Comparison of the Transition State Energies of Acid-Catalyzed Hydrations of Some 1-Methylcycloalkenes and Methylenecycloalkanes

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Hydration rates of 1-methylcyclobutene, methylenecyclobutane, 1-methylcyclopentene and methylenecyclopentane were measured spectrophotometrically in aqueous perchloric acid. The activation parameters and solvent deuterium isotope effects are in agreement with the rate-determining protonation of the double bond (A−S_E2 or Ad$_E$2 mechanism). The Gibbs energy difference between the transition states for hydration (protonation) of the *exo* and *endo* cycloalkenes was observed to be small (1.2 kJ mol^{-1}) in the case of the rigid cyclobutane derivatives and large (11.8 kJ mol^{-1}) in the case of the flexible cyclopentane derivatives, which is in agreement with earlier measurements with a rigid 2-methyl-2-norbornene/2-methylenenorbornane pair (0.8 kJ mol^{-1}) and with a flexible 1-methylcyclohexene/methylenecyclohexane pair (11.5 kJ mol^{-1}). The origin of the large differences is probably the changes of conformation occurring during the protonation of the flexible 1-methylcycloalkenes. The conformational changes possibly also cause small solvent deuterium isotope effects.

Recently, the transition state energies for acid-catalyzed hydration of the rigid olefins 2-methyl-2-norbornene (1) and 2-methylenenorbornane (2) were compared with those for the flexible olefins 1-methylcyclohexene (3) and methylenecyclohexane (4).[1] The energy difference between the *exo* and *endo* cycloalkenes was very small (0.8 kJ mol^{-1}) in the case of the bicyclic olefins 1 and 2, but rather large (11.5 kJ mol^{-1}) in the case of the monocyclic olefins 3 and 4. The mechanism of hydration was concluded to be the same, i.e. A−S_E2 of Ad$_E$2, in all cases, and thus the transition states for hydration are the transition states for the rate-determining protonation of the carbon-carbon double bond (Scheme 1).

The intermediate in the reaction, the 1-methyl-

1   2   3   4

5   6   7   8
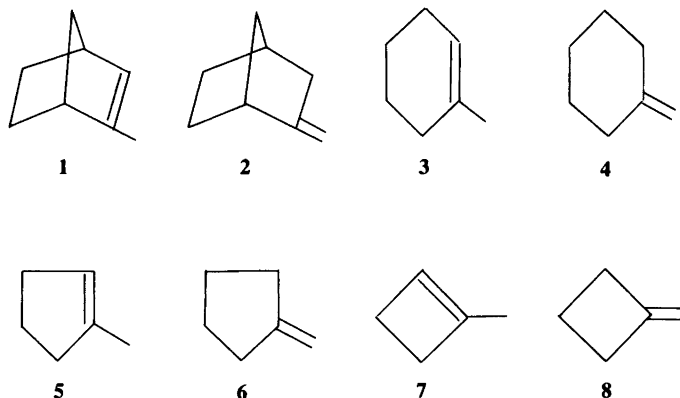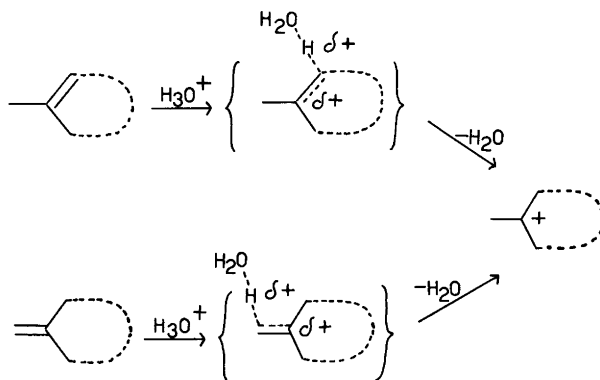
Scheme 1.

1-cycloalkyl cation, is common for the protonations of the *exo* and the *endo* cycloalkenes. Thus, the energies of the transition states should be quite similar (the transferring proton is very small) if the transition states lie close to the intermediate carbocation (this requirement is probably fulfilled),[2] and if there are no special effects prevailing in the protonation step. Evidently, such an effect does not exist in the protonation of the bicyclic olefins 1 and 2,[1] although the puckering of the double bond in the initial state could be a good candidate in the case of 2-methyl-2-norbornene.[3,4] The out-of-plane bending of the double bond and the unsymmetrical *p* orbitals would rationalize both the high rates of addition to norbornene and the occurrence of an attack mainly from the *exo* direction.[3,4] However, such a special effect seems to exist in the hydration of 1-methylcyclohexene, being probably a change of conformation during the protonation.[1]

To obtain more data for comparison, the acid-catalyzed hydrations of 1-methylcyclopentene (5) and methylenecyclopentane (6), which are rather flexible molecules like their cyclohexane analogs 3 and 4, and 1-methylcyclobutene (7) and methylenecyclobutane (8), which are quite rigid like their bicyclic analogs 1 and 2, were studied.

Experimental

Materials. 1-Methylcyclopentene (Aldrich, purity 99 % by GLC), methylenecyclopentane (Fluka AG, 98 %) and methylenecyclobutane (EGA-Chemie, 97 %, containing 3 % of spiropentane) were used without further purification. 1-Methylcyclobutene was prepared by isomerization of methylenecyclobutane on sodium-on-alumina

catalyst.[5] Its purity was 75 % and it contained 19 % of starting material, 3 % of spiropentane and a total of 3 % of three unidentified hydrocarbons. The substrates were analyzed by capillary gas chromatography (XE 60 column) and by IR, ^{1}H NMR and ^{13}C NMR spectroscopy.[5–9]

Kinetic measurements. The disappearance of the substrates in aqueous perchloric acid was followed by UV spectroscopy at 195 nm without nitrogen atmosphere.[1] The solubility of the olefins was poor and thus low initial concentrations (ca. 3×10^{-4} mol dm^{-3}) were used. The first-order rate constants were calculated from linear correlations between $\ln(A_t - A_\infty)$ (A = absorbance) and time (t). Fair linear correlations were obtained for 1-methylcyclopentene and methylenecyclobutane ($r \geq 0.999$), but the plots for methylenecyclopentane were generally slightly curved for the reaction in HClO$_4$ (linear for DClO$_4$), possibly due to isomerization of the substrate to its more stable isomer, 1-methylcyclopentene. In the case of the curved plots the initial slopes were employed for calculations of the rate constants.

The hydration rate constants for 1-methylcyclobutene (7), which contained 19 % of methylenecyclobutane (8), were calculated on an SM 5 computer from eqn. (1)

$$\frac{A_0 - A_t}{A_0 - A_\infty} = a(1 - e^{-k_7 t}) + (1 - a)(1 - e^{-k_8 t}) \quad (1)$$

where A_0, A_t and A_∞ are absorbances of the impure substrate in the beginning, at time t and at the end of a run (ca. 10 half-lives); a stands for $[A_7/(A_7 + A_8)]_0$, *i.e.* the contribution of 7 of the total initial absorbance (spiropentane causes no

253

noteworthy absorbance at 195 nm), and k_7 and k_8 are the first-order rate constants for isomers **7** and **8**. The rate constants calculated for the impurity by eqn. (1) were similar (to within 20 %) to those measured for pure methylenecyclobutane.

All measurements of the rate constants were repeated at least once, often several times, and their values were generally in agreement to within 5 %.

Product analyses. The hydration products of all four olefins were studied by stirring ca. 1 g of the substrate with 50 cm³ of 1 mol dm⁻³ HClO₄ at room temperature for 15–20 half-lives in a tightly stoppered flask. The solution was extracted with CH_2Cl_2, the organic solution was dried over K_2CO_3 and Na_2SO_4, the solvent was distilled off carefully and the residue was analyzed by GLC and IR, and by ¹H and ¹³C NMR spectroscopy.[10,11] The only product from 1-methylcyclopentene and methylenecyclopentane was 1-methyl-1-cyclopentanol and the only product from methylenecyclobutane was 1-methyl-1-cyclobutanol, which was also the dominant

Table 1. Rate constants for hydration of 1-methylcyclopentene (**5**), methylenecyclopentane (**6**), 1-methylcyclobutene (**7**) and methylenecyclobutane (**8**) in 1.00 mol dm⁻³ aqueous HClO₄ at different temperatures, and activation parameters and solvent deuterium isotope effects at 298.2 K.

Substrate	Temp./K	$k_1/10^{-4}$ dm³ mol⁻¹ s⁻¹	Activation parameters and solvent isotope effects.
5	283.2	2.59	
	288.2	5.18	
	293.2	9.68	
	298.2	18.3	
	298.2	17.5[a]	$\Delta G^{\neq} = 88.76 \pm 0.06$ kJ mol⁻¹
	298.2	15.2[b]	$\Delta S^{\neq} = -11 \pm 7$ J K⁻¹ mol⁻¹
	303.2	30.1	$\Delta H^{\neq} = 86 \pm 2$ kJ mol⁻¹
	308.2	41.9[c]	$k_H/k_D = 1.20 \pm 0.01$
6	283.2	38.9	
	288.2	70.1	
	293.2	116.0	
	298.2	164	$\Delta G^{\neq} = 83.12 \pm 0.08$ kJ mol⁻¹
	298.2	170[a]	$\Delta S^{\neq} = -65 \pm 10$ J K⁻¹ mol⁻¹
	298.2	98.2[b]	$\Delta H^{\neq} = 64 \pm 3$ kJ mol⁻¹
	303.2	256	$k_H/k_D = 1.67 \pm 0.06$
7	288.2	0.383	
	293.2	0.884	
	298.2	1.60	
	298.2	1.59[a]	$\Delta G^{\neq} = 94.70 \pm 0.09$ kJ mol⁻¹
	298.2	1.134[b]	$\Delta S^{\neq} = +4 \pm 13$ J K⁻¹ mol⁻¹
	303.2	2.81	$\Delta H^{\neq} = 96 \pm 4$ kJ mol⁻¹
	308.2	6.02	$k_H/k_D = 1.41 \pm 0.14$
8	283.2	0.650	
	288.2	1.45	
	293.2	2.86	
	298.2	5.89	
	298.2	5.63[a]	$\Delta G^{\neq} = 91.57 \pm 0.07$ kJ mol⁻¹
	298.2	4.12[b]	$\Delta S^{\neq} = 17 \pm 8$ J K⁻¹ mol⁻¹
	303.2	10.38	$\Delta H^{\neq} = 97 \pm 2$ kJ mol⁻¹
	308.2	17.7[c]	$k_H/k_D = 1.43 \pm 0.02$

[a]Calculated from the activation parameters. [b]Measured in DClO₄(D₂O). [c]Excluded from the calculations of the activation parameters.
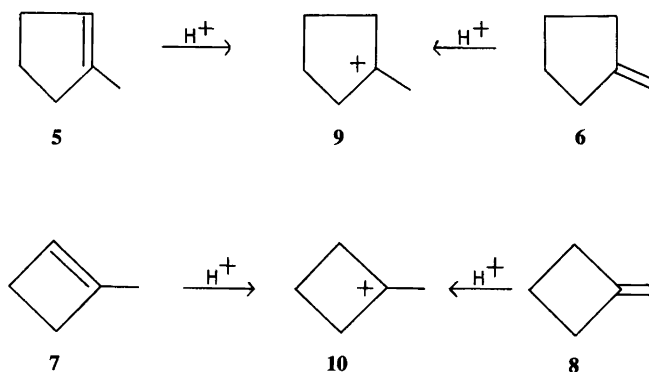
Scheme 2.

($\geqslant 90\%$) product from 1-methylcyclobutene (small, unidentified extra peaks were seen in the ^{13}C NMR spectrum).

Results and discussion

The hydration rate constants for the cycloalkenes 5–8 in 1.00 mol dm^{-3} aqueous perchloric acid at different temperatures are listed in Table 1 together with the activation parameters and solvent deuterium isotope effects. The rate constants and isotope effect for 1-methylcyclopentene at 298.2 K are very similar to those measured by Tidwell *et al.*[12] in 1 mol dm^{-3} sulfuric acid, and the rate constants for the cyclobutane derivatives 7 and 8 are in fair agreement with those measured by Taft *et al.*[13] in 0.973 mol dm^{-3} nitric acid, especially

when one takes into account the rather complicated experimental method used by the Taft group.

The negative activation entropies of hydration for the cyclopentane derivatives 5 and 6 (Table 1) are typical of the slow proton transfer from a hydronium ion to the carbon-carbon double bond (A–S$_E$2 or Ad$_E$2 mechanism),[14] but the slightly positive values for the cyclobutane derivatives are not general in the case of this mechanism, although not unique either.[15] The solvent deuterium isotope effects are also typical of the slow protonation of the double bond in strong mineral acid.[1,12,14]

1-Methylcyclopentene and methylenecyclopentane produce on protonation (Scheme 2) a 1-methyl-1-cyclopentyl cation (9), which is
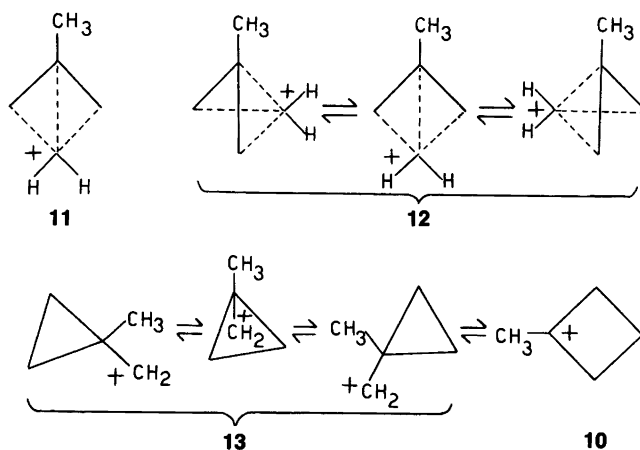
Scheme 3.

quickly decomposed by water to 1-methyl-1-cy-clopentanol. In the protonation of 1-methylcyclo-butene and methylenecyclobutane, the interme-diate is a 1-methyl-1-cyclobutyl cation (10), which produces 1-methyl-1-cyclobutanol in the aqueous solution. The structure of the cation 10 has been of great interest.[10,16–18] According to the most recent deuterium isotope perturbation stud-ies, the ^{13}C NMR spectra of the cation under sta-ble ion conditions are consistent with a symmetri-cal σ-bridged methylcyclobutonium structure (11) at 119 K[17,18] and with either the degenerate equilibrium mixture of three bicyclobutonium ions (12)[17] or the rapidly equilibrating bisected σ-delocalized 1-methylcyclopropylcarbinyl cations (13) exchanging through the classical 1-methylcy-clobutyl cation (10)[18] at higher temperatures (183–223 K) (Scheme 3).

If the equilibrium constants for the 1-methylcy-cloalkenes and methylenecycloalkanes are known, the energy differences between the tran-sition states for protonation can be calculated for the *endo* and *exo* cycloalkenes from their Gibbs energies of activation (Table 1). The equilibrium constants have been measured at 298.2 K without solvent over sodium-on-alumina catalyst for the cyclopentane compounds [$K(6 \rightleftharpoons 5)$ = 1084 ± 54 kJ mol^{-1}] and for the cyclobutane derivatives [$k(8 \rightleftharpoons 7)$ = 5.66 ± 0.16 kJ mol^{-1}].[19] The former value is in fair agreement with that (1144 ± 51) measured in acetic acid with *p*-toluenesulfonic acid as catalyst at the same temperature.[20] Thus, it is probable that the equilibrium constants are also similar in aqueous perchloric acid.

The Gibbs energy diagrams are presented in Figs. 1 and 2. They show that the energies of the transition states for protonation of the methylene-cycloalkanes are higher than those for the 1-methylcycloalkenes in both cases. The differ-ence is large (11.8 kJ mol^{-1}) for the cyclopentane derivatives and very similar to that (11.5 kJ mol^{-1}) measured for the corresponding cyclohex-
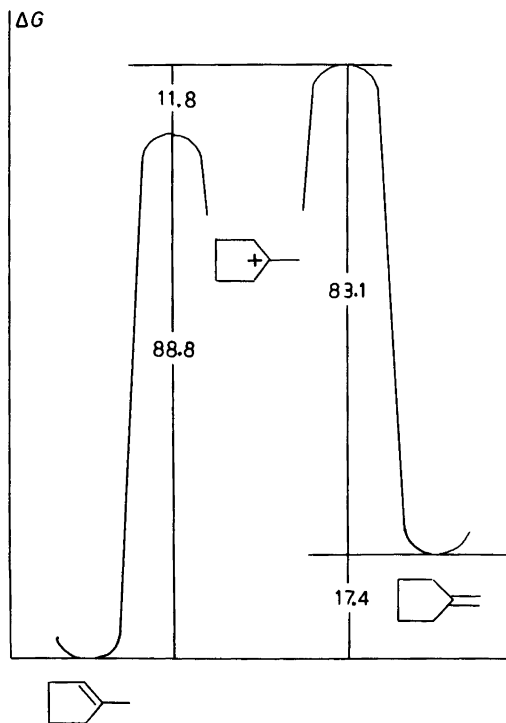

Fig. 1. The Gibbs energy diagrams for protonation (hydration) of 1-methylcyclopentene and methylene-cyclopentane in 1.0 mol dm⁻³ aqueous perchloric acid at 298.2 K (numerical values in kJ mol⁻¹).
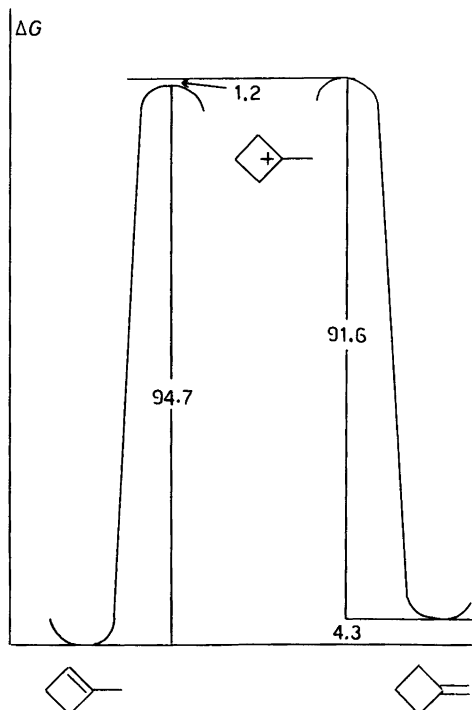
Fig. 2. The Gibbs energy diagrams for protonation (hydration) of 1-methylcyclobutene and methylene-cyclobutane in 1.0 mol dm⁻³ aqueous perchloric acid at 298.2 K (numerical values in kJ mol⁻¹).

ane derivatives 3 and 4; however, the difference is small (1.2 kJ mol^{-1}) for the cyclobutane derivatives, as it was (0.8 kJ mol^{-1}) for the norbornane compounds 1 and 2.[1] The observations inspired us to search for similarities in the protonations of the cyclopentane and cyclohexane olefins, and in the protonations of the cyclobutane and norbornane olefins.

The large difference in the transition state energies for protonation of 1-methylcyclohexene and methylenecyclohexane was recently suggested to be due to the conformational change between 1-methylcyclohexene and the 1-methylcyclohexyl cation, and not due to any change of conformation in the protonation of methylenecyclohexane.[1] A similar rationalization is also possible for the protonation of the cyclopentane olefins. The most stable conformation of 1-methylcyclopentene is an envelope, and that of methylenecyclopentane is a twist or half-chair,[21,22] the latter also being the probable conformation of the 1-methylcyclopentyl cation according to NMR deuterium isotope perturbation studies[23] (MINDO/3 calculations, however, suggest a flat envelope conformation, although both planar and slight twist conformations are very close to it in energy[23]). Thus, the favourable conformational change takes place in the protonation of 1-methylcyclopentene but not in that of methylenecyclopentane.

The conformation of 1-methylcyclobutene is evidently rigid planar, and that of methylenecyclobutane is nearly planar according to molecular models (a slight pucker is, however, probable when the barrier to planarity is 1.92 kJ mol^{-1}).[24,25] The conformation of the 1-methylcyclobutyl cation in aqueous media at ambient temperatures is unknown, because its structure is unknown (see above). According to MO calculations (which refer to the gas phase), it may be a planar classical 1-methylcyclobutyl cation (10), a puckered methylbicyclobutonium cation (11) or a bisected 1-methylcyclopropylcarbinyl cation (13), all of which represent energy minima, or it may be an equilibrium mixture of them all.[26–28] The possibility of the planar cation 10 being the initial 1-methylcyclobutyl cation formed in protonation is consistent with the small difference between the energies of the transition states for protonation of 1-methylcyclobutene and methylenecyclobutane, since no marked conformational changes are needed.

The solvent deuterium isotope effects are of interest because of the rather low value (k_H/k_D = 1.20) measured for the hydration (protonation) of 1-methylcyclopentene. A still lower value (1.13) was recently measured for 1-methylcyclohexene.[1] They both possibly reflect the conformational changes occurring between the initial states and the transition states, since the values measured for methylenecyclopentane (1.67) and methylenecyclohexane (1.51) are normal, as are also those for 1-methylcyclobutene (1.41), methylenecyclobutane (1.43) and 2-methylenenorbornane (1.67),[1] whose protonation does not cause any considerable changes of conformation. The high value for the rigid 2-methyl-2-norbornene (2.15), however, shows that there are also other factors, e.g. reaction rate and/or acid concentration, which influence the isotope effect.[12,29]

Generally, the magnitudes of isotope effects seem to be within narrower limits (1.43–1.86) for the protonation of the methylenecycloalkanes than for the protonation of the 1- (or 2-) methylcycloalkenes (1.13–2.15; data for 7 pairs of isomers from this work and from Refs. 1 and 15). An explanation may be the smaller structural changes occurring in the former case than in the latter case.

References

1. Lajunen, M. and Hiukka, R. *J. Org. Chem. 51* (1986) 1522.
2. Lajunen, M. and Andersson, A. *Acta Chem. Scand., Ser. A 36* (1982) 371.
3. Inagaki, S., Fujimoto, H. and Fukui, K. *J. Am. Chem. Soc. 98* (1976) 4054.
4. Spanget-Larsen, J. and Gleiter, R. *Tetrahedron 39* (1983) 3345.
5. Shabtai, J. and Gil-Av, E. *J. Org. Chem. 28* (1963) 2893.
6. Pouchert, C. J. *The Aldrich Library of Infrared Spectra,* Aldrich Chemical Co. 1970, pp. 29G and 30G.
7. Becker, K. B. *Helv. Chim. Acta 60* (1977) 68.
8. Thummel, R. P. and Nutakul, W. *J. Org. Chem. 43* (1978) 3170.

9. Klessinger, M., van Megen, H. and Wilhelm, K. *Chem. Ber. 115* (1982) 50.
10. Kirchen, R. P. and Sorensen, T. S. *J. Am. Chem. Soc. 99* (1977) 6687 and references therein.
11. Servis, K. L. and Shue, F.-F. *J. Am. Chem. Soc. 102* (1980) 7233.
12. Chwang, W. K., Nowlan, V. J. and Tidwell, T. T. *J. Am. Chem. Soc. 99* (1977) 7233.
13. Riesz, P., Taft, R. W., Jr. and Boyd, R. H. *J. Am. Chem. Soc. 79* (1957) 3724.
14. Lajunen, M. *Acc. Chem. Res. 18* (1985) 254 and references therein.
15. Lajunen, M. and Lyytikäinen, H. *Acta Chem. Scand., Ser. A 35* (1981) 131.
16. Olah, G. A., Prakash, G. K. S., Donovan, D. J. and Yavari, I. *J. Am. Chem. Soc. 100* (1978) 7086.
17. Siehl, H.-U. *J. Am. Chem. Soc. 107* (1985) 3390.
18. Prakash, G. K. S., Arvanaghi, M. and Olah, G. A. *J. Am. Chem. Soc. 107* (1985) 6017.
19. Herling, J., Shabtai, J. and Gil-Av, E. *J. Am. Chem. Soc. 87* (1965) 4107.
20. Cope, A. C., Ambros, D., Ciganek, E., Howell, C. F. and Jacura, Z. *J. Am. Chem. Soc. 82* (1960) 1750.
21. Scholz, M. and Köhler, H.-J. *Tetrahedron 25* (1969) 1863.
22. Allinger, N. L., Dodziuk, H., Rogers, D. W. and Naik, S. N. *Tetrahedron 38* (1982) 1593.
23. Botkin, J. H., Forsyth, D. A. and Sardella, D. J. *J. Am. Chem. Soc. 108* (1986) 2797.
24. Scharpen, L. H. and Laurie, V. W. *J. Chem. Phys. 49* (1968) 3041.
25. Burkert, U. and Allinger, N. L. *Molecular Mechanics,* ACS Monograph 177, The American Chemical Society, Washington 1982, p. 125.
26. Davis, R. E., Murthy, A. S. N. and Ohno, A. *Tetrahedron Lett.* (1968) 1595.
27. Olah, G. A., Spear, R. J., Hiberty, P. C. and Hehre, W. J. *J. Am. Chem. Soc. 98* (1976) 7470.
28. Levi, B. A., Blurock, E. S. and Hehre, W. J. *J. Am. Chem. Soc. 101* (1979) 5537.
29. Kresge, A. J., Sagatys, D. S. and Chen, H. L. *J. Am. Chem. Soc. 99* (1977) 7228.