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SUBSTITUTED LACTONES AND THEIR REACTIONS

VII. Preparation of 2-Methyl-3-alkyltetrahydropyrans and 3-Alkylhexane-2,6-diols by Reducing δ-Methyl-γ-alkyl-δ-valerolactones*

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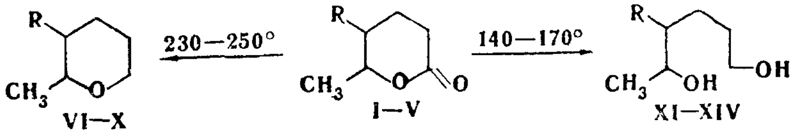
Hydrogenation of δ-methyl-γ-alkyl-δ-valerolactones with copper-chromium catalyst at 230°–250° gives 2-methyl-3-alkyltetrahydropyrans. Reduction of these lactones at 140°–170° gives 3 alkylhexane-2, 6-diols.

Continuing our research on converting α-alkyl- and α, γ-dialkylbutyrolactones to mono- and dialkyltetrahydrofurans, by reduction in the presence of copper-chromium catalyst [1, 2], it proved of interest to effect a similar conversion of δ-methyl-γ-alkyl-δ-valerolactones to the corresponding alkyltetrahydropyrans.

It had previously been found [1, 2] that reduction of alkylbutyrolactones using copper-chromium catalyst at 210°–220° C gave mainly 2-alkylbutane-1, 4-diols, while the corresponding alkyltetrahydrofurans were obtained almost exclusively by raising the temperature to 250°.

The present research deals with conversion of a number of δ-methyl-γ-alkyl-δ-valerolactones (I–V) by hydrogenation with copper-chromium catalyst. The same dependence was observed, reduction at 140°–170° C giving 3-alkylhexane-2, 6-diols (XI–XIV), and the main product at 250° C being the corresponding 2-methy-3-alkyltertetrahydropyrans (VI–X). Formation of the tetrahydropyran ring obviously involves first opening of the lactone ring to give the 3-alkylhexane-2, 6-diol, which then subsequently undergoes intramolecular dehydration.



I, VI, XI R=C_3H_7 IV, IX, XII R=C_6H_{13}
II, VII R=C_4H_9 V, X, XIII R=C_7H_{15}
III, VIII R=C_5H_{11} XIV R=H

The fact that these products contained a pyran ring was confirmed by their having zero ester and hydroxyl values, as well as by their IR spectra, which show the absence of carbonyl and hydroxyl groups, and the presence of an ethereal linkage. The gas chromatograms of the tetrahydropyrans VI–X exhibited two peaks close together and of approximately equal size, so that the products were apparently mixtures of stereoisomers, differing with respect to the spatial dispositions of the alkyl and methyl groups. Such mixtures are to be expected, as the starting lactones I–V are largely mixtures of the corresponding stereoisomers [3–5]. For the same reason the 3-alkylhexane-2, 6-diols (XI–XIV) prepared were also mixtures of diastereoisomers. Possibly for that reason derivatives of them obtained by reacting the hydroxyl group could not be isolated pure. These derivatives (bis-p-nitrobenzoates and bisphenylurethanes) were invariably oils which did not crystallize. However, it was worth passing to the lactone without a γ alkyl substituent, i.e., to the δ-methyl-δ-valerolactone, as the hexane-1, 5-diol derived from it gave an urethane with a characteristic sharp melting point.

It should be mentioned that on passing from lactones I–V to the tetrahydropyrans VI–X the floral tendency of the odor characteristic of the lactones is retained, and only a fruity tone is acquired, this being particularly manifest with 2-methyl-3-propyltetrahydropyran (VI), and decreasing with increase in the number of C atoms in the γ alkyl substituent.

Experimental

The lactones I–V were synthesized as previously described [3–5].

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* For Part VI see [1].

Table 1

Properties of 2-Methyl-3-alkyltetrahydropyrans

Compound number	Name	Bp (pressure mm)	d_4^{20}	n_D^{20}	MR_D		Formula	Found, %		Calculated,%		Yield, %
					Found	Calc.		C	H	C	H	
VI	2-Methyl-3-propyltetrahydropyran	65 (3)	0.8574	1.4407	43.75	43.56	$C_9H_{18}O$	76.12 76.11	12.66 12.71	76.01	12.75	27
VII	2-Methyl-3-butyltetrahydropyran*	65 (7)	0.8604	1.4404	47.95	48.18	$C_{10}H_{20}O$	76.62 76.74	12.83 12.87	76.89	12.89	66
VIII	2-Methyl-3-amyltetrahydropyran	80—81 (7)	0.8578	1.4439	52.71	52.85	$C_{11}H_{22}O$	77.65 77.83	13.03 13.21	77.58	13.02	45
IX	2-Methyl-3-hexyltetrahydropyran	99—102 (13)	0.8523	1.4462	57.68	57.45	$C_{12}H_{24}O$	78.16 78.04	12.98 13.00	78.19	13.13	63
X	2-Methyl-3-heptyltetrahydropyran	131—132 (16)	0.8523	1.4475	62.23	62.15	$C_{13}H_{26}O$	78.79 78.79	13.26 13.05	78.72	13.21	58

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* The IR spectrum of VII had intense bands at 1090 and 1100 cm^{-1}, showing that the molecule contained the C–O–C group. The spectrum was observed by I. V. Nikitin, with a UR-10 instrument.

Table 2

Properties of 3-Alkylhexane-2, 6-diols

Compound number	Name	Bp (pressure mm)	d_4^{20}	n_D^{20}	MR_D		Formula	Found, %		Calculated,%		Yield, %
					Found	Calc.		C	H	C	H	
XI	3-Propylhexane-2, 6-diol	145 (9)	0.9399	1.4593	46.61	46.89	$C_9H_{20}O_2$	67.14 67.38	12.56 12.41	67.45	12.58	81
XII	3-Hexylhexane-2, 6-diol	137—138 (2)	0.9160	1.4612	60.59	60.78	$C_{12}H_{26}O_2$	71.29 71.38	13.12 12.94	71.23	12.95	58
XIII	3-Heptylhexane-2, 6-diol*	155—156 (3)	0.9135	1.4624	65.16	65.47	$C_{13}H_{28}O_2$	72.36 72.18	13.03 13.14	72.16	13.05	83
XIV	Hexane-2, 6-diol**	115—116 (5)	0.9774	1.4520	32.64	32.95	$C_6H_{14}O_2$	—	—	—	—	52

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* Diacetate XIII: bp 170° (15 mm), d_4^{20} 0.9419, n_D^{20} 1.4432, the ester value shows 97.2% purity. Found: C 68.85, 68.71; H 12.43, 12.45%; MR_D 84.59. Calculated for $C_{17}H_{32}O_4$: C 67.96; H 10.74%; MR_D 84.42.

** Diphenylurethane XIV, mp 129°–130° C (ex octane).

Preparation of 2-methyl-3-alkyltetrahydropyrans (VI-X). 10 g δ-methyl-γ-valerolactone (I-V) was hydrogenated in a 150 ml rotating autoclave, using 2 g Cu-Cr catalyst at 230°-250° and 100-150 atm, until 2 moles H_2 were absorbed per mole lactone, after which the same temperature was maintained for a further 3 hr to ensure complete conversion of the initial diol to tetrahydropyran. The catalyst was separated off, washed with EtOH, the filtrates bulked, evaporated and vacuum-fractionated. The results are given in Table 1.

Preparation of 3-alkylhexane-2, 6-diols (XI-XIV). Hydrogenation was effected in exactly the same way, except that the temperature was 140°-170° C, and the products were worked up in the same way. The results are given in Table 2. Acetylation showed that the diols XI-XIV were not less than 98.8% pure.

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