## PHOTOCHEMICAL CHLORINATION

## OF 2-TRICHLOROMETHYL-1,3-DIOXOLANE

A. S. Atavin, A. N. Mirskova, É. F. Zorina, and T. S. Proskurina UDC 542.944.1:547.729.07

The photochemical chlorination of 2-trichloromethyl-1,3-dioxolane proceeds only at the carbon atoms in the 4 and 5 positions. The structures of the resulting 2-trichloromethyl-4-chloro- and 2-trichloromethyl-4,5-dichloro-1,3-dioxolanes were proved by means of the IR spectra and chemical transformations.

The chlorination of 1,3-dioxolanes usually leads to ring opening and the formation of carbonyl compounds [1] or to an unseparable mixture of chlorinated products of cyclic structure [2]. In this connection, monochloro-substituted 1,3-dioxolanes are obtained from chlorine-containing epoxides and diols or from chlorocarbonyl compounds [3]. There is one communication [4] regarding the direct chlorination of 2trichloromethyl-1,3-dioxolane (I), which gives a mixture of 2-trichloromethyl-4-chloro-1,3-dioxolane (III) and 2-chloroethyl trichloroacetate (V).

The photochemical chlorination of 2-trichloromethyl-1,3-dioxolane (I) in  $CCl_4$  with gaseous chlorine is a convenient method for the direct preparation (depending on the reagent ratio) of 2-trichloromethyl-4chloro- (II) or 2-trichloromethyl-4,5-dichloro-1,3-dioxolane (III).



The chlorination of I at -10 to  $-13^{\circ}$ C proceeds without substitution at C<sub>2</sub>, since 2-chloroethyl trichloroacetate (V), which should be formed as a result of rearrangement of tetrachloride IV, is not detected in the reaction products. The absorption bands of a carbonyl group are absent in the IR spectra of II and III. The series of bands at 1000-1180 cm<sup>-1</sup> corresponds to the absorption characteristic for the acetal structure.

When a second chlorine atom was introduced into II, one might have expected substitution at the same carbon atom  $(C_4)$  to give 2-trichloromethyl-4,4-dichloro-1,3-dioxolane. However, hydrolysis of the reaction product does not give a glycolic acid but rather a glyoxal. Consequently, dioxolane III is formed as a result of chlorination.

It is also possible that the chlorination products contain 2-trichloromethyl-4,4-dichloro- and 2trichloromethyl-2-chloro-1,3-dioxolanes, but the percentage of these compounds does not exceed 3-5%, as indicated by the results of gas-liquid chromatography (GLC) and elementary analysis and also by acid hydrolysis.

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TABI	E 1. 1	Physical	Constan	ts of Ch	lorinatec	d 2-Tric	chlorom	ethyl-1,	3-di oxolanes	0						
Com-	,	s 		Ър, °С		5 7	IW	a <sup>5</sup>	Empirical		Found, %		Ŭ	Calc., %		B these
punod	×	ž	<sup>22</sup>	(mm)	at a	q.	punoj	calc.	formula	v	Ŧ	IJ	υ	Н	บี	rieid, %
II	CCI3	CHCI	CH <sub>2</sub>	56 (2)	1,5960	1,4960	41,348	41,176	C4H4Cl4O2	21,6	1,9	62,5	21,3	1,8	62,8	77
III	CCI	CHCI	CHCI	77 (2)	1,7011	1,5130	45,99	45,98	C4H3C15O2	18,3	1,2	68,4	18,5	1,2	68,1	84
		-			-		-				-				_	_

Compounds II and III fume in air and are readily hydrolyzed in hydroxylamine hydrochloride solution. The  $\alpha$ -chloro atoms are quantitatively titrated with alkali at room temperature. In this connection, there arises some doubt regarding the purity of the II described by Dietrich and co-workers [4], who used treatment with aqueous sodium carbonate and refluxing for 3 h with triethylamine to purify the substance. Unfortunately, the amount of 2-chloroethyl trichloroacetate (V) impurity and the formation of any other products are not indicated in [4].

Compound III is more stable than II. This is in good agreement with the literature data on the greater stability of  $\alpha$ , $\beta$ -dichloroalkyl esters as compared with  $\alpha$ -halo esters [5]. Monochlorinated dioxolane II gives a dehydrochlorination product in reactions with alkoxides and amines and on heating.

## EXPERIMENTAL

The IR spectra at  $600-3600 \text{ cm}^{-1}$  were recorded with a UR-10 spectrometer. 2-Trichloromethyl-1,3-dioxolane (I) was obtained by the method in [6] and had the following physical constants: bp 53-55° (2 mm) and mp 40-41° (mp 40° [6]). The samples were irradiated with an RS-4 quartz lamp.

<u>Chlorination of 2-Trichloromethyl-1,3-dioxolane (I).</u> <u>A</u>. A 38.2-g (0.2 mole) sample of I was dissolved in 200 ml of CCl<sub>4</sub>. The solution was cooled to -10 to  $-13^{\circ}$  and irradiated with UV light while Cl<sub>2</sub> (~ 1.1 mole) was bubbled through it for 2 h. Dry nitrogen was then bubbled through the solution, and the solvent was removed by distillation to give 4.5 g (9%) of III and 34.9 g (77%) of II with bp 56° (2 mm), d<sub>4</sub><sup>20</sup> 1.5960, and n<sub>D</sub><sup>20</sup> 1.4960. Found: C 21.6; H 1.9; Cl 62.5%; MR<sub>D</sub> 41.348. C<sub>4</sub>H<sub>4</sub>Cl<sub>4</sub>O<sub>2</sub>. Calculated: C 21.3; H 1.8; Cl 62.8%; MR<sub>D</sub> 41.176.

<u>B.</u> A 76.4-g (0.4 mole) sample of I was dissolved in 250 ml of  $CCl_4$ , and, under conditions similar to those described above,  $Cl_2$  (~ 2.1 mole) was bubbled through the solution for 5 h. Workup of the mixture gave 5.6 g (6%) of II and 87.1 g (84%) of III with bp 77° (2 mm),  $d_4^{20}$  1.7011, and  $n_D^{20}$  1.5130. Found: C 18.3; H 1.2; Cl 68.4%; MR<sub>D</sub> 45.99. C<sub>4</sub>H<sub>3</sub>Cl<sub>5</sub>O<sub>2</sub>. Calculated: C 18.5; H 1.2; Cl 68.1%; MR<sub>D</sub> 45.98.

The purity of II and III was monitored by GLC with a KhL-4 chromatograph; the stationary phase was polyphenyl ether (15% on Celite-545), the thermostat temperature was 250°, the vaporizer temperature was 300°, l = 4 m, the carrier gas was helium, and v = 2 liter/h. 2-Chloroethyl trichloroacetate obtained by the method in [6] was introduced as the reference compound.

Hydrolysis of 2-Trichloromethyl-4-chloro- and 2-Trichloromethyl-4,5dichloro-1,3-dioxolanes. A. Water (50 ml), 3.5 ml of concentrated HCl, and an alcohol solution of 5 g of 2,4-dinitrophenylhydrazine were added to 1.5 g (0.007 mole) of II, and the mixture was refluxed for 4 h. Workup gave 0.87 g (95%) of glyoxal 2,4-dinitrophenylosazone with mp 308° (mp 309° [7]). Found: N 26.09%.  $C_{15}H_{13}O_2N_8$ . Calculated: N 26.07%. Hydrolysis of 2 g (0.009 mole) of III was carried out under similar conditions to give 4.1 g (90%) of the 2,4-dinitrophenylosazone with mp 308°. Found: N 26.10; 25.97%.

The 2,4-dinitrophenylosazones obtained on hydrolysis of II and III had the same R<sub>f</sub> values (0.44), which coincided with the R<sub>f</sub> value of glyoxal 2,4-dinitrophenylosazone, during chromatography on  $Al_2O_3$  (activity II) in methanol-chloroform (1:9).

<u>B.</u> Compounds II and III were subjected to oxime titration. At room temperature, 22.9% of the carbonyl compound in II (calculated value 22.6%) and 26.9% of the carbonyl compound in III (calculated value 26.5%) were titrated after 30 min.

<u>C.</u> The hydrolysis of II and III was carried out with 0.2 N KOH via the method in [8] in the presence of MethylOrange. At room temperature, 15.5% of the  $\alpha$ -Cl (calculated value 15.7%  $\alpha$ -Cl) in II and 13.01% of the  $\alpha$ -Cl in III (calculated value 13.6%  $\alpha$ -Cl) were titrated.

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