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Chemistry of Dioxacyclanes: XI.[1] Synthesis and Properties of Unsaturated Derivatives of 1,3-Dioxolanes

A. Kh. Kerimov

Institute of Polymeric Materials, Academy of Sciences of Azerbaizhan, Sumgait, Azerbaidzhan

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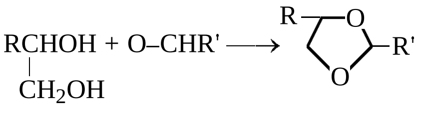
Abstract—1,3-Dioxolanes were synthesized by reactions of 3-cyclohexenecarboxaldehyde and 5-norbornene-2-*endo*-carboxaldehyde with 1,2-ethanedithiol and 3-(2-propenyloxy)- and 3-propoxy-1,2-propanediols, as well as of propionaldehyde, benzaldehyde, and trichloroacetaldehyde with the latter two thiols. Dichlorocarbene addition, bromination, and epoxidation of the ring C=C were accomplished, and activity of the resulting products as dienophiles in Dield–Alder reactions was assessed.

Dioxolane derivatives can be used as solvents [2], antiknock additives [3], synthetic intermediates for medicines [4], and monomers for useful polymers [5]. Cyclic acetals are produced from available starting materials, such as olefin hydrocarbons, organic oxides, glycols, and carbonyl compounds. However, there is very little information in the literature on the synthesis and properties of unsaturated 1,3-dioxolane derivatives which, apart from the above application fields, hold considerable synthetic promise [6].

The present communication describes the synthesis of 2-substituted or 2,4-disubstituted 1,3-dioxolanes by the reactions of 3-cyclohexenecarboxaldehyde and 5-norbornene-2-*endo*-carboxaldehyde with 1,2-ethanediol and 3-(2-propenyloxy)- and 3-propoxy-1,2-propanediols, as well as of propionaldehyde, benzaldehyde, and trichloroacetaldehyde with the latter two thiols in the presence of KU-2 cation exchanger (H^+ form) in toluene (Scheme 1).

Reaction progress was followed by GLC. Quantitation was performed by internal calibration technique [7] using diethyl or dipropyl phthalathe as standards. The chromatograms of the resulting compounds **IIIc**–**IIIj** contained two signals in the ratio ~55:45. These peaks were assigned to the *cis* and *trans* isomers of the dioxolanes. The mixtures could not be isolated, but the 1H NMR spectra gave evidence for the presence of the *cis* and *trans* isomers (see Experimental).

Scheme 1.



Ia–Ic **IIa–IIe** **IIIa–IIIj**

IIf

I, R = H (**a**), CH_2=$CHCH_2OCH_2$ (**b**), $C_3H_7OCH_2$ (**c**). **II**, R' = 3-cyclohexenyl (**a**), 5-norbornen-2-yl (b), C_2H_5 (**c**), C_6H_5 (**d**), Cl_3C (**e**). **III**, R = H, R' = 3-cyclohexenyl (**a**), 5-norbornen-2-yl (**b**); R = CH_2=$CHCH_2OCH_2$, R' = C_2H_5 (**c**), C_6H_5 (**d**), 3-cyclohexenyl (**e**), 5-norbornen-2-yl (**f**), Cl_3C (**g**); R = $C_3H_7OCH_2$, R' = C_6H_5 (**h**), 3-cyclohexenyl (**i**), 5-norbornen-2-yl (**j**).

When studying the effect of substituent R' in the carbonyl component on the reactivity of the CH=O group we found that in the optimal conditions [8] in the presence of KU-2 cation exchanger (H^+ form) the initial rate ($W_0 \times 10^4$) of the formation of dioxolane **IIId** from benzaldehyde is 1.35×10^4 mol l^{-1} s^{-1} and is much higher than the rates of the formation of dioxolanes **IIIe** and **IIIf** from aldehydes **IIa** (0.285×10^4 mol l^{-1} s^{-1}) and **IIb** (0.142×10^4 mol l^{-1} s^{-1}). The same conclusion follows from a comparison of the yields of the target reaction products, since, other conditions being equal, no by-products are formed (GLC data). Thus, in the optimal conditions providing high yields of the target products, the yield of dioxolane **IIId** is 76%, whereas the yields of dioxolanes **IIIe** and **IIIf** are 16 and 6%, respectively (see table).

The observed difference is hardly explicable in terms of the inductive or steric effects of the substi-

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[1] For communication X, see [1].

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Constants, yields, and elemental analyses of **IIIa**–**IIIj** and **IVa**–**IVh**

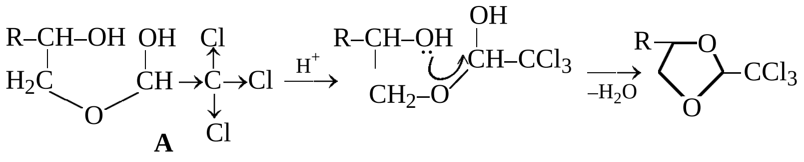
Comp. no	Yield, %	bp, °C (p, mm)	d_4^{20}	n_D^{20}	MR_D found	MR_D calculated	Found, % C	H	Cl	Formula	Calculated, % C	H	Cl
IIIa	87	80–81 (3)	1.0422	1.4770	41.82	42.18	69.94	9.11	–	$C_9H_{14}O_2$	70.09	9.15	–
IIIb	75	56–57 (1)	1.0837	1.4890	44.27	44.59	72.09	8.42	–	$C_{10}H_{14}O_2$	72.26	8.49	–
IIIc	63	63–65 (2)	0.9794	1.4400	46.35	46.02	62.58	9.24	–	$C_9H_{16}O_3$	62.76	9.37	–
IIId	76^a 89^b	125–128 (1)	1.0891	1.5115	60.49	60.89	70.74	7.18	–	$C_{13}H_{16}O_3$	70.89	7.32	–
IIIe	16^a 85^b	112–115 (2)	1.0354	1.4800	61.54	61.83	69.45	8.92	–	$C_{13}H_{20}O_3$	69.61	8.99	–
IIIf	6^a 76b	112–114 (1)	1.0670	1.4910	64.14	64.25	70.98	8.38	–	$C_{14}H_{20}O_3$	71.16	8.53	–
IIIg	30	112–115 (2)	1.3449	1.4850	55.73	56.01	36.64	4.17	–	$C_8H_{11}Cl_3O_3$	36.74	4.24	40.67
IIIh	79	124–126 (2)	1.0575	1.4960	61.40	61.36	70.09	8.11	–	$C_{13}H_{18}O_3$	70.24	8.16	–
IIIi	76	117–119 (1)	1.0158	1.4670	61.83	62.29	68.73	9.68	–	$C_{13}H_{22}O_3$	68.99	9.72	–
IIIj	64	120–122 (2)	1.0966	1.5040	64.35	64.71	70.28	9.23	–	$C_{14}H_{22}O_3$	70.56	9.30	–
IVa	78	95–97 (1)	1.1587	1.4800	41.73	42.09	63.35	8.22	–	$C_9H_{14}O_3$	63.50	8.29	–
IVb	56	88–90 (1)	1.1830	1.4950	44.92	44.51	65.78	7.68	–	$C_{10}H_{14}O_3$	65.91	7.74	–
IVc	73	180–183 (3)	1.8225	1.5352	71.96	71.63	22.69	2.57	62.75^c	$C_8H_{11}Br_2Cl_3O_3$	22.81	2.63	63.17^c
IVd	74	140–145 (2)	1.6196	1.5170	63.58	63.77	28.08	2.88	54.29^c	$C_8H_{10}BrCl_3O_3$	28.23	2.96	54.71^c
IVe	45	133–135 (3)	1.2880	1.5210	56.06	55.51	50.52	5.88	30.11	$C_{10}H_{14}Cl_2O_2$	50.65	5.95	29.90
IVf	34	169–171 (5)	1.3404	1.5330	59.02	58.95	52.85	5.60	28.14	$C_{11}H_{14}Cl_2O_2$	53.03	5.66	28.49
IVg	64	168–170 (1)	1.5302	1.5550	89.57	90.07	39.14	3.22	49.60	$C_{14}H_{14}Cl_2O_2$	39.38	3.30	49.88
IVh	71	163–165 (2)	1.4621	1.5260	93.44	93.82	37.66	3.57	47.69	$C_{14}H_{16}C_{16}O_3$	37.79	3.62	47.80

[a] Obtained in the presence of KU-2. [b] Obtained in the presence of TsOH. [c] Br + Cl.

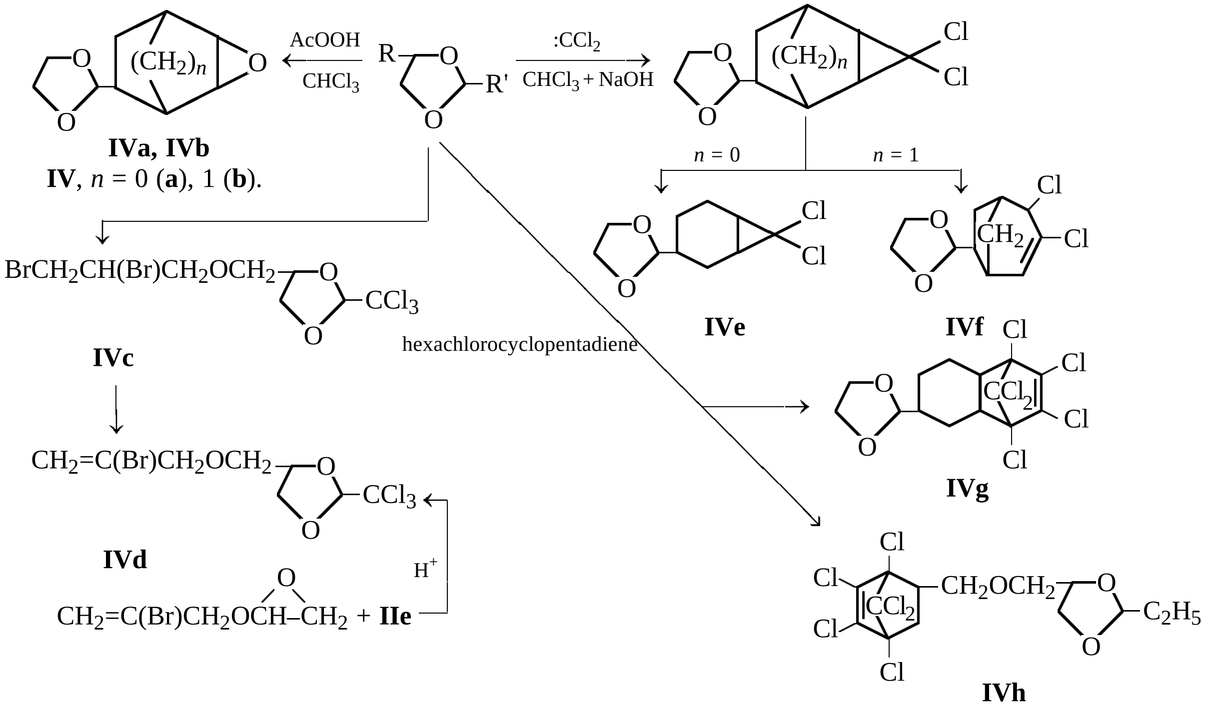
tuents in the carbonyl components and is inconsistent with published data [9]. Presumably, the difficulties with the synthesis of compounds **IIIe** and **IIIf** are associated with the activity of the catalyst rather than with the reactivity of compounds **IIa** and **IIb**. This assumption is confirmed by the fact that the yields of dioxolanes **IIIh**–**IIIj** from diol **Ic** (saturated analog of diol **Ib**) under the same conditions are 79, 76, and 64%, respectively. Moreover, with TsOH instead of KU-2, the yields of compounds **IIIe** and **IIIf** sharply increase (85 and 76%, respectively). Probably, if both components contain a double bond (preserved in the target product), they act together to saturate the cation-exchanger surface and deactivate it by blocking sulfo groups [10]. As a result, the cation exchanger loses activity, which does not happen in the case of homogeneous catalysis and a less saturated system (synthesis of compounds **IIIh**–**IIIj**). The higher yield of dioxolane **IIIe** compared with compound **IIIf** is assignable to conformational features of aldehydes **IIa** and **IIb** [11, 12].

It was found that strong electron-acceptor substituents (Cl_3C) in the aldehyde inhibit dioxolane formation. Thus, the reaction with aldehyde **IIe** in the optimal conditions gives traces of dioxolane **IIIg**, whereas in homogeneous medium its yield is 30%. It is known that the Cl_3C group activates the starting aldehyde, and its reactivity increases so much that it quantitatively converts into the corresponding semiacetal when simply mixed with diols (alcohols and thiols [13]. However, to convert into a cyclic acetal, the semiacetal should lose a water molecule (Scheme 2) [14, 15].

Scheme 2.



Scheme 3.



It was found that oxidation of compounds **IIIa** and **IIIb** with 50% peracetic acid gives rise respectively to *cis*-2-(1,2-epoxycyclohexyl)- and *cis*-2-(5,6-epoxynorbornan-2-yl)-1,3-dioxolanes (**IVa**, **IVb**) in good yields. Bromination of compound **IIIg** provides compound **IVc** which is easily dehydrobrominated to form compound **IVd**. It should be noted that the latter compound was obtained by independent synthesis from 3-(2-bromo-2-propenyloxy)-1,2-epoxypropane. Dichlorocarbene (generated from $CHCl_3$ and 50% aqueous NaOH [16]) reacts with compounds **IIIa** and **IIIb**, giving 2-(7,7-dichlorobicyclo[4.1.0]hept-4-yl)- and 2-(2,3-dichlorobicyclo[3.2.1]oct-3-en-6-yl)-1,3-dioxolanes (**IVe**, **IVf**). Thus we found that the dichlorocyclopropanation product **IIIb** is extremely unstable and undergoes isomerization with ring expansion and double bond formation, which agrees with published data [17]. The synthesis of adducts **IVg** and **IVh** shows that dioxolane derivatives with a double bond in the ring or in the side chain possess dienophilic activity and can be used in diene synthesis. The characteristic reactions were accomplished according to Scheme 3.

The compositions of compounds **IIIa**–**IIIj** and their transformation products were proved by elemental analysis, and the structures were assessed on the basis of MR_D, ^1H NMR, and IR data. Compound **IIIf** was also obtained by independent synthesis from 5-norbornene-2-carboxaldehyde dimethyl acetal in the presence of TsOH (Scheme 1).

EXPERIMENTAL

The IR spectra were recorded on a UR-20 instrument in thin films. The ^1H NMR spectra were obtained on a Tesla BS-487B spectrometer for CCl_4 solutions (80 MHz, internal reference HMDS). Gas chromatography was performed on a Chrom-4 chromatograph with a thermal conductivity detector and a stainless-steel column (3600.4 mm) packed with 5% Xð-60 on Chromaton N-AW-DMCS; temperature program 150–210°C; carrier gas helium (30 ml min^{-1}); detector current 80 mA.

4-(2-Propenyloxy)methyl-2-(5-norbornen-2-yl)-1,3-dioxolane (IIIf). *a*. A mixture of 24.4 g of aldehyde **IIb**, 27.8 g of diol **Ib**, 0.08 g of KU-2 cation exchanger, and 50 ml of toluene was heated at 130°C with azeotropic distillation of the reaction water. The reaction progress was controlled by GLC, taking samples every 30 min. After the reaction was complete (5 h), the reaction mixture was cooled to room temperature, the resin was filtered off, the solvent was removed, and the residue was distilled in a vacuum to isolate 2.28 g (6%) of compound **IIIf** (see table). ^1H NMR spectrum, δ, ppm: 0.80–3.00 group of signals (7H, carbon ring), 3.00–4.20 m (7H, $CH_2OCH_2CH\cdot CH_2O$), 4.42 d (1/2H, *trans*-OCHO, *J* 8 Hz), 4.52 d (1/2H, *cis*-OCHO, *J* 8 Hz), 4.95–5.30 m (2H, CH_2=C), 5.50–5.90 m (1H, C=CH). Compounds **IIIa**–**IIIe** were synthesized in a similar way.

b. A mixture of 19.5 g of aldehyde **IIb**, 22.5 g of diol **Ib**, 50 ml of toluene, and 0.06 g (0.3 wt% with respect to aldehyde) of TsOH was heated with azeotropic distillation of the reaction water under the above conditions and then washed with 5% potassium carbonate and water, dried with K_2CO_3, the solvent was removed, and the residue was distilled in a vacuum to isolate 28.9 g (76%) of compound **IIIf**, bp 110–112°C (1 mm), d_4^{20} 1.0592, n_D^{20} 1.4835. Compounds **IIId** and **IIIe** were synthesized in a similar way (see table).

c. A mixture of 33.6 g of 5-norbornene-2-carboxaldehyde dimethyl acetal (**IIf**), 29.0 g of diol **Ib**, 0.3 g (0.9 wt% with respect to **IIf**) of TsOH was heated with azeotropic distillation of the methanol formed. After cooling to room temperature, the reaction mixture was washed with 2% aqueous sodium hydroxide and water. The aqueous layer was treated with toluene, the extracts were combined with the organic layer, dried with $MgSO_4$, the solvent was removed, and the residue was distilled in a vacuum to isolate 39.3 g (79%) of compound **IIIf**, bp 110–111°C (1 mm), d_4^{20} 1.0672, n_D^{20} 1.4840.

4-(2-Propenyloxy)methyl-2-trichloromethyl-1,3-dioxolane (IIIg). A mixture of 79.3 g of diol **Ib**, 106 g of aldehyde **IIe**, 1.0 g (0.9 wt% with respect to **IIe**) of TsOH, and 100 ml of toluene was stirred with azeotropic distillation of the reaction water over the course of 12 h. After cooling to room temperature, the mixture was neutralized with 5% aqueous potassium carbonate, the aqueous layer was extracted with toluene, the extracts were combined with the organic layer, washed with water, dried with K_2CO_3, the solvent was removed, and the residue was distilled in a vacuum to isolate compound **IIIg** (see table). ^{1}H NMR spectrum, δ, ppm: 3.25–4.50 w.m (7H, $CH_2 \cdot OCH_2CHCH_2O$), 4.68 d (1/2H, *trans*-OCHO, *J* 7 Hz), 4.80 d (1/2H, *cis*-OCHO, *J* 7 Hz), 5.30 m (2H, CH_2=C), 5.90 m (1H, CH=C).

2-(3-Cyclohexenyl)-4-(propoxymethyl)-1,3-dioxolane (IIIi). A mixture of 33 g of aldehyde **IIa**, 45.6 g of diol **Ic**, 70 ml of toluene, and 0.1 g (0.3 wt% with respect to compound **IIa**) of KU-2 was stirred at 130C for 5 h with azeotropic distillation of the water formed, after which KU-2 was filtered off, the solvent was removed, and the residue was vacuum-distilled to isolate 51.6 g (76%) of compound **IIIi**. The reaction progress was controlled by GLC. ^{1}H NMR spectrum, δ, ppm: 0.95–1.00 group of signals (7H, $CH_3CH_2CH_2$), 1.25–2.15 m (7H, $CH_2OCH_2CH \cdot CH_2$), 3.15–4.25 m (3H, CH_2O, CHO), 4.50 d (1/2H, *trans*-OCHO), 4.60 d (1/2H, *cis*-OCHO), 5.45 m (2H, CH=CH). Compounds **IIIh** and **IIIj** were synthesized in a similar way (see table).

2-(5,6-Epoxynornornan-2-yl)-1,3-dioxolane (IVb). To a mixture of 31.6 g of compound **IIIb** and 50 ml of chloroform, 30.4 g of 50% peracetic acid was added with stirring at 18–20°C. The mixture was stirred at that temperature for an additional 1.5–2 h and then treated with 5% aqueous sodium bicarbonate, washed with water, and dried with $MgSO_4$. The solvent was removed in a vacuum to leave compound **IVb** (see table). ^{1}H NMR spectrum, δ, ppm: 0.70–2.68 group of signals (9H, carboring), 2.87 d (2H, oxirane 2CH), 3.00–4.20 m (4H, CH_2CH_2O), 4.60 d (1/2H, *trans*-OCHO, *J* 6 Hz), 4.79 d (1/2H, *cis*-OCHO, *J* 6 Hz). Compound **IVa** was synthesized in a similar way.

4-(2,3-Dibromopropoxymethyl)-2-(trichloromethyl)-1,3-dioxolane (IVc). Bromine, 15 g, was added with stirring to a mixture of 23.5 g of compound **IIIg** and 110 ml of CCl_4 at –10 to –5°C. The mixture was stirred for an additional 1.5–3 h, washed with 5% NaOH and water, the aqueous layer was treated with CCl_4, the organic layers were combined, washed with water, and dried with CaC_{12}. The solvent was removed, and the residue was distilled in a vacuum to obtain 27.8 g (73%) of compound **IVg** (see table). IR spectrum, ν, cm^{-1}: 570, 550, 810, 960, 1100, 1220, 1360, 2800.

4-(2-Bromo-2-propenyloxymethyl)-2-trichloromethyl-1,3-dioxolane (IVd). *a*. Powdered KOH, 17.4 g, was added in portions to a mixture of 126.4 g of compound **Ig** and 100 ml of dioxane. The mixture was stirred for 3–4 h under reflux. The organic layer was separated, the aqueous layer was treated with ether, the combined organic solutions were dried with $MgSO_4$; the solvents were removed, and the residue was distilled in a vacuum to obtain compound **IVd** (see table). IR spectrum, ν, cm^{-1}: 650, 760, 910, 980, 1100, 1169, 1320, 1620, 1280.

b. A mixture of 44.3 g of aldehyde **IIe**, 61.8 g of 3-(2-bromo-2-propenyloxy)-1,2-epoxypropane, 50 ml of toluene, and 3.9 g (0.9 wt % with respect to compound **IIe**) of H_2SO_4 (*d* 1.84) was refluxed for 12 h, cooled to 18–20C, and washed with 5% sodium bicarbonate and water. The aqueous layer was treated with toluene, combined with the organic layer, washed with water, and dried with $MgSO_4$; the solvent was removed, and the residue was distilled in a vacuum to obtain 15.6 g (20%) of compound **IVd**, bp 140–142°C (2 mm), d_4^{20} 1.6288, n_D^{20} 1.5164.

2-(2,3-Dichlorobicyclo[3.2.1]oct-3-en-6-yl)-1,3-dioxolane (IVf). Chloroform, 44.96 g, was added with stirring over the course of 45 min to a mixture of 50 ml of 50% aqueous NaOH, 10 ml of benzene, 0.4 g of triethylbenzylamonium chloride, and 19.9 g of compound **IIIb**. The mixture was stirred for an additional 3 h, diluted with ether, washed with 1% aqueous acetic acid and water, dried with $MgSO_4$; the solvent was removed, and the residue was distilled in a vacuum to obtain 10.2 g (43%) of compound **IVf**. ^1H NMR spectrum, δ, ppm: 0.60–2.95 m (9H, carboring), 3.05–4.30 m (4H, CH_2CH_2O), 4.45 d (1/2H, *trans*-OCHO, *J* 7 Hz), 4.55 d (1/2H, *cis*-OCHO, *J* 7 Hz), 5.80–6.20 m (1H, CH=C). Compound **IVe** was obtained in a similar way.

2-(1,8,9,10,11,11-Hexachlorotricyclo[6.2.1.0^{2,7}]-undec-9-en-4-yl)-1,3-dioxolane (IVg). A mixture of 20.2 g of compound **IIIa** and 54.4 g of hexachlorocyclopentadiene was stirred at 140–150°C for 12 h. Excess hexachlorocyclopentadiene was removed, and the residue was distilled in a vacuum to obtain compound **IVg**.

Compound **IVh** was synthesized in a similar way (see table).

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