ISSN 1070-4280, Russian Journal of Organic Chemistry, 2010, Vol. 46, No. 6, pp. 924–925. © Pleiades Publishing, Ltd., 2010.
Original Russian Text © B.F. Kukharev, V.K. Stankevich, N.A. Lobanova, G.R. Klimenko, G.A. Volkov, 2010, published in Zhurnal Organicheskoi Khimii, 2010, Vol. 46, No. 6, pp. 924–925.

SHORT COMMUNICATIONS

# Synthesis of 2-[2-Hydroxy-3-(vinyloxy)propoxy]benzaldehyde and Its Cyclization into *trans*- and *cis*-2-[(2-Methyl-1,3-dioxolan-4-yl)methoxy]benzaldehydes

**B. F. Kukharev, V. K. Stankevich, N. A. Lobanova, G. R. Klimenko, and G. A. Volkov**

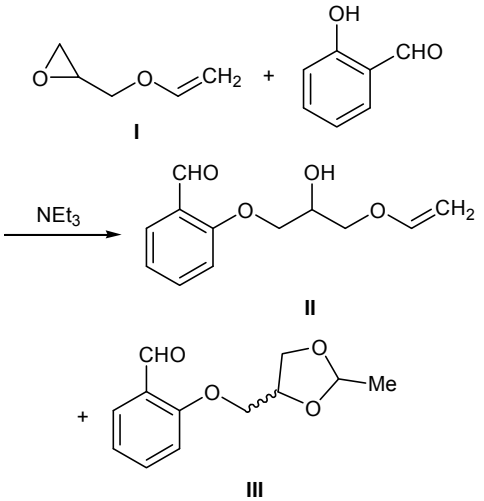
*Favorskii Irkutsk Institute of Chemistry, Siberian Division, Russian Academy of Sciences, ul. Favorskogo 1, Irkutsk, 664033 Russia*
*e-mail: irk_inst_chem@irioch.irk.ru*

Received December 30, 2009

**DOI:** 10.1134/S1070428010060242

1,3-Dioxolane derivatives exhibit a broad spectrum of biological activity [1]; in particular, various pesticides were found among these compounds [2]. With a view to further study pesticidal activity of 1,3-dioxolane derivatives, we have developed a procedure for the synthesis of 2-[(2-methyl-1,3-dioxolan-4-yl)-methoxy]benzaldehyde possessing salicylaldehyde and 1,3-dioxolane fragment.

We previously reported on the synthesis of 2-{2-hydroxy-3-[2-(vinyloxy)ethoxy]propoxy}benzaldehyde by reaction of 2-hydroxybenzaldehyde with ethylene glycol vinyl glycidyl ether, catalyzed by triethylamine [3]. The reaction of salicylaldehyde with glycidyl vinyl ether under analogous conditions, apart from expected 2-[2-hydroxy-3-(vinyloxy)propoxy]benzaldehyde (**II**), gave cyclic products, *trans*- and *cis*-isomeric dioxolanes **III**. According to the $^1$H NMR data, the ratio **II**:**III** (*cis* + *trans*) was 1:0.18, the ratio of isomeric dioxolanes *trans*-**III** and *cis*-**III** being 1:1.




No reaction occurred below 190°C. The optimal temperature was 210–220°C; therefore, the observed formation of dioxolanes **III** is likely to result from known thermal cyclization of vinyl ethers derived from polyols [4]. In fact, by heating vinyl ether **II** at 210°C over a period of 2 h we obtained an equimolar mixture of isomeric dioxolanes **III** in 28% yield together with resinous products.

Taking into account the poor yield of **III** in the thermal cyclization of vinyl ether **II**, the latter was subjected to acid-catalyzed cyclization. The reaction in the presence of a catalytic amount of hydrochloric acid was accompanied by weak heat evolution (the temperature rose by (2–3°C), and the products were stereoisomeric dioxolanes **III** at a ratio of 56:44 ($^1$H NMR data), the overall yield being 53%. Taking into account different fraction of the isomers, we succeeded in assigning with certainty most signals in the $^1$H and $^{13}$C NMR spectra to particular isomers. Presumably, the major stereoisomer is *trans*, and the minor, *cis*.

**2-[2-Hydroxy-3-(vinyloxy)propoxy]benzaldehyde (II).** A mixture of 26.1 g (0.26 mol) of vinyl ether **I**, 30.5 g (0.25 mol) of 2-hydroxybenzaldehyde, and 0.75 g (0.75 mmol) of triethylamine was quickly heated to 215°C, cooled, and distilled under reduced pressure. Yield 58%, bp 177–179°C (3 mm), $n_D^{20}$ = 1.5504. IR spectrum, ν, cm$^{-1}$: 3444, 3116, 3077, 3042, 2986, 2936, 2878, 2762, 1687, 1678, 1638, 1619, 1600, 1583, 1485, 1458, 1399, 1321, 1304, 1288,

1243, 1198, 1163, 1105, 1082, 1044, 1031, 999, 962, 864, 842, 810, 760, 722, 691, 653, 636, 598, 531, 440. $^1$H NMR spectrum, δ, ppm: 3.92 m (2H, $OCH_2$, OH), 4.03 d.d (1H, *cis*-HC=CO, $^2J$ = 2.3, $^3J_{cis}$ = 6.8 Hz), 4.15 m (3H, ArOC**H**$_A$H$_B$C**H**CH$_A$**H**$_B$), 4.21 d.d (1H, *trans*-HC=CO, $^2J$ = 2.3, $^3J_{trans}$ = 14.3 Hz), 4.32 m (1H, ArOCH$_A$**H**$_B$), 6.45 d.d (1H, OCH=C, $^3J_{cis}$ = 6.8, $^3J_{trans}$ = 14.3 Hz), 7.02 m (2H, 3-H, 5-H), 7.49 d.d (1H, 4-H, $^3J$ = 7.3, $^4J$ = 1.8 Hz), 7.76 d.d (1H, 6-H, $^3J$ = 7.6, $^4J$ = 1.8 Hz), 10.37 s (1H, CHO). $^{13}$C NMR spectrum, $\delta_C$, ppm: 68.33 (CHOH), 68.50 ($CH_2O$), 69.63 ($ArOCH_2$), 87.44 (=$CH_2$), 112.92 ($C^3$), 121.21 ($C^5$), 125.01 ($C^1$), 129.41 ($C^6$), 135.99 ($C^4$), 151.33 (OCH=), 160.61 ($C^2$), 189.80 (C=O). Found, %: C 65.00; H 6.45. $C_{12}H_{14}O_4$. Calculated, %: C 64.85; H 6.35.

**Cyclization of 2-[2-hydroxy-3-(vinyloxy)propoxy]benzaldehyde (II).** Concentrated hydrochloric acid, 0.05 g, was added under stirring at room temperature to 11.1 g (0.05 mol) of vinyl ether **II**, and the mixture was stirred for 1 h and distilled under reduced pressure to isolate a mixture of *trans* and *cis* isomers of compound **III**. Yield 53%, bp 187–190°C (4 mm), $n_D^{20}$ = 1.5431. IR spectrum, ν, cm$^{-1}$: 3076, 3042, 2989, 2937, 2875, 2788, 2761, 1688, 1657, 1600, 1583, 1486, 1458, 1401, 1368, 1350, 1304, 1287, 1257, 1242, 1225, 1201, 1191, 1160, 1151, 1116, 1106, 1092, 1043, 1033, 979, 959, 938, 930, 899, 862, 845, 807, 761, 729, 693, 648, 634, 597, 531, 515, 441. Found, %: C 64.91; H 6.40. $C_{12}H_{14}O_4$. Calculated, %: C 64.85; H 6.35.

**2-[*trans*-(2-Methyl-1,3-dioxolan-4-yl)methoxy]benzaldehyde (IIIa).** $^1$H NMR spectrum, δ, ppm: 1.39 t (3H, Me, $^3J$ = 4.9 Hz), 3.78–4.55 m (5H, $CH_2CHCH_2$), 5.19 q (1H, C**H**Me, $^3J$ = 4.9 Hz), 6.88–7.02 m (2H, 3-H, 5-H), 7.48–7.54 m (1H, 4-H), 7.77–7.86 m (1H, 6-H), 10.47 s (1H, CHO). $^{13}$C NMR spectrum, $\delta_C$, ppm: 19.79 (Me), 67.12 (ArO**C**$H_2$), 68.68 (**C**$H_2$OCHMe), 73.61 (**C**HOCHMe), 102.02 (OCO), 112.51 ($C^3$), 121.21 ($C^5$), 124.96 ($C^1$), 128.42 ($C^6$), 135.84 ($C^4$), 160.71 ($C^2$), 189.16 (C=O).

**2-[*cis*-(2-Methyl-1,3-dioxolan-4-yl)methoxy]benzaldehyde (IIIb).** $^1$H NMR spectrum, δ, ppm: 1.36 t (3H, Me, $^3J$ = 4.9 Hz), 3.78–4.55 m (5H, $CH_2CHCH_2$), 5.07 q (1H, C**H**Me, $^3J$ = 4.9 Hz), 6.88–7.02 m (2H, 3-H, 5-H), 7.48–7.54 m (1H, 4-H), 7.77–7.86 m (1H, 6-H), 10.48 s (1H, CHO). $^{13}$C NMR spectrum, $\delta_C$, ppm: 19.76 (Me), 67.32 (ArO**C**$H_2$), 69.19 (**C**$H_2$OCHMe), 73.83 (**C**HOCHMe), 102.34 (OCO), 112.64 ($C^3$), 121.14 ($C^5$), 124.99 ($C^1$), 128.25 ($C^6$), 135.81 ($C^4$), 160.79 ($C^2$), 189.35 (C=O).

The $^1$H and $^{13}$C NMR spectra were recorded at 26°C on a Bruker DPX-400 spectrometer at 400 and 100 MHz, respectively, using $CDCl_3$ as solvent and hexamethyldisiloxane as internal reference. The IR spectra were measured on a Bruker Vertex-70 spectrometer from samples prepared as thin films.

## REFERENCES

1. Elderfield, R.C. and Short, F., *Heterocyclic Compounds*, Elderfield, R.C., Ed., New York: Wiley, 1957, vol. 5. Translated under the title *Geterotsiklicheskie soedineniya*, Moscow: Inostrannaya Literatura, 1961, vol. 5, p. 7.
2. Mel'nikov, N.N., *Pestitsidy. Khimiya, tekhnologiya i primenenie* (Pesticides. Chemistry, Technology, and Application), Moscow: Khimiya, 1987, p. 530.
3. Kukharev, B.F., Stankevich, V.K., Klimenko, G.R., Kukhareva, V.A., and Bragin, E.V., *Russ. J. Org. Chem*., 2008, vol. 44, p. 1494.
4. Trofimov, B.A., *Geteroatomnye proizvodnye atsetilena* (Heteroatom Acetylene Derivatives), Moscow: Nauka, 1981, p. 8.