SYNTHESIS AND PROPERTIES OF 5-METHYLENE-1,3-DIOXOLAN-4-ONES

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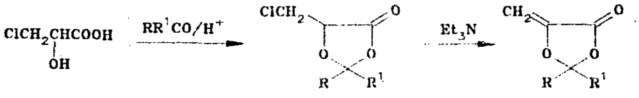
UDC 547.729.7.07

A general method, which consists in the dehydroxypropanoic of 5-chloromethyl-1,3-dioxolan-4-ones, is proposed for the synthesis of 5-methylene-1,3-dioxolan-4-ones. With respect to their structure, the synthesized compounds are simultaneously derivatives of acrylic acid and vinyl ethers.

5-Methylene-1,3-dioxolan-4-ones constitutes a group of unsaturated compounds, the exocyclic double bond of which is simultaneously in conjugation with a carbonyl group and bonded to an enol oxygen atom.

In their synthesis [1] we started from 3-chloro-2-hydroxypropionic acid, which, in analogy with the known cyclization of 2-hydroxy carboxylic acids [2, 3], reacted readily with aldehydes and ketones to give 5-chlormethyl-1,3-dioxolan-4-ones (Ia-f).



Ia-f IIa-f

I, II a,b,d,f R=H, c R=CH_3, e R+R^1=$(CH_2)_5$; a R^1=H, b,c R^1=CH_3, d R^1=CCl_3. f R^1=C_6H_5

In the reaction we used 60-65% aqueous solutions of 3-chloro-2-hydroxypropanoic acid [4] with sulfuric acid as the catalyst. The water formed during the synthesis and introduced with the acid was removed by azeotropic distillation with benzene.

As a result, we synthesized 5-chloromethyl-1,3-dioxolan-4-one (Ia), 2-methyl- (Ib), 2,2-dimethyl- (Ic), and 2-trichloromethyl-5-chloromethyl-1,3-dioxolan-4-one (Id), cyclohexane-spiro-2'-(5'-chloromethyl-1',3'-dioxolan-4'-one) (Ie), and 2-phenyl-5-chloromethyl-1,3-dioxolan-4-one (If). Depending on the character of the substituent in the 2 position, these compounds are either colorless, mobile, vacuum-distillable liquids or stable crystalline substances, the structures of which were proved by the results of elementary analysis and IR and PMR spectroscopic data (Tables 1 and 2).

Dioxolanones lb,f were obtained in the form of mixtures of cis and trans isomers, and dioxolane Id is the trans isomer. The percentages of the isomers in the mixtures were determined with respect to the integral intensities of the PMR signals (Table 2). These results are in agreement with the data in [3, 5]. In contrast to 2,5-dialkyl-substituted dioxolanones [6, 7], these isomers can be separated by gas—liquid chromatography (GLC). The assignment of the peaks on the chromotograms was made on the basis of the PMR spectra. The percentages of the cis and trans isomers were determined from the areas of the peaks in the case of dioxolanone Ib. The results obtained by these two methods were close to one another.

With respect to their structures, dioxolanones Ia-f are simultaneously acetals and lactones. For their dehydrochlorination one therefore cannot use alkalis, ammonia, and primary and secondary amines, which give rise to cleavage of the ring [2]. On the other hand, splitting out of hydrogen chloride proceeded smoothly in the presence of triethylamine as the base. The reaction was usually carried out in an inert organic solvent in the presence of inhibitors of free-radical polymerization. The selection of the temperature conditions for the dehydrochlorination depends to a pronounced degree on the nature of the substituent in the 2 position of the ring. For example, unsaturated dioxolanone Ia reacts with the amine at 80°C, derivatives Ib, c, e with electron-donor substituents react only at 100°C or higher, and dioxolanone Id with an electron-acceptor substituent is dehydrochlorinated smoothly at ~0°C.

Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1316-1318, October, 1985. Original article submitted October 2, 1984.

0009-3122/85/2110-1077$09.50

TABLE 1. Characteristics of Dioxolanones Ia-f

Compound*	bp (hPa) or mp, °C	n_D^{20}	d_4^{20}	IR spectrum, cm⁻¹ (C = O)	Found, %			Empirical formula	Calc., %			Yield, %
					C	H	Cl		C	H	Cl	
Ia	76 (2,00)	1,4622	1,4221	1812	35,4	4,1	25,8	$C_4H_5ClO_3$	35,2	3,7	26,0	87
Ib	59 (1,33)	1,4510	1,3028	1810	39,2	4,5	23,2	$C_5H_7ClO_3$	39,6	4,6	23,6	80
Ic	58—59			1810	43,6	5,5	21,6	$C_6H_9ClO_3$	43,8	5,5	21,6	39
Id	50—51			1820	23,7	1,6	55,6	$C_5H_4Cl_4O_3$	23,6	1,6	55,9	75
Ie	124 (5,30)	1,4842	1,2049	1812	52,5	6,3	17,3	$C_9H_{13}ClO_3$	52,8	6,3	17,3	88
If	55—56			1815	56,2	4,3	17,1	$C_{10}H_9ClO_3$	56,4	4,2	16,7	29

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*Compounds Ic, d, f were recrystallized from ether—n-hexane with cooling.

TABLE 2. PMR Spectra of Dioxolanones Ia-d, f

Compound	δ, ppm				J (cis; trans), Hz	Isomer ratio (cis/trans), %
	2-R	2-R¹	CH_2Cl	5-H		
Ia	5,50 s	5,61 d	3,83 d	4,50 dt	$J_{5\text{-H}, CH_2Cl}=3{,}3$; $J_{2\text{-H}, 5\text{-H}}=1{,}0$	
cis-Ib	5,77 dq	1,60 d	3,84 dd	4,65 dt	$J_{5\text{-H}, CH_2Cl}=(3{,}5; 3{,}6)$; $J_{2\text{-H}, CH_3}=(4{,}9; 5{,}0)$; $J_{2\text{-H}, 5\text{-H}}=(1{,}1; 1{,}2)$	60/40
trans-Ib	6,01 dq	1,53 d	3,87 dd	4,73 dt		
Ic	1,56 s	1,65 s	3,75 d	4,63 t	$J_{5\text{-H}, CH_2Cl}=3{,}4$	
Id	5,95 d		3,89 d	4,95 dt	$J_{5\text{-H}, CH_2Cl}=2{,}8$; $J_{2\text{-H}, 5\text{-H}}=1{,}4$	0/100
cis-If	6,35 s	7,65—7,25 m	3,86 d	4,67 t	$J_{5\text{-H}, CH_2Cl}=(3{,}7; 3{,}8)$	67/33
trans-If	6,70 s		3,87 d	4,76 t		

The formation of IIa-f evidently proceeds via an ElcB mechanism, which is the standard mechanism in the formation of α,β-unsaturated carbonyl compounds [8]. 5-Methylene-1,3-dioxolan-4-one (IIa), 2-methyl- (IIb), 2,2-dimethyl- (IIc), and 2-trichloromethyl-5-methylene-1,3-dioxolan-4-one (IId), cyclohexanespiro-2'-(5'-methylene-1,3'-dioxolan-4'-one) (IIe), and 2-phenyl-5-methylene-1,3-dioxolan-4-one (IIf) were synthesized.

The synthesized compounds are either colorless vacuum-distillable liquids or stable crystalline substances, the structures of which were proved by the results of elementary analysis and IR spectroscopic data (Table 3).

EXPERIMENTAL

The IR spectra of the liquid substances in the form of thin films between KBr plates and of KBr pellets of the solid substances were recorded with a UR-20 spectrometer. The PMR spectra of 20% solutions of the compounds in CCl_4 were recorded with a BS-478C spectrometer (80 MHz) with hexamethyldisiloxane (HMDS) as the internal standard. Chromatography was carried out with a Tsvet chromatograph with a flame-ionization detector; the sorbent was 3% neopentyl glycol succinate on Celite-545, the column temperature was 100°C, and the carrier-gas (nitrogen) flow rate was 33 ml/min.

5-Chloromethyl-1,3-dioxolan-4-one (Ia). A reactor equipped with a stirrer, a reflux condenser, and a Dean—Stark trap was charged with 211 g (1 mole) of a 59% aqueous solution of 3-chloro-2-hydroxypropanoic acid, 75 g (2.5 moles) of paraformaldehyde, 5 g of sulfuric acid, and 270 ml of benzene, and the mixture was heated to the boiling point. The water was removed by azeotropic distillation with benzene, and the benzene solution was washed successively with 50 ml of water, 60 ml of a 5% solution of sodium bicarbonate, and 50 ml of water. The solvent was removed by distillation at reduced pressure at 50-60°C, and the residue was distilled in vacuo.

Dioxolanones Ib-f (Table 1) were similarly synthesized. According to the GLC data, dioxolanone Ib contained 61% of the cis isomer (t_R = 11.8 min) and 39% of the trans isomer (t_R = 10.1 min).

TABLE 3. Characteristics of Dioxolanones IIa-f

Compound*	bp (hPa) or mp, °C	n_D^{20}	d_4^{20}	IR spectrum, cm⁻¹		Found, %		Empirical formula	Calc., %		Yield, %
				(C=O)	(C=C)	C	H(Cl)		C	H(Cl)	
IIa	38,0 (5,3) 20,0—20,5	1,4638	1,2640	1820 1804	1670	48,1	4,2	$C_4H_4O_3$	48,0	4,0	80
IIb	44 (8,0)	1,4528	1,1400	1809	1668	52,4	5,1	$C_5H_6O_3$	52,6	5,3	75
IIc	44 (11,3)	1,4380	1,0860	1809	1671	56,6	6,5	$C_6H_8O_3$	56,2	6,2	71
IId	42,0—42,5			1830	1680	27.7	1,5 (48,5)	$C_5H_3Cl_3O_3$	27,6	1,4 (48,9)	60
IIe	63 (2,6)	1,4842	1,1172	1809	1670	64,2	7,1	$C_9H_{12}O_3$	64,4	7,1	63
IIf	90 (2,6) 33—34			1812	1671	68,2	4,5	$C_{10}H_8O_3$	68,7	4,2	60

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*Compounds IIa, d, f were recrystallized from ether–n-hexane with cooling.

5-Methylene-1,3-dioxolan-4-one (IIa). A reactor equipped with a stirrer, a dropping funnel, a thermometer, and a reflux condenser fitted with a calcium chloride drying tube was charged with 75.8 g (0.75 mole) of triethylamine, 120 ml of benzene, 0.1 g of p-methoxyphenol, and 0.1 g of phenothiazine, and the mixture was heated to the boiling point and treated dropwise with stirring in the course of 1 h with 68.3 g (0.5 mole) of dioxolanone Ia in 50 ml of benzene. The end of the reaction was monitored by GLC from the disappearance of the chlorine-containing starting compound (t_R = 13.2 min). The mixture was cooled, the triethylamine hydrochloride was removed by filtration, and the filtrate was washed successively with 30 ml of 5% hydrochloric acid solution, 30 ml of 5% sodium bicarbonate solution, and 25 ml of water and dried with magnesium sulfate and potassium carbonate. The benzene was removed at reduced pressure in a stream of an inert gas, and the residue was distilled in vacuo. PMR spectrum: 5.61 ($2H_c$, $-OCH_2O-$), 5.01 ($1H_a$, d, J = 2.55 Hz, $>C{=}CH_aH_b$), and 4.76 ppm ($1H_b$, d, $>C{=}CH_aH_b$).

Dioxolanones IIb, c, e, f were similarly synthesized; IId was obtained in ether at –5°C (Table 3).

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