tion time of toluene, and one unknown component to be present in addition to benzene. The area under the unknown peak was slightly larger than that corresponding to toluene. Dimethyl oxalate was not detected. Calculations from vapor chromatograms, using *p*-xylene as an internal standard, showed the yields of methyl benzoate and toluene to be 21 and 12%, respectively [based on the amount of II (X = I) charged, assuming 0.5 mole of substituted benzene per mole of II]. Both methyl benzoate and toluene were separated by preparative scale vapor chromatography. Methyl benzoate was identified by comparison of its infrared spectrum with that of an authentic sample. A poor spectrum was obtained for the compound thought to be toluene since only a very small amount of material was isolated. An unequivocal assignment of structure could therefore not be made; however, bands at 727 and 692 cm.$^{-1}$ were indicative of toluene.

Reaction of Carbomethoxymercuric Acetate (I) with Ethylene.—A 2-l. stirred autoclave was charged with a mixture of 100 g. (0.314 mole) of carbomethoxymercuric acetate and 500 ml. of absolute methanol. The autoclave was pressurized with ethylene (800 p.s.i.g. at 12°) and heated to 60° (1340 p.s.i.g.) over a period of 5 hr. The reaction mixture was then stirred at 60–66° under ethylene pressure for a total of 18.5 hr. There was no noticeable pressure drop. The autoclave was cooled and discharged and the blue-green reaction mixture was filtered from a small amount of gray sediment. The filtrate was evaporated to dryness under vacuum to yield 88.1 g. of blue-green crystals. Recrystallization of 19.74 g. of this material from *n*-pentane yielded 14.94 g. of pale blue needles, m.p. 39–42.5°. The yield of partially purified β-methoxyethylmercuric acetate was calculated at 66.8%. An analytical sample (m.p. 42–43.5°, hot stage) was prepared by further recrystallization from *n*-pentane. The infrared spectrum of this material (chloroform solution) was identical with that of the β-methoxyethylmercuric acetate prepared from ethylene and methanolic mercuric acetate. The mixture melting point of these two compounds was 42–43° (hot stage).

Anal. Calcd. for $C_5H_{10}HgO_3$: C, 18.84; H, 3.16. Found: C, 19.0; H, 3.26.

Acknowledgment.—The author thanks Dr. R. D. Closson for helpful suggestions.

Carbonimidoyl Dihalides as Organic Intermediates.[1] I. The Preparation of 2-Aryl Aminobenzimidazoles[2]

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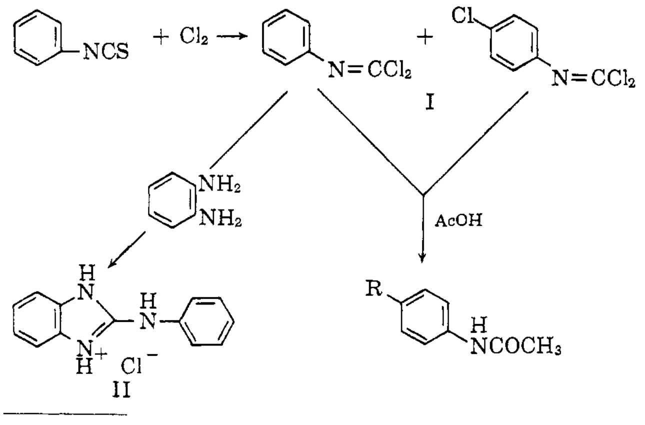
Received December 2, 1963

Phenyl- and *p*-chlorophenylcarbonimidoyl dichlorides, prepared by chlorination of phenyl isothiocyanate, react with *o*-phenylenediamines in a suitable solvent to form the corresponding 2-aryl aminobenzimidazoles. Moderate to almost quantitative yields are obtained, and the procedure affords a convenient route to this class of compounds.

The carbonimidoyl dichlorides I are reactive compounds which offer obvious promise as organic intermediates. They nevertheless have received little attention since the preparation of phenylcarbonimidoyl dichloride was reported in 1874.[3] These compounds may be prepared by addition of chlorine to isocyanides,[4] or more conveniently by direct chlorination of the isothiocyanates in an appropriate solvent at 0–5°.[3,4a,5]



The odor of these compounds is similar to, although not quite so obnoxious as, that of the isocyanides. The vapors are extremely irritating to the eyes. Prolonged exposure to phenylcarbonimidoyl dichloride is reported to cause corneal ulceration and temporary loss of vision, leading to its limited use as "blinding gas" during the first World War.[5a]

Nef[4a] claimed that under the conditions employed by Sell and Zierold for phenyl isothiocyanate, namely chlorination at 0° in chloroform solution, appreciable ring chlorination took place, the actual product being a mixture of phenylcarbonimidoyl dichloride and the *p*-chloro derivative. Bly, Perkins, and Lewis[5a] used carbon tetrachloride or phenylcarbonimidoyl dichloride itself as the solvent, and found no evidence of ring chlorination. In the present study it has been found that the solvent plays an important part in determining whether halogenation will occur on the ring. When chlorination was carried out in chloroform solution and the solution was then allowed to stand overnight or longer at room temperature without first removing the excess dissolved chlorine, the major product was *p*-chlorophenylcarbonimidoyl dichloride, identified by its acetolysis to *p*-chloroacetanilide.[5b] A small amount of the unsubstituted compound was also recovered, together with a little yellow oil believed to be largely 2,4-dichlorophenylcarbonimidoyl dichloride.[5a] No ring chlorination took place when the excess chlorine was aspirated from the solution *in vacuo* at room tempera-

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(1) These compounds, which may be considered as derivatives of the hypothetical carbonimidic acid, HN=C(OH)$_2$, have been known variously as isocyanide dihalides, carbylamine halides, and carbonimidyl halides, and are currently indexed by *Chemical Abstracts* as imidocarbonyl halides. The author is indebted to Dr. Leonard T. Capell, Nomenclature Director of the Chemical Abstracts Service, for suggesting the name "carbonimidoyl dihalides" as conforming with I.U.P.A.C. practice.

(2) Presented before the Division of Organic Chemistry at the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1963.

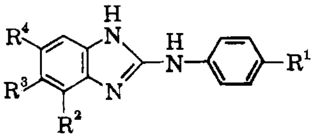
(3) E. Sell and G. Zierold, *Ber.*, **7**, 1228 (1874).

(4) (a) J. U. Nef, *Ann.*, **270**, 267 (1892); (b) P. A. S. Smith and N. W. Kalenda, *J. Org. Chem.*, **23**, 1599 (1958).

(5) (a) R. Bly, G. Perkins, and W. Lewis, *J. Am. Chem. Soc.*, **44**, 2896 (1922); (b) G. M. Dyson and T. Harrington, *J. Chem. Soc.*, 191 (1940); 150 (1942); (c) K. A. Petrov and A. A. Neĭmysheva, *Zh. Obshch. Khim.*, **29**, 2165 (1959).

TABLE I

2-ARYL AMINOBENZIMIDAZOLES



						Reflux, hr.	Yield, %		M.p., °C., base	Calcd., %			Found, %		
R¹	R²	R³	R⁴	Solvent[a]	Diamine[b]		HCl salt	Base		C	H	N	C	H	N
H	H	H	H	A	C	3	81	50	195–199	74.61	5.31	20.08	74.69	5.58	19.91
Cl	H	H	H	A	C	3	68	25	193–195	64.06	4.14	17.25	64.26	4.36	17.50
H	H	CH_3	H	A	D	3	..	44	167–169[c]	75.30	5.88	...	75.03	5.88	...
Cl	H	CH_3	H	A	D	7	83	..	205–207	65.24	4.70	...	64.95	4.84	...
H	H	Cl	H	A	E	3	42	19	215–217	64.06	4.14	...	64.06	4.21	...
Cl	H	Cl	H	A	E	48	66	..	169–173[d]	49.63	3.21	13.36	49.35	3.42	13.20[e]
H	H	NO_2	H	B	F	1.5	98	37	276–279	61.40	3.96	...	61.79	4.00	...
H	NO_2	H	Cl	B	G	1	...[f]	95	247–252	54.08	3.14	...[g]	53.44	3.13	...[g]
Cl	NO_2	H	Cl	B	G	0.5	...[f]	90	280–283	48.32	2.49	17.34	48.26	2.84	17.25

[a] A, 1,2-dichloroethane; B, nitrobenzene. [b] C, *o*-phenylenediamine; D, 3,4-toluenediamine; E, 4-chloro-*o*-phenylenediamine; F, 4-nitro-*o*-phenylenediamine; G, 5-chloro-3-nitro-*o*-phenylenediamine. [c] A. Keller [*Ber.*, **24**, 2498 (1891)] reported m.p. 166–167°. [d] Melting point of hydrochloride was 277–282°. [e] As hydrochloride. [f] Free base separated directly during reflux period. [g] Calcd.: Cl, 12.28. Found: Cl, 11.94.

ture immediately after the initial chlorination was complete, nor did it occur when carbon tetrachloride was used as the solvent. In carbon tetrachloride, a 90% yield of phenylcarbonimidoyl dichloride was obtained even when the solution, saturated with chlorine, was allowed to stand for 5 days at room temperature. These results suggest that the polar chloroform is acting as a halogen carrier for ring substitution through solvation of the chlorine molecule. The solid intermediate which forms from the isothiocyanate during chlorination in chloroform[5b,6] did not precipitate when carbon tetrachloride was used as the solvent.

Since phenylcarbonimidoyl dichloride reacts with aniline to form 1,2,3-triphenylguanidine,[3,5a] it was reasonable to expect it to react in similar fashion with *o*-phenylenediamine to give 2-anilinobenzimidazole (II). When *o*-phenylenediamine and phenylcarbonimidoyl dichloride were mixed without a solvent, no reaction took place until the temperature was raised to 83°, at which point a violent reaction ensued with the formation of a green melt, not further identified. Reaction proceeded to only a small extent in boiling chloroform at 61°, but in 1,2-dichloroethane (b.p. 83°), an 85% yield of crude 2-anilinobenzimidazole hydrochloride precipitated over a 3-hr. period. Conversion to the base yielded a product melting at 195–199°, whose infrared spectrum was identical with that of 2-anilinobenzimidazole prepared by heating N,N′-diphenyl-S-methylisothiourea and *o*-phenylenediamine in a sealed tube at 140°.[7,8] A mixture melting point showed no depression.

The preparation is quite general, and both phenyl- and *p*-chlorophenylcarbonimidoyl dichloride reacted smoothly with *o*-phenylenediamines when heated under reflux in a suitable solvent (Table I). Although 1,2-dichloroethane was generally satisfactory, nitrobenzene gave better results with *o*-phenylenediamines containing nitro groups. Benzene and toluene were unsuitable solvents for the reaction, producing poor yields of tarry product. In nearly every case, a purple or red color appeared immediately upon mixing the reagents. After a few minutes of reflux, the color faded and crystals of the benzimidazole hydrochloride began to separate. No color was observed when *o*-phenylenediamine and phenylcarbonimidoyl dichloride were mixed in 1,2-dichloroethane, but in chloroform a violet color appeared which soon faded, although very little over-all reaction took place.

The reaction was usually complete within 1 to 3 hr. *p*-Chlorophenylcarbonimidoyl dichloride was less reactive than the unsubstituted compound, and the reaction was further retarded by the presence of a nitro group in the diamine. No product was obtained from *p*-chlorophenylcarbonimidoyl dichloride and 4-nitro-*o*-phenylenediamine, the amine being recovered unchanged. Both 2-anilino-4-nitro-6-chlorobenzimidazole and 2-(*p*-chloro)anilino-4-nitro-6-chlorobenzimidazole precipitated as the free bases in 90–95% yield after 10 min. of reflux in nitrobenzene.

Experimental[9]

Phenylcarbonimidoyl Dichloride.—Chlorine gas was bubbled through a solution of 60 ml. (67.5 g., 0.5 mole) of phenyl isothiocyanate in 200 ml. of carbon tetrachloride with stirring and ice cooling, and at such a rate that the temperature did not rise above 3°. The reaction was complete after 3–4 hr., at which time chlorine was no longer rapidly absorbed, and the solution had turned a deep red. The solvent and the sulfur dichloride produced in the reaction were removed by distillation and the residue was fractionated through a 30-cm. column packed with glass helices. The product (74–78 g., 85–90% yield) distilled at 103–106° (31 mm.), lit.[5a] b.p. 107–109° (30 mm.), as a colorless oil, n^{25}_{D} 1.5713.

The infrared spectrum (Fig. 1) shows an intense C═N stretching absorption at 1650 cm.$^{-1}$, bands at 3311, 3067, 1754, 1587, 1481, 1447, 1205, 1072, 1026, 1002, 757.6, and 692 cm.$^{-1}$, and

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(6) O. Helmers, *Ber.*, **20**, 786 (1887).

(7) J. F. Deck and F. B. Dains, *J. Am. Chem. Soc.*, **55**, 4986 (1933).

(8) The first time that this procedure was followed, a product was obtained which gave the proper elemental analysis and exhibited the same infrared spectrum, but which melted at 151–152° after recrystallization from benzene, rather than at 188° as reported by Deck and Dains, and which seemed appreciably more soluble in benzene. After these crystals had stood for several months at room temperature, they were found to melt at 193–195°, suggesting that the low- and high-melting crystals were polymorphs. The products of subsequent sealed-tube preparations all melted between 195–200° after recrystallization.

(9) Melting points were determined in a calibrated Thomas-Hoover capillary melting point apparatus and are corrected. Analyses were by Schwartzkopf Microanalytical Laboratory, Woodside, N. Y.

broad absorption at about 913 and 845 cm.$^{-1}$. After several months, a band, absent in the spectrum of the freshly distilled product, appeared at 2262 cm.$^{-1}$. This is attributed to the isocyanate group[10] and indicates that some hydrolysis took place on exposure to the atmosphere.

***p*-Chlorophenylcarbonimidoyl Dichloride.**—Sixty milliliters of phenyl isothiocyanate dissolved in 200 ml. of chloroform was chlorinated in the same manner as above. After a short while a solid intermediate separated, gradually redissolving as the reaction progressed. Chlorination was complete after 5 hr., and the clear red solution, saturated with chlorine, was allowed to stand overnight or longer at room temperature. After removal of solvent and sulfur dichloride, fractionation afforded 63.5 g. (61% yield) of a faintly yellow oil, b.p. 135–141° (31 mm.), lit.[5a] b.p. 135–137° (30 mm.), n^{25}D 1.5862; together with 12 g. (14% yield) of phenylcarbonimidoyl dichloride; and about 5 g. of a yellow oil, n^{25}D 1.5904, distilling between 141–165° (31 mm.), which was probably largely 2,4-dichlorophenylcarbonimidoyl chloride.[5a]

In addition to C═N absorption at 1653 cm.$^{-1}$, the infrared spectrum (Fig. 2) shows bands at 3279, 3030, 1653, 1587, 1481, 1205, 1087, 1062, 1014, 942.5, 826.4, 754.7, 708.2, and 686.3 cm.$^{-1}$ with broad absorption centered at 900 cm.$^{-1}$. The isocyanate band again appeared at 2262 cm.$^{-1}$ upon exposure to the atmosphere.

***o*-Phenylenediamines.**—*o*-Phenylenediamine, 3,4-toluenediamine, 4-chloro-*o*-phenylenediamine, 4-nitro-*o*-phenylenediamine, and 5-chloro-3-nitro-*o*-phenylenediamine were purchased from Eastman Kodak Co. and recrystallized from water or alcohol.

Acetolysis of Phenylcarbonimidoyl Dichloride.[5a]—One milliliter of *p*-chlorophenylcarbonimidoyl dichloride was heated under reflux with 3 ml. of glacial acetic acid until evolution of hydrogen chloride ceased. The mixture was poured into cold water, and the precipitate, after recrystallization from water, was identified by its infrared spectrum as *p*-chloroacetanilide, m.p. 178–180°. In similar fashion, phenylcarbonimidoyl dichloride formed acetanilide, m.p. 114°.

2-Aryl Aminobenzimidazoles (Table I).—Equimolar amounts of phenyl- or *p*-chlorophenylcarbonimidoyl dichloride and the *o*-phenylenediamine were heated under reflux in about 10–20 ml. of 1,2-dichloroethane or nitrobenzene per gram of amine. Both 2-anilino- and 2-(*p*-chloro)anilino-4-nitro-6-chlorobenzimidazole precipitated as the free bases which were filtered, washed with a little ether, and recrystallized from dilute alcohol. The other benzimidazoles prepared separated as the hydrochlorides. Allowing the mixture to stand for 24–48 hr. after reflux afforded a more crystalline product. The crystals were filtered, washed with a little fresh solvent, and recrystallized at least twice from 6 *N* hydrochloric acid. The purified salt was then dissolved in water and converted to the base by addition of 6 *N* sodium hydroxide. The base occasionally precipitated as a gum which crystallized very slowly. This could usually be avoided by adding the sodium hydroxide solution to a hot, well-stirred solution of the hydrochloride until the mixture was strongly basic. The base was then recrystallized from dilute alcohol or benzene.

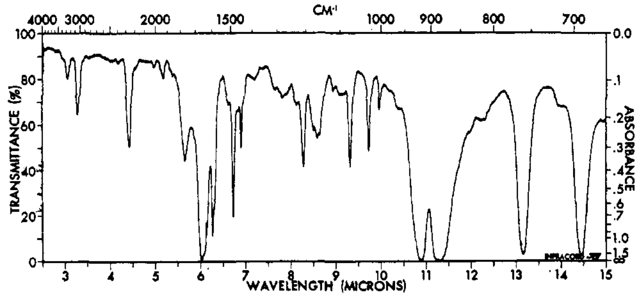

Fig. 1.—The infrared absorption spectrum of phenylcarbonimidoyl dichloride (as a liquid film). The band which appears at 2262 cm.$^{-1}$ after storage in air is attributed to the isocyanate group (see Experimental).

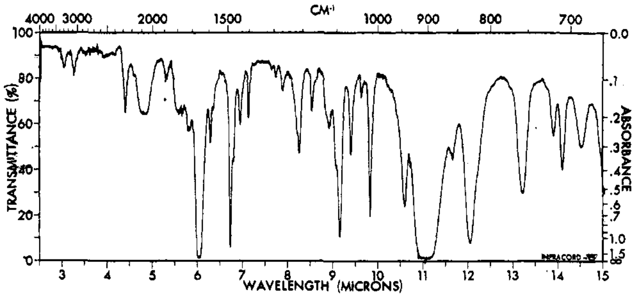

Fig. 2.—The infrared spectrum of *p*-chlorophenylcarbonimidoyl dichloride (as a liquid film). The band which appears at 2262 cm.$^{-1}$ after storage in air is attributed to the isocyanate group (see Experimental).

Acknowledgment.—Sincere appreciation is extended to Miss Jeannette Musco and Mr. Arthur Schwartz, graduate students at Hunter College, for technical assistance.

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[10] K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1962, p. 28; H. W. Johnson, Jr., and P. H. Daughhetee, Jr., *J. Org. Chem.*, **29**, 246 (1964).