Structural Effects in Solvolytic Reactions. 48. Rates of Ethanolysis of Camphene Hydrochloride and Related α-Methyl-Substituted 1-Chloro-1-methylcyclopentanes. Is the Rate of Ethanolysis of Camphene Hydrochloride Exceptionally High?[1]

Herbert C. Brown,* Frank J. Chloupek,[2a] and Ken'ichi Takeuchi[2b]

Richard B. Wetherill Laboratory, Purdue University, West Lafayette, Indiana 47907

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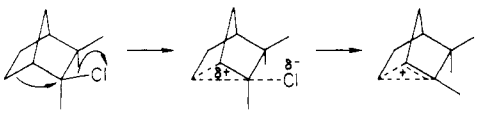
The rate of ethanolysis of camphene hydrochloride at 25 °C is remarkably faster (×13600) than that of *tert*-butyl chloride. To understand whether this is indicative of nonclassical participation of the C1–C6 electron cloud in the ionization of camphene hydrochloride, the rates of ethanolysis of 1-chloro-1-methylcyclopentane and its α-methyl-, α,α,α′-trimethyl-, and α,α,α′,α′-tetramethyl-substituted derivatives and of *exo*-2-chloro-*endo*-2-methylnorbornane were measured at 25 °C. The results show not only that the rates of ethanolysis of the 1-chloro-1-methylcyclopentanes increase progressively with increasing methyl substitution but also that the rate of ethanolysis of camphene hydrochloride is only 5.7 times higher than that of 1-chloro-1,2,2,5-tetramethylcyclopentane (a far better model than *tert*-butyl chloride for camphene hydrochloride). This shows clearly that the ethanolysis rate of camphene hydrochloride is not exceptionally high and provides no justification to invoke nonclassical participation of the C1–C6 bond in its ionization. It would have been highly desirable to have the endo isomer of camphene hydrochloride for a solvolysis study. Regretfully, it is not accessible. However, the rates of solvolysis of *exo*- and *endo*-2,3,3-trimethyl-2-norbornyl *p*-nitrobenzoates were studied in 80% acetone at 25 °C. A comparison of these rates with those of 1-methylcyclopentyl and *exo*- and *endo*-2-methyl-2-norbornyl *p*-nitrobenzoates clearly shows that the exo compounds reveal comparable modest factors (relative rate: 1-methylcyclopentyl, 1.00; 2-methyl-*exo*-2-norbornyl, 4.7; 2,3,3-trimethyl-*exo*-2-norbornyl, 49). It is the rates for the endo derivatives that reveal far more significant factors (relative rate: 1-methylcyclopentyl, 1.00; 2-methyl-*endo*-2-norbornyl, 0.00536; 2,3,3-trimethyl-*endo*-2-norbornyl, 0.0109). Consequently, compared to a reasonable model, 1-methylcyclopentyl, it is not the fast rates of the *exo*-norbornyl derivatives that are distinctive but rather the exceptionally slow rates of the *endo*-norbornyl derivatives.

Three major foundations have been proposed supporting the intervention of σ-bridged (nonclassical) cations in the solvolysis of 2-norbornyl derivatives: (i) unusually fast rates of solvolysis for the exo derivatives,[3] (ii) high exo:endo rate ratios in the solvolysis of 2-norbornyl substrates,[4] (iii) high exo substitution products in the solvolysis of both exo and endo derivatives.[5]

The first foundation is indicated by the Ingold proposal[3] that the solvolysis of camphene hydrochloride (1) must proceed with σ-bridging to a nonclassical ("synartetic") ion (eq 1). He observed that the rate of ethanolysis of



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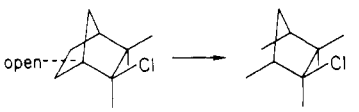
camphene hydrochloride is 13600 times[6] that of *tert*-butyl chloride. It was his opinion that this very high rate could not be accounted for by relief of steric strain as the chloride ion departs the highly sterically congested environment at C2 (1). Consequently, he proposed to account for the fast rate of **1** in terms of σ-participation (eq 1).

In such rate comparisons it is essential that a valid model be used. It appeared to us that *tert*-butyl chloride was not a valid model. It had none of the conformational forces present in norbornyl and similar derivatives. A better model would be the cyclopentane derivative **2**, obtained by opening the C5–C6 bond of **1**.



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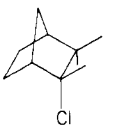
Accordingly, we undertook to examine the rates of solvolysis of 1-chloro-1-methylcyclopentane and its various methyl-substituted derivatives.[7] We report the details of that study in this paper. We also thought that another way of checking whether the rate for camphene hydrochloride is really "unusual" would be to study the rate of solvolysis of the endo isomer of camphene hydrochloride (**3**). Regretfully this compound is not accessible. However,



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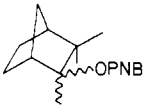
both the exo and endo isomers of 2,3,3-trimethyl-2-norbornyl *p*-nitrobenzoates (**4**) are readily synthesized.



4a, exo, OPNB; endo, CH_3
b, exo, CH_3; endo, OPNB

(1) For a preliminary communication, see: Brown, H. C.; Chloupek, F. J. *J. Am. Chem. Soc.* **1963**, *85*, 2322.

(2) (a) Postdoctoral research associate on a grant provided by the United States Atomic Energy Commission. (b) Graduate research assistant on grants (G 19878 and GP 6492X) from the National Science Foundation.

(3) Brown, F.; Hughes, E. D.; Ingold, C. K.; Smith, J. F. *Nature (London)* **1951**, *168*, 65.

(4) Winstein, C.; Trifan, D. S. *J. Am. Chem. Soc.* **1952**, *74*, 1147, 1154.

(5) (a) Berson, J. A. In "Molecular Rearrangements"; de Mayo, P., Ed.; Interscience: New York, 1963; Vol. 1, Chapter 3. (b) Reference 4.

(6) Ingold reports a rate factor of 6000 between camphene hydrochloride and *tert*-butyl chloride. Our results, however, show that it is 13600. The apparent discrepancy arises from the rate constant for *tert*-butyl chloride, which was not given explicitly in ref 3.

(7) Suitably substituted 1-chloro-1-methylcyclopentanes are better models for camphene hydrochloride than *tert*-butyl chloride is, since they possess many of the bond opposition forces present in camphene hydrochloride, which are partially relieved during ionization.

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Table I. Rates of Ethanolysis at 25 °C of Camphene Hydrochloride, *exo*-2-Chloro-*endo*-2-methylnorbornane, and Related α-Methyl-Substituted 1-Chloro-1-methylcyclopentanes

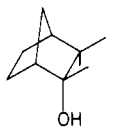
compd	10^6k_1, s^{-1}	rel rates			
tert-butyl chloride	0.85	1.00			
camphene hydrochloride (1)	1160	13600[a,b]	206	5.7	
exo-2-chloro-*endo*-2-methylnorbornane (7)	30.2	355	5.4		2.1
1-chloro-1-methylcyclopentane (8)	5.62	66	1.00		
1-chloro-1,2-dimethylcyclopentane (9)	14.5[c]	171	2.6		1.0
	10.6[d]	125	1.9		
1-chloro-1,2,2,5-tetramethylcyclopentane (10)	202	2380	36	1.00	
1-chloro-1,2,2,5,5-pentamethylcyclopentane (11)	458	5390	82		

[a] Our rate constant at 0 °C, 37.2×10^{-6} s^{-1}, is in reasonable agreement with the earlier value.[3] [b] See ref 6 for an explanation. [c] Chloride from *cis*-1,2-dimethylcyclopentanol. [d] Chloride from *trans*-1,2-dimethylcyclopentanol.

Consequently, we studied their rates of solvolysis in 80% aqueous acetone. In this paper, we compare the rates of solvolysis of **4a,b** with suitable model compounds such as 1-methylcyclopentyl and *exo*- and *endo*-2-methyl-2-norbornyl *p*-nitrobenzoates.

Results and Discussion

Synthesis. Camphene hydrochloride (1) was prepared from camphene and dry HCl as well as from methyl camphenilol (5) by the reported procedure.[8] The various



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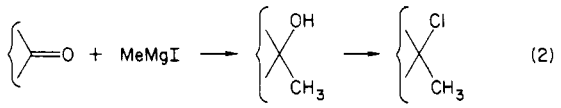
methyl-substituted 1-chloro-1-methylcyclopentanes were prepared by the conversion of the corresponding tertiary alcohols into the chlorides by reported procedure.[8] The tertiary alcohols were prepared by the treatment of the corresponding ketones with MeMgI (eq 2). 2-*exo*-



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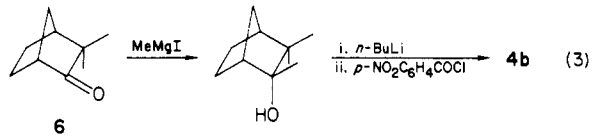
Chloro-2-*endo*-methylnorbornane was prepared by the method of Toivonen et al.[9]

2,3,3-Trimethyl-*endo*-2-norbornyl *p*-nitrobenzoate (**4b**) was prepared by the addition of MeMgI to camphenilone (6), followed by esterification with *p*-nitrobenzoyl chloride[10] (eq 3). The exo ester **4a**, was prepared by the conversion



6 5 (3)

of the endo alcohol **5** into the chloride, followed by solvolysis of the chloride to yield the *exo*-alcohol,[11] which was subsequently esterified (eq 4).

5 (4)

(8) Brown, H. C.; Kornblum, R. B. *J. Am. Chem. Soc.* **1954**, *76*, 4510.
(9) Toivonen, N. J.; Siltanen, E.; Ojala, K. *Ann. Acad. Sci. Fenn., Ser. A2* **1955**, *64*, 11.
(10) Brown, H. C.; Peters, E. N. *J. Am. Chem. Soc.* **1975**, *97*, 1927.
(11) Brown, H. C.; Takeuchi, K.; Ravindranathan, M. *J. Am. Chem. Soc.* **1977**, *99*, 2684.

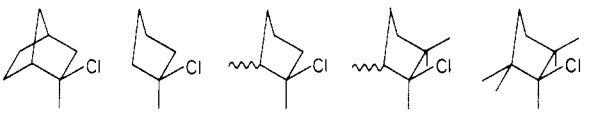
Table II. Rates of Solvolysis of 2,3,3-Trimethyl-2-norbornyl *p*-Nitrobenzoates and Related Derivatives in 80% Aqueous Acetone at 25 °C

p-nitrobenzoate	10^6k_1, s^{-1} 25 °C[a]	rel rate	rate ratio exo:endo
1-methylcyclopentyl[b]	2.11×10^{-3}	1.00	
2-methyl-*exo*-norbornyl[c]	1.00×10^{-2}	4.74	885
2-methyl-*endo*-norbornyl[c]	1.13×10^{-5}	0.00536	
2,3,3-trimethyl-*exo*-norbornyl[d]	1.04×10^{-1}	49.3	4500
2,3,3-trimethyl-*endo*-norbornyl[e]	2.31×10^{-5}	0.0109	

[a] Calculated from higher temperatures. [b] Brown, H. C.; Hammar, W. J. *J. Am. Chem. Soc.* **1967**, *89*, 6378. [c] See ref 14 for details. [d] $k_1^{50} = 3.25 \times 10^{-6}$ s^{-1}; $k_1^{75} = 61.8 \times 10^{-6}$ s^{-1}; $\Delta H^{\ddagger} = 25.8$ kcal/mol^{-1}; $\Delta S^{\ddagger} = -4.1$ eu. [e] $k_1^{100} = 0.867 \times 10^{-6}$ s^{-1}; $k_1^{125} = 12.0 \times 10^{-6}$ s^{-1}; $\Delta H^{\ddagger} = 30.4$ kcal/mol^{-1}; $\Delta S^{\ddagger} = -5.1$ eu.

Rates of Solvolysis. The rates of ethanolysis of camphene hydrochloride, *tert*-butyl chloride, 1-chloro-1-methylcyclopentane, 2-*exo*-chloro-*endo*-methylnorbornane, and the various methyl-substituted 1-chloro-1-methylcyclopentane derivatives were determined by a titrimetric procedure[10] at 25 °C. The data are provided in Table I. The rates of solvolysis of *exo*- and *endo*-2,3,3-trimethyl-2-norbornyl *p*-nitrobenzoates, along with those of the models in 80% acetone at 25 °C,[10] are provided in Table II.

Rates of Ethanolysis of Camphene Hydrochloride and the Related Tertiary Chlorides. The rate of ethanolysis of camphene hydrochloride (1) is 13600 times greater than that of *tert*-butyl chloride.[6] As discussed before, *tert*-butyl chloride is not a valid model for evaluating whether the rate of ethanolysis of **1** is unusual or not. The ideal model would be **2**, realized formally by opening the 5,6-bond of camphene hydrochloride. However, the difficulties involved in the synthesis of this particular structure led us to examine somewhat simpler model compounds (7–11). The data, provided in Table I, show



7 8 9 10 11

clearly that compared to 1-chloro-1-methylcyclopentane (8), camphene hydrochloride solvolyzes only 206 times faster. Introduction of a methyl group in the α-position of 1-chloro-1-methylcyclopentane increases the rate of solvolysis by a factor of approximately 2. Two more methyl groups in the α′-position increase the solvolysis rate sharply. Thus, 1-chloro-1,2,2,5-tetramethylcyclopentane (10) undergoes ethanolysis 36 times faster than 1-chloro-1-methylcyclopentane (8). 1-Chloro-1,2,2,5,5-pentamethylcyclopentane reacts even faster. These rate enhancements are clearly explicable in terms of steric assistance to ionization.[12]

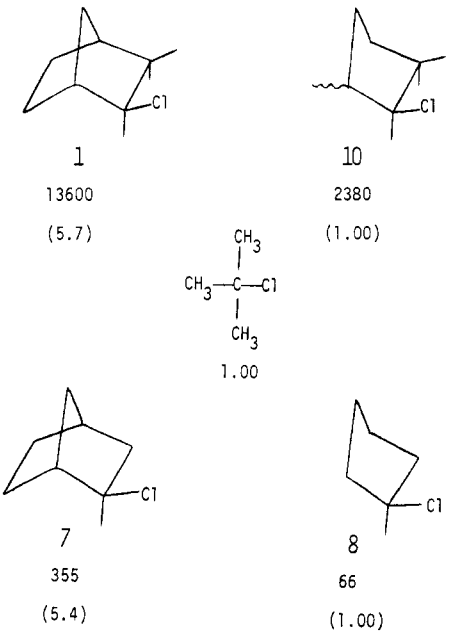


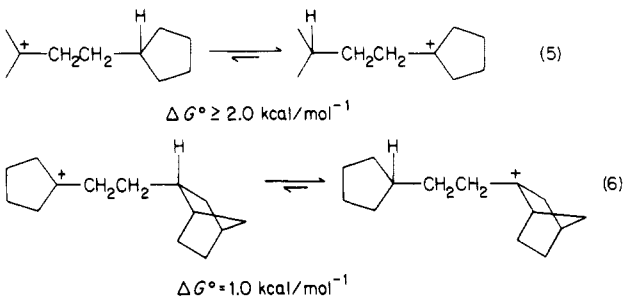
Figure 1. Relative rates of ethanolysis at 25 °C for camphene hydrochloride and *exo*-2-chloro-*endo*-2-methylnorbornane compared to *tert*-butyl chloride and suitably substituted 1-chloro-1-methylcyclopentanes as models.

A comparison of the relative rates of solvolysis of camphene hydrochloride (**1**) and *exo*-2-chloro-*endo*-2-methylnorbornane (**7**) with those of *tert*-butyl chloride and suitably substituted 1-chloro-1-methylcyclopentanes as models is illustrated in Figure 1. The cyclopentane derivative **10** is a very good model for camphene hydrochloride. The latter reacts only 5.7 times faster than this model although the rate factor is 13 600 with respect to *tert*-butyl chloride. Similarly, *exo*-2-chloro-*endo*-2-methylnorbornane (**7**) reacts only 5.4 times faster than 1-chloro-1-methylcyclopentane (**8**). (Again, **7** solvolyzes 355 times faster than *tert*-butyl chloride.) These rate factors (×5.7, ×5.4), modest in magnitude, probably arise from the differences in the conformational rigidity between the rigid bicyclic systems (**1** and **7**) and the relatively flexible monocyclic model systems (**10** and **8**). Certainly, these modest rate factors cannot be considered to require the incursion of a major new phenomenon, such as nonclassical stabilization involving the σ-electron cloud.

It is possible to calculate from the rate data the extent of stabilization of the transition state for the solvolysis of camphene hydrochloride with respect to the model **10** ($\Delta\Delta G^{\ddagger}$ = 1.0 kcal/mol^{-1}). Likewise, the $\Delta\Delta G^{\ddagger}$ for *exo*-2-chloro-*endo*-2-methylnorbornane and 1-chloro-1-methylcyclopentane is also 1.0 kcal/mol^{-1}. The $\Delta\Delta G^{\ddagger}$ for *tert*-butyl chloride and 1-chloro-1-methylcyclopentane is 2.3 kcal/mol^{-1}.

A related comparison by Okazawa and Sorensen[13] under stable-ion conditions (−90 °C) gives data in excellent agreement with the above results (eq 5 and 6).

These data also emphasize the importance of having a suitable model compound for comparison with the norbornyl derivative. A direct comparison of 2-norbornyl with isopropyl, in Sorensen's equilibrium study, gives an equilibrium strongly favoring the positive charge on norbornyl, closely paralleling Ingold's comparison of the rate of solvolysis of camphene hydrochloride with *tert*-butyl chloride. It is only the comparison of 2-norbornyl with



cyclopentyl, a preferable model, that provides a measurable equilibrium.

Rates of Solvolysis of *exo*- and *endo*-2,3,3-Trimethyl-2-norbornyl *p*-Nitrobenzoates. As pointed out just before, there is nothing unusual in the behavior of camphene hydrochloride (**1**, *exo*-Cl) and of *exo*-2-chloro-*endo*-2-methylnorbornane compared to suitable models (**10** and **8**, respectively). Consequently, it was of interest to compare *endo*-2-chloro-*exo*-2-methylnorbornane (**12**) and the endo isomer of camphene hydrochloride (**3**) with 1-chloro-1-methylcyclopentane. Regretfully, the synthetic problem for synthesizing such labile tertiary *endo*-norbornyl chlorides has not yet been solved. In one case it has been possible to prepare both the exo and endo isomers of 2-chloro-1,2-dimethylnorbornane and to measure their rates of ethanolysis.[14] We could have used the factor exo/endo, measured in this system (~200), to calculate the rates for the endo isomers. Instead, we adopted another solution. We compared the rates for the solvolysis in 80% aqueous acetone of 1-methylcyclopentyl,[15] *exo*- and *endo*-2-methyl-2-norbornyl,[15] and 2,3,3-trimethyl-2-norbornyl *p*-nitrobenzoates.[16] The data are summarized in Table II.

It will be noted that the exo isomers undergo solvolysis faster than the standard by modest factors of 4.7 and 49, comparable to the factors observed for the corresponding chlorides, 5.4 and 206, respectively. On the other hand, the endo compounds reveal relative rates that are much more significant: 1-methylcyclopentyl, 1.00; 2-methyl-*endo*-norbornyl, 0.005 36; 2,3,3-trimethyl-*endo*-2-norbornyl, 0.0109. Consequently, if 1-methylcyclopentyl is a reasonable model for the tertiary norbornyl derivatives, it is the rates for the endo isomers, not the exo isomers, that appear exceptional.[17]

In the past, the high exo:endo rate ratio exhibited in the solvolysis of 2-norbornyl derivatives has generally been interpreted in terms of a fast exo rate and a normal endo rate. The present results suggest the desirability of reconsidering this position. High exo:endo rate ratios could also arise from normal exo rates and very slow endo rates. Steric retardation of ionization in rigid bicyclic systems could be a factor.[18] In a forthcoming study we examine the importance of steric factors on the exo:endo rate ratios of tertiary 2-norbornyl derivatives.[15]

(12) Brown, H. C.; Fletcher, R. S.; Johannesen, R. B. *J. Am. Chem. Soc.* **1951**, *73*, 212.
(13) Okazawa, N.; Sorensen, T. S. *Can. J. Chem.* **1982**, *60*, 2180.
(14) Brown, H. C.; Ravindranathan, M.; Rao, C. G.; Chloupek, F. J.; Rei, M.-H. *J. Org. Chem.* **1980**, *43*, 3667.
(15) Brown, H. C.; Ikegami, S.; Vander Jagt, D. *J. Org. Chem.*, in press.
(16) Bunton, C. H.; O'Connor, C.; Whittaker, D. *J. Org. Chem.* **1967**, *32*, 2812. These authors have reported the rates of solvolysis of *exo*- and *endo*-2,3,3-trimethyl-2-norbornyl *p*-nitrobenzoates in 80% aqueous ethanol (v/v). Our values are in 80% acetone, which can be directly compared with the rates of the model compounds available in this solvent medium.
(17) Bentley (Bentley, T. S. *Annu. Rep.* **1974**, 119) has concluded that even in secondary 2-norbornyl solvolyses approximately half of the exo:endo rate ratio is due to steric hindrance to solvation and half due to σ-participation.
(18) Brown, H. C.; Rothberg, I.; Schleyer, P. v. R.; Donaldson, M. M.; Harper, J. J. *Proc. Natl. Acad. Sci. U.S.A.* **1966**, *56*, 1653.

Experimental Section

Preparation of *exo*-2-Chloro-*endo*-2-methylnorbornane. This compound was prepared by the method of Toivonen et al.[9]

Preparation of Camphene Hydrochloride. Camphene hydrochloride was prepared from camphene and dry HCl and from methylcamphenilol or camphene hydrate by reported procedure.[8] All of the three samples gave identical rate of solvolysis.

Preparation of the Various α-Methyl-Substituted 1-Chloro-1-methylcyclopentanes 8-11. 2,2-Dimethylcyclopentanone was prepared by the procedure of Bartlett.[19] The other cyclopentanones were obtained commercially or as a donation of K. Greenlee (ChemSampCo). The tertiary alcohols were obtained by the addition of MeMgI to the ketone. The alcohols were converted to the chlorides by our earlier reported procedure.[8]

Preparation of *exo*- and *endo*-2,3,3-Trimethyl-2-norbornyl *p*-Nitrobenzoates (4a,b). The endo alcohol (mp 144-145 °C) was obtained by the addition of MeMgI to camphenilone. The *exo*-alcohol was obtained by converting the *endo*-alcohol into the chloride by using HCl. The crude chloride mixture was hydrolyzed to give the crude *exo*-alcohol, which was purified by recrystallization, mp 105.5-106 °C. The alcohols were converted into their *p*-nitrobenzoates by using an earlier reported procedure.[10]

Kinetics Measurements. The rates of ethanolysis of the chlorides and the solvolysis of *p*-nitrobenzoates in 80% aqueous acetone were measured by the titrimetric procedure described earlier.[10]

Registry No. 1, 465-30-5; 7, 19138-54-6; 8, 6196-85-6; 9, 94944-56-6; 10, 94944-57-7; 11, 91138-79-3; 1-methylcyclopentyl *p*-nitrobenzoate, 19013-42-4; 2-methyl-*exo*-norbornyl *p*-nitrobenzoate, 22467-58-9; 2-methyl-*endo*-norbornyl *p*-nitrobenzoate, 13351-30-9; 2,3,3-trimethyl-*exo*-norbornyl *p*-nitrobenzoate, 13421-46-0; 2,3,3-trimethyl-*endo*-norbornyl *p*-nitrobenzoate, 13389-76-9; 2,3,3-trimethyl-*endo*-norbornan-2-ol, 13429-57-7; 2,3,3-trimethyl-*exo*-norbornan-2-ol, 13429-40-8; MeMgI, 917-64-6; camphenilone, 13211-15-9; HCl, 7647-01-0; *tert*-butyl chloride, 507-20-0.

(19) Bartlett, P. D.; Bavley, A. *J. Am. Chem. Soc.* **1938**, *60*, 2416.

^{17}O NMR Studies on 5-Substituted Uracils

Subramanian Chandrasekaran, W. David Wilson, and David W. Boykin*

Department of Chemistry and Laboratory for Microbial and Biochemical Sciences, Georgia State University, Atlanta, Georgia 30303

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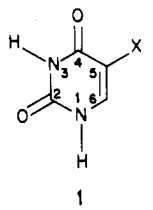
The ^{17}O NMR chemical shifts of eight ^{17}O-enriched 5-substituted uracils have been measured at 95 °C in ^{17}O-depleted water. The chemical shift range from the methoxy to the nitro compound for oxygen 2 is 40 ppm; the range for oxygen 4 for the same compounds is 20 ppm. The ^{17}O data for oxygen 2 gives a good correlation with Hammett and DSP treatments. A plot of the ^{17}O chemical shifts with the data for oxygen 2 and with the ^{17}O data for para-substituted anisoles gives a good correlation. Data for oxygen 4, an ortho-type position, does not correlate as well with the Hammett relationship.

Adenine–thymine base pair specificity of certain small molecules that intercalate with DNA has been attributed to hydrogen bonding between hydroxyl functions on the intercalator and the 2-carbonyl of thymine.[1] ^{17}O NMR spectroscopy is an excellent potential method to examine directly such interactions. As a first step in such investigations it is important to understand the effects of structural changes on the ^{17}O chemical shift of the carbonyl groups of the bases. The investigation reported here examines one aspect of structural changes on these pyrimidine bases carbonyl resonances: the effect of varying substituents at the 5-position of uracil (1). Several 5-



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substituted uracils and their nucleotide analogues have found use as chemotherapeutic agents[2] and, consequently, an understanding of the influence of substituents on the carbonyl oxygen chemical shifts, and the resulting inferred electronic changes, should add to the understanding of how these agents function.

Previous NMR studies on 5-substituted uracils have included proton,[3] nitrogen-15,[4] and carbon-13[5] investigations. Fiat and co-workers[6] reported the initial oxygen-17 study on uracil and thymine including assignment of the chemical shifts of their two carbonyl oxygen resonances. By carrying out this study on eight 5-substituted uracils, an evaluation of electronic properties of all nuclei in these pyrimidine systems by NMR will be completed. The determination of the oxygen chemical shifts in this system will also provide evidence of the value of using ^{17}O NMR to study tautomeric systems.

Experimental Section

The ^{17}O spectra were recorded on a JEOL GX-270 Spectrometer equipped with a 10-mm broad-band probe operated at 36.5 MHz. The instrument settings were 30-KHz spectral width, 1 K data points, 90° pulse angle (28-μs pulse width), 200-μs acquisition delay, and 16.9-ms acquisition time. The spectra were recorded

(1) Wilson, W. D.; Jones, R. L. In "Advances in Pharmacology and Chemotherapy"; Hawking, F., Ed.; Academic Press: New York, 1981; pp 117-222.

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