

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

2,2,3,3-Tetrachloro-1,4-dioxane¹BY R. K. SUMMERBELL, R. R. UMHOEFFER² AND GERALD R. LAPPIN^{3,4}

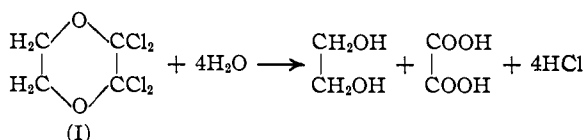
The chlorination of 2,3-dichloro-1,4-dioxane has been reported to give four stereoisomers of 2,3,5,6-tetrachloro-1,4-dioxane,^{5,6,7} 2,2,3,5-tetrachloro-1,4-dioxane,⁵ and 2,2,3,6-tetrachloro-1,4-dioxane.⁵ However, the isolation of 2,2,3,3-tetrachloro-1,4-dioxane (I) has not been previously reported. In fact, Böeseken and Tellegen,^{8,9} after carrying out a large number of chlorinations of 2,3-dichloro-1,4-dioxane under a wide variety of conditions, concluded that (I) could not be prepared by this method.

In the course of an investigation of the chlorination of 2,3-dichloro-1,4-dioxane in this Laboratory a fraction was obtained which gave a considerable amount of oxalic acid on hydrolysis. Further research established that (I) could be prepared in good yield by the slow chlorination of the dichlorodioxane at high temperatures using iodine as a catalyst. The optimum temperature was found to be 155–160° and the optimum rate of chlorine input to be 0.0010–0.0025 mole per minute. If the temperature was lowered to 110° the yield was decreased to 10% and if the rate of chlorine input was raised to 0.0050 mole per minute at 155–160° the yield was only 8%. The omission of the iodine catalyst decreased the yield to a considerable extent. Using the optimum conditions a yield of 55% could be consistently obtained.

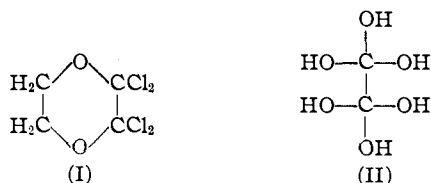
Vacuum fractionation of the reaction product gave a constant boiling mixture which contained about 85% of (I) as shown by hydrolysis and analysis for oxalic acid. Distillation of this mixture at atmospheric pressure destroyed the other components and gave a distillate which contained only (I) and some colored impurities. Fractionation of this distillate *in vacuo* gave pure (I). The purified 2,2,3,3-tetrachloro-1,4-dioxane was a colorless liquid, b. p. 204° (755 mm.), 75° (6 mm.), n_D^{20} 1.4812, d_4^{25} 1.496. It had an acid chloride-like odor and reacted violently with water, differing in this respect from other chlorinated dioxanes which react only slowly with water. In the ab-

sence of moisture the compound was very stable, a sample remaining unchanged in color and refractive index after standing two years in a sealed tube. This high degree of stability is in distinct contrast to that of other chlorinated 1,4-dioxanes which decompose on standing.

The structure of this tetrachloro-1,4-dioxane was established by its hydrolysis to ethylene glycol and oxalic acid, 2,2,3,3-tetrachloro-1,4-dioxane being the only one which would give these hydrolysis products. Analysis for the amount of oxalic acid formed showed the product to be at least 99% pure.

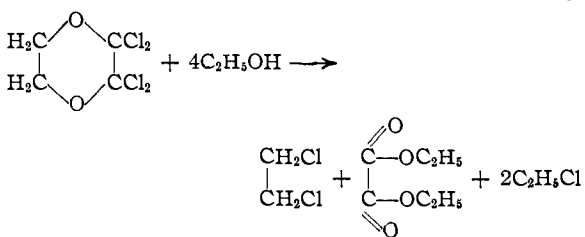


Structurally (I) can be related to orthoöxalic acid (II) and may be considered to be an ester



acid chloride of this acid. Very few examples of this α -dichloro ether or ester acid chloride type of structure have been reported and nothing is known of their behavior in the ordinary reactions of chloro ethers. Therefore, both as a source of hitherto unavailable derivatives of 1,4-dioxane and as an example of this unique type of structure, the behavior of (I) in the ordinary reactions of chloroethers was of great interest.

The reaction of 2,3-dichloro-1,4-dioxane with alcohols or sodium alkoxides has been reported to give good yields of the corresponding 2,3-dialkoxy-1,4-dioxanes.¹⁰ The corresponding reaction with (I) should give rise to 2,2,3,3-tetraalkoxy-1,4-dioxanes which would be esters of orthoöxalic acid, a type of compound which has never been reported. The tetrachlorodioxane reacted very



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(5) Butler and Cretcher, *THIS JOURNAL*, **54**, 2987 (1932).

(6) Christ and Summerbell, *ibid.*, **55**, 3029 (1933).

(7) Baker, *J. Chem. Soc.*, 2666 (1932).

(8) Böeseken, Tellegen and Henriquez, *THIS JOURNAL*, **55**, 1284 (1933).

(9) Tellegen, "Dioxaan en derivaten," Delft Technical University, Delft, Holland, 1934, pp. 34–46.

(10) Böeseken, Tellegen and Henriquez, *Rec. trav. chim.*, **50**, 909 (1931).

vigorously with alcohols but no tetraalkoxydioxanes could be isolated. With primary and secondary alcohols the products were the alkyl oxalate, ethylene dichloride, and the alkyl chloride. The results of these reactions are summarized in Table I. The formation of these products leads us to

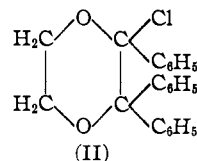


TABLE I

YIELD OF PRODUCTS IN THE REACTION OF (I) WITH PRIMARY AND SECONDARY ALCOHOLS

Alcohol	Alkyl oxalate, %	RCl, %	C ₂ H ₄ Cl ₂ , %
Methyl	85	Undetd.	80
Ethyl	90	36	79
<i>i</i> -Propyl	86	70	Undetd.

believe that the ortho-oxalate esters were formed as intermediates but were immediately cleaved by the evolved hydrogen chloride to give the observed products. No explanation can be advanced at this time for the fact that cleavage occurred exclusively to give the alkyl oxalate rather than a mixture of this ester and ethylene oxalate. With tertiary alcohols no oxalate ester was isolated, the products in this case being oxalic acid, ethylene dichloride and the olefin formed by dehydration of the alcohol. The reaction of oxalic acid with tertiary alcohols results in dehydration and oxalate esters of tertiary aliphatic alcohols have not been prepared. The cleavage mechanism is supported by the fact that, when the reaction was carried out in hexane solution so that the evolved hydrogen chloride would be partially removed from the field of reaction, a mixture apparently consisting of partial cleavage products was obtained. When sodium alkoxides were treated with (I) the product consisted of a very complex mixture from which no pure compound could be separated. Hydrolysis of this mixture and analysis for the amount of oxalic acid formed showed that the oxalate structure had, to a considerable extent, been destroyed during the course of the reaction. This leads us to believe that the chief mode of reaction of sodium alkoxides with (I) is one of dehalogenation. This is known to be the mode of reaction of sodium ethoxide with the similar compound, hexachloroethane.¹¹

The reaction of 2,3-dichloro-1,4-dioxane with arylmagnesium bromides gives a good yield of diaryldioxanes.¹² However, with alkylmagnesium halides the chief reaction is dehalogenation of the dichlorodioxane to give *p*-dioxene.¹² The substitution of cadmium alkyls for the Grignard reagent gave good yields of 2,3-dialkyl-1,4-dioxanes.¹³ The reaction of (I) with phenylmagnesium bromide gave a good yield of a compound, C₂₂H₁₉ClO₂, for which the most probable structure is 2-chloro-2,3,3-triphenyl-1,4-dioxane (II). The chlorine atom in this substance was very inert and would not react with methylmagnesium bromide in re-

fluxing toluene nor with sodium ethoxide. Heating with a solution of potassium hydroxide in ethylene glycol for several weeks converted it partially to a compound, C₄₄H₃₈O₄, the structure of which was not established. With alkyl Grignard reagents (I) gave a very complex mixture of products which could not be separated. During the course of the reaction a considerable amount of gaseous substance was evolved, which, in the case of butylmagnesium bromide, was shown to consist of a mixture of butane and butene. The chief mode of reaction of (I) with alkylmagnesium halides was thus shown to be dehalogenation. Substitution of cadmium alkyl gave identical results and no tetraalkyldioxane could be isolated.

Experimental

2,2,3,3-Tetrachloro-1,4-dioxane.—In a three-necked one-liter flask, fitted with a mechanical stirrer, a chlorine inlet tube and a reflux condenser attached to a hydrogen chloride trap, were placed 624 g. (4.0 moles) of purified 2,3-dichloro-1,4-dioxane and 5 g. of iodine. The reaction mixture was maintained at 155–160° by means of an electrically heated oil-bath. Dry chlorine gas, measured by means of an orifice-type flow meter, was passed in at the rate of 0.0025 mole per minute for a total time of fifty-four hours. The mixture was allowed to cool and dry air was passed in to remove dissolved gases. Distillation under reduced pressure through a 20-cm. Vigreux column gave 605 g., b. p. 101–102° at 16 mm. This fraction was distilled from an ordinary distilling flask at atmospheric pressure to give 520 g., b. p. 200–205°. Redistillation under reduced pressure gave 510 g. (56%) of (I), b. p. 75–76° at 6 mm., *n*_D²⁰ 1.4812, *d*₄²⁵ 1.496. This material reacted vigorously with water to give a solution from which oxalic acid dihydrate, m. p. 101–101.5°, crystallized on standing. Ethylene glycol was confirmed as the dibenzoate by means of a Schotten-Baumann reaction. Because of the high reactivity of (I) analysis for halogen was carried out by determining gravimetrically the silver chloride produced when a weighed sample of the substance reacted with an aqueous solution of silver nitrate. The oxalic acid was determined gravimetrically as calcium oxalate after allowing a weighed sample of (I) to stand with dilute sodium hydroxide solution.

Anal. Calcd. for C₄H₄Cl₄O₂: Cl, 62.80; oxalate, 1 mole per mole substance. Found: Cl, 62.51; oxalate, 0.988 mole per mole substance.

Reaction of (I) with Primary and Secondary Alcohols.—The procedure used in the reaction with ethanol will be described. With other alcohols the procedure was essentially the same, the isolation techniques being modified according to the nature of the products obtained.

In a three-necked flask fitted with stirrer, dropping funnel and a reflux condenser attached to a Dry Ice-cooled trap was placed 250 g. of absolute ethanol. To this was added dropwise 52 g. (0.22 mole) of (I), the temperature being maintained at 0–10° by means of an ice-bath. After all of the tetrachlorodioxane had been added the mixture was refluxed for one hour. The system was then arranged for distillation, all low-boiling material being caught in the vapor trap. The flask was heated on the steam-bath until no further distillation occurred. The vapor trap was found to contain 10 g. of ethyl chloride, b. p. 12–13°. The distillate was diluted with a large volume of water and the

(11) Geuther and Brockhoff, *J. prakt. Chem.*, [2] **7**, 107 (1873).

(12) Summerbell and Bauer, *THIS JOURNAL*, **57**, 2364 (1936).

(13) Summerbell and Bauer, *ibid.*, **58**, 759 (1936).

heavy non-aqueous layer was collected and dried over calcium chloride. Distillation of this liquid gave 18 g. (79%) of ethylene chloride. The residue in the distillation flask was distilled through a 20-cm. Vigreux column to give 30 g. (90%) of ethyl oxalate, b. p. 184–185°, n_D^{20} 1.4100.

When this reaction was carried out in refluxing hexane as a solvent considerable hydrogen chloride was evolved and the product was a very complex mixture of unstable substances which hydrolyzed to give oxalic acid. No pure compounds were isolated.

Reaction of (I) with Tertiary Alcohols.—Only the reaction with 2-methyl-2-propanol will be described in detail.

In a three-necked flask fitted with a mechanical stirrer, a dropping funnel and a reflux condenser attached to a Dry Ice-cooled vapor trap was placed 29.6 g. (0.40 mole) of dry 2-methyl-2-propanol. The flask and contents were cooled to 10° while 11.3 g. (0.05 mole) of (I) was slowly added. When the addition was complete the reaction mixture was refluxed until the evolution of gas ceased. The residue in the flask was distilled through a 20-cm. glass helices-packed column to give 8.7 g. (93%) of 2-chloro-2-methylpropane and 4.4 g. (89%) of ethylene chloride. The residue from this distillation crystallized to give 6.0 g. (95%) of oxalic acid dihydrate. The vapor trap contained 10.7 g. (96%), based on 0.30 mole of excess alcohol) of an unsaturated liquid which boiled below 0°. This was shown to be 2-methylpropene by its reaction with benzene in the presence of concentrated sulfuric acid to give *p*-di-*t*-butylbenzene.

With 2-methyl-2-butanol no attempt was made to isolate ethylene chloride or 2-methyl-2-chlorobutane. An unsaturated fraction, b. p. 30–36°, was presumed to be a mixture of 2-methyl-1-butene and 2-methyl-2-butene. Based on this assumption the conversion of excess alcohol to olefin was 93%.

Reaction of (I) with Phenylmagnesium Bromide.—To a well-stirred solution of 0.25 mole of phenylmagnesium bromide in 200 ml. of dry ether was added over a period of four hours a solution of 9.1 g. (0.04 mole) of (I) in 50 ml. of dry ether. The mixture was then refluxed with stirring for two hours and allowed to stand overnight at room temperature. The mixture was hydrolyzed with ice and ammonium chloride solution. The ether layer was separated, washed with water, dried over sodium sulfate, and the ether removed *in vacuo*. The residual oil was steam distilled to remove biphenyl and the non-volatile portion was recovered from the pot by extraction with ether. Removal of the solvent after drying the ether solution over sodium sulfate gave a pasty white solid which, after two recrystallizations from ethanol-water mixture gave 10.5 g. (71%) of white needles, m. p. 141.0–141.5°.

*Anal.*¹⁴ Calcd. for $C_{22}H_{19}ClO_2$: Cl, 10.10; C, 75.0; H, 5.40; mol. wt., 350. Found: Cl, 9.92; C, 74.8; H, 5.36; mol. wt. (Rast), 356.

The product was recovered unchanged after refluxing for four hours with a solution of methylmagnesium iodide in dry toluene and after heating for four hours with a solution of sodium ethoxide in absolute alcohol. A 2.0-g. sample of this substance was refluxed for two months with

5% alcoholic potassium hydroxide solution. Repeated crystallization from ethanol of the material recovered from this treatment gave 0.2 g. of a white solid, m. p. 159–160°.

*Anal.*¹⁴ Calcd. for $C_{44}H_{38}O_4$: C, 83.7; H, 6.02; mol. wt., 630. Found: C, 83.4; H, 5.82; mol. wt. (Rast), 615.

Reaction of (I) with Sodium Ethoxide.—The reaction of (I) with sodium ethoxide in various solvents and under different conditions of time and temperature gave rise to a product which distilled without separation into fractions, b. p. 50–150° at 0.05 mm. Hydrolysis of this product followed by precipitation of calcium oxalate which was dried and weighed showed that only about 30% of the theoretical amount of oxalate ion was formed. Both ethyl alcohol and ethylene glycol were identified in the hydrolyzate. No pure compound could be obtained from this reaction. Similar products were obtained with other sodium alkoxides.

Reaction of (I) with Alkyl Grignard Reagent.—The reaction of 0.10 mole of (I) with an excess of butylmagnesium bromide gave a gaseous product which contained 0.13 mole of butane and 0.12 mole of butene. Hydrolysis of the reaction mixture followed by the usual procedure gave a product which could not be separated into constant boiling fractions by distillation, b. p. 75–150° at 1 mm. All fractions (taken at 10° intervals) rapidly decolorized a solution of bromine in carbon tetrachloride and all contained chlorine. Similar results were obtained when cadmium alkyls were substituted for the Grignard reagent.

Conclusions

1. The new compound, 2,2,3,3-tetrachloro-1,4-dioxane (I), has been prepared for the first time and in good yield by the slow chlorination of 2,3-dichloro-1,4-dioxane at high temperature using iodine as a catalyst.

2. (I) has been found to react with primary and secondary alcohols to give high yields of alkyl oxalates, the other products being ethylene chloride and the alkyl chloride. With tertiary alcohols only ethylene chloride, oxalic acid, and the olefin formed by dehydration of the alcohol could be isolated.

3. (I) reacted with phenylmagnesium bromide to give a compound, $C_{22}H_{19}ClO_2$, which most probably had the structure 2-chloro-2,3,3-triphenyl-1,4-dioxane.

4. (I) was found to react with alkyl magnesium halides and with sodium alkoxides to give, as the chief products, complex mixtures apparently derived from (I) by dehalogenation.

(14) Micro carbon and hydrogen analyses by Mrs. M. Ledyard.