Russian Journal of General Chemistry, Vol. 73, No. 1, 2003, pp. 131–134. Translated from Zhurnal Obshchei Khimii, Vol. 73, No. 1, 2003, pp. 139–142.
Original Russian Text Copyright © 2003 by Kerimov.

Chemistry of Dioxacyclanes: X.[1] Synthesis and Properties of Chlorinated 1,3-Dioxolanes Derived from 4-Cyclohexenecarbaldehydes

A. Kh. Kerimov

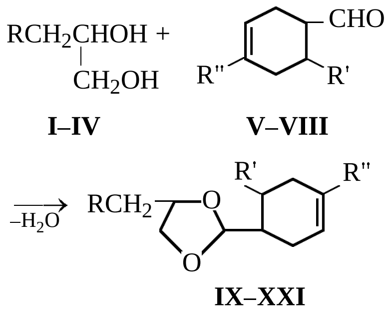
Institute of Polymetic Materials, National Academy of Sciences of Azerbaidzhan, Sumgait, Azerbaidzhan

Received April 24, 2000

Abstract—4-Cyclohexenecarbaldehyde and its 2-methyl-, 4-methyl-, and 2,4-dimethyl derivatives were reacted with 1,2-diols [1,2-propanediol and 3-chloro-, 3-(2-chloroethoxy)-, and 3-(2-chloro-1-chloromethylethoxy-1,2-propandiol] to synthesize the corresponding 2,4-disubstituted 1,3-dioxolanes. Epoxidation and bromination of the products were performed, as well as their condensation with hexachlorocyclopentadiene.

It is known that reactions of aldehydes with 1,2-propanediols provide a convenient synthetic route to 1,3-dioxolane derivatives [2, 3] which are prospective plastifiers [4], solvents [5], and corrosion inhibitors [6]. Moreover, these compounds are applied as thermally stable nonfreezing liquids [7], intermediate products in the synthesis of drugs and biologically active compounds [8], etc.

The present work reports the synthesis of 2,4-disubstituted 1,3-dioxolanes **IX**–**XXI** from 4-cyclohexenecarbaldehyde and its 2-methyl-, 4-methyl-, and 2,4-dimethyl derivatives under the action of 1,2-propanediol, as well as 3-chloro-, 3-(2-chloroethoxy)-, and 3-(2-chloro-1-chloromethylethoxy)-1,2-propanediols in the presence of KU-2 cation-exchange resin (H^+ form).



R = R' = R" = H (**I, V, IX**); R = Cl, R' = R' = H (**II, X**), R' = CH_3, R" = H (**VI, XI**), R' = H, R" = CH_3 (**VII, XII**), R' = R" = CH_3 (**VIII, XIII**); R = $Cl(CH_2)_2O$, R' = R" = H (**III, XIV**), R' = CH_3, R" = H (**XV**), R' = H, R" = CH_3 (**XVI**), R' = R' = CH_3 (**XVII**); R = $\mathrm{ClCH_2\underset{\displaystyle CH_2Cl}{\underset{|}{C}}HO}$, R' = R" = H (**IV, XVIII**), R' = CH_3, R" = H (**XIX**), R' = H, R" = CH_3 (**XX**), R' = R' = CH_3 (**XXI**).

The reaction progress was followed by GLC by the concentration the reaction product. Quantitative measurements were performed by the internal calibration technique. The internal standards were dimethyl and diethyl phthalates. The accumulation degrees of the reaction products were calculated by the areas of chromatographic peaks with use of calibration factors obtained by analysis of calibration mixtures [9]. In order of increasing retention time, the components of the reaction mixtures (on an example of compound **X**) rank as follows: toluene (solvent), 4-cyclohexenecarbaldehyde, 3-chloro-1,2-propanediol, 4-(chloromethyl)-2-(4-cyclohexenyl)-1,3-dioxolane (**X**), and dimethyl phthalate (standard). According to GLC data, compounds **XIV**–**XXI** are mixtures of two isomers. The isomers could not be isolated individual, but, as judged from the ^1H NMR spectra, these are *cis* and *trans* isomers differing in the arrangement of the substituents at the dioxolane C^2 and C^4 atoms.

In studying the effect of the substituent in the diol on its relative reactivity we established that in the optimal conditions found in [10] the initial rates ($W_0 \times 10^4$) of formation of dioxolanes **IX**, **X**, **XIV**, and **XVIII** are 2.75 ± 0.22, 5.60 ± 0.48, 3.95 ± 0.32, and 2.60 ± 0.19 mol l^{-1} s^{-1}, respectively (calculated by the least-squares procedure [11]). As follows from the above data, an electron-acceptor substituent (Cl) in the methyl group of 1,2-propanediol (taken as reference) increases the reaction rate more than two times [12]. However, replacement of chlorine by the bulkier electron-acceptor substituents $Cl(CH_2)_2O$ and

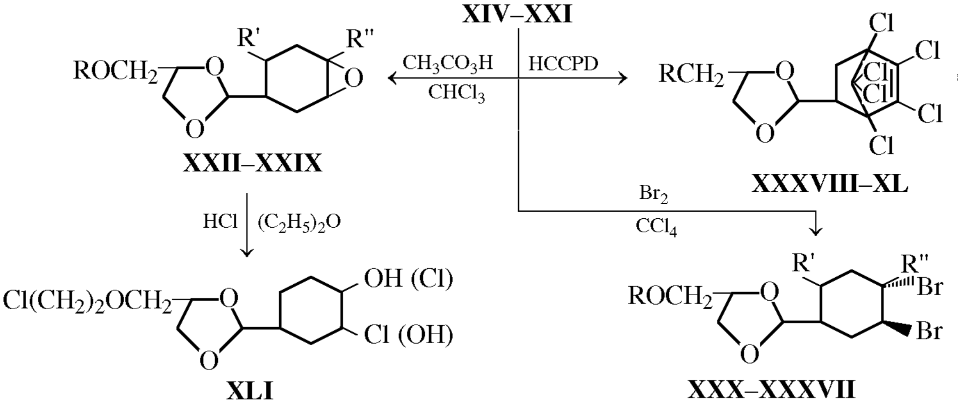
---

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

1070-3632/03/7301-0131 $25.00 © 2003 MAIK “Nauka/Interperiodica”

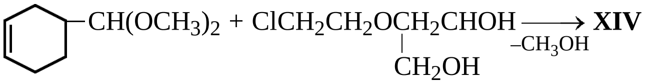
$\mathrm{ClCH_2\underset{\displaystyle CH_2Cl}{\underset{|}{C}}HO}$ results in gradual decrease in the reaction rate, and finally, with diol **IV**, the reaction rate gets even lower than the rate of formation of dioxolane **IX**.

Oxidation of compounds **XIV**–**XXI** with 55% peracetic acid in chloroform yields 4-(chloroalkoxymethyl)-2-*cis*-(1,2-epoxycyclohexyl)-1,3-dioxolanes **XXII**–**XXIX**, and bromination, 4-(chloroalkoxymethyl)-2-*trans*-(1,2-dibromocyclohexyl)-1,3-dioxolanes **XXX**–**XXXVII**. The example of the synthesis of cycloadducts **XXXVIII**–**XL** by reactions of compounds **X**, **XIV**, and **XVIII** with hexachlorocyclopentadiene (HCCPD) was used to show that 1,3-dioxolane derivatives with a double bond in the ring possess dienophilic activity and can be used in the Diels–Alder reaction.



R = $\mathrm{Cl(CH_2)_2}$, R' = R" = H (**XXII, XXX**); R' = $\mathrm{CH_3}$, R" = H (**XXIII, XXXI**); R' = H, R" = $\mathrm{CH_3}$ (**XXIV, XXXII**); R' = R" = $\mathrm{CH_3}$ (**XXV, XXXIII**); R = $\mathrm{ClCH_2\underset{\displaystyle CH_2Cl}{\underset{|}{C}}H}$, R' = R" = H (**XX, VI, XXXIV**); R' = $\mathrm{CH_3}$, R" = H (**XXVII, XXXV**); R' = H, R" = $\mathrm{CH_3}$ (**XXVIII, XXXVI**); R' = R" = $\mathrm{CH_3}$ (**XXIX, XXXVII**); R = Cl (**XXXVIII**), $\mathrm{Cl(CH_2)_2O}$ (**XXXIX**), $\mathrm{ClCH_2\underset{\displaystyle CH_2Cl}{\underset{|}{C}}HO}$ (**XL**).

The composition of compounds **XIV**–**XXI**[2] and their conversion products was proved by elemental analysis, and the structure of these compounds, by the MR_D values (see values) and ^1H NMR and IR spectra. Compound **XIV** was also synthesized from 4-cyclohexenecarbaldehyde dimethylacetal by the procedure in [13] in 80% yield.



$$\mathrm{C_6H_9CH(OCH_3)_2 + ClCH_2CH_2OCH_2\underset{\displaystyle CH_2OH}{\underset{|}{C}}HOH \xrightarrow[-CH_3OH]{} \mathbf{XIV}}$$

The IR spectra of compounds **XIV**–**XXI** contain absorption bands at 750–780 cm^{-1} [ν(C–Cl)] and weak bands at 1060, 1170, and 1260 cm^{-1} (C–O–C) [14]. The band at 1645–1650 cm^{-1} is formed by C=C stretching vibrations. The strong absorption bands at 660–670 cm^{-1} belong to bending vibrations and those at 3030–3040 cm^{-1}, to CH=CH stretching vibrations.

The bands at 850 and 920 cm^{-1} in the spectra of compounds **XXII**–**XXIX** point to the presence of epoxy groups. The presence of an epoxy group in compound **XXII** was confirmed by chemical transformations, specifically by the synthesis of chlorohydrin **XLI**. The IR spectrum of compound **XLI** contains a strong broad band at 3450–3500 cm^{-1} (associated OH group).

EXPERIMENTAL

The IR spectra were obtained on a UR-20 spectrophotometer in thin layer. The ^1H NMR spectra were measured on a Tesla BS-487B spectrometer (80 MHz) in CCl_4, internal reference HMDS. Gas chromatography was performed on a Chrom-4 instrument with a thermal conductivity detector and a stainless-steel

---

[2] The constants of compounds **IX–XIII** are published in [2].

Yields, constants, and elemental analyses of compounds **XIV**–**XLI**

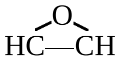
Comp. no.	Yield, %	bp, °C (*p*, mm)	d_4^{20}	n_D^{20}	MR_D		Found, %			Formula	Calculated, %		
					found	calcu-lated	C	H	Hlg		C	H	Hlg
XIV	82	130–131 (2)	1.1450	1.4880	62.08	62.54	58.12	7.87	14.73	$C_{12}H_{19}ClO_3$	58.41	7.76	14.36
XV	74	145–148 (3)	1.1178	1.4850	66.86	67.16	59.68	8.04	13.45	$C_{13}H_{21}ClO_3$	59.88	8.12	13.59
XVI	79	148–151 (3)	1.1242	1.4870	66.71	67.16	59.95	8.14	13.75	$C_{13}H_{21}ClO_3$	59.88	8.12	13.59
XVII	71	152–155 (3)	1.1033	1.4850	71.38	71.78	61.29	8.44	12.98	$C_{14}H_{23}ClO_3$	61.19	8.44	12.90
XVIII	72	155–158 (3)	1.2043	1.4980	71.85	72.03	52.79	6.93	23.95	$C_{13}H_{20}Cl_2O_3$	52.89	6.83	24.02
XIX	60	175–178 (3)	1.1805	1.4940	76.26	76.65	54.55	7.21	22.78	$C_{14}H_{22}Cl_2O_3$	54.38	7.17	22.93
XX	70	179–181 (3)	1.1756	1.4965	76.84	76.65	54.30	7.10	23.00	$C_{14}H_{22}Cl_2O_3$	54.38	7.17	22.93
XXI	58	183–185 (3)	1.1507	1.4920	81.50	81.27	55.63	7.56	22.05	$C_{15}H_{24}Cl_2O_3$	55.74	7.48	21.94
XXII	73	168–170 (8)	1.2092	1.4905	62.82	62.46	54.70	7.24	13.55	$C_{12}H_{19}ClO_4$	54.86	7.29	13.49
XXIII	75	173–175 (3)	1.1683	1.4765	66.80	67.07	56.25	7.58	12.92	$C_{13}H_{21}ClO_4$	56.42	7.65	12.81
XXIV	78	175–178 (3)	1.1916	1.4890	67.03	67.07	56.22	7.60	12.93	$C_{13}H_{21}ClO_4$	56.42	7.65	12.81
XXV	70	180–182 (3)	1.1457	1.4740	71.32	71.69	57.75	8.03	12.11	$C_{14}H_{23}ClO_4$	57.83	7.97	12.19
XXVI	55	168–170 (3)	1.2765	1.5000	71.70	71.94	50.03	6.51	22.93	$C_{13}H_{20}Cl_2O_4$	50.17	6.48	22.79
XXVII	53	180–182 (1)	1.2158	1.4860	76.80	76.56	51.81	6.78	21.72	$C_{14}H_{22}Cl_2O_4$	51.70	6.82	21.80
XXVIII	58	183–185 (2)	1.2496	1.4985	76.29	76.56	51.58	6.80	21.95	$C_{14}H_{22}Cl_2O_4$	51.70	6.82	21.80
XXIX	50	188–190 (1)	1.1919	1.4795	80.72	81.18	53.18	7.25	21.15	$C_{15}H_{24}Cl_2O_4$	53.11	7.13	20.90
XXX	53	185–188 (3)	1.5567	1.5100	78.11	78.54	35.35	4.66	48.23	$C_{12}H_{19}Br_2ClO_3$	35.45	4.71	48.03
XXXI	43	165–168 (3)	1.4914	1.5000	82.94	83.16	37.26	5.12	46.55	$C_{13}H_{21}Br_2ClO_3$	37.13	5.03	46.42
XXXII	48	169–170 (3)	1.5076	1.5050	82.74	83.16	37.15	5.08	46.25	$C_{13}H_{21}Br_2ClO_3$	37.13	5.03	46.42
XXXIII	40	173–175 (3)	1.4603	1.4990	87.38	87.78	38.58	5.28	44.77	$C_{14}H_{23}Br_2ClO_3$	38.69	5.33	44.93
XXXIV	46	172–177 (3)	1.5538	1.5120	87.74	88.03	34.38	4.45	50.78	$C_{13}H_{20}Br_2Cl_2O_3$	34.32	4.43	50.70
XXXV	43	200–205 (1)	1.4916	1.5030	92.95	92.65	35.71	4.83	49.05	$C_{14}H_{22}Br_2Cl_2O_3$	35.85	4.73	49.19
XXXVI	45	188–190 (1)	1.5130	1.5080	92.41	92.65	36.00	4.68	49.25	$C_{14}H_{22}Br_2Cl_2O_3$	35.85	4.73	49.19
XXXVII	40	220–223 (1)	1.4594	1.4970	96.85	97.26	37.15	4.96	47.56	$C_{15}H_{24}Br_2Cl_2O_3$	37.30	5.01	47.76
XXXVIII	65	220–223 (5)	1.4221	1.5100	100.00	99.55	37.76	3.25	52.13	$C_{15}H_{15}Cl_7O_2$	37.89	3.18	52.20
XXXIX	55	250–255 (2)	1.4771	1.5370	109.84	110.44	39.45	3.58	47.62	$C_{17}H_{19}Cl_7O_3$	39.30	3.69	47.77
XL	42	270–275 (1)	1.5043	1.5450	119.39	119.92	38.17	3.48	49.85	$C_{18}H_{20}Cl_8O_3$	38.06	3.55	49.94
XLI	74	194–196 (2)	1.2168	1.4720	68.96	69.40	48.07	6.73	23.64	$C_{12}H_{20}Cl_2O_4$	48.17	6.74	23.70

column (3600 × 4 mm) packed with 5% XE-60 on Chromaton N-AW-DMCS, oven temperature 170–210°C, carrier gas helium (30 ml/min), detector current 75 mA.

4-(2-Chloroethoxymethyl)-2-(4-cyclohexenyl)-1,3-dioxolane (XIV). *a*. A mixture of 39.7 g of 4-cyclohexenecarbaldehyde (**V**), 69.6 g of diol **III**, and 0.12 g of KU-2 (H^+ form) in 50 ml of toluene was heated with stirring with azeotropic distillation of the water formed. The reaction competion was detected by GLC. To this end, samples of the reaction mixture were taken every 30 min. The reaction was complete in 5 h. After cooling to room temperature, the reaction mixture was filtered to separate KU-2, the solvent was removed by vacuum distillation, and compound **XIV** was isolated by distillation. ^1H NMR spectrum, δ, ppm: 1.50–2.50 m (7H, carboring $CH_2CH_2CHCH_2$), 3.15–4.25 m (7H, CH_2O, CHO, $ClCH_2CH_2O$), 4.64 d (1H, *trans*-OCHO, *J* 6 Hz), 4.76 d (1H, *cis*-OCHO, *J* 6 Hz), 5.60 s (2H, CH=CH).

Compounds **XV**–**XXI** were synthesized in a similar way.

b. A mixture of 31.2 g of 4-cyclohexenecarbaldehyde dimethylacetal, 34 g of diol **III**, and 0.32 g (0.9% of the weight of the first reagent) of *p*-toluenesulfonic acid in 50 ml of toluene was heated with azeotropic distillation of the methanol formed. After cooling to room temperature, the residue was washed with 2% aqueous sodium hydroxide and water. The aqueous layer was treated with toluene, the extracts were combined with the organic layer and dried with $MgSO_4$. The solvent was removed, and the residue was distilled in a vacuum to isolate 39.3 g (80%) of compound **XIV**, bp 128–130°C (1 mm), d_4^{20} 1.1468, n_D^{20} 1.4900.

4-(2-Chloroethoxymethyl)-2-*cis*-(1,2-epoxycyclohexyl)-1,3-dioxolane (XXII). To a stirred mixture of 24.7 g of compound **XIV** and 50 ml of chloroform (18–20°C) we added over the course of 30 min, 18.6 g of 55% peracetic acid. Stirring was continued for an additional 1.5–2 h, after which the reaction mixture was treated with 5% aqueous sodium carbonate, washed with water, and dried with $MgSO_4$. The solvent was removed, and the residue was distilled in a vacuum to isolate compound **XXII**. ^1H NMR spectrum, δ, ppm: 1.25–2.25 m (7H, carboring $CH_2CH_2 \cdot CHCH_2$), 2.95 d (2H,  $\overset{O}{HC—CH}$), 3.25–4.30 m (7H, CH_2O, CHO, $ClCH_2CH_2O$), 4.55 d (1H, *trans*-OCHO, *J* 8 Hz), 5.70 d (1H, *cis*-OCHO, *J* 8 Hz).

Compounds **XXIII**–**XXIX** were synthesized in a similar way.

4-(2-Chloroethoxymethyl)-2-(1,2-dibromocyclohexyl)-1,3-dioxolane (XXX). Bromine, 33.6. g, was added dropwise at –10 to –5°C to a stirred mixture of 49.3 g of compound **XIV** and 110 ml of carbon tetrachloride. The reaction mixture was stirred for an additional 1.5–2 h at that temperature and washed with 5% aqueous sodium hydroxide and water. The aqueous layer was treated with carbon tetrachloride, the extract was combined with the organic layer and dried with $MgSO_4$. The solvent was removed, and the residue was distilled in a vacuum to isolate compound **XXX**. IR spectrum, ν, cm^{-1}: 660, 680 (C–Br), 690, 820 (C–Cl), 1020, 1225 (O–C–O). ^1H NMR spectrum, δ, ppm: 1.30–1.60 m (7H, carboring $CH_2CH_2CHCH_2$), 3.25–4.40 m (7H, CH_2O, CHO, $ClCH_2CH_2O$), 4.68 d (3H, 3HCBr).

Compounds **XXXI**–**XXXVII** were synthesized in a similar way.

2-(1,8,9,10,11,11-Hexachlorotricyclo[6.2.1.0^{2,7}]undec-9-en-5-yl)-4-(2-chloroethoxymethyl)-1,3-dioxolane (XXXIX). A mixture of 24.7 g of compound **XIV** and 54.6 g of HCCPD was stirred for 12 h at 140–150°C. Excess HCCPD was removed by distillation, and the residue was distilled in a vacuum to obtain compound **XXXIX**.

Compounds **XXXVIII** and **XL** were obtained in a similar way (see table).

2-[2(1)-Chlorocyclohexyl-1(2)-hydroxy]-4-(2-chloroethoxymethyl)-1,3-dioxolane (XLI). Hydrogen chloride was passed through a mixture of 39.4 g of compound **XXII** and 50 ml of ether at –10 to –5°C (the weight gain was determined by weighing). The ether was removed by distillation, and the residue was istilled in a vacuum to isolate compound **XLI**. The IR spectrum of dioxolane **XLI** contains no bands at 800 and 920 cm^{-1} and contains a broad band at 3450–3500 cm^{-1}, characteristic of associated OH group.

ACKNOWLEDGMENTS

The author is deeply grateful to M.G. Babaev for help in determining reaction rates and designing the paper.

REFERENCES

1. Babaev, M.G., Kerimov, A.Kh., and Khalilov, Kh.D., Abstracts of Papers, *2 Mezhdunarodnaya nauchnaya konferentsiya "Tonkii organicheskii sintez i kataliz"* (2nd Int. Scientific Conf. "Fine Organic Synthesis and Catalysis," Baku, 2002, pp. 102–103.
2. Kerimov, A.Kh., Babaev, M.G., and Mishiev, D.E., *Zh. Org. Khim.*, 1985, vol. 21, no. 3, p. 645.
3. Kerimov, A.Kh., Babaev, M.G., and Mishiev, D.E., *Zh. Org. Khim.*, 1987, vol. 23, no. 6, p. 1194.
4. US Patent 2113454, *Chem. Abstr.*, 1972, vol. 77, no. 25, N 164665.
5. Lebedev, N.N., *Khimiya i tekhnologiya osnovnogo organicheskogo i neftekhimicheskogo sinteza* (Chemistry and Technology of the Ground Organic and Petrochemical Synthesis), Moscow: Khimiya, 1975, pp. 671–673.
6. Taganliev, A., Berdieva, E., Rol'nik, L.Z., Zlotskii, S.S., Rakhmankulov, D.L., and Samirkhanov, Sh.M., USSR Inventor's Certificate no. 1553532, *Byull. Izobret.*, 1990, no. 12.
7. Trofimov, B.A., Atavin, A.S., and Gavrilova, G.M., USSR Inventor's Certificate no. 281461, *Byull. Izobret.*, 1973, no. 25.
8. Böhm, R., *Wiss. Z. Univ.*, 1980, vol. 29, no. 2, p. 97.
9. Ol'shanova, K.M., Potapova, M.A., and Morozova, N.M., *Praktikum po khromatograficheskomu analizu* (Manual on Chromatographic Analysis), Moscow: Vysshaya Shkola, 1970, pp. 63–66.
10. Babaev, M.G., Kerimov, A.Kh., Mishiev, D.E., Ragimov, A.V., and Shteinberg, B.Ya., Available from VINITI, 1985, Moscow, no. 6895-B-85.
11. Leidler, K., *Kinetika organicheskikh reaktsii* (Kinetics of Organic Reactions), Moscow: Mir, 1966, pp. 341–345.
12. Sykes, P., *A Guidebook to Mechanism in Organic Chemistry*, 2nd ed., London: Longmans, 1966. Translated under the title *Mekhanizmy reaktsii v organicheskoi khimii*, Moscow: Khimiya, 1991, pp. 31–33.
13. Luknitskii, F.I., *Chem. Rev.*, 1975, vol. 75, no. 3, p. 259.
14. *Laboratornye raboty po organicheskoi khimii* (Laboratory Works in Organic Chemistry), Ginzburg, O.F. and Petrov, A.M., Moscow: Vysshaya Shkola, 1982, pp. 240–254.