# On the Mechanism of the Dimerization of Phenoxy Radicals

*Sir:*

In recent work from our laboratory it was shown that the steady-state rate constants for the reactions

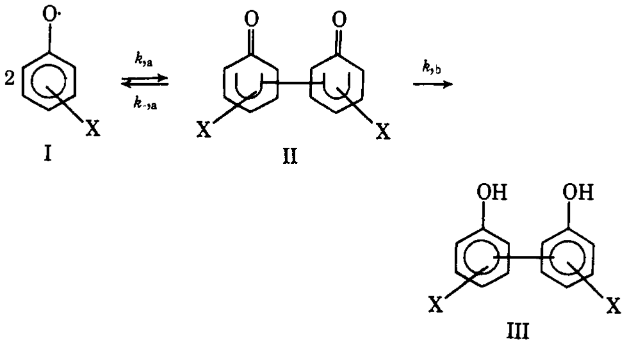
$$2\text{ArO}\cdot \longrightarrow \text{nonradical products} \quad (1)$$

$$2\text{KH}\cdot \longrightarrow \text{nonradical products} \quad (2)$$

are related by the expression

$$k_1 = k_2 \frac{(\text{KH}\cdot)^2 \text{ steady state}}{(\text{ArO}\cdot)^2 \text{ steady state}} \quad (3)$$

where KH· and ArO· are the semidione radicals and phenoxy radicals produced by photolysis in an esr cavity of α-diketones in benzene in the presence of phenols.[1] The results of a systematic mechanistic study of the dimerization of 14 substituted phenoxy radicals[2] were then found to be consistent with the general reaction scheme



where I is a substituted phenoxy radical, and II and III are the carbon–carbon bonded nonenolized and enolized dimers of I, respectively. We now wish to report the results of experiments which provide strong evidence for the validity of this mechanism.

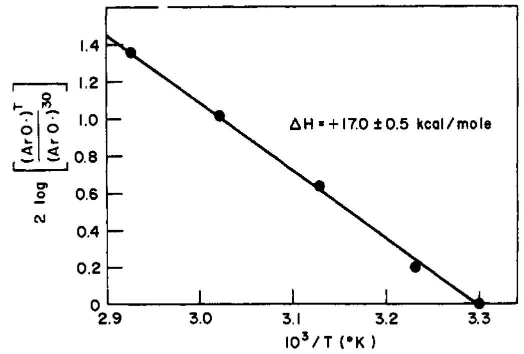


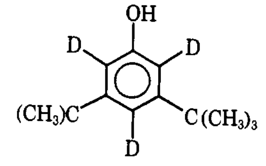
Figure 1. Plot of the log of the relative concentrations of the 3,5-di-*tert*-butylphenoxy radical V, as a function of temperature *vs.* $1/T$.

**Table I.** Summary of Kinetic and Thermochemical Results

| Phenoxy radical derived from | $k_1 \times 10^8$,[a] $M^{-1}$ sec$^{-1}$ | $k_1[\text{H}^+] \times 10^8$,[a] $M^{-1}$ sec$^{-1}$ | $\Delta E_1^{\ddagger}$[b] kcal/mol | ΔH₁, kcal/mol Exptl | Calcd[c] |
|---|---|---|---|---|---|
| IV | 0.11 ± 0.03 | 19 ± 5 | 2.6 ± 0.8 | 16.9 ± 0.8 | 17.6 |
| V | 1.1 ± 0.3[c] | 25 ± 6[c] | 1.2 ± 1.5[c] | 17.0 ± 0.5[c] | 17.6 |
| VI | 0.31[c] | 3 ± 1[c] | 6.8 ± 1.0[c] | 15.1 ± 1.4[c] | 14.0 |

[a] Based on a value of $k_2$ equal to $18 \pm 4 \times 10^8$ $M^{-1}$ sec$^{-1}$ for biacetylsemidione in benzene solution in the absence of and in the presence of $6 \times 10^{-3}$ $M$ *p*-toluenesulfonic acid.[2] [b] Based on a value of $\Delta E_a^{\ddagger}$ equal to 4.2 ± 0.4 kcal/mol for biacetylsemidione in benzene solution.[2] [c] From ref 2.

Compound IV was prepared from 3,5-di-*tert*-butylphenol (V), by the method of Kirby and Ogunkoya.[3] Analysis by nmr and mass spectral methods revealed



IV

that the isotopic purity of IV, *i.e.*, $d_3$ content, was greater than 95%. Photolysis of biacetyl in benzene at 30° in the presence of IV resulted in an esr spectrum which consisted of a composite of the spectrum of the biacetylsemidione radical and the spectrum predicted for the phenoxy radical derived from IV.[4] The value of $k_1$ (*cf.* Table I) for the phenoxy radical derived from IV was determined from the experimental ratio of ·KH/ArO· and eq 3. That value together with the earlier value of $k_1$ for the phenoxy radical from V yields an apparent isotope effect for reaction 1 equal to 10 ± 2 at 30°.[5] As we see from Table I this isotope effect also manifests itself in the apparent activation energies. Finally, the addition of $6 \times 10^{-3}$ $M$ *p*-toluenesulfonic acid results in values of $k_1$ for the phenoxy radicals from IV and V which are equal within experimental error and are consistent with diffusion-controlled dimerization. These results demand that the rate-controlling step in the dimerization of the 3,5-di-*tert*-butylphenoxy radical involves the breaking of a C–H bond. Within the context of our mechanism, $k_{-1a} \gg k_{1b}$ in the absence of added acid and the rate-controlling step is the enolization of II to III, while in the presence of acid $k_{-1a} \ll k_{1b}$ and the dimerization is diffusion controlled.

Upon interruption of the photolysis the steady-state concentrations of semidione and phenoxy radicals instantaneously decay. However, upon increasing the instrument sensitivity (20 times) well-resolved spectra of the phenoxy radicals from IV, V, and 2,6-di-*tert*-

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(1) S. A. Weiner, *J. Amer. Chem. Soc.*, in press.

(2) L. R. Mahoney and S. A. Weiner, *ibid.*, in press.

(3) G. W. Kirby and L. Ogunkoya, *J. Chem. Soc.*, 6914 (1965).

(4) For the 3,5-di-*tert*-butylphenoxy radical, $a_p$ equals 10.00 G and $a_o$ equals 6.60 G.[1] Based on the gyromagnetic ratio of H to D, we would predict that for the phenoxy radical derived from IV $a_p$ equals 1.53 G and $a_o$ equals 0.92 G. We observed that $a_p$ equals 1.56 G and $a_o$ equals 0.96 G.

(5) The error limits for the isotope effects are smaller than for the absolute values of $k_1$ since they do not depend upon the absolute value of $k_2$.

butylphenol (VI) are observed.[6] Moreover, the radical concentrations decay only slowly with time and increase with increasing temperature in a reversible manner. On the reasonable assumption that the source of the radicals is the presence of and the reversible disassociation of dimers formed from these radicals, the experimental values of the heats of formation of the dimers were obtained from the plots of 2 log [ArO·]$T$/[ArO·]30° *vs.* 1/$T$ (*cf.* Figure 1) and are summarized in Table I. These experimentally derived values are in quantitative agreement with the values calculated in the earlier work[2] for the heats of formation of the carbon–carbon nonenolized dimers II of the phenoxy radicals from V and VI.

(6) A similar observation is made for the 4-phenylphenoxy radical. However, the concentration of that radical decays to zero within a few minutes at 30°.

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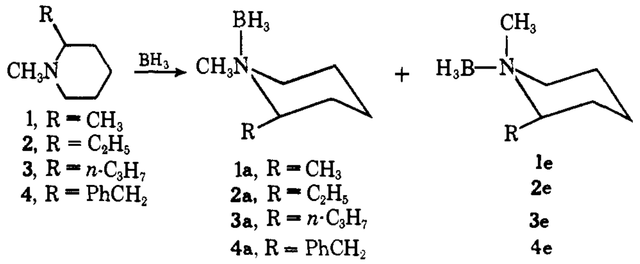
## Stereochemistry of Amine–Boranes. I. Amine–Boranes from 1-Methyl-2-substituted Piperidines[1]

*Sir:*

The reaction of borane with conformationally biased piperidines has been shown to be similar in energetics to the quaternary salt formation with methyl halides or tosylates giving a preferential axial B–N bond formation.[1] Reaction of 1-methyl-4-*tert*-butylpiperidine with diborane in THF or with pyridine–borane gave a mixture of diastereomeric amine–boranes containing 85% of the isomer having an axial BH$_3$. This result is similar to that obtained for the quaternary salt formation with trideuteriomethyl tosylate.[2]

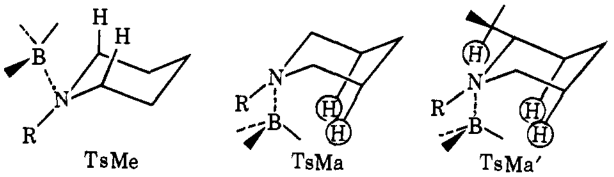
The stereoselectivity of quaternization of 1-methyl-2-substituted piperidines is less than that for the 3- or 4-substituted isomers,[3] and to test the similarity of amine–borane formation and quaternary salt preparation the reactions of borane in THF with 1,2-dimethylpiperidine (**1**), 1-methyl-2-ethylpiperidine (**2**), 1-methyl-2-*n*-propylpiperidine (**3**), and 1-methyl-2-benzylpiperidine (**4**) were investigated.[1] In each reaction a mixture of diastereomeric amine–boranes was formed and the composition could be determined from the integrated intensities of the NCH$_3$ signals of the amine–boranes in the pmr spectra of the mixtures. The assignment of pmr signals to the two diastereomeric structures was made on the basis of relative chemical shifts of the NCH$_3$ signals in the proton spectrum[4] and in the $^{13}$C spectrum.[5] The results are given in Chart I. It can be seen that as the size of the 2 substituent increases, the relative amount of the diastereomer with the alkyl groups cis, formed by equatorial B–N bond formation, also increases.

**Chart I**



| | Analysis of product mixture | Analysis after heating at 77° |
|---|---|---|
| 1 | 84% **1a**; 16% **1e** | 48% **1a**; 52% **1e** |
| 2 | 79% **2a**; 21% **2e** | 48% **2a**; 52% **2e** |
| 3 | 71% **3a**; 29% **3e** | 43% **3a**; 57% **3e** |
| 4 | 68% **4a**; 32% **4e** | 36% **4a**; 64% **4e** |

The factors affecting the relative stabilities of the diastereomeric transition states for the amine salt formation can be compared with those described for nucleophilic addition to cyclohexanones, for both reactions involve conversion of a tercovalent ring atom to a quadricovalent state. The data obtained in the amine–borane formation can readily be rationalized by considering the postulate proposed by Cherest and Felkin.[6] Thus, in the transition state of the formation of an equatorial B–N bond there would be the unfavorable torsional strain resulting from near eclipsing of the $\sigma$ bonds of the axial 2 and 6 bonds with the developing B–N bond (transition-state model TSM-e). On the other hand, the developing B–N bond from the axial side introduces a steric, nonbonding interaction with the axial groups on the 3 and 5 positions (TSM-a).



The steric strain is smaller than the torsional strain in simple piperidines such as 1-methyl-3- or -4-substituted piperidines. Thus, axial B–N bond formation is favored as observed.[1] The introduction of a 2 substituent introduces a third nonbonded interaction (TSM-a′) which increases the energy of this transition state as the size of the 2 substitutent increases. This is reflected by a decrease in the stereoselectivity of the reaction.[7] These opposing effects in the transition states can be used to rationalize much of the quaternization data relating the effect of the structure of the

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(1) Portions of this research were discussed at the 161st National Meeting of the American Chemical Society, Los Angeles, Calif., March 28–April 2, 1971, and at the IUPAC, Section Organo-Inorganic Chemistry, Boston, Mass., July 25–30, 1971. The research received financial support from research Grant No. PRF 3441-A1,4 from the American Chemical Society Petroleum Research Fund. The authors express their appreciation to the donors of this fund. All amine–boranes gave acceptable analyses for nitrogen and active hydrogen.

(2) H. O. House, B. A. Tefertiller, and C. G. Pitt, *J. Org. Chem.*, **31**, 1073 (1966).

(3) Reviews on the stereochemistry of quaternary salt formation are: (a) J. McKenna, *Top. Stereochem*, **5**, 275 (1970); (b) A. T. Bottini in "Selective Organic Transformations," B. S. Thyagarajan, Ed., Wiley-Interscience, New York, N. Y., 1970, pp 89–142.

(4) The relative chemical shifts of the proton resonance in the nmr spectra of *N*,*N*-dialkylpiperidinium salts determined in CDCl$_3$ (A. T. Bottini and M. K. O'Rell, *Tetrahedron Lett.*, 429 (1967)) usually shows the resonance signal for the protons on the axial substituent at higher field than those on the equatorial group: ref 2 and G. Fodor, J. D. Medina, and N. Mandava, *Chem. Commun.*, 581 (1968).

(5) The authors express their appreciation to Professor Ernest Wenkert and David W. Cochran of Indiana University for determination of the $^{13}$C magnetic resonance spectra. The discussion of these spectra will be published in a later paper.

(6) M. Cherest and H. Felkin, *Tetrahedron Lett.*, 2205 (1968).

(7) Reference 3b, pp 114–115.