ARYLOXYDIHYDROPYRANS

IX*. THE DIENE CONDENSATION OF ARYL VINYL ETHERS WITH CROTONALDEHYDE AND CINNAMALDEHYDE

V. G. Kozyrev, G. G. Skvortsova,
and M. F. Shostakovskii

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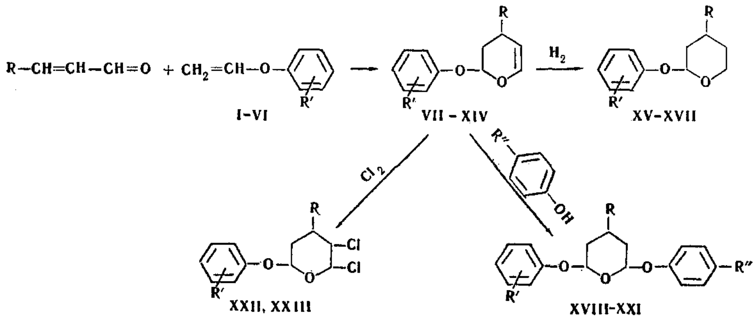
Heating aryl vinyl ethers with crotonaldehyde and cinnamaldehyde forms 2-aryloxy-4-methyl(phenyl)-3,4-dihydropyrans. In these adducts, the double bond of the dihydropyran ring possesses a high reactivity and readily adds hydrogen, halogens, and phenols.

Crotonaldehyde and cinnamaldehyde readily form adducts by the diene synthesis with alkyl vinyl ethers [1, 2]. We have established previously that aryl vinyl ethers play the role of dienophiles on reaction with acrolein [3].

The present work was devoted to a study of the condensation of vinyl ethers of phenol (I), of o-, m-, and p-cresols (II-IV), of 2,4-xylenol (V), and of o-fluorophenol (VI) with crotonaldehyde and cinnamaldehyde. The reactions take place in 10-12 h at 180-200°C, i.e., they require a longer time at a higher temperature than in the case of acrolein. The properties of the adducts are given in Table 1. The presence in the IR spectra of these compounds of absorption bands at 1080, 1093, and 1108 cm^{-1} shows their pyran structure, and the bands in the 1650-1660 cm^{-1} region indicate the presence of a double bond in this ring. Their purity was confirmed by thin-layer chromatography.

The 2-aryloxydihydropyrans VII and X readily react with phenols in the presence of acid catalysis with the formation of the mixed acetals XVIII-XXI as the sole products. No disproportionation of the products of this reaction, as in earlier studies, was found [4].



R = CH_3, C_6H_5; R' = H, 2-, 3-, 4-CH_3, 2,4-$(CH_3)_2$, o-F; R'' = H, Cl

The chlorination of compound VII and X must be carried out in the cold in carbon tetrachloride solution, and the chlorine must be added to the adducts. The reverse order of mixing the reactants leads to

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*For Communication VIII, see [5].

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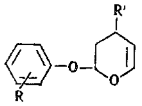
TABLE 1



Compound	R	R'	mp, °C (pressure, mm)	d_4^{20}	n_D^{20}	MR_D		Empirical formula	Found, %		Calc., %		Yield, %
						found	calc.		C	H	C	H	
VII	H	CH_3	128 (7)	1,0604	1,5229	54,72	54,63	$C_{12}H_{14}O_2$	75,83	7,25	75,79	7,37	75
VIII	2-CH_3	CH_3	135 (7)	1,0371	1,5185	59,64	59,25	$C_{13}H_{16}O_2$	76,21	7,80	76,47	7,84	70
IX	3-CH_3	CH_3	133 (8)	1,0400	1,5220	59,81	59,25	$C_{13}H_{16}O_2$	76,42	7,68	76,47	7,84	65
X	4-CH_3	CH_3	143,5 (7)	1,0363	1,5200	59,84	59,25	$C_{13}H_{16}O_2$	76,30	7,52	76,47	7,84	72
XI	2,4-$(CH_3)_2$	CH_3	150 (10)	1,0280	1,5195	64,40	63,87	$C_{14}H_{18}O_2$	76,94	8,09	77,06	8,25	68
XII	2-F	CH_3	136 (10)	1,1751	1,5159	49,26	49,91	$C_{12}H_{13}FO_2$	69,57	6,31	69,45	6,25	87
XIII	H	C_6H_5	mp 85—88	—	—	—	—	$C_{17}H_{16}O_2$	80,42	6,71	80,95	6,35	63
XIV	2-CH_3	C_6H_5	mp 90—92	—	—	—	—	$C_{18}H_{18}O_2$	81,12	7,01	81,20	6,77	58

pronounced resinification. The presence of a methyl group in the pyran ring apparently increases the mobility of the halogen atoms in compounds XXII and XXIII. Thus, the products of the chlorination of 4-methyl-2-phenoxy-3,4-dihydropyrans are less stable than the analogous derivatives of 2-cresoxy-3,4-dihydropyran [5].

EXPERIMENTAL

The initial vinyl ethers were obtained from the corresponding phenols and acetylene in an autoclave [6].

4-Methyl-2-phenoxy-3,4-dihydropyran (VII). A mixture of 60 g (0.5 mole) of I and 35 g (0.5 mole) of crotonaldehyde was heated in an autoclave at 180°C for 10 h. Distillation of the reaction products yielded 10 g of I, 6 g of crotonaldehyde, and 71.2 g (75%) of VII. Compounds VIII-XII were obtained similarly. Mixtures of I and II with cinnamaldehyde were kept at 200°C for 15 h. The adducts XIII and XIV were crystallized from dioxane or hot ethanol.

4-Methyl-2-phenoxytetrahydropyran (XV). A mixture of 19 g (0.01 mole) of VII, 0.3 g of Raney nickel, and 30 ml of ethanol was saturated with hydrogen for 16 h. Distillation yielded 1.76 g (92%) of XV with bp 133°C (10 mm); n_D^{20} 1.5101; d_4^{20} 1.0326. Found, %: C 74.86; H 8.54; MR_D 55.61. $C_{12}H_{16}O_2$. Calculated, %: C 75.00; H 8.33; MR_D 55.10.

2-(p-Cresoxy)-4-methyltetrahydropyan (XVI) was obtained similarly with a yield of 96%, bp 161°C (17 mm); n_D^{20} 1.5080; d_4^{20} 1.0176. Found, %: C 75.53; H 8.91; MR_D 60.34. $C_{13}H_{18}O_2$. Calculated, %: C 75.72; H 8.78; MR_D 59.72.

2-Phenoxy-4-phenyltetrahydropyran (XVII) was obtained by hydrogenating XIII in absolute dioxane, yield 76%, mp 76-78°C. Found, %: C 80.23; H 7.00. $C_{17}H_{18}O_2$. Calculated, %: C 80.31; H 7.09.

2-(p-Cresoxy)-4-methyl-6-phenoxytetrahydropyran (XX). Three drops of dioxane saturated with hydrogen chloride was added to a mixture of 4.1 g (0.02 mole) of IV and 1.88 g (0.02 mole) of phenol. The temperature of the mixture rose to 43°C. After 30 min, the solidifying reaction product was crystallized from ethanol. This gave 5.6 g (95%) of XX with mp. 89-91°C. Found, %: C 76.29; H 7.45. $C_{19}H_{22}O_3$. Calculated, %: C 76.51; H 7.38.

The following were obtained under the same conditions:

4-Methyl-2,6-diphenoxytetrahydropyran (XVIII) (yield 92%, mp 71-73°C. Found %: C 76.21; H 7.04. $C_{18}H_{20}O_3$. Calculated, %: C 76.21; H 6.93). 6-(p-Chlorophenoxy)-4-methyl-6-phenoxytetrahydropyan (XIX) (Yield 95%, mp 106-109°C. Found, %: C 67.81; H 5.96; Cl 11.14. $C_{18}H_{19}ClO_3$. Calculated, %: C 67.81; H 5.96; Cl 11.38). 2-(p-Chlorophenoxy)-6-(p-cresoxy)-4-methyltetrahydropyran (XXI) (Yield 98%, mp 105-107°C. Found, %: C 68.69; H 6.11; Cl 11.03. $C_{19}H_{21}ClO_3$. Calculated, %: C 68.57; H 6.32; Cl 10.68).

2,3-Dichloro-4-methyl-6-phenoxytetrahydropyran (XXII). At −20°C, 1.42 g (0.02 mole) of chlorine in 30 ml of CCl_4 was added to a solution of 3.8 g (0.02 mole) of VII in 50 ml of CCl_4. After an hour, the solvent was distilled off in vacuum to constant weight. This gave 5.22 g (~100%) of XXII: n_D^{20} 1.5358; d_4^{20} 1.2985. Found, %: C 54.31; H 5.25; Cl 28.3. $C_{12}H_{14}Cl_2O_2$. Calculated, %: C 54.88; H 5.31; Cl 27.75.

2,3-Dichloro-6-(p-cresoxy)-4-methyltetrahydropyran (XXIII) was obtained in a similar manner to XXII, n_D^{20} 1.5330; d_4^{20} 1.2801. Found, %: C 56.47; H 5.88; Cl 26.34. $C_{13}H_{16}Cl_2O_2$. Calculated, %: C 56.73; H 5.82; Cl 25.82.

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