STUDIES IN THE FIELD OF OXYGEN-CONTAINING HETEROCYCLES

XIV.* REACTION OF CHLOROTETRAHYDROPYRANS WITH ENOL ACETATES

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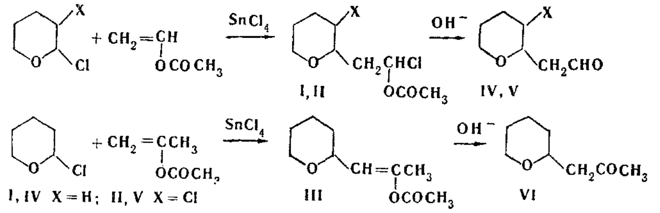
2-Chloro- and 2,3-dichlorotetrahydropyrans add to vinyl acetate in the presence of $SnCl_4$ with the formation of the corresponding gem-acetoxychlorides. The addition of 2-chlorotetrahydropyran to isopropenyl acetate is accompanied by the splitting out of HCl and the formation of the corresponding substituted enol acetate. The reaction products have been hydrolyzed to aldehydes and ketones.

We have previously shown [1] that various aldehydes of the tetrahydrofuran series can be obtained from 2-chlorotetrahydrofurans. In the present work we have established the possibility of obtaining other carbonyl compounds of the tetrahydropyran series similarly.

2-Chloro- and 2,3-dichlorotetrahydropyrans react with vinyl acetate in the presence of $SnCl_4$ in CCl_4 with the formation of addition products. 2-Chlorotetrahydropyran adds to isopropenyl acetate with the simultaneous splitting out of hydrogen chloride. The compounds obtained are hydrolyzed to aldehydes and ketones:



The hydrolysis of I and II was effected in aqueous dioxane solution in the presence of sodium bicarbonate, while III was hydrolyzed with alcoholic alkali.

The structures of compounds I and III were confirmed by their NMR spectra (see Fig. 1). The spectrum of compound I has the following signals: a triplet of the proton of the side chain most remote from the nucleus (δ 6.60 ppm, J = 7 Hz; the proton apparently interacts with the 2-proton of the ring with J = 2 Hz); the signals of the 2-proton of the ring (the two components with δ 3.90 and 4.00 ppm are most probably due to two diastereomers of compound I); the signals of the 6-protons (δ about 3.4 ppm); a strong signal of the acetyl protons (apparently of two diastereomers with δ 2.09 and 2.11 ppm) superimposed on the signals of the methylene group of the side chain (the extreme components can be seen); and the signals of the 3,4,5-protons of the ring (δ about 1.5 ppm).

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*For Communication XIII, see [1].

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TABLE 1.

Compound	bp, °C (pressure mm)	d_4^{20}	n_D^{20}	MR_D		Empirical formula	Found %			Calc. %			Yield, %
				found	calc.		C	H	Cl	C	H	Cl	
I	100(2)	1,1267	1,4569	49,63	49,95	$C_9H_{15}ClO_3$	—	—	17,27	—	—	17,18	48
II	94(1)	1,2391	1,4729	54,52	54,91	$C_9H_{14}Cl_2O_3$	—	—	29,25	—	—	29,42	55
III	108(2)	1,0069	1,4549	49,45	49,44	$C_{10}H_{16}O_3$	65,13	9,52	—	65,22	9,52	—	54
IV	98(15)	1,0268	1,4512	34,18	33,95	$C_7H_{12}O_2$*	65,50	9,43	—	65,59	9,44	—	66
V	94(3)	1,1842	1,4709	38,99	39,05	$C_7H_{11}ClO_2$†	—	—	21,78	—	—	21,54	76
VI	55(2)	0,9914	1,4484	38,91	39,60	$C_8H_{14}O_2$‡	66,90	9,43	—	67,56	9,92	—	45

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*2,4-Dinitrophenylhydrazone: mp 104°C. Found %: N 16.85; $C_{13}H_{16}N_4O_5$. Calculated %: N 16.29.

†2,4-Dinitrophenylhydrazone: mp 114°C. Found %: N 17.75. $C_{13}H_{15}ClN_4O_5$. Calculated %: N 18.10.

‡2,4-Dinitrophenylhydrazone: mp 122°C. Found %: N 15.23. $C_{14}H_{18}N_4O_5$. Calculated %: N 15.65.

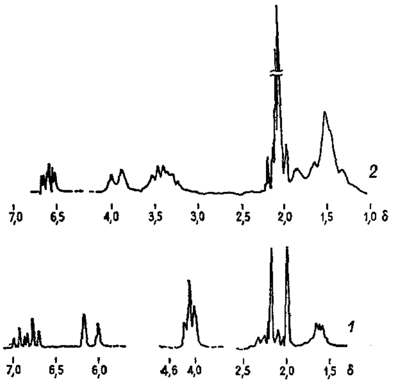

Fig. 1. NMR spectra: 1) 2-(2'-acetoxyprop-1'-enyl)tetrahydropyran (III); 2) 2-(2'-acetoxy-2'-chloroethyl)tetrahydropyran (I).

The NMR spectrum of compound III is similar to the spectrum of the analogous ester of the tetrahydrofuran series, published previously [1]. The 2-proton of the ring is characterized by δ 6.85 ppm and interacts with the olefinic proton and the 3-protons of the ring with J values of, respectively, 17 and 7 Hz. The spectrum also has the doublet of the olefinic proton (δ 6.09 ppm), the signals of the 6-protons (4.08 ppm), and the singlets of the methyl groups on a background of the signals of the other protons of the ring.

EXPERIMENTAL

Reaction of the Chlorides with Enol Acetates. A solution of 0.3 mole of a freshly distilled chloride in 80 ml of dry CCl_4 was treated with 8 ml of a 10% solution of $SnCl_4$ in CCl_4. With stirring, 0.3 mole of an enol acetate was added dropwise, and the mixture was stirred for another 1-2 h (25°C) and left for two days, after which 1 ml of pyridine and 30 ml of petroleum ether were added and, after 40 min, it was filtered through a layer of alumina (2 cm). The solvent was evaporated off and the residue was distilled in vacuum (see Table 1).

Tetrahydropyran-2-ylacetaldehyde (IV). A mixture of 6.2 g of compound I, 50 ml of dioxane, 20 ml of water, and 3 g of $NaHCO_3$ was heated at 75-90°C with vigorous stirring. The course of the hydrolysis was followed by thin-layer chromatography on alumina. After the disappearance of the starting material, the reaction mixture was stirred with 50 ml of ether, and the organic layer was separated off and dried with $MgSO_4$, the solvent was evaporated off, and the residue was distilled in vacuum (see Table 1).

(3-Chlorotetrahydropyran-2-yl)acetaldehyde (V) was obtained similarly from 11.8 g of compound II, 175 ml of dioxane, 20 ml of water, and 5.5 g of $NaHCO_3$ (see Table 1).

Tetrahydropyran-2-ylacetone (VI). With vigorous stirring at 50°C, a 20% solution of KOH in ethanol was added dropwise to a solution of 1.5 g of compound III in 50 ml of ethanol containing thymolphthalein. A minimum excess of alkali in the solution was maintained in accordance with the color of the indicator. The course of the hydrolysis was followed by thin-layer chromatography on alumina. After the disappearance of the starting material, the solution was diluted twofold with water and extracted with ether, the extract was dried with $MgSO_4$, the solvent was evaporated off, and the residue was distilled in vacuum.

The NMR spectra were taken on a JNM-3H-100 (100 MHz) instrument using 30% solutions in CCl_4 with hexamethyldisiloxane as internal standard. The authors are grateful to A. V. Golovin for taking the spectra.

LITERATURE CITED

1. Yu. I. Tarnopol'skii and A. K. Nadelyaeva, Chemistry of Heterocyclic Compounds, Collection 2 (1970).