2800 ml. of ether. Stirring was continued for 4 hr. after the addition had been completed. The excess hydride was destroyed by the dropwise addition of water. The ether solution was acidified with hydrogen chloride and the solvent was removed *in vacuo*. The residue was dissolved in 175 ml. of 2% hydrochloric acid, filtered, neutralized with ammonium hydroxide solution to pH 8.5, and filtered. The solution on acidification with perchloric acid gave, after recrystallization from methanol, 0.7 g. (33%) of a crystalline solid, m.p. 214–216°. Further recrystallization gave a sample, m.p. 219.5–220.5 (lit.[10] m.p. 223–227°).

1,2,3,4,6,7,12,12b-Octahydroindolo[2,3-*a*]quinolizine.—To a solution of 366 mg. of 1,2,3,4,6,7-hexahydro-12H-indolo[2,3-*a*]-quinolizinium perchlorate in 120 ml. of ethanol was added 137 mg. of platinum oxide and the mixture was hydrogenated unti uptake ceased. The catalyst was removed by filtration and the alcohol was removed *in vacuo*. The residue was treated with a mixture of 10% sodium hydroxide solution and ether. The ether layer was washed with water and dried over sodium sulfate. Removal of the solvent gave 198 mg. of a crystalline solid, m.p. 149.5–151°. Recrystallization from petroleum ether gave a sample, m.p. 151–152°.

This sample was shown to be identical with an authentic sample[11] by the methods of mixture melting point and infrared analysis.

N-1,1-Trichlorocyanoacetimidoyl Chloride

WAYNE R. CARPENTER AND PATRICIA ARMSTRONG

Chemistry Division, Research Department, U. S. Naval Ordnance Test Station, China Lake, California

Received January 6, 1964

Ott and Löpmann[1] isolated a by-product, $C_3N_2Cl_4$ (II), in the preparation of dichloromalononitrile (I) by the aqueous chlorination of malononitrile. The name tetrachloromalononitrile was given to II but a structure was not proposed. A third compound, dichlorocyanoacetamide (III), was also isolated.[2]

$$CH_2(CN)_2 \xrightarrow[H_2O]{Cl_2} \underset{I}{CCl_2(CN)_2} + \underset{II}{C_3N_2Cl_4} + \underset{III}{NCCl_2CONH_2}$$

The procedure of Ott and Löpmann[1] called for the addition of 2 moles of chlorine to 1 of malononitrile in an ice-cold aqueous solution; no yields were reported. By using a 3:1 mole ratio of chlorine to malononitrile under similar conditions we isolated 74% of I, 8.5% of II, and none of III. Ammonium chloride (13%) was also isolated but no dichloroacetamide, as noted by Rosenblatt and Broome in chlorination of malononitrile with aqueous sodium hypochlorite.[3] No attempt was made to optimize the yield of III, but in one variation of the reaction which failed to produce any of I or II (see Experimental) the yield of III was 8.5%.

On the basis of the following evidence, it is proposed that tetrachloromalononitrile (II) is N-1,1-trichlorocyanoacetimidoyl chloride (IIa). Infrared spectra of I and II both show cyano group absorption at about 4.45 μ; whereas the spectrum of I has no peak in the C=N bond region, the spectrum of II has a strong band at 6.3 μ (see Table I). Reaction of both I and II with excess sodium iodide in acetone caused the formation of free iodine and sodium chloride in the molar amounts listed in Table II.

TABLE I

SIGNIFICANT INFRARED ABSORPTION MAXIMA[a]

Compd.	Wave length, μ
I	4.45 (m), 9.22 (s), 10.00 (m), 10.50 (s), 10.76 (m), 12.65 (s) broad,
II	4.48 (w), 5.79 (w), 6.32 (s), 6.49 (w), 8.72 (s), 9.02 (w), 9.91 (s), 10.25 (w), 10.40 (w), 11.62 (s), 12.60 (s) broad, 14.35 (s)

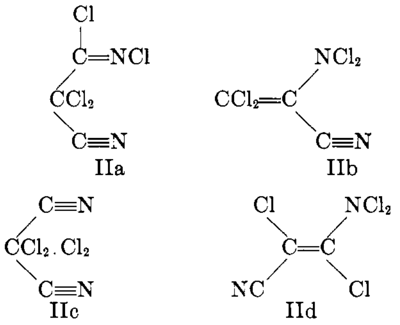
[a] Intensity: s, strong: m, medium; w, weak.

TABLE II

PRODUCT STOICHIOMETRY OF SODIUM IODIDE REACTION

Compound	Moles of I_2/mole of compound	Moles of NaCl/mole of compound
I	1.10	2.16
II	2.15	4.03

The presence of a nitrile group and two positive chlorines reduces the number of possible structures for a monomeric form to four, where IIb and IId represent rearrangements and IIc represents a molecular complex.



Structure IIb can be eliminated because I and II are interconvertible. Chlorine reacted with I to form II, which was converted back to I by treatment with zinc. It is very unlikely that the rearrangements required in going from I to IIb would be so readily reversible. Structure IIc is also improbable in view of the good thermal stability of II. Furthermore, IIc would not be expected to absorb at 6.3 μ, whereas the C=N bond of IIa would. IId is improbable because the rearrangement involved in its formation from I would require the removal of a chlorine atom from a carbon atom in exchange for placing a chlorine atom on a nitrogen atom. Thermodynamically, this exchange would be unfavorable because the N–Cl bond has a much lower bond energy than that of C–Cl. Molecular weight determinations eliminated the possibility that II could be anything but monomeric.

$$I \underset{Zn}{\overset{Cl_2}{\rightleftarrows}} II$$

The addition of halogen to the triple bond of a nitrile group is unusual, but not without precedent. One of the products of the action of mercuric fluoride on acetonitrile is N-fluoroacetimidoyl fluoride.[4]

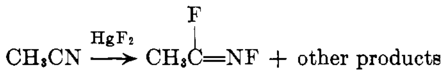
---

(1) E. Ott and B. Löpmann, *Ber.*, **55B**, 1255 (1922).

(2) It is interesting that the infrared spectrum of III does not show a nitrile group absorption. However, this result is consistent with the fact that chlorodicyanoacetamide also does not have a nitrile group absorption [S. Trofimenko, E. L. Little, Jr., and H. F. Mower, *J. Org. Chem.*, **27**, 433 (1962)]. The infrared spectrum of III also has a doublet at 2.93 and 3.15 and a strong band at 5.85 μ. These figures are consistent with expected values for NH and C=O stretching frequencies in an electronegatively substituted primary amide.

(3) D. H. Rosenblatt and G. H. Broome, *ibid.*, **26**, 2116 (1961).

(4) F. Nerdel, *Naturwissenschafen*, **39**, 209 (1952).



$$CH_3CN \xrightarrow{HgF_2} CH_3\overset{F}{C}=NF + \text{other products}$$

Experimental

Dichloromalononitrile and N-1,1-Trichlorocyanoacetimidoyl Chloride.—A solution of 33.0 g. of malononitrile (0.5 mole) and 500 ml. of water was added to a 1-l. flask equipped with stirrer, thermometer, Dry Ice–acetone reflux condenser, inlet tube, and external ice–water cooling bath. Chlorine gas (118.3 g., 1.67 moles) was introduced slowly with stirring over a period of 4 hr., taking care to keep the temperature at or below 5°. The cooling bath was removed and the stirring was continued another 3 hr., during which time the upper portion of the flask was heated gently with warm air in order to decompose the solid chlorine hydrate. The reaction mixture was then separated. The upper aqueous phase was evaporated to 3.2 g. of white solid, identified as ammonium chloride by infrared spectrum. It gave positive tests for ammonia and chloride ion. The lower, organic phase was fractionated. At atmospheric pressure, 46.9 g. of dichloromalononitrile was collected at 86–93°, with an additional 3.0 g. at 41° when the pressure was reduced to 105 mm. The total yield amounted to 74.0% based on malononitrile. Continuation of the distillation at 45 mm. yielded 8.9 g. (8.5% of theory) of N-1,1-trichlorocyanoacetimidoyl chloride boiling at 93–97°. Redistillation at 45 mm. furnished pure material at 97°.

Anal. Calcd. for $C_3Cl_4N_2$: C, 17.50; H, 0.00; Cl, 68.89; N, 13.61; mol. wt., 205.9. Found: C, 17.23; H, 0.05; Cl, 68.90; N, 13.95; mol. wt., 226.9 (ebulioscopic in carbon tetrachloride).

Both dichloromalononitrile and N-1,1-trichlorocyanoacetimidoyl chloride are lachrymatory and extremely irritating.

Dichlorocyanoacetamide.—The operations in the above procedure were carried out with the following changes: 150 ml. of water and 150 ml. of chloroform were used. After reaction, the aqueous phase yielded 8.2 g. of ammonium chloride upon evaporation. The organic phase yielded 5.7 g. of white solid (III) when diluted with 200 ml. of hexane. Evaporation of the filtrate at room temperature yielded only a small amount of oily solid. After recrystallization of III from ethanol–water, it melted at 90–93°.

Anal. Calcd. for $C_3H_2Cl_2N_2O$: C, 23.55; H, 1.32; Cl, 46.36; N, 18.31. Found: C, 23.90; H, 1.58; Cl, 46.39; N, 18.36.

Reaction with Sodium Iodide.—A weighed sample (0.2–0.3 g.) of dichloromalononitrile or N-1,1-trichlorocyanoacetimidoyl chloride was added to 10 ml. of a 20% solution of sodium iodide in acetone. After about 10 min. the mixture was filtered through a weighed fine-fritted funnel. The filter cake was washed thoroughly with acetone until all of the iodine was removed. The funnel was then dried at 110° and reweighed to determine sodium chloride. The acetone filtrate was diluted with water and titrated with 0.1 N sodium thiosulfate to a starch end point to determine iodine.

Conversion of Dichloromalononitrile to N-1,1-Trichlorocyanoacetimidoyl Chloride.—Five grams of dichloromalononitrile was treated with 2.6 g. of chlorine at room temperature in an apparatus which allowed reflux of chlorine. After the reaction had proceeded for about 2 hr., the mixture was allowed to stand overnight to permit evaporation of unused chlorine. Based on the infrared spectrum of the product mixture, the reaction had converted 40% of I into II. No other constituents were evident from the spectrum.

Conversion of N-1,1-Trichlorocyanoacetimidoyl Chloride to Dichloromalononitrile.—A solution of 2.0 g. of pure N-1,1-trichlorocyanoacetimidoyl chloride (II) in 10 ml. of dimethylformamide was added dropwise to a stirred mixture of 2.0 g. of zinc powder in 10 ml. of sulfolane, which was used as a moderator for the reaction. The reaction flask was kept at 50° with a water bath, and a reduced pressure of 20 mm. was maintained throughout the reaction. The effluent from the flask was fed through a cold trap at −78°. The contents of the trap (0.31 g.) consisted of nearly pure dichloromalononitrile, as shown by infrared spectral comparison.

Acknowledgment.—The authors express their gratitude to Dr. R. A. Henry for his helpful suggestions and encouragement.

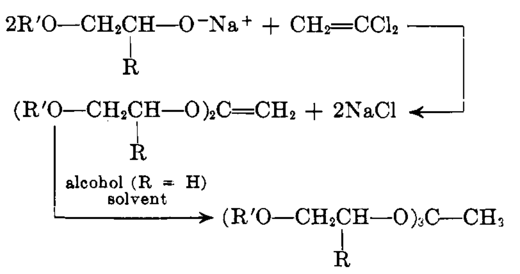
Ketene Acetals. I. A New Synthesis of Ketene Acetals and Ortho Esters[1]

WILLIAM C. KURYLA AND DONALD G. LEIS

Union Carbide Corporation, Chemicals Division, Research and Development Department, South Charleston, West Virginia 25303

Received March 23, 1964

We have found that ketene acetal and ortho ester derivatives of β-alkoxy alcohols may be synthesized by a simple one-step process which involves the slow addition of vinylidene chloride to a sodium β-alkoxy alcoholate, dissolved or suspended in a solvent. This process results in an exothermic reaction which yields either the ketene acetal or ortho ester derivative of the alcohol, with the concomitant precipitation of solid sodium chloride. The resultant product depends on the solvent conditions used, and the steric nature of the β-alkoxy alcohol.



$$2R'O-CH_2\underset{R}{CH}-O^-Na^+ + CH_2=CCl_2 \longrightarrow (R'O-CH_2\underset{R}{CH}-O)_2C=CH_2 + 2NaCl$$

$$(R'O-CH_2\underset{R}{CH}-O)_2C=CH_2 \xrightarrow[\text{solvent}]{\text{alcohol }(R = H)} (R'O-CH_2\underset{R}{CH}-O)_3C-CH_3$$

When tetrahydrofurfuryl alcohol was used in this synthesis as both the reactant and solvent, the ortho acetate (IX) was obtained in a 53.4% yield. However, when diethylene glycol dimethyl ether was used as the solvent, the ketene acetal (II) was obtained in a 48.3% yield.

Using 2-ethoxyethanol (Cellosolve solvent), or diethylene glycol monomethyl ether (Methyl Carbitol solvent), as both the reactant and solvent, only the corresponding ortho acetates (VII and VIII) were isolated in yields of 56.6 and 40.5%, respectively. However, when 1-methoxypropanol-2 (Ucar solvent LM) was used as both the reactant and solvent, the ketene acetal derivative (I) was obtained in a 46.8% yield, thus demonstrating the steric effect of the α-methyl group $(R = CH_3)$.

Attempts to prepare ketene acetals or ortho esters from simple alcohols, such as methanol, ethanol, 1-butanol, and 2-butanol in this process, resulted in failure as neither the exotherm nor salt precipitation was observed.

The methyl ketene acetal derivative (III) of 1-methoxypropanol-2 was obtained in an 8.3% yield when 1,1-dichloropropene-1 was used in the place of vinylidene chloride. Similarly, using 1,1,2-trichloroethylene and tetrahydrofurfuryl alcohol, the chloroortho ester (X) was obtained in a 13.6% yield. A tabulation of ketene acetals and ortho esters made by this synthesis, together with their analyses and physical properties, is found in Table I.

The assignment of structures was based on the elemental analyses, ebullioscopic molecular weight deter-

---

[1] Presented in part at the 146th National Meeting of the American Chemical Society, Denver, Colo., Jan., 1964.