

AROXYDIHYDROPYRANS

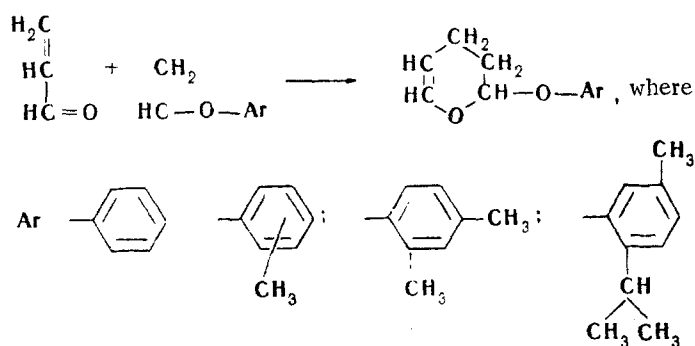
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2-o-, -m-, -p-cresoxy-, 2-xyleneoxy-, 2-thymoxy-2-cyclohexoxy-3,4-dihydropyrans are synthesized for the first time by a Diels-Alder reaction between vinylaryl ethers and acrolein. The ability of the products to undergo cationic polymerization is demonstrated.

It is known that heating vinylalkyl ethers with unsaturated aldehydes and ketones leads to formation, by the Diels-Alder reaction, of adducts which are 2-alkoxy-3,4-dihydropyrans [1-5]. Such compounds can be used as starting materials for various syntheses, in particular for preparing 1,5-pentanediols, which are plasticizers for cellulose, heat-resistant rubbers, etc. [6-7]. Tetrahydropyran derivatives are also used as solvents, and intermediates for synthesizing insecticides and polymers [8]. However, the patent literature does not contain any information about reaction of unsaturated aldehydes with aromatic vinyl ethers, which latter are interesting and readily accessible reactive starting materials. It is true, however, that there is very scanty and contradictory information about the properties of 2-phenoxy-3,4-dihydropyran [6, 9].

This paper deals with the Diels-Alder reaction between acrolein and vinyl ethers of phenol, o-, m-, p-cresol, thymol, and 2,4-xenol. This diene synthesis involving acrolein and vinylaryl ethers was run without catalyst or solvent at 150°-200° C, time 6-7 hours. Yields of adducts reach 52-99% based on the vinyl ether reacted. Due to the



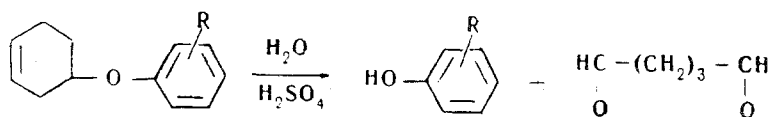
absence of any side reactions, unreacted starting materials are recovered almost quantitatively by distilling the products.

It was found that the optimum reaction temperature is equal to, or close to, the melting point of the starting ether. Thus at 150° C acrolein and vinylphenyl ether react to give a 99.4% yield of product. When the ether is replaced by vinyl-m-cresol ether the temperature has to be 170° C for a 77% yield of adduct to be obtained, while if it is replaced by vinyl-p-cresyl ether, the temperature has to be 180° C to obtain this latter yield. As the substituents in the benzene ring of the vinyl ether increase in number and complexity, increasingly drastic conditions are required to effect the diene synthesis. Later, using the information about the optimum reaction conditions for each individual vinylaryl ether, the Diels-Alder reaction was run between acrolein and a mixture of vinylaryl ethers, prepared from a technical cresol cut from Cheremkhovo coal semicoking tar.

Reaction of acrolein with the vinyl ether derived from cyclohexanol gives a low yield of adduct, 2-cyclohexoxy-3,4-dihydropyran, an unstable compound prone to polymerize on storage.

All the aroxydihydropyrans synthesized are high-boiling colorless liquids, and their purities check by good agreements between found and calculated molecular refractions, analytical data, and gas chromatography, which latter indicates 99.5-99.9% of a single component.* IR spectra indicated absence of a free aldehyde group, and frequencies 1080, 1093, 1108, 1105 cm^{-1} characteristic of vibrations of C-O-C in the pyran ring [10, 11]. The structures of the 2-aroxydihydropyrans are shown by their abilities to undergo hydrolysis, in acid solution, to the corresponding phenol and glutaraldehyde, identified as its bis-2,4-dinitrophenylhydrazone.

* We thank V. V. Keiko for chromatographic analysis.



Phenoxydihydropyran is very easily polymerized by cationic polymerization catalysts, the reaction involving the double bond of the dihydropyran ring. High (80–90%) yields of polymers are obtained as white or yellowish powders.

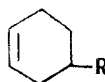
Experimental

The starting vinyl ethers were prepared by treating the appropriate phenols with acetylene in an autoclave [12].

Vinylphenyl ether bp 44.5° (10 mm), n_D^{20} 1.5227; vinyl-o-cresyl ether bp 59° (3 mm), n_D^{20} 1.5170; vinyl-m-cresyl ether bp 176° (726 mm), n_D^{20} 1.5186; vinyl p-cresyl ether bp 175° (760 mm), n_D^{20} 1.5180; vinyl-2,4-xylenyl ether 82° (6 mm); n_D^{20} 1.5076; vinyl-cyclohexyl ether 47.5° (15 mm), n_D^{20} 1.4547. The acrolein used was freshly distilled, bp 52°–53° (720 mm), n_D^{20} 1.3990.

2-Phenoxy-3,4-dihydropyran. 60 g (0.5 mole) vinylphenyl ether and 28 g (0.5 mole) acrolein were charged into a 2-liter rotating autoclave, and heated for 6 hr at 150° C. The autoclave was cooled and its liquid contents fractionated first at atmospheric pressure, to give 5.1 g acrolein bp 53°, n_D^{20} 1.4010, and then under vacuum, to give 29.7 g vinylphenyl ether, bp 62°–62.5° (19 mm), n_D^{20} 1.5220, and 43.75 g diene synthesis adduct. Yield of 2-phenoxy-3,4-dihydropyran 99.4% (on reacted vinyl ether), bp 115° (9 mm), d_4^{20} 1.0950; n_D^{20} 1.5357. Found: C 75.05, 74.43; H 6.94, 7.04%; mol. wt. 178, 175.5; MR_D 50.08. Calculated for $C_{11}H_{12}O_2$: C 74.97; H 6.87%; mol. wt. 176; MR_D 50.02. IR spectrum: [v = very, s = strong, w = weak, a = area, m = medium] 3080 (vs), 2944 (vs), 2864 (s) 1652 (m), 1592 (s), 1494 (s), 1448 (m), 1368 (m), 1350 (ma), 1290 (m), 1238 (s), 1214 (vs), 1170 (s), 1110 (ma), 1086 (s), 1040 (vs) 998 (m), 956 (vs), 928 (ma), 752 (vs), 720 (vs), 692 (s) cm^{-1} .

Properties of 2-Aroxy-3,4-dihydropyrans



R	Bp (mm pressure)	d_4^{20}	n_D^{20}	MR_D		Formula	Found, %		Calc., %		Yield, %
				Found	Calc.		C	H	C	H	
Phenoxy	62–62.5 (19)	1.0950	1.5357	50.08	50.02	$C_{11}H_{12}O_2$	75.05	6.94	74.97	6.87	99.4
o-Cresoxy	94–97 (3)	1.0735	1.5300	54.62	54.63	$C_{12}H_{14}O_2$	75.46	7.33	75.78	7.36	78.2
m-Cresoxy	148–150 (11)	1.0758	1.5310	54.63	54.63	$C_{12}H_{14}O_2$	75.69	7.48	75.78	7.36	76.7
p-Cresoxy	112–113 (4)	1.0730	1.5303	54.71	54.63	$C_{12}H_{14}O_2$	75.75	7.57	75.78	7.36	87.1
2,4-xylenoxy	170 (32)	1.0376	1.5238	60.24	59.25	$C_{13}H_{16}O_2$	76.71	8.11	76.43	7.89	52.1
Thymoxy	144.5 (6)	1.0215	1.5200	69.02	68.48	$C_{15}H_{20}O_2$	77.65	8.54	77.54	8.61	76.0
Cyclohexoxy	70–92 (2.5)	1.0070	1.4795	51.14	51.42	$C_{11}H_{18}O_2$	72.46	10.07	72.48	9.96	12.2

Treatment of 2-phenoxy-3,4-dihydropyran in EtOH with 2,4-dinitrophenylhydrazine reagent gave glutaraldehyde bis-2,4-dinitrophenylhydrazone, mp 187° C (the literature gives [13] mp 186°–187°).

The other aroxydihydropyrans were synthesized similarly. The table lists their properties.

Diels-Alder reaction between cresol cut vinyl ethers and acrolein. 50 g (0.37 mole) of a cresols vinyl ether cut bp 173°–175°, obtained from complex mixed vinyl ethers of Cheremkhovo coal semicoking tar phenols, was charged into an autoclave, along with 22 g (0.38 mole) acrolein. The reactants were maintained at 170° C for 7 hr, and the products vacuum-fractionated to give 38.3 g cresoxy-3,4-dihydropyran (yield 78.8% on the vinyl ether reacted), bp 150°–152° (31 mm); d_4^{20} 1.0760; n_D^{20} 1.5300; MR_D 54.54. Calculated for $C_{12}H_{14}O_2$: MR_D 54.63.

Poly(thymoxy-3,4-dihydropyran). A solution of 0.2 g $SnCl_4 \cdot 5H_2O$ in 3 ml Et_2O was added to 10 g (0.05 mole) thymoxydihydropyran. The resultant viscous brown resin was dissolved in 15 ml acetone and precipitated with 300 ml Et_2O . Reprecipitation was effected twice. Drying to constant weight in a vacuum-desiccator gave 9.86 g white polymer powder, mp 78°, η_{sp} 0.04, yield 98.6%.

2-o-Cresoxy-3,4-dihydropyran. IR spectrum*: 1642 (m), 1585 (m), 1484 (s), 1453 (m), 1437 (m), 1366 (w),

* The IR spectra were determined with a IKS-14 spectrometer, using a NaCl prism.

1340(w), 1288(w), 1233(s), 1211(s), 1180(s), 1173(s), 1157(w), 1115(s), 1080(s), 1059(s), 1037(m), 988(w), 956(w), cm^{-1} .

2-m-Cresoxy-3,4-dihydropyran. IR spectrum: 1640(w), 1585(s), 1498(s), 1479(s), 1437(s), 1362(s), 1336(m), 1314(m), 1275(s), 1246(s), 1213(s), 1176(s), 1146(s), 1078(s), 1054(s), 1037(s), 996(s), 956(s), cm^{-1} .

2-p-Cresoxy-3,4-dihydropyran. IR spectrum: 1640(s), 1603(m), 1574(m), 1493(s), 1437(m), 1367(m), 1339(m), 1275(m), 1240(s), 1206(s), 1176(s), 1104(m), 1081(s), 1065(s), 1038(m) cm^{-1} .

2-(2', 4'-Xylenoxy)-3,4-dihydropyran. IR spectrum: 1639(s), 1490(s), 1435(s), 1367(s), 1360(m), 1336(m), 1300(m), 1284(s), 1245(s), 1206(s), 1174(s), 1152(s), 1122(s), 1080(s), 1059(s), 1037(s), 990(m), 962(s) cm^{-1} .

2-Thymoxy-3,4-dihydropyran. IR spectrum: 1639(m), 1606(m), 1565(m), 1492(m), 1437(m), 1408(m), 1370(m), 1357(m), 1274(m), 1245(s), 1213(s), 1174(m), 1158(s), 1108(m), 1093(s), 1076(m), 1058(s), 1034(s), 1004(m), 969(s) cm^{-1} .

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