12 R=H
I R=COCH₃

13 R=H
14 R=COCH₃

15 R₁, R₂, R₃, = H
16 R₁=H, R₂=CH₃
    R₃=COCH₃

generates both 1,2- and 1,4-diols in a ratio which is highly dependent on solvent and acid. Under thus-far optimum conditions (1:1 THF:10% HOAc, room temperature, 20 h), trans-1,2-diol **12** is produced in 30% yield along with **13** (30%) and **15** (30%). Additional experiments have shown that tetraol **15** arises from **12,** a fact which has important mechanistic consequences.[12] Diol **12,** obtained pure by chromatography, can be acetylated (94%) and thereby produces *dl*-senepoxide, mp 97–98 °C, whose IR, NMR, and TLC characteristics are identical with those of an authentic sample. The methanolysis of **1** catalyzed by perchloric acid additionally confirms its structure by producing seneol **16,** a metabolite of senepoxide in *Uvaria catocarpa*.[2a]

References and Notes

(1) For part II see N. Ikota and B. Ganem, *J. Am. Chem. Soc.,* preceding paper in this issue.
(2) Senepoxide: (a) R. Hollands, D. Becher, A. Gaudemer, and J. Polonsky, *Tetrahedron,* **24,** 1633 (1968); (b) A. Ducruix, C. Pascard, and J. Polonsky, *Acta Crystallogr., Sect. B,* **32,** 1589 (1976). Crotepoxide: (c) S. M. Kupchan, R. J. Hemingway, and R. M.Smith, *J. Org. Chem.,* **34,** 3898 (1969). LL-Z1220: (d) D. B. Borders and J. E. Lancaster, *ibid.,* **39,** 435 (1974). Pipoxide: (e) J. Singh, K. L. Dhar, and C. K. Atal, *Tetrahedron,* **26,** 4403 (1970). Triptolide: (f) S. M. Kupchan, W. A. Court, R. G. Dailey, C. J. Gilmore, and R. F. Bryan, *J. Am. Chem. Soc.,* **94,** 7194 (1972).
(3) Senepoxide: (a) A. Ichihara, K. Oda, M. Kobayashi, and S. Sakamura, *Tetrahedron Lett.,* 4235 (1974). Crotepoxide: (b) K. Oda, A. Ichihara, and S. Sakamura, *ibid.,* 3187 (1975); (c) M. R. Demuth, P. E. Garrett, and J. D. White, *J. Am. Chem. Soc.,* **98,** 634 (1976).
(4) All drawings except for structures 1 and 2 are meant to connote racemic mixtures. The fact that arene oxides 3a and 3b can racemize via their respective oxepin tautomers has interesting biosynthetic consequences: B. Ganem and G. W. Holbert, *Bioorg. Chem.,* **6,** 393 (1977).
(5) H. Plieninger and G. Ege, *Chem. Ber.,* **94,** 2095 (1961).
(6) W. E. Barnett and L. L. Needham, *J. Org. Chem.,* **40,** 2843 (1975).
(7) Satisfactory elemental analyses were obtained for all new compounds.
(8) G. W. Holbert, L. B. Weiss, and B. Ganem, *Tetrahedron Lett.,* 4435 (1976).
(9) Epoxidation of the corresponding alcohol 5 is a considerably slower reaction and produces a 1:1 mixture of stereoisomers. Carboxyl groups have been shown to exert specific syn-directing effects by S. A. Cerefice and E. K. Fields, *J. Org. Chem.,* **41,** 355 (1976).
(10) A similar result has been obtained with benzene epoxide using chemically generated singlet oxygen: C. H. Foster and G. A. Berchtold, *J. Org. Chem.,* **40,** 3743 (1975).
(11) For related examples see (a) G. O. Pierson and O. A. Runquist, *J. Org. Chem.,* **34,** 3654 (1969); (b) J. E. Baldwin and O. W. Lever, *J. Chem. Soc., Chem. Commun.,* 344 (1973).
(12) The trisubstituted oxirane ring is much more readily hydrolyzed in **12** than it is in **11.** We point out in this regard that **12** is remarkably similar in

i
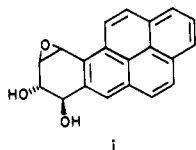
structure to acid-labile diolepoxide i, produced by metabolism of benzo[a]pyrene in hepatic tissue. The epoxide's pronounced electrophilicity

in i, presumably due to anchimeric assistance from the benzylic hydroxyl, is thought to be responsible for the potent activity of benzpyrene as an environmental carcinogen: D. L. Whalen, J. A. Montemarano, D. R. Thakkar, H. Yagi, and D. M. Jerina, *J. Am. Chem. Soc.,* **99,** 5523 (1977), and references cited therein.

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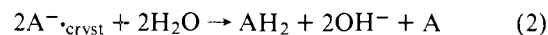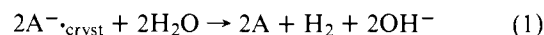*Received September 12, 1977*

Production of Hydrogen from Interaction of an Anion Radical and Water

Sir:

Solvated hydrocarbon anion radicals and dianions have been known to be rapidly protonated (without exception) upon the addition of protic solvents such as water or alcohols for over 30 years (Birch reduction).[1] In fact, there exists a vast number of reports including those that elucidate the kinetics and mechanisms involved in these protonation reactions.[2] Even solid anion radical and dianion salts are rapidly protonated upon water addition.[3] However, we wish to report here the cleavage of water to yield hydrogen gas via anion radical reduction as opposed to anion radical protonation.

During our investigation into the heats of formation of organic anion radicals,[3] the reactions of the solid sodium salts of the polyacene series (pentacene, tetracene, anthracene, and naphthalene) were studied. The anion radicals were generated from a 1.5- to 2-fold excess of neutral hydrocarbon to sodium metal in tetrahydrofuran (THF). After complete dissolution of the sodium mirror, the anion radical solution was passed through a sintered-glass frit and the solvent (THF) distilled off under high vacuum (10^{-6} Torr).[4] A large excess (~2 mL) of degassed water was then added to the solid salt. The noncondensable gasses resulting form the reaction of the water with the salt (NaA) were allowed to pass into a vacuum system connected with a Toepler pump fitted with a gas buret.[5]

From 1 mmol of NaA, 0.5 mmol of hydrogen would be expected if eq 1 rather than eq 2 describes the reaction. The 0.5 mmol of H_2 would generate about half of an atmosphere of pressure in the 10-mL bulb of the gas buret. For A = pentacene, tetracene, and anthracene no gas was detected indicating that at least 99.9% of the reaction procedes via eq 2. However, for the reaction of water with the naphthalene anion radical, large quantities of H_2 are evolved.[6]

$$2A^{-} \cdot _{cryst} + 2H_2O \rightarrow 2A + H_2 + 2OH^{-} \qquad (1)$$

$$2A^{-} \cdot _{cryst} + 2H_2O \rightarrow AH_2 + 2OH^{-} + A \qquad (2)$$

After pumping all of the H_2 into the gas buret, the remaining reaction mixture was titrated with HCl to yield the initial amount of anion radical. From 10 such reactions 42 ± 8% of the reaction procedes via eq 1 rather than eq 2. The large standard deviation in this percent may be due to the fact that the pathway may vary with the crystal size of the $NaC_{10}H_8$. NMR analysis of the reaction mixture substantiates these conclusions as to the reaction pathway, in that ~80% of the organic material is naphthalene and 20% is dihydronaphthalene. When eq 2 describes the reaction pathway, a 50:50 mixture of A and AH_2 is obtained.

The possibility existed that the H_2 production could be explained by a partial microscopic reversal of the sodium reduction back to naphthalene and sodium metal upon solvent removal. If this were the case, the added water would simply react with the Na^0. This is not the situation, however, as naphthalene cannot be sublimed from the salt after solvent evaporation when an excess of sodium is used to ensure com-

plete reduction of the naphthalene. When the sodium reduction of the naphthalene is not complete, it is readily sublimed from the solid mixture at room temperature.

All of the above mentioned data indicate that the solid salt of the naphthalene anion radical reacts with water to yield ~40% of the theoretical amount of hydrogen gas expected from eq 3. This production of H_2 compared with the lack of it from

$$2 \bigcirc\!\bigcirc^{\cdot-} + 2H_2O \longrightarrow 2 \bigcirc\!\bigcirc + H_2 + 2OH^- \quad (3)$$
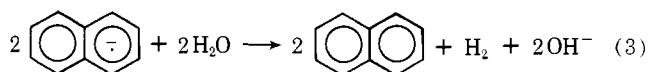
the other polyacene systems is probably associated with its lower electron affinity (larger energy difference between the neutral molecule and the anion radical). It seems reasonable that the reaction proceeds through an intermediate that consists of a hydrogen bond between the water and the charged π cloud of the anion radical.[7] The extra electron could then be pulled out of the antibonding MO and into the hydrogen 1s orbital with simultaneous breaking of the H–O bond in water.

This H_2 evolution via anion radical cleavage of water is in sharp contrast to the fact that only protonation has been observed previously. The possibility of photogeneration of anion radicals to be used for water cleavage and H_2 production with recovery of the neutral substrate should not be overlooked.

References and Notes

(1) (a) A. J. Birch, *J. Chem. Soc.*, 430 (1944); (b) A. J. Birch, *ibid.*, 593 (1946); (c) A. J. Birch and H. Smith, *Q. Rev., Chem. Soc.*, **12**, 17 (1958).
(2) Citation of a few examples: (a) S. Bank and B. Bockrath, *J. Am. Chem. Soc.*, **94**, 6076 (1972); (b) E. R. Minnich, L. D. Long, J. M. Ceraso, and J. L. Dye, *ibid.*, **95**, 1061 (1973); (c) J. F. Garst and J. A. Pacifici, *ibid.*, **97**, 1802 (1975).
(3) (a) G. R. Stevenson, I. Ocasio, and A. Bonilla, *J. Am. Chem. Soc.*, **98**, 5469 (1976); (b) unpublished results.
(4) The technique is identical with that described in G. R. Stevenson and I. Ocassio, *J. Phys. Chem.*, **79**, 1387 (1975).
(5) G. Stevenson and L. Echegoyen, *J. Am. Chem. Soc.*, **96**, 3381 (1974).
(6) The noncondensable gas evolved from the reaction was shown to be hydrogen by first passing it through a liquid nitrogen trap and then into a CuO oven. The gas reduced the CuO to Cu and formed water.
(7) The existence of hydrogen bonds to charged π clouds has been demonstrated for the anions of cyclooctatetraene; see G. R. Stevenson and A. Vassos, *J. Phys. Chem.*, **81**, 1526 (1977).

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A Self-Consistency Criterion for Two-Structure Theories

Sir:

Two-structure theories have been proposed for systems where the properties are thought to be intermediate between those of the individual structures. Thus water[1] has been described as a mixture of regions of ice-like material and regions of more closely packed molecules (or normal liquid). Aqueous electrolytes have been described[2,3] as mixtures of ionic lattice-like regions with "Debye–Hückel" ("D–H") regions of random structure modified by electrostatic forces. It is not my

purpose at this time to discuss the over-all merits of any of these theories, but there is a self-consistency criterion which should be imposed upon any two-structure theory. The relative proportion of material in each structure should be given by the appropriate expression for equilibrium between the two structures. Thus the total Gibbs energy must be at its minimum with respect to distribution of material between the two structures. Also the activity or chemical potential for a component of the system must be the same for one structure as for the other structure.

Many recent theories[4] conform either exactly or approximately to this equilibrium criterion. However, certain two-structure theories for strong electrolytes grossly violate this principle. Both the theory of Singh[2] and the earlier theory of Lietzke, Stoughton, and Fuoss[3] use arbitrary transfer functions to shift the proportion of "D–H" solute to that of "lattice" solute with increasing concentration. For the first example of Singh, namely HCl, and with his equations and parameters, the chemical potential of the "D–H" solute is lower at all substantial concentrations than that of the "lattice" solute. This difference in chemical potential in favor of the "D–H" structure increases with concentration. Thus, at equilibrium there would be no shift to the "lattice" structure and the expected properties of the two-structure model, treated consistently, would be just those of the "D–H" structure.

References and Notes

(1) Such theories for water are reviewed by D. Eisenberg and W. Kauzmann, "The Structure and Properties of Water", Oxford University Press, London, 1969, Chapter 5; and by M. S. Jhon and H. Eyring, *Ann. Rev. Phys. Chem.*, **27**, 45 (1976).
(2) P. P. Singh, *J. Am. Chem. Soc.*, **99**, 1312 (1977).
(3) (a) G. R. Stevenson, I. Ocasio, and R. M. Fuoss, *Proc. Natl. Acad. Sci. U.S.A.*, **59**, 39 (1968); **61**, 775 (1968).
(4) For example, G. Nemethy and H. A. Scheraga, *J. Chem. Phys.* **36**, 3382 (1962); **41**, 680 (1964).

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Nitroxide Radical as a Nuclear Spin Decoupling Reagent. Application to Carbon-13 Nuclear Magnetic Resonance Studies of Organothallium Compounds[1]

Sir:

We wish to report here a novel use of a stable nitroxide radical as a nuclear spin decoupling reagent in the ^{13}C NMR spectra of organothallium compounds which are very complicated owing to large ^{13}C–Tl nuclear spin couplings. We have currently been interested in the use of stable free radicals as NMR spin probes (paramagnetic shift and relaxation reagents) for studying the intermolecular interaction associated with hydrogen bonding,[2] charge transfer interaction,[3] and π-stacking interaction.[4] Here we are concerned with the Lewis acid–base interaction[5] between thallium in organothallium compounds and nitroxide radical which manifests itself as decoupling effect of long range [13]C–[205]Tl coupling and simplifies the spectra enough to be assigned very easily.

It is well established that thallium in organothallium compounds serves as a Lewis acid toward electron-donating Lewis bases such as pyridine and triphenylphosphine oxide.[6] This suggests that nitroxide radical may also form a weak complex with organothallium compounds at the central metal atom, resulting in effective relaxation of thallium nuclei. This nitroxide–thallium interaction may lead to Tl–[13]C nuclear spin decoupling.