TETRAFLUOROBORIC ACID – A NEW CATALYST FOR THE SYNTHESIS OF 1,3-DIOXOLANES. PREPARATION OF HYDROXYACETONE

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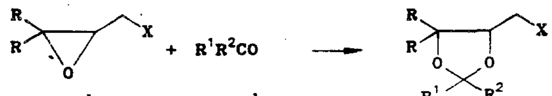
It is established that tetrafluoroboric acid (HBF_4) is an effective catalyst for halogen substitution reactions of oxiranes (epichlorohydrin and 1-bromo-3-methyl-2,3-epoxybutane) with aldehydes and ketones, forming 1,3-dioxolanes in high yields.

The formation of five-membered, cyclic acetals and ketals, 1,3-dioxolanes, by the reaction of carbonyl compounds with oxiranes usually takes place in the presence of a small number of acid catalysts, and high yields are obtained, as a rule, with the use of ketones but not aldehydes [1].

We have found a new catalyst for this process – tetrafluoroboric acid. This acid, discovered at the beginning of the last century [2], has only been used as a catalyst for the polymerization of oxirane compounds [3] and hydration reactions [4].

We have shown that the commercial acid (40% aqueous solution) is able to catalyze the formation of 1,3-dioxolanes in the reaction of epichlorohydrin (Ia) or 1-bromo-3-methyl-2,3-epoxybutane (Ib) with a number of aldehydes and ketones (IIa-h). A major advantage of this catalyst is that, in contrast to the known methods, it ensures high yields of reaction products, III, not only in the case of ketones, but of aldehydes as well (Table 1).

The best results are obtained with an epichlorohydrin:carbonyl compound:catalyst mole ratio of 1:(2-3):(0.003-0.005). Temperature and duration of the process depend on the carbonyl compound (Table 1). It must be noted that, in the case of epoxide Ib, the lower yields of dioxolanes IIIi, j are explained by its isomerization to bromomethyl isopropyl ketone by the known mechanism [7]. This is not observed when $CuSO_4$ is used as the catalyst [10]. It was noted that compounds IIIc, d are formed as a mixture of two stereoisomers in a ratio of (40-50):(60-50). This is shown by the signal from the OCH group proton in the PMR spectrum, which has the form of two multiplets (see Experimental).



Ia,b IIa-h

Compound*	R¹	R²	Compound*	R¹	R²	Compound*	R¹	R²
IIa	CH_3	CH_3	IIg	CH_3	C_6H_5	IIIe	$(CH_2)_5$	
IIb	CH_3	C_2H_5	IIh	H	$CH_3CH{=}CH$	IIIf	H	C_6H_5
IIc	H	$i\text{-}C_3H_7$	IIIa	CH_3	CH_3	IIIg	CH_3	C_6H_5
IId	H	$i\text{-}C_4H_9$	IIIb	CH_3	C_2H_5	IIIh	H	$CH_3CH{=}CH$
IIe	$(CH_2)_5$		IIIc	H	$i\text{-}C_3H_7$	IIIi	CH_3	CH_3
IIf	CH_3	C_6H_5	IIId	H	$i\text{-}C_4H_9$	IIIj	H	$i\text{-}C_3H_7$

*Ia, IIIa-h· R=H, X=Cl; Ib, IIIi,j R=CH_3, X=Br.

The dehydrochlorination of dioxolanes IIIa, e by the action of sodium diethyleneglycolate according to the procedure described in [10] gives methylene derivatives IVa, e

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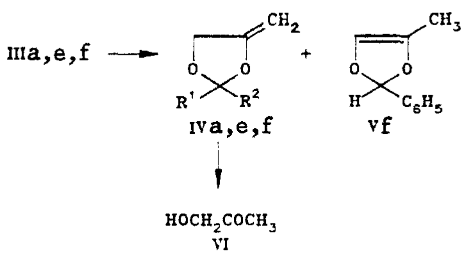

It was found that the action of potassium hydroxide (either dry or under the conditions of interphase catalysis) does not bring about dehydrochlorination. Potassium hydroxide did prove to be effective for the dehydrochlorination of 2-phenyl-4-chloromethyl-1,3-dioxolane (IIIf). However, in this case the reaction does not take place regiospecifically, as it does with sodium glycolate, but regioselectively: a mixture of compounds IVf and Vf is formed in a 30:70 ratio (PMR, GLC). This contradicts the data in [11], according to which isomer IVf is formed exclusively under analogous conditions.

The resultant methylenedioxolanes proved to be convenient intermediates for the preparation of 1-hydroxy-2-propanone (hydroxyacetone) (VI). Thus, on treatment of dioxolane IVa with an equimolar amount of water containing 5% sulfuric acid, 60% hydroxyacetone is formed. Moreover, the hydroxyacetone can be prepared even in the presence of catalytic amounts of TsOH (as the crystalline hydrate) without adding water. The yield in this case is 54%. This synthetic route to hydroxyacetone avoids the use of the toxic, mercury compounds used to prepare the material by the hydration of propargyl alcohol [12] or bromoacetone [13].

EXPERIMENTAL

The IR spectra were recorded on a UR-20 instrument in thin layer. The PMR spectra were obtained on a Perkin–Elmer R-12B (60 MHz) instrument in CCl_4 and, in the case of VI, in D_2O; internal standard HMDS. Purity and identity of the compounds synthesized were determined by means of GLC on an LKhM-8MD instrument with a cathetometer on a column (2000 × 3 and 3000 × 3 mm) with 5% OV-17 on Chromaton Super; carrier gas (helium) flow rate, 40-60 ml/min; temperature 100-200°C.

TABLE 1. Yields and Reaction Conditions for the Formation of Dioxolanes in the Presence of HBF_4 ($3.8 \cdot 10^{-3}$ %)

Compound	I:II, mole	T_r, °C	t_r, h	HBF_4, g(%)	Yield of III, %	Literature data		
						literature	yield of III, %	catalyst
IIIa	Ia:IIa=1:3	60	2	0,6 ($2,9 \cdot 10^{-3}$)	96	[5]	59	$BF_3 \cdot OEt_2$
	Ia:IIa=1:2	55	2	1,0 ($4,8 \cdot 10^{-3}$)	96			
	Ia:IIa=1:2,5	60	2	1,0 ($4,8 \cdot 10^{-3}$)	96			
	Ia:IIa=1:1,5	60	2	1,0 ($4,8 \cdot 10^{-3}$)	86			
IIIb	Ia:IIb=1:2,5	70	2	0,8	96	[5]	60	$BF_3 \cdot OEt_2$
IIIc	Ia:IIc=1:2,5	90	4	0,8	75			
IIId	Ia:IId=1:2,5	95	4	0,8	75			
IIIe	Ia:IIe=1:2,5	100	2,5	0,8	98	[6]*	—	TsOH
IIIf	Ia:IIf=1:2,5	160	2	0,8	72	[8]*	50	HCl
IIIg	Ia:IIg=1:2,5	80	2	0,8	86	[6]*	—	TsOH
IIIh	Ia:IIh=1:2,5	50	0,3	0,8	73	[9]*	40	TsOH
IIIi	Ib:IIa=1:2,5	60	2	0,8	60	[10]*	89	$CuSO_4$
IIIj	Ib:IIc=1:2,5	60	4	0,8	52	[10]**	49	$BF_3 \cdot OEt_2$

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*Product III obtained from glycerol monochlorohydrate.

**The low yield is due to the secondary isomerization of the bromoepoxide to bromomethyl isopropyl ketone [7].

Preparation of 2,2-R,R^1-4-halomethyl-5,5-R^2-1,3-dioxolanes (IIIa-j). The halooxirane is added dropwise with stirring to a mixture of the carbonyl compound and catalyst (exothermic reaction). The reaction mixture is then held at the specified temperature, after which it is vacuum distilled. The reaction conditions and yields of III are shown in Table 1. The characteristics of the hitherto-undescribed dioxolanes IIIc, d are given below. Their elementary analyses for C, H, and Cl correspond to the calculated values.

2-Isopropyl-4-chloromethyl-1,3-dioxolane (IIIc, $C_7H_{13}ClO_2$). Bp 65-68°C (11.5 mm Hg), n_D^{20} 1.4416, d_4^{20} 1.0845. IR spectrum: 1080 cm^{-1} (C–O). PMR spectrum: 0.90 [6H, d, J = 6.9 Hz, $(CH_3)_2$], 1.50-1.90 [1H, m, CH–$(CH_3)_2$], 3.42-3.70 (2H, m, CH_2Cl), 3.85-4.05 (1H, m, $ClCH_2CH$), 4.12-4.30 (2H, m, CH_2O), 4.60 and 4.75 ppm (1H, m, m, OCH).

2-Isobutyl-4-chloromethyl-1,3-dioxolane (IIId, $C_8H_{15}ClO_2$). Bp 44-46°C (3.5 mm Hg), n_D^{20} 1.4432, d_4^{20} 1.0588. IR spectrum: 1060 cm^{-1} (C–O). PMR spectrum: 0.99 [6H, d, J = 6.8 Hz, $(CH_3)_2$], 1.40-1.90 [3H, m, $(CH_3)_2CH_2$-CH], 3.42-3.70 (2H, m, CH_2Cl), 3.85-4.10 (1H, m, $ClCH_2CH$), 4.18-4.40 (2H, m, CH_2O), 4.93 and 5.11 ppm (1H, m, m, OCH).

Preparation of 2-R^1,R^2-4-methylene-1,3-dioxolanes (IVa, b). Dehydrochlorination with sodium ethyleneglycolate according to the procedure described in [10] were carried out and with potassium hydroxide by the procedure in [11].

2,2-Dimethyl-4-methylene-1,3-dioxolane (IVa, $C_6H_{10}O_2$). Bp 102-104°C (680 mm Hg), n_D^{20} 1.4260, d_4^{20} 0.9712. IR spectrum: 1052 (C–O), 1680 (C=C), 3125 cm^{-1} (=CH_2). PMR spectrum: 1.40 [6H, s, $(CH_3)_2$], 3.75 and 4.20 (2H, m, m, CH_2), 4.44 ppm (2H, m, =CH_2). Yield 81%.

2,2-Pentamethylene-4-methylene-1,3-dioxolane (IVb, $C_9H_{14}O_2$). Bp 192-196°C (680 mm Hg), n_D^{20} 1.4660. IR spectrum: 1180 (C–O), 1660 (C=O), 3070 cm^{-1} (=CH_2). PMR spectrum: 1.35-1.80 [10H, m, $(CH_2)_5$], 4.10 (br. s, 2H, CH_2), 4.38-4.60 ppm (2H, m, =CH_2). Yield 71%.

Dehydrochlorination of 4-Chloromethyl-2-phenyl-1,3-dioxolane (IIIf). A mixture of 12.3 g (62 mmoles) of IIIf and 10.4 g (190 mmoles) of potassium hydroxide are held, with stirring, at 120-125°C for 6 h. Then 50 ml water is added and it is extracted three times with benzene. The extract is dried with magnesium sulfate. Distillation yields 7.2 g (72%) of a mixture of 4-methylene-2-phenyl-1,3-dioxolane (IVf) and 4-methyl-2-phenyl-4,5-dehydro-1,3-dioxolane (Vf) in a 30:70 ratio (PMR, GLC) which boils at 101-114°C (10 mm Hg), n_D^{20} 1.5274. IR spectrum of mixture: 1080 (C–O), 1600 (C–C–arom.), 1690 (C=C), 3060 (CH–arom.), 3075 cm^{-1} (=CH_2). PMR spectrum of mixture: 1.80 (d.d, J = 10 Hz, CH_3), 3.85 and 4.29 (m, H_A and H_B, CH_2), 4.45 (m, J = 1.0 Hz, =CH_2), 6.02 (br. s, CH), 6.45 (br. s, =CH), 7.25-7.50 ppm (5H, m, C_6H_5).

Preparation of 1-Hydroxy-2-propanone (VI). A. A mixture of 1.1 ml of water (60 mmoles) and 0.05 g of H_2SO_4 is slowly added dropwise (exothermic reaction) to 6.8 g (60 mmoles) of dioxolane IVa at 20°C (cooling water). The reaction mixture is stirred for another 2 h, neutralized with dry soda, and extracted with ether. Distillation gives 2.7 g (60.2%) of hydroxyacetone, bp 61-63°C (50 mm Hg), n_D^{20} 1.4230. IR spectrum: 1080 (C–O), 1725 (C=O), 3280-3520 cm^{-1} (OH). PMR spectrum: 1.98 (3H, s, CH_3), 4.12 ppm (2H, s, CH_2).

B. A mixture of 6.8 g (60 mmoles) of dioxolane IVa and a catalytic amount of p-toluenesulfonic acid is held at 60°C, and the composition of the mixture is monitored by means of GLC. Yield 2.4 g (54%) of hydroxyacetone.

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SYNTHESIS OF 5-ALKENYL-1,3-DIOXANES

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Cyclic acetals containing alkenyl groups were obtained from 5-methyl-5-acyl-1,3-dioxane. The 1,3-dioxane fragment does not interfere in reduction of the carbonyl group, nor in participation of the carbonyl group in Wittig and Grignard reactions.

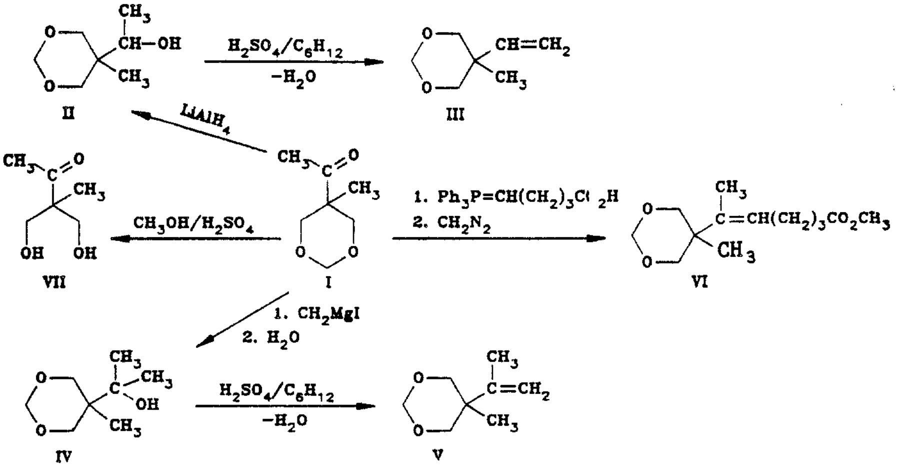
The synthesis of 2- and 4-alkenyl-1,3-dioxanes by acetalization of unsaturated aldehydes and by condensation of dienes with formaldehyde, respectively, has been described [1-3].

Because these compounds have been found to be of interest in the preparation of homo- and copolymers, the purpose of the present investigation is the development of different methods for preparation of cyclic acetals containing unsaturated substituents.

We synthesized 1,3-dioxanes containing alkenyl groups in the 5 position from a product of the condensation of methyl ethyl ketone with formaldehyde, namely 5-methyl-5-acyl-1,3-dioxane (I) [4].

The reduction of dioxane I to 5-methyl-5-(α-hydroxyethyl)-1,3-dioxane (II) and subsequent dehydration gave 5-methyl-5-vinyl-1,3-dioxane (III). In a reaction with CH_3MgI, ketone I formed tertiary alcohol 5-methyl-5-(α-methyl-α-hydroxyethyl)-1,3-dioxane (IV) in quantitative yield, and acid dehydration of (IV) gave 5-methyl-5-isopropenyl-1,3-dioxane (V). Wittig's reagent was used to obtain 5-methyl-5-[α-(methyloxycarbonylbutylidene)ethyl]-1,3-dioxane (VI).

During dehydration of dioxane alcohols II and IV, ring cleavage was practically not observed, and 3,3-bis(hydroxymethyl)-2-butanone (VII) was obtained in low yield (24%) only during acid methanolysis of I.



According to the obtained data, the cycloacetal fragment does not interfere in the occurrence of conversions at side functional groups, and 5-acyl-1,3-dioxanes can be used in the synthesis of polyfunctional cyclic acetals.

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