MIXED AROMATIC-ALIPHATIC ACETALS; THEIR PREPARATION, ^{1}H AND ^{13}C-NMR SPECTRA AND HYDROGENOLYSIS BY ETHEREAL SOLUTION OF CHLOROALANE

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The corresponding *p*-X-phenylisobutyl acetals of acetaldehyde (*I*), 2-(*p*-X-phenoxy)tetrahydropyrans (*II*), 2-(*p*-X-phenoxy) tetrahydrofurans (*III*), and cyclohexyl(*p*-X-phenyl)acetals of acetaldehyde (*IV*) were prepared by addition of *p*-X-substituted phenols to isobutyl vinyl ether, 2,3-dihydro-4*H*-pyran, 2,3-dihydrofuran, and cyclohexyl vinyl ether, respectively. The structures of acetals *I*—*IV* were confirmed by their ^{1}H and ^{13}C-NMR spectra. Diastereotopic protons of the methylene and geminal methyl groups are anisochronous in the ^{1}H-NMR spectra of acetals *I*. ^{13}C-NMR spectra of acetals *IV* demonstrate anisochronous behaviour of cyclohexane ring diastereotopic carbon atoms. The constants σ_p^+ for several groups calculated using ^{13}C-NMR spectra are: 1-isobutoxy-1-ethoxy-(—0·56), 2-tetrahydropyranyloxy- (—0·58), 2-tetrahydrofuryloxy- (—0·59), and 1-cyclohexyloxy-(1-ethoxy) (—0·57). Experimental relative rate constants of hydrogenolysis of acetals *I* and *II* by ethereal solution of chloroalane yield best correlations with σ_p^+ constants of the substituent X, providing the values $\varrho = 2{\cdot}61$ and $\varrho = —1{\cdot}09$ for compounds of the series *I* and *II*, respectively. The importance of these results for finding the rate determining step of the studied reaction is discussed.

In our previous papers[1,2], we measured relative rates of hydrogenolysis of 2-alkoxy- and 2-alkoxy-3-substituted tetrahydrofurans by chloroalane. We came to the conclusion that this reaction was controlled by dissociation of the reagent-substrate complex into alkoxycarbenium ions (Scheme 1, step *B*). This finding agrees with results obtained by non-kinetic methods in studies of different series of aliphatic acetals[3,4].

This work is intended to supplement the missing data on the course of reaction of chloroalane with acetals containing aromatic groups where hypotheses on the governing role of the complex formation (*i.e.* step *A*) were formulated in some cases[1,5].

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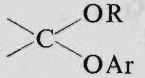
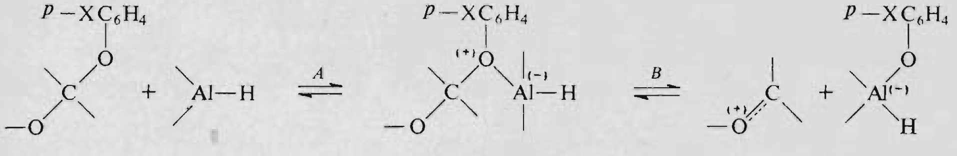
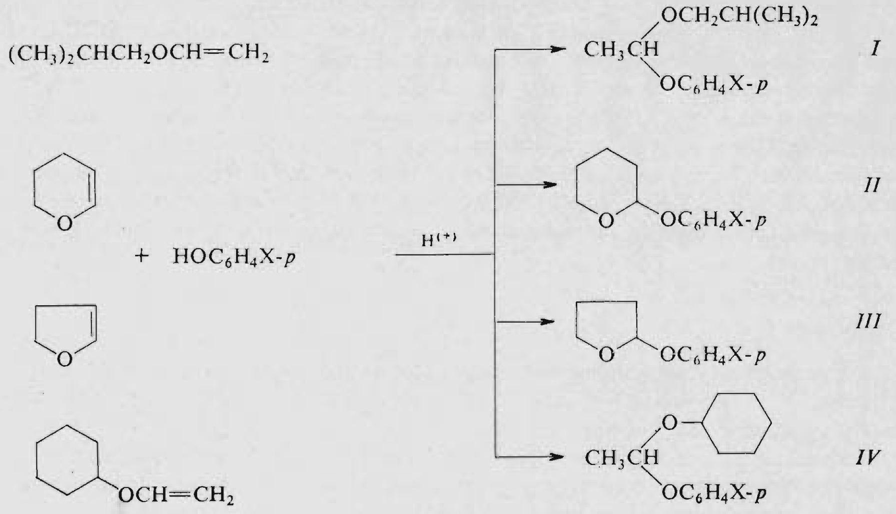
* Part of the Thesis of J.D.

The cleavage of acetals  by chloroalane takes place exclusively on the C—OAr bond[1,5,6], as depicted in Scheme 1. Both main alternatives for the reaction controlling step, *A* and *B*, have quite different reaction center requirements with respect to the electronic effect of the substituents. The complex formation step *A* will be supported by donors and the decomposition step *B* will be supported by acceptors. From this point of view, we selected as a model for the study of hydrogenolysis of acetals containing an aromatic group the series of acetals given in Scheme 2.



SCHEME 1



In formulae *I*, *II*, *III* and *IV*: *a*, X = Cl; *b*, X = H; *c*, X = CH_3; *d*, X = $(CH_3)_3C$; *e*, X = OCH_3.

SCHEME 2

The groups inert to chloroalane and including both donors and acceptors were selected as the X-substituents. The compounds belonging to the series of *p*-X-phenyl-isobutyl acetals of acetaldehyde (*I*), 2-(*p*-X-phenoxy)tetrahydropyrans (*II*), 2-(*p*-X-

-phenoxy)tetrahydrofurans (*III*), and cyclohexyl (*p*-X-phenyl)acetals of acetaldehyde (*IV*) were prepared by an acid catalyzed addition of *p*-X-substituted phenols to the corresponding vinyl ethers. With selected acetals, we carried out the reaction in the preparative scale to confirm that their hydrogenolysis by chloroalane took place at the C—OAr bond exclusivelly. The relative rate constants of the reactions of acetals *I* and *II* chloroalane were determined and used in the linear free energy relationship correlations with the substitution constants of the X-substituents.

EXPERIMENTAL

Temperature data are uncorrected. The purity of acetals *I*—*IV* was checked by a high-pressure liquid chromatograph Varian 8 500 using a 250 × 2 mm Micro Pack SI 10 column. The eluent was 3 : 1 mixture of heptane and 0·2 % solution of 2-propanol in heptane, solvent flow was 30 ml/h, UV detection was performed at 220 nm. A Chrom 3 (Laboratory Instruments, Prague) instrument was employed for gas-chromatographic analyses; the column was loaded with 5% SE 30 on Chromaton N-AW DMCS 0·20—0·25 mm; katharometric detection, hydrogen as a carrier gas. ^{1}H-NMR spectra of pure compounds were measured on a Tesla BS 487C spectrometer in tetrachloromethane containing tetramethylsilane as an internal standard. Quantitative analysis of the substrates ratio was made on a pulse spectrometer Bruker WP-80 DS. One-pulse spectra were evaluated; the solvent was deuteriochloroform, internal standard was tetramethylsilane. ^{13}C-FT-NMR spectra were measured on a Bruker WP-80 DS spectrometer at 20·12 MHz. Proton broad-band decoupling (8 W) was applied at 4·5 ppm with respect to tetramethylsilane. Samples were measured in 10 mm coaxial Wilmad sample tubes with 1,4-dioxane (20% in ^2H_2O) as an external standard at 30°C. Internal deuterium lock was used. For every spectrum, 128 FID's were collected. Flip angle was 23°, digital resolution used was 0·915 Hz/point. Chemical shifts are expressed with respect to tetramethylsilane using the relation $\delta_{1,4\text{-dioxane}} = 67{\cdot}4$ ppm. The accuracy of chemical shift determination was 0·05 ppm. The activity of the stock ethereal solutions of lithium aluminium hydride was determined iodometrically[7]. Aluminium trichloride was sublimed before use.

Compounds *I*—*IV*

Several crystals of *p*-toluenesulfonic acid were added to the mixture of 0·05 ml of vinyl ether and 0·05 ml of corresponding *p*-X-substituted phenol in 10 ml of diethyl ether. After a short period of exothermic reaction, the mixture was refluxed for 1 h, cooled and washed by 10 ml of 4·8M aqueous–methanolic (1 : 4) potassium hydroxide. The ethereal layer was separated and the aqueous one extracted by 5 × 10 ml of diethyl ether. Combined extracts were dried over magnesium sulfate, their volume was reduced by distillation at atmospheric pressure and distillation at reduced pressure gave the products. Purity of products was checked by high-pressure liquid chromatography and their structures were confirmed by ^{1}H and ^{13}C-NMR spectra. The yields and physical constants are given in Table I, the ^{1}H and ^{13}C-NMR spectra in Tables II—V.

Hydrogenolysis of Phenylisobutyl Acetal of Acetaldehyde *Ib* and 2-Phenoxytetrahydropyran *IIb* by Chloroalane

The reaction of 0·15 mol of *Ib* with 100% excess of chloroalane provided, after separation of products soluble in 10% aqueous sodium hydroxide, isobutyl ether as the only product. No phenylethyl ether was detected by gas chromatography. Similarly was in the reaction of *IIb* with excess of chloroalane isolated tetrahydropyran only; no products of the tetrahydropyran ring cleavage were found.

Determination of Relative Rate Constants of the Hydrogenolysis of Acetals *I—IV* by Chloroalane

The equal amounts (10^{-3} mol) of both measured acetal and the acetal used as a standard were weighted into small glass vials. The vials were then thrown into $0·5 . 10^{-3}$ mol solution of chloroalane in diethyl ether (prepared from 0·89 ml of 0·281M solution of lithium aluminium hydride in diethyl ether, 0·54 ml of 0·463M solution of aluminium trichloride in diethyl ether and 10 ml of diethyl ether). The solution was refluxed 1 h under stirring and exclussion of air moisture. Test experiments proved that chloroalane is consumed after 5—8 minutes. The mixture was afterwards washed by 5 ml of 10% aqueous sodium hydroxide, the ethereal layer was separated and the aqueous one extracted by 5 × 5 ml of diethyl ether. Combined extracts were

TABLE I

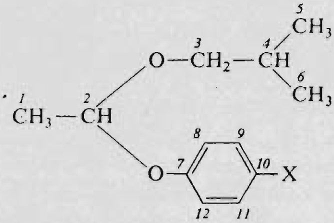
List of prepared *p*-X-phenylisobutyl acetals of acetaldehyde (*I*), 2-(*p*-X-phenoxy)tetrahydropyrans (*II*), 2-(*p*-X-phenoxy)tetrahydrofurans (*III*), and cyclohexyl (*p*-X-phenyl) acetals of acetaldehyde (*IV*)

Acetal[a]	B.p., K/kPa	n_D	Yield, %
Ia	404·7—405·7/1·73	1·4948/294·7	63·8
Ib	376·7—377·7/1·47	1·4790/296·2	72·4
Ic	395·2/2·0	1·4793/295·2	73·0
Id	422·2—422·7/1·73	1·4798/297·2	66·0
Ie	415·7—416·7/1·73	1·4863/291·7	75·4
IIa	381·2/2·53	1·5447/291·2	48·0
IIb	393·2/1·67[b,c]	1·5211/294·2	62·2
IIc	406·2—409·2/1·60[b]	1·5155/295·2	44·4
IId	438·2/1·73	1·5059/293·2	41·8
IIe	398·7—400·7/2·06	1·5335/292·7	47·6
IIIa	409·2—411·2/1·60	1·5365/295·7	34·0
IIIb	383·2—384·2/1,73[d]	1·5221/296·2	41·6
IIIc	398·2/1·60	1·5192/296·2	39·3
IIId	429·2—431·2/1·87	1·5100/292·2	41·3
IIIe	433·2—433·7/2·13	1·5250/295·2	69·7
IVa	448·2—452·2/1·93	1·5159/291·7	66·1
IVb	416·7/1·47	1·5050/295·2	63·0
IVc	425·2—427·2/1·47	1·5022/295·2	67·4
IVd	459·2—461·2/1·73	1·4975/292·7	48·2
IVe	460·2—460·7/2·20	1·5092/291·2	58·1

[a] All prepared acetals gave satisfactory results of elemental analysis; [b] compare lit.[6]; [c] compare lit.[8]; [d] compare lit.[5].

TABLE II

Chemical shifts $\delta^1H_{CCl_4}$, $\delta^{13}C_{neat}$ and coupling constants J (Hz) in the ^1H and ^{13}C-NMR spectra of *p*-X-phenylisobutyl acetals of acetaldehyde (*I*)



X	Cl	H	CH_3	$(CH_3)_3C$	OCH_3
H in X	—	—	2·24	1·28	3·61
H_1	1·43	1·44	1·40	1·43	1.34
H_2	5·26	5·31	5·23	5·24	5·11
$J_{1,2}$	6·0	6·0	5·0	6·0	6·0
$H_3{}^a$	3·38	3·39	3·41	3·41	3·42
$H_{3'}{}^a$	3·14	3·13	3·15	3·14	3·15
$\lvert J_{3,3'}\rvert$	9·1	9·15	9·1	9·13	9·1
H_4	1·74	1·75	1·73	1·76	1·71
$J_{3,4}{}^a$	6·67	6·56	6·61	6·66	6·61
$J_{3',4}{}^a$	6·43	6·44	6·49	6·49	6·39
H_5	0·85	0·85	0·85	0·88	0·82
H_6	0·88	0·88	0·88	0·90	0·85
$J_{4,5} = J_{4,6}$	7·0	7·5	7·5	6·5	7·0
$H_{8,12}{}^b$	6·84	6·75—7·30	6·76	6·81	6·63
$H_{9,11}{}^b$	7·11	6·75—7·30	6·92	7·16	6·77
$J_{8,9} + J_{8,11}$	9·0	—	9·0	9·0	10·0
H_{10}	—	6·75—7·30	—	—	—
C in X	—	—	20·6	—	55·3
$C_{(1)}$	20·1	20·3	20·2	—	20·3
$C_{(2)}$	99·9	99·5	99·6	—	100·5
$C_{(3)}$	72·1	72·0	71·9	—	72·3
$C_{(4)}$	28·9	29·0	28·9	—	29·0
$C_{(5),(6)}$	19·7	19·8	19·6	—	19·7
$C_{(7)}$	156·1	157·8	155·5	—	155·2
$C_{(8),(12)}$	119·1	117·7	117·7	—	119·3
$C_{(9),(11)}$	129·7	129·7	130·1	—	114·8
$C_{(10)}$	127·0	122·0	130·7	—	151·4

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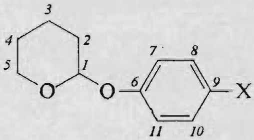
[a] Calculated from the AB quartets. Since the X-part of the spectrum cannot be solved owing to the coupling to the geminal methyl groups, a difference method of calculation was used. This method yields positive values of the vicinal couplings $J_{3,4}$ and $J_{3',4}$; [b] calculated from the pseudo-quartet of the aromatic protons.

dried over magnesium sulfate, ether was evaporated at room temperature and the residue was quantitatively analysed by ^{1}H-NMR. The ratio of unreacted substrates was determined as the ratio of the integral curves of their acetal protons.

The relative rate constants k_{rel} were calculated using the relations derived in the ref.[11]. A program LFER-C was written for this purpose in Tesla Fortran language (Laboratory of Computing Machinery, Technical University, Brno). It allows to perform both one-parameter correlation of logarithms k_{rel} with the constants σ and the two-parameter correlation of logarithms k_{rel} with the constants σ and E_S. Simultaneously the characteristics of these correlation are calculated. Calculated values of k_{rel}, found values of ϱ and the coefficients of correlation, r, for the equation $\log k_{rel} = \varrho \cdot \sigma$ are given in Table VI.

TABLE III

Chemical shifts $\delta^1H_{CCl_4}$, $\delta^{13}C_{neat}$ and coupling constants J (Hz) in the ^{1}H and ^{13}C-NMR spectra of 2-(*p*-X-phenoxy)tetrahydropyrans (*II*)



X	Cl	H	CH_3	$(CH_3)_3C$	OCH_3
H in X	—	—	2·24	1·20	3·58
H_1	5·20	5·30	5·26	5·23	5·17
$H_{2,3,4}$	1·12—1·87	1·38—2·0	1·37—2·0	1·25—1·87	1·37—2·0
H_5	3·24—4·0	3·24—4·0	3·24—4·0	3·24—4·0	3·24—4·0
$H_{8,10}$[a]	6·95	6·62—7·25	6·91	7·08	6·81
$H_{7,11}$[a]	6·55	6·62—7·25	6·80	6·81	6·63
$J_{7,8} + J_{7,10}$	9·0	—	9·0	9·0	10·0
H_9	—	6·62—7·25	—	—	—
C_α in X	—	—	20·6	34·3	—
C_β in X	—	—	—	32·0	—
$C_{(1)}$	96·8	96·4	96·5	96·4	—
$C_{(2)}$	30·7	30·8	30·8	30·9	—
$C_{(3)}$	19·1	19·1	19·1	19·1	—
$C_{(4)}$	25·7	25·7	25·8	25·8	—
$C_{(5)}$	61·9	61·7	61·5	61·5	—
$C_{(6)}$	156·5	157·9	155·8	155·6	—
$C_{(7),(11)}$	118·4	116·9	116·8	116·5	—
$C_{(8),(10)}$	129·7	129·7	130·1	126·3	—
$C_{(9)}$	126·7	121·8	130·6	144·0	—

[a] Calculated from the pseudo-quartet of the aromatic protons.

Calculation of σ_p^+ Constants from the ^{13}C-NMR Spectra

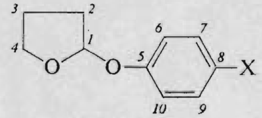
The correlation equation (*1*) succesfully applied

$$S_p = 9{\cdot}81\sigma_p^+ - 0{\cdot}81\,, \qquad (1)$$

where $S_p = \delta^{13}C_p - \delta^{13}C_{benzene}$,
(coefficient of correlation $r = 0{\cdot}99$) in the series of 14 substituted benzenes[12] was used to evaluate the σ_p^+ constants for the substituents 1-isobutoxy-1-ethoxy,- 2-tetrahydropyranyloxy-, 2-tetrahydrofuryloxy- and 1-cyclohexyloxy-1-ethoxy-. The S_p values based on the ^{13}C-NMR spectra of acetals *Ib*, *IIb*, *IIIb*, and *IVb* together with the calculated values of the σ_p^+ constants are given in Table VII.

TABLE IV

Chemical shifts $\delta^1H_{CCl_4}$, $\delta^{13}C_{neat}$ and coupling constants J Hz in the ^{1}H and ^{13}C-NMR spectra of 2-(*p*-X-phenoxy)tetrahydrofurans (*III*)



X	Cl	H	CH_3	$(CH_3)_3C$	OCH_3
H in X	—	—	2·20	1·18	3·58
H_1	5·58	5·62	5·57	5·55	5·50
$H_{2,3}$	1·62—2·24	1·62—2·24	1·62—2·24	1·37—2·12	1·62—2·24
H_4	3·62—4·00	3·62—4·00	3·62—4·00	3·50—4·00	3·62—4·00
$H_{6,10}$[a]	7·09	6·50—7·24	6·89	7·08	6·81
$H_{7,9}$[a]	6·82	6·50—7·24	6·76	6·80	6·62
$J_{9,10} + J_{6,9}$	9·0	—	9·0	9·0	8·0
H_8	—	6·50—7·24	—	—	—
C in X	—	—	20·5	—	55·5
$C_{(1)}$	103·1	102·7	102·8	—	103·6
$C_{(2)}$	33·2	33·1	33·0	—	33·0
$C_{(3)}$	24·0	23·8	23·8	—	23·9
$C_{(4)}$	68·5	68·0	67·8	—	68·0
$C_{(5)}$	156·7	158·1	155·9	—	155·1
$C_{(6),(10)}$	118·6	117·0	116·9	—	118·4
$C_{(7),(9)}$	129·7	129·7	130·1	—	114·9
$C_{(8)}$	126·7	121·7	130·6	—	152·0

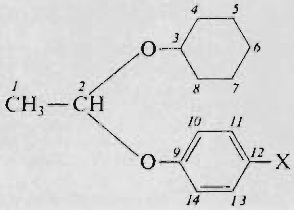
[a] Calculated from the pseudo-quartet of the aromatic protons.

RESULTS AND DISCUSSION

The protons of prochiral methylene group and geminal methyl groups are anisochronous in the ^{1}H-NMR spectra of acetals *I*. The ^{3}CHH′—^{4}CH part of the iso-

TABLE V

Chemical shifts $\delta^1H_{CCl_4}$, $\delta^{13}C_{neat}$ and coupling constants J (Hz) in the ^{1}H and ^{13}C-NMR spectra of cyclohexyl (*p*-X-phenyl) acetals of acetaldehyde (*IV*)



X[a]	Cl	H	CH_3	$(CH_3)_3C$	OCH_3
H in X	—	—	2·24	1·23	3·55
H_1	1·35	1·41	1·38	1·35	1·30
H_2	5·30	5·36	5·30	5·28	5·20
$J_{1,2}$	5·8	6·0	5·5	5·2	5·8
H_3	3·3—3·8	3·3—3·8	3·4—3·8	3·3—3·8	3·3—3·8
$H_{4,8}$	1·68	1·75	1·75	1·68	1·65
$H_{5,6,7}$	1·0—1·5	1·0—1·5	1·0—1·5	1·0—1·5	1·0—1·5
$H_{10,14}$[b]	7·06	6·67—7·29	6·91	7·11	6·76
$H_{11,13}$[b]	6·83	6·67—7·29	6·75	6·76	6·64
H_{12}	—	6·67—7·29	—	—	—
$J_{13,14} + J_{13,10}$	9·0	—	9·0	9·0	9·0
C_α in X	—	—	20·8	34·5	55·5
C_β in X	—	—	—	32·1	—
$C_{(1)}$	21·3	21·3	21·3	21·4	21·4
$C_{(2)}$	98·5	98·5	98·6	98·6	99·4
$C_{(3)}$	74·0	74·0	73·9	74·1	74·4
$C_{(4),(8)}$	34·1	34·1	34·1	34·2	34·1
	32·9	32·8	32·8	32·9	32·8
$C_{(5),(7)}$	24·5	24·5	24·5	24·6	24·5
	24·4	24·3	24·3	24·5	24·4
$C_{(6)}$	26·3	26·3	26·3	26·4	26·3
$C_{(9)}$	156·2	157·7	155·5	155·4	155·4
$C_{(10),(14)}$	118·1	118·1	118·1	117·7	119·8
$C_{(11),(13)}$	129·7	129·7	130·2	126·4	114·9
$C_{(12)}$	126·9	121·9	130·7	144·2	151·3

[a] Carbon-13 signals in the cyclohexane ring were assigned according to lit.[9,10]; [b] calculated from the pseudo-quartet of the aromatic protons.

butoxy group containing diastereotopic protons $H_{(3)}$ and $H_{(3')}$ gives rise to an ABX-type spectrum whose AB part can be solved to obtain the data given in Table II. The anisochrony of protons $H_{(3)}$ and $H_{(3')}$ ($\delta H_{(3)} - \delta H_{(3')}$ is 0·24−0·28 ppm in tetrachloromethane at *c.* 10% volume concentration corresponds to 19·2−22·4 Hz at 80 MHz) is only slightly dependent on the substituent X and is substantially greater than that reported[13,14] for α-phenylisobutyl ether(V) (*cca* 0·25 Hz in 10% tetrachloromethane solution at 80 MHz). It was proved[14] that besides intrinstic chemical shift non-equivalence due to the diastereoisotopy of protons $H_{(3)}$ and $H_{(3')}$ the subtantial contribution to the magnitude of this effect originates in conformational preference that causes the proximity of one diastereotopic proton to the benzene ring. Inspection

TABLE VI

Values of k_{rel} for the hydrogenolysis of *p*-X-phenylisobutyl acetals of acetaldehyde (*I*), 2-(*p*-X-phenoxy)tetrahydropyrans (*II*), 2-(*p*-tolyloxy)tetrahydrofuran (*IIIc*) and cyclohexylphenyl acetal of acetaldehyde (*IVb*) by ethereal chloroalane and characteristics of linear free energy relationships correlations

Acetal k_{rel}	*Ia*[a] 2·09	*Ib*[a] 1·75	*Ic*[a] 0·15	*Id*[a] 0·38	*Ie*[a] [d]	*IIb*[b] 0·042	*IIc*[b] 0·097	*IIe*[b] 0·301	*IIb*[a] 0·015[e]	*IIIc*[c] 2·36	*IVb*[a] 0·41
ϱ/r at σ_p^+	2·61 ± 0·49/0·9667					—1·09 ± 0·04/0·9995			—		
ϱ/r at σ_p	— /0·7727					— /0·5196			—		
ϱ/r at σ_r	— /0·0008					— /0·9832			—		

[a] Standard *IIIb*; standard *IIIc*; [c] standard *Ic*; [d] unmeasurably small; [e] calculated from the experimental values k_{rel} *Ic*/*IIIb* and *IIIc*/*Ic*.

TABLE VII

Values of S_p and calculated values of σ_p^+ constants

Substituent	S_p[a]	σ_p^+
Iso-$C_4H_9OCH(CH_3)O$-	—6·30	—0·56
2-Tetrahydropyranyloxy-	—6·50	—0·58
2-Tetrahydrofuryloxy-	—6·55	—0·59
Cyclo-$C_6H_{11}OCH(CH_3)O$-	—6·40	—0·57

[a] The chemical shift of benzene $\delta^{13}C_{benzene}$ = 128·3 ppm used in the calculation of S_p values was obtained by measurements under identical conditions as that used for the ^{13}C-NMR spectra of acetals *I*—*IV*.

of models of acetals *I* leads to a conclusion that the different extent of the chemical shift non-equivalence in compounds *I* and *V* corresponds to the difference in their structures (*p*-X-phenoxy group instead of phenyl group) and that the preferred conformation of *I* type acetals has the aromatic ring close to the methylene group and that the mutual position of the oxygen lone pairs is gauche. The chemical shift non-equivalence of geminal methyl groups in acetals *I* (0·02 – 0·03 ppm, *i.e.* 1·6 – 2·4 Hz at 80 MHz) is substantially greater than the comparable value for the compound *V* (0·4 Hz at 80 MHz)[14]. However, it corresponds well to this value for α-phenylisopentyl ether *VI* (3·2 Hz at 80 MHz)[14]. We think that this fact also supports the view that the benzene ring is the main cause of the magnitude of the chemical shift non-equivalence because its distance from the geminal methyl groups is the same as in the compound *VI*. Again, according to the Newman's[15] "rule of six" and the discussion in ref.[14], the magnitude of the chemical shift non-equivalence of the geminal methyl groups in acetals *I* might be well affected by a conformation-caused differences in their shielding by the benzene ring. No anisochronous behaviour was observed in the ^{13}C-NMR spectra of acetals *I*. As evident from Table V, the diastereotopic carbon atoms $C_{(4)}$, $C_{(8)}$, and $C_{(5)}$, $C_{(7)}$ of the cyclohexane ring are anisochronous in the ^{13}C-NMR spectra of acetals *IV*. According to our best knowledge, this phenomenon was so far observed for the carbons of a monosubstituted cyclohexane ring only with 2-cyclohexyl-2,3,3-trimethyloxetane[16,17]. The magnitude of magnetic non-equivalence sharply decreases with increasing distance from the chirality center and is practically independent of the nature of the substituent X ($\delta C_{(4)} - \delta C_{(8)}$) is 1·2 – 1·3 ppm, ($\delta C_{(5)} - \delta C_{(7)}$) is 0·1 – 0·2 ppm). We measured ^{13}C-NMR spectra of acetal *IVb* in the range 175 – 400 K and in various solvents (at low temperatures in the mixture of fluorotrichloromethane and tetrachloromethane 1 : 0·6, at 295 K as a neat liquid and in ($^{2}H_{4}$)-methanol at higher temperatures in ($^{2}H_{6}$)-dimethyl sulfoxide). The spectrum does not change much over the temperature range investigated and in the various solvents used. Therefore it was concluded that the difference in free energy between the axial and the equatorial conformer of acetal *IVb* is at least 12·5 kJ mol^{-1} and that the magnitude of the chemical shift non-equivalence of the diastereotopic cyclohexane ring carbons was mainly due to the chirality of the molecule since it is practically temperature independent.

A reversed conformational equilibrium with respect to the acetals *IV* is expected on the basis of the anomeric effect in 2-(*p*-X-phenoxy)tetrahydropyrans (*II*). Marked preference of conformations having an electronegative substituent at the position 2 axially oriented even in the crystalline state was demonstrated in many tetrahydropyran derivatives[18–21]. The magnitude of the anomeric effect was determined for 2-methoxy-, 2-chloro- and 2-bromotetrahydropyran and was equal to 5·5, 11·3 and more than 13·4 kJ mol^{-1} (ref.[22]). We measured the ^{13}C-NMR spectrum of the acetal *IIb* at 198 K in ($^{2}H_{4}$)-methanol and did not found any changes even if it is known that the individual conformers of 2-substituted tetrahydropyrans exhibit different carbon-13 chemical shifts[23]. Therefore we think that acetals *II* are present in the conformation with an axial substituent to such an extent that the presence of a second conformation is not directly detectable; the free energy difference must be at least $-12{\cdot}5\ \mathrm{kJ\ mol^{-1}}$. The results of the ^{1}H-NMR spectra measurements in the presence of tris (dipivaloylmethanato) europium also show that the type *II* acetals predominantly exist in the conformation with the axial substituent. Increasing the concentration of the shift reagent, the signal in the region of $H_{(5)}$ protons is first narrowed and then again broadened. This effect is explained by a shift of axial protons initially resonating at higher magnetic field and exhibiting a substantially larger induced downfield shift than their equatorial counterparts. Assuming the coordination site of the shift reagent located somewhere between both oxygen atoms (which is reasonable according to the magnitude of the induced shifts of other protons signals), the agreement of our model with the reality is good. Thus, the results correspond to an axial orientation of the *p*-X-phenoxysubstituent on the tetrahydropyran ring.

The correlation of obtained k_{rel} value for the hydrogenolysis of acetals *I* and *II* by ethereal solution of chloroalane with various constants of the substituents shows that the linear dependence holds for the substitution constants σ_p^+ only. That indicates that in the transition state of the reaction a positive charge is formed on the acetal oxygen next to the aromatic ring. There is a lot of evidence for the similar reaction course with the carbon analogs of our acetals. For example, following reactions also provide satisfactory correlations with the σ_p^+ constants: hydration of *p*-X-substituted styrenes[24], hydration of *p*-X-substituted phenylacetylenes[25], solvolysis of *p*-X-substituted 1,1-dimethylbenzylchlorides[26], and thermolysis of *p*-X-substituted chlorobenzylmethyl ethers[27]. In all cases mentioned, the reaction controlling step is the positive charge formation on the benzyl carbon. Found signs of the ϱ constants show that the hydrogenolysis of acetals *I* is controlled by step *B* whereas the same reaction with acetals *II* is controlled by step *A* (Scheme 1).

We believe that the control of hydrogenolysis by reagent–substrate complex formation with acetals *II* is the first case of the reaction of acetals with electrophiles that is not controlled by alkoxycarbenium ion formation. The reason is probably a difficult accessibility of the more nucleophilic oxygen atom that is expressed also in the reaction rate. From the Table VI it follows that

$$k_{\mathrm{rel}}\,Ib > k_{\mathrm{rel}}\,IIIb > k_{\mathrm{rel}}\,IVb \gg k_{\mathrm{rel}}\,IIb$$

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