AROXYDIHYDROPYRANS

VII. Condensation of Acrolein with Vinyl Ethers of Fluoro-, Chloro-, and Bromophenols.*

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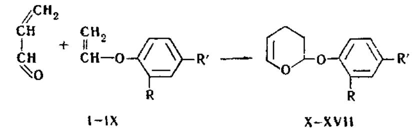
The vinyl ether of o-fluorophenol by diene condensation with acrolein forms an adduct and this with a higher yield than the vinyl ethers of chloro- and bromophenols. Eight 2-halogenaroxy-3, 4-dihydropyrans were synthesized. New halogen-containing acetals and polymers of the tetrahydropyran series were obtained.

We had previously studied the reaction of acrolein with vinylaryl ethers having mainly electron donating substituents in the benzene ring [2, 3]. As is known, the best dienophiles are those compounds having double bonds activated by conjugation with electron accepting substituents [4, 8]. Continuing our investigations of the diene condensation using acrolein as starting material, we studied the behavior of the vinyl ethers of various halogenated phenols, as well as the properties of the synthesized 2-halogenaroxy-3, 4-dihydropyrans with respect to reactions of hydrogenation, acetal formation and polymerization. As dienophiles we employed the vinyl ethers of o-fluorophenol (I), of o-, m-, and p-chlorophenols (II–IV), of o-, p-bromophenols (V, VI), of 2, 4-dichlorophenol (VII), of 2, 4-dibromophenol (VIII), and of 2, 4, 6-trichlorophenol (IX). The interaction of these compounds with acrolein proceeds at 170–180° C (the process is accompanied by some resinification, but at 150–160° C the yields of adducts sharply decrease), in the course of 6–8 hr according to the following scheme:



R=H, F, Cl, Br; R'=H, Cl, Br

Under the given conditions, a substantial influence on the yield of the desired product is exerted by the nature of the halogen, the number of atoms and their position in the benzene ring. Thus, the yields of o-fluoro-, O-chloro- and O-bromophenoxy-3, 4-dihydropyrans amounted to 92, 85, and 74% respectively. With respect to the yield of adduct with acrolein, the isomeric vinyl ethers of chlorophenols may be arranged in the following order: o > p > m.

In previous papers it had been shown that the optimum temperature for the condensation of vinylaryl ethers having electron donating substituents in the ring are temperatures close to the boiling points of the ethers under study [2]. Probably due to the electron accepting properties of the halogens, the double bond of dienophiles I–VI is more activated, and, therefore, their diene synthesis with acrolein proceeds at a much lower temperature. More difficult was to carry out the reaction with dichloro-, dibromo-, and all the more with trichloroderivatives of vinyl ethers (VI–IX). These require more severe conditions, which promote the occurrence of side reactions, the partial decomposition and resinification of the reacting substances. For this reason the yield of 2-(o-, p-dichlorophenoxy)-3, 4-dihydropyran (XVI) amounted to 67%, and that of 2-(o-, p-dibromophenoxy)-3, 4-dihydropyran (XVII) to only 14%. It was not possible to obtain the adduct of the trichloro derivative (IX) and acrolein at 190–200° C, and stronger heating led to the decomposition of the reaction mixture. Table 1 presents the properties of the dihydropyrans synthesized.

Their structure was proved by chemical conversions to aroxy- and polyaroxytetrahydropyrans. The double band of the dehydropyran cycle in compounds X–XVII became less reactive due to the influence of the halogens, which is transmitted through the double oxygen bridge, and this was confirmed by infrared spectroscopy data [9].

Under the action of nickel catalyst, hydrogen attached itself to dihydropyran XIII to form 2-(p-chlorophenoxy)tetrahydropyran (XVIII). In the presence of catalytic quantities of hydrogen chloride, XV reacted with ethanol to form two symmetric and one mixed acetals according to the following scheme:

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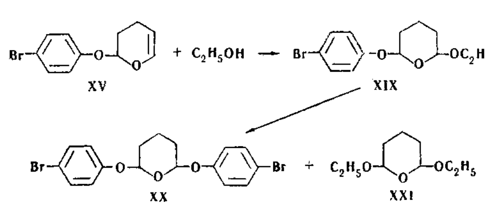
*For part VI, see [1].



As a result of the reaction of XV with propargyl alcohol, p-cresol,and p-chlorophenol, formation of a symmetrical structure was not observed in the reaction products, and only mixed acetals of the tetrahydropyran series (**XXII–XXIV**) were obtained. With the highest yield, about 90%, calculated on reacting dihyropyran XV, was obtained 2-(p-bromophenoxy)-6-(p-chlorophenoxy)tetrahydropyran.

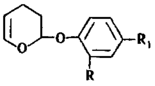
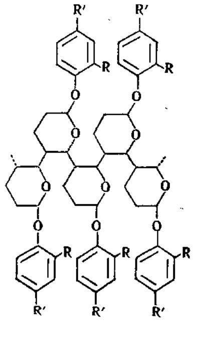


Table 1. 2-Halogenaroxy-3, 4-dihydropyrans

Compound	R	R′	Bp °C (pressure in nm)	d_4^{20}	n_D^{20}	MR_D found	MR_D calculated	Molecular formula	Found, % C	Found, % H	Calculated, % C	Calculated, % H	Yield, %
X		H	136 (10)	1.1751	1.5179	50.02	49.91	$C_{11}H_{11}FO_2$	67.98	5.71	68.04	5.67	92
XI	Cl	H	138 (9)	1.2100	1.5452	54.89	54.88	$C_{11}H_{11}ClO_2$	63.03	5.06	62.85	5.24	85
XII	H	Cl[a]	112 (2)	1.2129	1.5475	55.06	54.88	$C_{11}H_{11}ClO_2$	62.91	5.25	62.85	5.24	71
XIII	H	Cl	95,5 (1)	1.2100	1.5471	55.08	54.88	$C_{11}H_{11}ClO_2$	62.41	5.32	62.85	5.24	80
XIV	Br	H	155 (7)	1.4240	1.5629	58.14	57.78	$C_{11}H_{11}BrO_2$	51.83	4.24	51.76	4.31	74
XV[b]	H	Br	160 (13)	1.4270	1.5640	58.11	57.78	$C_{11}H_{11}BrO_2$	51.90	4.36	51.76	4.31	71
XVI	Cl	Cl	111 (0.5)	1.3400	1.5629	59.37	59.75	$C_{11}H_{10}Cl_2O_2$	53.76	4.15	53.88	4.08	67
VII[c]	Br	Br	c			—	—	$C_{11}H_{10}Br_2O_2$	39.38	2.90	39.52	3.00	14

*(a) m-Isomer; (b) mp 46° C; (c) mp 62° C.

The synthesized compounds X, XII–XV were able to open the double bond of the pyran cycle to form 2-polyhalogenaroxytetrahydropyrans with molecular weights from 2000 to 3500. The basic ring of these compounds has the following structure (by analogy with previous investigations):



EXPERIMENTAL

The original vinyl ethers were obtained from halogenated phenols in an autoclave under pressure, according to the Favorski-Shostakovskii reaction [10, 13]. Their properties [bp °C (pressure, nm), n_D^{20}, respectively] were as follows: I) 60(10), 1.4970; II), 69(9), 1.5420; III) 67(7), 1.5399; IV) 53(4), 1.5400; V) 83(5), 1.5680; VI) 38(0.5), 1.5677; VII) 105(8), 1.5571; VIII) 145(17), 1.6035; IX) 114(12), 1.5609, mp 37° C. The acrolein utilized in the reaction was dehydrated and freshly distilled, bp 51–52° C (720 mm), n_D^{20};1.3990.

2-(o-Fluorophenoxy)-3, 4-dihydropyran (X). In an autoclave of 0.2 *l* capacity were placed 27.6 g (0.2 mole) of I and 11.2 g (0.2 mole) of acrolein. A current of nitrogen was blown through, and the reaction mixture was maintained at 190° C during 8 hr. The reaction product was submitted to distillation 1.9 g of acrolein, 4.7 g of I and 29.1 g of compound X were recovered. This corresponded to a 92% yield, calculated on the quantity of I that had reacted. The remaining 2-halogenaroxy-3, 4-dihydropyrans XI–XVII were prepared in a similar way. They dissolved well in acetone and in carbon tetrachloride, but with difficulty in ethanol.

2-(p-Chlorophenoxy)tetrahydropyran (XVIII). Into a reaction vessel for hydrogenation, were placed 2.5 g (0.012 mole) of XIII, 0.5 g of Rainey nickel, and 15 g of absolute ethanol. A current of hydrogen was then passed through. 2.4 g (95%) of XVIII was obtained, bp 140° C (9 mm); d_4^{20} 1.1821; n_D^{20} 1.5325. Found, %: C 62.25; H 6.01; MR_D 55.84. Calculated for $C_{11}H_{13}ClO_2$, %: C 62.11; H 6.11. MR_D 55.35. According to the literature [11], bp 127° C (3 mm).

2-(p-Bromophenoxy)-6-ethoxytetrahydropyran (XIX). From 12.77 g (0.05 mole) of XV and 2.3 g (0.05 mole) ethanol, and following the procedure described in [12], 2.56 g (17%) of XIX was obtained, bp 161° C (3 mm); d_4^{20} 1.3895; n_D^{20} 1.5103. Found, %: C 51.76; H 5.60; MR_D 69.32. Calculated for $C_{13}H_{17}BrO_3$, %: C 51.82; H 5.65; MR_D 69.13. Furthermore, 1.2 g (30%) of 2,6-diethoxytetrahydropyran (XXI) was obtained, with constants which agreed with those recorded in the literature [3], and 1.21 g (12%) of 2,6-di-(p-bromophenoxy)tetrahydropyran (XX), mp 101° C. Found, %: C 47.51; H 3.67. Calculated for $C_{17}H_{16}Br_2O_3$, %; C 47.66; H 3.74.

2-(p-Bromophenoxy)-6-propinoxytetrahydropyran (XXII). From 2.55 g (0.0105 mole) of XV and 0.56 g (0.01 mole) of propargyl alcohol, 0.87 g (28%) of **XXII** was obtained, bp 182° C (8 mm); d_4^{20} 1.4121; n_D^{20} 1.5662. Found, %: C 52.01; H 4.78. MR_D 71.83. Calculated for $C_{14}H_{15}BrO_3$, %: C 52.34; H 4.67. MR_D 71.74.

2-(p-Bromophenoxy)-6-(p-cresoxy)tetrahydropyran (XXII). In an acid medium, 2.55 g (0.0105 mole) of XV and 1.08 g (0.01 mole) of p-cresol yielded 2.8 g (77%) of **XXIII**, mp 93.5° C. Found, %: C 59.05; H 5.31. Calculated for $C_{18}H_{19}BrO_3$, %: C 59.30; H 5.23.

2-(p-Bromophenoxy)-6-(p-chlorophenoxy)tetrahydropyran (XXIV). From 2.55 g (0.0105 mole) of XV and 1.28 g (0.01 mole) of p-chlorophenol, 3.45 g (90%) of **XXIV** was obtained, mp 85.5° C. Found, %: C 53.21; H 4.20. Calculated for $C_{17}H_{16}ClO_3Br$, %: C 53.19; H 4.17.

Table 2. Poly(2-halogenaroxy)tetrahydropyrans.

R	R′	mp, °C	[η]	M	yield, %
F	H	107	0.295	2100	73
H	Cl*	115	0.319	2270	70
H	Cl	120	0.340	2400	78
Br	H	142	0.481	3200	88
H	Br	146	0.493	3350	81

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*m-Isomer.

Poly(2-o-fluorophenoxy)tetrahydropyran (XXV). Into a flat-bottomed flask, 5 g of X were placed, and under stirring 0.075 g of hydrated stannic chloride was added. After 12 hr a viscous reaction product was formed, was dissolved in 10 ml of acetone and then precipitated with 200 ml of ethanol. The precipitated polymer was dried under vacuum to constant weight at 50° C. 3.65 g (73%) of poly(2-o-fluorophenoxy)tetrahydropyran was obtained. The remaining 2-halogenaroxy-3,4-dihydropyrans were polymerized under similar conditions. Table 2 summarizes the properties of the polymers obtained.

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