilled at reduced pressure and high temperature (over 100°). In the case of o-nitrobenzaldoxime, a violent explosion occurred during vacuum distillation (pot temperature 130°).*

Preparation of 3,4-Diphenylfuroxan.[38a]—Benzhydroxamic chloride (2 g, 0.013 mol) was dissolved in 50 ml of ether. The solution was cooled in ice and an excess of 10% aqueous sodium hydroxide (10 ml) was added dropwise, with shaking. The solution was shaken occasionally for 30 min at 0°. The ether layer was separated and dried over anhydrous sodium sulfate. The ether solution was allowed to stand over the weekend at room temperature and condensed. The residual solid was crystallized from ethanol to give 0.77 g (64%), mp 117–118° (lit.[38a] 114–115°), of the desired product: ir (Nujol) 1575 and 1590 cm^{-1} (>C=N–); uv λ max 237 and 280 mμ (ε 27,223 and 8831, respectively).

Anal. Calcd for $C_{14}H_{10}N_2O_2$: C, 70.50; H, 4.23; N, 11.76. Found: C, 70.37; H, 4.25; N, 11.73.

Chlorination of Benzaldoxime in Methylene Chloride.—The benzaldoxime (a mixture of α and β isomers) (10 g, 0.0526 mol) was dissolved in 400 ml of methylene chloride at 0°. Chlorine gas was passed through this solution for 30 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 this solution. The solvent was removed *in vacuo* and the residue was vacuum distilled. Benzonitrile was collected in 23% yield [1.96 g, bp 74–81° (0.8 mm)] as the low-boiling fraction. The crystalline material obtained from the high-boiling fraction [bp 110–111° (0.8 mm)] was collected by filtration and crystalized from ethyl acetate: 1.07 g (9%); mp 136–137° of X obtained; ir spectrum (Nujol) 3260 (OH) and 1735 cm^{-1} (PhC=N); uv spectrum λ max 258 mμ (ε 19,900, PhC=N); mass spectrum *m/e* (rel intensity) 274 (2) (parent peak), 155 (9.1), 119 (55), and 103 (100).

Anal. Calcd for $C_{14}H_{11}N_2ClO_2$: C, 61.21; H, 4.04; N, 10.20; Cl, 12.91. Found: C, 61.33; H, 3.89; N, 10.18; Cl, 12.91.

The solid residue (after vacuum distillation) was extracted with ether and the ether insoluble solid was crystallized from ethanol to give 1.15 g (12%), mp 109–110° (lit.[39] 109°), of *O*-benzoylbenzhydroxamic chloride: ir spectrum (Nujol) 1760 cm^{-1} (C=O); uv λ max 260 mμ (ε 25,714, PhC=N); mass spectrum *m/e* (rel intensity) 259 (2) (parent peak), 204 (15), 138 (3), 122 (27), 119 (10) 105 (100), and 103 (100).

Anal. Calcd for $C_{14}H_{10}NClO_2$: C, 64.75; H, 3.88; N, 5.39; Cl, 13.66; mol wt, 260. Found: C, 64.58; H, 3.88; N, 5.20; Cl, 13.99; mol wt, 262 (vaporimetric).

Chlorination of *o*-Hydroxybenzaldoxime (XI) in Methylene Chloride.—XI (2 g, 0.0146 mol) was dissolved in 250 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 this solution. The solvent was removed at reduced pressure and the oily residue was dissolved in 5 ml of ethanol. After standing at room temperature for several days, a crystalline material was collected from the ethanolic solution. The com-

(38) See ref 7, p 103.
(39) See ref 27, p 214.

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

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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).