

is 1.45 Å,⁸ and in N₂O₄ it is 1.75 Å.⁹ Therefore in N₂O₃ this distance is unusually long although it is still considerably shorter than twice the van der Waal's radius for nitrogen of 3 Å.¹⁰ The infrared analysis has also favored a long bond.²

A complete structure determination independent of any assumptions is not possible without data from another isotopic species. From calculations it is clear, however, that the observed data will fit a range of planar ON-NO₂ models with C_s symmetry and $d(\text{NN}) = 1.85 \text{ \AA}$., and with N-O bond lengths and interatomic angles similar to those observed in other molecules.^{11,12} This is the model for N₂O₃ which has been generally accepted and supported in the literature.^{1,2}

In summary, the basis for asserting that the observed spectra arises from N₂O₃ is as follows. (1) The reaction of NO and NO₂ produces the spectra which have intensity and pressure-temperature dependence of the intensity in agreement with equilibrium calculations. (2) The spectrum arises from a species containing two nonequivalent nitrogen atoms separated by $1.85 \pm 0.03 \text{ \AA}$. (3) The moments of inertia will fit a planar ON-NO₂ model with C_s symmetry, a long N-N bonded distance and with N-O bond lengths and angles similar to other compounds.

Acknowledgment. The author thanks Dr. David R. Lide, Jr., and Dr. William H. Kirchhoff for numerous helpful discussions concerning this work.

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Electron Spin Resonance Studies of Deuterium Isotope Effects. A Novel Resonance-Integral Perturbation¹

Sir:

Recent electron spin resonance (e.s.r.) studies of aromatic radicals have demonstrated that the replacement of a hydrogen atom by deuterium can produce significant modifications in the proton hyperfine splitting constants (a^{H}) for ring positions other than the one of substitution. The most dramatic effect is observed in the benzene anion²; smaller changes occur in the deuterated naphthalene anions³ and in the N-deuterated dihydropyrazine cation and its methyl derivatives.⁴ In striking contrast to the result for benzene, deuteration does not alter the proton hyperfine splittings in the cyclooctatetraene anion radical.⁵ In this communication, we propose that a consistent explanation of these

(1) Research supported in part through U. S. Air Force Office of Scientific Research Grants No. AF-AFOSR-285-63 and -65.

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data is provided by a vibrational perturbation of the Hückel resonance-integral parameter β . The nature of the effect, which is different from the electron donation usually associated with deuteration,⁶ is such that it should occur in general on isotopic substitution of aromatic hydrocarbons.

To provide a qualitative description of the alteration of the electronic wave function on deuteration, we consider a very simple model. If the carbon-atom $2p\pi$ orbitals follow the out-of-plane bending motion of the C-H or C-D bonds, the integral β depends on the hydrogen or deuterium position. For adjacent carbon atoms r and s , we express the effective resonance integral as $\beta_{rs} \cong \beta_0(\cos \theta)_{rs}$, where β_0 is the resonance-integral parameter corresponding to a pair of parallel $2p\pi$ orbitals, θ is a function of the angle between them, and $\langle \rangle$ signifies a vibrational average. Expanding $\cos \theta$, we obtain $\delta_{rs} = \beta_{rs}^{\text{D}} - \beta_{rs}^{\text{H}} \cong (\beta_0/2)[\langle \theta^2 \rangle_{rs}^{\text{H}} - \langle \theta^2 \rangle_{rs}^{\text{D}}]$ for the change in β_{rs} on the substitution of deuterium at carbon atom r (or s). Although quantitative evaluation of β_{rs} requires an exact knowledge of the degree of orbital following⁷ and a complete vibrational analysis for the deuterated and undeuterated species, it is evident that $\langle \theta^2 \rangle_{rs}^{\text{H}} > \langle \theta^2 \rangle_{rs}^{\text{D}}$, and therefore that $\delta_{rs} < 0$. The energy shift of the Hückel molecular orbital ψ_k for a species deuterated at position r is then⁸

$$\Delta \epsilon_k \cong 2\delta_{r,r+1}c_r^{(k)}c_{r+1}^{(k)} + 2\delta_{r,r-1}c_r^{(k)}c_{r-1}^{(k)} \quad (1)$$

where $c_r^{(k)}$ is the coefficient of the $2p\pi$ orbital on atom r in ψ_k .

To apply eq. 1 to the benzene-1-*d* anion we must consider the degenerate pair of antibonding orbitals that are available for the unpaired electron. The orbital which is antisymmetric with respect to the symmetry plane through position 1 is unaltered by the perturbation ($c_1 = 0$), while the symmetric orbital is destabilized by $-(2/3)\delta$, where $\delta = \delta_{1,2} = \delta_{1,6}$. Thus, in agreement with experiment, the degeneracy is lifted by deuteration and the unpaired electron is predicted to be predominantly in the antisymmetric orbital. A considerable contribution from the symmetric orbital is also expected, however, because of thermal excitation⁹ and vibronic coupling.¹⁰ A crude estimate¹¹ for C₆H₅D⁻ gives $(\delta/\beta_0) \cong 0.0025$, and on the basis of thermal mixing (with $\beta_0 \cong -40 \text{ kcal./mole}$) yields the hyperfine constants $a_{\text{para}}^{\text{H}} = -3.4 \text{ gauss}$, $a_{\text{ortho}}^{\text{H}} \cong a_{\text{meta}}^{\text{H}} = -3.9 \text{ gauss}$, in agreement with the measured values.^{2,12} For the cyclooctatetraene-1-*d* anion, application of eq. 1 does not remove the degeneracy because a pair of nonbonding orbitals is involved; the model thus predicts no change in the proton hyperfine splittings on deuteration, which is again in agreement with the observed results.¹³ The naphthalene negative

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(13) An alternative model given by Carrington, *et al.*,⁵ also explains the qualitative differences between the behavior of C₆H₅D⁻ and C₈H₇D⁻, but a rough quantitative estimate based on force-constant data [H. P. Fritz, *Advan. Organometal. Chem.*, **1**, 239 (1964)] suggests that the effect is too small to account for the hyperfine constant change in C₆H₅D⁻.

ion has the unpaired electron in a nondegenerate orbital so that the energy shift obtained on deuterium substitution does not lead to a first-order effect on the proton splittings; however, the perturbation produces a change in the atomic orbital coefficients which, with $(\delta/\beta_0) \sim 0.004$, provides good agreement with the experimental data for all of the deuterionaphthalene compounds studied.³

It is of interest to contrast the resonance-integral perturbation with an alternative model based on the treatment of deuterium as an electron-donating substituent.⁶ The simplest way to introduce such an effect into Hückel theory is to use an atomic integral of the form $\alpha_r = \alpha_0 + \delta_r\beta$, where α_0 is the Coulomb integral of an aromatic C-H carbon atom, r is the substituted position, and $\delta_r < 0$. The resulting energy change is $\Delta\epsilon_k \cong \delta_r\beta[c_r^{(k)}]^2$. Application of this formula to the pair of degenerate orbitals in benzene and cyclooctatetraene shows that for both systems the antisymmetric orbital is unaffected while the symmetric orbital is destabilized, and the magnitude of the effect for $C_8H_5D^-$ indicates that there would be an observable perturbation for $C_8H_7D^-$, in disagreement with experiment. For the naphthalene-1,4,5,8- d_4 and naphthalene-2,3,6,7- d_4 anions, the atomic-integral perturbation model also gives incorrect results.^{3,14} Of course, these discrepancies do not demonstrate that no atomic-integral deuterium isotope effect exists; they show only that if there is such an effect, it must make a considerably smaller contribution to the changes in the e.s.r. spectra than the resonance-integral perturbation.

The resonance-integral perturbation model can be easily applied to other radicals. For example, it predicts that the unpaired electron should be predominantly in the *antisymmetric* orbitals of the deuterio-benzene positive ion ($C_6H_5D^+$),¹⁵ the deuteriocyclopentadienyl radical ($C_5H_4D\cdot$), and the deuteriocycloheptatrienyl radical ($C_7H_6D\cdot$). Corresponding calculations can also be made for radicals with multiple deuterium substitution.^{3,12} Since the atomic-integral perturbation model predicts that the unpaired electron should be predominantly in the *symmetric* orbitals of $C_6H_5D^+$ and $C_5H_4D\cdot$, an e.s.r. study of these deuterated radicals would be of particular interest.

Acknowledgment. We wish to thank Professors T. Katz and K. Morokuma for helpful discussions.

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(15) For $C_6H_5D^+$, the model of Carrington, *et al.*,⁵ predicts that the unpaired electron would be predominantly in the symmetric orbital.

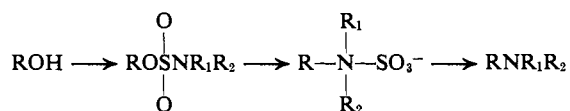
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The Conversion of Alcohols into Amines

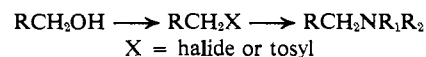
Sir:

We wish to report a useful method for the conversion of alcohols into amines, the key step of which is of special interest in that it is another member in the list,

small but growing, of S_N1 reactions.¹ The method involves the conversion of alcohols into sulfamate esters, the rearrangement of these esters into betaine analogs through alkyl migration from oxygen to nitrogen, and the final hydrolysis to the amine. The



method works well for alcohols that yield moderately stable carbonium ions,² and thus it complements the



two-step route³ which, because of the displacement nature of the steps, is usually restricted to primary alcohols.

Typical yields for the new method (for the version in which N,N -dimethylsulfamates are used) are given in Table I. Since dialkylamino groups are very often

Table I. Data for the Process
 $ROH \longrightarrow ROSO_2N(CH_3)_2 \longrightarrow RN(CH_3)_2$

| R | Solvent | Yield of amine, % ^a | Retention of configuration, % |
|-----------------------------|----------------------|--------------------------------|-------------------------------|
| $C_6H_5CH(CH_3)$ | $CH_3OCH_2CH_2OCH_3$ | 60 ^b | Complete racemization |
| | CCl_4 | 20 | 7 |
| | $CHCl_3$ | 11 ^c | 24 |
| | CH_3CO_2H | 11 ^d | 67 |
| $C_6H_5CHC_6H_5$ | $CH_3OCH_2CH_2OCH_3$ | 76 | |
| $p\text{-ClC}_6H_4CHC_6H_5$ | $CH_3OCH_2CH_2OCH_3$ | 80 | |
| $C_6H_5CH=CHCH_2$ | $CH_3OCH_2CH_2OCH_3$ | 69 | |

^a The yields were not optimized. ^b 19% styrene was also isolated. ^c Plus 48% of the ethyl ether (from C_2H_5OH in $CHCl_3$) and 27% styrene. ^d Plus 50% 1-phenylethyl acetate (3% inversion of configuration) and 10% styrene.

present in alkaloids and in certain classes of drugs,⁴ the new method should be of special interest in the synthesis of these compounds. Slight modifications of the reagents will permit, in addition, the synthesis of primary amines.⁵

The new reaction proceeds with over-all *retention* of configuration in polar solvents (Table I), and as such may be useful in the stereochemical correlation of alcohols and amines. The increase in the retention of configuration in polar solvents parallels that found for the nitrosoamide decomposition^{1d}; in part, this re-

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