ARYLOXYDIHYDROPYRANS

VIII. Halogenation*

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The action of chlorine and bromine on 2-aryloxy-3,4-dihydropyrans has been studied; a series of 6-aryloxy-2,3-dihalogenotetrahydropyrans has been obtained. The stability of the compounds synthesized rises with the introduction of electron-accepting substituents into the benzene ring. On being heated in the presence of alkalis, they split off a molecule of hydrogen halide and open the tetrahydropyran ring.

It is known that the halogenation of dihydropyran takes place at a low temperature in diethyl ether solution [2–5]. The halogens in the reaction products possess a high activity and can be replaced by various functional groups [6,7].

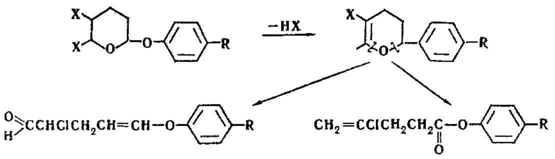
In this work we have studied for the first time the chlorination and bromination of 2-phenoxy-, 2-(o-, m-, and p-methylphenoxy)-, 2-(o-fluorophenoxy)-, and 2-(o- and p-chlorophenoxy(3,4-dihydropyrans (I–VII), respectively). The investigations carried out have shown that the two halogen atoms add to the double bond of the dihydropyran ring with the formation of 6-aryloxy-2,3-dihalogenotetrahydropyrans (VIII–XVI).

The reaction of chlorine with 2-phenoxy- and, especially, 2-methylphenoxy-3,4-dihydropyrans (I–IV) must be carried out at −15° C with the gradual addition of the halogen solution to the dihydropyran solution. The presence of electronegative substituents in the benzene ring enables the reaction to be carried out at higher temperatures (0–5° C).

The 6-aryloxy-2,3-dihalogenotetrahydropyrans (VIII–XII) are unstable and deliquesce and fume at room temperature, splitting off hydrogen halides. The dibromo derivatives begin to decompose immediately after their isolation from solutions, just like the products of the halogenation of vinyl ethers [8–10].

The introduction into the aryloxy group of I of such substituents as fluorine and chlorine increases the stability of the corresponding halogenation products XIV–XVI. These compounds can be stored for a long time without change.

On being heated in the presence of caustic potash, XII and XIII split off a molecule of hydrogen halide like the monohalogen derivatives of pyran [11,12]. We assume, by analogy with vinyl ethers [13], that the chlorine atom in the β- position is the more stable and the action of alkali on XII and XIII gives the 2-aryloxy-5-halogeno-3,4-dihydropyrans (XVII–XVIII) with a yield of 60–70%. The elementary composition of dehydrochlorination products of XII and XIII confirms their structure. In addition, the given structure of XVII and XVIII is shown by their IR spectra. The appearance of an absorption band of XVII in the 1660 cm^{-1} region (figure) is due to the vibrations of the C=C bond in the dihydropyran ring. Strong absorption at 1600 and 1500 cm^{-1}, and also at 3040 cm^{-1}, confirms the presence of an aromatic structure. The broadest and strongest bands in the spectrum—at 1220–1225 cm^{-1}—is due to ether bonds, including the C—O bonds of the ring. The strong band at 694 cm^{-1} must be ascribed to the C—Cl stretching vibrations. In spite of the presence in the spectrum of bands characteristic for the dihydropyran ring, there is absorption at 1740 and 1735 cm^{-1}, respectively, for XVII and XVIII. This may be caused by the vibrations of the carbonyl group. Apparently, dehydrochlorination is accompanied by the opening of the ring due to the instability of the 2-aryloxy-5-chlorodihydropyran formed:



However, we have been unable to identify the products not containing a pyran ring.

Under the action of an excess of halogens on the 2-aryloxy-3,4-dihydropyrans in addition to the saturation of the

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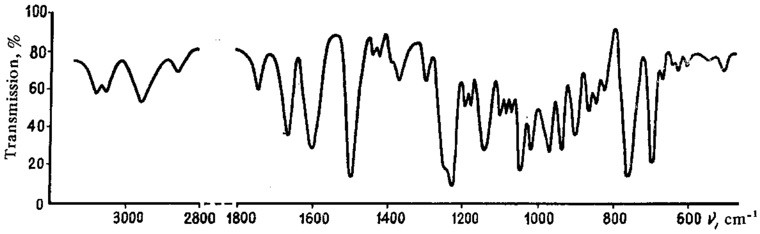
*For part VII, see [1].

double bond the replacement of hydrogen atoms of the ring by the halogens takes place. The replacement occurs most readily at temperatures from −5 to −10° C in compounds II–IV having a methyl group in the benzene ring. To perform this reaction with I, the temperature must be raised to 0° C. Compounds V–VII exchange hydrogen for chlorine only at room temperature. We assume that in these cases substitution takes place primarily in the pyran ring.



IR spectrum of 2-(p-methylphenoxy)-5-chloro-3,4-dihydropyran (XVII).

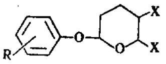
EXPERIMENTAL

The IR spectra were taken on a UR-10 spectrophotometer.

The initial 2-aryloxy-3,4-dihydropyrans, obtained as described by Shostakovskii et al. [15] have the following constants [number of compounds, bp° C (mm); n_D^{20}]: I, 93 (4), 1.5367; II, 107 (8), 1.5300; III, 145 (11), 1.5312; IV, 115 (5), 1.5300; V, 136 (10), 1.5179; VI, 138 (9), 1.5452; VII, 95.5 (1), 1.5471.

2,3-Dibromo-6-phenoxytetrahydropyran (VIII). At −10° C, 3.4 g (19.6 mM) of I in 30 ml of ether was added dropwise to 1 ml (19.6 mM) of bromine in 50 ml of absolute diethyl ether. After 2 hr, the solvent was distilled off and the residual product was washed with petroleum ether and dried to constant weight in vacuum. This gave 6.36 g (98%) of VIII (table). IR spectrum, cm^{-1}: 2950, 1595 (s), 1503,(s), 1495 (m), 1448 (m), 1405, 1360 (w), 1320 (w), 1294, 1270, 1230(v.s),1123, 1094 (s), 1063 (s), 1035(s), 960, 890, 855, 780 (m), 755 (s), 694 (v.s), 653 (s), 628 (s), 604 (s), 524 (v.s), 506 (s).

6-Aryloxy-2,3-dihalogenotetrahydropyrans



Compound	R	X	d_4^{20}	n_D^{20}	MR_D		Empirical formula	Found, %			Calculated, %			yield, %
					found	calculated		C	H	halogen	C	H	halogen	
VIII	H	Br	1,7010	1,5850	66,19	66,01	$C_{11}H_{12}Br_2O_2$	38,76	3,71	47,90	39,28	3,57	47,62	98
IX	4-CH₃	Br	1,6350	1,5751	70,73	70,63	$C_{12}H_{14}Br_2O_2$	40,81	3,95	46,12	41,14	4,00	45,71	96
X	2-CH₃	Cl	1,2647	1,5409	64,84	64,83	$C_{12}H_{14}Cl_2O_2$	55,13	5,21	27,15	55,17	5,36	27,20	96
XI	3-CH₃	Cl	1,2647	1,5405	64,80	64,83	$C_{12}H_{14}Cl_2O_2$	55,42	5,28	27,38	55,17	5,36	27,20	94
XII	4-CH₃	Cl	1,2658	1,5412	64,80	64,83	$C_{12}H_{14}Cl_2O_2$	55,11	5,33	27,31	55,17	5,36	27,20	98
XIII[a]	H	Cl	—	—	—	—	$C_{11}H_{12}Cl_2O_2$	53,21	4,80	29,03	53,44	4,86	28,74	98
XIV[b]	2-F	Cl	—	—	—	—	$C_{11}H_{11}Cl_2FO_2$	49,39	4,02	34,11	49,81	4,15	33.96[д]	92
XV[c]	2-Cl	Cl	—	—	—	—	$C_{11}H_{11}Cl_3O_2$	46,70	4,13	37,81	46,89	3,90	37,83	93
XVI[d]	4-Cl	Cl	—	—	—	—	$C_{11}H_{11}Cl_3O_2$	46,83	4,20	37,87	46,89	3,90	37,83	93

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[a] Rectangular prisms, plates, mp 103-105° C. [b] Octahedra, mp 108-110° C. [c] Needles, mp 98-103° C. [e] Sum of the halogens.

2,3-Dichloro-6-(p-fluorophenoxy)tetrahydropyran (XIV). With cooling to 0° C, 3.88 g (0.02 mole) of V dissolved in 30 ml of CCl_4 was added dropwise to a solution of 1.42 g (0.02 mole) of chlorine in 50 ml of carbon tetrachloride. The mixture was kept for 1 hr and then the solvent was evaporated off at 10 mm. This gave 4.87 g (92%) of XIV in the form of white crystals with mp 110° C (from diethyl ether). IR spectrum, cm^{-1}: 2951 (m), 2861, 1615 (m), 1990 (w), 1520 (v.s) 1445 (m), 1425 (m), 1360, 1340, 1290 (m), 1230 (v.s, broad), 1180, 1122 (s), 1909 (s), 1060 (s), 1033 (s), 965 (s), 890, 858, 815 (s), 778 (s), 753 (s), 704, 650 (m), 602, 555 (w), 717 (s).

The halogenation of the other dihydropyrans; II–IV, VI–VII, was carried out under similar conditions (table).

5-Chloro-2-phenoxy-3,4-dihydropyran (XVIII). A mixture of 4.9 g of XIII and 0.3 g of KOH was heated in vacuum.

This gave 2.66 g (63%) of XVIII in the form of a light yellow mobile liquid soluble in acetone, dioxane, and ethanol. Bp 137° C (2 mm); d_4^{20} 1.2290; n_D^{20} 1.5442. Found, %: C 62.25; H 5.24; Cl 17.63; MR_D 54.88. $C_{11}H_{11}ClO_2$. Calculated, %: C 62.85; H 5.24; Cl 16.86; MR_D 54.01.

5-Chloro-2-(p-methylphenoxy)-3,4-dihydropyran (XVII). This was obtained in a similar manner to XVIII. Yield 71%, bp 161° C (7 mm); d_4^{20} 1.1632; n_D^{20} 1.5405. Found, %: C 64.44; H 5.93; Cl 15.43; MR_D 60.47. $C_{12}H_{14}ClO_2$. Calculated, %: C 64.14; H 5.83; Cl 15.62; MR_D 59.50.

REFERENCES

1. G. G. Skvortsova and V. G. Kozyrev, KhGS [Chemistry of Heterocyclic Compounds], 6, 17, 1970.
2. R. Paul, C. R., 218, 122, 1944.
3. R. Paul, Bull. soc. chim. France, [5]1, 1397, 1934.
4. W. A. Bonner, P. I. Werth, and M. Roth, J. Org. Chem., 27, 1575, 1962.
5. S. M. Makin, V. M. Likhosherstov, and M. I. Shelemina, ZhOKh, 34, 1809, 1964.
6. R. C. Brandon, J. M. Derfer, and C. E. Boord, J. Am. Chem. Soc., 72, 2120, 1950.
7. I. C. Montaign, Ann. chim., 9, 310, 1954, C. A., 49, 10942, 1955.
8. Yu. V. Pokonova, Halogenoethers [in Russian], Moscow, 1966.
9. H. I. Barber, R. F. Fuller, and M. B. Green, J. Appl. Chem., 3, 409, 1953.
10. H. I. Barber, R. F. Fuller, M. B. Green, and H. F. Swartow, J. Appl. Chem., 3, 266, 1953.
11. O. Riobe, Ann. chim., [12]4, 593, 1949; C. A., 44, 2983, 1950.
12. R. Hawkins and N. Bennet, British patent no. 571265, 1945; C. A., 41, 998, 1947.
13. M. F. Shostakovskii, Vinyl Ethers [in Russian], Moscow, 1952.
14. L. Bellamy, Infrared Spectra of Complex Molecules [Russian translation], Moscow, 1963.
15. M. F. Shostakovskii, G. G. Skvortsova, K. V. Zapunnaya, and V. G. Kozyrev, USSR patent no. 168717, 1964; Byull, izobr., no. 5, 26, 1965.

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