styrene oxide and gave exclusively **8,** and *cis*-β-methylstyrene oxide gave a mixture of **9** and **10,** in the same proportion as in the reaction with the TMT:ZnCl$_2$:O$_2$ mixture. In fact, treatment of the epoxides with a mixture of TMT and ZnCl$_2$ gave the same products.[8] The case for an epoxide intermediate was further strengthened by the observation that treatment of cyclooctene with TMT:ZnCl$_2$:O$_2$ mixture in the THF gave a 12% isolated yield of cyclooctene oxide **11.** This epoxide is extraordinarily unreactive toward nucleophilic ring opening. No amino alcohol was formed when **11** was treated with dimethylamine or with the TMT:ZnCl$_2$ mixture.[9]

There is some evidence that mechanism 4 may be competing with the epoxidation mechanism under our conditions. The reaction of indene oxide with dimethylamine of the TMT: ZnCl$_2$ complex fails to give any **6,** and yet this product is formed in the reaction with the TMT:2nCl$_2$:O$_2$ mixture. A small (5%) but significant yield of 1-dimethylamino-2-octanol was obtained in the reaction of 1-octene with TMT:ZnCl$_2$:O$_2$. This product was also formed when octane-1,2-epoxide was stirred with dimethylamine for several days. However, there was also obtained a small amount of *N,N*-dimethyl-6-hydroxy-1-octylamine in the TMT:ZnCl$_2$:O$_2$ reaction. This product could only have been formed by intramolecular H-atom transfer in the intermediate 1-dimethylamino-2-octyl radical, followed by reaction with oxygen.

Reaction 1 is reversible. Little or no amino alcohols were formed if the temperature of the reaction was raised to 100 °C or if the oxygen flow was restricted. The main product under those conditions was the addition of two dimethylamino groups to the double bond.[10] In the absence of ZnCl$_2$ the epoxidation reaction does not proceed well. Only a trace of (<1%) was obtained when TMT was photolyzed in the presence of cyclooctene and oxygen. The role of ZnCl$_2$ is not understood yet. It may force the equilibrium (eq 1) further to the right or it may stabilize the nitroxyl radical (or both).[11] There is little precedent for reactions 1 and 2 in the literature. Reaction 1 is reminiscent of the formation of peroxy nitrogen trioxide from nitric oxide and oxygen,[12] but the closest analogy for eq 2 are reactions such as those of acylperoxy radicals with alkenes to give epoxides and the corresponding carboxylic acids.[13] The latter, however, may have an alternative explanation. The present data indicate the epoxide formation is stereospecific and consequently the reaction seems to be a concerted transfer of an oxygen atom from **1** to the alkene. This type of reaction may be a fairly general phenomenon. In fact, something like this may be occurring during biological epoxidations where atmospheric oxygen is introduced stereospecifically into double bonds (such as in squalene [14]) or aromatic systems (such as carcinogenic polynuclear aromatic hydrocarbons[15]). Further work on this reaction is progressing in our laboratory.

Acknowledgment. We are grateful to the National Science Foundation (Grant No. MPS 7411792) for support of this research, and to Dr. W. C. Danen, Kansas State University, and Mr. David Sieh, University of Nebraska, for their help with ESR experiments.

References and Notes

(1) This is paper 3 of a series dealing with complexed radicals. Paper 2 is V. W. Day, D. H. Campbell, and C. J. Michejda, *J. Chem. Soc., Chem. Commun.*, 118 (1975).

(2) The neutral fraction was also examined, but not in as much detail. No epoxides were found in this fraction for the first groups of alkenes discussed.

(3) The components of interest were also compared with authentic samples and, where these were not available, satisfactory microanalytical data were obtained. Details of the structural assignments will be published in a full paper.

(4) F. Minisci and R. Galli, *Tetrahedron Lett.*, 3197 (1964).

(5) C. F. Huebner, E. M. Donaghue, C. J. Novak, L. Dorfman, and E. Wenkert, *J. Org. Chem.*, **35,** 1149 (1970).

(6) Structure confirmed by single-crystal x-ray structure analysis of the hydrobromide salt (to be submitted for publication).

(7) These products were formed in low yields (ca. 5%), but trace amounts of the other isomers would have been detected by our analytical procedure.

(8) The nucleophilic opening of the epoxides may be a fairly complicated reaction. Some dimethylamine is formed in the disproportionation of amino radicals. However, TMT may also react with the epoxides in a manner similar to that of its' reactions with other alkylating agents. Cf. C. J. Michejda and D. Romans, *Tetrahedron Lett.*, 281 (1968).

(9) A referee made a reasonable suggestion that 11 could be formed by an autooxidation mechanism (cf. D. E. Van Sickle, F. R. Mayo, E. S. Gould, and R. M. Arluck, *J. Am. Chem. Soc.*, **89,** 977 (1967)). This does not seem to be the case here. An increase in O$_2$ pressure over the reaction (up to 3 atm) did not inhibit epoxide formation, as seems to be the case in the autooxidation reaction. An increase in temperature (up to 100 °C), however, did decrease the amount of epoxide, presumably because of the reversibility of eq 1, but contrary to what is expected for an autooxidation reaction.

(10) C. J. Michejda and D. H. Campbell, *J. Am. Chem. Soc.*, **96,** 929, (1974).

(11) Nitroxyl radicals, which have an H-atom next to the nitrogen, decompose primarily by disproportionation (K. Adamic, D. F. Bowman, J. Gillian, and K. U. Ingold, *J. Am. Chem. Soc.*, **93,** 902 (1971)). Consonant with that, we find dimethylhydroxylamine in the products of the reaction. When the reaction is carried out in the cavity of an ESR spectrometer, the spectrum of the very stable tetramethyl hydrazine radical cation is observed, together with the spectrum of another, unstable, nitrogen radical. The spectrum of the unstable radical (obtained by subtracting away the $TMH\cdot^+$ spectrum) is consistent with that of dimethylnitroxyl. The spectrum could be simulated by assuming $a_N = 15.2$ G, $a_H = 12.3$ G, line width of 3.9 G.

(12) W. A. Guillory and H. S. Johnston, *J. Chem. Phys.*, **42,** 2457 (1965).

(13) P. I. Valov, E. A. Blyumberg, and N. M. Emanuel, *Izv. Akad. Nauk*, 1334 (1966); cf. N. M. Emanuel in Special Lectures, XXIIIrd International Congress, IUPAC, Boston, Mass., Butterworths, London, 1971, p 337.

(14) S. Yamamoto and K. Bloch in "Natural Substances Formed from Mevalonic Acid", T. W. Goodwin, Ed., Academic Press, New York, N.Y., 1969, p. 35.

(15) P. L. Grover, P. Sims, E. Huberman, H. Marquardt, T. Kuroki, and C. Heidelberger, *Proc. Natl. Acad. Sci. USA*, **68,** 1098 (1971).

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A Novel Stereospecific Alkenyl–Alkenyl Cross-Coupling by a Palladium- or Nickel-Catalyzed Reaction of Alkenylalanes with Alkenyl Halides

Sir:

Direct and selective coupling of two unlike alkenyl groups by the reaction of an alkenylmetal derivative with an alkenyl halide has been difficult. None of the known alkenylmetals of the main group elements appears to undergo satisfactorily a stereospecific substitution reaction with an alkenyl halide.[1] Although the reaction of alkenylcuprates with alkenyl halides is promising, it does not appear to have been well developed.[2]

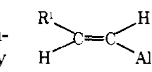
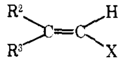
We wish to report that a general and selective procedure for the synthesis of conjugated (*E,E*)- and (*E,Z*)-dienes can now be provided by the reaction of (*E*)-alkenylalanes, readily obtainable via hydroalumination of alkynes,[3] with alkenyl halides in the presence of suitable palladium or nickel complexes (eq 1).

The scope of the new procedure is indicated by the results summarized in Table I and a few representative examples shown below.

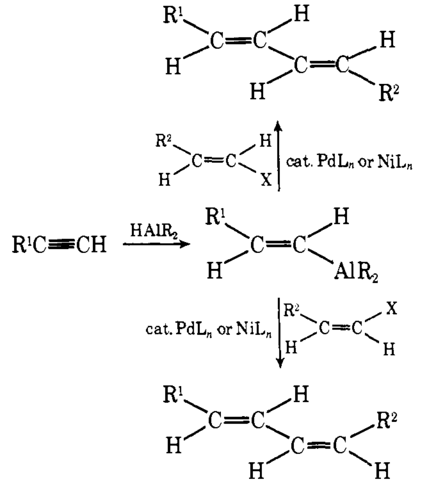
Although no detailed mechanistic study has been made, the initial step must involve the oxidative addition of an alkenyl halide to a Pd or Ni complex to form the intermediate (**1**),[4] since no other binary combinations induce any noticeable reaction under these conditions. The following mechanism which is analogous to those proposed for other related cross-coupling reactions[4] seems to accommodate all of the experimental results (eq 5).

The following observations and interpretations may be worth noting. (1) The Pd-catalyzed reaction in each case is highly stereospecific (≥97%), supporting an assumption that all steps proceed with retention of configuration.[5] Moreover, no ho-

Table I. Alkenyl–Alkenyl Cross-Coupling by the Palladium- or Nickel-Catalyzed Reaction of (*E*)-Alkenylalanes with Alkenyl Halides[a]

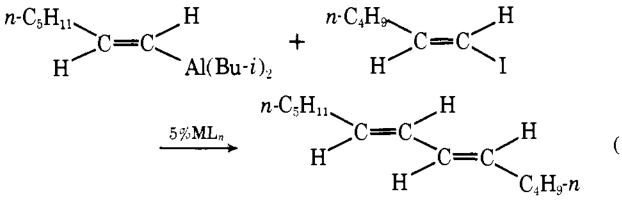
Entry	R^1 of 	R^2 	R^3	X	M of $M(PPh_3)_n$	Cross-coupled product Yield,[b] %	*E,E*/*E,Z*	Homocoupled product[c] (yield, %)
1	n-C_5H_{11}	n-C_4H_9	H	I	Pd	74 (60)	>99/1	Traces
2	n-C_5H_{11}	n-C_4H_9	H	I	Ni	70	95/5	n-C_{12} (2), n-C_{14} (15)
3	n-C_5H_{11}	H	n-C_4H_9	I	Pd	55	>99/1	n-C_{12} (2), n-C_{14} (trace)
4	n-C_5H_{11}	H	n-C_4H_9	I	Ni	55	90/10	n-C_{12} (4), n-C_{14} (trace)
5	n-C_4H_9	t-C_4H_9	H	I	Pd[d]	82 (71)	>99/1	Traces
6	n-C_4H_9	t-C_4H_9	H	I	Ni	48	93/7	n-C_{12} (6), t-C_{12} (8)
7	t-C_4H_9	n-C_4H_9	H	I	Ni	15	93/7	—
8	t-C_4H_9	H	n-C_4H_9	I	Pd[d]	36	97/3	n-C_{12} (2), t-C_{12} (2)
9	n-C_4H_9	$COOCH_3$	CH_3	Br	Pd[d]	75 (61)	97/3	Traces

[a] The amount of a catalyst in each case is 5 mole %. The Ni catalyst was prepared by the reaction of anhydrous $Ni(acac)_2$ with 2 equiv of diisobutylaluminum hydride in the presence of 4 equiv of triphenylphosphine. The Pd catalyst was prepared from dichlorobis(triphenylphosphine)palladium and 2 equiv of diisobutylaluminum hydride. Unless otherwise stated, the reaction was carried out in a mixture of ether–hexane at room temperature (ca. 25 °C). [b] By GLC. The numbers in parentheses are isolated yields. [c] n-C_{12} = (n-$C_4H_9CH{=}CH-)_2$, n-C_{14} = (n-$C_5H_{11}CH{=}CH-)_2$, t-C_{12} = (t-$C_4H_9CH{=}CH-)_2$. [d] In THF–hexane.



(1)

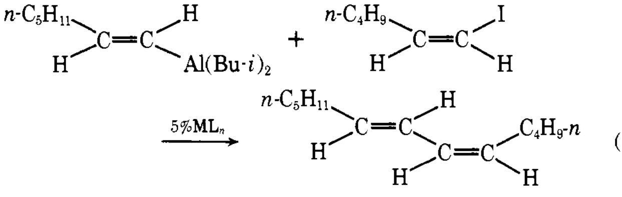
R^1, R^2 = alkyl; R = i-Bu; X = Br or I; L = PPh_3



(2)

M = Pd, 74%, >99%*E*, *E*

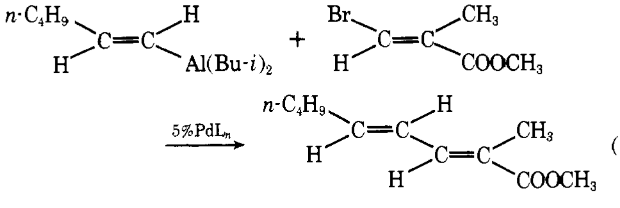
M = Ni, 70%, 95%*E*,*E*, 5%*E*,*Z*



(3)

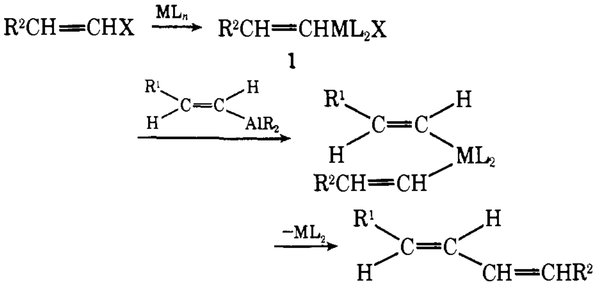
M = Pd, 55%, >99%*E*,*Z*

M = Ni, 55%, 90%*E*,*Z*



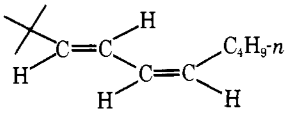
(4)

75%, 97%*E*,*E*

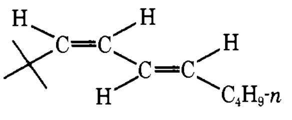


(5)

mocoupled products are formed in any significant amounts (<2%), thereby making palladium complexes the catalysts of choice. (2) The stereospecificity of the Ni-catalyzed (*E*,*E*)-diene synthesis is ca. 95%, whereas that of the (*E*,*Z*)-diene synthesis is ca. 90%. To establish unequivocally the stereochemistry of the isomeric by-product in the (*E*,*E*)-diene synthesis (*E*)-1-hexenyldiisobutylalane was reacted with (*E*)-1-iodo-3,3-dimethyl-1-butene under the influence of $Ni(PPh_3)_4$. The major by-product has been identified as (*E*,*Z*)-2,2-dimethyl-3,5-decadiene (**2**) by GLC coinjection with an authentic sample prepared stereospecifically by the Pd-catalyzed reaction of (*Z*)-1-iodo-1-hexene with (*E*)-3,3-dimethyl-1-butenyldiisobutylalane.[6] The amount of the *Z*,*E* isomer (**3**),[6] which has a longer GLC retention time (SE-30) than **2**, was negligible (<1%). This and other results presented here appear consistent with a view that the presumed oxidative addition of alkyl-substituted alkenyl halides to nickel(0) complexes is highly stereospecific, somewhat contrary to a suggestion made in the paper on the homodimerization of alkenyl halides.[7] However, a more definitive conclusion on this point must await further clarification. (3) In the Ni-catalyzed cross-coupling reaction, the amount of the dimer of the alkenyl halide formed competitively is less than 5% of the cross-coupled product, indicating that the cross-coupling reaction is considerably faster than the dimerization.[7] (4) It should be emphasized that the use of (*E*)-alkenylalanes permits a highly facile stereoselective introduction of one of the alkenyl groups which does not require isolation or purification of any alkenyl intermediate.[8] Among alkenylmetal derivatives readily obtainable as discrete species via hydrometalation of alkynes, alkenylalanes appear almost uniquely suited. For, the corresponding alanates have given the desired products in much



2



3

lower yields, and the corresponding boranes and borates have failed to provide the desired products in any significant amounts.[9] (5) Proper selection of solvents appears to be of crucial importance. Ethyl ether is satisfactory for the Ni-catalyzed reactions and some of the Pd-catalyzed reactions. In more polar solvents such as THF these reactions proceed appreciably faster. However, the relative amounts of undesired isomers and homocoupled products also increase, especially in the Ni-catalyzed reactions. (6) Although our study with functionalized alkenes is limited, the ester group can be tolerated as indicated in eq 4. (7) Finally, the product yield is low, when the alkyl substituent of alkenylalanes is sterically demanding (entry 7). However, the same product can be obtained in considerably higher yields by using the corresponding iodide (entry 5 or 6).

The following procedure for the preparation of methyl (*E,E*)-2-methyl-2,4-nonadienoate is representative. To 0.74 g (1 mmol) of dichlorobis(triphenylphosphine)palladium[10] suspended in 20 ml of THF were added sequentially 0.37 ml (2 mmol) of neat diisobutylaluminum hydride (25 °C, 10 min), (*E*)-1-hexenyldiisobutylalane, prepared in a separate flask from 1.64 g (2.28 ml, 20 mmol) of 1-hexyne dissolved in 20 ml of hexane and 2.84 g (3.68 ml, 20 mmol) of diisobutylaluminum hydride, and 3.58 g (20 mmol) of methyl (*E*)-3-bromo-2-methylpropenoate[11] (25 °C). The reaction mixture was refluxed for 15 min, treated with 3 N hydrochloric acid, and extracted with ethyl ether. After the organic layer was dried over $MgSO_4$, filtered, and concentrated at reduced pressure, distillation provided 2.2 g (61%) of methyl (*E,E*)-2-methyl-2,4-nonadienoate: bp 78–79 °C (1 mm); ^1H NMR (CCl_4, Me_4Si) δ 0.90 (t, J = 6 Hz, 3 H), 1.1–1.6 (m, 4 H), 1.90 (s, 3 H), 2.0–2.5 (m, 2 H), 3.67 (s, 3 H), 5.7–6.6 (m, 2 H), and 7.10 (d, J = 10 Hz, 1 H) ppm; ir (neat) 1715 (s), 1645 (s), 1620 (w), 1245 (s), 1105 (s), 975 (s), 750 (s) cm^{-1}.

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References and Notes

(1) We have recently developed a few selective conjugated diene syntheses via organoboranes which, however, do not involve the interaction of an alkenylmetal derivative with an alkenyl halide. (a) E. Negishi and T. Yoshida, *J. Chem. Soc., Chem. Commun.*, 606 (1973); (b) E. Negishi, G. Lew, and T. Yoshida, *ibid.*, 874 (1973).

(2) For a review on the cross-coupling reactions via organocoppers, see G. H. Posner, *Org. React.*, **22**, 253 (1975). In the only example of alkenyl–alkenyl cross-coupling cited in this extensive review, the desired diene was obtained in 27% yield. Moreover, it is not clear whether homocoupled products were obtained or not. G. Büchi and J. A. Carlson, *J. Am. Chem. Soc.*, **90**, 5336 (1968); *ibid.*, **91**, 6470 (1969).

(3) G. Wilke and H. Muller, *Justus Liebigs Ann. Chem.*, **629**, 222 (1960).

(4) (a) K. Tamao, K. Sumitani, and M. Kumada, *J. Am. Chem. Soc.*, **94**, 4374 (1972); (b) R. J. P. Corriu and J. P. Masse, *J. Chem. Soc., Chem. Commun.*, 144 (1972); (c) M. Kumada, "Organotransition-Metal Chemistry", Y. Ishii and M. Tsutsui, Ed., Plenum, New York, N.Y., 1975, p 211, and references cited therein; (d) M. Yamamura, I. Moritani, and S.-I. Murahashi, *J. Organomet. Chem.*, **91**, C39 (1975).

(5) Mechanisms involving double or multiple inversions cannot be ruled out on a rigorous basis, but the essential absence of the *Z,Z* isomer appears incompatible with such mechanisms.

(6) All isolated products were adequately characterized by spectroscopic analyses. The *E,E*, *E,Z*, and *Z,E* isomers of 2,2-dimethyl-3,5-decadiene are distinguishable by GLC (SE-30) and NMR. In particular, the ^{13}C NMR spectra of these isomers show the following distinct olefinic carbon peaks: ^{13}C NMR ($CDCl_3$, Me_4Si) δ *E,E* isomer, 125.7, 131.4, 132.7, and 143.3 ppm; *E,Z* isomer, 120.8, 129.6, 130.2, and 145.4 ppm; *Z,E* isomer, 126.9, 127.4, 135.5, and 139.4 ppm. Their ^1H NMR spectra exhibit singlets for the *tert*-butyl protons at δ 1.02, 1.04, and 1.16 ppm, respectively. The *Z,E* isomer (**3**) was prepared by the procedure recently reported by us[1b] from *tert*-butylethyne and 1-hexyne. Our attempts to prepare **3** by the procedure reported here have not been fruitful due to the tendency of (*Z*)-iodo-3,3-dimethyl-1-butene to isomerize into the *E* isomer during its preparation.

(7) M. F. Semmelhack, P. M. Helquist, and J. P. Gorzynski, *J. Am. Chem. Soc.*, **94**, 9234 (1972).

(8) A related alkenyl-aryl coupling reaction has recently been reported, E. Negishi and S. Baba, *J. Chem. Soc., Chem. Commun.*, 596 (1976).

(9) A study with alkenylzirconium derivatives is in progress.

(10) Neither preformed tetrakis(triphenylphosphine)palladium nor the catalyst prepared in situ from palladium chloride, 2 equiv of triphenylphosphine, and 2 equiv of diisobutylaluminum hydride induces the desired alkenyl–alkenyl coupling.

(11) Prepared stereoselectively (>99% *E*) from methyl methacrylate via bromination–dehydrobromination (85% yield) (P. Canbere, *Bull. Soc. Chim. Fr.*, 144 (1964)).

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The Role of Distance in Electron Transfer in Solution. Experimental Verification of the Hush–Marcus Theory Using Mixed-Valence Complexes

Sir:

Hush and Marcus have shown that for an outer-sphere electron transfer reaction in solution (e.g., $Fe(H_2O)_6^{3+} + Ru(NH_3)_6^{2+} \rightarrow Fe(H_2O)_6^{2+} + Ru(NH_3)_6^{3+}$) the activation free energy ΔG_{12}^* is given by eq 1.[1-5]

$$\Delta G_{12}^* = w_r + \frac{\lambda}{4}\left(1 + \frac{\Delta G_R^{\circ\prime}}{\lambda}\right)^2 \tag{1}$$

In eq 1, w_r is the work needed to bring together the reactants, $\Delta G_R^{\circ\prime}$ is the free energy change on electron transfer within the ion-pair or association complex of the reactants,[6] and $\lambda/4$ is the reorganizational energy arising from rearrangements of the inner- and outer-coordination spheres (eq 2).

$$\lambda = \lambda_i + \lambda_o \tag{2}$$

If it is further assumed that λ is related to the reorganizational λ values for the individual self-exchange reactions ($Fe(H_2O)_6^{3+/2+}$, $Ru(NH_3)_6^{3+/2+}$) as in eq 3,[7]

$$\lambda = (\lambda_{11} + \lambda_{22})/2 \tag{3}$$

the relationship in eq 4 can be derived which has been tested extensively, generally with good success.[1-9]

$$k_{12} = (k_{11}k_{22}K_{12}f)^{1/2} \tag{4}$$

However, correlations using eq 4 are limited in that they fail to give direct insight either into the partitionings of λ suggested in eq 2 and 3, or into other factors such as the effect of distance between reactants on the activation barrier for electron transfer.

In the mixed-valence ion $[(bpy)_2ClRu(pyz)RuCl(bpy)_2]^{3+}$ (bpy is 2,2′-bipyridine) there are discrete Ru(II) and Ru(III) sites and delocalization is slight.[9,10] For such ions, Hush has shown that the energy of the intervalence transfer (IT) band, E_{op} (eq 5; pyz is pyrazine),

$$[(bpy)_2ClRu^{II}(pyz)Ru^{III}Cl(bpy)_2]^{3+} \xrightarrow[E_{op}]{h\nu} [(bpy)_2ClRu^{III}(pyz)Ru^{II}Cl(bpy)_2]^{3+*} \tag{5}$$

is related to the activation energy for the related thermal process, E_{th} (eq 6),

$$[(bpy)_2ClRu^{II}(pyz)Ru^{III}Cl(bpy)_2]^{3+} \xrightarrow[E_{th}]{} [(bpy)_2ClRu^{III}(pyz)Ru^{II}Cl(bpy)_2]^{3+} \tag{6}$$

as in eq 7,[12]

$$E_{op} \sim 4E_{th} = \lambda = \lambda_i + \lambda_o \tag{7}$$

Using a dielectric continuum model, λ_o as given by eq 8 is predicted to hold both for outer-sphere reactions and for in-