water, dilute sodium carbonate solution and saturated sodium chloride solution before being filtered through Drierite and then concentrated to yield 3.79 g. (97%) of light yellow solid, m.p. 69–74°. After the first recrystallization from methanol the yield was 2.79 g. (71%) of yellow needles, m.p. 71.5–74°. The infrared spectrum indicated that both the cyano and nitro groups were present. The analytical sample, m.p. 72–75°, was prepared by three subsequent crystallizations from methanol.

Anal. Calcd. for $C_{14}H_{10}O_2N_2$: C, 70.6; H, 4.2; N, 11.8. Found: C, 70.6; H, 4.4; N, 11.8.

2-(2'-Nitrophenyl)-phenylacetonitrile (X) with Sodium Hydroxide.—In duplicate runs 0.205 g. (0.87 mmole) of X in 0.55 ml. of methanol was mixed with 0.20 g. (5 mmoles) of sodium hydroxide. Twenty-four seconds after the beginning of the addition of the base a yellow precipitate began separating; the temperature had risen from 33 to 38° in about 1 min. After about 8 min. from the time of mixing the precipitate was filtered and washed. The reaction mixture had been kept below room temperature with ice-water about 5 of the 8 min. The yield was 0.166 g. (87%) of yellow crystals, m.p. 218.5–220.5° with no depression in m.m.p. with authentic XII.

In another run duplicating the above except that the reaction mixture was refluxed for 5 min., a yellow precipitate formed instantaneously but it dissolved and no pure XII could be isolated by the above procedure.

MORGANTOWN, W. VA.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY]

Rearrangements of α-Halogenated Ethers. I. 2,2,3,3-Tetrachloro-*p*-dioxane

BY R. K. SUMMERBELL AND DANIEL R. BERGER[1]

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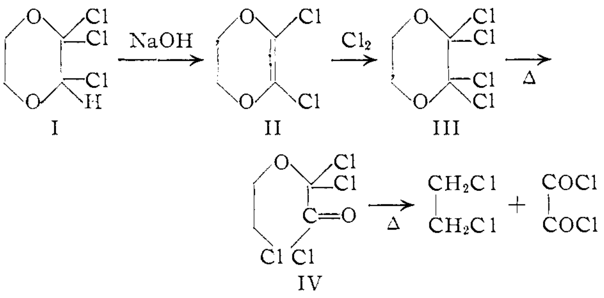
The compound previously assigned the structure 2,2,3,3-tetrachloro-*p*-dioxane (III) has been shown to be (2-chloroethoxy)-dichloroacetyl chloride (IV). III has been synthesized, its structure proved, and the formation of IV from III by a thermal rearrangement has been demonstrated.

Discussion

Some ten years ago the high temperature chlorination of *trans*-2,3-dichloro-*p*-dioxane[2] was described,[3] and the liquid product, obtained in 55% yield, was assigned the structure 2,2,3,3-tetrachloro-*p*-dioxane. This assignment seemed justified as solid derivatives of both ethylene glycol and oxalic acid were isolated from the hydrolysate; no other tetrachlorodioxane could give these derivatives. We recently have had occasion to prepare this compound, and a routine examination of its infrared spectrum revealed a strong absorption at 5.55 μ, entirely inconsistent with its formulation as tetrachlorodioxane.

In order to resolve this inconsistency, the tetrachlorodioxane was prepared by an alternate route. Addition of chlorine to 2-chloro-*p*-dioxene gave 2,2,3-trichloro-*p*-dioxane (I). Removal of hydrogen chloride from I by means of sodium hydroxide gave 2,3-dichloro-*p*-dioxene (II), which upon addition of chlorine gave the desired 2,2,3,3-tetrachloro-*p*-dioxane (III). However, III is entirely different from the previously described liquid, IV. III is a stable white solid melting at 140°, whereas IV is a water-white mobile liquid boiling at 205°. Compound IV reacts "violently" with water and alcohols; III can be recrystallized successfully from aqueous ethanol and is stable to a humid atmosphere. Furthermore, III does not absorb in the region of 5–6 μ.

The structural relationship between III and IV was established as follows: Both gave correct analyses for $C_4H_4O_2Cl_4$, and after hydrolysis both gave derivatives of oxalic acid and ethylene glycol. When III was heated under reflux in tetrachloroethane solution, with the periodic withdrawal of aliquots for spectral examination, the infrared spectrum of III was observed to change slowly to that of IV, the apparently first-order reaction requiring approximately 30 hours for the disappearance of III. Finally, on heating IV at 190° without solvent, there was a very slow distillation, the products being ethylene chloride and oxalyl chloride. On the basis of these observations, the liquid IV is *not* 2,2,3,3-tetrachloro-*p*-dioxane, but rather must be (2-chloroethoxy)-dichloroacetyl chloride. It is entirely possible that in the previously described preparation of IV[3], III is actually formed as an intermediate. However, the reaction temperature (155°) and the time taken for the reaction (54 hours) are more than are required to permit essentially complete isomerization of III to IV; should any III still be present at the end of the reaction, it would be isomerized in the atmospheric distillation used in the purification scheme for IV. Confirmation of this was obtained by heating III at 210° for 30 minutes. On cooling, the liquid did not solidify, and the infrared spectrum of III was no longer present, having been replaced by that of IV.



The observation that both III and IV could be hydrolyzed to yield derivatives of ethylene glycol requires some comment. Hydrolysis of III would be expected to yield the glycol, whereas the hydrolysis of IV should instead give ethylene chloro-

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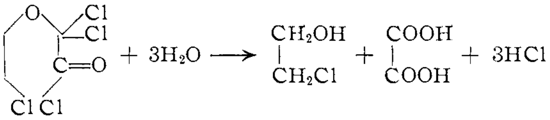
[1] Northwestern University Fellow, 1955–1956; Allied Chemical and Dye Corp. Fellow, 1956–1957.

[2] See R. K. Summerbell and H. E. Lunk, THIS JOURNAL, **79**, 4802 (1957), for the structures of *cis*- and *trans*-2,3-dichloro-*p*-dioxane.

[3] R. K. Summerbell, R. R. Umhoefer and G. R. Lappin, *ibid.*, **69**, 1352 (1947).

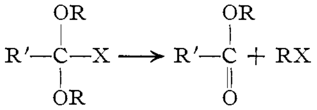
hydrin. In the previous work,[3] the glycol was not isolated as such, but rather was identified as its dibenzoate prepared by a Schotten–Baumann reaction. Under the basic conditions employed, the



chlorohydrin, which was formed by the hydrolysis, would be dehydrochlorinated to give ethylene oxide, which would then react with water to give the glycol.[4] It was therefore necessary, in order to firmly establish the structure of IV, to isolate ethylene chlorohydrin (or a derivative which could be formed from ethylene chlorohydrin but not from ethylene glycol) from the hydrolysis products of IV. This was accomplished by neutralizing the hydrolysis solution with ammonium hydroxide, care being taken not to allow the solution to become basic. The chlorohydrin was removed by distillation as its azeotrope with water, and the distillate was treated with *p*-anisidine according to the method of Jacobs and Heidelberger[5] to give 2-(*p*-anisidino)-ethanol, *p*-$CH_3OC_6H_4NHCH_2CH_2OH$, a compound which, under the conditions used, could not be formed from ethylene glycol.

The rearrangement of III to give IV proceeds at a lower temperature than does the rearrangement of IV to give ethylene chloride and oxalyl chloride, as is evidenced by the fact that IV was isolated from its original preparation. A satisfactory explanation is found in a consideration of the bulk of the chlorine atoms of III, and the fact that III is constrained in a ring system. On both III and IV, the migrating chlorine atoms may be in a favorable position for the rearrangement; the rearrangement of III to IV, however, gives a much greater relief of strain than does the corresponding rearrangement of IV, and consequently the former requires a lower energy input.

Rearrangements of α-haloethers to give alkyl halides and carbonyl derivatives are not unknown. Over a century ago, Malaguti[6] reported perchloroethyl ether to give, on pyrolysis, trichloroacetyl chloride and hexachloroethane. Shostakovsky and Bogdanova have reported[7] α-bromoethyl butyl ether to give, on slow distillation, 97% of butyl bromide and traces of acetaldehyde. Most of the oxygen, however, was recovered as water. The same bromoether, after three weeks in a sealed tube in diffuse light, gave 80% of butyl bromide and again, water. α-Bromoethyl ethyl ether similarly gave, on heating, 89% of ethyl bromide, with the formation of some acetaldehyde. Hall and Sirel[8] obtained a 20% yield of 1,3-dichloropropanone as the only isolated product from the low temperature (−20°) chlorination of isopropyl ether. The isolation was achieved by a distillation at 83–88°, during which the type of rearrangement under discussion probably occurred. In a similar reaction of an α-haloester, α-chloroethyl acetate is reported[9] to give acetyl chloride and acetaldehyde upon heating to 560–590°. The yield is 88%, with a conversion of 41%. There are also related reactions in the literature[10–13] for which the authors are led to postulate the formation of a halogenated acetal followed by a similar type of rearrangement to give an alkyl halide and ester.



$$R'-\overset{\displaystyle OR}{\underset{\displaystyle OR}{C}}-X \longrightarrow R'-\overset{\displaystyle OR}{\underset{\displaystyle O}{C}} + RX$$

Pyrolysis of 2,3-dibromo-2,3-dichloro-*p*-dioxane (V) gives a rearrangement analogous to that of III. 2,3-Dichloro-*p*-dioxene, on addition of bromine, gave the solid compound V. On pyrolysis of V at atmospheric pressure, a liquid, VI, was obtained. VI has not as yet been completely characterized, but its infrared spectrum is quite similar to that of IV, so that its structure is most probably that of (2-bromo-[or chloro]ethoxy)-bromochloroacetyl chloride (or bromide).

Experimental[14]

2-Chloro-*p*-dioxene was prepared by the method of Summerbell and Lunk.[2]

2,2,3-Trichloro-*p*-dioxane (I) was prepared by the method of Lunk[15]; b.p. 60–61° (1 mm.), m.p. 20–21°.

2,3-Dichloro-*p*-dioxene (II).—A mixture of 6.0 g. (0.15 mole) of sodium hydroxide in 5 ml. of water and 20 ml. of carbitol held at 200–205° (bath) was treated dropwise with 19.2 g. (0.10 mole) of I in 20 ml. of carbitol. The slow addition took about 0.5 hour, and from time to time small amounts of water were added to replace that which distilled. The distillate was milky and boiled from 110–140°. After the addition of the trichlorodioxane was completed, 20 ml. of water was added in small portions and allowed to distil.

The heavy organic layer of the distillate was taken into ether, washed with water and dried over magnesium sulfate. The filtered solution was freed of ether and the residue was distilled *in vacuo*. There was very little forerun, and practically no residue. The yield of 2,3-dichloro-*p*-dioxene, b.p. 55° (2.5 mm.), $n^{25}D$ 1.4930, was 8 g. (52%).

Anal. Calcd. for $C_4H_4O_2Cl_2$: C, 31.00; H, 2.60. Found: C, 31.33; H, 2.70.

2,2,3,3-Tetrachloro-*p*-dioxane (III).—A solution of 20 g. (0.129 mole) of II in 50 ml. of methylene chloride was stirred with cooling on the ice-bath. Chlorine was added slowly until the solution turned yellow; the yellow color was removed by "back-titrating" with a few drops of the dioxene. The solution was cooled on a Dry Ice–acetone-bath, and three crops of crystals were obtained, which, after recrystallization from ether, gave 20 g. (0.088 mole, 67%) of the white solid. A satisfactory melting point could not be obtained by recrystallization; however, a sublimed sample (50° (0.5 mm.)) melted at 137–140° (sealed tube) The compound can be recrystallized from aqueous ethanol with no change in its infrared spectrum. Infrared absorption bands are (s = strong; m, medium; w, weak; sh, shoulder; re-

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[4] The reaction of ethylene chlorohydrin with base to give ethylene glycol is well described in the literature. For references, see G. O. Curme and F. Johnston, "Glycols," A.C.S. Monograph No. 114, Reinhold Publishing Corp., New York, N. Y., 1952, p. 15.

[5] W. A. Jacobs and M. Heidelberger, *J. Biol. Chem.*, **21**, 421 (1915).

[6] M. J. Malaguti, *Ann. chim. et phys.*, [3] **16**, 5 (1846).

[7] M. F. Shostakovsky and A. V. Bogdanova, *Zhur. Obshchei Khim.*, **21**, 388 (1951); English translation, *J. Gen. Chem. U. S. S. R.*, **21**, 429 (1951).

[8] G. E. Hall and I. Sirel, THIS JOURNAL, **74**, 836 (1952).

[9] Cons. Elektrochem. Industrie, PB 74539, frames 7431–34.

[10] S. M. McElvain and D. Kundiger, THIS JOURNAL, **64**, 254 (1942).

[11] E. N. Marvell and M. J. Joncich, *ibid.*, **73**, 973 (1951).

[12] S. M. McElvain and C. H. Stammer, *ibid.*, **75**, 2154 (1953).

[13] J. B. Wright, *ibid.*, **77**, 4883 (1955).

[14] Microanalyses were performed by Miss H. Beck. Unless otherwise stated, melting points were taken on a Fisher-Johns block and are uncorrected.

[15] H. E. Lunk, Ph.D. Thesis, Northwestern University, 1957.

ported as microns in carbon tetrachloride solution): 6.85w, 6.91w, 7.86w, 7.98w, 8.82s, 9.00s, 9.38m, 9.60m, 10.16s, 10.65s, 11.80m, 13.9s, 14.2sh. A very weak carbon-hydrogen band appears at 3.42 μ.

Anal. Calcd. for $C_4H_4O_2Cl_4$: C, 21.27; H, 1.78; mol. wt., 225.90. Found: C, 21.41; H, 1.75; mol. wt., 234 (in benzene).

Hydrolysis of 2,2,3,3-Tetrachloro-*p*-dioxane (III).—Compound III, 1.0 g., and water, 30 g., were heated overnight on the steam-bath. Then 1.1 g. of calcium nitrate was added, and the mixture was heated for another hour. The precipitate was filtered and dried, and had an infrared absorption spectrum (potassium bromide pellet) identical with that of calcium oxalate prepared from oxalic acid.

Sodium hydroxide, 2.0 g., was added to the filtrate. A precipitate appeared, which was removed by filtration and discarded. To the filtrate was then added 0.7 g. of benzoyl chloride, and the solution was heated for 10 minutes on the steam-bath. After sitting overnight at room temperature, the solid which had formed was removed, washed with ethanol, and dried, to give a compound, m.p. 67–69°. It was identical in all respects with authentic ethylene glycol dibenzoate.

(2-Chloroethoxy)-dichloroacetyl chloride (IV) was prepared by the method of Summerbell, Umhoefer and Lappin.[3] The product, n^{25}_D 1.4805, boiled at 205° (760 mm.) and 76–78° (6 mm.). Infrared absorption bands are (reported as microns in carbon disulfide solution): 5.55s, 7.01w, 7.66m, 8.52s, 9.24m, 9.75s, 9.90sh, 10.30m, 11.50w, 11.76w, 12.4sh, 13.2s, broad, 14.7m, 15.3m, broad.

Isomerization of 2,2,3,3-Tetrachloro-*p*-dioxane (III) to (2-Chloroethoxy)-dichloroacetyl Chloride (IV).—Compound III was dissolved in redistilled *sym*-tetrachloroethane in a concentration of 54 mg./ml. and heated under reflux (144.5°) using a calcium chloride tube to ensure dryness. Aliquots were withdrawn periodically for spectral analysis. An attempt was made to determine the rate of disappearance of III by using its band at 10.65 μ; however, the results of different runs were not consistent and no reproducible rate constant was found. The various runs did, however, all follow first order kinetics, and the bands due to III disappeared after 24–36 hours, being replaced gradually with the spectrum of IV. In refluxing carbon tetrachloride solution (77°), III is unchanged after three days.

Pyrolysis of 0.5 g. of III at 210° for 30 minutes led to complete isomerization to IV. The infrared spectrum of the liquid product was mostly that of IV, with a small amount of ethylene chloride and oxalyl chloride present. III was totally absent.

Hydrolysis of (2-Chloroethoxy)-dichloroacetyl Chloride (IV).—Hydrolysis of IV to yield oxalic acid and ethylene glycol dibenzoate already has been described.[3] The isolation of ethylene chlorohydrin as 2-(*p*-anisidino)-ethanol was accomplished as described below.

Compound IV (15 g., 0.067 mole) and 50 ml. of water were allowed to stand together overnight; during the first hour the reaction was exothermic. On cooling, crystals, probably oxalic acid, separated and were removed by filtration. The solution was then neutralized with ammonium hydroxide, care being taken that it be no more basic than *p*H 7 (the color changes from water-white to yellow as the neutralization point is neared). On cooling in ice, crystals (presumably ammonium oxalate) formed which were filtered and discarded. The filtrate was distilled through a 10-inch Vigreux column, and the first 30 ml. was collected in three 10-ml. fractions, n^{25}_D 1.3535, 1.3430, 1.3393, respectively. (Ethylene chlorohydrin is reported to form an azeotrope, containing 58% water, boiling at 97.8°.[16]) The first two fractions were recombined and distilled; the first 6 ml. was collected, n^{25}_D 1.3591.

The above 6 ml., estimated from the refractive index to contain approximately 4 g. (0.05 mole) of ethylene chlorohydrin, was heated under reflux for two hours with 12 g. (0.10 mole) of *p*-anisidine and 10 ml. of water.[17] The mixture was made basic with sodium hydroxide and extracted with ether. After drying over magnesium sulfate, the ether was removed on the steam-bath and the residue distilled *in vacuo*. A micro distillation apparatus, having a column of only 1.5 inches, was used, and no real attempt at a careful separation of *p*-anisidine from 2-(*p*-anisidino)-ethanol was made. The distillate was taken in three fractions, the last of which comprised about 35% of the total. After two recrystallizations of the third fraction from ether at −78°, 1.1 g. of compound, m.p. 41.0–42.0°, was obtained, identical in the infrared with 2-(*p*-anisidino)-ethanol prepared by the method of Jacobs and Heidelberger.[5] The yield was 0.007 mole (10%).

Anal. Calcd. for $C_9H_{13}O_2N$: C, 64.65; H, 7.84. Found: C, 64.53; H, 7.58.

Pyrolysis of (2-Chloroethoxy)-dichloroacetyl Chloride (IV).—Compound IV, 15 g., was heated to 190° on a sand-bath (b.p. of IV is 205°). A very slow distillation through a 4-inch vacuum-jacketed Vigreux column occurred; after 60 hours, 5 g. of distillate had been collected. The infrared spectrum showed, by comparison with the known compounds, that the distillate consisted entirely of oxalyl chloride and ethylene chloride.

Aniline was added dropwise to 0.5 ml. of the distillate until no more vigorous reaction was noted. The precipitate was triturated in ethanol, leaving a solid which melted at 252–253°. The infrared spectrum was identical with that of oxanilide (m.p. 253°) prepared from authentic oxalyl chloride in a similar manner.

2,3-Dibromo-2,3-dichloro-*p*-dioxane (V).—Compound II (8.3 g., 0.054 mole) was dissolved in 50 ml. of carbon tetrachloride. To it was added, with stirring over 0.5 hour, a solution of 8.65 g. (0.054 mole) of bromine in carbon tetrachloride to make 50 ml. An ice-bath was used to cool the reaction. After standing for three hours, the solution was heated under reflux for 0.5 hour and the solvent removed by distillation from the steam-bath. The residue, on standing overnight, deposited white crystals which were filtered and washed with cold ethanol to give 6.3 g. (37%) of V melting over a wide range up to 140°. Recrystallization from ethanol gave a m.p. of 103–130° (sealed tube). The material can also be purified by sublimation, but it is not stable enough to give a satisfactory melting point. On standing, V decomposes to give fumes with ammonia vapor; it is, however, fairly stable when stored in a desiccator over sodium hydroxide pellets.

Anal. Calcd. for $C_4H_4O_2Br_2Cl_2$: C, 15.26; H, 1.27. Found: C, 15.27; H, 1.24.

Pyrolysis of 2,3-Dibromo-2,3-dichloro-*p*-dioxane (V).—Compound V (2.50 g., 0.00794 mole) was placed in a 5-ml. flask fitted to a short distillation head. Distillation at atmospheric pressure gave 2.02 g. of a red-orange liquid, b.p. 180–185°. Redistillation gave a colorless liquid, b.p. 55° (0.3 mm.), n^{25}_D 1.5167. The infrared absorption spectrum was quite similar to that of IV, a strong carbonyl band at 5.53 μ being the most prominent absorption.

NOTE ADDED IN PROOF.—The chlorination of *p*-dioxane to give a 30% yield of trichloroacetyl chloride, along with some hexachloroethane, has been reported recently.[18] This result, obtained in a chlorination at temperature above 160°, quite probably involves the formation of halogenated intermediates followed by rearrangements of the type discussed in the present paper.

EVANSTON, ILLINOIS

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(16) "Azeotropic Data," Advances in Chemistry Series, No. 6, American Chemical Society, Washington, D. C., 1952, p. 5.

(17) The procedure from this point is modified from that of Jacobs and Heidelberger, ref. 5.

(18) N. B. Lorette, *J. Org. Chem.*, **22**, 843 (1957).