

Thermodynamic, spectroscopic, and density functional theory studies of allyl aryl and prop-1-enyl aryl ethers. Part 1.

Thermodynamic data of isomerization

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A chemical equilibration study of the relative thermodynamic stabilities of seventy isomeric allyl aryl ethers (**a**) and (*Z*)-prop-1-enyl aryl ethers (**b**) in DMSO solution has been carried out. From the variation of the equilibrium constant with temperature the Gibbs energies, enthalpies, and entropies of isomerization at 298.15 K have been evaluated. Because of their low enthalpies, the (*Z*)-prop-1-enyl aryl ethers are strongly favored at equilibrium, the Gibbs energies of the **a**→**b** isomerization ranging from −12 to −23 kJ mol^{−1}. The entropy contribution is negligible in most reactions, but occasionally small positive values less than +10 J K^{−1} mol^{−1} of the entropy of isomerization are found. The equilibration studies were also extended to involve two pairs of related isomeric ethers with a Me substituent on C(2) of the olefinic bond. The Me substituent was found to increase the relative thermodynamic stability of the allylic ethers by *ca.* 3.4 kJ mol^{−1}.

Introduction

In a thermodynamic sense, alkyl allyl ethers ROCH₂CH=CH₂ are much less stable than their isomers, alkyl prop-1-enyl ethers ROCH=CHMe, a fact which may be used to convert alkyl allyl ethers “quantitatively” into alkyl prop-1-enyl ethers.¹ In more precise terms, the Gibbs energy of isomerization of allyl methyl ether to (*Z*)-prop-1-enyl methyl ether is known to be −19.9 kJ mol^{−1} in DMSO solution at 298.15 K,² corresponding to an equilibrium constant $K([(\textit{Z})\text{-prop-1-enyl}]/[\text{allyl}])$ of *ca.* 3100. With increasing bulkiness of the alkyl group R, the relative stability of the (*Z*)-prop-1-enyl isomer is further enhanced: for R = Bu^t, ΔG_m° (298.15 K) = −24.9 kJ mol^{−1} ($K = 23000$).² The high thermodynamic stability of alkyl (*Z*)-prop-1-enyl ethers arises almost completely from the enthalpy term: in the majority of reactions studied, the entropy contribution proved to be negligible (−2 to +2 J K^{−1} mol^{−1}).² The low enthalpy of alkyl prop-1-enyl ethers is mainly due to the strong stabilization (comparable to that in ethyl vinyl ether³) brought about by p–π conjugation in the –O–C=C moiety.

In addition to the thermodynamics of isomerization of alkyl allyl ethers to alkyl (*Z*)-prop-1-enyl ethers, that of allyl vinyl ethers (CH₂=CHCH₂OCH=CH₂, and related compounds) to (*Z*)-prop-1-enyl vinyl ethers (MeCH=CHOCH=CH₂) has also been studied.⁴ In these reactions both the reactant and product are stabilized by p–π conjugation. Although the O atom of the reaction product may thus conjugate with *two* adjacent olefinic linkages, the stabilization arising from this π–p–π conjugation is not strong enough to favor the reaction product to the extent that alkyl (*Z*)-prop-1-enyl ethers are favored relative to alkyl allyl ethers. Thus, for the reaction allyl vinyl ether→(*Z*)-prop-1-enyl vinyl ether the Gibbs energy change, −16.1 kJ mol^{−1} in DMSO solution at 298.15 K,⁴ is *ca.* 4 kJ mol^{−1} less negative than that for the allyl methyl ether→(*Z*)-prop-1-enyl methyl ether isomerization.

Allyl vinyl ethers are structurally related to allyl aryl ethers and prop-1-enyl vinyl ethers to prop-1-enyl aryl ethers. As ring-substituted allyl aryl ethers are readily accessible from the corresponding phenols and allyl halides, the thermodynamics of the isomerization of allyl aryl ethers to prop-1-enyl aryl

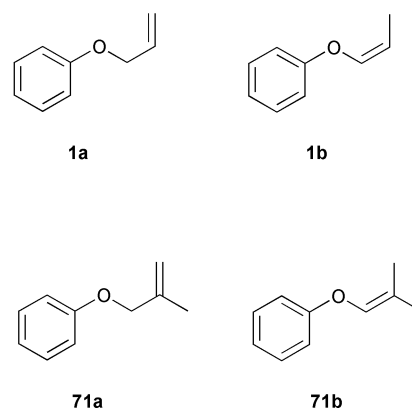


Fig. 1 The parent compounds of the two series of compounds of the present study.

ethers may thus be studied in great detail using an extensive number of compounds. In the present investigation, two series of isomeric ring-substituted allyl aryl ethers and (*Z*)-prop-1-enyl aryl ethers were prepared (for the parent compounds **1a**, **1b**, **71a**, and **71b**, see Fig. 1), and the thermodynamics of the **a** to **b** reaction were studied by Bu^tOK catalyzed chemical equilibration in DMSO solution. Under these experimental conditions, the thermodynamic equilibrium is readily established only between the allyl aryl and (*Z*)-prop-1-enyl aryl ethers: for a full thermodynamic equilibrium involving the *E* isomer, more drastic experimental conditions (high temperatures, prolonged reactions times, and possibly a different catalyst) are required. The compounds prepared were characterized by accurate molecular masses and various NMR spectroscopic (¹H, ¹³C, and ¹⁷O NMR) methods; in addition, 70 eV EI mass spectra, as well as IR and UV spectra for several representatives of the compounds, were also determined. Because of the large amounts of data obtained, the results will be published in several papers. The thermodynamic part of the study, including the synthetic work, accurate molecular masses and ¹H NMR chemical shifts, is described here; an analysis of the structural information present in the ¹H, ¹³C,

Table 1 Values of the mean equilibrium constant K for the isomerization of allyl aryl ethers (**1–70**) to (*Z*)-prop-1-enyl aryl ethers and of 2-methylallyl aryl ethers (**71** and **72**) to 2-methylprop-1-enyl aryl ethers in DMSO solution at various temperatures

No.	Substitution	T/K							No.	Substitution	T/K						
		299.2	323.2	348.2	373.2	398.2	423.2	443.2			299.2	323.2	348.2	373.2	398.2	423.2	443.2
1	H	912	548	337	242	164	119.7	99.1	37	2-Me	981	593	397	291	208	161	128.7
2	4-Me		590	371	257	184	133.3	102.8	38	2-Et		706	464	321	237	165	139
3	4-Et		500	321	223	162	117.7	96.8	39	2-Pr ⁱ		833	510	342	228	177	138
4	4-Pr ⁱ	892	575	340	231	168	121.6	96.4	40	2-Bu ^s		806	494	314	229	166	133
5	4-Bu ^s		601	375	261	177	134.3	103.8	41	2-Bu ⁱ		1023	608	413	287	210	159
6	4-Bu ⁱ		572	373	261	183	135.1	105.6	42	2-Ph		502	357	237	177	129.7	106.8
7	4-MeO			426	288	205	148.4	115.2	43	2-MeO		556	390	269	189	151	126.0
8	4-EtO		653	421	281	195	144.0	117.3	44	2-EtO		577	375	265	184	135	113.5
9	4-MeS				176	127	94.6	78.1	45	2-Pr ⁱ O		548	358	249	169	127.3	100.7
10	4-F	855	519	319	225	151	112.9	95.0	46	2-F	408	278	204	149	110.9	91.6	81.4
11	4-Cl	503	350	220	150	108.5	85.7	70.5	47	2-Cl		360	239	168	125.0	99.7	86.5
12	4-Br		330	213	150	111.1	84.8	71.8	48	2-Br	359	253	172	132	99.6	81.6	69.8
13	4-I		319	218	150	110.7			49	4-Cl-2-Me	607	400	266	189	135.3	103.3	85.1
14	3,5-di-Me		628	419	263	195	142.0	114.7	50	2,3,5-tri-Me		689	452	318	224	175	
15	3,5-di-Bu ⁱ		628	393	257	182	133.8	103.8	51	2-(CH ₃) ₄ -3		623	379	268	190	141.4	116.0
16	4-Cl-3,5-di-Me		444	279	190	140	101.1	78.8	52	2-Bu ⁱ -4-Me				492	333	239	186
17	3,5-di-MeO			253	173	125.4	95.3	77.6	53	2,4-di-Bu ⁱ			704	465	324	224	175
18	3,5-di-Cl		188	124.2	94.5	68.2	55.0	46.6	54	2,3-di-MeO		503	317	223	160	114.9	92.7
19	3,5-di-F	274	196	135.8	102.3	81.4			55	2,3-di-F	245	179	131.3	101.4	81.0		
20	3,4,5-tri-MeO		232	170	129.9	105.6	85.3		56	2,4-di-F		257	177	138.1	103.1	80.7	72.4
21	3-Me		552	357	246	173	130.8	102.3	57	2-Cl-5-Me		288	197	145	105.0	81.5	68.2
22	3-Et		494	335	230	159	119.4	95.8	58	2-Cl-4,5-di-Me			242	170	125.6	95.9	80.5
23	3-Pr ⁱ		553	344	244	174	131.8	100.2	59	2,3-di-Cl		195	134.7	103.1	78.2	61.2	54.6
24	3-Bu ⁱ	872	521	319	223	156	120.0	93.8	60	2,4-di-Cl	291	199	134.6	101.4	79.7		
25	3-MeO		499	320	225	166	128.0	108.5	61	2,5-di-Cl		168	120.6	93.5	72.1	60.4	52.1
26	3-F		279	201	148	110.2	86.7	71.2	62	2-Cl-4-F		243	177	130.3	101.8	79.6	
27	3-Cl		297	202	152	113.2	89.8	76.8	63	2,6-di-Me		2615	1430	942	606	416	330
28	3-Br	426							64	2,4,6-tri-Me				1005	651	453	340
29	4-Cl-3-Et		385	249	174	126.4	92.7	74.9	65	4-Br-2,6-di-Me			1090	679	452	318	256
30	3-(CH ₃) ₃ -4			382	255	178	137.3	107.2	66	2,6-di-Pr ⁱ		3890	2270	1400	947	671	508
31	3,4-di-MeO		637	386	264	180	130.6	105.3	67	2-Bu ⁱ -6-Me				3470	2170	1460	1090
32	3-OCH ₂ O-4			361	242	168	128.6	104.4	68	2,6-di-MeO		975	560	375	262	179	148
33	3-Cl-5-MeO	376	267	181	134	99.0	78.0	66.7	69	2,6-di-F			248	182	141	110.0	
34	3,4-di-F		270	187	141	110.7	88.0		70	2,6-di-Cl					788	556	432
35	3,4-di-Cl		232	164	120.5	89.5	71.4	59.5	71	H		147	103.1	75.5	56.7	44.2	37.1
36	3-Cl-4-F	412	266	187	135	101.6	81.9	66.9	72	2,6-di-Me		562	361	248	164	125.7	98.9

and ¹⁷O NMR chemical shifts will be reported in the next contribution.

To facilitate interpretation of the thermodynamic data of isomerization, some DFT (density functional theory) calculations on the stable conformations of **1a** and **1b** were also carried out. A more extensive computational study of the accurate molecular geometries of some key compounds of the present study will be published later.

Results and discussion

The primary results of the thermodynamic work, *i.e.* the values of the mean equilibrium constant K at various temperatures, are shown in Table 1. From the variation of the value of the mean equilibrium constant with temperature, the thermodynamic parameters ΔG°_m , ΔH°_m and ΔS°_m of isomerization at 298.15 K (Table 2) were calculated by the van't Hoff equation, employing a linear least-squares treatment of $\ln K$ vs. T^{-1} . The uncertainties of the thermodynamic parameters given in Table 2 are twice the standard errors of the regression analyses, rounded to one decimal. However, because of the reactivity of the halogen atom of the 3-Br derivatives (**28**) toward the strongly basic catalyst-solvent system, the equilibration experiments on this pair of isomers were not successful at elevated temperatures; thus the reported uncertainty of the value of ΔG°_m for **28a**→**28b** is twice the standard error of the mean of the parallel determinations at 299.2 K. Moreover, because of some experimental difficulties, the equilibrium between the 2,6-di-Cl derivatives **70a** and **70b** was studied at only three temperatures from 398.2 to 443.2 K. The uncertainties given in Table 2 for this reaction are estimated errors, since a

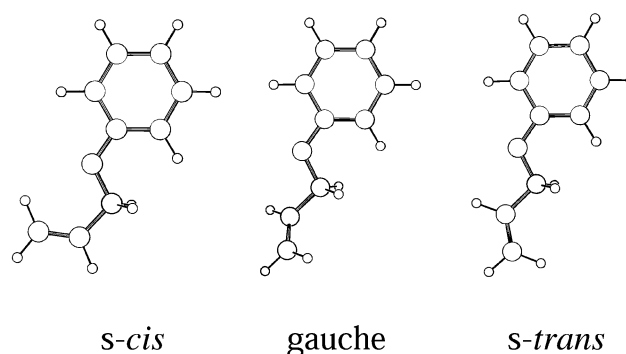


Fig. 2 ORTEP-3 view¹⁶ of the stable *s-cis* and *gauche* conformers, and that of the unstable *s-trans* structure, of allyl phenyl ether **1a** according to the B3LYP/6-31G* calculations.

regression analysis on only three data points gave unrealistically small error limits.

Conformations of allyl phenyl ether **1a** and (*Z*)-prop-1-enyl phenyl ether **1b**

Prior to discussion of the thermodynamic data, it is helpful to consider the stable conformations of the parent compounds **1a** and **1b** as found by the DFT calculations at the B3LYP/6-31G* level of theory. Two energy minima (of different energy) on the potential energy surface (PES) of **1a** were found. One of them corresponds to a stable conformer with a planar heavy atom skeleton, the other to a nonplanar *gauche* conformer with the torsion angles $\tau(C_{ar}=C_{ar}-O-C)$ and $\tau(O-C-C=C)$ equal to -2.6° and -129° , respectively (see Fig. 2). The former conformer, with

Table 2 Values of the thermodynamic parameters ΔG_m° (298.15 K), ΔH_m° , and ΔS_m° of the isomerization of allyl aryl ethers (**1–70**) to (*Z*)-prop-1-enyl aryl ethers and of 2-methylallyl aryl ethers (**71** and **72**) to 2-methylprop-1-enyl aryl ethers in DMSO solution^a

No.	Substitution	ΔG_m° / kJ mol ⁻¹	ΔH_m° / kJ mol ⁻¹	ΔS_m° / J K ⁻¹ mol ⁻¹	No.	Substitution	ΔG_m° / kJ mol ⁻¹	ΔH_m° / kJ mol ⁻¹	ΔS_m° / J K ⁻¹ mol ⁻¹
Symmetrically substituted, without <i>ortho</i> -substituents					Mono- <i>ortho</i> -substituted				
1	H	-17.0 ± 0.1	-17.1 ± 0.4	-0.4 ± 1.1	37	2-Me	-17.1 ± 0.1	-15.3 ± 0.4	6.0 ± 1.0
2	4-Me	-17.2 ± 0.2	-17.1 ± 0.6	0.2 ± 1.5	38	2-Et	-17.6 ± 0.2	-16.3 ± 0.6	4.3 ± 1.7
3	4-Et	-16.7 ± 0.1	-16.3 ± 0.3	1.2 ± 0.7	39	2-Pr ⁱ	-18.0 ± 0.2	-17.8 ± 0.6	0.8 ± 1.5
4	4-Pr ⁱ	-16.9 ± 0.1	-17.0 ± 0.6	-0.3 ± 1.5	40	2-Bu ^s	-17.9 ± 0.1	-17.8 ± 0.5	0.3 ± 1.3
5	4-Bu ^s	-17.2 ± 0.1	-17.3 ± 0.5	-0.3 ± 1.3	41	2-Bu ^t	-18.6 ± 0.1	-18.2 ± 0.5	1.4 ± 1.4
6	4-Bu ^t	-17.1 ± 0.1	-16.7 ± 0.5	1.3 ± 1.4	42	2-Ph	-16.7 ± 0.2	-15.6 ± 0.7	3.7 ± 1.9
7	4-MeO	-17.6 ± 0.2	-17.6 ± 0.6	0.0 ± 1.5	43	2-MeO	-16.9 ± 0.2	-15.0 ± 0.7	6.2 ± 1.8
8	4-EtO	-17.4 ± 0.1	-17.2 ± 0.3	0.8 ± 0.7	44	2-EtO	-17.0 ± 0.1	-16.3 ± 0.5	2.4 ± 1.3
9	4-MeS	-16.0 ± 0.1	-16.1 ± 0.4	0.0 ± 0.9	45	2-Pr ⁱ O	-17.0 ± 0.1	-16.9 ± 0.5	0.4 ± 1.3
10	4-F	-16.8 ± 0.1	-16.9 ± 0.4	-0.5 ± 1.2	46	2-F	-14.9 ± 0.1	-12.6 ± 0.5	7.9 ± 1.3
11	4-Cl	-15.6 ± 0.2	-15.4 ± 0.6	0.5 ± 1.7	47	2-Cl	-15.6 ± 0.2	-14.3 ± 0.7	4.5 ± 1.9
12	4-Br	-15.5 ± 0.1	-15.2 ± 0.4	1.2 ± 1.1	48	2-Br	-14.6 ± 0.1	-12.7 ± 0.3	6.7 ± 0.9
13	4-I	-15.5 ± 0.1	-15.2 ± 0.5	1.0 ± 1.5	<i>ortho</i> -Alkyl-substituted				
14	3,5-di-Me	-17.3 ± 0.2	-17.0 ± 0.6	1.0 ± 1.7	37	2-Me	-17.1 ± 0.1	-15.3 ± 0.4	6.0 ± 1.0
15	3,5-di-Bu ^t	-17.4 ± 0.1	-17.8 ± 0.3	-1.4 ± 0.7	49	4-Cl-2-Me	-16.0 ± 0.1	-15.0 ± 0.4	3.1 ± 1.0
16	4-Cl-3,5-di-Me	-16.4 ± 0.1	-16.9 ± 0.5	-1.7 ± 1.3	50	2,3,5-tri-Me	-17.4 ± 0.1	-15.6 ± 0.3	5.9 ± 0.7
17	3,5-di-MeO	-16.0 ± 0.1	-15.9 ± 0.2	0.3 ± 0.6	51	2-(CH ₂) ₄ -3	-17.2 ± 0.1	-16.6 ± 0.5	2.0 ± 1.3
18	3,5-di-Cl	-14.0 ± 0.2	-13.8 ± 0.6	0.7 ± 1.5	41	2-Bu ^t	-18.6 ± 0.1	-18.2 ± 0.5	1.4 ± 1.4
19	3,5-di-F	-14.0 ± 0.1	-12.3 ± 0.5	5.5 ± 1.4	52	2-Bu ^t -4-Me	-19.2 ± 0.1	-19.1 ± 0.2	0.5 ± 0.6
20	3,4,5-tri-MeO	-15.4 ± 0.2	-13.3 ± 0.6	7.2 ± 1.6	53	2,4-di-Bu ^t	-19.0 ± 0.2	-18.8 ± 0.7	0.6 ± 1.7
Mono- <i>meta</i> -substituted					<i>ortho</i> -Methoxy-substituted				
21	3-Me	-17.0 ± 0.1	-16.6 ± 0.3	1.1 ± 0.9	43	2-MeO	-16.9 ± 0.2	-15.0 ± 0.7	6.2 ± 1.8
22	3-Et	-16.7 ± 0.1	-16.3 ± 0.4	1.3 ± 1.1	54	2,3-di-MeO	-16.7 ± 0.1	-16.7 ± 0.4	0.1 ± 1.1
23	3-Pr ⁱ	-16.9 ± 0.2	-16.6 ± 0.6	1.2 ± 1.7	<i>ortho</i> -Fluoro-substituted				
24	3-Bu ^t	-16.8 ± 0.1	-16.9 ± 0.4	-0.5 ± 1.0	46	2-F	-14.9 ± 0.1	-12.6 ± 0.5	7.9 ± 1.3
25	3-MeO	-16.5 ± 0.1	-15.2 ± 0.5	4.6 ± 1.4	55	2,3-di-F	-13.7 ± 0.1	-11.0 ± 0.3	8.9 ± 0.9
26	3-F	-15.1 ± 0.1	-13.6 ± 0.5	5.0 ± 1.2	56	2,4-di-F	-14.7 ± 0.2	-12.7 ± 0.6	6.7 ± 1.6
27	3-Cl	-15.1 ± 0.1	-13.4 ± 0.3	5.7 ± 0.8	<i>ortho</i> -Chloro-substituted				
28	3-Br ^b	-15.1 ± 0.1			47	2-Cl	-15.6 ± 0.2	-14.3 ± 0.7	4.5 ± 1.9
<i>meta</i> -Alkyl-substituted					57	2-Cl-5-Me	-15.2 ± 0.1	-14.4 ± 0.3	2.7 ± 0.7
22	3-Et	-16.7 ± 0.1	-16.3 ± 0.4	1.3 ± 1.1	58	2-Cl-4,5-di-Me	-15.7 ± 0.1	-14.9 ± 0.3	2.7 ± 0.7
29	4-Cl-3-Et	-16.0 ± 0.1	-16.2 ± 0.3	-0.5 ± 0.7	59	2,3-di-Cl	-14.0 ± 0.1	-12.8 ± 0.5	4.3 ± 1.3
30	3-(CH ₂) ₃ -4	-17.2 ± 0.2	-17.0 ± 0.6	0.6 ± 1.6	60	2,4-di-Cl	-14.1 ± 0.1	-12.9 ± 0.5	3.8 ± 1.5
<i>meta</i> -Alkoxy-substituted					61	2,5-di-Cl	-13.6 ± 0.1	-11.6 ± 0.3	6.6 ± 0.9
25	3-MeO	-16.5 ± 0.1	-15.2 ± 0.5	4.6 ± 1.4	62	2-Cl-4-F	-14.6 ± 0.1	-12.7 ± 0.4	6.5 ± 0.9
31	3,4-di-MeO	-17.4 ± 0.1	-17.9 ± 0.3	-1.6 ± 0.8	<i>ortho,ortho'</i> -Disubstituted				
32	3-OCH ₂ O-4	-17.0 ± 0.2	-16.8 ± 0.6	0.7 ± 1.6	63	2,6-di-Me	-21.1 ± 0.2	-20.5 ± 0.6	1.8 ± 1.6
17	3,5-di-MeO	-16.0 ± 0.1	-15.9 ± 0.2	0.3 ± 0.6	64	2,4,6-tri-Me	-21.4 ± 0.2	-21.2 ± 0.5	0.7 ± 1.1
33	3-Cl-5-MeO	-14.8 ± 0.1	-13.5 ± 0.4	4.5 ± 1.1	65	4-Br-2,6-di-Me	-20.1 ± 0.2	-19.7 ± 0.6	1.5 ± 1.6
20	3,4,5-tri-MeO	-15.4 ± 0.2	-13.3 ± 0.6	7.2 ± 1.6	66	2,6-di-Pr ⁱ	-22.0 ± 0.1	-20.1 ± 0.3	6.5 ± 0.7
<i>meta</i> -Fluoro-substituted					67	2-Bu ^t -6-Me	-24.8 ± 0.1	-22.7 ± 0.3	6.9 ± 0.7
26	3-F	-15.1 ± 0.1	-13.6 ± 0.5	5.0 ± 1.2	68	2,6-di-MeO	-18.5 ± 0.2	-18.7 ± 0.7	-0.8 ± 1.7
34	3,4-di-F	-14.8 ± 0.1	-12.6 ± 0.4	7.3 ± 1.0	69	2,6-di-F	-15.6 ± 0.1	-13.2 ± 0.3	7.9 ± 0.8
19	3,5-di-F	-14.0 ± 0.1	-12.3 ± 0.5	5.5 ± 1.4	70	2,6-di-Cl ^c	-21.5 ± 0.2	-19.6 ± 0.6	6.2 ± 1.5
<i>meta</i> -Chloro-substituted					Reactions 71a → 71b and 72a → 72b				
27	3-Cl	-15.1 ± 0.1	-13.4 ± 0.3	5.7 ± 0.8	71	H	-13.5 ± 0.1	-13.7 ± 0.2	-0.9 ± 0.4
35	3,4-di-Cl	-14.6 ± 0.1	-13.5 ± 0.2	3.4 ± 0.6	72	2,6-di-Me	-17.1 ± 0.2	-17.3 ± 0.6	-0.8 ± 1.5
36	3-Cl-4-F	-14.9 ± 0.1	-13.8 ± 0.2	3.9 ± 0.6					
18	3,5-di-Cl	-14.0 ± 0.2	-13.8 ± 0.6	0.7 ± 1.5					
33	3-Cl-5-MeO	-14.8 ± 0.1	-13.5 ± 0.4	4.5 ± 1.1					

^a The errors are twice the standard errors. ^b At 299.2 K. ^c The errors are estimated errors.

an *s-cis* structure about the C–C(sp²) single bond [*i.e.* $\tau(\text{O}=\text{C}=\text{C})=0^\circ$], has an energy (at 0 K, including ZPE) of only 0.1 kJ mol⁻¹ below that of the nonplanar gauche form. After thermochemistry corrections to 298.15 K, the enthalpy of the *s-cis* conformer was calculated to be 0.3 kJ mol⁻¹ lower than that of the gauche form. On the other hand, the entropy of the gauche conformer was calculated to be 1.7 J K⁻¹ mol⁻¹ higher than that of the *s-cis* form. Thus, adding the term $R\ln 2$ (= 5.8 J K⁻¹ mol⁻¹) to the computational molar entropy of the gauche form, statistically favored by a factor of 2 over the *s-cis* form, the equilibrium constant $K\{\text{[gauche]}/\text{[s-cis]}\}$ is calculated to be *ca.* 2.2 at 298.15 K, and thus the conformational mixture of

allyl phenyl ether **1a** is estimated to consist of *ca.* 70% of the nonplanar gauche form.

In addition to these two energy minima, another stationary point, corresponding to a planar *s-trans* heavy atom structure [$\tau(\text{O}=\text{C}=\text{C})=180^\circ$] on the PES of allyl phenyl ether was found. However, a thermochemistry analysis of this structure revealed it not to be a stable conformer but a transition state (one imaginary frequency was found). This unstable *s-trans* structure was calculated to have an enthalpy about 3.2 kJ mol⁻¹ higher than that of the *s-cis* conformer at 298 K. (At 0 K, the corresponding energy difference, including the difference in zero-point energies, was calculated to be 4.8 kJ mol⁻¹).

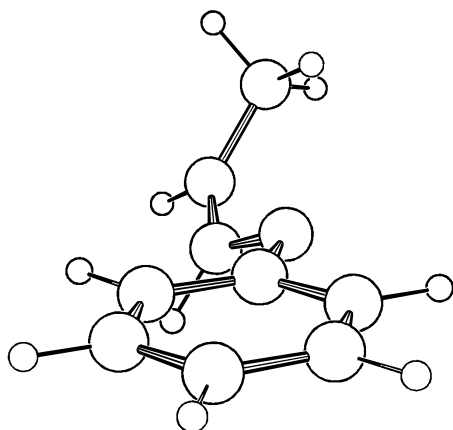


Fig. 3 ORTEP-3 view of one of the four energetically equivalent conformers of (Z)-prop-1-enyl phenyl ether according to the B3LYP/6-31G* calculations.

For **1b**, only a single stable conformer (in four energetically equivalent forms, however) was found (Fig. 3). The nonplanar nature of this gauche conformer is illustrated by the values, -27° and 150° , of the torsion angles $\tau(\text{C}_{\text{ar}}=\text{C}_{\text{ar}}-\text{O}-\text{C})$ and $\tau(\text{C}=\text{C}-\text{O}-\text{C}_{\text{ar}})$, respectively. In this conformer, neither the $\text{C}=\text{C}$ bond nor the phenyl group is perfectly aligned for unhindered conjugation with lone-pair electrons of the O atom.

A general survey of the thermodynamic data of isomerization

For clarity of presentation, the thermodynamic data of Table 2 are divided into internally related groups of reactions, allowing substituent effects on the thermodynamic parameters of isomerization to be seen in an easy-to-follow manner, at the expense of some repetition of the data in successive sections of the table. The main division is between reactions involving compounds with one, two, or no *ortho*-substituents.

The thermodynamic parameters $\Delta G^\circ_{\text{m}}$ and $\Delta H^\circ_{\text{m}}$ display the high stability of the **b** isomers relative to that of their allylic counterparts **a**, in line with our previous findings on the high thermodynamic stabilities of alkyl (Z)-prop-1-enyl and vinyl (Z)-prop-1-enyl ethers relative to those of their allylic isomers.^{2,4} The value of $\Delta G^\circ_{\text{m}}$ for **1a**→**b**, $-17.0 \text{ kJ mol}^{-1}$ at 298.15 K, is 0.9 kJ mol^{-1} more negative than that for allyl vinyl ether→(Z)-prop-1-enyl vinyl ether,⁴ but 2.9 kJ mol^{-1} less negative than that for methyl allyl ether→methyl (Z)-prop-1-enyl ether.² In each of the three reactions quoted, the entropy contribution is negligible. For the reactions shown in Table 2, the values of $\Delta H^\circ_{\text{m}}$ are seen to depend considerably on the position, number, and nature of substituents, varying from -11.0 to $-22.7 \text{ kJ mol}^{-1}$ for the 2,3-di-F (**55**) and 2-Bu'-6-Me (**67**) derivatives, respectively. The entropy contribution, although negligible in most reactions, can occasionally achieve positive values clearly different from zero but always smaller than $+10 \text{ J K}^{-1} \text{ mol}^{-1}$.

Compounds without *ortho*-substituents (1–36)

The first twenty entries of Table 2 for reactions between symmetrically substituted derivatives of the parent compounds **1a** and **1b** show values of $\Delta G^\circ_{\text{m}}$ ranging from -14.0 to $-17.6 \text{ kJ mol}^{-1}$ for the 3,5-di-Cl (**18**) and 4-MeO (**7**) derivatives, respectively. A decreasing relative stability of the allylic ethers **a** with increasing electron donating power of the ring substituents is revealed by the data. Electron-donating substituents tend to decrease the strength of $\text{p}-\pi$ interaction between the O atom [on C(1)] and the aryl ring in both isomers, but the weakening of conjugation proves to be more severe in the allylic ethers. In view of the structural differences between the **a** and **b** isomers, this is not unexpected. First, $\text{p}-\pi$ conjugation is likely to be stronger in the ArO system of the **a** isomers, owing to the

closely planar structure of the $\text{C}_{\text{ar}}=\text{C}_{\text{ar}}-\text{O}-\text{C}$ moiety. Thus, the electronic character of ring substituents will have a more significant effect on the strength of $\text{p}-\pi$ conjugation in the allylic ethers. Second, the O atom of the **b** isomers has a possibility to conjugate with *two* unsaturated moieties: thus, a reduced strength of conjugation in the ArO moiety may, at least in part, be compensated for by enhanced conjugation in the $-\text{O}-\text{CH}=\text{CHMe}$ moiety. The reality of this phenomenon has been documented previously by multinuclear NMR spectroscopic studies of divinyl ethers,⁵ structurally related to the **b** isomers.

Among the 4-halo-substituted ethers, the Cl (**11**), Br (**12**), and I (**13**) derivatives have remarkably similar values of the thermodynamic parameters of isomerization, whereas the values of $\Delta G^\circ_{\text{m}}$ and $\Delta H^\circ_{\text{m}}$ for the 4-F derivatives (**10**) are clearly more negative, reflecting the higher electron-donating conjugative power of the F atom.

The **a**→**b** reaction of the 3,4,5-tri-MeO derivatives (**20**), in comparison with that of the 3,5-di-MeO derivatives **17**, is interesting. The additional 4-MeO group in **20** leads to a significant decrease of *ca.* 3.6 kJ mol^{-1} in the exothermic character of the reaction and to an increase of *ca.* 0.6 kJ mol^{-1} in the value of $\Delta G^\circ_{\text{m}}$. For comparison, introduction of a 4-MeO substituent to **1** leads to small *negative* changes of -0.5 to -0.6 kJ mol^{-1} in the values of both $\Delta G^\circ_{\text{m}}$ and $\Delta H^\circ_{\text{m}}$. The markedly different effects of the 4-MeO substituent in the 3,4,5-tri-MeO and 4-MeO derivatives are likely to arise from obvious differences in the stereochemical orientation of this group in these compounds. In the 4-MeO derivatives **7**, the MeO group is coplanar with the plane of the aromatic ring, contrary to the situation in **20** where the 4-MeO group is forced to a nonplanar conformation about the $\text{C}_{\text{ar}}-\text{O}$ bond.⁶ As the 4-MeO group in **20** is thus effectively isolated from conjugative interaction with the aromatic ring, the electron-attracting *inductive* character of the MeO group leads to an enhanced $\text{p}-\pi$ conjugation in the ArO moiety, thus promoting the relative stability of the allylic ether.

In this group of reactions the entropy contributions are usually negligible: thus the positive reaction entropies of *ca.* 6 to $7 \text{ J K}^{-1} \text{ mol}^{-1}$ for the 3,5-di-F (**19**) and 3,4,5-tri-MeO (**20**) derivatives are exceptional. They possibly arise from unexpected changes in the composition of the mixture of conformers present in each isomeric species, or from exceptional solvation effects by the DMSO molecules.

meta-Substituted compounds

The substitution of a single alkyl group at the *meta*-position of the parent compounds has only a marginal effect on the thermodynamics of the **a**→**b** reaction.

All the 3-halo-substituted compounds have remarkably similar values of the parameters of isomerization. It is noteworthy that the reaction entropies are clearly positive for the 3-halo and 3-MeO derivatives, contrary to the negligible reaction entropies for the 3-alkyl derivatives. An amazing pattern of substituent effects on reaction thermodynamics thus appears in the *meta*-halo and *m*-MeO compounds. Whereas the 3,5-di-MeO and 3,5-di-Cl substitutions in **17** and **18**, respectively, have no detectable effect on reaction entropy, the unexpected positive effect of 3,5-di-F substitution on reaction entropy is comparable to that of the 3-F mono-substitution. Moreover, a 3-Cl-5-MeO substitution (in **33**), unlike the symmetrical 3,5-di-Cl and 3,5-di-MeO substitutions, leads to a positive reaction entropy.

Further, it may be noted that while the reaction entropy for the 3-MeO derivatives **25** is positive by *ca.* $5 \text{ J K}^{-1} \text{ mol}^{-1}$, introduction of an additional MeO group to the 4-position (**31**) decreases the reaction entropy to essentially zero. The effect remains the same if the 3,4-di-MeO system is replaced by the fragment $-\text{O}-\text{CH}_2-\text{O}-$ of a 1,3-dioxole ring (**32**). For comparison, introduction of an additional F or Cl atom to the 4-carbon of the 3-F (**26**) or 3-Cl derivatives (**27**) has only a small effect on the positive reaction entropies.

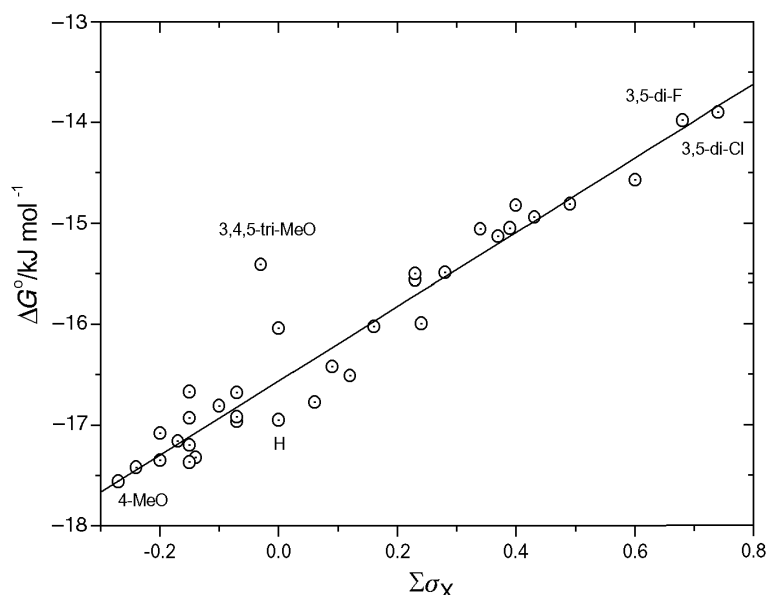


Fig. 4 The standard Gibbs energy of the **a**→**b** isomerization of the present non-*ortho*-substituted aromatic ethers in DMSO solution at 298.15 K as a function of the sum of the Hammett σ values¹⁷ for the substituents.

Gibbs energies of isomerization vs. Hammett σ values of substituents

The previous discussion has suggested that the Gibbs energy of isomerization of the non-*ortho*-substituted aromatic ethers is a function of the electronic nature of the substituents. To find out a possible quantitative relationship between these properties, the Gibbs energies of isomerization of the *meta*- and/or *para*-substituted derivatives of **1** were plotted against the sum of the Hammett σ values ($\Sigma\sigma_x$) for the substituents (see Fig. 4). Excluding the exceptional data point for the 3,4,5-tri-MeO derivatives, a least-squares treatment of the data gives a fairly good linear relationship, $\Delta G^\circ_{\text{m}}(298.15 \text{ K})/\text{kJ mol}^{-1} = -16.56 + 3.7\Sigma\sigma_x$, with a correlation coefficient of 0.977, for the **a**→**b** reaction. The significant deviation of the data point for the 3,4,5-tri-MeO derivatives from the correlation line probably arises from the nonplanar orientation of the 4-MeO group which is likely to have a σ value different from that of a conjugated, in-plane MeO group.

Mono-*ortho*-substituted compounds

***ortho*-Alkyl-substituted compounds.** A single *o*-Me substituent has only a negligible effect on the Gibbs energy of the **a**→**b** reaction; the reaction enthalpy, however, becomes *ca.* 1.8 kJ mol⁻¹ less negative and the reaction entropy 6 J K⁻¹ mol⁻¹ more positive. On successive replacements of the H atoms of the *o*-Me substituent by Me groups (Me→Et→Pr^{*i*}→Bu^{*i*}), the Gibbs energy of isomerization becomes more negative by *ca.* 0.5 kJ mol⁻¹ for each Me group introduced. In the same sequence, the exothermic character of the reaction increases but the reaction entropy decreases to effectively zero for the *o*-Pr^{*i*} and *o*-Bu^{*i*} derivatives.

In these 2-monoalkyl-substituted aromatic ethers the dominating effect of the *ortho*-substituent is steric in nature. Apparently, any alkyl group on C(2) is bulky enough to strongly disfavor a planar arrangement of the allyloxy moiety with the torsion angle $\tau[\text{C}_{\text{ar}}(2)=\text{C}_{\text{ar}}(1)-\text{O}-\text{C}] = 0^\circ$ (*cf.* 2-substituted anisoles⁷). Thus the number of conformers of the allyloxy moiety in these 2-alkyl-substituted allyl aryl ethers is likely to be only half of that in **1a**. However, because of the nonplanar nature of **1b**, an *o*-Me substituent is not bulky enough to cause a similar reduction in the number of the conformers of the (*Z*)-prop-1-enyloxy moiety: the DFT calculations show that the 2-Me substituent only leads to a marked widening to 84° of the torsion angle $\tau[\text{C}_{\text{ar}}(2)=\text{C}_{\text{ar}}(1)-\text{O}-\text{C}]$ from that, 27°, in **1b**.

With increasing bulkiness of the *ortho*-substituent, however, repulsive steric interactions between the substituent and the prop-1-enyl group lead to a similar reduction in the number of conformers present in the reaction product, thus restoring the entropy change to that found for **1a**→**1b**. The enhancing exothermic character of the **a**→**b** reaction in the same sequence suggests that the repulsions between the *ortho*-substituent and the RO moiety on C(1) become more severe in the allylic ethers.

Interestingly, a Ph group (in **42**) has an *ortho*-substituent effect comparable to that of a Me group. This shows that the plane of the 2-Ph substituent is markedly rotated out of the plane of the parent Ph group, thus avoiding strong steric interactions between the substituent and the RO side chain.

***ortho*-Alkoxy-substituted compounds.** The effects of an *o*-MeO substituent (in **43**) on the thermodynamic parameters of the **a**→**b** isomerization are almost identical to those of an *o*-Me group, despite the marked electronic interactions of the MeO group with the aromatic moiety. Further, while the exothermic character of the reaction increases and the entropy contribution decreases with increasing bulkiness of the alkoxy group (MeO→EtO→Pr^{*i*}O), there is hardly any change in the Gibbs energy of isomerization at 298.15 K in the same sequence. Thus, a compensation of the changes in reaction enthalpy by simultaneous changes in reaction entropy takes place in these reactions.

***ortho*-Halo-substituted compounds.** Among the three 2-halo-substituted derivatives **46–48**, the smallest (F) and largest (Br) halogen atoms have quite similar substituent effects on the thermodynamic parameters of isomerization, whereas the Gibbs energy and enthalpy of isomerization are slightly more negative for the 2-Cl derivatives. In view of the marked differences between the three halogen atoms in the factors (steric, inductive, and conjugative) contributing to the substituent effect, finding a tenable explanation for these facts is not easy.

Di- and trisubstituted derivatives with a single *ortho*-substituent

In many cases, introduction of additional *meta*- or *para*-substituents to mono-*ortho*-substituted derivatives of **1a** and **1b** shows the substituent effects on thermodynamic data of isomerization to be comparable to those observed for a similar substitution in the absence of the *ortho*-substituent. Thus, substitution of a Cl atom for the 4-H atom of the 2-Me derivatives, **37** increases the value of the $\Delta G^\circ_{\text{m}}$ by 1.1 kJ mol⁻¹, and that of

the parent compounds **1** by 1.4 kJ mol⁻¹. Placing two additional Me groups at the *meta*-positions of the 2-Me derivatives, **37** leads to a change of *ca.* -0.3 kJ mol⁻¹ in ΔG°_m (see **50a**→**50b**); this agrees with the corresponding changes in ΔG°_m on replacement of the *meta*-hydrogens of the parent compounds **1a** and **1b** by Me or Bu^t groups (*cf.* reactions **14a**→**14b** and **15a**→**15b** with **1a**→**1b**).

4-Me- and 4-Bu^t-substituents have only negligible effects on the thermodynamics of isomerization of the parent compounds **1**. However, for the *o*-Bu^t-substituted derivatives the 4-Me- and 4-Bu^t-substituents lead to a slight increase of *ca.* -0.5 kJ mol⁻¹ in the negative character of both the Gibbs energy and enthalpy of isomerization, without any detectable effect on the entropy of isomerization. A 2,3-fusion of a 6-membered saturated carbocyclic ring to the parent compounds, leading to **51**, gives rise to a value of ΔG°_m of isomerization comparable to that of the 2-Me derivatives **37**. On the other hand, the values of ΔH°_m and ΔS°_m for **51a**→**51b** are more similar to those of the 2-Et derivatives **38** suggesting, not unexpectedly, that the steric effects of the 2-Et group in **38** are comparable to those of the fused carbocyclic ring in the tetralin moieties of **51a** and **51b**.

Introduction of a second MeO substituent to the 3-position of the 2-MeO derivatives **43** decreases the reaction entropy from *ca.* 6.2 to 0.1 J K⁻¹ mol⁻¹ (reaction **54a**→**54b**). Simultaneously, a 1.7 kJ mol⁻¹ enhancement in the exothermic character of the reaction is observed so that the Gibbs energy of isomerization remains essentially unaffected. In both isomers of **54** the 2-MeO group is likely to have an almost orthogonal orientation with respect to the plane of the aromatic system (*cf.* the orientation of the 2-MeO group in 1,2,3-trimethoxybenzene⁶). It is surprising to find that the effect of the 3-MeO group in **54** is to decrease the reaction entropy by *ca.* 6 J K⁻¹ mol⁻¹, whereas the effect of the 4-MeO group in the 3,4,5-tri-MeO derivatives **20** is to *increase* the reaction entropy by approximately the same amount. (The structural feature common to **20** and **54** is the presence of a perpendicular MeO group between two other ethereal moieties.)

Expectedly, introduction of an additional F atom to the 4-position of the 2-F derivatives **46** has only a marginal effect on the thermodynamics of isomerization, see reaction **56a**→**56b**. However, the 2,3-di-F substitution in **55**, relative to the 2-F substitution in **46**, decreases the exothermic character of the reaction by *ca.* 1.6 kJ mol⁻¹, whereas the reaction entropy remains unchanged. The reaction enthalpy of -11.0 kJ mol⁻¹ for the 2,3-di-F derivatives is the least negative one among the reactions studied in this work. For these compounds, the reaction entropies are generally more positive than those for the other reactions studied. The relatively mild exothermic character of these reactions, together with the markedly positive reaction entropies, suggest that the allylic isomers of these fluorine-containing compounds are more strongly stabilized by solvation with the DMSO molecules than the other allyl aryl ethers.

If an additional halogen atom is introduced to the 2-Cl derivatives, the reaction entropy remains essentially unchanged whereas the reaction becomes 2–3 kJ mol⁻¹ less exothermic. In the 2,4-dichloro derivatives (**60**), the effect of +1.6 kJ mol⁻¹ of the 4-Cl substituent on the Gibbs energy of isomerization is comparable to that, +1.4 kJ mol⁻¹, of the Cl atom in the 4-Cl-substituted derivatives of the parent compounds **1a** and **1b**. However, the corresponding effect of +1.0 kJ mol⁻¹ of the 4-F atom in the 2-Cl-4-F derivatives (**62**) is unexpectedly large in comparison with the substituent effect of only +0.2 kJ mol⁻¹ of the 4-F atom in **10**.

Compounds with two *ortho*-substituents

Excluding the **a**→**b** reaction of the 2,6-difluoro derivatives **69**, the other reactions in this group of *ortho,ortho'*-disubstituted

Table 3 Comparison of the substituent effects (in kJ mol⁻¹) of the first (X) and second (Y) *ortho*-substituents on the enthalpy of isomerization of allyl aryl ethers to (Z)-prop-1-enyl aryl ethers in DMSO solution

First <i>ortho</i> -substituent		Second <i>ortho</i> -substituent		Difference
X	SE(X)	Y	SE(Y)	SE(Y) – SE(X)
Me	1.8	Me	-5.2	-7
Me	1.8	Bu ^t	-7.4	-9
Pr ⁱ	-0.7	Pr ⁱ	-2.3	-2
Bu ^t	-1.1	Me	-4.5	-3
MeO	2.1	MeO	-3.7	-6
F	4.5	F	-0.6	-5
Cl	3.8	Cl	-5.3	-9

compounds (**63**–**70**) are characterized by markedly negative reaction enthalpies. The most exothermic reaction, $\Delta H^\circ_m = -22.7$ kJ mol⁻¹, was found for the 2-Bu^t-6-Me derivatives **67**. Similarly, the other 2,6-dialkyl-substituted compounds, as well as the 2,6-di-MeO (**68**) and 2,6-di-Cl (**70**) derivatives, also have high negative reaction enthalpies of -19 to -21 kJ mol⁻¹. Thus the low reaction enthalpy, -13.2 ± 0.3 kJ mol⁻¹, for the 2,6-di-F derivatives is clearly exceptional in this group of reactions, being *ca.* 6 kJ mol⁻¹ less negative than that for the 2,6-di-Cl derivatives.

The relatively high exothermic character of these isomerization reactions shows, not unexpectedly, that *ortho*-substituent effects are not additive. Introduction of two *ortho*-substituents to **1a** and **1b** has a marked destabilizing effect on both isomers, but the destabilization is seen to be larger for the allyl aryl ethers. This is reasonable, because the loss of stabilization arising from a marked reduction of the strength of p- π conjugation in the ArO moiety of these non-planar compounds is greater in the allylic ethers. In the absence of two *ortho*-substituents the allylic ethers may assume planar (or nearly planar) structures of the C_{ar}=C_{ar}-O-C moiety, with no steric hindrance for efficient p- π conjugation. On the other hand, the loss of conjugative stabilization in the ArO moiety of the **b** isomers may be compensated for by an increased conjugative interaction of the O atom with the olefinic C=C bond.

The non-additivity of *ortho*-substituent effects on the thermodynamic data of isomerization is illustrated quantitatively in Table 3. The substituent effect on reaction enthalpy on introduction of the first *ortho*-substituent X to the parent compounds **1** is given by the term SE(X) in Table 3; this term is generally positive, excluding the cases X = Prⁱ and X = Bu^t for which it is slightly negative. On introduction of the second *ortho*-substituent Y, invariably negative substituent effects SE(Y) are found. The highest of these, -7.4 kJ mol⁻¹, applies to the case (Y = Bu^t, X = Me), the lowest (-0.6 kJ mol⁻¹) to Y = X = F. The values of SE(Y) for Y = Me are remarkably similar, *ca.* -5 kJ mol⁻¹, for both X = Me and X = Bu^t. On the other hand, although there is no significant difference in the values of the term SE(X) between X = F and X = Cl, the value of SE(Y) is *ca.* 5 kJ mol⁻¹ more negative for Y = X = Cl than for Y = X = F. This is likely to arise from the bulkiness of the Cl atom which forces the allyloxy group of the 2,6-di-Cl derivative **70a** to assume a more nonplanar conformation about the C_{ar}-O bond than that in the respective 2,6-di-F derivative **69a**.

The difference, SE(Y) – SE(X), between the substituent effects of the second and first *ortho*-substituents is shown in the last column of Table 3. Among the symmetrically 2,6-disubstituted compounds, the difference is largest (-9 kJ mol⁻¹) for X = Y = Cl and, surprisingly, smallest (-2 kJ mol⁻¹) for X = Y = Prⁱ. Intermediate values of -5 to -7 kJ mol⁻¹ of the difference SE(Y) – SE(X) are found for the F-, MeO- and Me-substituents.

The reaction entropies of these *ortho,ortho'*-substituted compounds fall in two groups, being either negligible or positive by 6 to 7 J K⁻¹ mol⁻¹. Giving a tenable explanation for this fact is not easy, but differences in the entropy of mixing of varying numbers of conformers present in each compound may be involved.

Stabilization of the olefinic C=C bond of the present ethers by methyl substitution

The value of ΔH_m° for **71a**→**71b** is -13.7 kJ mol⁻¹, to be compared with that, -17.1 kJ mol⁻¹, for **1a**→**1b**. Thus the Me group on C(2) of the olefinic side chain R of the ROAr moiety has a double-bond stabilizing effect *ca.* 3.4 kJ mol⁻¹ stronger in the reactant than in the reaction product. Similarly, the enthalpies of isomerization, -17.3 and -20.5 kJ mol⁻¹, of **72a** to **72b** and of **63a** to **63b**, respectively, show the double-bond stabilization energy of the Me group to be about 3.2 kJ mol⁻¹ stronger in the allylic ether **72a**.

Similarly, the stabilizing effect of the olefinic Me group in EtOCH₂C(Me)=CH₂ is known to be *ca.* 2.3 kJ mol⁻¹ stronger than that of the *E*-Me group in the isomeric form EtOCH=C(Me)₂.^{2,4} Moreover, a difference of 4.8 kJ mol⁻¹ has been found between the double bond stabilizing energies of the Me group in CH₂=CHOCH₂C(Me)=CH₂ and its isomer CH₂=CHOCH=C(Me)₂.⁴

On average, the double-bond stabilization energy of the Me group thus appears to be *ca.* 3.4 kJ mol⁻¹ stronger in the allylic ethers. The relatively weak double-bond stabilizing effect of methyl (and other alkyl) groups in the β -position of α,β -unsaturated ethers (like the present **b** compounds) has been documented previously in several thermodynamic studies.⁸ It is ascribable to the electron-repelling nature of the alkyl group which suppresses the strength of p- π conjugation in the vinyl-oxy group, a phenomenon clearly demonstrated by ¹⁷O NMR spectroscopy.⁹

According to Table 2, the effect of 2,6-di-Me substitution of **1a** and **1b** on the value of the ΔG_m° of the isomerization is -4.1 kJ mol⁻¹. For comparison, an almost equal effect of -3.6 kJ mol⁻¹ is found on replacement of the two *ortho*-hydrogens of **71a** and **71b** by Me groups. This suggests that the CH₂=C(Me)CH₂- group of **72a** adopts an orientation in which the Me group has no significant steric interaction with the *o*-Me groups, in line with the prevailing conformations of the parent compound **1a**.

Conclusion

In this work, thermodynamic data of isomerization of ring-substituted allyl aryl ethers **a** to (*Z*)-prop-1-enyl aryl ethers **b** in DMSO solution are given. In each case, the relative equilibrium concentration of the **a** form is negligible. The concentration of the allylic ether at equilibrium is increased by electron-withdrawing ring-substituents, but decreased by 2,6-disubstitution, particularly 2,6-dialkyl and 2,6-di-Cl substitution. The reaction entropy is usually negligible, sometimes slightly positive, but always smaller than +10 J K⁻¹ mol⁻¹. Thus, the **a**→**b** reaction is enthalpy driven, the values of ΔH_m° ranging from -11.0 kJ mol⁻¹ for the 2,3-di-F derivatives (**55**) to -22.7 kJ mol⁻¹ for the 2-Bu'-6-Me derivatives (**67**). In isomerization reactions between structurally related compounds, a compensation of varying reaction enthalpies by varying reaction entropies is often found, thus leading to remarkably similar Gibbs energies of isomerization. The origin of this phenomenon is not clear, but it may be caused by solvation effects or changes in the conformer compositions. Methyl substitution at the olefinic C=C bond has a stronger stabilizing effect of *ca.* 3.4 kJ mol⁻¹ on the allylic ethers, in line with previous findings on related nonaromatic ethers.

Experimental

Materials

The allyl aryl ethers, typically in a 0.1 mol scale of reagents, were prepared from commercially available phenols and allyl bromide (or allyl chloride with KI) in acetone solution in the presence of K₂CO₃.¹⁰ The allyl aryl ethers obtained were isomerized to (*Z*)-prop-1-enyl aryl ethers by Bu'OK in DMSO solution,¹ usually with some heating of the reaction mixture. The progress of isomerization was monitored by GLC. After disappearance of the reagent, the cooled reaction mixture was extracted with hexane, washed with water, and dried (MgSO₄). The final product was purified by fractional distillation; it usually consisted of *ca.* 90–95% of the *Z* isomer **b**, together with 5–10% of the *E* form, and trace amounts of the allyl aryl ether **a**.

Compounds **71a** and **72a** were similarly prepared from 2-methylallyl bromide and the respective phenols. The products were isomerized to the ethers **71b** and **72b** as described above for the allyl aryl ethers.

The compounds prepared, together with their boiling points, yields, and accurate molecular masses, are shown in Table 4. The ¹H NMR chemical shifts δ_H (JEOL GX 400 MHz, CDCl₃, TMS) are reported in Tables 5 and 6.

Chemical equilibration

The equilibration studies were conducted in DMSO solution (*ca.* 20 vol% of substrate) with Bu'OK (*ca.* 40–80 mg ml⁻¹) as catalyst.² To facilitate the achievement of thermodynamic equilibrium, the equilibrations were run on mixtures of isomers initially close to the final relative equilibrium concentrations. The process of isomerization was monitored by GLC on 50 m capillary columns of types Silar 9C and SE-30. A flame ionization detector (FID) was used on a Perkin-Elmer 8500 gas chromatograph equipped with a GP-100 graphic printer. The equilibration times varied from *ca.* 15 minutes at the highest temperatures to several months at the lowest temperatures. At suitable time intervals, an equilibrated sample (*ca.* 10 μ l in a glass ampoule) was rapidly cooled in an ice-water bath, and analyzed by GLC. The gas-chromatographic analysis was immediately performed on the cooled sample, without any pre-treatment of its contents. Our experience on this and related systems² has shown this to be the best experimental procedure: the compounds studied are sufficiently unreactive so that no significant change of the composition of the equilibrated sample occurs during the analysis provided that an accumulation of the catalyst in the injector is prevented by keeping the glass liner clean. For comparison, if the isomers were extracted from the reaction mixture by a solvent prior to gas-chromatographic analysis, this would introduce additional sources of error like that arising from possible differences in the distribution coefficients of the isomers between the two phases.

At each temperature, the reported value of the equilibrium constant is an average of typically 5 to 6 determinations; occasionally, more than 10 parallel determinations were performed. The standard errors (standard deviation divided by the square root of the number of parallel determinations) of the mean equilibrium constant were typically *ca.* 1% of the value of the equilibrium constant.

Computations

The DFT calculations^{11,12} of the geometry-optimized conformations of the parent compounds (**1**) were performed with the Gaussian 94W software¹³ at the B3LYP/6-31G* level of theory, using the Berny gradient optimization method.¹⁴ The thermochemistry analyses (1 bar, 298.15 K, scaling factor¹⁵ 0.9804) were carried at the same level of calculation.

Table 4 Boiling points, yields, and accurate molecular masses^a of the compounds studied in this work

No.	Substitution	Formula	<i>M</i> (calcd)	Bp (°C/Torr)	Yield (%)	<i>M</i> (obsd)	Bp (°C/Torr)	Yield (%)	<i>M</i> (obsd)
<i>Allyl aryl ethers</i>					<i>(Z)-Prop-1-enyl aryl ethers</i>				
1	H	C ₉ H ₁₀ O	134.0732	Commercial product		134.0751	78/16	62	134.0738
2	4-Me	C ₁₀ H ₁₂ O	148.0888	97–98/14	71	148.0873	95/15	55	148.0874
3	4-Et	C ₁₁ H ₁₄ O	162.1045	89–90/7	62	162.1001	86–87/6	53	162.1001 (new)
4	4-Pr ⁱ	C ₁₂ H ₁₆ O	176.1201	93–94/6	55	176.1193	93–94/7	59	176.1183 (new)
5	4-Bu ^s	C ₁₃ H ₁₈ O	190.1358	110–113/7	63	190.1342 (new)	110–112/10	58	190.1346 (new)
6	4-Bu ^t	C ₁₃ H ₁₈ O	190.1358	115–116/8	59	190.1356	112–113/8	75	190.1358 (new)
7	4-MeO	C ₁₀ H ₁₂ O ₂	164.0837	111–112/9	56	164.0814	108–109/10	45	164.0810
8	4-EtO	C ₁₁ H ₁₄ O ₂	178.0994	118–120/9	68	178.0966	107–108/7	25	178.0964 (new)
9	4-MeS	C ₁₀ H ₁₂ OS	180.0609	85–87/1	31	180.0585	72–74/1	24	180.0593 (new)
10	4-F	C ₉ H ₉ FO	152.0637	87–88/18	72	152.0673	78/15	74	152.0665 (new)
11	4-Cl	C ₉ H ₉ ClO	168.0342	97–98/10	68	168.0343	91–92/10	44	168.0341
12	4-Br	C ₉ H ₉ BrO	211.9837	109–111/9	97	211.9846	101–102/9	54	211.9820
13	4-I	C ₉ H ₉ IO	259.9698	125–127/7	66	259.9661	116–118/7	44	259.9661 (new)
14	3,5-di-Me	C ₁₁ H ₁₄ O	162.1045	99/9	46	162.1030	94–95/11	58	162.1029
15	3,5-di-Bu ^t	C ₁₇ H ₂₆ O	246.1984	130–132/7	65	246.1969	132–133/7	56	246.1988 (new)
16	4-Cl-3,5-di-Me	C ₁₁ H ₁₃ ClO	196.0655	79–80/1	48	196.0648	68–70/1	59	196.0664 (new)
17	3,5-di-MeO	C ₁₁ H ₁₄ O ₃	194.0943	161–165/15	50	194.0918	144–146/12	27	194.0918 (new)
18	3,5-di-Cl	C ₉ H ₈ Cl ₂ O	201.9952	129–130/15	78	201.9894	118–119/12	58	201.9938 (new)
19	3,5-di-F	C ₉ H ₈ F ₂ O	170.0543	68–69/12	32	170.0551 (new)	54–55/8	29	170.0558 (new)
20	3,4,5-tri-MeO	C ₁₂ H ₁₆ O ₄	224.1049	109–112/1	34	224.1037	121–123/2	48	224.1058 (new)
21	3-Me	C ₁₀ H ₁₂ O	148.0888	94–95/13	56	148.0874	90–92/14	62	148.0874
22	3-Et	C ₁₁ H ₁₄ O	162.1045	103–105/12	68	162.1025 (new)	98–99/12	66	162.1031 (new)
23	3-Pr ⁱ	C ₁₂ H ₁₆ O	176.1201	100/9	55	176.1208 (new)	96–98/10	48	176.1205 (new)
24	3-Bu ^t	C ₁₃ H ₁₈ O	190.1358	124–125/15	91	190.1343	115–118/12	67	190.1344 (new)
25	3-MeO	C ₁₀ H ₁₂ O ₂	164.0837	117–118/11	55	164.0822	106–107/9	41	164.0809
26	3-F	C ₉ H ₉ FO	152.0637	79/15	63	152.0614	78/20	21	152.0619 (new)
27	3-Cl	C ₉ H ₉ ClO	168.0342	99/11	67	168.0338	93–95/11	50	168.0344
28	3-Br	C ₉ H ₉ BrO	211.9837	117–118/12	85	211.9831	107–108/9	65	211.9831 (new)
29	4-Cl-3-Et	C ₁₁ H ₁₃ ClO	198.0625	115–117/7	72	196.0630 (new)	107–109/7	63	196.0651 (new)
30	3-(CH ₂) ₃ -4	C ₁₂ H ₁₄ O	174.1045	72–73/1	62	174.1032 (new)	69–70/1	39	174.1038 (new)
31	3,4-di-MeO	C ₁₁ H ₁₄ O ₃	194.0943	136–138/7	58	194.0931	128–130/7	45	194.0919 (new)
32	3-O-CH ₂ -O-4	C ₁₀ H ₁₀ O ₃	178.0630	102–103/2	62	178.0638	75–77/1	55	178.0643 (new)
33	3-Cl-5-MeO	C ₁₀ H ₁₁ ClO ₂	198.0448	143–145/15	74	198.0459 (new)	133–134/12	60	198.0436 (new)
34	3,4-di-F	C ₉ H ₈ F ₂ O	170.0543	78–79/13	52	170.0547 (new)	61–62/11	47	170.0545 (new)
35	3,4-di-Cl	C ₉ H ₈ Cl ₂ O	201.9952	123–124/10	76	201.9924 (new)	107–108/7	59	201.9914 (new)
36	3-Cl-4-F	C ₉ H ₈ ClFO	186.0248	92–93/9	77	186.0221 (new)	84–86/7	45	186.0224 (new)
37	2-Me	C ₁₀ H ₁₂ O	148.0888	92/11	76	148.0871	92–93/20	74	148.0872
38	2-Et	C ₁₁ H ₁₄ O	162.1045	90/8	66	162.1018	82/7	58	162.1020 (new)
39	2-Pr ⁱ	C ₁₂ H ₁₆ O	176.1201	93–95/8	66	176.1196	90–92/10	48	176.1193 (new)
40	2-Bu ^t	C ₁₃ H ₁₈ O	190.1358	100–101/7	73	190.1339	96–97/7	47	190.1327 (new)
41	2-Bu ^t	C ₁₃ H ₁₈ O	190.1358	108–109/9	43	190.1341	100/9	59	190.1339 (new)
42	2-Ph	C ₁₅ H ₁₄ O	210.1045	148–150/7	75	210.1028 (new)	144–147/7	57	210.1033 (new)
43	2-MeO	C ₁₀ H ₁₂ O ₂	164.0837	109/10	70	164.0829	110–111/13	35	164.0819 (new)
44	2-EtO	C ₁₁ H ₁₄ O ₂	178.0994	105–108/8	84	178.0994	102–103/8	42	178.0965 (new)
45	2-Pr ⁱ O	C ₁₂ H ₁₆ O ₂	192.1150	106–107/9	79	192.1133 (new)	103/9	73	192.1141 (new)
46	2-F	C ₉ H ₉ FO	152.0637	74–75/9	63	152.0620	66–67/10	50	152.0626 (new)
47	2-Cl	C ₉ H ₉ ClO	168.0342	100–101/10	63	168.0344	102–103/15	30	168.0347
48	2-Br	C ₉ H ₉ BrO	211.9837	124/15	68	211.9827	110–111/12	56	211.9840 (new)
49	4-Cl-2-Me	C ₁₀ H ₁₁ ClO	182.0498	105–107/7	64	182.0479	101–102/8	55	182.0500 (new)
50	2,3,5-tri-Me	C ₁₂ H ₁₆ O	176.1201	128–129/20	25	176.1183	120–121/18	50	176.1186 (new)
51	2-(CH ₂) ₄ -3	C ₁₃ H ₁₆ O	188.1201	142–143/12	47	188.1206	78–79/0.5	62	188.1210 (new)
52	2-Bu ^t -4-Me	C ₁₄ H ₂₀ O	204.1514	80–81/1	27	204.1507	118–119/14	60	204.1516 (new)
53	2,4-di-Bu ^t	C ₁₇ H ₂₆ O	246.1984	94–96/1	15	246.1976	99–101/2	50	246.1981 (new)
54	2,3-di-MeO	C ₁₁ H ₁₄ O ₃	194.0943	128–130/8	63	194.0928	122–125/7	49	194.0930 (new)
55	2,3-di-F	C ₉ H ₈ F ₂ O	170.0543	90–91/18	77	170.0535 (new)	80/18	55	170.0527 (new)
56	2,4-di-F	C ₉ H ₈ F ₂ O	170.0543	64–65/8	73	170.0543 (new)	56–57/7	70	170.0536 (new)
57	2-Cl-5-Me	C ₁₀ H ₁₁ ClO	182.0498	105–107/7	77	182.0499 (new)	102–104/7	56	184.0471 (new)
58	2-Cl-4,5-di-Me	C ₁₁ H ₁₃ ClO	196.0655	126–128/7	64	196.0656 (new)	122–124/7	61	196.0656 (new)
59	2,3-di-Cl	C ₉ H ₈ Cl ₂ O	201.9952	128–129/10	60	201.9900	117–119/9	69	201.9901 (new)
60	2,4-di-Cl	C ₉ H ₈ Cl ₂ O	201.9952	116–118/8	64	201.9903	115–116/10	44	201.9896 (new)
61	2,5-di-Cl	C ₉ H ₈ Cl ₂ O	201.9952	121–123/12	75	201.9936 (new)	106–108/8	57	201.9911 (new)
62	2-Cl-4-F	C ₉ H ₈ ClFO	186.0248	93–94/11	66	186.0257 (new)	84–85/8	68	186.0245 (new)
63	2,6-di-Me	C ₁₁ H ₁₄ O	162.1045	100–101/14	62	162.1030	96–97/18	75	162.1027
64	2,4,6-tri-Me	C ₁₂ H ₁₆ O	176.1201	64–65/1	52	176.1191	104–106/15	37	176.1212 (new)
65	4-Br-2,6-di-Me	C ₁₁ H ₁₃ BrO	240.0150	82–83/1	75	240.0116	72–73/1	40	242.1015 (new)
66	2,6-di-Pr ⁱ	C ₁₅ H ₂₂ O	218.1671	126–127/16	38	218.1673	117–118/12	69	218.1668 (new)
67	2-Bu ^t -6-Me	C ₁₄ H ₂₀ O	204.1514	76–78/1	47	204.1500	120/15	47	204.1512 (new)
68	2,6-di-MeO	C ₁₁ H ₁₄ O ₃	194.0943	140–141/15	47	194.0920	136–138/12	40	194.0938 (new)
69	2,6-di-F	C ₉ H ₈ F ₂ O	170.0543	55/7	76	170.0528 (new)	68–69/14	18	170.0528 (new)
70	2,6-di-Cl	C ₉ H ₈ Cl ₂ O	201.9952	123–124/18	79	201.9944	122–123/18	35	201.9935 (new)
<i>2-Methylallyl aryl ethers</i>					<i>2-Methylprop-1-enyl aryl ethers</i>				
71	H	C ₁₀ H ₁₂ O	148.0888	85–86/10	61	148.0878	81–82/11	56	148.0880
72	2,6-di-Me	C ₁₂ H ₁₆ O	176.1201	103–105/11	50	176.1196	99/12	61	176.1195 (new)

^a For halogen-containing compounds, accurate molecular masses of the ³⁵Cl and ⁷⁹Br isotopic species.

Table 5 ¹H NMR chemical shifts of allyl aryl ethers (**1a–70a**) and 2-methylallyl aryl ethers (**71a** and **72a**)^a

No.	Substitution	H-2	H-3	H-4	H-5	H-6	H-α ^b	H-β ^b	H-γ (E) ^b	H-γ (Z) ^b	Substituents
1a	H	6.91	7.27	6.94	7.27	6.91	4.52	6.05	5.28	5.41	
2a	4-Me	6.81	7.10		7.10	6.81	4.49	6.05	5.27	5.39	2.28
3a	4-Et	6.84	7.10		7.10	6.84	4.51	6.05	5.27	5.40	2.59 (2 H), 1.21 (3 H)
4a	4-Pr ⁱ	6.84	7.12		7.12	6.84	4.50	6.04	5.26	5.39	2.85 (1 H), 1.22 (6 H)
5a	4-Bu ^s	6.84	7.07		7.07	6.84	4.48	6.04	5.25	5.39	2.52 (1 H), 1.55 (2 H), 1.20 (3 H), 0.80 (3 H)
6a	4-Bu ^t	6.85	7.29		7.29	6.85	4.51	6.05	5.26	5.41	1.29
7a	4-MeO	6.83	6.84		6.84	6.83	4.48	6.04	5.26	5.39	3.75
8a	4-EtO	6.82	6.84		6.84	6.82	4.48	6.05	5.27	5.40	3.98 (2 H), 1.39 (3 H)
9a	4-MeS	6.83	7.21		7.21	6.83	4.45	5.99	5.25	5.37	2.39
10a	4-F	6.96	6.84		6.84	6.96	4.49	6.03	5.28	5.40	
11a	4-Cl	6.79	7.18		7.18	6.79	4.43	5.99	5.25	5.37	
12a	4-Br	6.76	7.33		7.33	6.76	4.45	6.00	5.27	5.38	
13a	4-I	6.65	7.50		7.50	6.65	4.44	5.99	5.27	5.37	
14a	3,5-di-Me	6.55		6.59		6.55	4.49	6.04	5.26	5.39	2.28
15a	3,5-di-Bu ^t	6.78		7.02		6.78	4.54	6.08	5.29	5.43	1.30
16a	4-Cl-3,5-di-Me	6.62				6.62	4.43	6.00	5.25	5.37	2.31
17a	3,5-di-MeO	6.08		6.08		6.08	4.44	6.01	5.24	5.37	3.70
18a	3,5-di-Cl	6.78		6.92		6.78	4.46	5.98	5.29	5.38	
19a	3,5-di-F	6.42		6.39		6.42	4.46	6.00	5.30	5.39	
20a	3,4,5-tri-MeO	6.18				6.18	4.51	6.07	5.31	5.43	3.84 (6 H), 3.79 (3 H)
21a	3-Me	6.74		6.74	7.15	6.74	4.51	6.05	5.27	5.40	2.32
22a	3-Et	6.76		6.76	7.14	6.70	4.45	6.02	5.22	5.37	2.58 (2 H), 1.20 (3 H)
23a	3-Pr	6.80		6.80	7.18	6.72	4.50	6.04	5.26	5.40	2.85 (1 H), 1.23 (6 H)
24a	3-Bu ^t	6.97		6.97	7.19	6.70	4.50	6.03	5.25	5.39	1.29
25a	3-MeO	6.50		6.50	7.17	6.50	4.51	6.05	5.28	5.41	3.77
26a	3-F	6.60		6.60	7.17	6.60	4.46	6.00	5.26	5.38	
27a	3-Cl	6.91		6.91	7.18	6.79	4.51	6.02	5.29	5.40	
28a	3-Br	7.05		7.04	7.08	6.80	4.44	5.98	5.26	5.37	
29a	4-Cl-3-Et	6.79			7.20	6.66	4.48	6.02	5.27	5.39	2.69 (2 H), 1.21 (3 H)
30a	3-(CH ₂) ₃ -4	6.79			7.07	6.69	4.47	6.04	5.23	5.38	2.8 (4 H), 2.07 (2 H)
31a	3,4-di-MeO	6.36			6.72	6.52	4.43	6.01	5.24	5.38	3.79, 3.77
32a	3-O-CH ₂ -O-4	6.49			6.30	6.66	4.41	6.00	5.24	5.36	5.85
33a	3-Cl-5-MeO	6.51		6.51		6.35	4.47	6.01	5.28	5.39	3.74
34a	3,4-di-F	6.59			7.03	6.71	4.46	6.00	5.29	5.39	
35a	3,4-di-Cl	6.99			7.30	6.76	4.49	6.01	5.31	5.40	
36a	3-Cl-4-F	6.93			7.03	6.75	4.48	6.01	5.30	5.40	
37a	2-Me		7.14	6.85	7.13	6.80	4.53	6.06	5.26	5.43	2.25
38a	2-Et		7.14	6.89	7.13	6.81	4.53	6.06	5.26	5.43	2.68 (2 H), 1.21 (3 H)
39a	2-Pr ⁱ		7.21	6.92	7.13	6.82	4.54	6.07	5.26	5.43	3.38 (1 H), 1.23 (6 H)
40a	2-Bu ^s		7.17	6.93	7.13	6.84	4.54	6.07	5.26	5.43	3.16 (1 H), 1.60 (2 H), 1.20 (3 H), 0.85 (3 H)
41a	2-Bu ^t		7.26	6.89	7.15	6.85	4.57	6.10	5.27	5.44	1.40
42a	2-Ph		7.1–7.6	6.99	7.1–7.6	6.91	4.47	5.93	5.15	5.28	6.9–7.6
43a	2-MeO		6.9	6.9	6.9	6.9	4.61	6.08	5.27	5.40	3.86
44a	2-EtO		6.83	6.83	6.83	6.83	4.51	6.03	5.20	5.37	4.00 (2 H), 1.38 (3 H)
45a	2-Pr ⁱ O		6.88	6.88	6.88	6.88	4.55	6.04	5.23	5.41	4.48 (1 H), 1.33 (6 H)
46a	2-F		7.03	6.96	7.06	6.88	4.60	6.06	5.29	5.42	
47a	2-Cl		7.36	6.88	7.18	6.90	4.60	6.06	5.30	5.46	
48a	2-Br		7.52	6.80	7.21	6.85	4.56	6.03	5.28	5.47	
49a	4-Cl-2-Me		7.09		7.06	6.69	4.49	6.04	5.27	5.41	2.21
50a	2,3,5-tri-Me			6.60		6.51	4.47	6.05	5.25	5.42	2.28 (3 H), 2.23 (3 H), 2.15 (3 H)
51a	2-(CH ₂) ₄ -3			6.67	7.01	6.59	4.48	6.03	5.22	5.41	2.71 (4 H), 1.75 (4 H)
52a	2-Bu ^t -4-Me		7.08		6.93	6.73	4.50	6.06	5.24	5.42	2.27 (3 H), 1.39 (9 H)
53a	2,4-di-Bu ^t		7.34		7.15	6.77	4.53	6.07	5.24	5.43	1.42 (9 H), 1.30 (9 H)
54a	2,3-di-MeO			6.57	6.95	6.57	4.59	6.06	5.26	5.41	3.85, 3.86
55a	2,3-di-F			6.75	6.94	6.72	4.58	6.03	5.30	5.42	
56a	2,4-di-F		6.71		6.9	6.8	4.55	6.02	5.28	5.41	
57a	2-Cl-5-Me		7.21	6.69		6.72	4.58	6.05	5.29	5.45	2.30
58a	2-Cl-4,5-di-Me		7.10			6.70	4.56	6.05	5.28	5.44	2.15 (3 H), 2.20 (3 H)
59a	2,3-di-Cl			7.04	7.10	6.80	4.59	6.04	5.31	5.46	
60a	2,4-di-Cl		7.34		7.14	6.81	4.57	6.02	5.30	5.44	
61a	2,5-di-Cl		7.24	6.84		6.85	4.55	6.03	5.31	5.46	
62a	2-Cl-4-F		7.11		6.88	6.83	4.54	6.03	5.29	5.42	
63a	2,6-di-Me		7.00	6.91	7.00		4.30	6.11	5.25	5.43	2.28
64a	2,4,6-tri-Me		6.80		6.80		4.26	6.08	5.23	5.41	2.23 (6 H), 2.22 (3 H)
65a	4-Br-2,6-di-Me		7.12		7.12		4.25	6.05	5.24	5.40	2.22
66a	2,6-di-Pr ⁱ		7.14	7.14	7.14		4.33	6.15	5.31	5.50	3.37 (2 H), 1.27 (12 H)
67a	2-Bu ^t -6-Me		7.02	6.92	7.16		4.34	6.07	5.25	5.48	2.28 (3 H), 1.38 (9 H)
68a	2,6-di-MeO		6.56	6.97	6.56		4.52	6.11	5.17	5.30	3.82
69a	2,6-di-F		6.87	6.94	6.87		4.63	6.05	5.24	5.36	
70a	2,6-di-Cl		7.28	6.98	7.28		4.57	6.15	5.28	5.43	
71a	H	6.96	7.30	6.97	7.30	6.96	4.43		5.02	5.15	1.86
72a	2,6-diMe		6.99	6.90	6.99		4.15		4.97	5.17	2.27 (6 H), 1.88 (3 H)

^a In ppm from internal TMS. ^b The designations α, β, and γ refer to the positions of the hydrogens in the allyl group.

Table 6 ¹H NMR chemical shifts of (*Z*)-prop-1-enyl aryl ethers (**1b–70b**) and 2-methyl-prop-1-enyl aryl ethers (**71b** and **72b**)^a

No.	Substitution	H-2	H-3	H-4	H-5	H-6	H-α	H-β	H-γ	Substituents
1b	H	6.99	7.30	7.02	7.30	6.99	6.37	4.88	1.72	
2b	4-Me	6.88	7.09		7.09	6.88	6.34	4.83	1.71	2.30
3b	4-Et	6.91	7.12		7.12	6.91	6.35	4.83	1.71	2.60 (2 H), 1.21 (3 H)
4b	4-Pr ⁱ	6.92	7.15		7.15	6.92	6.35	4.83	1.71	2.87 (1 H), 1.23 (6 H)
5b	4-Bu ⁱ	6.92	7.09		7.09	6.92	6.35	4.83	1.71	2.53 (1 H), 1.56 (2 H), 1.21, 0.80
6b	4-Bu ^t	6.92	7.32		7.32	6.92	6.36	4.84	1.71	1.30
7b	4-MeO	6.93	6.84		6.84	6.93	6.29	4.79	1.71	3.77
8b	4-EtO	6.92	6.83		6.83	6.92	6.30	4.79	1.71	3.99 (2 H), 1.40 (3 H)
9b	4-MeS	6.91	7.22		7.22	6.91	6.30	4.84	1.69	2.40
10b	4-F	6.9–7.0 ^b			6.9–7.0 ^c		6.30	4.86	1.71	
11b	4-Cl	6.87	7.20		7.20	6.87	6.33	4.94	1.70	
12b	4-Br	6.82	7.35		7.35	6.82	6.27	4.88	1.68	
13b	4-I	6.73	7.54		7.54	6.73	6.28	4.89	1.69	
14b	3,5-di-Me	6.62		6.67		6.62	6.35	4.83	1.70	2.29
15b	3,5-di-Bu ^t	6.87		7.13		6.87	6.41	4.85	1.75	1.33
16b	4-Cl-3,5-di-Me	6.69				6.69	6.28	4.84	1.69	2.31
17b	3,5-di-MeO	6.15		6.15		6.15	6.34	4.84	1.69	3.71
18b	3,5-di-Cl	6.87		7.00		6.87	6.28	4.98	1.68	
19b	3,5-di-F	6.51		6.47		6.51	6.29	4.99	1.69	
20b	3,4,5-tri-MeO	6.25				6.25	6.32	4.87	1.72	3.85 (2 MeO), 3.80
21b	3-Me	6.81		6.84	7.17	6.79	6.36	4.85	1.71	2.33
22b	3-Et	6.84		6.85	7.18	6.80	6.36	4.83	1.71	2.61 (2 H), 1.22 (3 H)
23b	3-Pr	6.85		6.85	7.20	6.79	6.36	4.84	1.71	2.87 (1 H), 1.22 (6 H)
24b	3-Bu ^t	7.03		7.05	7.21	6.79	6.37	4.83	1.72	1.30
25b	3-MeO	6.6		6.6	7.19	6.6	6.36	4.87	1.72	3.78
26b	3-F	6.7		6.7	7.20	6.7	6.32	4.91	1.70	
27b	3-Cl	6.99		7.00	7.21	6.88	6.33	4.94	1.70	
28b	3-Br	7.14		7.14	7.14	6.90	6.31	4.92	1.69	
29b	4-Cl-3-Et	6.86			7.22	6.75	6.31	4.87	1.70	2.70 (2 H), 1.21 (3 H)
30b	3-(CH ₂) ₃ -4	6.85			7.10	6.75	6.32	4.80	1.70	2.83 (4 H), 2.05 (2 H)
31b	3,4-di-MeO	6.60			6.76	6.49	6.31	4.80	1.72	3.84, 3.82
32b	3-O-CH ₂ -O-4	6.56			6.41	6.70	6.25	4.80	1.69	5.91
33b	3-Cl-5-MeO	6.59		6.59		6.44	6.31	4.93	1.70	3.77
34b	3,4-di-F	6.81			7.06	6.69	6.26	4.93	1.69	
35b	3,4-di-Cl	7.08			7.33	6.84	6.28	4.97	1.68	
36b	3-Cl-4-F	7.03			7.05	6.85	6.27	4.93	1.70	
37b	2-Me		7.16	6.93	7.13	6.89	6.35	4.85	1.73	2.29
38b	2-Et		7.17	6.97	7.14	6.89	6.36	4.84	1.73	2.70 (2 H), 1.23 (3 H)
39b	2-Pr ⁱ		7.24	7.01	7.14	6.90	6.35	4.84	1.73	3.35 (1 H), 1.25 (6 H)
40b	2-Bu ⁱ		7.20	7.01	7.14	6.91	6.34	4.84	1.73	3.12 (1 H), 1.63 (2 H), 1.23, 0.85
41b	2-Bu ^t		7.31	6.98	7.16	6.91	6.32	4.84	1.75	1.41
42b	2-Ph			7.0–7.6 ^d			6.31	4.77	1.62	7.0–7.6
43b	2-MeO			6.9–7.0 ^d			6.28	4.89	1.74	3.88
44b	2-EtO		6.96	6.94	6.94	6.96	6.29	4.83	1.74	4.06 (2 H), 1.41 (3 H)
45b	2-Pr ⁱ O		6.9	6.9	6.9	6.9	6.31	4.83	1.73	4.47 (1 H), 1.34 (6 H)
46b	2-F			6.9–7.1 ^d			6.33	4.92	1.74	
47b	2-Cl		7.38	6.96	7.19	6.99	6.33	4.97	1.75	
48b	2-Br		7.54	6.89	7.23	6.96	6.33	4.97	1.75	
49b	4-Cl-2-Me		7.14		7.09	6.81	6.31	4.95	1.74	2.26
50b	2,3,5-tri-Me			6.63		6.56	6.26	4.75	1.70	2.21, 2.19, 2.12
51b	2-(CH ₂) ₄ -3			6.74	7.01	6.68	6.34	4.81	1.71	2.73 (4 H), 1.75 (4 H)
52b	2-Bu ^t -4-Me		7.10		6.95	6.80	6.27	4.80	1.74	2.29 (3 H), 1.39 (9 H)
53b	2,4-di-Bu ^t		7.35		7.17	6.84	6.31	4.80	1.74	1.42 (9 H), 1.31 (9 H)
54b	2,3-di-MeO			6.62	6.95	6.62	6.32	4.86	1.74	3.85, 3.88
55b	2,3-di-F			6.8	6.95	6.8	6.32	4.97	1.73	
56b	2,4-di-F		6.78		6.99	6.87	6.25	4.89	1.72	
57b	2-Cl-5-Me		7.24	6.78		6.81	6.31	4.95	1.74	2.29
58b	2-Cl-4,5-di-Me		7.13			6.79	6.28	4.90	1.74	2.20, 2.17
59b	2,3-di-Cl			7.10	7.10	6.88	6.32	5.03	1.74	
60b	2,4-di-Cl		7.37		7.15	6.91	6.28	5.00	1.73	
61b	2,5-di-Cl		7.27	6.93		6.97	6.30	5.05	1.73	
62b	2-Cl-4-F		7.10		6.90	6.90	6.24	4.93	1.73	
63b	2,6-di-Me		7.01	6.94	7.01		5.95	4.58	1.77	2.29
64b	2,4,6-tri-Me		6.79		6.79		5.91	4.53	1.76	2.18 (6 H), 2.22 (3 H)
65b	4-Br-2,6-di-Me		7.12		7.12		5.87	4.59	1.75	2.18
66b	2,6-di-Pr ⁱ		7.16	7.16	7.16		6.03	4.58	1.82	
67b	2-Bu ^t -6-Me		7.02	6.96	7.16		5.94	4.57	1.77	2.22 (3 H), 1.38 (9 H)
68b	2,6-di-MeO		6.56	6.98	6.56		6.11	4.57	1.79	3.79
69b	2,6-di-F		6.91	6.98	6.91		6.28	4.76	1.77	
70b	2,6-di-Cl		7.29	7.01	7.29		6.05	4.79	1.81	
71b	H	6.95	7.26	6.96	7.26	6.95	6.18		1.71	1.67 (3 H)
72b	2,6-di-Me		6.97	6.91	6.97		5.81		1.80	2.22 (6 H), 1.58 (3 H)

^a In ppm from internal TMS. The designations α, β, and γ refer to the positions of the hydrogens of the prop-1-enyl group. ^b H-2 and H-3. ^c H-5 and H-6. ^d H-3–H-6.

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