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# CHLORINATION OF 1,3-DIOXOLAN-4-ONES

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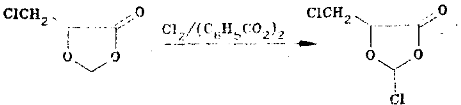
It is shown that the direction of chlorination of 1,3-dioxolan-4-ones in the presence of benzoyl peroxide is determined by the nature of the substituent at the 5-position of the ring. In this case a chloromethyl group, having a —I effect, promotes a selective replacement of hydrogen at the 2-position, while a methyl group mainly causes replacement of hydrogen at the 5-position.

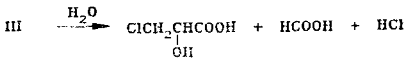
The present work is devoted to the reaction of 1,3-dioxolan-4-ones with chlorine and aims to establish the effect of the substituent at the 5-position of the ring on the direction of chlorination.

5-Methyl- (I) and 5-chloromethyl-1,3-dioxolan-4-one (II) underwent chlorination. Replacement of hydrogen by chlorine proceeds only at an increased temperature (80-100°C) and in the presence of free-radical initiators. In the case of dioxolanone I on chlorination to an increase in weight equal to the replacement of one atom of hydrogen by chlorine, determination of the composition of the reaction mixture was not achieved. In the second case chlorination proceeds selectively and leads to 2-chloro-5-chloromethyl-1,3-dioxolan-4-one (III). This, evidently, can be accounted for by the influence of the substituent with a —I effect, which to a large extent lowers the reactivity of the C—H bond at the 5-position of the ring to attack by an electrophilic chlorine radical.



II III

It was established (GLC) that the compound synthesized was a mixture of cis and trans isomers; it showed thermal stability and was readily distilled, but was unstable on hydrolysis. Among the products of hydrolysis were identified 3-chloro-2-hydroxypropionic, formic, and hydrochloric acids.



$$\text{III} \xrightarrow{H_2O} ClCH_2\underset{OH}{\underset{|}{C}}HCOOH + HCOOH + HCl$$

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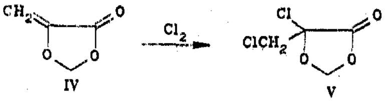
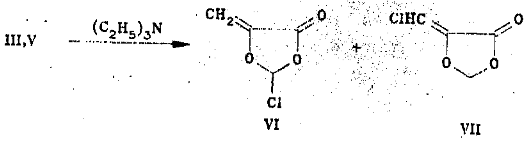
It could be supposed that in the case of dioxolanone I, chlorine would, on the contrary, replace hydrogen at the 5-position, forming a thermally unstable compound. For proof of this hypothesis we chlorinated 5-methylene-1,3-dioxolan-4-one (IV). The reaction proceeded smoothly at 0-5°C. The 5-chloro-5-chloromethyl-1,3-dioxolan-4-one (V) obtained was a substance of low thermal stability, and it was not possible for us to isolate it by vacuum distillation.



The dioxolanones III and V synthesized are isomers, being at the same time both lactones and α-chlorethers. It is well known that such compounds display exceptionally high reactivity in reactions with various nucleophilic reagents. We established that in the presence of triethylamine as a base, in both cases splitting off of hydrogen chloride occurred and 2-chloro-5-methylene-1,3-dioxolan-4-one (VI) and 5-chloromethylene-1,3-dioxolan-4-one (VII), respectively, were obtained in high yield.



The properties of the unsaturated compounds obtained were dependent on the nature of the substituents at the 2- and 5-positions. The first was a mobile, colorless liquid with an odor similar to that of acid chlorides; it could be distilled under vacuum and hydrolyzed with the formation of pyruvic, formic, and hydrochloric acids. The second was a stable, crystalline substance. Their composition and structure were confirmed from the data of elemental analysis and IR spectroscopy.

## EXPERIMENTAL

IR spectra were recorded on a UR-20 instrument using a thin film between KBr plates. Chromatographic analysis was carried out on a Tsvet series chromatograph, with flame ionization detector, and 3% neopentyl glycol succinate on cellite 545 as adsorbent. Dioxolanone I was obtained according to a standard method [1].

2-Chloro-5-chloromethyl-3-dioxolan-4-one (III). Into a reaction vessel fitted with bubbler, thermometer, and reflux condenser with calcium chloride tube were inserted 136.5 g (1 mole) dioxolanone II [2] and 0.0014 g (0.001 wt. %) benzoyl peroxide; and this was heated to 90-95°C. Chlorine dried with sulfuric acid was passed through until there was a gain in weight of 35 g and the mixture was distilled under vacuum. 10 g (7%) initial product was obtained as well as 120 g (75% based on initial reactant) cis,trans-dioxolanone III, mp 57-58°C (1.33 hPa), $n_D^{20}$ 1.4680, $d_4^{20}$ 1.4740. IR spectrum: 1831 $cm^{-1}$ (C=O). Found: C 28.0; H 2.3; Cl 41.7%; MW 169. $C_4H_4Cl_2O_3$. Calculated: C 27.5; H 2.3; Cl 42.0%; MW 171.

Hydrolysis of dioxolanone III was carried out on a boiling water bath, and after the suspension was dissolved vacuum evaporation was carried out at 50°C. The residue was 3-chloro-2-hydroxypropionic acid, mp 77-78°C (from an ether—chloroform mixture), according to [3]: mp 78-79°C. A test mixture with a known sample melted without depression.

2-Chloro-5-methylene-1,3-dioxolan-4-one (VI). Into a reaction vessel fitted with stirrer, thermometer, dropping funnel, and reflux condenser with calcium chloride tube were inserted 20 g (0.118 mole) dioxolanone III, 50 ml ether, and free-radical polymerization inhibitors (p-methoxyphenol and phenothiazine); and at −5°C over the course of 0.5 h was added dropwise a solution of 12 g (0.119 mole) triethylamine in 40 ml ether. Stirring was continued for a further 2 h at the temperature indicated. The triethylamine salt was filtered off, the solvent was removed, and the residue was distilled under vacuum. 12.5 g (77%) was obtained, mp 40°C (5.32 hPa), $n_D^{20}$ 1.4724, $d_4^{20}$ 1.4579. IR spectrum: 1830 $cm^{-1}$ (C=O), 1680 $cm^{-1}$ (C=C). Found: C 35.5; H 2.3; Cl 26.4%; MW 135.0. $C_4H_3ClO_3$. Calculated: C 35.7; H 2.2; Cl 26.4%; MW 134.5. The product was easily hydrolyzed by water, undergoing quantitative conversion to pyruvic acid (determined by polarography), formic and hydrochloric acids.

5-Chloro-5-chloromethyl-3,3-dioxolan-4-one (V). Into a reaction vessel with stirrer, thermometer, bubbler, and calcium chloride tube were inserted 10 g (0.1 mole) of compound IV [4], 20 ml carbon tetrachloride, and free-radical polymerization inhibitors. At −5°C 7.5 g (0.107 mole) chlorine was passed in, and the mixture was maintained with stirring at room temperature for 4 h. Completion of reaction was determined chromatographically according to the disappearance of initial dioxolanone IV. The solvent was removed under vacuum, and 16.3 g (95%) crude dioxolanone V was obtained, which on heating decomposed with the formation of tarry products. In a subsequent synthesis it was used without purification.

5-Chloromethylene-1,3-dioxolan-4-one (VII). Into a reaction vessel with stirrer, dropping funnel, thermometer, and calcium chloride tube were inserted 10.6 g (0.105 mole) triethylamine and 20 ml benzene. At 20-25°C a solution of 17.1 g (0.1 mole) dioxolanone V in 30 ml benzene was further added. The mixture was maintained for 5 h; then triethylamine hydrochloride salt was filtered off, and the filtrate was washed successively with 5% solutions of hydrochloric acid and sodium carbonate, and then with water. The solvent was removed, and 9.5 g (71%) was obtained, mp 7.52-73.0°C (from an ether—n-hexane mixture in the presence of grade A activated carbon). IR spectrum: 1817, 1805 $cm^{-1}$ (C=O), 1680 $cm^{-1}$ (C=C). Found: C 35.9; H 2.3; Cl 26.5%; MW 138.5. $C_4H_3ClO_3$. Calculated: C 35.7; H 2.2; Cl 26.4%; MW 134.5.

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# REACTION OF 2-METHYL-5,6-DIHYDRO-2H-PYRAN WITH DICHLOROCARBENE

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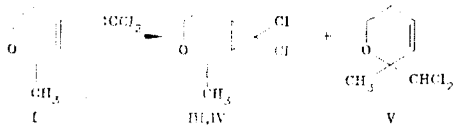
543.422:541.634

Upon treatment of 2-methyl-5,6-dihydro-2H-pyran with dichlorocarbene there are formed products of addition to the double bond and insertion at the C—H bond giving cis- and trans-7,7-dichloro-2-methyl-3-oxabicyclo[4.1.0]heptane and 2-dichloromethyl-2-methyl-5,6-dihydro-2H-pyran.

The reaction of dihalocarbenes with alkenes usually yields the corresponding adduct via addition to the double bond (including 5- and 6-membered cyclic vinyl ethers [1, 2]).

We have found that three compounds are formed from 2-methyl-5,6-dihydro-2H-pyran (I) in 37% overall yield: cis- (III) and trans- (IV) 7,7-dichloro-2-methyl-3-oxabicyclo[4.1.0]-heptane and 2-dichloromethyl-5,6-dihydro-2H-pyran (V) in the ratio 1.0:5.7:3.3.



It can be proposed that the C—H insertion product appearing together with the adducts III and IV is due to the allyl structure of I, the same course of reaction having earlier been observed in the case of 2,5-dihydrofuran [3].

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