

## 112. Steric Effects on Reaction Rates – III. Application of Force-Field Calculations to Chromic Acid Oxidation of Alcohols

by Paul Müller and Jacky Blanc,

Département de Chimie Organique, Université de Genève, CH-1211 Genève 4

and Dieter Lenoir

Organisch-chemisches Institut der Technischen Universität München

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### Summary

The rates of oxidation with chromic acid of 15 bi- and polycyclic secondary alcohols have been measured and correlated with strain changes calculated by the MM1-program between the alcohols and the corresponding ketones. A correlation of the same quality is obtained upon representation of OH-strain by CH<sub>3</sub>-strain. The significance of the correlations with respect to the oxidation mechanism as well as the limitations of the applicability of force-field calculations to reactivity problems are discussed.

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**Introduction.** – Steric effects may have profound influences on the reactivity of molecules [1], but their interpretation is difficult. In favorable cases they are due to strain effects alone [2], but even then their understanding requires considerable knowledge about the reaction mechanism which usually is difficult to evaluate. Further, thermochemical data allowing evaluation of strain in the reacting molecules are often not available with the desired accuracy [3]. The situation is even less satisfactory when it comes to evaluation of strain in transition states. Although significant improvement in calculating transition states by quantum mechanical methods has recently been advanced [4], very often transition state structures are controversial and to our knowledge there are no theoretical methods available which would allow calculations of structures and energies of transition states of complex reactions with the required reliability, say to  $\pm 1$  kcal/mol.

In previous communications [5] we have applied a simple model, using force-field calculations, to the interpretation of reactivity of secondary alcohols towards chromic acid. This particular reaction was selected because of its relative simplicity, the kinetically relevant steps involving only transformation of an alcohol to a ketone by Cr(VI). The reaction mechanism is well understood [6]. The entropies of activation are constant within experimental error for unhindered alcohols [7], so that reactivity changes can be attributed to variations in  $\Delta H^\ddagger$ . Polar effects are small in the absence of strong electron-withdrawing substituents, therefore the dominating

factor consists in strain changes occurring between the alcohol and the respective transition state. Previously we assumed the strain in alcohols to be equal to that of the corresponding methyl-substituted hydrocarbon [5]. A choice had to be made for the selection of a suitable model for the transition state. The ketone was used mostly for reasons of convenience, an appropriate force-field being available [9]. This choice has the advantage that the calculated strain energies of ketones can be experimentally verified. Further, it was found that the strain changes between alcohol and ketone correlate reasonably with the rates of alcohol oxidation.

In the meantime more elaborate force-fields [10] including one for alcohols [11] have become available and we decided to study a new series of alcohols. A particular effort was made to extend the rate range and to obtain a satisfactory distribution of the experimental points within this range. With the exception of cyclohexanol, which was used for reference purposes, only rigid molecules were studied, since conformationally flexible compounds can lead to difficulties [5] [12].

**Results and Discussion.** – Oxidation rates were measured spectrophotometrically at 25.0° in 80% (v/v) acetic acid. For very reactive compounds measurements were carried out in 30 and 40% acetic acid. Acidity was kept constant by working in presence of 10<sup>-2</sup> N H<sub>2</sub>SO<sub>4</sub>. The rate constants reported in *Table 1* (last entry) were obtained by use of appropriate reference compounds for the different solutions. Since strained alcohols such as *Sendo*-bicyclo[2.1.1]hexanol (**3**) and 7-norbornanol (**4**) undergo extensive cleavage upon chromic acid oxidation in acetic acid [13] the rate constants of these compounds were verified by competition experiments under the conditions of the *Jones* oxidation. 7-Norbornanol (**4**) had the same reactivity relative to cyclohexanol in both systems; however, for **3** the relative rate dropped from 0.14 in the spectrophotometric method to 0.08 in the competitive method. The latter value was retained because it is considered more representative for the carbonyl-forming process than that measured in acetic acid [13].

Strain energies for alcohols, methyl-substituted hydrocarbons and ketones were calculated using *Allinger's* MM1-program, QCPE-No. 318 (Quantum Chemistry Program Exchange, Bloomington), to which *Allinger's* force-field for alcohols [11] was incorporated.

Whenever possible, the calculated enthalpies of formation (*Table 1*, entry 4) are compared with experimental data (entry 5). Agreement between the two sets of data is on the average 1.8 kcal/mol; the sparse data prohibit identification of trends in the deviations. Structures and energies of polycyclic and strained molecules have been widely calculated by various force-field methods [14]. While for alkanes [15] and alkenes reasonable agreement between experimental and calculated values were found, functional groups attached to polycyclic frameworks [16] give rise to more serious problems. Therefore, enthalpies of formation of alcohols (for example *3exo*-isomer of **10** and the *4exo*-isomer of **11** have been experimentally determined and compared with values calculated by MM1-program [17]. Discrepancies of 4–7 kcal/mol were found. *Steele* [17] suggests that these are due to deficiencies in the H↔H potential energy function which are in part based upon unreliable thermodynamic data. Although the significance of the thermochemical data has been questioned [23], we believe that some source of error must be in the

Table 1. Force-field calculations<sup>a)</sup> of alcohols and ketones, and rate constants for alcohol oxidation

Structure	No.	Derivative	$-AH_{\text{fcalc}}^{\circ}$	$-AH_{\text{fexp}}^{\circ}$	$E_{\text{st}}^{\text{b)}$	$\Delta E_{\text{st}}^{\text{c)}$	$k_2^{\text{d)}$	$\log k_{\text{rel}}$	
	1	OH	–	–	–	–	1.01	0.0	
		CH <sub>3</sub>	36.99 <sup>e)</sup>	36.98 <sup>f)</sup>	1.05	1.60			
		oxo	55.32 <sup>e)</sup>	+ 54.43 <sup>g)</sup>	2.79	–			
	2	2-OH	20.70		42.12	1.83	0.97	0.96	
		2-CH <sub>3</sub>	– 12.41		42.11	1.83			
		2-oxo	4.73		43.95	–			
	3	5endo-OH	+ 19.46		43.36	6.56	0.144		
		5endo-CH <sub>3</sub>	– 14.50		44.20	5.72		– 1.09	
		5-oxo	– 1.25		49.92	–		0.08 <sup>l)</sup>	
	4	7-OH	52.09	52.0 <sup>h)</sup>	16.31	3.47	0.145	– 0.88	
		7-CH <sub>3</sub>	18.57		16.72	3.06			
		7-oxo	34.46	32.0 <sup>h)</sup>	19.78	–			
	5	2-OH	63.70	68.0 <sup>i)</sup>	10.30	– 0.32	7.18	0.85	
		2-CH <sub>3</sub>	30.10		10.80	– 0.82			
		2-oxo	49.87	52.2 <sup>i)</sup>	9.98	–			
	6	9-OH	69.98		9.59	0.67	7.24	0.86	
		9-CH <sub>3</sub>	35.50		10.96	– 0.70			
		9-oxo	55.17	57.13 <sup>i)</sup>	10.26	–			
	7	2-OH	72.70	74.3 <sup>k)</sup>	4.16	0.90	6.76	0.83	
		2-CH <sub>3</sub>	38.38		5.35	– 0.29			
		2-oxo	57.65	55.1 <sup>k)</sup>	5.06	–			
	8	2endo-OH	49.95		26.90	– 2.56	25.5	3.15	
		2endo-CH <sub>3</sub>	13.50		30.24	– 5.90	(30% AcOH)		
		2-oxo	38.37		24.34	–			
	9	4-OH	67.82		14.62	– 2.22	31.2	1.47	
		4-CH <sub>3</sub>	33.71		15.61	– 3.21	0.53		
		4-oxo	55.90		12.40	–	(30% AcOH)		
	10	4endo-OH	27.66		52.06	– 7.58	44.5	3.24	
		4endo-CH <sub>3</sub>	– 6.80		53.40	– 8.92	(40% AcOH)		
		4-oxo	21.20		44.48	–			
	11	11endo-OH	35.34		44.38	– 7.99	78.3	3.45	
		11endo-CH <sub>3</sub>	– 7.95		54.56	– 18.17	(40% AcOH)		
		11-oxo	29.19		36.39	–			
	12	4endo-OH	17.25		54.17	– 9.05	297	4.22	
		4endo-CH <sub>3</sub>	– 18.22		56.52	– 11.39	(30% AcOH)		
		4exo-OH	23.45		47.96	– 2.84	0.54	1.48	
	13	4exo-CH <sub>3</sub>	– 12.71		51.01	– 5.89	(30% AcOH)		
		4-oxo	16.82		45.12	–			
		4endo-OH	28.87		42.55	– 2.44	7.76	2.63	
	14						(30% AcOH)		
							10.95		
								(40% AcOH)	
		4endo-CH <sub>3</sub>	– 6.03		44.33	– 4.22			
		4exo-OH	31.84		39.57	0.54	0.19	0.87	
	15	4exo-CH <sub>3</sub>	– 3.26		41.56	– 1.45	(40% AcOH)		
		4-oxo	17.17		40.11	–			

<sup>a)</sup> In kcal/mol. <sup>b)</sup> Strain energy. <sup>c)</sup> Strain difference between ketone and alcohol of CH<sub>3</sub>-derivative.

<sup>d)</sup> Experimental rate constant, in 80% AcOH, 10<sup>–2</sup> NH<sub>2</sub>SO<sub>4</sub>; 25.0°, in M<sup>–1</sup>·min<sup>–1</sup>. <sup>e)</sup> [5]. <sup>f)</sup> [18]. <sup>g)</sup> [19].

<sup>h)</sup> [20]. <sup>i)</sup> [21]. <sup>k)</sup> [22]. <sup>l)</sup> Competition experiment.

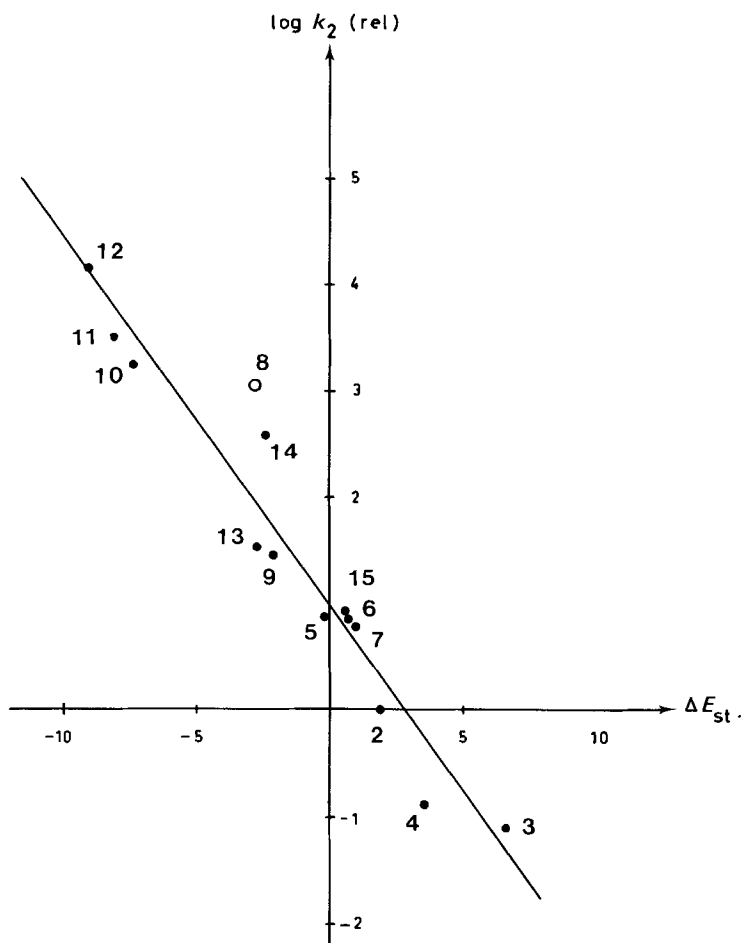


Fig. 1. Correlation of  $\log k$  vs.  $\Delta E_{st}$  (ketone-ROH). Slope  $-0.34$ , intercept  $0.89$ ,  $r=0.9717$ ,  $\sigma=0.37$ .  
 ○ excluded.

calculations. Clearly, errors of 4–7 kcal could invalidate the entire approach. However, since we are only interested in relative strain energies obtained upon variation of the functional group in a fixed position of the same molecular structure and not in absolute values, it is reasonable to expect at least partial compensation of systematic errors. Nevertheless, better force-fields for structure reactivity correlations are needed.

Correlations of  $\log k$  for alcohol oxidation and strain differences  $\Delta E_{st}$  are shown in *Figure 1* ( $\Delta E_{st}$ (ketone-ROH)) and *Figure 2* ( $\Delta E_{st}$ (ketone-RMe)). The general aspect of the correlations is the same. Both have correlation coefficients of 0.97–0.98 and standard deviations of 0.32–0.37 in  $\log k$ . This represents significant improvement in comparison to our previously published results [5]; we ascribe this to the extension of the rate range, to the more favorable distribution of the experi-

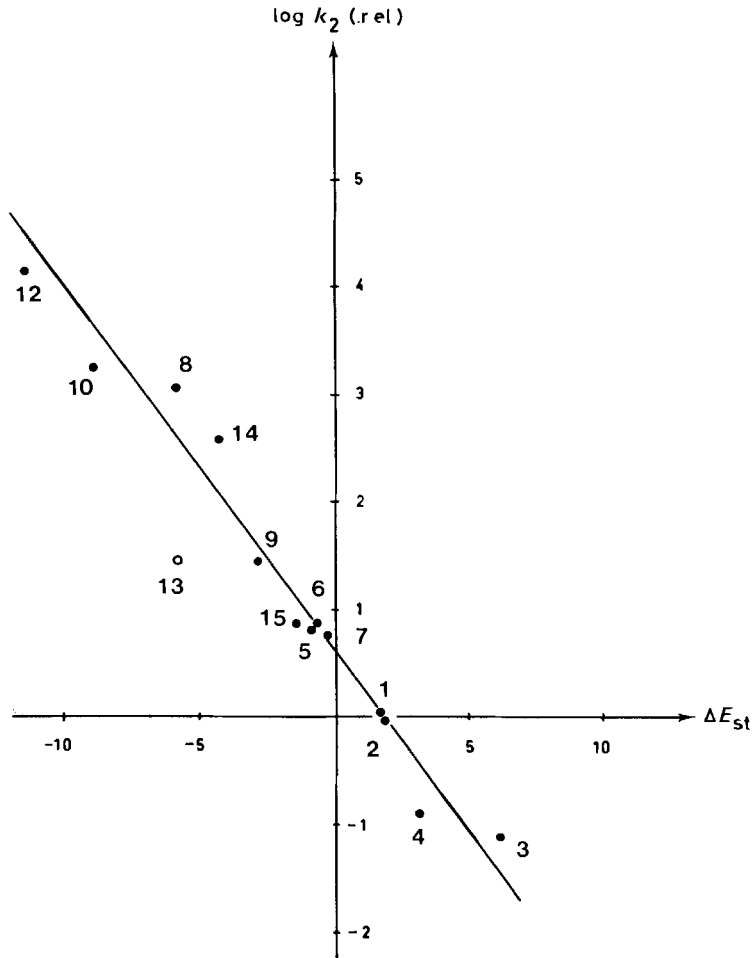


Fig. 2. Correlation of  $\log k$  vs.  $\Delta E_{st}$  (ketone-RMe). Slope  $-0.35$ , intercept  $0.63$ ,  $r=0.9783$ ,  $\sigma=0.32$ .  $\circ$  excluded.

mental points over this range, and to the fact that we restrict ourselves to conformationally rigid molecules. The fit is remarkable in view of the approximations involved in our approach [5] [6]. The correlation between strain differences ( $\Delta E_{st}$ ) and  $\log k$  demonstrates that the carbonyl group is a reasonable model for the transition state of oxidation. In other words, the properties of the ketone product must in part be reflected in the transition state. In general, one should not *a priori* expect such correspondence between properties of product and transition state. However, in the case of this particular reaction there are indications that it should exist. *Sicher* [12] has shown that a correlation exists between the relative stability and rate of chromic acid oxidation of epimeric alcohols. Since oxidation of epimeric alcohols leads to the same ketone, and since their relative reactivity is determined only by their difference in stability, it follows that their transition states must be

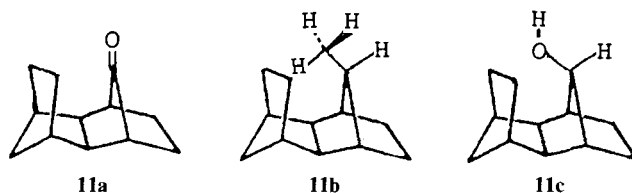
similar in energy. This is only possible if substantial rehybridization has occurred on going to the transition state. The force-field approach is an extension of *Sicher's* correlation. It allows to express the stability of the alcohol not with respect to its epimer, but rather to a transition state model.

It is appropriate to discuss also the shortcomings of this model. If reactivities of the alcohols in *Figures 1* and *2* are expressed in terms of  $\Delta H^\ddagger$ , the correlations have slopes of 0.47. An ideal model for the transition state would lead to a slope of unity. Therefore our calculations overestimate the strain changes occurring between alcohol and transition state by a factor of 2. It would be more appropriate to use a model with hybridization intermediate between  $sp^3$  and  $sp^2$ ; however, our theoretical understanding of the reaction mechanism is not sufficiently advanced to provide safe grounds for such a procedure which, further, would require the extension of the force-field approach into an area where its applicability is questionable.

The correlations in *Figures 1* and *2* confirm our previous findings [5]. Alcohols leading to strained ketones are unreactive and alcohols suffering severe non-bonded interactions and leading to unstrained ketones react very rapidly. With respect to the foregoing discussion alcohol **11c** represents an interesting case; it is highly strained and at the same time leads to a highly strained ketone, namely a 7-norbornanone derivative. The enhanced reaction rate of this alcohol demonstrates that release of non-bonded interactions contributes more to the reactivity than strain in the product. Previously we have used  $CH_3$ -groups in order to simulate the steric requirements of OH-groups. *Figures 1* and *2* compare  $\Delta E_{st}$ -values for alcohols and the corresponding methyl derivatives. Since both correlations obtained are of comparable quality, the general conclusion is that OH-strain is well represented by  $CH_3$ -strain. In mono- and bicyclic molecules we find a small strain increase of 0.5 to 1 kcal/mol upon replacement of OH by  $CH_3$ . In polycyclic systems this increase is somewhat larger with one extreme exception, namely compound **11** where the difference is 10 kcal/mol (*Table 1*). In the  $CH_3$ -derivative **11b** at least one of the H-atoms will be close to the 1,8-ethane bridge, while in the alcohol **11c** the only H-atom present is oriented outwards (*Scheme 1*). For this reason the  $CH_3$ -model leads to a serious overestimation of strain in **11** and is no longer representative for OH-strain.

Recently force-field calculations have been used by *Smith & Harris* [25] and by *Lenoir & Frank* [26] to rationalize rates of solvolysis of secondary tosylates in terms of strain differences between carbenium ion and the parent hydrocarbon or its methyl derivative. Although satisfactory correlations were obtained for acetolysis

Scheme 1



with substrates, solvolyzing *via* unassisted carbenium ion mechanism ( $k_c$ -substrates) we note that these correlations suffer from the same inadequacies as ours. The use of the carbenium ion as transition state models leads to an overestimation of  $\Delta$  strain by a factor of *ca.* 2. In this respect the correlation of *Schneider & Thomas* [27] which models the transition state properties for solvolysis of cycloalkyltosylates in trifluoroethanol by means of a carbonyl group is more satisfactory [28]. Further, the model used by *Smith & Harris* [25] does not consider effects due to leaving group hindrance which are undoubtedly present in his  $k_c$ -substrates. If substrates such as 2-adamantyl or 7-norbornyl *p*-toluenesulfonate suffer rate retardations, the procedure of *Harris* must lead to overestimation of anchimeric assistance in solvolysis. The question should be reexamined in the light of the approach of *Schneider & Thomas* [27].

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### Experimental Part

*Origin and/or syntheses of alcohols.* 9-Bicyclo[3.3.1]nonanol (**6**) and 2-adamantanol (**7**) were obtained by  $\text{LiAlH}_4$  reduction of the commercially available ketones. Bicyclo[2.1.1]hexan-2-ol (**2**) was synthesized by photocyclization of 1,5-hexadiene-3-one [29], followed by reduction with  $\text{LiAlH}_4$ . The *5endo*-isomer **3** was accessible by reductive cleavage of 2-oxatricyclo[3.2.0.0<sup>3,7</sup>]heptane [30]. 7-Norbornanol (**4**) [31], bicyclo[2.2.2]octan-2-ol [32] and *endo*-trimethylene-*2endo*-norbornanol [33] were synthesized in our laboratory by known procedures. Similarly, *4endo-endo-endo*-tetracyclo[6.2.1.1<sup>3,6</sup>.0<sup>2,7</sup>]dodecan-4-ol (**10**) [34] and *4endo*- and *4exo*-hydroxypentacyclo[6.2.1.1<sup>3,6</sup>.0<sup>2,7</sup>.0<sup>5,11</sup>]dodecan-11-ol (**11**) was accessible *via* reduction of the ketone [26] [36]. 4-Homoadamantanol (**9**) (tricyclo[3.3.2.1<sup>3,7</sup>]undecan-9-ol) and the isomers of pentacyclo[6.2.1.1<sup>3,6</sup>.0<sup>2,7</sup>.0<sup>5,9</sup>]dodecan-4-ol [37] were gifts of Prof. *P. v. R. Schleyer*, Erlangen, and Dr. *T. Fukunaga*, Du Pont de Nemours.

*Kinetic measurements.* Stock solutions of 30, 40 and 80% AcOH were prepared by introducing 10.0 ml of  $10^{-1}\text{N}$   $\text{H}_2\text{SO}_4$  into a 100 ml volumetric flask. To this was added the appropriate amount (by volume) of AcOH (*Merck*) and the solution was made up to the mark with deionized water. The chromic acid solutions were prepared by dissolving a weighed amount of *ca.* 35 mg of dried ammonium dichromate in a 10-ml volumetric flask with the corresponding acetic acid solution. The alcohol was weighed in a UV, quartz cell. After addition of AcOH (3.0 ml) the solution was thermostatted in the compartment of a spectrophotometer which allowed measuring of the temperature within the cell. Reaction was initiated upon addition of thermostatted chromic acid solution to the cell with a micro-pipette. For reasons of solubility and reactivity of the alcohols three different systems were used with the following characteristics.

Table 2. Solvent systems for kinetic measurements

	80% AcOH	30 and 40% AcOH
$[\text{H}_2\text{SO}_4]$	$10^{-2}\text{N}$	$10^{-2}\text{N}$
$[\text{Cr(VI)}]_0$	$10^{-3}\text{N}$	$10^{-4}\text{N}$
$[\text{ROH}]$	$3 \times 10^{-2} - 6 \times 10^{-2}\text{M}$	$10^{-3} - 2 \times 10^{-3}\text{M}$
Optical path	1.0 cm	5.0 cm
Volume	3.0 ml	12.0 ml
T	$25 \pm 0.1^\circ$	$25 \pm 0.1^\circ$

Reaction rates were determined by monitoring the change in optical density at 350 nm. First-order rate constants ( $k_1$ ) were obtained by linear regression on plots of  $\ln(A_t - A_\infty)$  vs.  $t$ . In all cases the correlation coefficient  $r$  was better than 0.999. The second-order rate constants were calculated by division of  $k_1$  by the concentration of alcohol used. The rate constants given in the *Table 1* are averages of three runs with a variation of  $\pm 5\%$  [38].

*Competition experiments.* Equimolar quantities of two alcohols (2-propanol/7-norbornanol (**4**) or 7-norbornanol (**4**)/5-endo-bicyclo[2.1.1]hexan-5-ol (**3**) and a known amount of *p*-xylene as internal standard were dissolved in 60% aq. acetone, 0.3N in  $H_2SO_4$ . To this was added at 0°, 2.67M chromic acid solution in water to allow for *ca.* 50% conversion of the alcohols. At the end of the reaction the mixture was neutralized with  $Na_2CO_3$  and analyzed by GC. (direct injection, column 5% FFAP on chromosorb W). Relative rate constants were determined from the amount of unreacted alcohols a and b at time  $t$  by use of the expression:

$$k_a/k_b = \frac{\ln([a]_t/[a]_0)}{\ln([b]_t/[b]_0)}$$

The relative rate of **4** over 2-propanol is 0.24, that of **3** over **4** 0.64. Using the known rate constant for isopropanol oxidation in the kinetic system (0.54 relative to cyclohexanol) it is possible to convert the results of the competition experiments to the kinetic scale (*Table 3*).

Table 3. Alcohol reactivity from kinetic and competition experiments

Alcohol	$k_a/k_b$	$k_{rel}$ (competition)	$k_{rel}$ (kinetic)
2-Propanol	–	–	0.54
7-Norbornanol ( <b>4</b> )	0.24	0.13	0.14
5-endo-Bicyclo[2.1.1]hexan-5-ol ( <b>3</b> )		0.083	0.14

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