41. Parallelism Between Nucleophilically Solvent-Assisted and Phenyl-Assisted Reactions. Possible Existence of Nucleophilically β-Phenyl-Solvated Ion Pairs

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Summary

Solvolysis rate constants in MeOH and *t*-BuOH are compared for β-methyl and β-phenyl derivatives of two cycloalkyl systems. It appears that the β-phenyl derivatives solvolyse at the same rate as the β-methyl ones. The lack of deceleration is attributed to phenyl assistance. It is established by configurational analysis of the reaction products, that those products which necessarily originate from a cationic species are the most abundant ones. It is suggested that these reactions could proceed through ion-pair intermediates, which are nucleophilically solvated by phenyl or by the solvent. A parallel between phenyl assistance and 'S_N2 (intermediate)' mechanism, suggested by *Bentley & Schleyer,* is drawn.

The 'S_N2 (intermediate)' mechanism proposed by *Bentley & Schleyer* [1a] seems to be the most general mechanism for solvolyses of secondary substrates. It implies a large spectrum of transition states and takes place between purely unassisted S_N1 (limit k_c) and purely concerted one-step S_N2 mechanisms. In the transition state of a 'S_N2 (intermediate)' reaction a partial positive charge is developing on the reacting C-atom which is weakly bound with the solvent. This bond to the solvent, reduces the activation energy compared with an S_N1 mechanism without any assistance (k_c) [2]. Consequently, the reaction is accelerated and the value of the rate ratio k_s/k_c, representative of the extent of solvent assistance [3], must be greater than 10. This two-step reaction involves an intermediate which is a nucleophilically solvent-solvated ion pair [1]. We have brought experimental evidences of such a mechanism [4]. Solvent assistance was characterized by high values for k_s/k_c ratios and the ionic intermediate by the analysis of the reaction products. In anchimerically assisted processes, the migrating group is an 'internal' nucleophile. So, there is the possibility that a similarly-graded mechanism exists with the neighboring phenyl group playing the role of the solvent. In this case, the positive reacting C-atom would be nucleophilically phenyl-solvated in the intermediate, but the reaction products would not necessarily be those from a symmetrical phenonium ion but, as in 'S_N2 (intermediate)' reactions, could be the same as those that would be obtained from a classical cation. Generally, in the solvolyses of secondary

β-phenylalkyl substrates, two discrete solvent-assisted (k_s) and aryl-assisted (k_Δ) pathways, between which there is no crossover, are competing [5]: $k_t = k_s + Fk_\Delta$ (F represents the internal return). The k_s-route would be the solvent-assisted 'S_N2 (intermediate)' mechanism. Good correspondence of rates and products are often observed for these two pathways. Nevertheless, the problem of the concomitant formation of olefins and tertiary rearrangement products is very little studied. They are included in the k_s-term [6b]. But the question could be asked whether such products, rather expected for a carbocationic process, could not likewise arise from the k_Δ-pathway. We studied solvolyses of secondary β-phenyl bicyclic compounds, under conditions expected to lead to 'S_N2 (intermediate)' mechanism for the solvent-assisted path k_s, in order to check if phenyl assistance k_Δ can proceed similarly, *i.e.*, through a cationic intermediate which involves a nucleophilic assistance (here from the phenyl group), but leads to products similar to those that would be obtained from a classical cation. We have chosen as substrates bicyclo[4.2.0]octane **I**(R=C_6H_5) and bicyclo[4.4.0]decanec[1]) **I'**(R=C_6H_5) derivatives. These compounds involve the widely studied 3-phenyl-2-butyl structure [8] which displays kinetically weak phenyl assistances in the usual solvents. However, owing to their conformational rigidity[2]), a more detailed and fruitful analysis of the products could be anticipated.

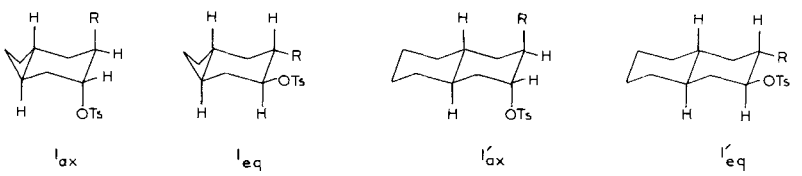

Fig. 1. *Formulae of compounds* $\mathbf{I}_{ax}$, $\mathbf{I}_{eq}$, $\mathbf{I'}_{ax}$, $\mathbf{I'}_{eq}$

Comparative Kinetic Study of Secondary Diaxial β-Methyl and β-Phenyl Compounds. – The rate data summarized in *Table 1* reveal that for diaxial tosylates $\mathbf{I}_{ax}$ and $\mathbf{I'}_{ax}$ the β-phenyl derivatives solvolyse in MeOH and *t*-BuOH practically at the same rate as the analogous methyl derivatives. This similarity is unexpected since it implies in the case of the phenyl tosylates, that two retarding factors are to be balanced: a) the electron-withdrawing inductive effect of phenyl and b) the decrease of solvent assistance in connection with the difficulty of the solvent approach parallel to a bulkier β-substituent [2b] [4] [9] (phenyl more hindering than methyl).

The electron-withdrawing effect of phenyl would lead to a noticeable decrease of the β-phenylalkyl compound rate [12], while, owing to the weak electron-donating effect of the methyl group [13], the solvolysis of the β-methylalkyl tosylate would be slightly accelerated, compared to the unsubstituted compound. Commonly, a factor of

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[1]) For these compounds, the nomenclature previously used in [7] was adopted.

[2]) Diaxial compounds always react in chair form, but the reactions of the diequatorial ones can still proceed *via* non-chair conformations.

10 is used for the rate-retarding inductive effect of phenyl (k_H/k_Φ) [12][3]). The retarding effect expected for the tosylate $\mathbf{I}_{ax}$ (R = C_6H_5) and $\mathbf{I}'_{ax}$ (R = C_6H_5) can be estimated by the comparison of the reaction rates of the analogous β-methyl and β-phenyl diequatorial derivatives $\mathbf{I}_{eq}$ and $\mathbf{I}'_{eq}$ *(Table 2)*.

Table 1. *Rate Constants for Solvolyses of Analogous Diaxial β-Phenyl and β-Methyl Tosylates*

Tosylate	R	10^6 k [s^{-1}]	
		MeOH[a])	t-BuOH[b])
$\mathbf{I}_{ax}$	CH_3	2.95[c])	0.94 ± 0.01[d])
$\mathbf{I}_{ax}$	C_6H_5	2.57[e])	1.08 ± 0.03
$\mathbf{I}'_{ax}$	CH_3	2.37 ± 0.04[d])	0.429 ± 0.08[d])
$\mathbf{I}'_{ax}$	C_6H_5	2.09 ± 0.02	0.476 ± 0.01

[a]) ROTs = 5×10^{-2}M, t = 45 °C. [b]) ROTs = 7×10^{-2}M, t = 65 °C. [c]) [10]. [d]) [4]. [e]) [11].

Table 2. *Rate Constants for Methanolysis of Diequatorial [4.2.0] and [4.4.0] Bicyclic Tosylates* $\mathbf{I}_{eq}$ *and* $\mathbf{I}'_{eq}$

R	$\mathbf{I}_{eq}$		$\mathbf{I}'_{eq}$	
	CH_3	C_6H_5	CH_3	C_6H_5
k [s^{-1}] 110 °C	3.94×10^{-4}	1.18×10^{-4}	5.65×10^{-4}	1.17×10^{-4}
100 °C	1.58×10^{-4}	4.28×10^{-5}	2.02×10^{-4}	4.05×10^{-5}
90 °C	5.34×10^{-5}	1.34×10^{-5}	7.02×10^{-5}	1.26×10^{-5}
80 °C	1.87×10^{-6}	4.05×10^{-6}	2.10×10^{-5}	4.00×10^{-6}
$\Delta H^{\neq}$ [kcal/mol]	26.8	29.6	28.6	29.6
$\Delta S^{\neq}$ [eu]	−4.7	0.3	0.9	0.3
extrapol., 45 °C	2.51×10^{-7}	3.55×10^{-8}	2.15×10^{-7}	3.41×10^{-8}
$k_{CH_3}/k_{C_6H_5}$, 45 °C	7.1		6.3	

For diequatorial compounds, solvent assistance implies a non-chair conformation [14]. In the methanolyses of $\mathbf{I}_{eq}$ (R = C_6H_5) and $\mathbf{I}_{eq}$ (R = CH_3), the product structures argue against purely S_N2 or $E2$ mechanisms [11] [15]. Therefore, the mechanism is well of the S_N2 (intermediate) type. As solvent approach is easier for diequatorial compounds in non-chair conformation than for diaxial ones, it can be supposed that for the latter the transition state must be more ionic than for the former. Consequently a retarding factor, due to the inductive effect of the phenyl group, higher than 6–7 (observed value for diequatorial compounds: *Table 2*) could be expected for diaxial ones. Moreover, as solvent assistance must be weaker for β-phenylalkyl than for β-methylalkyl substrates (where the back of the leaving group is much more accessible) [16] a further increase of the difference between the rates, with the β-methylalkyl derivatives more reactive than the β-phenyl ones, was to be anticipated: $k_s^{CH_3} = \alpha k_s^{\Phi}$ with a minimum value of 10 estimated for α. Thus, the similarity of the observed rates for diaxial β-phenyl and β-methyl compounds $\mathbf{I}_{ax}$ and $\mathbf{I}'_{ax}$, is surprising. In fact, it reflects an acceleration for β-phenyl compounds, which can only arise from phenyl assistance Fk_Δ. Since $k_s^{CH_3} \simeq k_s^{\Phi} + Fk_\Delta^{\Phi}$, it can be concluded that Fk_Δ^{Φ} is much greater than k_s^{Φ}.

[3]) Several different estimates of this kinetic correction factor are found in the literature coming to 33, a value predicted for the $k_{2\text{-Propyl}}/k_{1\text{-Phenyl-2-propyl}}$ rate ratio in the absence of participation [12d], and even to 47.6 [12e].

Reaction Products. – The kinetic data suggest that in the considered reactions, the β-phenyl compounds $\mathbf{I}_{ax}$($R = C_6H_5$) and $\mathbf{I}'_{ax}$ ($R = C_6H_5$) essentially react by a phenyl-assisted mechanism. As we have previously proved, by the analysis of reaction products, the occurrence of a nucleophilically solvent-solvated ion pair intermediate for the solvolysis in *t*-BuOH of the β-methyl analogues of these compounds [4], the analysis of reaction products of $\mathbf{I}_{ax}$ and $\mathbf{I}'_{ax}$ ($R = C_6H_5$) in this solvent was performed. The percentages of the reaction products are given in *Table 3*.

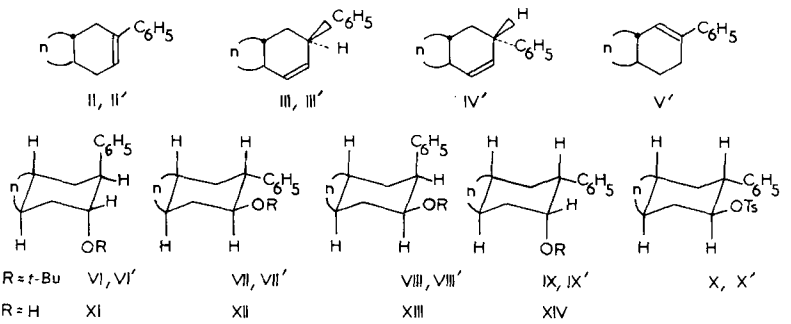

Fig. 2. *Structure of products in* t-*BuOH Solvolysis from* ($R = C_6H_5$, $n = 2$) *and* **I′** ($R = C_6H_5$, $n = 4$)

Table 3. *Percentages of Products for* t-*BuOH Solvolysis from* $\mathbf{I}_{ax}$ ($R = C_6H_5$) *and* $\mathbf{I}'_{ax}$ ($R = C_6H_5$)

Products			$\mathbf{I}_{ax}$		$\mathbf{I}'_{ax}$	
			[Py][a]) = 0	[Py] = 0.18M	[Py] = 0.37M	
Tosylate	**X** or	**X′**	15	12	9	
Olefins	**II**	**II′**	74	80	57	
	III	**III′**	5	5	24	
		IV′			2	
		V′			4	
Ethers	**VI**	**VI′**	2	3	3	42
	VII	**VII′**		22		13
	VIII	**VIII′**		34		45
	IX			40		
				4		
Alcohols[b])	**XI**		4			
	XII		19	undetectable	undetectable	
	XIII		35			
	XIV		42			
			4			

$[\mathbf{I}_{ax}$ ($R = C_6H_5$)$] = [\mathbf{I}'_{ax}$ ($R = C_6H_5$)$] = 7 \times 10^{-2}$M; t = 65 °C.

[a]) [Py] = Pyridine.

[b]) Due to the formation of water from dehydration of *t*-BuOH by TsOH liberated.

In non-buffered solvolyses, the presence of alcohols is observed, due to the progressive formation of water from the dehydration of *t*-BuOH by the liberated TsOH. Buffering the medium with pyridine roughly prevents the formation of water. We have verified that the 2,3-olefin **III** is not isomerized by TsOH and that the latter does not induce an addition reaction. Examination of *Table 3* shows that the presence

of water in *t*-BuOH slightly decreases the proportions of elimination, which remains very markedly predominant with respect to substitution. This phenomenon is not surprising, the addition of water to anhydrous EtOH slightly reduces elimination, whether the latter is first- or second-order [17]. The low proportion of 2,3-olefin (5% for **III**, 24% for **III'**), and the even lower percentage of inverted substitution products (**VIII**, **XIII** and **VIII'**) show that the solvent does not induce concerted mechanisms like *E*2 and S_N2, respectively. The diequatorial tosylate **X** (or **X'**), and the substitution products **VI**, **VII**, **XI** and **XII**, **VI'** and **VII'**, cannot have another origin than either the attack of the leaving group (internal return) or the attack of the solvent on a phenonium ion. The Σ(alcohols)/Σ(ethers) ratio decreases with the quantity of water present in the medium. Thus, it must be assumed that for the non-buffered solvolyses, there is a competition between the two nucleophiles (*t*-BuOH and H_2O) with regard to the different ions present. The direction of the opening of the phenonium ion formed from $\mathbf{I}_{ax}$ ($R = C_6H_5$) remains constant regardless of the attacking nucleophile. The proportion of tosylate $\mathbf{I}_{ax}$ and $\mathbf{I}'_{ax}$ formed by the reverse reaction can thus be evaluated from the amount of diequatorial tosylate produced, using the same diaxial/diequatorial ratio as for the solvent attack [18]. The products **X**, **VI**, **VII**, **XI**, **XII**, **IX** and **XIV** (reaction of **X**), and $\mathbf{I}_{ax}$ (return) on the one hand, and **X'**, **VI'**, **VII'**, **IV'** [8] and $\mathbf{I}'_{ax}$ (return) on the other hand, can thus be considered as arising from phenonium ions derived from $\mathbf{I}_{ax}$ and $\mathbf{I}'_{ax}$ ($R = C_6H_5$), respectively. Furthermore, the olefins **II**, **II'** and **V'** seem to originate from the secondary cations obtained by heterolysis of the C-OTs bond, and from the tertiary cations formed by migration of the H-atom α to the phenyl group from the secondary cations. This classification of the products according to their supposed origin is given in *Table 4*.

Table 4. *Product Analysis for t-BuOH Solvolysis from* $\mathbf{I}_{ax}$ *(*$R = C_6H_5$*) and* $\mathbf{I}'_{ax}$ *(*$R = C_6H_5$*)*

	$\mathbf{I}_{ax}$		$\mathbf{I}'_{ax}$	
	CH_3[a])	C_6H_5	CH_3[b])	C_6H_5
% Necessarily originating from a phenonium ion		20		32
% Necessarily originating from a cationic species	90	74	63	48
% Possibly originating from solvent assistance[c])	10	6	37	20
k_s/k_c[b])	100		60	

[a]) [10]. [b]) [4]. [c]) All these compounds can likewise have the secondary cation as precursor.

It is noteworthy that, within the same series, there is an analogy between the products formed by the phenylalkyl and the methylalkyl tosylates. In all cases, the products which could be considered as deriving from a classical cation are the most abundant. However, for the β-phenyl compounds, the products originating from a phenonium ion (Fk_Δ^ϕ) are, by far, more abundant than those possibly arising from the solvent assistance (k_s^ϕ). Moreover, the latter are fewer than the products possibly originating from solvent assistance for the methylalkyl substrate ($k_s^{CH_3}$). Consequently, for the β-phenylalkyl compounds, it can be supposed that the percentage of olefins arising from the k_s^ϕ path is also strongly decreasing.

For the solvolyses of methylalkyl tosylates [4], the discrepancy between kinetic data implying solvent assistance, which was characterized by a substantial value for k_s/k_c ratio, and the reaction products, in majority seeming to arise from a cationic species led us to assume the nucleophilic involvement of the solvent in the transition state leading to ion pairs. For solvolyses of β-phenylalkyl tosylates, kinetic results suggest that phenyl assistance (Fk_Δ^ϕ) is taking in a large extent the place of solvent assistance (k_s^ϕ). But also here, most of the products seem to arise from a classical cation. Under these conditions, it appears necessary to put forward the intervention of an ion pair intermediate, nucleophilically solvated by the phenyl group, which could explain the formation of these products and in particular that of the Δ-3,4 olefin, the major product of the reaction. Such an ion was previously proposed by *Ramsey & Das* [19]. But they considered that it was the only precursor of all the products (no k_s route from the covalent substrate), and this last hypothesis was refuted by *Schleyer et al.* [6b]. For their part, *Brown et al.* [20a, b], *Winstein et al.* [20c] and *Cram et al.* [20d, e] proposed for symmetrical systems, two simultaneous π-cations of this sort, in rapid equilibrium. Furthermore, owing to the particular structure of 1-phenyl-2-propyl tosylate, the intermediate formed during the trifluoroacetolysis of this compound [5] [12c, d] can only be a very unsymmetrical phenonium ion similar to the one we are postulating.

Conclusion. – β-Phenylalkyl substrates solvolyse by two competing phenyl-assisted and solvent-assisted discrete pathways. For the considered solvolyses, kinetic results provide the proof of a large involvement of phenyl assistance. But as most of the products obtained in *t*-BuOH are those which could be formed from a classical ion, consequently it appears that only a very unsymmetrical phenonium ion, precursor of the majority of the products, can be invoked to explain both these results. The competitive solvent-assisted pathway would be of minor importance owing to the difficult approach to the reacting C-atom close to the bulky β-phenyl group, and it would only account for a small part of the obtained olefins. Therefore, phenyl- and solvent-solvated ionic species could coexist in the medium. Weak nucleophilic bonds (Δ or S) lower the energy of the transition state for the rate-determining ionization step, but are not sufficient to induce the course of the second step of product formation from the nucleophilically solvated intermediates. As it was suggested for the S_N2 (intermediate) mechanism, a gradual spectrum of nucleophilic attachment could be anticipated for phenyl-assisted mechanisms.

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Experimental Part

General. ^{1}H-NMR spectra were obtained on either a *Varian T-60* or *Varian XL 100* NMR spectrometer, using TMS as an internal standard (δ in ppm).The IR spectra were recorded on *Perkin-Elmer* (model *257* or *325*) instruments (ν in cm^{-1}). Analytical vapor-phase chromatography (VPC) was performed on a *Perkin-Elmer F 11* gas chromatograph (flame ionization detector) with 1/8 in × 10 ft. columns of 10% QF1 on *Diatoport* 60–80 Mesh or 10% FFAP on *Chromosorb W* DMCS 60–80 Mesh.

Materials. – Solvents. MeOH and *t*-BuOH were distilled after treatment with Na and K, respectively. They were stored under N_2 atmosphere. Pyridine was distilled and stored over KOH pellets.

Tosylates. The preparation and characterization of the alcohols of structures $\mathbf{I}_{ax}$ (R = CH_3) and $\mathbf{I}_{eq}$ (R = CH_3) have already been reported [21]. Those of the other alcohols of the type $\mathbf{I}_{ax}$, $\mathbf{I}_{eq}$ (R = C_6H_5), $\mathbf{I'}_{ax}$, $\mathbf{I'}_{eq}$ (R = CH_3 or C_6H_5) were carried out as described in [21]. The tosylates were prepared from high purity alcohols and TsCl in pyridine at 0°. They were recrystallized several times from petroleum ether/Et_2O mixtures at low temperatures or were purified by TLC. The characteristics of the tosylates $\mathbf{I}_{ax}$ (R = CH_3), $\mathbf{I}_{eq}$ (R = CH_3), $\mathbf{I}_{ax}$ (R = C_6H_5) and $\mathbf{I}_{eq}$ (R = C_6H_5), $\mathbf{I'}_{ax}$ (R = C_6H_5) and $\mathbf{I'}_{eq}$ (R = C_6H_5), $\mathbf{I'}_{ax}$ (R = CH_3) were reported in [10][15][11][7][4b], respectively. $\mathbf{I'}_{eq}$ (R = CH_3): F = 85.1°. IR (CCl_4) 1370, 1185, 1175 (SO_2); 910, 925, 965 (C–O). ^{1}H-NMR (CCl_4): 0.75 (*d*, *J* = 6, 3H, CH_3); 2.42 (*s*, 3H, tosyl-CH_3); 4.06 (*m*, 1H, C*H*OTs); 7.26 (*d*, *J* = 8, 2H, C_6H_4); 7.70 (*d*, *J* = 8, 2H, C_6H_4). Anal. calc. for $C_{18}H_{26}SO_3$: C 67.05, H 8.13, O 14.88; found: C 66.88, H 8.17, O 15.01.

Kinetics Procedures. Kinetics were performed by the sealed-ampule technique, in constant temperature baths at 45° and 65° (± 0.05°), for methanolyses and *t*-butanolyses, respectively.

Diaxial Compounds. The initial substrate concentration was 0.05M for methanolyses and 0.07M for *t*-butanolyses. Liberated TsOH was titrated under N_2 with standard NaOH solutions, and phenolphthalein as indicator. *t*-Butanolyses were carried out in presence of pyridine to prevent the solvent dehydration promoted by TsOH. Practically, the same rates were observed up to 60% and to 30% reaction with and without buffer, respectively. Above these percentages, curved plots were obtained owing to presence of H_2O. Each run involved at least 9 ampules, and was carried out at least in duplicate.

Diequatorial Compounds. Solvolyses were followed conductimetrically. Owing to the low solubility of these derivatives and especially the phenyl-substituted ones, about 4×10^{-4}M solutions were used. Conductivity measurements were performed in *CM/02/55/G* cells with bright Pt electrodes using approximatively 2 ml of solution. The cell glass vessel was immersed in a temperature bath at 25.0° ± 0.1°. Readings were taken with a *Tacussel* model *CD 7N* conductimeter, capable of 0.5–1% accuracy depending on the used scale. A calibrated curve: conductivity = f(TsOH) was established with standard solutions of TsOH. The raw kinetic data were fitted to the first-order rate equation by means of a linear regression method, with correlation coefficients $r \geqslant 0.999$. For the diequatorial tosylates, kinetics were carried out at four different temperatures and the rate constant was extrapolated to 45° ($r \geqslant 0.9997$ for the four diequatorial tosylates).

Isolation and Characterization of Solvolysis Products. Upon completion of the solvolysis reaction, the solution was cooled, diluted with H_2O, then extracted several times with twice distilled pentane. Precipitated diequatorial phenyl tosylate was filtered on a tared fritted funnel, washed with pentane, H_2O, then dried to constant weight. The combined org. portions were washed with H_2O until all the alcoholic solvent was removed, and dried over anh. Na_2SO_4. The concentration of the solution was carried out by distillation of the pentane through a 20 cm vacuum-jacketed column packed with glass helices, with the H_2O bath temp. less than 50°. Analytical VPC was performed on the residue (accuracy 2% on the measurement). The relative proportions of ether oxides were determined by integration of the ^{1}H-NMR signal, obtained with a *Varian XL100* spectrometer. The different constituents were separated by TLC. The identification of these products was performed by VPC and ^{1}H-NMR comparisons with authentical samples. Olefins were obtained as reported in [11] and [7]. *t*-Butoxides were prepared from the corresponding alcohols obtained as described previously [21] from the [4.2.0]- and [4.4.0]epoxides.

(3ax)-Hydroxy-(4ax)-phenylbicyclo[4.2.0]octane. M.p. 75–75.5°. IR (CCl_4): 3623 (free OH), 3592 (intra bound OH), 975 (C–O). ^{1}H-NMR (CCl_4): 7.16 (*s*, 5H, C_6H_5); 4.22 (*m*, 1H, C*H*OH), 3.02 (*m*, 1H, C*H*C_6H_5). MS: 202 (M^+ ($C_{14}H_{18}O$)).

(3eq)-Hydroxy-(4ax)-phenylbicyclo[4.2.0]octane. M.p. 50–50.5°. IR (CCl_4): 3580 (O–H), 1030 (C–O). ^{1}H-NMR (CCl_4): 7.22 (*m*, 5H, C_6H_5); 3.78 (*m*, 1H, C*H*OH); 3.10 (*m*, 1H, C*H*C_6H_5). MS: 202 (M^+ ($C_{14}H_{18}O$)).

(3eq)-Hydroxy-(4eq)-phenylbicyclo[4.2.0]octane. M.p. 78°. IR (CCl_4): 3580 (O–H), 1030 (C–O). ^{1}H-NMR (CCl_4): 7.15 (*s*, 5H, C_6H_5); 3.52 (*m*, 1H, C*H*OH); *ca* 2.4 (br. *m*, 1H, C*H*C_6H_5). MS: 202 (M^+ ($C_{14}H_{18}O$)).

(3ax)-Hydroxy-(4eq)-phenylbicyclo[4.2.0]octane. M.p. 49°. IR (CCl_4): 3585 (O–H), 985 (C–O). ^{1}H-NMR (CCl_4): 7.13 (*s*, 5H, C_6H_5); 3.88 (*m*, 1H, C*H*OH); 2.7 (*d* of *m*, *J* = 11, 1H, C*H*C_6H_5). MS: 202 (M^+ ($C_{14}H_{18}O$)).

tert-*Butoxy Derivatives.* In a stirred solution of *ca.* 200 mg (5×10^{-4} mole) of alcohol in 10 ml of CH_2Cl_2, isobutene was bubbled over a 30 min period, at r.t. Then 0.05 ml of concentrated H_2SO_4 was added and the bubbling was continued for 4 h. The solution was allowed to stand overnight. It was washed in turn with H_2O, sat. $NaHCO_3$ and H_2O, prior to drying and solvent evaporation without warming. The residue was purified by TLC.

(3ax)-tert-*Butoxy-(4ax)-phenylbicyclo[4.2.0]octane.* IR ($CDCl_3$): 1390, 1365 (*t*-Bu), 1190, 1030, 995 (C–O). ^{1}H-NMR ($CDCl_3$): 7.25 (*s*, 5H, C_6H_5); 4.03 (*m*, 1H, C*H*O*t*Bu); 3.03 (*m*, 1H, C*H*C_6H_5); 1.106 (*s*, 9H, *t*-Bu). MS: 258 (M^+ ($C_{18}H_{26}O$)).

(3eq)-tert-*Butoxy-(4ax)-phenylbicyclo[4.2.0]octane.* IR ($CDCl_3$): 1385, 1360 (*t*-Bu), 1190, 1085, 1050 (C–O). ^{1}H-NMR ($CDCl_3$): 7.33 (*m*, 5H, C_6H_5); 3.74 (*m*, 1H, C*H*O*t*Bu); 3.16 (*m*, 1H, C*H*C_6H_5); 1.004 (s, 9H, *t*-Bu). MS: 258 (M^+ ($C_{18}H_{26}O$)).

(3eq)-tert-*Butoxy-(4eq)-phenylbicyclo[4.2.0]octane.* IR ($CDCl_3$): 1390, 1365 (*t*-Bu), 1190, 1080, 1050 (C–O). ^{1}H-NMR ($CDCl_3$): 7.22 (*s*, 5H, C_6H_5); 3.48 (*m*, 1H, C*H*O*t*Bu); 2.56 (br. *m*, 1H, C*H*C_6H_5); 0.692 (*s*, 9H, *t*-Bu). MS: 258 (M^+ ($C_{18}H_{26}O$)).

(3ax)-tert-*Butoxy-(4eq)-phenylbicyclo[4.2.0]octane.* IR ($CDCl_3$): 1390, 1360 (*t*-Bu), 1190, 1170, 1120, 1035, 1015, 995 (C–O). ^{1}H-NMR ($CDCl_3$): 7.17 (*s*, 5H, C_6H_5); 3.71 (*m*, 1H, C*H*O*t*Bu); 2.63 (*d* of *m*, *J* = 11, 1H, C*H*C_6H_5); 0.700 (*s*, 9H, *t*-Bu). MS: 258 (M^+ ($C_{18}H_{26}O$)).

(3ax)-Hydroxy-(4ax)-phenylbicyclo[4.4.0]decane. IR (CCl_4): 3610 H–O), 1025, 995, 965 (C–O). ^{1}H-NMR ($CDCl_3$): 7.23 (*s*, 5H, C_6H_5); 4.35 (*m*, 1H, C*H*OH); 3.08 (*m*, 1H, C*H*C_6H_5). MS: 230 (M^+ ($C_{16}H_{22}O$)).

(3eq)-Hydroxy-(4ax)-phenylbicyclo[4.4.0]decane. IR (CCl_4): 3580 (O–H), 1055, 1040, 1015 (C–O). ^{1}H-NMR ($CDCl_3$): 7.3 (*m*, 5H, C_6H_5); 3.9 (*m*, 1H, C*H*OH); 3.32 (*m*, 1H, C*H*C_6H_5). MS: 230 (M^+ ($C_{16}H_{22}O$)).

(3eq)-Hydroxy-(4eq)-phenylbicyclo[4.4.0]decane. IR (CCl_4): 3590 (O–H) 1055, 1045, 1030 (C–O). ^{1}H-NMR ($CDCl_3$): 7.27 (*s*, 5H, C_6H_5); 3.67 (*m*, 1H, C*H*OH); *ca.* 2.4 (br. *m*, 1H, C*H*C_6H_5). MS: 230 (M^+ ($C_{16}H_{22}O$)).

(3ax)-tert-*Butoxy-(4ax)-phenylbicyclo[4.4.0]decane.* IR (CCl_4): 1385, 1360 (*t*-Bu), 1190, 1040, 1010 (C–O). ^{1}H-NMR (CCl_4): 7.20 (*s*, 5H, C_6H_5); 4.01 (*m*, 1H, C*H*O*t*Bu); 2.94 (*m*, 1H, C*H*C_6H_5); 1.228 (*s*, 9H, *t*-Bu). MS: 286 (M^+ ($C_{20}H_{30}O$)).

(3eq)-tert-*Butoxy-(4ax)-phenylbicyclo[4.4.0]decane.* IR (CCl_4): 1385, 1360 (*t*-Bu), 1195, 1070, 1020. ^{1}H-NMR (CCl_4): 7.28 (*m*, 5H, C_6H_5); 3.78 (*m*, 1H, C*H*O*t*Bu); 3.18 (*m*, C*H*C_6H_5); 1.150 (*s*, 9H, *t*-Bu). MS: 286 (M^+ ($C_{20}H_{30}O$)).

(3eq)-tert-*Butoxy-(4eq)-phenylbicyclo[4.4.0]decane.* IR (CCl_4): 1390, 1360 (*t*-Bu), 1195, 1070, 1060 (C–O). ^{1}H-NMR (CCl_4): 7.16 (*s*, 5H,C_6H_5); 3.28 (*m*, 1H, C*H*O*t*Bu); 2.44 (*m*, 1H, C*H*C_6H_5); 0.682 (*s*, 9H, *t*-Bu). MS: 286 (M^+ ($C_{20}H_{30}O$)).

Product Stability. To the normal solvent system (containing or not containing the buffer) was added TsOH and the product to be tested in equimolar amounts. The solution was subjected to usual solvolysis and workup conditions. Resulting product(s) was analysed by VPC and ^{1}H-NMR.

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