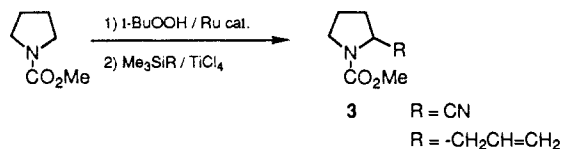


corresponding dichloroacetate upon oxidation of **1** in a mixture of AcOH and Cl₂CHCO₂H (1:1).

The present oxidation reaction provides a novel and convenient method for introduction of substituents at the α -position of amino compounds. Although α -substitution is important in connection with the synthesis of nitrogen-containing biologically active compounds, only a few methods to achieve such substitution are reported.¹³ Selective carbon-carbon bond formation at the α -position of amides can be performed readily by alkylation, allylation, and cyanation. Thus, TiCl₄-induced reaction of 1-(*tert*-butyldioxy)-2-(methoxycarbonyl)-1,2,3,4-tetrahydroisoquinoline with benzylmagnesium bromide at -78 °C gave 1-benzyl-2-(methoxycarbonyl)-1,2,3,4-tetrahydroisoquinoline (71%). Furthermore, 2-(*tert*-butyldioxy)-1-(methoxycarbonyl)pyrrolidine derived from 1-(methoxycarbonyl)pyrrolidine was converted into 2-cyano-1-(methoxycarbonyl)pyrrolidine (**3a**) (77%) or 2-allyl-1-(methoxycarbonyl)pyrrolidine (**3b**) (66%) by TiCl₄-induced



reactions with cyanotrimethylsilane and allyltrimethylsilane at -78 °C, respectively. Stereoselective carbon-carbon bond formation at the β -position of 4-acetoxyazetidione **2** has been extensively studied using various nucleophiles.⁹

Work is in progress to provide definitive mechanistic information and to apply the present new method to other systems.

Supplementary Material Available: IR, ¹H NMR, and ¹³C NMR spectral data for products of ruthenium-catalyzed oxidation of amides and lactams (4 pages). Ordering information is given on any current masthead page.

(13) (a) Meyers, A. I. *Aldrichimica Acta* **1985**, *18*, 59-68. Meyers, A. I. *Lect. Heterocycl. Chem.* **1984**, *7*, 75. Meyers, A. I.; Fuentes, L. M.; Boes, M.; Dickman, D. A. *Chem. Scr.* **1985**, *25*, 25. (b) Beak, P.; Reitz, D. B. *Chem. Rev.* **1984**, *84*, 471. (c) Seebach, D.; Enders, D. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 15.

Acid-Catalyzed Dehydration of Naphthalene Hydrates

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We wish to report measurements of rates of acid-catalyzed dehydration of the three isomeric hydrates of naphthalene (**1-3**). These hydrates have been isolated recently in optically active forms as intermediates in biotransformations of 1,2- and 1,4-dihydronaphthalene by a mutant strain of *Pseudomonas putida*^{1,2} and rat liver systems.³ Preparation of the (racemic) 2-hydroxy-1,2-dihydronaphthalene (**2**) was first reported by Bamberger,⁴ and synthetic routes to all three hydrates have since been developed.^{5,6}

(1) Boyd, D. R.; McMordie, R. A. S.; Sharma, N. D.; Dalton, H.; Gray, D. J., manuscript submitted.

(2) Boyd, D. R.; McMordie, R. A. S.; Sharma, N. D.; Dalton, H.; Williams, P.; Jenkins, R. O. *J. Chem. Soc., Chem. Commun.* **1989**, 339.

(3) Boyd, D. R.; van Bladeren, P. J., manuscript in preparation.

(4) Bamberger, E.; Lodter, W. *Justus Liebigs Ann. Chem.* **1985**, *288*, 100.

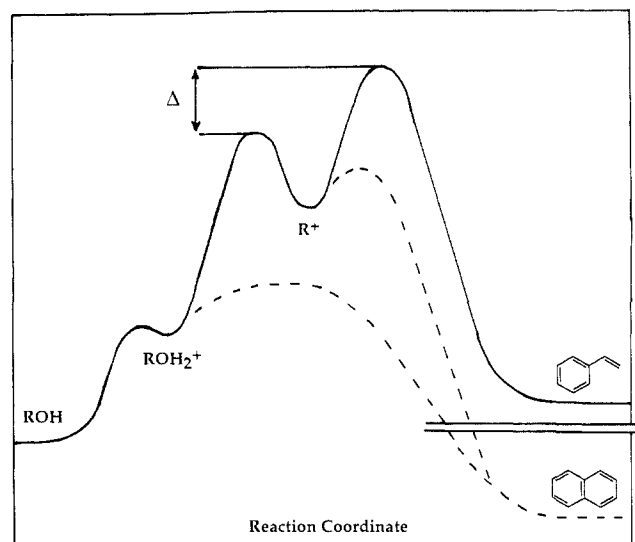
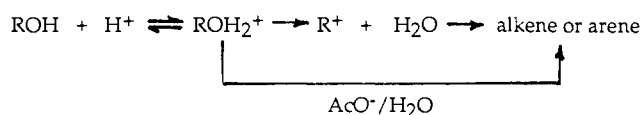
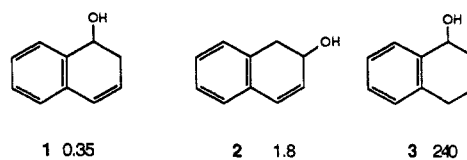


Figure 1.

Scheme I



It was shown by Jeffrey and Jerina that dehydration of **1** and **2** to naphthalene occurs in 1-butanol in the presence of 0.01 M HCl.⁶ The reaction also takes place in dilute aqueous solutions of strong acids, and the more reactive 1,4-hydrate **3** dehydrates in acetic acid buffers. Second-order rate constants (M⁻¹ s⁻¹) for catalysis by H⁺ in aqueous solution, measured spectrophotometrically at 25 °C, are shown under the relevant structures below.



Comparisons with simple alcohols show that the hydrates are highly reactive molecules. Thus the saturated acyclic analogue of **1**, α -phenylethanol (**4**), dehydrates nearly 10⁸ and 10¹¹ times more slowly than the 1,2- and 1,4-hydrates, respectively.^{7,8} These differences are too large to be attributed to the activating effect of the vinyl substituent present in the hydrates, and it is natural to ask whether the aromatic stabilization of the naphthalene product is responsible. This stabilization is certainly large. The free energy of hydration of naphthalene may be estimated as ca. 20 kcal/mol,⁹ compared with the measured value of -2.2 kcal/mol⁷ for styrene, the product of dehydration of α -phenylethanol.

Dehydration of α -phenylethanol occurs in strongly acidic aqueous media, and the mechanism of its reaction is well-established as occurring via the protonated alcohol and the α -phenylethyl carbocation, as shown in the upper pathway of Scheme I.⁷ Deprotonation of the carbocation to form styrene is rate-determining, and for the related α -(*p*-methylphenyl)ethanol (**5**) in 1:1 aqueous trifluoroethanol, Jencks and Richard have shown that this occurs nearly 2000 times more slowly than the rate of carbocation formation.¹⁰

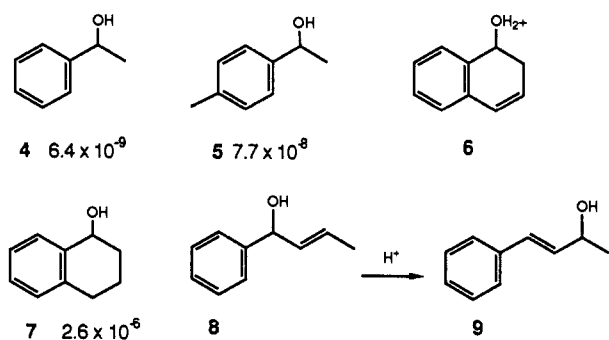
(5) Brown, H. C.; Vara Prasad, J. V. N. *J. Org. Chem.* **1985**, *50*, 3002. Marks, K.; Prajer-Janczewska, L. *Pol. J. Chem.* **1981**, *55*, 1037. Moss, R. J.; Rickborn, B. *J. Org. Chem.* **1985**, *50*, 1381. Boyd, D. R.; Agarwal, R.; O'Kane, G. A.; Porter, H. P.; Sharma, N. D., manuscript submitted.

(6) Jeffrey, A. M.; Jerina, D. M. *J. Am. Chem. Soc.* **1972**, *94*, 4048-4050.

(7) Schubert, W. M.; Keefe, J. R. *J. Am. Chem. Soc.* **1972**, *94*, 559.

(8) Modena, G.; Rivetti, F.; Scorrano, G.; Tonellato, U. *J. Am. Chem. Soc.* **1977**, *99*, 3392.

(9) More O'Ferrall, R. A.; Kelly, S., unpublished.



According to Scheme I, aromatic stabilization of the products could influence the reactivity of the hydrates in two ways. The first is by increasing the rate of proton loss from the carbocation. As may be seen from the potential energy profiles in Figure 1, however, the magnitude of this increase is limited by the difference in barrier heights (Δ) for formation and reaction of the phenylethyl cation which, if we extrapolate from Jencks and Richard's results for the *p*-methyl derivative,¹⁰ amounts to a factor of only 500 in reaction rates (in water). A more radical role for aromatic stabilization would be implied if the naphthalene were formed directly from the protonated hydrates (e.g., **6**) in a concerted reaction, as shown in the lower pathway of Scheme I and the lower dashed line in Figure 1.

The two possibilities may be distinguished because the concerted but not the stepwise reaction involves proton transfer in the rate-determining step and should be subject to catalysis by buffer acids. Since, in practice, measurements in acetic acid buffers (up to 0.4 M acid, $f = 0.5$) failed to reveal such catalysis, even for the reactive 1,4-hydrate **3**, it follows that proton transfer is not rate-determining and hence that breaking of the C-H and C-O bonds of the protonated hydrates is not concerted.

The absence of buffer catalysis further suggests that, in contrast to α -phenylethanol, deprotonation of the carbocation is also not rate-determining, consistent with the expectation that the rate of this step is increased by the aromatic stabilization. This conclusion is not unequivocal because buffer catalysis of deprotonation of reactive carbocations is weak.¹⁰ It is confirmed, however, by (i) failure to observe rearrangement of the 1,4- to the more stable (and more strongly absorbing) 1,2-hydrate in competition with dehydration, despite the reactions sharing a common benzallylic carbocation intermediate; (ii) absence of diminished product absorption that would indicate trapping by azide ion when the 1,4-hydrate is reacted in the presence of 2 M sodium azide (9:1 NaN_3/HN_3 buffer, pH 5.5); and (iii) reasonable agreement between the spectrophotometrically measured rate constant for dehydration of **1** ($0.35 \text{ M}^{-1} \text{ s}^{-1}$) and an approximate polarimetric rate constant ($0.7 \pm 0.2 \text{ M}^{-1} \text{ s}^{-1}$) for loss of optical activity from a small amount of chiral **1** [(*R*)-(+)-1-hydroxy-1,2-dihydronaphthalene, $[\alpha]_D^{25} +52^\circ$ (CHCl_3)], both measured in 50% (v/v) aqueous trifluoroethanol.¹¹

It follows that dehydration rate constants for **1**–**3** refer to rate-determining carbocation formation, in contrast to those for **4** and **5**, which are for rate-determining deprotonation. The aromatic stabilization of the product does increase the reactivity of the hydrates, therefore, but as already noted, this accounts for only 500-fold of the rate differences of 5×10^7 between **1** and **4** and 5×10^{10} between **3** and **4**. Apparently, other factors also contribute to the differences.

One further contribution to the high reactivity of **1**–**3** is that reaction occurs more readily in the cyclic than open-chain phenethyl structure. This is apparent from measurements of rate constants for dehydration and carbocation formation from the dihydro derivative of **1** and **3**, α -tetralol (**7**), which show that these reactions occur respectively 400 and 200 times more rapidly than the corresponding reactions of α -phenylethanol. The rate constant

for carbocation formation was measured polarimetrically, from racemization of the *R*-(+) substrate, as $\sim 6 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ (extrapolated to water from aqueous trifluoroethanol mixtures), which is 230 times greater than for the dehydration reaction and only 500 times slower than dehydration of the 1,2-naphthalene hydrate **1**. Solvolyses of open-chain alkyl and cyclohexyl substrates lacking a phenyl substituent show little difference in rates.¹² The high reactivity of the tetralol therefore probably reflects an absence of steric¹² and entropic inhibition of resonance stabilization of the carbocation by the phenyl group.

The remaining difference between **7** and **1** is sensibly ascribed to stabilization of the carbocation by a vinyl substituent. Thus, comparison of the 1,4-hydrate **3** with its open-chain vinyl analogue **8**, for which the rate of carbocation formation is measured as $0.58 \text{ M}^{-1} \text{ s}^{-1}$ by monitoring rearrangement to its stable isomer **9**, shows a rate difference of 400 (k_3/k_8), which is close to the difference (170) between the cyclic and open-chain structures **7** and **4** (k_7/k_4). The 130-fold difference between **2** and **3** can be attributed to the lower energy of a conjugated than unconjugated double bond in the reactants and corresponds roughly to the energy difference between 1,2- and 1,4-dihydronaphthalene.¹³ Finally, the small (5-fold) difference between **1** and **2** presumably reflects a difference in stability of their carbocations.

In summary, the higher reactivity of naphthalene hydrates than α -phenylethanol may be understood in terms of contributions from a number of factors, none of which, individually, is unusually large and all of which have straightforward explanations. Aromatic stabilization is one of these (contributing a factor of 5×10^2), but enhanced resonance in the cyclic cation (2×10^2), the effect of a vinyl substituent (5×10^2), and deconjugation of the double bond in the reactants (1.5×10^2) are also important.

Acknowledgment. We thank the Department of Education for Northern Ireland (R.A.S.McM.) and the British Science and Engineering Research Council (N.D.S.) for financial support.

(12) Streitwieser, A. *Solvolytic Displacement Reactions*; McGraw-Hill: New York, 1962.

(13) Stull, D. R.; Westrum, E. F., Jr.; Kirby, S. P. *The Chemical Thermodynamics of Organic Compounds*; Wiley: New York, 1969.

Novel Heterocycles Comprising Alternating Phosphorus Atoms and Alkyne Units¹

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As part of our program directed toward synthesis of the unknown cage compounds **1**, **2**, and related "phosphocarbons" (C_nP_m), we have prepared the first heterocycles comprising alternating phosphorus atoms and alkyne units. Herein we report our syntheses and some properties of 1,4,7-tri-*tert*-butyl-1,4,7-triphospha[3]pericyclyne (**3**) and 1,4,7,10-tetra-*tert*-butyl-1,4,7,10-tetraphospha[4]pericyclyne (**4**).² Such heterocycles and phosphocarbons are expected to exhibit a variety of unusual structural and electronic properties.

Our syntheses began with *tert*-butylphosphonous dichloride (**5**), prepared in 48% yield by the addition of *tert*-butylmagnesium chloride to phosphorous trichloride.³ Treatment of **5** with excess

(1) Part 8 in the series "Cyclines". This work was first presented at the International Meeting of Pacific Basin Chemical Societies (PACIFICHEM 89) in Honolulu, Hawaii, Dec 1989. Part 7: Scott, L. T.; Cooney, M. J.; Johnels, D. *J. Am. Chem. Soc.* **1990**, *112*, 4054–4055.

(2) All-carbon [M]pericyclynes have previously been reported: Scott, L. T.; DeCicco, G. J.; Hyun, J. L.; Reinhardt, G. *J. Am. Chem. Soc.* **1985**, *107*, 6546–6555.

(10) Richard, J. P.; Jencks, W. P. *J. Am. Chem. Soc.* **1984**, *106*, 1373.

(11) A Perkin-Elmer 241 spectropolarimeter with continuous data collection and signal averaging was used for the polarimetric measurements.