Anal. Calcd. for $C_6H_{14}Br_2Si$: C, 26.28; H, 5.11; Br, 58.39. Found: C, 26.31; H, 5.31; Br, 58.28.

γ-Chloropropyl(chloromethyl)dimethylsilane. A.—To 29.7 g. (0.25 mole) of thionyl chloride was added in small portions (caution) 41.7 g. (0.25 mole) of γ-hydroxypropyl(chloromethyl)-silane. After the evolution of gases had subsided, the mixture was heated at reflux for 1 hr. and distilled without further work-up to yield 28.9 g. (63%) of the dichloro derivative, b.p. 212°, $n^{23}D$ 1.4656. Yields using this procedure varied from 63 to 80%. Reactions using pyridine as solvent gave yields ranging from 32 to 40%.

Anal. Calcd. for $C_6H_{14}ClSi$: C, 38.92; H, 7.56; Cl, 38.37. Found: C, 38.90; H, 7.54; Cl, 38.18.

B.—A mixture of 81.3 g. (0.685 mole) of thionyl chloride and 114 g. of the residue from the preparation of 3,3-dimethyl-3-sila-1-oxacyclohexane yielded, after a 3-hr. reflux and distillation, 100.8 g. of the dichloro derivative.

1,1-Dichloro-3,3-dimethyl-1,3-disilacyclohexane.—Using the general procedure as outlined by Cason and Rapoport,[18] the di-Grignard reagent of γ-bromopropyl(bromomethyl)dimethylsilane (54.2 g., 0.19 mole) was prepared using 9.2 g. (0.38 g.-atom) of magnesium turnings and 200 ml. of ether. The Grignard reagent was then transferred to a dropping funnel and added dropwise to a solution of 32.4 g. (0.19 mole) of silicon tetrachloride in 500 ml. of ether. The mixture was heated under reflux for 19 hr., then filtered with suction using Filter-Cel. The filtrate was distilled to yield 25.4 g. (62%) of the disilacyclohexane, b.p. 97° (20 mm.), $n^{23}D$ 1.4798. An analytical sample was obtained using a gas phase preparative column.

Anal. Calcd. for $C_6H_{14}Cl_2Si_2$: C, 33.80; H, 6.57. Found: C, 34.04; H, 6.55.

3,3-Dimethyl-3-sila-1-thiacyclohexane.—A mixture of 29.7 g. (0.104 mole) of γ-bromopropyl(bromomethyl)dimethylsilane, 26.2 g. (0.109 mole) of sodium sulfide, 50 ml. of water, and 200 ml. of ethanol was heated under reflux for 16 hr. The reaction mixture then was distilled to dryness. The first 75 ml. of the distillate, b.p. 79–81°, was diluted with water, and the oil which separated was extracted with 50 ml. of petroleum ether (b.p. 30–60°). A saturated solution of mercuric chloride was added to the remainder of the distillate until solid material ceased to form (*ca.* 1 l. was required). The solid mercuric salt was collected, washed with ethanol and water, then steam distilled. About 500 ml. of distillate was collected. The organic material was extracted from the distillate with petroleum ether (b.p. 30–60°). Combination of the extracts followed by drying over magnesium sulfate and distillation yielded 10.9 g. (69%) of the silathiacyclohexane, b.p. 181°, $n^{26}D$ 1.4978.

Anal. Calcd. for $C_6H_{14}SSi$: C, 49.31; H, 9.59; S, 21.91; Si, 19.17. Found: C, 49.53; H, 9.65; S, 21.62; Si, 19.19.

In a run using the same conditions except that γ-chloropropyl-(chloromethyl)dimethylsilane was used in place of the dibromo derivative, there was obtained a 47% yield of the silathiacyclohexane.

3,3-Dimethyl-3-sila-1-butyl-1-azacyclohexane Hydrobromide.—To 30.0 g. (0.11 mole) of γ-bromopropyl(bromomethyl)dimethylsilane was added 16.1 g. (0.22 mole) of *n*-butylamine. A spontaneous exothermic reaction occurred almost immediately, the temperature rising to 170°. After the reaction had subsided, the mixture was heated to 260°. Upon cooling, the mixture solidified. The solid was dissolved in boiling water, clarified with activated carbon, and crystallized, yielding 15.1 g. (52%) of the crude product. Recrystallization from ethanol (95%) gave an analytical sample, m.p. 210–211°.

Anal. Calcd. for $C_{10}H_{24}BrNSi$: C, 45.11; H, 9.02; N, 5.26; Si, 10.54. Found: C, 45.37; H, 8.88; N, 5.11; Si, 10.61.

Some Reactions of Carbomethoxymercuric Salts

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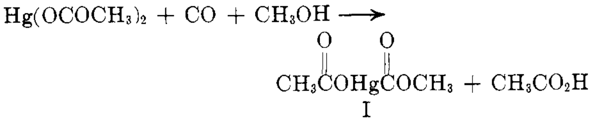
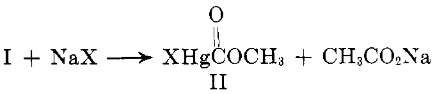
Carbomethoxymercuric acetate (I) yielded benzyl acetate and methyl benzyl ether when treated with excess benzyl bromide. Carbomethoxymercuric bromide (II, X = Br), mercurous bromide, and mercuric bromide were also isolated. On reaction with benzyl bromide, carbomethoxymercuric bromide yielded methyl benzyl ether, carbon monoxide, and mercuric bromide. Photochemical decomposition of carbomethoxymercuric iodide (II, X = I) in benzene solution afforded methyl benzoate and a compound tentatively identified as toluene. Reaction of a methanolic solution of I with ethylene yielded β-methoxyethylmercuric acetate.

A methanolic solution of mercuric acetate will react readily with carbon monoxide to form carbomethoxymercuric acetate (I) (eq. 1). Furthermore, the acetate group of I may be easily replaced by halide (eq. 2) to form compounds of structure II[2] (X = Cl, Br, or I). Although the structures for these compounds caused some controversy in the early literature,[2-5] a recent investigation by Halpern and Kettle[6] has proven structures I and II to be correct.



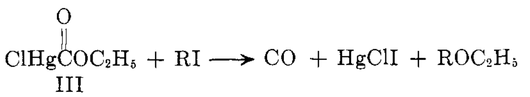
$$\mathrm{Hg(OCOCH_3)_2 + CO + CH_3OH \longrightarrow \underset{I}{CH_3\overset{\overset{O}{\|}}{C}OHg\overset{\overset{O}{\|}}{C}OCH_3} + CH_3CO_2H} \quad (1)$$



$$\mathrm{I + NaX \longrightarrow \underset{II}{XHg\overset{\overset{O}{\|}}{C}OCH_3} + CH_3CO_2Na} \quad (2)$$

Since the chemistry of this class of organomercury compounds appears to have been little studied, the reactions of I and II (X = Br) with benzyl bromide, the photochemical decomposition of II (X = I), and the reaction of I with ethylene were investigated. The results of these studies are herein reported.

Reaction with Benzyl Bromide.—In 1920, Manchot reported the reactions of methyl iodide with carbomethoxymercuric acetate (I) and *n*-propyl iodide with carbethoxymercuric chloride (III), although the structures he proposed for I and III were incorrect.[4] The former reaction was reported to yield carbon monoxide, mercuric iodide, and mercuric acetate, whereas carbon monoxide and mercury halides were isolated from the latter. Equation 3 was suggested to account for the latter reaction, although the ethyl ether apparently was not isolated.



$$\mathrm{\underset{III}{ClHg\overset{\overset{O}{\|}}{C}OC_2H_5} + RI \longrightarrow CO + HgClI + ROC_2H_5} \quad (3)$$

Since Manchot identified no organic compounds from his reactions, the reaction of compound I with an ex-

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[1] Northern Regional Research Laboratory, Peoria, Ill.

[2] W. Schoeller, W. Schrauth, and W. Essers, *Ber.*, **46**, 2864 (1913).

[3] W. Schoeller, *ibid.*, **53**, 2144 (1920).

[4] W. Manchot, *ibid.*, **53**, 984 (1920).

[5] W. Manchot, *ibid.*, **54**, 571 (1921).

[6] J. Halpern and S. F. A. Kettle, *Chem. Ind.* (London), 668 (1961).

cess of benzyl bromide was run in chloroform solution. Analysis of the volatile products by vapor phase chromatography (v.p.c.) showed two major components which were separated by preparative scale v.p.c. and identified as methyl benzyl ether and benzyl acetate by their infrared spectra. The yield of benzyl acetate, calculated from the vapor chromatogram, appeared quantitative, and the calculated yield of methyl benzyl ether was 20%, based on I. Mercurous bromide, mercuric bromide, and carbomethoxymercuric bromide were isolated from the solid portion of the reaction mixture in yields of 22.7, 20.5, and 36.7%, respectively, based on I.

When carbomethoxymercuric bromide (II, X = Br) was allowed to react with benzyl bromide, carbon monoxide and methyl benzyl ether were obtained along with a 92% crude yield of mercuric bromide. The yield of methyl benzyl ether, calculated from the vapor chromatogram, appeared quantitative.

The above data suggest that the first reaction to occur when compound I is treated with benzyl bromide is that represented by eq. 4. The excess benzyl bromide present in the system then reacts with II to form methyl benzyl ether, carbon monoxide, and mercuric bromide according to eq. 5, which is essentially the same as that proposed by Manchot.[4] The path by which mercurous bromide is formed is unknown.

$$\text{I} + C_6H_5CH_2Br \longrightarrow C_6H_5CH_2OAc + \text{II}\ (X = Br) \quad (4)$$

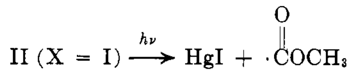
$$\text{II}\ (X = Br) + C_6H_5CH_2Br \longrightarrow C_6H_5CH_2OCH_3 + CO + HgBr_2 \quad (5)$$

The reaction of I with benzyl bromide to form benzyl acetate and II (X = Br) is analogous to the known reactions of mercuric acetate with acetyl chloride[7] and alkyl halides.[8] Equation 5 is analogous to the reaction path formulated by Dessy and Paulik[9] for the decomposition of II (X = Cl) with acids.

Photochemical Decomposition of Carbomethoxymercuric Iodide.—Corbett and Williams[10] have studied the photochemical decomposition of methylmercuric iodide in benzene solution and have isolated toluene from the reaction mixture. The suggested mechanism involved the cleavage of methyl mercuric iodide to mercurous iodide and methyl radical followed by reaction of methyl radical with the aromatic ring. On the basis of these results, it was of interest to see if the carbomethoxy radical (IV) could be generated from II (X = I) in the presence of ultraviolet light and similarly trapped by reaction with benzene.

Photolysis of a benzene solution of II (X = I) for 6 hr. at 6–10° gave a 56% yield of crude mercurous iodide. Concentration of the benzene solution afforded methyl benzoate and a compound with the retention time of toluene in yields of 21 and 12%, respectively, as calculated from the vapor chromatogram. Owing to the small scale of the reaction, the latter compound could not be isolated in an amount sufficient to afford positive identification by infrared. On the basis of the mechanism suggested below, the above yields were calculated assuming 0.5 mole of substituted benzene per mole of carbomethoxymercuric iodide. One unknown compound was also present in the mixture. The peak area on the vapor chromatogram corresponding to this material was slightly larger than that of toluene.

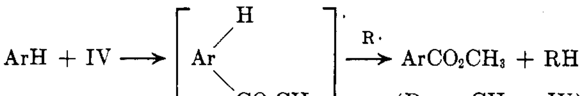
Methyl benzoate was probably formed by a route analogous to that proposed for the methylmercuric iodide decomposition[10] (eq. 6 and 8). The decomposition of radical IV to carbon dioxide and methyl (eq. 7) has been observed[11] and would account for the formation of toluene.



$$\text{II}\ (X = I) \xrightarrow{h\nu} HgI + \cdot\overset{O}{\overset{\|}{C}}OCH_3 \quad (6)$$

IV

$$\text{IV} \longrightarrow CO_2 + \cdot CH_3 \quad (7)$$

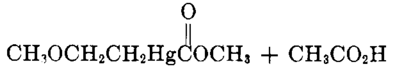


(R = ·CH₃ or IV) (8)

Reaction of Carbomethoxymercuric Acetate with Ethylene.—When a methanolic solution of carbomethoxymercuric acetate (I) was allowed to react with ethylene, a crystalline solid was obtained. Both melting point and elemental analysis suggested that this material was β-methoxyethylmercuric acetate (V). The proposed structure was confirmed by both mixture melting point and comparison of the infrared spectrum with that of a sample of V prepared by the known reaction of ethylene with mercuric acetate in methanol.[1,12]

Two explanations for the formation of V from I may be suggested. Perhaps the most obvious route is the reaction of I with ethylene with loss of the carbomethoxy group to yield V directly. Mercuric methoxyacetate ($CH_3CO_2HgOCH_3$) could possibly be formed from I through loss of carbon monoxide prior to reaction with ethylene.[13] Another possibility is shown in eq. 9. Here, reaction of ethylene with I

$$\text{I} + CH_2{=}CH_2 + CH_3OH \longrightarrow$$



$$CH_3OCH_2CH_2Hg\overset{O}{\overset{\|}{C}}OCH_3 + CH_3CO_2H$$

VI

$$\text{VI} + CH_3CO_2H \longrightarrow CH_3OH + CO + \underset{\text{V}}{CH_3OCH_2CH_2HgOCOCH_3} \quad (9)$$

in a manner analogous to that with mercuric acetate could occur to yield VI and acetic acid followed by reaction of acetic acid with VI to yield V and carbon monoxide. The data at hand, however, do not permit a choice between the various alternatives.

Experimental[14]

Preparation of Carbomethoxymercuric Acetate (I).—Carbon monoxide was passed through a methanolic solution of 100 g. (0.314 mole) of mercuric acetate according to the method of Schoeller.[2] The crude material was dissolved in warm chloroform (below 45°), filtered, and precipitated with petroleum ether to yield 88.8 g. (88.8%) of material, m.p. 103.5–107° dec. (lit.[2] m.p. 109° dec.). The n.m.r. spectrum (40 Mc.) of a sample

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[7] R. C. Paul, D. Singh, and S. S. Sandhu, *J. Chem. Soc.*, 319 (1959).

[8] M. M. Koton, T. M. Zorina, and E. G. Osberg, *J. Gen. Chem. USSR*, **17**, 59 (1947); *Chem. Abstr.*, **42**, 141*d* (1948).

[9] R. E. Dessy and F. E. Paulik, *J. Am. Chem. Soc.*, **85**, 1812 (1963).

[10] G. E. Corbett and G. H. Williams, *Proc. Chem. Soc.*, 240 (1961).

[11] J. C. J. Thynne and P. Gray, *ibid.*, 141 (1962), and references quoted therein.

[12] J. Chatt, *Chem. Rev.*, **48**, 7 (1951).

[13] Suggested by a referee.

[14] Melting points are uncorrected and were determined in capillary tubes unless otherwise specified.

further purified by recrystallization from chloroform–petroleum ether was in agreement with the published spectrum.[6] Sharp singlets were observed at τ 7.95 and 6.25, and the areas under these two signals were in the ratio of 1.0:0.8, respectively.

Preparation of Carbomethoxymercuric Bromide (II, X = Br).—To a solution of 20.04 g. (0.0629 mole) of carbomethoxymercuric acetate in 100 ml. of absolute methanol was added a solution of 8.39 g. (0.0815 mole) of sodium bromide in 50 ml. of water. The addition was carried out at room temperature. After addition was complete, the reaction mixture was stirred for a few minutes at room temperature, cooled, and filtered to yield 17.96 g. of crude carbomethoxymercuric bromide. This material was crystallized from diethyl ether to afford 11.97 g. (56.2% yield) of purified material, m.p. 125–128° dec. (lit.[2] m.p. 127–128° dec.).

Preparation of Carbomethoxymercuric Iodide (II, X = I).—To a cold stirred solution of 50 g. (0.157 mole) of carbomethoxymercuric acetate in 250 ml. of absolute methanol was added a solution of 32.3 g. (0.215 mole) of sodium iodide in 125 ml. of water. Addition was made over a 10–15-min. period, while the reaction mixture was cooled in ice. The gray crystalline solid was removed by filtration, dried under vacuum (wt. 36.5 g.), and recrystallized from ether to yield 23.43 g. of purified material (38.6% yield).

β-Methoxyethylmercuric acetate (V) was prepared by passing ethylene through a methanolic solution of 20.0 g. (0.0627 mole) of mercuric acetate according to the method of Schoeller.[2] The crude solid was extracted with hot pentane. On cooling, the pentane extracts deposited 14.4 g. (72%) of crystalline β-methoxyethylmercuric acetate. A small portion of this material was recrystallized a second time from pentane. The melting point (hot stage) of this purified material was 41.5–42.5° (lit.[2] m.p. 42°).

Reaction of Carbomethoxymercuric Acetate (I) with Benzyl Bromide.—A mixture of 10.12 g. (0.0318 mole) of carbomethoxymercuric acetate, 5 ml. (0.0421 mole) of benzyl bromide and 10 ml. of chloroform was heated under reflux (internal temperature of 78°) for a total of 22.7 hr. and cooled to room temperature. The reaction mass was then filtered; the gray precipitate was washed with n-pentane. The weight of dry solid was 9.71 g. The final filtrate, after decantation from 0.40 g. of gummy solid, was concentrated to a volume of about 50 ml. by distillation at atmospheric pressure. This material was then stirred vigorously for 1 hr. at room temperature with a solution of 7.30 g. (0.0430 mole) of silver nitrate in 50 ml. of water. The mixture was filtered; the precipitate was washed with bothpen tane and diethyl ether. The two-phase filtrate was separated and the aqueous phase was washed with ether. The combinedo rganic phase was washed with water, dried over magnesium sulfate, and concentrated by distillation at atmospheric pressure to a weight of 9.35 g. Vapor chromatographic analysis of this material showed two major components and two minor components in addition to solvent and some low-boiling minor components which came off the column quite close to solvent. The two major components were separated by preparative scale v.p.c. and were identified as methyl benzyl ether and benzyl acetate by comparison of their infrared spectra with those of authentic samples. Only traces of benzyl alcohol were detected, and no methyl phenylacetate was found. Approximate yields were calculated from the vapor chromatogram using the method of Eastman[15] (the molecular weights of the unknown minor components were estimated from their retention times). The calculated yield of benzyl acetate was quantitative (calculated yield figure was over 100%), and that of methyl benzyl ether was 20% (based on carbomethoxymercuric acetate charged). The two higher boiling minor components taken together amounted to about 10% by weight of the 9.35 g. of material originally analyzed. These components were not identified.

Fractional crystallization of the 9.71 g. of gray solid obtained earlier afforded 2.02 g. (22.7%) of crude mercurous bromide, 2.35 g. (20.5%) of mercuric bromide, and 3.94 g. (36.7%) of carbomethoxymercuric bromide. Mercurous bromide was isolated owing to its insolubility in diethyl ether. The latter two compounds were separated by fractional crystallization from chloroform. The per cent yields given are based on carbomethoxymercuric acetate charged. Mercuric bromide and the bromo compound II were identified by the melting points of purified samples and also by comparison of their infrared spectra with those of authentic samples. The observed melting point of mercuric bromide was 229–233.5° (sample appeared to start subliming about 200°), and that of bromo compound II was 124–128.5° dec. Mercurous bromide was identified by a positive ammonium hydroxide test for mercurous ion[16] and elemental analysis of a partially purified sample obtained by submitting the crude material to a single sublimation.

Anal. Calcd. for HgBr: Hg, 71.51; Br, 28.49. Found: Hg, 71.1; Br, 27.6.

Reaction of Carbomethoxymercuric Bromide (II, X = Br) with Benzyl Bromide.—A mixture of 10.10 g. (0.0298 mole) of carbomethoxymercuric bromide, 5 ml. (0.0421 mole) of benzyl bromide, and 10 ml. of chloroform was heated under reflux for 17.5 hr. and allowed to cool to room temperature. The volume of gas given off was 800 ml. (theoretical yield of carbon monoxide, assuming an ideal gas, was 733 ml.). In another experiment, this gas was collected and identified as carbon monoxide by its mass spectrum. The reaction mixture was filtered and the crude mercuric bromide was washed with n-pentane. The weight of this material was 9.88 g. (92% crude yield). The crude mercuric bromide was readily purified by sublimation and was identified by its melting point of 229–233.5° (sample appeared to start subliming around 200°) and also by comparison of its infrared spectrum with that of an authentic sample.

The filtrate obtained from the removal of crude mercuric bromide was diluted with n-pentane to a volume of about 200 ml., decanted from a very small amount of gummy solid, and concentrated to a volume of about 50 ml. by distillation at atmospheric pressure. This material was added to a solution of 7.24 g. (0.0426 mole) of silver nitrate in 50 ml. of water and the resulting mixture was stirred vigorously at room temperature for 1 hr. The mixture was then filtered from silver bromide. The two-phase filtrate was separated; the aqueous layer was extracted with ether. The combined organic phase was dried over magnesium sulfate and concentrated to a weight of 9.66 g. by distillation at atmospheric pressure. Vapor chromatographic analysis of this material showed two major components and two minor components in addition to the solvent peaks. The major components were separated by preparative scale v.p.c. and identified as methyl benzyl ether and benzyl alcohol by comparison of their infrared spectra with those of authentic samples. Methyl phenylacetate was not detected. Approximate yields were calculated from the vapor chromatogram using the method of Eastman.[15] The yield of methyl benzyl ether was quantitative, based on carbomethoxymercuric bromide charged (calculated yield figure was over 100%). A 23% recovery of benzyl bromide (as benzyl alcohol) was obtained. The two minor components taken together amounted to about 3% by weight of the 9.66 g. of material originally analyzed. These components were not identified.

The Photochemical Decomposition of Carbomethoxymercuric Iodide (II, X = I) in Benzene.—A clear solution of 3.00 g. (0.00777 mole) of carbomethoxymercuric iodide in 250 ml. of benzene was cooled to 6°. The stirred solution was then irradiated in a nitrogen atmosphere with a 70-watt Hanau PL 313 immersion-type ultraviolet source for 6 hr. During this time, the internal temperature remained between 6 and 10°, and a grayish yellow precipitate formed. Filtration of the reaction mixture afforded 1.43 g. of solid. Elemental analysis of this material indicated that it was crude mercurous iodide. The crude yield was 56.3%.

Anal. Calcd. for HgI: Hg, 61.25; I, 38.75. Found: Hg, 58.7; I, 37.8.

The clear filtrate was distilled at atmospheric pressure. After removal of excess benzene, the distillation residue was separated, by decantation into a liquid phase, plus 0.40 g. of orange solid (probably thermal decomposition products of unchanged II). After removal of more benzene from the liquid phase by atmospheric distillation, the higher boiling residue was subjected to a one-plate distillation at reduced pressure to yield 2.74 g. of distillate. Sublimation of the solid residue from the one plate distillation yielded 0.09 g. of a light yellow solid (m.p. 83–135°) whose infrared spectrum was similar to that of dimethyl terephthalate. Purification of this material, however, could not be achieved. Vapor chromatography of the above 2.74 g. of distillate indicated methyl benzoate, a compound with the reten-

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(15) R. H. Eastman, *J. Am. Chem. Soc.*, **79**, 4243 (1957).

(16) C. J. Engelder, T. H. Dunkelberger, and W. J. Schiller, "Semi-Micro Qualitative Analysis," John Wiley and Sons, Inc., New York, N. Y., 1936, p. 109.

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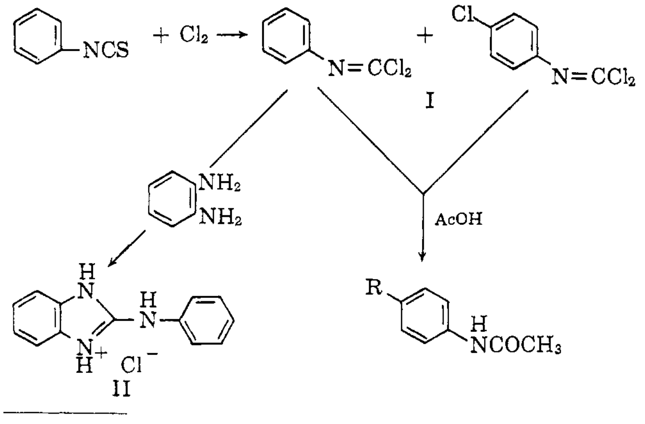
Phenyl- and *p*-chlorophenylcarbonimidoyl dichlorides, prepared by chlorination of phenyl isothiocyanate, react with *o*-phenylenediamines in a suitable solvent to form the corresponding 2-aryl aminobenzimidazoles. Moderate to almost quantitative yields are obtained, and the procedure affords a convenient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