REACTION OF 2-SUBSTITUTED 4,4-DIMETHYL-5-METHYLENE-1,3-DIOXOLANES WITH DICHLOROCARBENE AND CERTAIN TRANSFORMATIONS OF ADDUCTS OBTAINED

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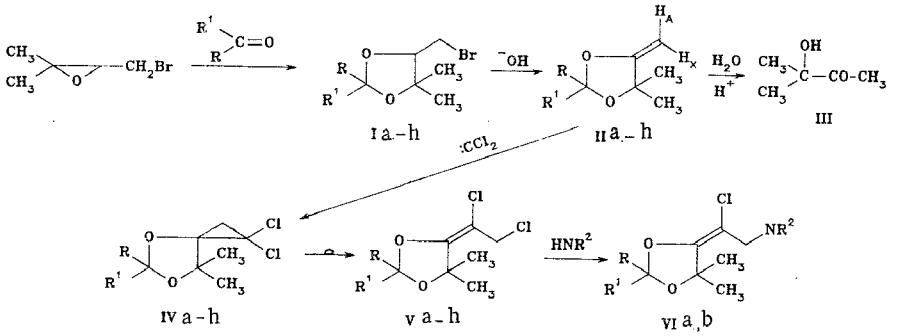
A series of derivatives of 4,4-dimethyl-5-methylene-1,3-dioxolane has been synthesized, and their reaction with dichlorocarbene, obtained under interphase catalysis conditions, has been studied. The adducts obtained undergo thermal isomerization into dichloroethylidene derivatives.

In reaction with acid reagents, unsaturated dioxolanes undergo recyclization into furan derivatives [1], enter addition reactions at the double bond [2], or are fragmented into acyclic compounds [3].

It was interesting to recyclize 2-substituted 4,4-dimethyl-5-methylene-1,3-dioxolanes II (Table 1), synthesized from the corresponding 5-(bromomethyl)dioxolanes I (Table 2), which is readily obtained from the available 1-bromo-3-methyl-2,3-epoxybutanes [4] and carbonyl compounds. The structure of dioxolanes I and II was confirmed by PMR spectroscopy (Tables 1 and 2). These data show that in the case of asymmetric carbonyl compounds, two isomeric diolanes I are formed, as shown by the presence of two sets of certain signals in the PMR spectra of compounds Ib, e-h.

Studies carried out showed that under the conditions described in [1], compounds II do not recyclize. It was interesting to clarify whether this is due to a higher tendency of dioxolanes II to undergo other types of reactions [2, 3] than recyclization.



I, II, IV, V a R=R¹=CH₃; b R=CH₃, R¹=C₂H₅; c R—R¹=—(CH₂)₄; d R—R¹=—(CH₂)₅; e R=H, R¹=CH₃; f R=H, R¹=*i*-C₃H₇; g R=H, R¹=C₃H₇; h R=H, R¹=C₆H₅; VI a R=R¹=R²=CH₃; b R=R¹=CH₃, R²—R²=—(CH₂)₅—

We found that, in fact, the hydrolysis of dioxolane IIa leads to a ketoalcohol III (GLC) and in the reaction of dioxolanes IIa-h with dichlorocarbene, obtained under interphase catalysis conditions [5], 5-(2,2-dichlorocyclopropyl)-1,3-dioxolanes IVa-h are formed (Table 3). The structure of these compounds is confirmed by the presence of signals in the region of δ 1.5-1.7 ppm in the PMR spectrum, which are characteristic of an AB type spin system with J_{AB} = 9.3 Hz (the dichlorocyclopropane fragment). It should also be noted that dichlorides IVb, e-h are formed in the form of a mixture of two isomers (Table 3).

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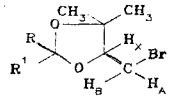
TABLE 1. 5-Methylene-1,3-dioxolanes II

Compound	Bp, °C (650 mm)	n_D^{20}	d_4^{20}	δ, ppm (J, Hz)					Found, %		Empirical formula	Calculated %		Yield, %
				4-CH_3	H_A[a]	H_X[a]	R	R'	C	H		C	H	
IIa[b]	112—114	1,4150	0,8985	1,38	3,64	4,07	1,35	1,35	67,4	9,8	$C_8H_{14}O_2$	67,6	9,9	75[c]
IIb	138—140	1,4260	0,9042	1,38	3,69	4,14	1,41	0,9 t (CH_3, 7,2); 1,66 q (CH_2)	69,2	10,1	$C_9H_{16}O_2$	69,2	10,3	78
IIc[b]	171—173	1,4580	0,9718	1,36	3,65	4,07	1,75 sh $(CH_2)_4$		71,4	9,4	$C_{10}H_{16}O_2$	71,4	9,5	82
IId	190—193	1,4665	0,9797	1,37	3,68	4,13	1,60 sh $(CH_2)_5$		72,2	9,7	$C_{11}H_{18}O_2$	72,5	9,9	71
IIe	106—109	1,4180	0,9124	1,30; 1,40	3,66	4,08	5,34 q (4,7)	1,36	65,8	9,2	$C_7H_{12}O_2$	65,6	9,4	67
IIf	142—145	1,4260	0,9052	1,28; 1,37	3,62	4,04	5,17 t (4,0)	0,95 (CH_3, 7,2); ~1,5 sh (CH_2CH_2)	69,1	10,1	$C_9H_{16}O_2$	69,2	10,3	85
IIg	150—152	1,4265	0,9099	1,31; 1,39	3,64	4,08	4,97 d (4,1)	0,94 d (CH_3, 6,8); 1,3—2,0 m (CH)	68,4	10,1	$C_9H_{16}O_2$	69,2	10,3	82
IIh	114—117[d]	1,5080	1,0423	1,40; 1,45	3,76	4,22	6,06	7,2—7,5	75,4	7,0	$C_{12}H_{14}O_2$	75,8	7,4	59

[a] J_{AX} = 2.5 Hz. [b] Also described in [3], but differs somewhat in n_D value. [c] From chloride yield 77%. [d] At 14 mm.

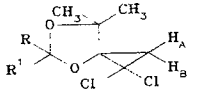
TABLE 2



Compound	Bp, °C (pressure, mm)	n_D^{20}	d_4^{20}	Ratio between isomers, %	δ, ppm (J, Hz)						Found, %			Empirical formula	Calculated, %			Yield, %
					4-CH_3	H_A[a]	H_B[a]	H_X[a]	R	R^1	C	H	Br		C	H	Br	
Ia	72—74 (13)[b]	1,4600	1,2859	—	1,14; 1,34	3,30	3,45	3,97	1,30	1,36	42,9	6,7	35,7	$C_8H_{15}BrO_2$	43,1	6,7	35,9	69; 89 c
Ib	82—85 (12)	1,4670	1,2602	50	1,11; 1,35	3,27	3,36	3,92	1,25	0,89 t (CH_3); 1,4—2,0 m (CH_2)	45,7	7,0	33,6	$C_8H_{15}BrO_2$	45,6	7,2	33,8	54; 60 c
				50	1,15; 1,37	3,27	3,36	4,06	1,29									
Ic	109—112 (12)	1,4935	1,3275	—	1,14; 1,34	3,27	3,40	3,87	1,70 sh		48,4	6,8	32,0	$C_{10}H_{17}BrO_2$	48,2	6,8	32,1	57
Id	130—132 (13)	1,4910	1,2667	—	1,13; 1,35	3,28	3,39	3,98	1,53 sh		50,5	7,1	30,4	$C_{11}H_{19}BrO_2$	50,2	7,2	30,4	47
Ie	70—72 (13)	1,4695	1,3456	65	1,19; 1,34	3,29	3,49	3,88	5,08 q	1,27 d (4,8)	39,9	6,2	38,0	$C_7H_{13}BrO_2$	40,1	6,2	38,3	54
				35	1,21; 1,39	3,26	3,50	3,87	5,21 q	1,29 d (4,8)								
If	91—93 (13)	1,4620	1,2449	60	1,19; 1,32	3,24	3,34	3,85	4,93 t (4,5)	0,94 t (CH_3);	45,9	7,3	33,5	$C_9H_{17}BrO_2$	45,6	7,2	33,8	49
				40	1,19; 1,40	3,29	3,39	3,82	5,06 t (4,5)	1,5 sh (CH_2); 0,98 t (CH_3)								
Ig	100—102 (14)	1,4640	1,2513	56	1,19; 1,33	3,1—3,7		3,85	4,74 d (4,5)	0,92 d (7,5)	45,3	7,2	33,6	$C_9H_{17}BrO_2$	45,6	7,2	33,8	52
				44	1,19; 1,39	3,1—3,7		3,95	4,84 d (4,5)									
Ih	124—126 (2)	1,5342	1,3468	55	1,18; 1,34	3,22	3,36	3,91	5,80 q	7,2—7,5 m	53,5	5,6	29,2	$C_{12}H_{15}BrO_2$	53,1	5,5	29,5	45
				45	1,18; 1,46	3,25	3,39	3,98	5,93									

[a] J_{AB} = 10.5, J_{AX} = 7.6, J_{BX} = 6.0 Hz. [b] Described also in [3], but differs somewhat in n_D value. [c] Catalyst $CuSO_4$.

TABLE 3



Compound	Bp, °C (pressure, mm)	n_D^{20}	d_4^{20}	Ratio between isomers, %	δ, ppm (J, Hz)				Found, %			Empirical formula	Calculated, %			Yield, %
					4-CH_3	H_A, H_B[a]	R	R^1	C	H	Cl		C	H	Cl	
IVa	82—83 (12)	1,4605	1,1796	—	1,24; 1,49	1,59; 1,68	1,35, 1,52		47,7	6,2	31,3	$C_9H_{14}Cl_2O_2$	48,0	6,2	31,6	88
IVb	94—96 (10)	1,4660	1,1605	50	1,22; 1,55	1,50; 1,56	1,31	0,89 m (CH_3); 1,5 m (CH_2)	50,5	6,5	29,4	$C_{10}H_{16}Cl_2O_2$	50,2	6,7	29,7	82
				50	1,24	1,67; 1,67	1,43	0,99 m (CH_3); 1,5 m (CH_2)								
IVc	76—78 (2)	1,4830	1,2026	—	1,25; 1,53	1,61; 1,65	1,3—1,9 m $(CH_2)_4$		52,5	6,1	29,0	$C_{11}H_{16}Cl_2O_2$	52,6	6,4	29,3	80
IVd	88—90 (2)	1,4885	1,1854	—	1,25; 1,53	1,59; 1,66	~1,6 sh $(CH_2)_5$		54,2	6,4	26,5	$C_{12}H_{18}Cl_2O_2$	54,3	6,8	26,8	52
IVe	78—80 (12)	1,4640	1,2073	60	1,20; 1,50	1,57; 1,61	5,14 q (4,9)	1,33 d	45,4	5,6	33,4	$C_8H_{12}Cl_2O_2$	45,5	5,7	33,7	65
				40	1,43; 1,56	1,57; 1,61	5,46 q (4,9)	1,35 d								
IVf	99—101 (12)	1,4630	1,1501	50	1,20; 1,49	1,56; 1,60	4,95 t (4,2)	0,95 m (CH_3)	50,4	6,4	29,9	$C_{10}H_{16}Cl_2O_2$	50,2	6,7	29,7	72
				50	1,26; 1,55	1,56; 1,60	5,27									
IVg	103—106 (12)	1,4650	1,1533	50	1,22; 1,49	1,48; 1,52	4,71 d (4,3)	0,91 d (7,1)	50,0	6,4	29,9	$C_{10}H_{16}Cl_2O_2$	50,2	6,6	29,7	75
				50	1,26; 1,56	1,56; 1,60	5,08	0,97								
IVh	119—123 (2)[b]			50	1,24; 1,55	1,57; 1,62	5,78 s	7,3 m	56,9	5,1	26,1	$C_{12}H_{14}Cl_2O_2$	57,1	5,13	26,0	75
				50	1,30; 1,64	1,59; 1,65	6,14 s	7,3 m								

[a] J_{AB} = 9.3 Hz. [b] Mp 55-58°C.

TABLE 4. 5-(1,2-Dichloroethylidene)-1,3-dioxolanes V

Compound	Bp, °C (pressure, mm)	n_D^{20}	d_4^{20}	Ratio, between isomers, %	δ, ppm (J, Hz)				Found, %			Empirical formula	Calculated, %			Yield, %
					4-CH_3	CH_2Cl	R	R'	C	H	Cl		C	H	Cl	
Va	95—98 (12)	1,4765	1,1647	—	1,58	4,35	1,48	1,48	48,2	6,1	31,9	$C_9H_{14}Cl_2O_2$	48,0	6,2	31,6	91
Vb	117—120 (16)	1,4789	1,1462	65	1,58	4,36	1,43	0,93 t (CH_3, 7,2)	50,1	6,7	29,4	$C_{10}H_{16}Cl_2O_2$	50,2	6,7	29,7	87
				35	1,59	4,32	1,45	1,75 m (CH_2)								
Vc	133—136 (13)	1,4980	1,1944	—	1,56	4,38	1,83 sh (CH_2)$_4$		52,7	6,5	29,1	$C_{11}H_{16}Cl_2O_2$	52,6	6,3	29,3	88
Vd	100—102 (2)	1,5010	1,1782	—	1,57	4,34	1,65 sh (CH_2)$_5$		54,1	6,4	26,5	$C_{12}H_{18}Cl_2O_2$	54,3	6,8	26,8	84
Ve	94—97 (12)	1,4790	1,1997	75	1,47; 1,62	4,29[a]; 4,31	5,41 q	1,45 d (4,5)	45,4	5,6	33,4	$C_8H_{12}Cl_2O_2$	45,5	5,7	33,6	82
				25	1,47; 1,62	4,27[a]; 4,28	5,48 q	1,47 d (4,5)								
Vf	113—117 (12)	1,4768	1,1408	—	1,47; 1,60	4,30[a]; 4,32	5,30 t (4,1)	0,97 m(CH_3); ~1,5 m (CH_2CH_2)	49,9	6,8	29,7	$C_{10}H_{16}Cl_2O_2$	50,2	6,7	29,7	84
Vg	123—126 (13)	1,4780	1,1469	—	1,49; 1,63	4,37	5,14 d (4,7)	0,98 d (CH_3; 6,5); 1,4—2,1 m(CH)	49,9	6,6	29,5	$C_{10}H_{16}Cl_2O_2$	50,2	6,7	29,7	88
Vh	131—135 (2)[b]				1,57	4,28	6,11 s	7,37	57,4	5,3	25,9	$C_{13}H_{14}Cl_2O_2$	57,1	5,1	26,0	70

[a]Type AB system, J_{AB} = 12.0 Hz. [b]Crystallizes, forming hygroscopic crystals.

On transition to higher dioxolanes II, not only dichlorocyclopropane derivatives are formed, but also the isomeric compounds V. An analysis of the IR and PMR spectra indicates that compounds Va-h are products of thermal isomerization of dichlorocyclopropyl derivatives. Further studies showed that compounds IV can isomerize completely into dichlorides V (Table 4) when heated to 80-90°C.

The allyl chlorine atom in dichlorides V has an appreciable reactivity, and is readily replaced by secondary amines. According to the PMR data, the amino derivatives VIa, b consist of a mixture of cis,trans-isomers in a ratio of 1:5. It should be noted that in the PMR spectra of the initial chloride Va, the second isomer is not observed.

EXPERIMENTAL

The PMR spectra were obtained on the Perkin-Elmer R-12B spectrometer (60 MHz) in CCl_4, with HMDS as internal standard. The purity and identity of the products synthesized were determined by the GLC method on the LKhM-8MD apparatus on a column (200 × 3 mm and 300 × 3 mm) with 5% SE-30 on N-AW-HMDS Chromaton; the flow rate of the carrier gas (helium) was 40-60 ml/min; temperature 120-180°C.

5-Bromomethyl-1,3-dioxolanes I (Table 2). A. A mixture of 100 mmoles of 1-bromo(chloro)-3-methyl-2,3-epoxybutane, 300 mmoles of a ketone, and 10% (with respect to the weight of the halide) of boron trifluoride ethereate was boiled for 8-12 h. It was then treated by a solution of sodium carbonate and extracted with ether; the extract was dried over magnesium sulfate and distilled in vacuo.

For compounds Ie-h, 120 mmoles of aldehyde are used.

5-Chloromethyl-2,2,4,4-tetramethyl-1,3-dioxolane was obtained by the same procedure. Yield 80%. Bp 55-57°C (12 mm); n_D^{20} 1.4395; d_4^{20} 1.0443. Found, %: C 53.6; H 8.7; Cl 19.5. $C_8H_{15}ClO_2$. Calculated, %: C 53.8; H 8.4; Cl 19.9.

B. A mixture of 50 mmoles of 1-bromo(chloro)-3-methyl-2,3-epoxybutane, 60 ml of a ketone, and 4.1 g of anhydrous copper sulfate is stirred for 3 h at 55-60°C. The reaction mixture is filtered and distilled in vacuo. Dioxolanes Ia, b were obtained by this method.

4,4-Dimethyl-5-methylene-1,3-dioxolanes IIa-h (Table 1). A 50 mmole-portion of bromide I is added dropwise in the course of 30 min, with stirring, at 60-70°C, to an alcoholate obtained from 125 mmoles of diethylene glycol and 100 mmoles of sodium. The mixture is then stirred for another 3 h, and the dehydrobromination product is distilled from the reaction mixture. IR spectra: 1675-1682 (C=C); 3128-3132 cm^{-1} (=CH_2).

1,3-Dioxolane-4-spirocyclopropanes IV (Table 3). A 100-mmole portion of chloroform is added dropwise, with stirring, to a mixture of 50 mmoles of of dioxolanes II, 24 ml of a 50% solution of sodium hydroxide, and catalytic amounts of TEBA, while the reaction temperature of the mixture is maintained at 30-35°C. The mixture is stirred at room temperature for another 2-3 h and extracted with ether; the extract is dried over magnesium sulfate, and distilled.

5-(1,2-Dichloroethylidene)-1,3-dioxolanes (Va-h). Compounds IVa-h are boiled for 1 h in an equal volume of benzene, and then benzene is distilled off, and the dichlorides Va-h are isolated by distillation (Table 4). IR spectra: 1662-1669 cm^{-1} (C=C).

2,2,4,4-Tetramethyl-5-(1-chloro-2-piperidinoethylidene)-1,3-dioxolane (VIb). An 11.3-g (50 mmoles) portion of dichloride Va is added dropwise and slowly, at room temperature, to 8.5 g (100 mmoles) of piperidine in 30 ml of dry benzene. The mixture is stirred for another 5-6 h at 75-80°C, the salt that precipitates is filtered, and the filtrate is distilled in vacuo. Yield 10.9 g (80%) of amine VIb, bp 146-147°C (13 mm); n_D^{20} 1.4810, d_4^{20} 1.0520. PMR spectrum: 1.39 (s, 2-CH_3); 1.54 (s, 4-CH_3); 2.28-2.48 (4H, m); 1.43-1.49 (6H, m); 3.15 ppm (s, CH_2). IR spectrum: 1676 cm^{-1} (C=C). Found, %: 61.2; H 8.8; N 5.5. $C_{14}H_{24}ClNO_2$. Calculated, %: C 61.4; H 8.8; N 5.1.

2,2,4,4-Tetramethyl-5-(1-chloro-2-dimethylaminoethylidene)-1,3-dioxolane (VIa) is obtained by passing dry dimethylamine at −30°C into an ethereal solution of chloride Va. Yield 84%, bp 101-104°C (13 mm); n_D^{20} 1.4608, d_4^{20} 1.0269; PMR spectrum: 1.41 (s, 2-CH_3), 1.55 (s, 4-CH_3); 2.20 [δ, $N(CH_3)_2$]; 3.13 ppm (s, CH_2); IR spectrum: 1670 cm^{-1} (C=C). Found, %: C 56.5; H 8.4; Cl 15.5; N 5.6. $C_{11}H_{20}ClNO_2$. Calculated, %: C 56.5; H 8.6; Cl 15.2; N 6.0.

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THE LIQUID-PHASE FREE RADICAL ISOMERIZATION OF CYCLIC DIMETHYLFORMAMIDE ACETALS

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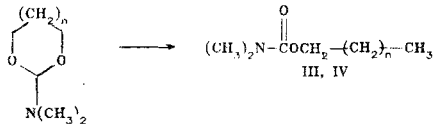
In the presence of tert-butyl peroxide, 2-dimethylamino-1,3-dioxacyclanes are converted to esters of dimethylcarbamic acid. The reaction is described by a kinetic equation for an unbranched chain reaction with quadratic chain termination. The five-membered heterocycle is more reactive than the six-membered heterocycle. The predominant site for free radical attack is the methine group adjacent to the three heteroatoms.

In our previous work [1-3], we showed that cyclic acetals of aliphatic aldehydes are converted in the presence of free radical donors to the isomer esters. Under analogous conditions, the corresponding carbonates and their derivatives are formed from 2-alkoxy-1,3-dioxacyclanes and their analogs [4, 5]. In order to investigate the effect of ring size and the nature of substituents on this reaction, we studied the kinetics of the liquid-phase radical isomerization of cyclic acetals of dimethylformamide induced by tert-butyl peroxide (TBP).

2-Dimethylamino-1,3-dioxacyclanes I and II are converted to the isomeric dimethylcarbamate esters III and IV with an initial rate V_{ef}. The $V_{ef}/\sqrt{V_{TBA}}$ (V_{TBA} is the rate of formation of tert-butyl alcohol in the system which reflects the initiation rate) remains satisfactorily invariant in the PTB concentration range from 0.05 to 0.5 mole/liter (Table 1). Hence, esters III and IV are formed by an unbranched radical chain mechanism with quadratic chain termination



I, II — I, III n= 0; II, IV n= 1

The value for V_{ef} increases linearly with increasing substrate concentration, while the rate of formation of tert-butyl alcohol (V_{TBA}) remains constant (Fig. 1). This linear increase indicates the participation of one acetal molecule in the rate-limiting step of the isomerization. The invariance of V_{TBA} indicates that all the tert-butoxyl radicals are completely consumed in the hydrogen abstraction step at acetal concentrations greater than 2.0 mole/liter. The lines giving the dependence of V_{ef} on the substrate concentration passes through the origin. Thus the rearrangement of the cyclic radical to a linear radical is not the slow step in the ester formation. These experimental results and our previous data [1, 4] indicate that acetals I and II isomerize according to our previously proposed mechanism [1]:

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