PREPARATION OF γ-BUTYROLACTONES BY OXIDATION OF MONOFUNCTIONAL TETRAHYDROFURAN DERIVATIVES

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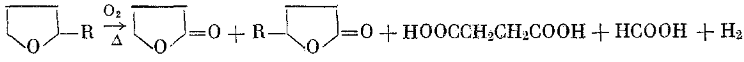
The reaction of tetrahydrofuran (THF) with oxygen, which occurs in the presence of peroxides or salts of metals of variable valence, or is initiated by UV irradiation, results in the formation of α-hydroxytetrahydrofuran and γ-butyrolactone [1-8]. γ-Hydroxyketones are obtained by the oxidation of α-alkyltetrahydrofurans, probably as a result of decomposition of the hydroperoxides which precede them; the formation of lactones is not observed in this case [7, 8].

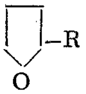
In this paper we have investigated the liquid-phase oxidation of monofunctional THF derivatives: tetrahydrofurfuryl alcohol (I), its formate (II) and acetate (III), and methyl 2-tetrahydrofurancarboxylate (IV). Two products, via., γ-butyrolactone and the corresponding substituted γ-butyrolactone with a functional group in the γ-position (Table 1), are principally formed from these compounds. Their overall yields, allowing for the degree of conversion of the starting substance are: 76% from (I), 72% from (II), 95% from (III), and 81% from (IV); γ-butyrolactone is, as a rule, formed in the greatest amounts.

A small amount of succinic acid, which apparently arises due to oxidation of a portion of the lactones to succinic anhydride with subsequent hydrolysis [9], is detected in the reaction products. The cleaved side functional group is converted to formic acid:



R=CH_2OH (I), $CH_2OC(O)H$ (II), $CH_2OC(O)CH_3$ (III), $C(O)OCH_3$ (IV).

TABLE 1. Conditions and Results of the Oxidation of



Compound No.	Starting compound			T, °C	Time, h	Reaction products, mole				
	R	No. of moles used in the reaction	conversion, %			γ-butyrolactone	γ-R-γ-butyrolactone †	formic acid	succinic acid	water
I	$-CH_2OH$	1.0	0.59	115	10	0.37	0.06 0.02	0.09	0.01	0.78
II	$-CH_2O\overset{\overset{O}{\|}}{C}-H$	0.5	0.48	115	10	0.22	0.04 0.08	0.13	0.02	0.22
III	$-CH_2O\overset{\overset{O}{\|}}{C}CH_3$	0.5	0.47	115	25	0.22	0.07 0.158	0.09	0.03	0.28
IV	$-\overset{\overset{O}{\|}}{C}OCH_3$	0.615	0.59	70 *	18	0.29	0.19	0.25	0.07	0.20

* The reaction was carried out in the presence of 0.5 g of $(CH_3COO)_2Mn \cdot 4H_2O$.

† The upper number refers to γ-hydroxymethyl-γ-butyrolactone, while the lower number refers to its formate (oxidation of I and II) or acetate (III).

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Under the reaction conditions, the formic acid partially esterifies (I) [10] and γ-hydroxymethyl-γ-butyrolactone. On the other hand, in the oxidation of (II) and (III) a certain amount of the ester groups in the reaction products are saponified, as a result of which γ-hydroxymethyl-γ-butyrolactone is obtained along with its fprmate and acetate.

Thus the reaction of oxygen with monofunctional THF derivatives, like the oxidation of α-methyl tetrahydrofuran [11], proceeds at two reaction centers, viz., C_2 and C_5. UV irradiation accelerates the oxidation and makes it possible to carry out the reaction at a lower temperature.

EXPERIMENTAL METHOD

The oxidation was carried out in a 150 ml cylindrical glass reactor equipped with a horizontal porous diaphragm, a tube for supplying oxygen to its lower portion, a reflux condenser, and a trap at the gas outlet cooled to –70°. The reactor was heated with a thermostated bath. The oxygen was supplied at 10 liter/h during the oxidation of (I), (III), and (IV) and at 15 liter/h for the oxidation of (II).

The percentages of starting substances in the lactones formed in the oxidates of (I), (II), and (III) were determined by gas–liquid chromatography using standard samples (in particular, γ-hydroxymethyl-γ-butyrolactone [12] and an internal standard, γ-amyl-γ-butyrolactone, in the oxidate of (IV) by vacuum distillation and gas–liquid chromatography. Formic acid was identified by gas–liquid chromatography, and the amount of it was determined by titration of the oxidate and the fraction with bp up to 120° which was isolated from it. The water content was found by the Fischer method, and succinic acid with mp 190° was isolated from the oxidate by distillation and crystallization.

Oxidation of (I). Distillation from the oxidate yielded a mixture of 0.26 mole of (I) in 0.15 mole of its formate, γ-butyrolactone, and a mixture of γ-hydroxymethyl-γ-butyrolactone and its formate. The composition of the mixture of lactones (see Table 1) was determined from the integral intensities of the protons of the hydroxyl (δ 5.5 ppm) and formate (8 ppm) groups in the NMR spectrum; the IR spectrum contained the following bands (ν, cm^{-1}): 1775 (lactone C=O), 1725 (formyl group C=O), and 1050 and 3450 (OH group).

Oxidation of (II). The workup and analysis of the oxidate were carried out similarly.

Oxidation of (III). In addition to the compounds listed in Table 1, the reaction mass contained 0.26 mole of acetic acid. Distillation of it yielded γ-acetoxymethyl-γ-butyrolactone with bp 143-144° (10 mm); n_D^{20} 1.4515, d_4^{20} 1.1874. Found: C 52.64; H 6.70%; MR 35.89. $C_7H_{10}O_4$. Calculated: C 53.16; H 6.38%; MR 35.68. The characteristic bands in the IR spectrum (ν, cm^{-1}) were as follows: 1250, 1745 (CH_3COO), and 1785 (lactone C=O). Mass spectrum: $M^+ = 144$, m/e 100 (M – 44), 85 (M – 59), 59 ($COOCH_3$), and 44 (CO_2). Saponification of this compound yielded γ-hydroxymethyl-γ-butyrolactone with bp 107-108° (0.8); n_D^{20} 1.4650, d_4^{20} 1.2120. Found: C 50.92; H 7.15%; MR 26.25. $C_5H_8O_3$. Calculated: C 51.75; H 6.91%; MR 26.27. IR spectrum (ν, cm^{-1}): 1775 (lactone C=O), 1050 and 3450 (OH group). Mass spectrum: $M^+ = 116$, m/e 85 (M –31), 72 (M – 44), 44 (CO_2), 31 (CH_2OH).

Oxidation of (IV). Distillation yielded γ-carbomethoxy-γ-butyrolactone with bp 78-79° (0.1 mm); n_D^{20} 1.4520, d_4^{20} 1.1725. Found: C 49.42; H 5.82%; MR 31.20. $C_6H_8O_4$. Calculated: C 50.00; H 5.59%; MR 31.02. IR spectrum (ν, cm^{-1}): 1250, 1745 ($COOCH_3$), 1790 (lactone C=O). Mass spectrum: M^+ 158, m/e 100 (M – 44), 85 (M – 59), 59 ($COOC_2H_5$), and 44 (CO_2). Traces of the allyl methyl ester of oxalic acid were detected in the reaction products.

CONCLUSIONS

The major products in the oxygen-oxidation of tetrahydrofurfuryl alcohol, its esters, and an ester of 2-tetrahydrofurancarboxylic acid are γ-butyrolactone and the corresponding γ-substituted γ-butyrolactone.

LITERATURE CITED

1. V.J.Stenberg, Ch.T.Wang, and N.Kulevsky, J.Organ.Chem., 35, 1774 (1970).
2. K.Scherf and K.Schmeidl, German Patent No.1222034 (1966); Chem.Abstr., 65, 15238 (1966).
3. N.Kulevsky, Ch.T.Wang, and V.J.Stenberg, J.Organ.Chem., 34, 1345 (1969).
4. J.G.M.Bremner and D.G.Jones, British Patent No.608539 (1948); Chem.Abstr., 43, 2224 (1949).
5. Sh.Murai, N.Sonoda, and Sh.Tsutsumi, Bull.Chem.Soc.Japan, 35(5), 527 (1963); Chem.Abstr., 60, 2877 (1964).
6. A.Robertson, Nature, 162, 153 (1948).

7. Usines de Melle, British Patent No. 614392 (1948); Chem. Abstr., 44, 1531 (1950).
8. M. Maincon and P. Chassaing, Canadian Patent No. 496332 (1953); Referativnyi Zh. Khim., 13935P (1956).
9. K. Schmeidl and K. Scherf, German Patent No. 1183897 (1964); Chem. Abstr., 62, 6397 (1965).
10. G. J. Baumgarther and Ch. L. Willson, J. Amer. Chem. Soc., 81, 2440 (1959).
11. G. I. Nikishin, V. G. Glukhovtsev, M. A. Peikova, and A. V. Ignatenko, Izv. Akad. Nauk SSSR, Ser. Khim., 2320 (1971).
12. G. I. Nikishin, S. S. Spektor, and V. G. Glukhovtsev, Izv. Akad. Nauk SSSR, Ser. Khim., 397 (1971).