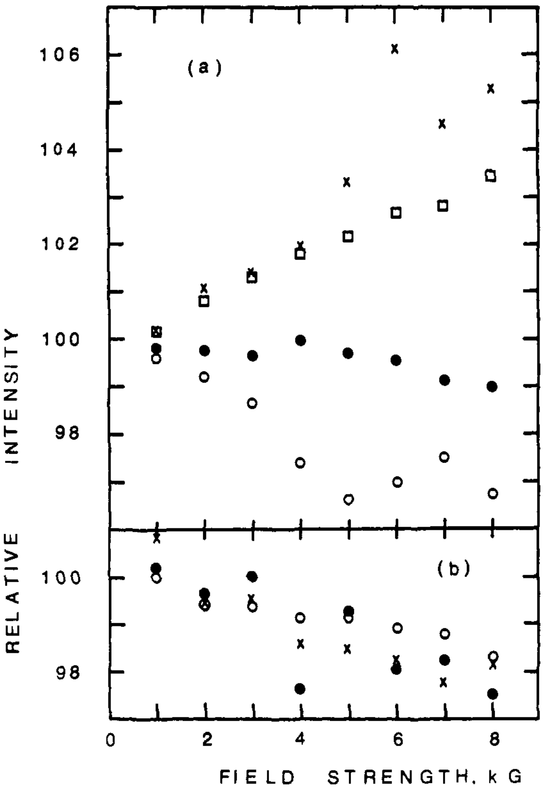

Figure 1. (a) Magnetic field effect on delayed fluorescence from 2.1 $\times$ 10^{-4} M anthracene and different amounts of oxygen in DMF: O, no oxygen, delayed fluorescence lifetime, τ = 4.3 msec; ●, 7.5 $\times$ 10^{-4} atm, τ = 3.9 msec; □, 3 $\times$ 10^{-3} atm, τ = 2.7 msec; $\times$, 6 $\times$ 10^{-3} atm, τ = 1.9 msec. (b) 2.5 $\times$ 10^{-4} M anthracene and different amounts of oxygen in acetonitrile: O, no oxygen, τ = 3.2 msec; $\times$, added oxygen, 1.5 $\times$ 10^{-3} atm, τ = 1.2 msec; ●, 3 $\times$ 10^{-3} atm, τ = 0.9 msec.

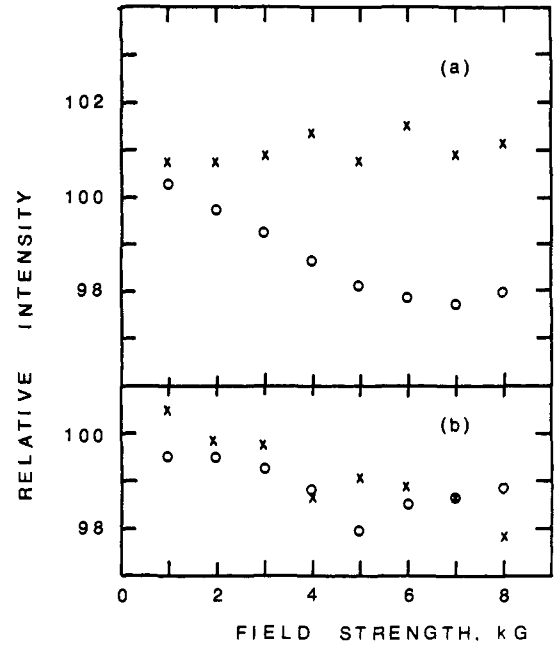

Figure 2. (a) Magnetic field effect on delayed fluorescence (emission at 390 nm) from a 2.6 $\times$ 10^{-4} M solution of pyrene in DMF: O, no oxygen, τ = 1.4 msec; $\times$, added oxygen, 6 $\times$ 10^{-3} atm, τ = 0.7 msec. (b) 2.0 $\times$ 10^{-4} M pyrene in acetonitrile: O, no oxygen, τ = 2.1 msec; $\times$, added oxygen, 2.2 $\times$ 10^{-5} atm, τ = 1.4 msec.

sample was prepared by at least eight freeze–pump–thaw cycles, then sufficient oxygen to partially quench the triplet state yet still yield detectable DF signals was introduced through the vacuum line, and finally the cell was sealed off with a torch. DF studies of anthracene and pyrene in N,N-dimethylformamide (DMF) and acetonitrile in the absence of oxygen showed the usual decrease in DF intensity with increasing magnetic field strength, caused by a decrease in the rate of the triplet–triplet annihilation reaction[1] (Figures 1 and 2). When oxygen was introduced into the samples, upon initial exposure to the excitation beam, no DF signal was observed. After several minutes the DF signal increased to measurable levels. This increase in DF signal with time has been observed previously in studies of DF in the solid state in the presence of oxygen[10] and is probably caused by a depletion in the concentration of oxygen by reaction with the triplet of the aromatic hydrocarbon to form the transannular peroxide. The DF signals in DMF solutions for both anthracene and pyrene show an increase in intensity with increasing magnetic field strength (Figures 1 and 2) indicating a decrease in the rate of reaction 1 at higher fields, paralleling the results observed for quenching of triplets by radical cations.[4] In acetonitrile, on the other hand, no change in DF behavior was observed upon addition of oxygen for both anthracene and pyrene, although oxygen quenching was occurring, as seen by a decrease in the lifetime (τ) of the aromatic triplet. A solvent dependency on the magnetic field effect on triplet–triplet annihilation was observed previously,[2,4] and these results lend further support to the importance of the role of the solvent in these processes.

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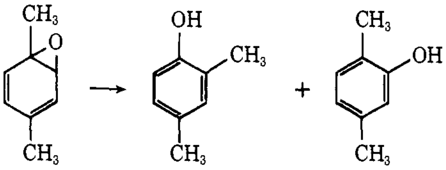
[10] R. C. Johnson, V. Ern, D. W. Wiley, and R. E. Merrifield, *Chem. Phys. Lett.*, **11**, 188 (1971).

The Oxygen Walk as a Complementary Observation to the NIH Shift

Sir:

Aromatization of arene oxides may occur with or without group migration (NIH shift[1]). A well-studied example is provided in eq 1.[2] From profiles of log



(1)

k_{obsd} *vs.* pH and lack of buffer acid catalysis, the aromatization reaction can be shown to occur both by spontaneous and *specific* acid catalysis (*i.e.*, $k_{\text{obsd}} = k_0 + k_{\text{H}}[\text{H}^+]$).[3] In addition, from values of $\Delta S^{\ddagger}$,

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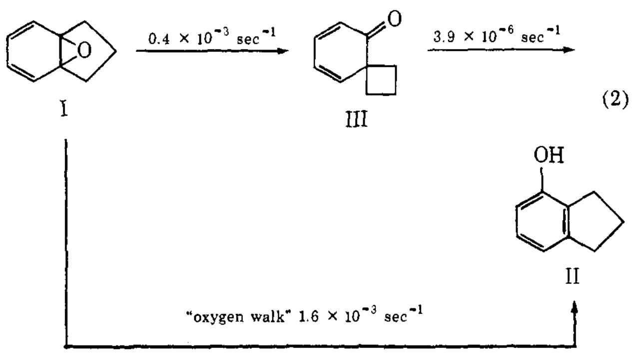
[1] (a) G. Guroff, J. W. Daly, D. M. Jerina, J. Renson, B. Witkop, and S. Udenfriend, *Science*, **157**, 1524 (1967); (b) J. W. Daly, D. M. Jerina, and B. Witkop, *Experientia*, **28**, 1129 (1972).

[2] (a) H. Yagi, D. M. Jerina, G. J. Kasperek, and T. C. Bruice, *Proc. Nat. Acad. Sci. U. S.*, **69**, 1985 (1972); (b) E. A. Fehnel, *J. Amer. Chem. Soc.*, **94**, 3961 (1972); (c) G. J. Kasperek, T. C. Bruice, H. Yagi, and D. M. Jerina, *ibid.*, **94**, 7876 (1972); (d) N. Kaubisch, J. W. Daly, and D. M. Jerina, *Biochemistry*, **11**, 3080 (1972).

[3] G. J. Kasperek and T. C. Bruice, *J. Amer. Chem. Soc.*, **94**, 198 (1972).

lack of deuterium solvent isotope effects,[3] establishment of great sensitivity to substituent electronic effects, plus lack of kinetic primary deuterium isotope effects for both benzene and naphthalene oxides, the rate-determining step for both k_0 and k_H has been established to be carbonium ion formation.[4] This being so, it might be anticipated that, for suitably favorable cases (stable carbonium ions), collapse of the carbonium ion to give an isomeric arene oxide could compete with collapse back to the original arene oxide prior to aromatization to a phenol. This would result in oxygen migration around the ring ("oxygen walk").

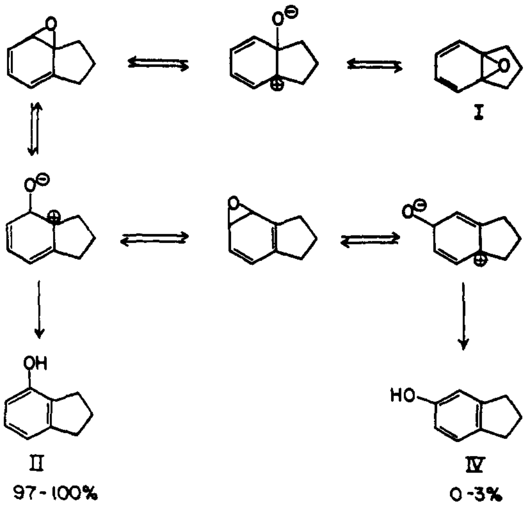
The isomerization of 8,9-indane oxide (I) to 4-indanol (II) was studied by Vögel and Günther,[5] who concluded from the isolation of a Diels-Alder adduct of the spiro ketone (III) that III was a requisite intermediate yielding II *via* dienone phenol rearrangement. We report herein kinetic studies (eq 2) which reveal that



(2)

the path through III is a minor one and that the major portion of II arises from I *via* a requisite "oxygen walk." Repetitive scanning (30°, 50% dioxane–H_2O, v/v, μ = 0.1 with KCl, pH 7–12) reveals a pH-independent first-order ($k_0 = 1.4 \times 10^{-3}$ sec^{-1}) disappearance of I (250 mμ) with simultaneous appearance of II (285 nm (ϵ 3.42 × 10), 275 (6.19 × 10^2 M^{-1} cm^{-1}))[6] and the spiro ketone III (320 mμ).[7] After complete disappearance of I, first-order disappearance of III commences ($k_1 = 3.9 \times 10^{-6}$ sec^{-1}), and at t_∞ the only species present is II.[6] Only 30% of II is produced *via* I → III → II. (In a separate experiment, it was shown that pure III aromatizes to II at the same rate that III produced *in situ* aromatizes to II.) Since II is produced before a significant amount of III has formed and is produced more rapidly than III → II, II must also be produced from I (eq 2) *via* an "oxygen walk" (Scheme I). A second oxygen walk is possible and would account for the minor amounts of 5-indanol[6] observed during the isomerization of I. The decreased stability of the carbonium ion leading to 5-indanol accounts for only a small amount of that compound being produced.

Scheme I



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[4] G. J. Kasperek, T. C. Bruice, H. Yagi, and D. M. Jerina, *J. Chem. Soc., Chem. Commun.*, 784 (1972).

[5] E. Vögel and H. Günther, *Angew. Chem., Int. Ed. Engl.*, **6**, 385 (1967).

[6] Isolated from reaction mixture and shown to be identical with an authentic sample by glc, tlc, and nmr. Trace amounts (2–3%) of a glc peak corresponding to 5-indanol have been detected.

[7] Identification of spiro[3,5]nona-6,8-dien-5-one (III): the 100-MHz spectrum (CS_2 solution, line position in δ relative to TMS, and coupling constants in hertz) was assigned as six methylene cyclobutane hydrogens 1.70–3.10 and four vinyl hydrogens with 1 H_6 5.87, 1 H_7 6.86, 1 H_8 6.10, and 1 H_9 6.72; ${}^3J_{6,7} = {}^3J_{8,9} = 9.5$, ${}^3J_{7,8} = 6$, ${}^4J_{6,8} = 1$, ${}^4J_{7,9} = 1.75$, and ${}^5J_{8,9} = 0.71$ Hz. Concentration of the CS_2 solution resulted in formation of a Diels–Alder dimer whose melting point and ir, nmr, and mass spectra were identical with those of the dimer previously identified among the rearrangement products of 8,9-indane oxide: M. Wiesel, Ph.D. Thesis, Der Universitaté Köln, 1966, p 61. The σ_{max} 318 nm (ϵ 4305 M^{-1} cm^{-1}) (50% dioxane–H_2O) for the spiroketone was based on the weight of dimer produced after concentration.

Transition Metal Catalyzed [2 + 2] Cross-Addition of Olefins. Nickel(0)-Catalyzed Cycloaddition of Norbornadiene and Methylenecyclopropane

Sir:

One of the most intriguing natures of transition metal complexes is the ability to catalyze cycloaddition of olefins leading to cyclobutane derivatives, since the reaction mode is formally envisaged as a thermally forbidden [$_\pi 2_s + {}_\pi 2_s$] process.[1] Although there exist

$$\| + \| \xrightarrow{M} \square$$

various examples of cyclodimerization reactions,[2,2i] only a few cases are known of coupling between two different olefins.[3,4] The essential intermediate in the cross-coupling reaction of olefins A and B is believed to be a

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[1] R. B. Woodward and R. Hoffmann, *Angew. Chem.*, **81**, 797 (1969).

[2] For example: (a) C. W. Bird, R. C. Cookson, and J. Hudec, *Chem. Ind. (London)*, 20 (1960); (b) C. W. Bird, D. L. Colinese, R. C. Cookson, J. Hudec, and R. O. Williams, *Tetrahedron Lett.*, No. **11**, 373 (1961); (c) P. W. Jolly, F. G. A. Stone, and K. MacKenzie, *J. Chem. Soc.*, 6416 (1965); (d) P. Heimbach and W. Brenner, *Angew. Chem.*, **79**, 813 (1967); (e) G. N. Schrauzer, *Advan. Catal.*, **18**, 373 (1968); (f) F. W. Hoover and R. V. Lindsey, Jr., *J. Org. Chem.*, **34**, 3051 (1969); (g) F. J. Weigert, R. L. Baird, and J. R. Shapley, *J. Amer. Chem. Soc.*, **92**, 6630 (1970); (h) P. Binger, *Angew. Chem.*, **84**, 352 (1972).

[2i] Note Added in Proof. Quite recently the intervention of a metallocyclic intermediate in metal catalyzed [2 + 2] cycloaddition reactions has been demonstrated: A. R. Fraser, P. H. Bird, S. A. Bezman, J. R. Shapley, R. White, and J. A. Osborn, *J. Amer. Chem. Soc.*, **95**, 597 (1973).

[3] A. Greco, A. Carbonaro, and G. Dall'Asta, *J. Org. Chem.*, **35**, 271 (1970); D. R. Coulson, *ibid.*, **37**, 1253 (1972).