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Stereoelectronic requirement and effect of ring size on silanol elimination: a kinetic study

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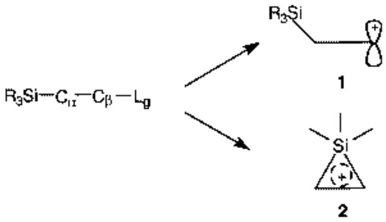
Acid catalyzed elimination of silanol from the cyclic *cis*-α,β-dihydroxysilanes **3**–**8** to cycloalkanones was studied at three different temperatures (298, 313 and 328 K). Silyldiols **3**–**7** hydrolyzed smoothly, while **8** was resistant to hydrolysis. The observed ease of elimination (reflected in the rate constants) was found to be related to the conformational flexibility of the ring and intramolecular hydrogen bonding. The results have confirmed the requirement of perfect antiperiplanar geometry of the eliminating groups, $SiMe_3$ and β-OH. The quantitation of the hydrolysis products, the cycloalkanones, was done using the gas chromatographic peak area normalization method using an internal standard. The rate data obtained at three different temperatures were employed to calculate $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta G^{\ddagger}$. The rate constants and thermodynamic parameters increase with the ring size. There is an interesting demarcation between these two values for common ring silyldiols and the larger ring silyldiols.

Introduction

Acid catalyzed silanol elimination of α,β-dihydroxysilanes to give carbonyl compounds is well documented.[1–3] The observations by Stork, Hudrlik, and Whitham have clearly demonstrated that the elimination proceeds *via* path (a) of Scheme 1. However, in a rare observation by Cunico,[4] it was revealed that the TFA-catalyzed reaction of α,β-dihydroxysilanes containing bulky groups on the silyl moiety (R = t-Bu, Scheme 1) yielded α-silylketones by silyl group migration, called silapinacol rearrangement. These α-silylcarbonyl compounds that are prone to protonic desilylation[5] can also lead to carbonyl compounds, path (b), (Scheme 1).

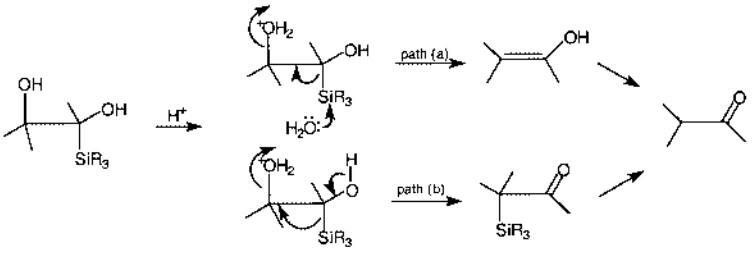
The process of silanol elimination begins with the protonation of β-OH leading to the formation of a cation stabilized by a β-silicon effect.[6] The stereochemistry of elimination is similar to that observed in E2 reactions. Instead of the base abstracting the proton β to the leaving group, the nucleophile (water) attacks the silyl group resulting in simultaneous fission of the $C–^{+}OH_2$ and $C–SiMe_3$ bonds. The rate of elimination depends on the magnitude of stabilization of the β-cation.[7,8] The inductive contribution (+I) from silicon is shown to be small and independent of dihedral angle, as it occurs through bonds.[6] The magnitude of β-silicon stabilization depends on the (p–σ)-C–Si hyperconjugation, which is maximized when the 2p orbital of the cationic β-carbon and the C–Si σ-bonding orbital are aligned in the same plane. Several studies[7–10] have shown that, in a system like $R_3Si–C_\alpha–C_\beta–Lg$ (Lg = leaving group), the incipient β-cation may be stabilized in two ways, either by hyperconjugation of the C–Si bond with the vacant p-orbital of the β-carbon (called vertical stabilization **1**) or by the formation of silacyclopropylium cation (non vertical stabilization **2**) (Scheme 2). Also, the amount of stabilization depends on $R_3Si–C_\alpha–C_\beta–Lg$ dihedral angle θ. The synperiplanar ($\theta = 0°$) β-effect is proven to be much smaller than the antiperiplanar ($\theta = 180°$) β-effect.[6–9]



Scheme 2

The β-effect providing low energy transition state and/or intermediates causing rate enhancement of up to 10^{12} with respect to model systems has been reported,[7] especially in solvolysis reactions of β-silylesters. The rate enhancement was remarkably high (~10^{12}) for antiperiplanar disposition, and moderately high (~10^4) when these groups are gauche or synperiplanar, compared with unsilylated analogues.

The existence of β-effect even in ground state has been noted by a low temperature X-ray structure study[10] of β-trimethylsilyl esters. The observed lengthening of the C–O bond when the Si–C–C–O dihedral angle is close to 180° is attributed to the β-effect. The measured lengthening of the ester C–O bond in



Scheme 1

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synperiplanar geometry was much smaller in comparison with that of antiperiplanar geometry and has been ascribed to much poorer vertical overlap between the σ-C–Si orbital and neighbouring σ*-C–O orbital.

The stereoelectronic requirement of β-silicon effect plays a crucial role in silanol elimination and has been extensively utilized in stereo- and regiospecific C=C bond forming reactions under acid as well as base-catalyzed conditions.[11] In acyclic systems of any diastereomeric form, a free rotation about the central C_α–C_β bond can bring the β-cation into the same plane as C–Si bond. However, in cyclic systems, only if ring conformations can allow antiperiplanar disposition of the silyl moiety with the β-OH group, the acid-catalyzed silanol elimination is possible.[3,12,13] Though some studies of acid-catalyzed hydrolysis of a few *cis*- and *trans*-1-trimethylsilyl-1,2-cycloalkanediols have been made, a thorough investigation on the conformational requirements of acid hydrolysis, and especially the related kinetic and thermodynamic data are lacking. The present study addresses these points.

The earlier studies by Lambert and co-workers[7–9] for assessing the β-silicon effect in different geometries were carried out for solvolysis reactions that are mechanistically quite different from silanol elimination.[1,2] The developing positive charge on β-carbon during silanol elimination, is predominantly stabilized by vertical participation **1** (Scheme 2). Thus, the dihedral angle of 180° is crucial for the silanol elimination.

In acyclic α,β-dihydroxysilanes, whether *erythro* or *threo*, the required antiperiplanar disposition of β-OH and $SiMe_3$ (*i.e.*, $\theta = 180°$) is easily attainable by free rotation about C_α–C_β bond. However, in cyclic systems the attainability of the all important 180° dihedral angle is decided by the conformational flexibility of the ring, which means the ring size of the silyldiol.

Stork and co-workers,[1] and Hudrlik and co-workers[2] have demonstrated smooth silanol elimination from both *erythro* and *threo* silyldiols of acyclic systems. Robbins and Whitham[3] observed that 1-trimethylsilyl-*trans*-1,2-cyclohexanediol obtained from acid hydrolysis of trimethylsilylcyclohexene epoxide was resistant to further reaction even under drastic conditions.

Though silanol eliminations have been studied for long, no attempt has been made to correlate their kinetic characteristics and thermodynamic parameters with ring structure. Most of the silanol eliminations were observed in *trans*-silyldiols derived from acyclic α,β-epoxysilanes and a few from the cyclic systems. In an earlier study[12] of the hydrolysis of cyclic α,β-epoxysilanes derived from different ring sizes (medium to large rings), we had noted that the medium ring (five and six membered) epoxysilanes provided the most stable *trans*-α,β-dihydroxysilanes which did not hydrolyze further to cycloalkanone while the 12-membered ring diol did.[12] The essentially *syn* stereochemistry of β-OH and $SiMe_3$ groups in medium rings prevented the attainment of antiperiplanar geometry, whereas in the large ring there was no such restriction. The trimethylsilylcycloheptene epoxide and the trimethylsilylcyclooctene epoxide did not give the expected silyldiols due to transannular hydride migration followed by loss of silyl group.[12,13]

Experimental

Materials

The silyldiols **3**–**8** were prepared as described previously.[14] All chemicals and solvents were purified by standard procedures. The identity and purity of the substrates and the products were ascertained by their physical and spectral data, and those of their derivatives.

GC analyses were carried out on a Varian Vista 6000 instrument using 15% FFAP on Chromosorb W column (2 m × 2 mm id). Temperature programming was as follows: initial temperature 80 °C, hold time 2 min, heating rate 5 °C min^{-1}, final temperature 180 °C. The injector and detector temperatures were 200 and 220 °C respectively.

Chromatographic methods

1 Thin layer chromatographic method. In a 25 mL flask, 1 mmol of the *cis*-diol was taken and dissolved in 3 mL of 1,4-dioxane. The flask was then placed in a water bath kept over a magnetic stirrer fitted with a temperature sensor (sensitivity ±0.2 °C). The desired temperature was set and when the bath had reached the set temperature, 0.5 mL of 1 M H_2SO_4 was added to the flask with a micro-pipette. The reaction was followed at regular intervals by TLC. The TLC was performed on glass plates coated with silica gel G and 10% ethyl acetate in petroleum ether was used as eluent. The chromatogram was developed in an iodine chamber. Initially the progress of the reaction was checked every 30 min. As the reaction proceeded, the rate slowed and the TLC was performed every hour. The diols had R_f values of 0.4 and the ketones 0.8. The reaction was taken to be complete when the diol spot could not be detected on the TLC plate. At this stage the contents of the flask were diluted with water (10 mL), the excess acid was neutralized with 10% $NaHCO_3$ solution and the ketone was extracted into ether (3 × 10 mL). The combined ether layers were washed with water (2 × 10 mL), saturated NaCl solution (10 mL) and dried over anhydrous Na_2SO_4. The solvent was removed on a rotary evaporator to obtain the ketone. The ketone was characterized by its IR spectrum and by its semicarbazone and oxime derivatives.

2 Gas chromatographic method. Into a 25 mL flask, 1 mmol of the *cis*-diol was weighed, and 3 mL of 1,4-dioxane and 150 mg of toluene were added. The flask was then placed in a water bath kept on a magnetic stirrer fitted with a temperature sensor (sensitivity ±0.2 °C). When the solution reached the desired temperature, 0.5 mL of 1 M H_2SO_4 was added to the flask with a micro-pipette. An aliquot of 0.1 mL was immediately drawn from the reaction mixture, two drops of saturated aqueous $NaHCO_3$ were added to neutralize the excess acid followed by 0.5 mL diethyl ether and shaken well. The ether layer was separated, dried, and injected (1 µL) into the GC. The peak areas of toluene and ketone were noted. The initial aliquot showed no ketone in the reaction mixture. Aliquots taken at regular intervals were worked up as above and injected (1 µL) into GC. The area percentage of ketone was found to increase with each injection. The percentage of ketone was measured relative to that of toluene. The reaction was assumed to be complete when the percentage of ketone relative to that of toluene remained constant for three successive measurements.

Quantitation of the chromatogram

Peak area normalization method was used to quantify the chromatogram.[15] To avoid the error due to variations in injection volume and aliquot dilution, the concentration of the cycloalkanone $[x]$ was measured relative to an internal standard. GC-pure toluene was used as an internal standard because it is inert under the reaction conditions and has a convenient retention time. The progress of hydrolysis was noted by increase in the concentration of cycloalkanone, and the reaction was assumed to be complete when three successive GC measurements showed the same concentration of cycloalkanone. Since a ketone is the only product of hydrolysis, its final concentration is a direct measure of the initial concentration of the diol [a]. The hydrolysis was carried out at three different temperatures (298, 313 and 328 K). Plotting ln $[a/a - x]$ against time (t) produced a straight line graph in each case, indicating that the rate of each reaction is first order in silyldiol. A typical kinetic plot is given in Fig. 1. The rate

Table 1 Hydrolysis of cyclic *cis*-α,β-dihydroxysilanes **3**–**6**. Rate constants and thermodynamic parameters

	Rate constant of hydrolysis $10^5\,k$ s^{-1}						
Diol	298 K	313 K	328 K	E_a/kJ mol^{-1}	$\Delta H^\ddagger$/kJ mol^{-1}	$\Delta S^\ddagger$/J K^{-1} mol^{-1}	$\Delta G^\ddagger$/kJ mol^{-1}
3	2.99	9.01	23.00	56.01	53.41 ± 0.11	−152.50 ± 3.17	101.13 ± 0.27
4	4.08	13.17	37.03	60.32	57.60 ± 0.06	−135.54 ± 3.42	100.17 ± 0.24
5	8.24	32.98	111.19	73.63	70.99 ± 0.06	−85.39 ± 4.20	97.82 ± 0.16
6	17.48	74.07	270.83	75.89	73.29 ± 0.06	−71.33 ± 4.31	95.65 ± 0.13

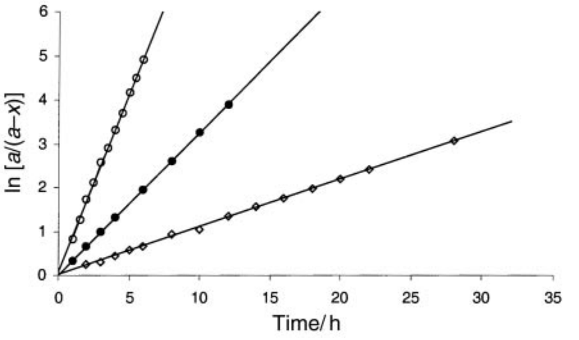


Fig. 1 Hydrolysis of silyldiol **3** at 298 K (○), 313 K (●), 328 K (◇).

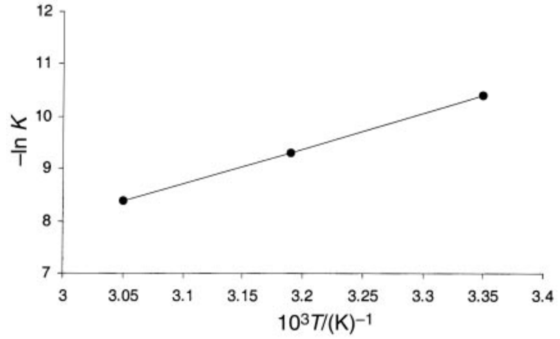


Fig. 2 Arrhenius plot (−ln k vs $1/T$) of hydrolysis of silyldiol **3**.

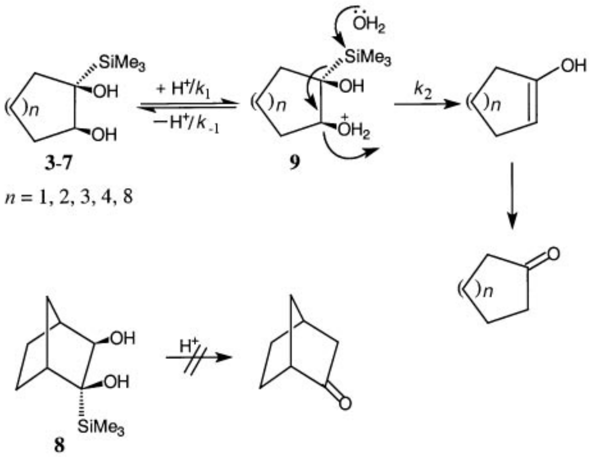
constants and energy of activation (E_a) were evaluated by standard procedures.[16] A representative Arrhenius plot (ln k vs. $1/T$) used to evaluate energy of activation is given in Fig. 2. The regression coefficient (r) was found to be >0.9997. The enthalpy of activation ($\Delta H^\ddagger$), entropy of activation ($\Delta S^\ddagger$), and the free energy of activation ($\Delta G^\ddagger$) were calculated using standard relations.[17] The rate constants and thermodynamic parameters are presented in Table 1.

Results and discussion

Complementary to our earlier observations, we have now observed that cyclic *cis*-α,β-dihydroxysilanes which have β-OH and SiMe$_3$ groups *anti* to each other in rings of all sizes hydrolyze smoothly to the corresponding cycloalkanones. A detailed kinetic study was carried out, and the findings clearly demonstrate the stereoelectronic requirement of β-silicon effect in silanol elimination reactions, and its relationship with the ring structure.

For the present study, six different cyclic *cis*-silyldiols comprising of five- and six-membered ring diols **3** and **4**, seven- and eight-membered ring diols **5** and **6**, one large ring (twelve-membered) diol **7**, and one rigid bicyclic diol **8** were used (Scheme 3), all of which evidently have the β-OH group *anti* to the SiMe$_3$ group. It should be noted that the two groups in **8** have the dihedral angle fixed at 120°, while in others it can attain 180°.

The silyldiols were prepared by *cis*-hydroxylation of the corresponding cyclic vinylsilanes using cetyltrimethylammonium permanganate.[14] The silanol elimination was carried out in 1,4-dioxane as the solvent and aqueous 1 M H_2SO_4 as catalyst (see Experimental section for details).



3-7

9

8

Scheme 3

As expected, the stereoelectronic requirement for silanol elimination could be easily attained by a small rotation in **3**–**7**, because the eliminating groups in the substrates have the *anti* stereochemistry. The diols **3**–**7** hydrolyzed smoothly to the corresponding cycloalkanones, while **8** was resistant to acid even at 75 °C, and decomposed on heating to 100 °C. A 60° rotation around C_2–C_3 bond in the anticlinal (120°) position of β-OH and SiMe$_3$ groups to secure the required perfect anti-periplanar geometry is prevented due to rigidity of the bicycloheptane system **8**.

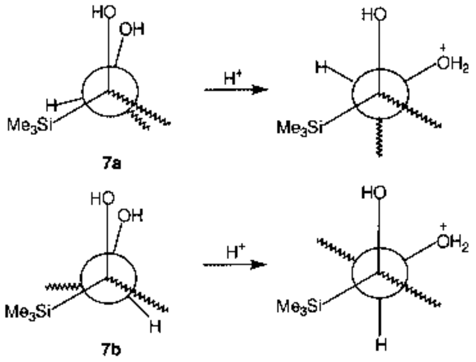
The hydrolytic elimination of diols **5** and **6** occurred smoothly without forming any transannular product. This is in contrast to what was noted during the hydrolytic opening of epoxides derived from trimethylsilylcycloheptene and trimethylsilylcyclooctene.[12]

The silyldiol **7** was a mixture of diastereomers **7a** and **7b**, formed from the *cis* hydroxylation of a 48 : 52 mixture of *cis*- and *trans*-trimethylsilylcyclododecene. Though the hydrolysis of the diastereomeric mixture was observed at room temperature, heating to 50 °C for 2 h was required for completion of the reaction. This may be attributed to the difference in solubilities of the diastereomers and the rapid conformational changes for attainment of antiperiplanar array (Scheme 4).

Kinetic results

To measure the rates of hydrolysis, the time required for each reaction was qualitatively estimated by TLC. However, the actual rate data were obtained by measuring the progress of the reaction by GC using an internal standard. The TLC method was useful in obtaining the approximate time required for hydrolysis and it also gave an idea about the susceptibility of the diol for hydrolysis. The method was applied to all the diols (**3**–**8**) at two different temperatures (298 and 313 K).

Kinetically, the silanol elimination is first order in silyldiol. Hence, by measuring the rate of consumption of the silyldiol

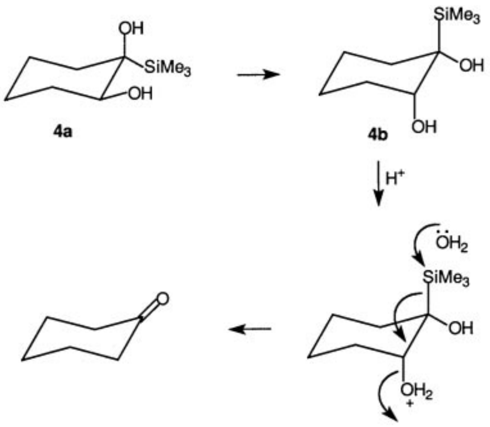


Scheme 4

or the rate of formation of cycloalkanone it is possible to get kinetic data. Since the hydrolysis product, the ketone, is a liquid, it is convenient to measure its concentration by the quantitation of gas chromatograms of aliquots taken at regular intervals during hydrolysis. However, this method was useful in measuring the concentration of cycloalkanones obtained in the hydrolysis of silyldiols **3**–**6**, but not **7** as it was not possible to measure accurately the concentration of cyclododecanone by GC.

The kinetic results were as expected. As the ring size increased, the conformational freedom increased,[18] and with that the rate of hydrolysis increased from the five-membered ring silyldiol to the eight membered one. The intramolecular hydrogen bonding is one factor that may influence the conformational characteristics of the silyldiols. This bonding is strongest in the five-membered ring *cis*-diol[18] and decreases along the series and reaches a minimum in the eight-membered ring, as observed in their IR spectra.[14] Though we have not been able to quantify this under our reaction conditions, the fact that each substrate has to follow a similar mechanistic pathway, as indicated by similar $\Delta G^\ddagger$ values, we consider that stronger intramolecular hydrogen bonding is at least partly responsible for the slower reaction rates in lower member diols (**3** and **4**) than in larger rings (**5** and **6**). Another factor that could influence the rate of elimination is the stereoelectronic effect, especially in six-membered ring silyldiol **4**. Since *trans* eliminations are most favoured in cyclohexane systems, the diol **4** was expected to hydrolyze faster than **5** and **6**. This turned out to be not the case. In the cyclohexane system (**4**) the only conformation that fulfills the requirement of leaving groups, *i.e.* $SiMe_3$ and β-OH, to be antiperiplanar is the one in which they are *trans* diaxial (**4b**). In **4** the preferred position for the bulky $SiMe_3$ group is naturally equatorial. Thus, the β-OH and $SiMe_3$ would be in a *trans*-diequatorial position (**4a**), which is a considerable deviation (60°) from the needed antiperiplanar geometry. For elimination to occur, the molecule has to transform such that $SiMe_3$ and β-OH groups attain the *trans*-diaxial geometry. This process entails some energy barrier that probably causes the hydrolysis of **4** to be slower than that of **5** and **6** (Scheme 5).

Though the rate of hydrolysis increased with ring size, it was noticed that the enthalpy of activation also increased along the series. The $\Delta H^\ddagger$ for the set of **3** and **4** are of similar value and those for the set of **5** and **6** are of similar value. Thus there is a significant difference between the $\Delta H^\ddagger$ values of the two sets. Though the reaction rates increased with temperature, which is on the expected lines, the rate enhancement for every 15 °C rise in temperature was higher for **5** and **6** (~4 times) than for **3** and **4** (~3 times). For an enthalpy controlled reaction, lower rate means higher enthalpy. However, in this case, though the rate of hydrolysis was higher for larger rings (**5** and **6**), the enthalpy of activation was also higher. This is an unexpected but interesting observation, which we believe may be explained in the following way.



Scheme 5

The silanol elimination is taking place from a protonated intermediate **9** (Scheme 3), which may be considered as the activated complex.[19] There would be a thermal equilibrium between the activated complex and the substrate. The critical configuration of **9**, *i.e.* antiperiplanar array, leads to the product. The rate at which **9** collapses to product would determine the rate of hydrolysis. The difference between the average energy of the reactant and that of the activated complex is the enthalpy of activation. It includes the difference in bond dissociation energy, conformational changes, strain, and solvation energy between the substrate and the activated complex. Since all these factors contribute to $\Delta H^\ddagger$, it is bound to vary from system to system. The activated complex seems to eliminate silanol faster in the larger ring diols (**5** and **6**) due to higher probability to attain the favourable conformation in these cases. This is perhaps determined by the proportion of different conformers present, governed by their relative energies and the Boltzmann distribution. The observed increasing trend in rate constants with increasing enthalpy must be ultimately controlled by entropy cancellation. The four atoms $Me_3Si–C_\alpha–C_\beta–{}^+OH_2$, and the attacking nucleophile H_2O must be in the same plane in the transition state. In order to achieve this specific orientation, the molecule must surrender the freedom it normally has to assume many possible forms in space, and adopt only the one that leads to elimination. Thus, there is a considerable loss of entropy, and $\Delta S^\#$ is negative. The $\Delta S^\ddagger$ for **3** and **4** involves reorganization of the conformationally more stable diequatorial geometry of the eliminating groups to the less stable diaxial geometry at some stage of formation of the transition state. It is reflected in the greater negative values of $\Delta S^\ddagger$ for these systems than in the case of the more agile **5** and **6** (Table 1). In the case of **8**, where this geometry is unattainable, the expected hydrolysis does not occur even at relatively high temperatures, and decomposition of the substrate takes place.

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References

1 (*a*) G. Stork and E. Colvin, *J. Am. Chem. Soc.*, 1971, **93**, 2080; (*b*) G. Stork and M. E. Jung, *J. Am. Chem. Soc.*, 1974, **96**, 3682; (*c*) G. Stork, *Pure. Appl. Chem.*, 1975, **43**, 553; (*d*) M. E. Jung, *Tetrahedron*, 1976, **32**, 3.

2 (*a*) P. F. Hudrlik and D. Peterson, *Tetrahedron Lett.*, 1974, 1133; (*b*) P. F. Hudrlik and D. Peterson, *J. Am. Chem. Soc.*, 1975, **97**, 1464; (*c*) P. F. Hudrlik, R. N. Misra, G. P. Withers, A. M. Hudrlik, R. J. Rona and J. P. Arcoleo, *Tetrahedron Lett.*, 1976, 1453;

(*d*) P. F. Hudrlik, J. P. Arcoleo, R. H. Schwartz, R. N. Misra and R. J. Rona, *Tetrahedron Lett.*, 1977, 591; (*e*) P. F. Hudrlik, R. H. Schwartz and A. K. Kulkarni, *Tetrahedron Lett.*, 1979, 2233.

3 C. Robbins and G. H. Whitham, *J. Chem. Soc., Chem. Commun.*, 1976, 697.

4 R. F. Cunico, *Tetrahedron Lett.*, 1986, **27**, 4269.

5 P. F. Hudrlik and A. K. Kulkarni, *J. Am. Chem. Soc.*, 1981, **103**, 6251.

6 J. B. Lambert, *Tetrahedron*, 1990, **46**, 2677; J. B. Lambert, *Acc. Chem. Res.*, 1999, **32**, 183.

7 J. B. Lambert, G. T. Wang, R. B. Finzel and D. H. Teramura, *J. Am. Chem. Soc.*, 1987, **109**, 7838.

8 (*a*) J. B. Lambert and E. C. Chelius, *J. Am. Chem. Soc.*, 1990, **112**, 8120; (*b*) J. B. Lambert, R. W. Emblidge and S. Malany, *J. Am. Chem. Soc.*, 1993, **115**, 1317.

9 (*a*) J. B. Lambert and G. T. Wang, *J. Phys. Org. Chem. I*, 1988, 169; (*b*) G. T. Wang, D. Li, E. C. Chelius and J. B. Lambert, *J. Chem. Soc., Perkin Trans. 2*, 1990, 331.

10 (*a*) V. Y. Chan, C. Clark, J. Giordano, A. J. Green, A. Karalis and J. M. White, *J. Org. Chem.*, 1996, **61**, 5227; (*b*) J. M. White and G. B. Robertson, *J. Org. Chem.*, 1992, **57**, 4638.

11 (*a*) I. Fleming, A. Barbero and D. Walter, *Chem. Rev.*, 1997, **97**, 2063; (*b*) D. J. Ager, *Org. React. (N.Y.)*, 1990, **38**, 1.

12 (*a*) G. Nagendrappa, *Tetrahedron*, 1982, **38**, 2429; (*b*) G. Nagendrappa and T. J. Vidyapathi, *J. Organomet. Chem.*, 1985, **31**, 280.

13 A. P. Davis, G. J. Hughes, P. R. Lowndes, C. M. Robbins, E. J. Thomas and G. H. Whitham, *J. Chem. Soc., Perkin Trans. 1*, 1981, 1934.

14 M. N. Mallya and G. Nagendrappa, *Synthesis*, 1999, 38.

15 (*a*) P. A. Sewell and B. Clarke, *Chromatographic Separations, ACOL (University of Greenwich)*, Wiley, Singapore, 1991, pp. 147–191; (*b*) I. A. Fowlis, *Gas Chromatography, ACOL (University of Greenwich)*, 2nd edn., Greenwich University press, Chichester, UK, 1995, pp. 158–175.

16 (*a*) J. March, *Advanced Organic Chemistry*, 4th edn., Wiley, New York, 1992, pp. 208–226; (*b*) N. S. Isaacs, *Physical Organic Chemistry*, Longman, UK, 1987, pp. 77–113.

17 K. J. Laidler, *Reaction Kinetics*, Pergamon Press, London, 1963, vol. 1.

18 E. L. Eliel, H. S. Wilen and L. N. Mander, *Stereochemistry of Organic Compounds*, Wiley, New York, 1994, pp. 665–811.

19 (*a*) G. W. Klumpp, *Reactivity in Organic Chemistry*, Wiley, New York, 1982, pp. 227–398; (*b*) K. J. Laidler, *Theories of Chemical Reaction Rates*, McGraw-Hill, New York, 1969, pp. 41–55.