Dimethylammonium N,N-Dimethylthiocarbamate (15).—Into a solution of 18 g (0.4 mol) of dimethylamine in 200 ml of absolute ether at 0° was bubbled carbonyl sulfide at such rate that the temperature did not rise above 5°. The gas was added until the reaction was no longer exothermic and then the slurry was stirred at 0° for 1 hr. The product, 27.8 g (46%), was collected by filtration and washed with ether. No further purification was attempted.

Lead N,N-Dimethylthiocarbamate (16).—To a stirred solution of 11.7 g (0.08 mol) of dimethylammonium salt, **15**, in 50 ml of water was added a solution of 25.5 g (0.08 mol) of lead acetate in 100 ml of water. Precipitation was immediate; however, the mixture was stirred for an additional 1 hr to ensure completeness of reaction. The product was collected by filtration and washed twice with acetone and finally twice with ether. The crystals were dried for 48 hr under vacuum affording 10.0 g (31%) of lead salt.

Dimethylcarbamoyl Thiocyanate (17) and Dimethylcarbamoyl Disulfide (18).—A slurry of 10.0 g (0.025 mol) of lead salt **16** and 6.0 g (0.056 mol) of dry cyanogen bromide in 50 ml of anhydrous benzene was stirred for 5 days at room temperature. The precipitate was removed by filtration and the filtrate was washed twice with 100-ml portions of water. The solution was dried and the solvent evaporated under vacuum keeping the temperature below 25°, giving 7.9 g of a mixture of **17** and **18**. The product mixture was an orange oil which resisted all attempts at separation of its components: infrared spectrum (film), 2160, 1710, 1675, 1360, 1245, 1090, and 680 cm^{-1}. It was stored at −20° for further use since a sample was discovered to isomerize substantially on standing, neat, for 2 days at room temperature.

Isomerizations of 17 to Dimethylcarbamoyl Isothiocyanate (9).—Distillation of 5.0 g of the crude mixture of **17** and **18** gave 1.2 g of the isomerized product, **9**, bp 40–42° (0.1 mm). No indication of the thiocyanate **17** could be discovered in the distillate or tarry pot residue.

A solution of 1.0 g of the thiocyanate–disulfide mixture in 10 ml of acetone was heated at reflux and the course of the isomerization followed by infrared. The characteristic -NCS absorption of **9** at 1990 cm^{-1} was observable after 5 min. The isomerization was assumed to be complete after 45 min with the complete disappearance of the -SCN absorption at 2160 cm^{-1}. When 0.5 g of potassium thiocyanate was additionally dissolved in the acetone solution the time for complete isomerization was again approximately 45 min. The dissolved salt gave no observable accelerating effect to the isomerization.

Registry No.—**6**, 4917-81-1; **7**, 3553-71-7; **9**, 16011-79-3; **10**, 14004-91-2; **11**, 16011-81-7; **13**, 16011-82-8; **17**, 16011-83-9; **18**, 16011-88-4; 1,1-dimethyl-4-thiobiuret, 16011-84-0; diethylcarbamoyl isothiocyanate, 16011-85-1; 1,1-diethyl-4-thiobiuret, 16011-86-2; 1,1-dimethyldithiobiuret, 14812-36-3.

Reaction of Chloral with Hydrazine

C. N. YIANNIOS, A. C. HAZY, AND J. V. KARABINOS

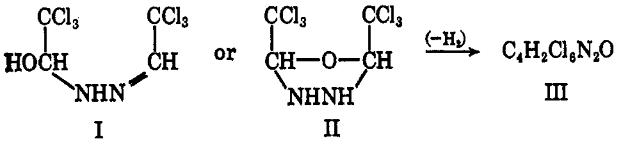
Olin Research Center, New Haven, Connecticut 06504

Received October 3, 1967

The reaction of chloral with hydrazine has been reinvestigated. Two products, trichloroethylidene trichloroacetic acid hydrazide and dichloroethylidene trichloroacetic acid hydrazide, were isolated and their structures were elucidated by spectral methods.

G. Knöpfer[1] reported the isolation of an "anhydrochloral" hydrazine derivative prepared by heating either hydrazine sulfate or hydrochloride in an excess of chloral hydrate.

Elemental analysis led to the assignment of the empirical formula $C_4H_2Cl_6N_2O$ to this product (III). When the compound was decomposed with aqueous potassium hydroxide, Knöpfer failed to isolate any chloroform. He proposed that this derivative resulted from dehydrogenation of either structure I or II, but favored II as the precursor since its isomer (I) should have been decomposed by alkali to give chloroform.



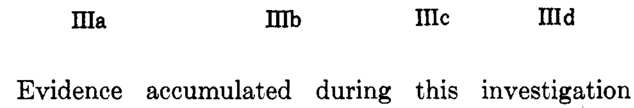
I II III

Compound III was subsequently prepared by Knöpfer[2] from hydrazine hydrate and chloral hydrate in glacial acetic acid. Upon investigation of the analogous reaction of hydrazine hydrate and bromal hydrate, Knöpfer discovered that, in the absence of a solvent, a product having the empirical formula $C_4H_2Br_6N_2O$ was produced. This same reaction in glacial acetic acid, however, gave a pentabromo derivative of formula $C_4H_3Br_5N_2O$. No mention was made of any analogous pentachloro derivative.

The present investigation sheds considerable light on the reaction of chloral with hydrazine. In addition to elucidating the structure of compound III, several other products, including a pentachloro derivative, have been obtained and identified.

Results and Discussion

Compound III was prepared from excess chloral hydrate and monohydrazine sulfate or chloral hydrazine [$Cl_3CCH(OH)NHNH_2$]. Knöpfer's[2] method (in glacial acetic acid) also gave III. The infrared spectra of samples obtained by either method were identical; the elemental analyses compared favorably with those reported by Knöpfer.[1] Several likely structures fitting the formula $C_4H_2Cl_6N_2O$ (IIIa–d) may be considered.



IIIa IIIb IIIc IIId

Evidence accumulated during this investigation points overwhelmingly to the acyclic structure IIId. The infrared spectrum (KBr pellet) showed absorption at 3.1 (m, secondary amide N—H stretch), 3.3 (w, H—C= vibration) and 5.83 μ (s, C=O stretch). Although the carbonyl absorption appeared at a lower wavelength than would be expected for an aliphatic secondary amide, this position coincides with that

---

[1] G. Knöpfer, *Monatsh. Chem.*, **34**, 769 (1913).

[2] G. Knöpfer, *ibid.*, **37**, 357 (1916).

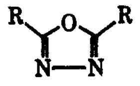
found by other workers[3] for polyhalogenated secondary amides. N-Alkyltrifluoromethyl amides of the type CF_3CONHR, for example, absorb in the range 5.8–5.9 μ in the solid state. Other bands found in the infrared spectrum of compound III were at 6.15 (w, C=N), 6.53 (m, amide II band), 11.63 and 12.14 μ (s, C—Cl stretch of a trichloromethyl group). The evidence that the carbon–chlorine stretch comes from a trichloromethyl group rather than a dichloromethyl group evolved from the observation that compounds which had been shown by other means to contain a dichloromethyl moiety invariably exhibited a strong absorption band near 12.8 μ. The 12.8-μ region of the infrared spectrum of compound III, however, showed no such absorption.

Further evidence for the proposed structure of III was obtained from the nmr spectrum (dioxane deuteriochloroform solution with tetramethylsilane as an internal standard) which consisted of two lines with no fine structure. The low-field proton (N—H) was exchanged with deuterium and the high-field resonance appeared at 528 cps (=C—H).

Structures IIIa and IIIb are inconsistent with the carbonyl absorption in the infrared. Additionally, these cyclic structures would not have produced the nmr spectrum found, since IIIa would not have one proton capable of deuterium exchange while the protons of IIIb would have produced splitting of the respective resonances. Although structure IIIc does have a carbonyl, its nmr spectrum should have only one singlet and no deuterium exchange should occur.

The cyclic structures were further excluded by comparison of the infrared spectrum with those of 1,3,4-oxadiazoles which were independently synthesized.

Compound IV, 2,5-bis(trichloromethyl)-1,3,4-oxadiazole,[4] was prepared by the action of phosphorus pentachloride on N,N′-bis(trichloroacetyl)hydrazine.



IV, R = CCl_3
V, R = $CHCl_2$

$Cl_2CH\overset{O}{\overset{\|}{C}}NHNH\overset{O}{\overset{\|}{C}}CHCl_2$

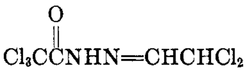
VI

This oxadiazole (IV) exhibited characteristic C–O–C absorption in the infrared at 9.9,[5] and trichloromethyl absorption at 11.6 with a broad band near 12.5 μ. Carbonyl absorption at 5.8–5.9 μ was absent. Catalytic hydrogenation of IV in ether resulted in the absorption of four atoms of hydrogen accompanied by loss of hydrogen chloride to form 2,5-bis(dichloromethyl)-1,3,4-oxadiazole (V). The infrared of V had no carbonyl absorption, a band at 10.1 (cyclic C—O—C), no band at 11.6, and strong absorption at 12.8 μ (dichloromethyl).

When compound IV was hydrogenated in glacial acetic acid in the presence of 70% aqueous perchloric acid,[6] once again four atoms of hydrogen were absorbed and hydrogen chloride was evolved. In this instance, however, ring cleavage occurred and N,N′-bis(dichloroacetyl)hydrazine (VI) was isolated. This product proved to be identical with that obtained from chloral hydrazine and dichloroacetyl chloride in glacial acetic acid. The infrared of VI had no absorption in the 9.9–10.1 region, but did show carbonyl absorption at 6.15 and dichloromethyl absorption at 12.8 μ. No bands were present in the 11.5–12.2-μ region indicating that the trichloromethyl was absent.

One of the most significant factors contributing to Knöpfer's assignment of a cyclic structure to III was the observation that base-catalyzed decomposition of the compound failed to produce any isolable chloroform. Since an acyclic structure such as IIId would, indeed, be expected to produce chloroform upon base decomposition, this point was reinvestigated by glpc and mass spectrometric methods. The results of our investigation have demonstrated incontrovertibly that chloroform was produced as one of the major products by the action of aqueous potassium hydroxide on compound III. The chloroform was identified by comparison of the retention time with that of an authentic sample when subjected to glpc under identical conditions, as well as by mass spectrometry. Among the other identifiable decomposition products were nitrogen, carbon dioxide (if an excess of potassium hydroxide were not present), and a minor amount of 1,1-dichloroethylene. This identification of chloroform as one of the major decomposition products should serve adequately to remove any last traces of ambiguity concerning the structure of compound III, trichloroethylidene trichloroacetic acid hydrazide.

The reaction of chloral with hydrazine in glacial acetic acid under anhydrous conditions produced a pentachloro derivative ($C_4H_3Cl_5N_2O$) (VII).[7] As for compound III, several analogous structures (both cyclic and acyclic) may be written for compound VII. Spectral evidence (both nmr and infrared) established the structure as that of dichloroethylidene trichloroacetic acid hydrazide (VII).



$Cl_3C\overset{O}{\overset{\|}{C}}NHN{=}CHCHCl_2$

VII

The infrared spectrum of VII had bands exactly as described for the spectrum of III with the addition of a strong absorption at 12.8 μ attributed to the presence of a dichloromethyl group. Again, no absorption occurred at 9.9 μ, indicating the absence of a cyclic C—O—C bond. The presence of a carbonyl absorption at 5.83 μ together with the previous observation eliminated any possible cyclic (1,3,4-oxadiazole) structures.

The nmr spectrum of VII had an AB-type spectrum with the A doublet centered at 388 cps and the B doublet centered at 476 cps ($J = 8$ cps) as well as a broad peak at 689 cps; the integrated areas of the peaks showed a 1:1:1 ratio. The low field resonance was due to the amide proton as demonstrated by deuterium exchange. Thus, the nmr spectrum served to eliminate structure VIII as a possibility for this pentachloro compound, since compound VIII would not produce an AB pattern. In view of these observations, the penta-

---

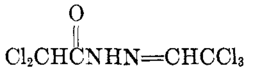
[3] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1964, p 212.

[4] R. Stolle and F. Helworth, *J. Prakt. Chem.*, **88**, 315 (1913).

[5] M. Milone and E. Borello, *Gazz. Chim. Ital.*, **81**, 368 (1951).

[6] R. H. Baker, K. H. Cornell, and M. J. Cron, *J. Amer. Chem. Soc.*, **70**, 1490 (1948). This procedure was found to cause ether cleavage.

[7] C. N. Yiannios and J. V. Karabinos, U. S. Patent 3,306,935 (Feb 1967).



$$Cl_2CHC(=O)NHN{=}CHCCl_3$$

VIII

bromo derivative described by Knöpfer[2] may well have been dibromoethylidene tribromoacetic acid hydrazide.

Experimental Section[8]

N-(1-Hydroxy-2,2,2-trichloroethyl)hydrazine (chloral hydrazine) may be prepared by the method of Knöpfer,[9] but the following procedure was found to be more convenient. Under a nitrogen atmosphere a solution of 147 g (1.0 mol) of anhydrous chloral in 500 ml of ether was treated dropwise with 32 g (1.0 mol) of anhydrous hydrazine while a temperature of −5 to 5° was maintained. When addition was complete, the reactants were digested for 1.5 hr at 20°. The product was then collected by suction filtration, washed with ether, and air dried to give a quantitative yield of white powder, mp 100°, dec pt 85° (lit.[9] mp 100°, dec pt 85°). The product had a tendency to decompose when *in vacuo* or at temperatures above 25°, but this difficulty was circumvented by storage of samples under ether with refrigeration.

Trichloroethylidene Trichloroacetic Acid Hydrazide (III).—To 165 g (1.0 mol) of chloral hydrate in 400 ml of glacial acetic acid was added 12.5 g (0.25 mol) of hydrazine hydrate in 200 ml of glacial acetic acid. The solution was heated to 65° and maintained at this temperature for 3 hr then cooled and poured slowly into 2.5 l. of vigorously stirred ice water. The resulting yellow solid was immediately collected by suction filtration, washed with water, and air dried to give 12.3 g (16% yield) of III. Repeated recrystallizations from benzene gave a white solid, mp 185–187°. Further purification was accomplished by passing a benzene solution of the compound through silica gel, eluting with benzene, and evaporating the solvent under a stream of nitrogen. The resulting crystals had mp 188–190° (Knöpfer[1] reported mp 187° for his "anhydrochloral hydrazine derivative").

Anal. Calcd for $C_4H_2Cl_6N_2O$: C, 15.66; H, 0.66; Cl, 69.34; N, 9.13. Found: C, 16.20; H, 0.70; Cl, 68.40; N, 9.22.[10]

The same product was also obtained when chloral hydrazine replaced the hydrazine hydrate and also when monohydrazine sulfate was melted with chloral hydrate.

2,5-Bis(trichloromethyl)-1,3,4-oxadiazole (IV) was prepared from N,N′-bis(trichloroacetyl)hydrazine and phosphorus pentachloride according to the procedure of Stolle and Helworth.[4] The product was obtained in 50% yield and had mp 47–48° and bp 119° (8 mm) (lit.[4] mp 48°, bp 121° (9 mm)).

2,5-Bis(dichloromethyl)-1,3,4-oxadiazole (V).—A heavy-walled flask equipped with a magnetic stirrer and gas burette was charged with 3 g of IV, 25 mg of palladium on carbon, and 50 ml of ether. The system was purged with nitrogen and hydrogen was then introduced at room temperature while the solution was stirred. After 455 ml of hydrogen was absorbed, the catalyst was removed by filtration, and the solvent was evaporated under nitrogen. The white powder residue was dried *in vacuo* and had mp 89–91°.

Anal. Calcd for $C_4H_2Cl_4N_2O$: C, 20.36; H, 0.85; Cl, 60.1; N, 11.88. Found: C, 20.75; H, 0.80; Cl, 59.8; N, 12.07.

1,2-Bis(dichloroacetyl) hydrazine (VI) was prepared by hydrogenation of 3 g of IV in 50 ml of glacial acetic acid with 25 mg of palladium on carbon and 1.4 ml of 70% aqueous perchloric acid.[6] During the hydrogenation, a white precipitate formed. After 660 ml of hydrogen had been absorbed, the reaction mixture was filtered and the solid was washed with water and dried. After treatment with ether and filtration to remove the catalyst, evaporation of the solvent gave a residue which was dissolved in ethanol and reprecipitated by the addition of a few drops of water to the cold solution. The product had mp 241–243°.

Anal. Calcd for $C_4H_4Cl_4N_2O_2$: C, 18.92; H, 1.59; Cl, 55.8; N, 11.00. Found: C, 19.15; H, 1.71; Cl, 55.5; N, 11.20.

In an alternative procedure for the preparation of VI, 26.6 g (0.18 mol) of dichloroacetyl chloride was added dropwise at 0° to 32.4 g (0.18 mol) of chloral hydrazine in 100 ml of glacial acetic acid. The mixture was stirred at room temperature for 4 hr, then poured into ice water. The resulting solid was collected, dissolved in ethanol, and reprecipitated with a few drops of water to give VI, mp 241–242°. A mixture of the samples prepared by the two methods had mp 241–243°.

Dichloroethylidene trichloroacetic acid hydrazide (VII) was prepared as described by Yiannios and Karbinos.[7] A chilled (−5°) well-stirred solution of 147 g (1.0 mol) of anhydrous chloral in 900 ml of ether was blanketed with a nitrogen atmosphere and treated, dropwise, with 32 g (1.0 mol) of anhydrous hydrazine. The hydrazine addition rate was controlled to maintain a temperature range of −3 to −5°. The chloral–hydrazine adduct precipitated as a white powder immediately. To this mixture was added 442 g (3.0 mol) of anhydrous chloral in 800 ml of glacial acetic acid and the mixture was stirred at 5° for 15 min. Most of the ether was then removed *in vacuo*. The temperature was allowed to rise gradually to 50° at atmospheric pressure while the last traces of ether were removed under nitrogen. (Several color changes occurred during the rise in temperature.) The resulting clear amber solution was stirred at 50° for 5 hr, then allowed to stand overnight at 0°. The white crystals which formed were collected by filtration and washed with water. The filtrate was added slowly, with agitation, to 3 l. of ice water to precipitate more product. The combined solids were recrystallized repeatedly from xylene to give 44 g (16% yield), mp 159–160°. An analytical sample was prepared by passing a xylene solution through silica gel and allowing the product to crystallize from the eluate to give mp 160–161°.

Anal. Calcd for $C_4H_3Cl_5N_2O$: C, 17.64; H, 1.11; Cl, 65.09; N, 10.29. Found: C, 17.90; H, 1.10; Cl, 64.50; N, 10.45.

Decomposition of III.—Samples (40–60 mg) of III were sealed in a 50-ml glass bulb and the air was removed. Aqueous potassium hydroxide was introduced by syringe through a rubber septum in the wall of the bulb. A reaction occurred which continuously produced gas. The bulb was warmed to 40° and after reaction subsided the liquid was dark brown in color. The vapors above the solution were analyzed by mass spectrometry and the samples were also examined by glpc using 30% polyethylene glycol 400 on Chromosorb W, at 83°, with a flow rate of 75 cc of helium/min. The analyses showed the presence of chloroform (26.5 mol %), 1,1-dichloroethylene (10.1 mol %), and nitrogen (53 mol %).

Registry No.—Chloral hydrate, 302-17-0; hydrazine, 302-01-2; IIId, 16054-39-0; V, 16054-40-3; VI, 16054-41-4; VII, 14918-94-6; N-(1-hydroxy-2,2,2-trichloroethyl)hydrazine, 16054-33-4.

---

[8] All melting and boiling points are uncorrected. Melting points were determined on a Mel-Temp capillary melting point apparatus. Infrared spectra were obtained on a Perkin-Elmer Model 137 spectrophotometer; the nmr spectra were run on a Varian A-60 spectrometer; mass spectra were obtained on a Consolidated Electrodynamics Corporation Model 21-103C spectrometer; glpc data were obtained on a Perkin-Elmer Model 154 fractometer.

[9] G. Knöpfer, *Monatsh. Chem.*, **32**, 767 (1911).

[10] As in Knöpfer's work, difficulty was encountered in efforts to obtain analytically pure material. In a series of samples Knöpfer reported results in the following ranges: C, 15.59–16.05; H, 0.80–0.98; Cl, 68.32–68.85; N, 9.30–9.74.