

peaks should be shifted and broadened, not sharp peaks as observed. This argument, however, is erroneous. According to the original proposal,¹⁸ the porphyrin cation radical of compound 1 of HRP is in the $^2A_{2u}$ state which has spin density only on the meso carbons and the nitrogen atoms;¹⁹ therefore, the methyl groups attached to the β positions should not be affected (J. Fajer, L. K. Hanson, and C. K. Chang, manuscript in preparation.)

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- (20) EPR and Mössbauer measurements of the green intermediate are in progress.
- (21) J. T. Groves, T. E. Nemo, and R. S. Myers, *J. Am. Chem. Soc.*, **101**, 1032 (1979), have recently reported similar hydroxylation reactions using iodobenzene. It may be worthwhile to point out that Fe^{III} TPP is a superior catalyst to Fe^{III} OEP since TPP is more stable toward meso cleavage.

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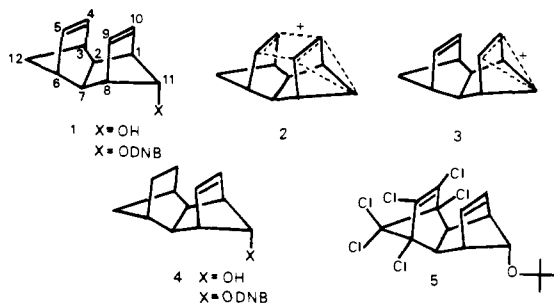
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Nonconjugated Charge Delocalization by Remote π Electrons via Relay through a Double Bond Proximate to a Solvolysis Center

Sir:

Diene **1** is of considerable fundamental interest regarding our understanding of factors which influence chemical reactivity because of its remarkably high reaction rate in solvolysis. Comparison of **1** with the historic *anti*-7-norbornenyl and 7-norbornyl systems¹ shows the relative rate ratio to be $10^{14}:10^{11}:1$ (at 25 °C), respectively.² The enormous reactivity of **1** was attributed to π -electron participation of the remote C_4C_5 double bond by relay through the C_9C_{10} double bond to give the extensively charge delocalized carbocation **2**.² Theoretical calculations agree with this and predict **2** to have considerable extra stabilization.³ However, it has been claimed by Paquette and Dunkin⁴ that, owing to leveling of the rate ratios, the three-carbon $C_9C_{10}C_{11}$ network shown in **3** prevails and $C_4=C_5$ does not *anchimerically assist* ionization.

We find the latter interpretation to be highly questionable. It appears that "leveling of rate ratios" refers to the observation that a diene-monoene combination like **1** and **4** has the same rate within a factor of ~ 2 .⁴ However, the Paquette cases⁴ and **1** and **4** (*vide infra*) all show *large rate* enhancements of 200–1000 (depending on the temperature of comparison) over the *anti*-7-norbornenyl system. Apparently this fact was not



considered to be important.⁴ Our reevaluation of the status of the whole problem has prompted us to initiate a detailed investigation seeking new experimental information.

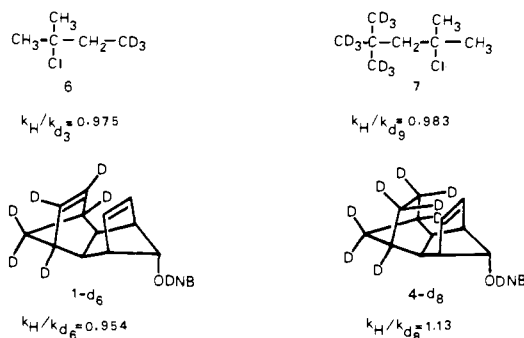
The logical first step is to see if the $C_4=C_5$ moiety is involved in the rate-determining step of the solvolysis reaction. Study of secondary deuterium isotope effects has proven to be a very informative investigative tool in this connection.⁵ Accordingly, **1**-ODNB and 3,4,5,6,12,12-**1**-ODNB- d_6 were prepared for such examination. Monoenes **4**-ODNB and

3,4,4,5,5,6,12,12-**4**-ODNB- d_8 also were obtained for comparison purposes.

Known compound **5**⁶ was converted to **1**-OH and **4**-OH. It was found to be advantageous to remove the *tert*-butyl group from **5** with $HClO_4$ in THF and protect the OH function as the tetrahydropyranyl ether by reaction with dihydropyran in dry ether containing a trace of HOTs. Dechlorination of the pyranyl ether with sodium in dry THF-*t*-BuOH, removal of the protecting group with aqueous $HClO_4$ -THF, washing of a combined ether solution of crude product with water and then aqueous $NaHCO_3$, followed by evaporation of the ether, and recrystallization of the oil from hexane gave **1**-OH.⁷ An ether solution of the residue was extracted with aqueous $AgNO_3$ and treated with aqueous $HClO_4$, followed by aqueous $NaHCO_3$, and the ether was removed. Recrystallization of this concentrate from hexane afforded **4**-OH.⁷ Preparation of **1**-OH- d_6 and **4**-OH- d_8 was achieved by using sodium in dry THF-*t*-BuOD⁸ in the dechlorination step; deuterium incorporation was $>97\%$.⁷ The desired dinitrobenzoates were obtained from reaction of the corresponding alcohols with 3,5-dinitrobenzoyl chloride in pyridine.⁷

Solvolysis studies were carried out in 80% aqueous dioxane at 85.00 ± 0.02 and 87.00 ± 0.01 °C for **1**-ODNB and **4**-ODNB, respectively. Product analyses after ~ 10 reaction half-lives by GC and NMR showed only formation of anti-retained alcohols from both diene and monoene systems. Kinetic measurements were made by following the changes in conductivity with a Radiometer Model CDM3 conductivity meter.⁹ Five concurrent **1**-ODNB and **1**-ODNB- d_6 runs were made in the same constant-temperature bath with *carefully* matched conductivity cells which had been degassed (N_2) and sealed.^{10a} In each successive run the cells used for **1**-ODNB and **1**-ODNB- d_6 were switched. The rate constants were calculated from the standard first-order rate law using a least-squares computer program. Average values were $k_H = 6.627 \times 10^{-5} s^{-1}$ and $k_D = 6.946 \times 10^{-6} s^{-1}$ with $k_H/k_D = 0.954 \pm 0.001$.^{10a} For **4**-ODNB and **4**-ODNB- d_8 four separate concurrent rate measurements were made in the same way.^{10b} Average values were $k_H = 6.662 \times 10^{-5} s^{-1}$ and $k_D = 5.920 \times 10^{-5} s^{-1}$ with $k_H/k_D = 1.13 \pm 0.02$.^{10b} A rate constant for **4**-ODNB also was determined at 85.00 °C for comparison purposes; $k = 4.23 \times 10^{-5} s^{-1}$. The **1**-ODNB:**4**-ODNB rate ratio is 1.57:1.

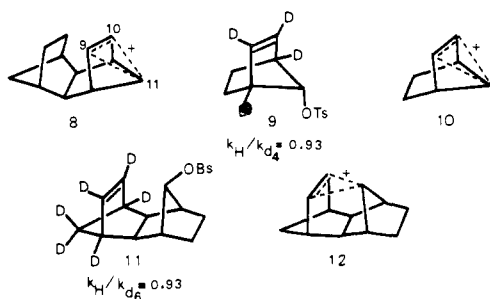
Rate effects on limiting solvolysis reactions caused by deuteration of remote saturated C-H positions not conjugated with the reaction site ordinarily show inverse isotope effects.^{5a,11} Solvolyses of **6**¹¹ and **7**^{5a} in 80% aqueous EtOH at 25 °C illustrate typical γ and δ effects. These kinds of k_H/k_D



values are ascribed to normal inductive interaction which attenuates by a factor of ~ 3 for each intervening saturated carbon and becomes minuscule per D at the δ position and almost nil beyond that.^{5a} Calculations based on this for **1**-ODNB- d_6 predicts k_H/k_D to be essentially unity (>0.998). It is evident that the inverse isotope effect found with **1**-ODNB- d_6 is significantly larger than can be accounted for by an inductive factor.

Comparison of **1**-ODNB- d_6 and **4**-ODNB- d_8 isotope effects is instructive. The diametric results are indicative that the reactivities of the diene and monoene differ in origin. In this regard, a k_H/k_D value substantially greater than unity for **4**-ODNB- d_8 is striking. Several observations, taken collectively, lead to a plausible explanation of the effect. First, **4**-ODNB has very high solvolytic reactivity. Comparison of **4**-ODNB with the *anti*-7-norbornenyl and 7-norbornyl systems show a relative rate ratio of $10^{14}:10^{11}:1$, respectively. This and the product results clearly indicate that solvolysis of **4**-ODNB proceeds by anchimeric assistance to give charge delocalized intermediate **8**. Second, an examination of scale molecular models shows that severe steric repulsion occurs between the C_4C_5 inside ϵ hydrogens and the C_9C_{10} π -electron bridge.¹² This indicates that the C_9C_{10} π electrons are forced closer to the C_{11} reaction site in the reactant state and that additional rate enhancement of 10^3 for **4**-ODNB over the *anti*-7-norbornenyl structure is a consequence of the severe sterically congested environment. Finally, it is well known that C-H bonds have greater vibrational amplitudes compared with analogous C-D bonds.¹³ These considerations predict $k_H/k_D > 1$.¹³ On the basis of information now available the best working hypothesis is that the remote ϵ deuterium isotope effect of $k_H/k_D = 1.13$ is of steric derivation.

All things considered, it is clear that the ϵ -D inverse isotope effect observed with **1**-ODNB- d_6 is neither inductive nor steric in nature. This result is accounted for best in terms of remote C_4C_5 π -electron participation in the rate-determining step by relay through the C_9C_{10} bridge to the C_{11} reacting site to give charge delocalized cation **2**. A net inverse effect is just what is expected for rehybridization going from sp^2 toward sp^3 C.¹⁴ Support for neighboring double-bond participation is found in the k_H/k_D value observed for solvolysis of **9** in 96% EtOH.^{15a} Participating π electrons in the rate-determining



step for **9** \rightarrow **10** is well documented. Additional confirmation is afforded by the similar magnitude of the ϵ -D isotope effect observed^{15b} for acetolysis of the closely analogous **11** \rightarrow **12** process.¹⁶

These new results provide clear-cut evidence that the near identity of solvolytic reactivity found with **1**-ODNB and **4**-ODNB is *not due* to the inability of the remote C_4C_5 π electrons of **1**-ODNB to assist ionization in the rate-determining step as maintained by Paquette and Dunkin.⁴ Instead the correspondence in rate acceleration is purely fortuitous and it is due to different reactivity factors operating with each system. For **4**-ODNB the rate enhancement is a consequence of severe steric strain. In the case of **1**-ODNB the remote π electrons are a part of the driving force for anchimerically assisted ionization.

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Photochemical Cyanation of Acetophenones. Acetyl Displacement

Sir:

In a previous communication Letsinger and Colb reported that a variety of methyl- and methoxy-substituted acetophenones underwent nucleophilic attack by cyanide upon irradiation.¹ From structure elucidation studies of the principal isolable products, three reaction modes were documented: rearrangement by acetyl migration, cyanation by methoxy-group displacement, and phthalide formation by cyanide incorporation and hydrogen transfer. This communication reports preliminary details of a fourth reaction type, the net displacement of acetyl by cyanide, a transformation which was discovered while investigating solvent effects upon the reported photochemical reactions. Acetyl displacement from acetophenones through either a photochemical or thermal process appears to be without prior precedent in the chemical literature. Indeed, Snyder² has reported that carbonyl compounds such as benzophenone and benzaldehyde are thermally unreactive toward cyanide in DMF, a potent cyanation medium.

In the transformations outlined below, the acetyl group of certain acetophenones (**1a-d**) was displaced by cyanide ion³ to form the corresponding benzonitriles (**2a-d**). On a preparative scale, the yields of methoxybenzonitriles were modest, the highest being $\sim 41\%$ overall of 2'-methoxybenzonitrile, equivalent to 64% yield at 65% conversion.⁴ In other prepar-