

Effect of a Substituent in the Benzene Ring upon the Kinetics of Acid-Catalyzed Hydrolysis of *exo*-2-Norbornyl Phenyl Ether

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The rate constants of hydrolysis for *exo*-2-norbornyl phenyl ether without substituent and with *p*-Me, *p*-Ac, *m*-CN, *p*-CN or *p*-NO₂ group in the benzene ring were measured in concentrated perchloric acid solutions spectrophotometrically and/or by capillary GC. The effect of the substituent on the rate constants and other kinetic parameters of hydrolysis is small. The parameters are in agreement with the *A*-1 mechanism. The ether oxygen of the *exo*-epimer is much more basic than that of the *endo*-epimer ($\text{p}K_{\text{a},\text{exo}} - \text{p}K_{\text{a},\text{endo}} \approx 2$), which causes a greater part of the *exo/endo* rate ratio than do the initial state energies and rate constants of the rate limiting stage, i.e. of the formation of the norbornyl cation and the substituted phenol.

Bicyclo[2.2.1]heptyl aryl ethers are both of practical interest, because of their fungicidal, insecticidal and acaricidal activity and also their possible effect on the growth of plants,^{1,2} and of theoretical interest because their hydrolysis produces a norbornyl cation.³ Recently, the acid-catalyzed hydrolysis of *exo*- and *endo*-2-bicyclo[2.2.1]heptyl (or 2-norbornyl) phenyl ethers in perchloric acid was studied, and the *exo/endo* rate ratio was observed to be very high (2570).³ This fact, together with the positive entropies of activation (14–17 J K⁻¹ mol⁻¹), the solvent deuterium isotope effect ($k_{\text{H}}/k_{\text{D}} \approx 0.47$) and the products of hydrolysis, showed that the bond between the carbon atom of the norbornane moiety and the ether oxygen is broken in the unimolecular rate-limiting stage of the reaction producing a norbornyl cation and phenol [the final products were *exo*- and *endo*-2-norborneols, phenol and *o*- and *p*-(*exo*-2-norbornyl)phenols].³ This *A*-1 mechanism was also supported by the marked effect of the alkyl (cycloalkyl or bicycloalkyl) group upon the rate of hydrolysis of secondary or tertiary alkyl phenyl ethers ($\rho^* \approx -4$).^{4,5}

This work extends the investigation of the acid-catalyzed hydrolysis of 2-norbornyl phenyl ethers to the effect of a substituent in the benzene ring of the *exo*-isomer. The preliminary results have recently been reported.⁴ The object of interest is not only the effect on the rate of hydrolysis, but also on the kinetic parameters, especially those of excess acidity plots.⁶

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Results and discussion

The rate constants of hydrolysis measured spectrophotometrically, or by capillary GC, for six *exo*-2-norbornyl phenyl ethers in aqueous perchloric acid solutions at different temperatures and acid concentrations are listed in Table 1. The activation parameters, solvent deuterium isotope effects and parameters for excess acidity plots^{6,7} are collected in Table 2.

The activation entropies are positive or slightly negative and thus in agreement with the unimolecular mechanism of hydrolysis (*A*-1). The solvent deuterium isotope effects are rather similar to the values measured for isopropyl, cyclopentyl and cyclohexyl phenyl ethers.⁴ The $k_{\text{H}}/k_{\text{D}}$ values are close to 0.5, except that (0.60) for the acetyl-substituted ether, which is slightly higher, this being possibly due to a deuteration of the methyl group of the acetyl substituent in DClO₄(D₂O).⁸ The isotope effects are between the values typical of the *A*-1 (≤ 0.5) and *A*-2 (≥ 0.5) hydrolysis mechanisms, but values such as these are rather common in the case of the acid-catalyzed ether hydrolysis.^{9–11}

The effect of a substituent in the benzene ring upon the rate of hydrolysis of *exo*-2-norbornyl phenyl ethers is slight (e.g. $k_{\text{p-Me}}/k_{\text{p-NO}_2} = 6.0$ in 6 M HClO₄ at 298 K; Table 2). The rate constants fairly follow the Hammett equation [eqn. (1)]

$$\log(k_{\text{X}}/k_{\text{H}}) = \rho\sigma \quad (1)$$

when employing the Hammett substituent constants σ

Table 1. Disappearance rate constants of *exo*-2-norbornyl phenyl ethers with substituent X in the benzene ring in aqueous perchloric acid solutions at different temperatures and acid concentrations.

X	T/K	$c(\text{HClO}_4)^a / \text{mol dm}^{-3}$	X_0^b	Method ^c	$k_\psi / 10^{-4} \text{ s}^{-1}$	
<i>p</i> -Me	288.2	6.01		GC	1.44(5)	
	293.2	6.01		GC	3.1(3)	
	298.2	6.00		GC	6.2(8)	
	303.2	5.98		GC	12.5(5)	
	308.2	5.98		GC	22.8(1)	
H	308.2	3.01	0.74	GC	0.127(2)	
	308.2	3.47	0.88	GC	0.268(5)	
	308.2	3.96	1.04	GC	0.576(8)	
	308.2	4.01	1.06	SP	0.565(2) ^d	
	308.2	4.50	1.24	SP	1.259(5) ^d	
	308.2	4.99	1.46	SP	2.92(13) ^d	
	308.2	4.99	1.46	GC	2.94(16)	
	308.2	5.93	1.92	SP	16.9(5) ^d	
	308.2	5.99	1.95	GC	18.9(3)	
	308.2	6.52	2.25	SP	46.5(21) ^d	
	308.2	7.02	2.56	SP	119(7) ^d	
	<i>p</i> -Ac	298.2	6.00		SP	1.49(2)
		298.2	6.02		SP	2.48(2) ^e
303.2		5.99		SP	2.92(2)	
308.2		5.97		SP	5.6(3)	
313.2		5.97		SP	10.3(2)	
318.2		5.95		SP	19.2(3)	
303.2		4.51	1.27	SP	0.174(19)	
303.2		5.01	1.50	SP	0.50(5)	
303.2		5.99	1.98	SP	2.92(2)	
303.2		6.53	2.30	SP	7.26(17)	
303.2		7.03	2.60	SP	17.7(2)	
303.2		7.59	2.98	SP	47(3)	
303.2		8.15	3.39	SP	103(6)	
<i>m</i> -CN		298.2	5.95		SP	1.64(8)
		298.2	5.91		SP	3.17(4) ^e
	303.2	5.94		SP	3.28(5)	
	308.2	5.93		SP	6.54(10)	
	314.7	5.92		SP	15.5(2)	
	318.2	5.90		SP	23.5(2)	
<i>p</i> -CN	298.2	5.89		SP	1.03(2)	
	308.2	5.87		SP	3.42(4)	
	318.2	5.85		SP	12.4(5)	
	328.2	5.81		SP	39.9(11)	
	<i>p</i> -NO ₂	288.2	6.03		GC	0.262(21)
298.2		6.03		GC	1.10(4)	
298.2		6.03		SP	1.07(4)	
308.2		5.93		GC	3.35(5)	
308.2		5.93		SP	3.40(3)	
318.2		5.99		GC	12.2(3)	
308.2		4.46	1.25	GC	0.182(3)	
308.2		4.96	1.45	GC	0.433(5)	
308.2		4.98	1.46	SP	0.505(17)	
308.2		5.01	1.47	SP	0.56(1)	
308.2		5.51	1.72	GC	1.51(3)	
308.2		5.93	1.92	SP	3.40(3)	
308.2		5.99	1.96	GC	3.35(5)	
308.2		6.45	2.23	GC	8.2(2)	
308.2		6.52	2.26	SP	9.8(8)	
308.2		6.81	2.44	GC	15.2(3)	
308.2		7.02	2.56	SP	20.0(11)	
308.2		7.33	2.78	GC	42.7(14)	
308.2	7.58	2.93	SP	47.8(9)		

^aTemperature corrected. ^bExcess acidity,⁷ temperature corrected. ^cGC, gas chromatographic; SP, spectrophotometric. ^dRef. 3. ^eMeasured in $\text{DClO}_4(\text{D}_2\text{O})$.

($\rho = -0.88 \pm 0.07$; $r = -0.990$) or the σ^+ substituent constants ($\rho^+ = -0.82 \pm 0.06$; $r = -0.989$).^{12a} The former reaction constant (ρ) is practically equal with that ($\rho_{\text{S} \rightarrow \text{SH}^+} = -0.9 \pm 0.1$) measured by Lambrechts and Cerfontain¹³ for the protonation of the ether oxygen of five *p*-substituted methyl phenyl ethers in aqueous sulfuric acid at 298 K. Thus the reaction constant of the rate-limiting stage of hydrolysis ($\rho_{\text{r.l.s.}} = \rho - \rho_{\text{S} \rightarrow \text{SH}^+}$) is close to zero, which means that the positive charge of the protonated substrate does not markedly transfer to the benzene ring during decomposition to the norbornyl cation and phenol (Scheme 1). This seems reasonable and rationalizes the small effect of a substituent in the benzene ring as compared to the large effect of a substituent ($\rho^* \approx -4$)⁴ in the alkyl moiety upon the hydrolysis rate.

The excess acidity method,⁶ which is an excellent tool to study the effect of acidity of a medium upon the rate and equilibrium of a reaction, can be applied to the hydrolysis of the substrates by employing eqn. (2),

$$\log k_\psi - \log c_{\text{H}^+} = m^\ddagger m^* X_0 - \log[1 + (c_{\text{H}^+}/K_{\text{SH}^+})10^{m^* X_0}] + \log(k_0/K_{\text{SH}^+}) \quad (2)$$

in which k_ψ is an observed rate constant in aqueous acid of concentration c_{H^+} and excess acidity X_0 ;^{7,12b} m^\ddagger and m^* are slope parameters and k_0 stands for the medium-independent rate constant of the rate-limiting stage (r.l.s.) and K_{SH^+} for the thermodynamic dissociation constant of the protonated substrate (Scheme 1).⁶ Equation (2) is a combination of the original eqns. (3) and (4),⁶

$$\log(c_{\text{SH}^+}/c_{\text{S}}) - \log c_{\text{H}^+} = m^* X_0 + pK_{\text{SH}^+} \quad (3)$$

$$\log k_\psi - \log c_{\text{H}^+} - \log[c_{\text{S}}/(c_{\text{S}} + c_{\text{SH}^+})] = m^\ddagger m^* X_0 + \log(k_0/K_{\text{SH}^+}) \quad (4)$$

which can be used separately for the evaluation of the pK_{SH^+} and m^* values [eqn. (3)] and of the m^\ddagger and k_0 [or $\log(k_0/K_{\text{SH}^+})$] values [eqn. (4)]. However, estimation of the same parameters via eqn. (2) is more convenient using the method of a nonlinear least-squares minimization provided that the experimental data are sufficiently accurate.^{5,14}

Sometimes the substituent itself can be protonated, thus markedly retarding the acid-catalyzed ether hydrolysis, because the ether oxygen must also be protonated. As a simplification one can assume that the substituent-protonated substrate does not react further in any way (Scheme 1). This approximation worked well in the case of the acid-catalyzed hydration of the double bond of 5-methyl-5-hydroxymethyl-2-norbornenes, when the partial protonation of the hydroxyl oxygen atom retarded the hydration.¹⁵ The protonation of the substituent can be taken into account by adding a second correction term, when the excess acidity equation obtains, for instance, a form of eqn. (5),

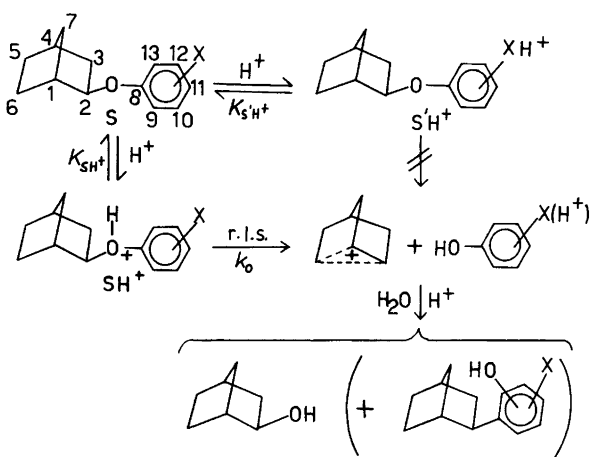
$$\log k_\psi - \log c_{\text{H}^+} - \log[c_{\text{S}}/(c_{\text{S}} + c_{\text{S}^+\text{H}^+})]$$

Table 2. Rate constants (in 6.0 M HClO₄), activation parameters and solvent deuterium isotope effects at 298.2 K and parameters of the excess acidity plot [eqn. (2)] for the acid-catalyzed hydrolysis of *exo*-2-norbornyl phenyl ethers with substituent X in the benzene ring in aqueous perchloric acid solutions.

X	k_{ψ}^a 10 ⁻⁴ s ⁻¹	ΔS^\ddagger / J K ⁻¹ mol ⁻¹	ΔH^\ddagger / kJ mol ⁻¹	k_H/k_D
H ^b	4.69(9)	14(4)	100.9(12)	0.47(2)
<i>p</i> -Me	6.15(16)	14(5)	99.8(13)	
<i>p</i> -Ac	1.49(1)	-3(1)	98.3(4)	0.60(1)
<i>m</i> -CN	1.65(2)	15(2)	103.4(6)	0.51(4)
<i>p</i> -CN	1.01(5)	-9(7)	98(2)	
<i>p</i> -NO ₂	1.02(7)	-20(8)	94(2)	

X	T/K	m^\ddagger	log(k_0/K_{SH^+})	m^*	pK _{SH⁺}
H ^c	308.2	1.43(2)	-6.42(2)	1.06(2)	-3.74(4)
H	308.2	1.55(5)	-6.51(3)	1.02(3)	-3.43(12)
<i>p</i> -Ac ^d	303.2	1.50(2)	-7.27(2)	1.00(1)	-3.92(4)
<i>p</i> -NO ₂	308.2	1.52(5)	-7.21(7)	1.01(3)	-3.56(10)

^aCalculated from the activation parameters. ^bRef. 3. ^cRef. 5. ^dThe following values were used to calculate [eqn. (3)] the first correction term in eqn. (5): pK_{SH⁺} = -3.76 and $m^\ddagger = 0.76$.¹⁶



Scheme 1.

$$= m^\ddagger m^* X_0 - \log[1 + (c_{H^+}/K_{SH^+})10^{m^\ddagger X_0}] + \log(k_0/K_{SH^+}) \quad (5)$$

where $c_{S'H^+}$ is the concentration of the substrate protonated on the substituent. The correction term can be calculated from eqn. (3) by making the following substitutions: $c_{S'H^+}/c_{SH^+}$, m^\ddagger/m^* and $pK_{S'H^+}/pK_{SH^+}$, if the thermodynamic dissociation constant of the substituent-protonated substrate, $K_{S'H^+}$, and the slope parameter m^\ddagger are known. If they are not known, it is, of course, possible to add an additional correction term, $-\log[1 + (c_{H^+}/K_{S'H^+})10^{m^\ddagger X_0}]$, on the right side of eqn. (2) and to attempt to evaluate six parameters with the aid of the nonlinear least-squares minimization, but experimental accuracy and the amount of experimental data must be higher in this case. Therefore it is more practical to use an equation such as eqn. (5).

A possible protonation of the substituents used can be estimated from the following literature pK_a (= $pK_{S'H^+}$) values: -3.76 for the carbonyl group of

p-methoxyacetophenone,¹⁶ -10.45 for benzonitrile¹⁷ and -11.3 for nitrobenzene.¹⁸ Thus the protonation of the acetyl group is probably the only one to be taken into account for the HClO₄ concentrations used (Table 1). A reversible protonation of the aromatic ring also takes place, though the portion of the protonated form is probably generally very small and may not cause further reactions,¹⁹ except perhaps in the case of the *p*-Me-substituted substrate,¹³ where the protonation of the tolyl ring might be the reason for the observed unusual kinetics at the beginning of the runs (see Experimental). The disappearance of the substrate via hydrolysis of the substituent is possible in the case of the cyano group, but the reaction is evidently extremely slow under the conditions used in this work.²⁰

The parameters of eqn. (2) are given in Table 2, and the strictly linear plots ($r=0.998$ - 0.9998) of eqn. (4), obtained by using the correction term (two in the case of the acetyl substituent) calculated from the parameters with eqn. (3), are presented in Fig. 1. The slope parameter m^\ddagger , which depends on the transition state, is close to 1.5 and does not markedly depend on the substituent in the benzene ring. It is close to the value (1.54-1.55)^{3,5} measured for the hydrolysis of *endo*-2-norbornyl phenyl ether at 308 K. [The older m^\ddagger values (1.37-1.43) evaluated for *exo*-2-norbornyl phenyl ether using six data points are probably less accurate.^{3,5} Their disagreement with the present value (1.55), calculated using eleven data points, shows an unfortunate sensitivity of m^\ddagger values due to experimental inaccuracy; the accordance between both the older and the present data points in Fig. 1 seems excellent.] The slope parameter m^* , which depends on the site of protonation, is close to 1.00, as was earlier observed for the protonation of the ether oxygen atom in aqueous perchloric acid.^{3-5,10,11,14}

The pK_{SH^+} values (Table 2) depend only slightly and randomly upon the substituent in the benzene ring, this

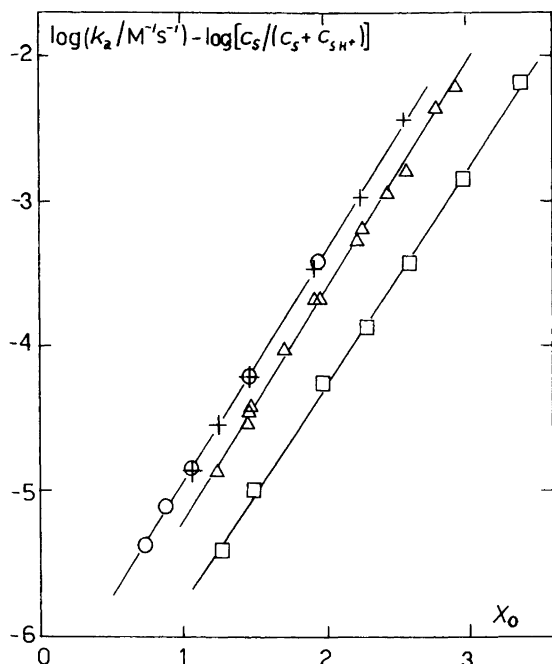


Fig. 1. The excess acidity plots for the hydrolysis of *exo*-2-norbornyl phenyl ethers with a substituent in the benzene ring in aqueous perchloric acid. Symbols in the case of the substituents: (+) H_3 ; (O) H (this work); (Δ) $p\text{-NO}_2$ (0.5 has been added to the $\log k_a$ values for clarity) and (\square) $p\text{-Ac}$.

result being different from that measured for five *p*-substituted methyl phenyl ethers¹³ (our values are probably less accurate; see above). The present pK_{SH^+} values are ca. two units less negative than those measured for *endo*-2-norbornyl phenyl ether { -5.56 at 288 K [eqn. (3)] and -5.73 at 308 K [eqn. (2)]}.^{3,5} Accordingly, the *exo* ether oxygen atom is much more basic than the *endo* one, as was recently preliminarily observed.⁵ (The pK_{SH^+} values for the *endo* epimers possibly need more comparative data, although they are close to the 'normal' values measured for isopropyl, cyclopentyl and cyclohexyl phenyl ethers.)^{4,5}

A Goering-Schewene diagram (Fig. 2) was constructed for the hydrolysis of *exo*- and *endo*-2-norbornyl phenyl ethers from the Gibbs energies obtained as follows: ΔG° for $\text{NBOPh} + \text{H}^+ \rightleftharpoons \text{NBO}(\text{H}^+)\text{Ph}$ (NB = 2-norbornyl) from the calculated [eqn. (3)] c_{SH^+}/c_S ratios in $7.0 \text{ mol dm}^{-3} \text{ HClO}_4$ at 308 K;⁵ ΔG^\ddagger for $\text{NBOPh} + \text{H}^+ \rightleftharpoons \text{transition state (TS)}$ from the k_ψ values measured under the same conditions;³ and ΔG° for $\text{exo-NBOPh} \rightleftharpoons \text{endo-NBOPh}$ from the equilibrium constants of *exo*- and *endo*-2-norborneols and 2-norbornyl acetates.^{21,22} The diagram shows that the big difference of the Gibbs energies of the *exo*- and *endo*-transition states (25.1 kJ mol^{-1}) is to a major extent caused by the difference in the pK_{SH^+} values ($\Delta G^\circ = 14.0 \text{ kJ mol}^{-1}$) and to a minor extent by the differences in both the initial state energies ($\Delta G^\circ = 5.0 \text{ kJ mol}^{-1}$) and the rates of the rate-limiting stages ($\Delta G = 6.1 \text{ kJ mol}^{-1}$), i.e. in the forma-

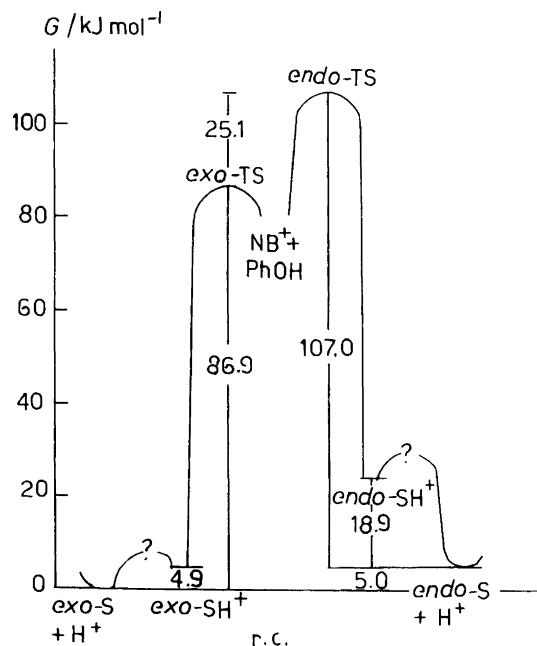
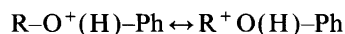


Fig. 2. The Goering-Schewene (Gibbs energies) diagram for the hydrolysis of *exo*- and *endo*-2-norbornyl phenyl ethers in $7.0 \text{ mol dm}^{-3} \text{ HClO}_4(\text{aq})$ at 308.2 K (S, substrate; TS, transition state; NB, norbornyl; r.c., reaction coordinate).

tion of the norbornyl cation and phenol via the nonclassical and classical transition states.²³ The result is rather surprising and evidently shows that the great thermodynamic stability of an intermediate cation (R^+ , e.g. *tert*-butyl⁵ or nonclassical 2-norbornyl²⁴) also markedly stabilizes the protonated substrate $[\text{RO}(\text{H}^+)\text{Ph}]$, but weakens the R-O^+ bond probably less than the resonance



would seem to demand. More investigations are needed.

Experimental

Syntheses. 2-Bicyclo[2.2.1]heptyl (or 2-norbornyl) phenyl ethers with *p*-Me, *p*-Ac, *m*-CN, *p*-CN and *p*-NO₂ substituents were mainly prepared as *exo-endo* mixtures from *exo*-2-norbornyl bromide and a properly substituted sodium phenoxide by refluxing for 9–20 h in absolute ethanol.^{2,3} The yields were always poor (2–8%) and the portions of the *endo*-epimers varied from 13% (*p*-Me) to 18% (*m*-CN). When dimethyl sulfoxide was used as solvent instead of ethanol in the case of the nitro-substituted ether, the yield was almost as poor (10%), but the portion of the *endo*-epimer increased to 35%. The products were purified by distillation in vacuum through an efficient column, but the epimers were not separated. The purities varied between 96 and 98%. The *exo*- and *endo*-epimers gave either a single peak or two merged peaks in capillary GC analyses. Their portions

were therefore analyzed and the epimers identified from the ^1H and ^{13}C NMR spectra. The ^{13}C chemical shifts (Table 3) are in agreement with those measured for the unsubstituted *exo*- and *endo*-2-norbornyl phenyl ethers.³

Kinetics. The disappearance of *exo*-2-norbornyl phenyl ethers with *p*-Ac, *m*-CN, *p*-CN and *p*-NO₂ substituents and the formation of the corresponding phenols in HClO₄(aq) were followed during 2–3 half-lives spectrophotometrically (SP; Cary 17 D, 218–230 nm). The much more slowly reacting *endo*-epimers practically did not hydrolyze during this time (see later). Trials to measure the hydrolysis rates of *exo*-2-norbornyl *p*-tolyl ether in the same way were not successful. Therefore its disappearance was followed by GC (an FFAP capillary column) with dichloromethane as extracting solvent and 3-nitrotoluene as internal standard.³ The GC method was also used to check and obtain additional rate measurements in the case of *exo*-2-norbornyl phenyl ether and its *p*-nitro derivative.

The disappearance of the ethers generally followed at least satisfactory first-order kinetics, but in the case of the methyl-substituted ether the GC peak of the substrate rapidly decreased at the beginning of the runs ca. 15%, after which the change became ca. 7 times slower (the reason is considered above). In these cases, the anomalous first values were rejected. The rate constants were calculated from the slopes of the linear correlation $\ln(A_t - A_\infty)$ vs. t , where A is the absorbance in the SP measurements and the ratio of integrals of the substrate and the internal standard in the GC measurements and t is time. The final sample or absorbance reading was taken after ten estimated half-lives of the *exo*-epimer, when the amount of the *endo*-epimer was practically equal to that at the beginning of the run. The two methods mostly gave equal rate constants within the experimental error limits (Table 1). The rate constant under each condition was measured two or more times, and less parallel runs were generally needed in the GC than in the SP method.

Table 3. Tentative assignments of ^{13}C NMR chemical shifts in CDCl₃ (TMS) for *exo*- and *endo*-2-bicyclo[2.2.1]heptyl phenyl ethers with substituent X in the benzene ring (numbering of the carbon atoms in Scheme 1).

X	C-1	C-2	C-3	C-4	C-5	C-6	C-7
<i>exo</i> -epimers							
H ^a	41.2	79.9	40.0	35.5	28.5	24.3	35.2
<i>p</i> -Me	41.1	80.2	40.0	35.5	28.5	24.4	35.2
<i>p</i> -Ac	41.2	80.5	40.0	35.5	28.4	24.2	35.2
<i>m</i> -CN	41.0	80.6	39.7	35.5	28.3	24.1	35.2
<i>p</i> -CN	41.1	80.7	39.9	35.4	28.3	24.2	35.2
<i>p</i> -NO ₂	41.3	81.3	39.9	35.6	28.4	24.2	35.3
X	C-8	C-9	C-10	C-11	C-12	C-13	C-X
<i>exo</i> -epimers							
H ^a	157.9	115.5	129.3	120.2	129.3	115.5	—
<i>p</i> -Me	155.5	115.5	129.8	129.4	129.8	115.5	20.4
<i>p</i> -Ac	162.0	115.1	130.6	129.9	130.6	115.1	26.2, 196.8
<i>m</i> -CN	157.9	118.3	113.0	123.9	130.0	120.6	118.7
<i>p</i> -CN	161.2	116.0	133.8	103.2	133.8	116.0	119.4
<i>p</i> -NO ₂	163.2	115.3	125.8	141.2	125.8	115.3	—
X	C-1	C-2	C-3	C-4	C-5	C-6	C-7
<i>endo</i> -epimers							
H ^a	40.6	77.9	37.5	36.9	29.4	20.8	37.3
<i>p</i> -Me	40.5	78.1	37.5	36.8	29.4	20.8	37.3
<i>p</i> -Ac	40.6	78.5	35.5	36.8	29.3	20.8	37.2
<i>m</i> -CN	40.4	78.6	36.7	37.2	29.2	20.6	37.2
<i>p</i> -CN	40.5	78.7	37.3	36.7	29.2	20.7	37.3
<i>p</i> -NO ₂	40.7	79.4	37.3	36.8	29.2	20.8	37.3
X	C-8	C-9	C-10	C-11	C-12	C-13	C-X
<i>endo</i> -epimers							
H ^a	158.7	115.4	129.4	120.2	129.4	115.4	—
<i>p</i> -Me	156.5?	115.5	129.8	129.4	129.8	115.5	20.4
<i>p</i> -Ac	162.8	115.5	130.9	127.4	130.9	115.5	26.2, 196.8
<i>m</i> -CN	158.8	118.3	113.0	123.9	130.2	120.6	118.7
<i>p</i> -CN	161.9?	115.2	133.8	103.2	133.8	115.2	119.4
<i>p</i> -NO ₂	164.0	115.3	125.8	141.2	125.8	115.3	—

^aRef. 3.

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