of tri- and tetrasubstituted olefins toward the Hofmann and Milas reagents is interesting. It seems likely that the osmate esters generated from highly substituted olefins could be slow to hydrolyze, thus creating a bottleneck in the catalytic sequence. The basic conditions used with our reagent probably facilitate hydrolysis[12] of such hindered osmate esters and enable a more rapid turnover of the osmium catalyst.[14]

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(2) OsO_4: (a) K. A. Hofmann, *Ber. Dtsch. Chem. Ges.*, **45**, 3329 (1912); (b) R. Criegee, *Justus Liebigs Ann. Chem.*, **522**, 75 (1936); (c) R. Criegee, B. Manchard, and H. Wannorvius, *Ibid.*, **550**, 99 (1942); (d) N. A. Milas and S. Sussman, *J. Am. Chem. Soc.*, **58**, 1302 (1936); (e) N. A. Milas and S. Sussman, *ibid.*, **59**, 2345 (1937); (f) N. A. Milas, J. H. Trepagnier, J. T. Nolan, and M. I. Iliopolus, *ibid.*, **81**, 4730 (1959).

(3) Because RuO_4 is both less expensive and less toxic than OsO_4, we attempted to control its reactions with olefins so as to produce diols rather than the usual cleavage products. Reaction of RuO_4 with *E*- and with *Z*-cyclododecene in EtOAc at −78°, followed by reduction at −78° with dimethylsulfide, afforded the threo and erythro diols, respectively (ca. 20% yield in each case). This proves for the first time that RuO_4 reacts with olefins, like MnO_4^- and OsO_4, by stereospecific cis addition to produce initially a cyclic ruthenium (VI) ester (K. B. Sharpless and A. Y. Teranishi, unpublished results). However, due to the poor yields, this is not a practical route to diols.

(4) The beneficial effect of basic conditions on the yield of diol in MnO_4^- oxidations of olefins is well known (see ref. 1b and K. B. Wiberg, "Oxidation in Organic Chemistry", Academic Press, New York, N.Y., 1965, pp. 42–43).

(5) The catalytic decomposition of H_2O_2, especially alkaline H_2O_2, by a variety of transition metals is well known (see J. A. Connor and E. A. V. Ebsworth, *Adv. Inorg. Chem. Radiochem.*, **6**, 359–360 (1964), and S. B. Brown, P. Jones, and A. Suggett, *Prog. Inorg. Chem.*, **13**, 159–204 (1970)).

(6) There is one earlier claim to the use of *tert*-butyl hydroperoxide, catalyzed by OsO_4, for the vicinal hydroxylation of an olefin (G. E. McCasland, S. Turuta, and L. J. Durham, *J. Org. Chem.*, **33**, 2835 (1968)). However, the experimental section of that paper reveals that hydrogen peroxide in *tert*-butyl alcohol (i.e., the Milas reagent), not *tert*-butyl hydroperoxide, was the oxidant actually used.

(7) Tetraethylammonium hydroxide was chosen as the base for its solubility in the organic medium. Use of sodium or potassium hydroxides resulted in heterogeneous reaction mixtures and lower yields.

(8) Cooling is more important for some olefins than for others. For example, at room temperature α-methylstyrene gives more cleavage to acetophenone and the 4-octenes afford less diol and more ketol and α-diketone.

(9) The impurities in commercial *tert*-butyl hydroperoxide are *tert*-butyl alcohol and water. Since neither of these impurities interferes with this reaction, *tert*-butyl hydroperoxide of any strength or purity can be used. By contrast, the molybdenum and vanadium catalyzed epoxidations of olefins are very sensitive to the purity of the hydroperoxide (K. B. Sharpless and R. C. Michaelson, *J. Am. Chem. Soc.*, **95**, 6136 (1973); S. Tanaka, H. Yamamoto, H. Nozaki, K. B. Sharpless, R. C. Michaelson, and J. D. Cutting, *ibid.*, **96**, 5254 (1974)).

(10) This catalyst solution was prepared as described by Daniels and Fischer (R. Daniels and J. L. Fischer, *J. Org. Chem.*, **28**, 320 (1963)) with the exception that *tert*-butyl hydroperoxide was used in place of H_2O_2 as the stabilizer. Recipe: 1 g of OsO_4, 199 ml of the specially purified *tert*-butyl alcohol, and 1 ml of 90% *tert*-butyl hydroperoxide; each milliliter contains 2×10^{-5} mol of OsO_4.

(11) K. B. Sharpless and D. R. Williams, *Tetrahedron Lett.*, 3045 (1975).

(12) It is well known that osmium(VI) glycol esters are often reluctant to hydrolyze. For this reason we believe that, in these catalytic systems, the osmium(VI) ester is first oxidized to an osmium(VIII) ester which then undergoes hydrolysis. Considerations of pK_a indicate that the principal base in our system will be the *tert*-butyl hydroperoxide anion. In addition to facilitating hydrolysis, this anion might also be expected to increase the rate of oxidation of osmium(VI) to osmium(VIII).

(13) Camille and Henry Dreyfus Teacher–Scholar Grant recipient; Alfred P. Sloan Fellow, 1973–1975.

(14) Note Added in Proof. A group at Upjohn has discovered a mild osmium catalyzed oxidation of olefins to vicinal diols using amine N-oxides as the oxidant (V. Van Rheenen, R. C. Kelly, and D. Y. Cha, *Tetrahedron Lett.*, in press). We are grateful to Dr. Robert Kelly for informing us of their results prior to publication.

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Free Energies of Hydration and Hydrolysis of Gaseous Acetamide

Sir:

Despite widespread interest in the biochemical properties of the acylamido function in aqueous solution, there seems to be little thermodynamic information about the strength of interaction between amides and solvent water. An absolute measure of the hydrophilic character of a solute is provided by its equilibrium of distribution between dilute solution and the dilute vapor phase, in which intermolecular forces are absent. This is to report that the hydrophilic character of acetamide, which is apparently the first amide to have been studied in this way, far surpasses that of other simple uncharged organic compounds which have been measured before.[1,2]

Initial attempts to measure the partial pressure of aqueous acetamide by conventional methods were in vain. Analysis by mass spectrometry showed that acetamide was not present at detectable levels (ca. 10^{-3} Torr) in samples removed from the gas space over stirred solutions of acetamide (1 M) in water at 25°. It was therefore necessary to resort to a dynamic technique, similar to that first developed by Shaw and Butler[3] for use with more volatile solutes, and use radioactivity as a means of detection.

In a typical experiment, water-pumped nitrogen was passed (at a rate of 40 ml/min) through a glass train consisting of a series of three wash bottles with fritted glass disks, each containing 100 ml of acetamide-*1*-^{14}C (0.01 M, 0.03 Ci/mol) in dilute KOH (0.01 M). The alkali was added to trap acetic acid, which was found to be generated in trace quantities during long-term experiments. Continuing through a spray trap, the effluent gas then passed through a second series of three wash bottles, each containing water (150 ml). At intervals, samples were removed from these traps for analysis of radioactivity accumulated as a function of the volume of gas passed through the train. Of the radioactivity transferred, more than 96% appeared in the first two receiving vessels, indicating the efficiency of the trapping system. The chemical nature of the radioactive substance transferred was determined by measuring its distribution coefficient between water, containing either HCl (0.05 M) or KOH (0.05 M), and 1-octanol at 25°. In both acidic and basic systems, the radioactive substance exhibited $K_d = 0.070$ toward octanol, identical with values measured with samples of authentic acetamide in separate experiments (and similar to a value extrapolated from the observed behavior of butyramide[4]). In contrast, the possible contaminant acetic acid gave $K_d = 0.60$ from 0.05 M HCl to octanol, and $K_d \leq 0.001$ from 0.05 M KOH to octanol (consistent with literature values[4]).

The rate of transfer of radioactive acetamide was found to be proportional to the rate of flow of gas, and to the concentration of radioactivity in the equilibrating vessels. The rate was unaffected by varying the concentration of nonradioactive acetamide in the equilibrating vessels in the range from 0.001 to 0.01 M (consistent with the known monomeric nature of acetamide in water[5]), or by increasing the volume and number of equilibrating vessels containing radioactive acetamide in solution (indicating that equilibration was complete under these conditions). The observed rate of transfer corresponded to an absolute distribution coefficient of 7.6×10^{-8} (with a standard deviation of 2.5×10^{-8} in eight experiments) from water to the vapor phase at 25°.

The most hydrophilic of simple organic compounds studied previously, acetic acid, gave $K_d = 1.1 \times 10^{-5}$ for distribution from aqueous solution (0.05 M) to the vapor phase by the present method, in good agreement with earlier de-

Table I. Absolute Distribution Coefficients for Transfer from Dilute Aqueous Solution to the Vapor Phase at 25 °C[a]

Ethane[b]	22
Ethylene[b]	9.6
Acetylene[b]	1.1
Dimethyl ether[c]	4.1×10^{-2}
Ethyl acetate[d]	5.4×10^{-3}
Acetone[d]	1.3×10^{-3}
Ethylamine[d]	4.1×10^{-4}
Ethanol[e]	2.1×10^{-4}
Acetic acid[f]	1.1×10^{-5}
Acetamide[f]	7.6×10^{-8}
Ammonia[g]	7.7×10^{-4}
Water[h]	2.5×10^{-5}

[a] Equilibria in mol/l. in vapor, divided by mol/l. in dilute aqueous solution. [b] Reference 8. [c] Reference 9. [d] Reference 10. [e] Reference 1. [f] This work. [g] Reference 11. [h] Reference 12.

Table II. Free Energies of Reaction in Dilute Solution and in the Vapor Phase

	Acetamide hydrolysis	Ethyl acetate hydrolysis	Ethyl acetate ammonolysis
ΔG for reaction in dilute aqueous solution at 25 °C[a]	+6.4[c]	+0.7[d]	−5.7
(ΔG for solvation of gaseous products) − (ΔG for solvation of gaseous reactants)[b]	+4.9	−2.4	−7.3
ΔG for reaction in the dilute vapor phase at 25 °C	+1.5	+3.1	+1.6

[a] Free energies in kcal based on uncharged reactants and products in dilute solution, with water activity taken as 55.6 M. [b] Free energies of solvation calculated from distribution coefficients in Table I. [c] Assumed equivalent to a value for propionamide, calculated from the data of Morawetz and Otaki using propionic acid $pK_a = 4.88$ (ref 14). [d] Reference 15.

terminations.[6] Values for simple representatives[7] of organic compounds of various classes, compared in Table I, are distributed over a range that exceeds eight orders of magnitude. The extreme position of acetamide is consistent with a relatively large shift in carbonyl stretching frequency that occurs when the compound is transferred to water from the vapor phase,[13] and with the possibility that the molecule in aqueous solution possesses some zwitterionic character.

Theoretical considerations suggest[16,17] that noncovalent hydration often plays a decisive role in determining biochemical energetics in aqueous solution. This is illustrated clearly by the equilibria for hydrolysis of amides and esters, which are actually shifted in opposite directions when these reactions are transferred between dilute aqueous solution and the vapor phase (Table II). This effect is so pronounced that solvation may be said to provide the entire driving force (−7.3 kcal) for the ammonolysis of ethyl acetate, a reaction which is strongly exergonic in water but slightly endergonic in the vapor phase (Table II). There is little doubt that changing solvation exerts an important influence on the equilibrium conformation of macromolecules, the catalytic activity of enzymes, and the behavior of biological receptors and energy transducing systems. It would therefore be useful to have information about the solvation of other polar molecules of biological interest.

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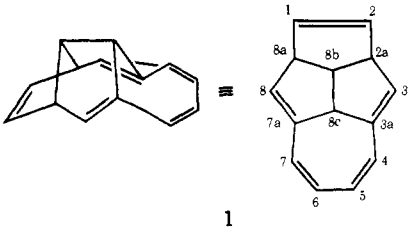
2a,8a,8b,8c-Tetrahydropentaleno[6,1,2-*aji*]azulene

Sir:

The triquinacenes have stimulated great interest for both theoretical and synthetic chemists.[1-3] A new member of this fascinating family of compounds, 2a,8a,8b,8c-tetrahydropentaleno[6,1,2-*aji*]azulene (**1**), has special significance because of its relationship to potentially antiaromatic [12]annulenes.[4] We wish to report the synthesis of **1**, which involves a new approach to the triquinacene system and which employs an unusually facile formal $_{\sigma}2_S + {}_{\sigma}2_S$ cycloreversion.



1

The synthetic path recognizes the relationship between **1** and norcaradiene **2** and is outlined in Scheme I. The ketone **3** is readily available by an amalgamation of the work of Baker[5] and Battiste.[6] Subjection of ketone **3** to condensation with the preformed methoxy Wittig reagent ($Ph_3P^+CH_2OCH_3Cl^-$, n-C_4H_9Li, THF) under forcing conditions (diglyme, room temp → reflux) gave the desired enol ether **4**[7] [NMR: δ 5.04 (s, 1 H), and 3.02 (s, 3 H); ir 1730 (=OCH_3), 1603 (aryl) cm^{-1}], which, without purification, was treated with 3 N aqueous hydrochloric acid at room temperature to smoothly give the desired aldehyde **5**,[7] mp 74–7 °C [NMR: δ 8.34 (s, 1 H), 6.8–7.2 (AA′BB′, 4 H), 6.29 (t (J = 2 Hz), 2 H), 3.35 (br s, 2 H), 3.22 (s, 2 H),