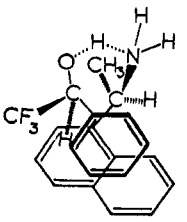

4

4, the aromatic rings of the amine and the carbinol overlap, the carbinyl proton being held above the naphthyl system where it is heavily shielded. The more distant trifluoromethyl group experiences comparatively less shielding by the naphthyl group. In the analogous conformer derived from enantiomer **3a**, the positions of the carbinyl proton and the trifluoromethyl group are reversed. The net average result is that the carbinyl proton of enantiomer **3a** is less shielded than is that of **3**, while the trifluoromethyl group of enantiomer **3a** is more highly shielded than is that of **3**. Weak charge-transfer interactions between the aromatic systems may stabilize conformations such as **4**. Such interaction may be invoked to account for the unusually large degree of spectral nonequivalence exhibited by the enantiomers of 2′,2′,2′-trifluoro-2,4-dinitrophenylethanol and 2′,2′,2′-trifluoro-3,5-dinitrophenylethanol when optically active amine **2** is used as a solvent.[1c] Significantly, a carbon tetrachloride solution 1.0 *M* in naphthalene and 0.01 *M* in 2′,2′,2′-trifluoro-2,4-dinitrophenylethanol shows absorption at 385 mμ which is not present in the spectra of the individual components. Enhanced long-wavelength absorption is characteristic of charge-transfer complex formation.

The foregoing model is probably oversimplified; steric effects doubtlessly important in determining conformational preferences have not been explicitly discussed. Even so, the model is an aid in rationalizing the observations. Tests of the validity of this model are in progress.

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Bis(trichloromethyl) Nitroxide. A Novel Electron Spin Resonance Spectrum

Sir:

Nitroxide radicals (R_2NO) stabilized by fluorocarbon substituents have recently been prepared and identified by their electron spin resonance spectra.[1-3] Nitroxide radicals carrying hydrocarbon substituents are also known and normally require a tertiary carbon adjacent to the nitrogen, or aromatic substituents, in order to achieve stability.[4,5] The identification, by electron spin resonance spectroscopy, of a relatively stable nitroxide radical containing chlorocarbon substituents, namely, bis(trichloromethyl) nitroxide, is now reported. It is believed that this is the first observed example of an esr spectrum containing resolved hyperfine splitting due to β-chlorine nuclei.

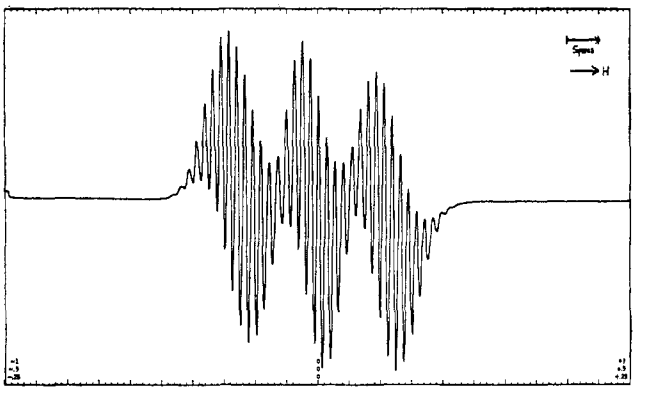

Figure 1. The electron spin resonance spectrum of bis(trichloromethyl) nitroxide.

Trichloronitrosomethane, a blue liquid at room temperature, was prepared by the method previously described[6] and stored at 77°K. The electron spin resonance spectrum shown in Figure 1 was obtained by measurement on trichloronitrosomethane at room temperature in the dark. This spectrum clearly demonstrates the presence, in trichloronitrosomethane, of a small concentration of a free radical containing several magnetic nuclei. A similar but less intense spectrum was obtained by measurement on a dilute solution of trichloronitrosomethane in carbon tetrachloride.

All the features of the spectrum may be interpreted in terms of the radical bis(trichloromethyl) nitroxide. Interaction of the unpaired electron with the ^{14}N nucleus gives rise to the main triplet with a splitting of 11.8 ± 0.1 gauss. Each component of this triplet is split further into a series of hyperfine lines with a coupling of 1.25 ± 0.05 gauss. Some overlapping of these lines occurs in the center of the spectrum, but examination of the amplified wings of the spectrum reveals all the expected hyperfine structure for bis(trichloromethyl) nitroxide. The tenth line of each hyperfine series is the most intense, approximately 600 times more so than the outermost line. This suggests that there are 19 hyperfine lines in each component of the main triplet. Such a pattern can arise by interaction of the unpaired electron with six equivalent chlorine nuclei. The theoretical intensity ratio of the strongest to the weakest line in the spectrum of an electron in this situation is 580:1.

The isotropic nitrogen splitting is larger than that observed for bis(trifluoromethyl) nitroxide,[1,2] much smaller than in dialkyl nitroxides,[7] and slightly smaller than in potassium nitrosodisulfonate (Fremy's salt).[8] This suggests that the magnitude of the nitrogen coupling is related to the electron-withdrawing power of the substituents. The rather poor resolution of the chlorine hyperfine lines may be attributed to the presence of two

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chlorine isotopes. Since the two isotopes have slightly different nuclear moments, slight differences in the hyperfine splitting will be expected. These small splittings are not resolvable and hence a composite splitting, due to the isotopic mixture, is observed.

The bis(trichloromethyl) nitroxide is not as stable as the fluorinated analog,[1,3] and the esr signal decays to one-half of its original intensity in 7 hr.

Bis(trichloromethyl) nitroxide is considered to be formed during the synthesis of trichloronitrosomethane by attack of a trichloromethyl radical on the nitroso compound.

$$CCl_3\cdot + CCl_3\cdot NO \longrightarrow (CCl_3)_2NO$$

A free-radical mechanism was suggested for the synthesis of trichloronitrosomethane, but free trichloromethyl radicals were not postulated.[6] In view of the present work it would appear that at least some trichloromethyl radicals must be formed during the synthesis of trichloronitrosomethane. A possible source of trichloromethyl radicals is the decomposition of the postulated sulfoxide intermediate

$$CCl_3SO_2\cdot \longrightarrow CCl_3\cdot + SO_2$$

although other sources could also be envisaged.

Further work on this, and related systems, is in progress.

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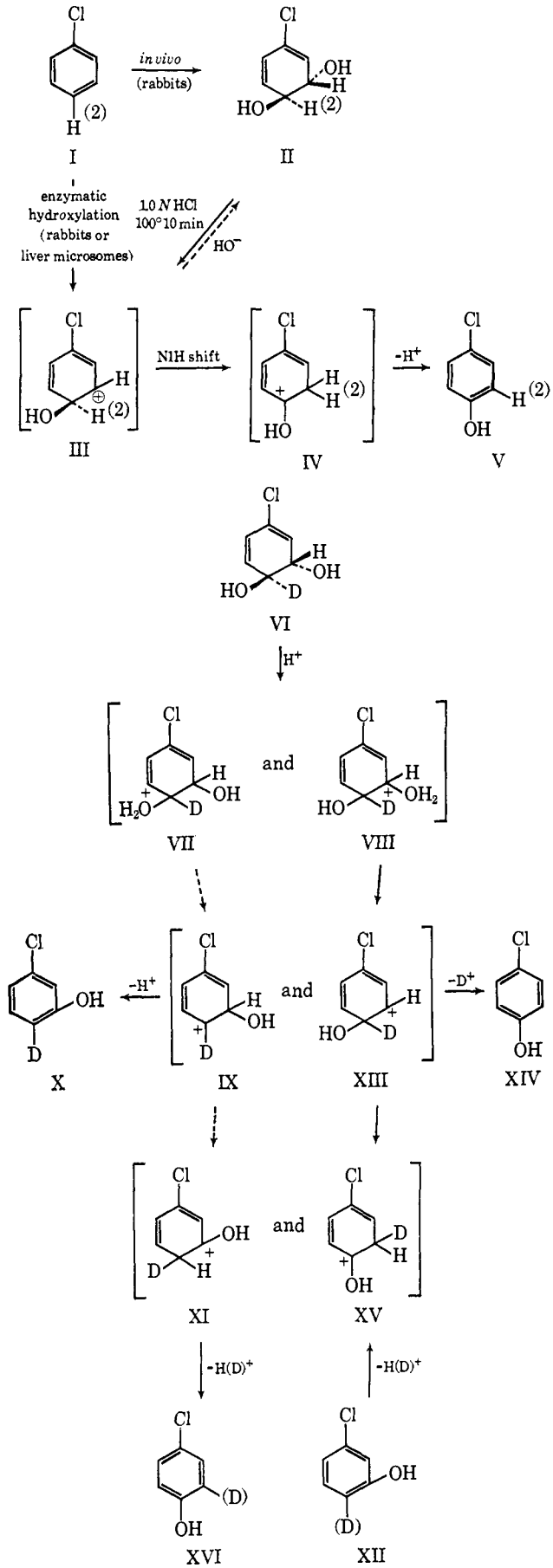
Deuterium Migration during the Acid-Catalyzed Dehydration of 6-Deuterio-5,6-dihydroxy-3-chloro-1,3-cyclohexadiene, a Nonenzymatic Model for the NIH Shift

Sir:

In most enzymatic hydroxylations of aromatic substrates the substituent (^2H, ^3H, or halogen) present at the position of the entering oxygen migrates to either one of the adjacent ring positions. This migration has been called the NIH shift.[1] In a variety of chemical hydroxylating systems only one reagent, trifluoroperacetic acid, produced these hydroxylation-induced migrations.[2] The electrophilic nature of trifluoroperacetic acid[3] suggests cationoid intermediates. A general mechanism involving such cationoid intermediates would conveniently rationalize the migration observed both in nonenzymatic and enzymatic hydroxylation reactions. This communication provides further evidence that enzymatic hydroxylations with concomitant migration and retention of isotopic label may proceed *via* cationoid intermediates. This has been accomplished by starting with a selectively deuterated aromatic substrate and by arriving at the same phenolic metabolite V by enzymatic (I → III → IV → V) and nonenzymatic (II → III → IV → V) pathways which intersect at the cationic intermediate III.



Following the procedure of Smith, *et al.*,[4] a dihydro-

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