distillate was discarded, and the residue then was made basic with 0.2 equiv. of 20% sodium hydroxide, after which the mixture again was steam distilled until 70 ml. of distillate possessing an amine-like odor had been collected. The distillate was extracted with ether (three 50-ml. portions) and, after the ether extracts had been dried over anhydrous magnesium sulfate, anhydrous hydrogen chloride was introduced to yield 88 mg. (33%) of 2-amino-3-methylbutane hydrochloride (VIa): m.p. 182–184°; a mixture melting point with an authentic specimen[19] showed no depression; $\nu_{\max}^{\text{KBr}}$ (cm.$^{-1}$) $CNH_3^+Cl^-$ 1605 (m), 2000 (m); identical with that of the authentic sample.

Anal. Calcd. for $C_5H_{14}ClN$: C, 48.58; H, 11.42; Cl, 28.69. Found: C, 48.38; H, 11.33; Cl, 28.84.

Also, a **p-nitrobenzoyl derivative** was prepared from 26 mg. (0.23 mmole) of 2-amino-3-methylbutane hydrochloride (VIa) and 43 mg. (0.25 mmole) of p-nitrobenzoyl chloride: yield 7 mg. (14%) after recrystallization from cyclohexane; m.p. 119–120°, lit.[20] m.p. 114–115°; a mixture melting point with a sample prepared from the alternate route showed no depression; $\nu_{\max}^{\text{KBr}}$ (cm.$^{-1}$) NH 3280 (s), CONH 1642 (s); identical with that of the authentic sample.

Anal. Calcd. for $C_{12}H_{16}N_2O_3$: C, 60.99; H, 6.83; N, 11.86. Found: C, 61.02; H, 7.12; N, 12.08.

1-(1-Aminoethyl)cyclohexanethiol Hydrochloride (Vb).—By the same procedure employed for Va, 35.0 g. (0.20 mole) of IVb yielded 22.0 g. (69%) of Vb as a colorless oil, b.p. 85–90° (0.06 mm.), which solidified upon cooling, m.p. 84–88°. Dry hydrogen chloride was passed through 20 ml. of anhydrous ether solution containing 1.00 g. (6.30 mmoles) of Vb to precipitate 960 mg. (77%) of the amine hydrochloride, m.p. 135–136°.

Anal. Calcd. for $C_8H_{18}ClNS$: C, 49.11; H, 9.27; Cl, 18.11. Found: C, 48.95; H, 9.39; Cl, 17.93.

A mixture of 1.00 g. (5.10 mmoles) of Vb and 10 ml. of cyclohexanone was heated until a homogeneous solution was obtained. After cooling to room temperature, the reaction mixture was poured slowly into 50 ml. of anhydrous ether to precipitate 750 mg. (53%) of **4′-methyldispiro[cyclohexane-1,2′-thiazolidine-5′,1′′-cyclohexane] hydrochloride** as a white hygroscopic material, m.p. 155–157°.

Anal. Calcd. for $C_{14}H_{26}ClNS$: C, 60.95; H, 9.51; Cl, 12.86. Found: C, 60.62; H, 9.46; Cl, 12.65.

In like manner, 1.00 g. (5.10 mmoles) of Vb and 10 ml. of benzaldehyde gave 825 mg. (56%) of **4′-methyl-2-phenylspiro[cyclohexane-1,5′-thiazolidine] hydrochloride**, m.p. 89–90°.

Anal. Calcd. for $C_{15}H_{22}ClNS$: C, 63.70; H, 7.49; Cl, 12.54. Found: C, 63.41; H, 7.76; Cl, 12.83.

2-Amino-3-methyl-3-pentanethiol (Vc).—As for Va, 15.0 g. (0.10 mole) of IVc yielded 6.50 g. (66%) of Vc: b.p. 55–58° (0.06 mm.); $n^{25}{}_D$ 1.5003; $d^{25}{}_4$ 0.998; $\nu_{\max}^{10\%\ CCl_4}$ (cm.$^{-1}$) NH_2 3340 (w), 3290 (w), SH 2560 (w).

Anal. Calcd. for $C_6H_{15}NS$: C, 54.08; H, 11.35; N, 10.15. Found: C, 53.95; H, 11.61; N, 10.23.

3-Mercapto-3-ethyl-2-aminopentane (Vd).—As for Va, 8.00 g. (0.05 mole) of IVd yielded 4.50 g. (62%) of IXd: b.p. 40–45° (0.03 mm.); $n^{25}{}_D$ 1.5149; $d^{25}{}_4$ 1.015; $\nu_{\max}^{10\%\ CCl_4}$ (cm.$^{-1}$) NH_2 3350 (w), 3280 (w), SH 2560 (w).

Anal. Calcd. for $C_7H_{14}NS$: C, 57.09; H, 11.64; S, 21.77. Found: C, 57.28; H, 11.51; S, 22.04.

The **hydrochloride** was formed from 1.00 g. (6.8 mmoles) of Vd in 25 ml. of anhydrous ether, yield 990 mg. (79%), m.p. 175–176°, which was placed in a vacuum desiccator immediately following the filtration.

Anal. Calcd. for $C_7H_{18}ClNS$: C, 45.76; H, 9.87; Cl, 19.28. Found: C, 45.92; H, 9.94; Cl, 19.09.

From 1.00 g. (5.40 mmoles) of Vd and 10 ml. of cyclohexanone was obtained **5′,5′-diethyl-4′-methylspiro[cyclohexane-1,2′-thiazolidine] hydrochloride** as colorless crystals, m.p. 232–234°.

Anal. Calcd. for $C_{13}H_{26}ClNS$: C, 59.16; H, 9.57; S, 12.16. Found: C, 59.02; H, 9.46; S, 12.25.

From 1.00 g. (5.40 mmoles) of the Vd and 10 ml. of benzaldehyde was obtained **5,5-diethyl-4-methyl-2-phenylthiazolidine hydrochloride**, m.p. 220–222°.

Anal. Calcd. for $C_{14}H_{22}ClNS$: C, 61.88; H, 8.13; S, 11.80. Found: C, 62.01; H, 8.03; S, 11.84.

Acknowledgment.—This investigation was supported by a research contract, DA-49-193-MD-2049, with the Office of the Surgeon General, U. S. Army Medical Research and Development Command, dealing with antiradiation agents, and in part by funds provided for biological and medical research by the State of Washington Initiative Measure No. 171. For the gracious hospitality of their laboratories, one of us (G. W. S.) wishes to thank Professor S. J. Angyal, University of New South Wales, Professor L. H. Briggs, University of Auckland, and Professor Lloyd M. Jackman, University of Melbourne.

---

[19] A sample of this substance was prepared from 2-amino-3-methylbutane obtained by hydrogenation of 3-methyl-2-butanone oxime [D. C. Iffland and T. Yen, *J. Am. Chem. Soc.*, **76**, 4180 (1954)].

[20] A. Michael and G. H. Carlson, *J. Org. Chem.*, **4**, 169 (1939).

The Effects of Metallic Ions on the Autoxidation of Phenylhydroxylamine to Azoxybenzene in Methanol

YOSHIRO OGATA AND TAKASHI MORIMOTO

Contribution No. 64 from the Department of Applied Chemistry, Faculty of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, Japan

Received July 13, 1964

The effects of metallic ions on the autoxidation of phenylhydroxylamine have been studied kinetically by estimating consumed oxygen. Cupric ion showed the strongest acceleration, some other ions had weaker effects in the order ferric > manganous > nickel ≅ chromium > cobaltous ion, while stannous and silver ions have no effect. The kinetics was studied more extensively on cupric ion catalysis. The rate was expressed as follows (p = partial pressure of oxygen): $v = k_M[C_6H_5NHOH]p + k_C[C_6H_5NHOH][Cu^{+2}]p$. The rate was retarded by the addition of a high concentration of methyl methacrylate or styrene but not by the addition of hydroquinone or diphenylamine. A mechanism involving the coupling of a radical, $C_6H_5\dot{N}OH$, produced from a complex between phenylhydroxylamine and cupric ion is postulated and discussed.

In our previous paper[1] it has been reported that the autoxidation of phenylhydroxylamine to form azoxybenzene in methanol follows the stoichiometry in eq. 1.

$$4C_6H_5NHOH + O_2 \longrightarrow 2C_6H_5NO{=}NC_6H_5 + 4H_2O \qquad (1)$$

The rate was expressed as

$$v = k[C_6H_5NHOH]p$$

where p is the partial pressure of oxygen and the reaction was accelerated by base and retarded by acid, but was not affected by the addition of radical initiators or inhibitors.

---

[1] Y. Ogata, Y. Sawaki, J. Mibae, and T. Morimoto, *J. Am. Chem. Soc.*, **86**, 3854 (1964).

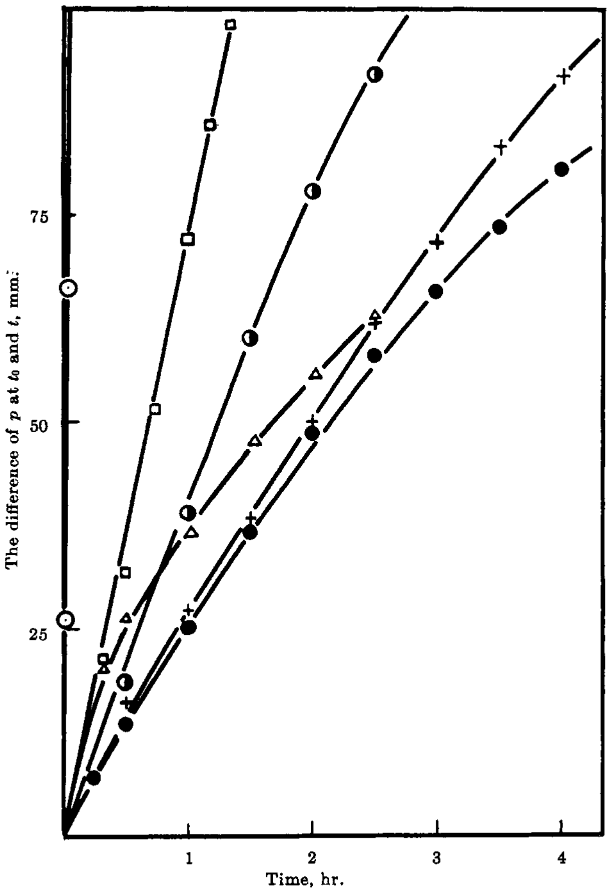

Figure 1.—The absorption curves of oxygen in the metallic ion catalyzed autoxidation of phenylhydroxylamine at 35° and constant volume: ●, uncatalyzed, silver (0.001 *M*) and stannous 0.001 *M*); +, nickel (0.001 *M*) and chromium (0.001 *M*); △, cobaltous (0.01 *M*); ◑, ferric (0.001 *M*); □, manganous (0.01 *M*); and ○, cupric ion (0.001 *M*).

The present paper reports the effects of metallic ions on the rate of autoxidation of phenylhydroxylamine in methanol. The rate was measured by estimating the consumption of oxygen. Among a number of metallic ions examined, cupric ion was an excellent catalyst for the reaction; hence, the kinetics with cupric nitrate was more precisely studied. It was of interest to note that the kinetics support the mechanism which the authors have previously suggested.[1]

It has been known that cupric ion accelerates the autoxidation of N-methyl-*p*-aminophenol,[2] durohydroquinone,[3] sodium sulfite,[4] aldehydes,[5] or hydrocarbons,[6] but nothing was known on the effect of metallic ions on the oxidation of phenylhydroxylamine.

Results

Effects of Metallic Ions.—The conversion curves for the autoxidation of phenylhydroxylamine in methanol with added cupric, ferric, manganous, nickel, cobaltous, and silver nitrates, stannous chloride, and chromium acetate are shown in Figure 1. Note that concentrations of manganous and cobaltous ions (0.01 *M*) are ten times as large as those of the others (0.001 *M*). Silver and stannous salts had no effect on the rate. Cupric nitrate was the strongest catalyst. The activity decreased in the order: cupric > ferric > manganous > nickel ≅ chromium > cobaltous salt. There was no influence from the addition of potassium chloride and nitrate. These effects are analogous with those in the autoxidation of hydrazine in an aqueous medium[7] except that chromium ion was a stronger catalyst there.

Rate Equation.—The rate was first order with phenylhydroxylamine and with oxygen at constant concentration of metallic ion and expressed as

$$-\frac{dp}{dt} = k[C_6H_5NHOH]p \qquad (2)$$

Here, p is the partial pressure of oxygen at time t. Although the apparent rate constant k increased with time owing to the presence of a small amount of hydrogen peroxide,[1] the constant at the start of reaction, k_0, was nearly constant with various initial concentrations of reactants as shown in Table I.

TABLE I

INITIAL SECOND-ORDER RATE CONSTANT OF AUTOXIDATION OF PHENYLHYDROXYLAMINE AT CONSTANT CUPRIC NITRATE CONCENTRATION (1.028×10^{-5} *M*) AT 35°

Initial concn. of C_6H_5NHOH, *M*	Initial *p*, mm.	$k_0 \times 10^2$, M^{-1} min.$^{-1}$
0.2898	219	1.62
0.3093	215	1.50
0.4074	213	1.43
0.2487	222	1.61
0.1951	217	1.51
0.2951	300	1.65
0.3054	117	1.48

The plot of k_0 *vs.* the concentration of cupric nitrate gave a straight line with a slope of 1.32×10^3 (Figure 2). The line indicates that k_0 has still a value of $2.0 \times 10^{-3} M^{-1}$ min.$^{-1}$ (k_M) at null concentration of cupric ion; therefore, the rate equation is expressed as

$$-\frac{dp}{dt} = \{k_C[Cu^{+2}]_s + k_M\}[C_6H_5NHOH]p \qquad (3)$$

where k_C is the catalytic rate constants and $[Cu^{+2}]_s$ is the stoichiometric concentration of cupric ion, *i.e.*, the sum of the concentrations of complexed and free cupric ions.

Effects of Radical Inhibitors.—If a fairly high concentration of methyl methacrylate or styrene was added to the cupric ion catalyzed reaction mixture, the reaction was considerably retarded. On the other hand, no retardation was observed with a lower concentration of styrene, hydroquinone, or diphenylamine as shown in Table II. No induction period was observed with all of these retarders.

Effects of Hydrochloric Acid or Metallic Salts.—On addition of hydrochloric acid to the cupric nitrate catalyzed system the reaction slowed down remarkably; it was of interest to see that the variation of rate constant is very small with tenfold variation of the acid concentration (0.0136–0.00136 *M*). Addition of lithium chloride to the cupric ion catalyzed system exerted the same retardation as hydrochloric acid, but lithium nitrate did not (Table III).

---

(2) W. Reinders and P. Dingemans, *Rec. trav. chim.*, **53**, 239 (1934).

(3) T. H. James and A. W. Weissberger, *J. Am. Chem. Soc.*, **60**, 98 (1938).

(4) A. Titoff, *Z. physik. Chem.* (Leipzig), **45**, 641 (1903); H. L. J. Bäckström, *J. Am. Chem. Soc.*, **49**, 1460 (1927).

(5) J. R. McNesby and C. A. Heller, Jr., *Chem. Rev.*, **54**, 325 (1954).

(6) K. U. Ingold, *ibid.*, **61**, 563 (1961).

(7) F. L. Audrieth and P. H. Mohr, *Ind. Eng. Chem.*, **43**, 1774 (1951).

Table II

Effects of Radical Inhibitors in a Methanolic Solution of 1.028×10^{-5} *M* Cupric Nitrate at 35°

Initial concn. of C_6H_5NHOH, *M*	Initial *p*, mm.	Inhibitor	Concn. of inhibitor, *M*	$k_0 \times 10^3$, M^{-1} min.$^{-1}$
0.6295	213	Methyl methacrylate	0.3178	2.84
0.2705	214	Styrene	0.6630	3.03
0.3967	201	Styrene	0.025	14.4
0.3583	205	Cyclohexene	0.4926	3.87
0.3082	216	Hydroquinone	0.021	14.1
0.3363	225	Diphenylamine	0.093	16.2

Table III

Effects of Acid and Salts in the Presence of 1.028×10^{-5} *M* Cupric Nitrate in Methanol at 35°

Initial concn. of C_6H_5NHOH, *M*	Initial *p*, mm.	Acid or salt	Concn. of acid or salt, *M*	$k_0 \times 10^3$, M^{-1} min.$^{-1}$
0.3039	220	HCl	0.3396	Very slow
0.3111	212	HCl	0.0678	1.70
0.3014	217	HCl	0.0136	2.40
0.3002	211	HCl	0.00136	2.50
0.3186	215	LiCl	0.00083	2.49
0.4943	320	$LiNO_3$	0.00102	7.78

Discussion

The acceleration of the autoxidation by cupric ion may be due to the formation of a complex I between phenylhydroxylamine and cupric ion, which then readily evolves radical $C_6H_5\dot{N}OH$. The following mechanism is suggested to explain the observed facts.

$$C_6H_5\ddot{N}HOH + Cu^{+2} \overset{\text{fast}}{\rightleftharpoons} \underset{\text{I}}{[(C_6H_5\dot{N}HOH)^{+}Cu^{+}]} \tag{4}$$

$$[(C_6H_5\dot{N}HOH)^{+}Cu^{+}] + O_2 \xrightarrow{\text{slow}} C_6H_5\dot{N}OH + Cu^{+2} + HO_2\cdot \tag{5}$$

$$C_6H_5NHOH + HO_2\cdot \xrightarrow{\text{fast}} {}_6H_5\dot{N}OH + H_2O_2 \tag{6}$$

$$2C_6H_5\dot{N}OH \xrightarrow{\text{fast}} C_6H_5NO{=}NC_6H_5 + H_2O \tag{7}$$

$$2C_6H_5NHOH + H_2O_2 \longrightarrow C_6H_5NO{=}NC_6H_5 + 3H_2O \tag{8}$$

Simultaneously, the uncatalyzed reaction may occur.[1]

$$C_6H_5\ddot{N}HOH + O_2 \xrightarrow{\text{slow}} C_6H_5\dot{N}OH + HO_2\cdot \tag{9}$$

Defining *k* and *K* to be the rate and equilibrium constants of the subscripted steps, *a*, the initial concentration of phenylhydroxylamine, and *x*, the consumed concentration of free and complexed phenylhydroxylamine at time *t*, the following equations are derived.

$$K_4 = \frac{[\text{I}]}{[C_6H_5NHOH][Cu^{+2}]}$$

$$a - x = [\text{I}][1 + (K_4[Cu^{+2}])^{-1}]$$

Therefore, the over-all rate is expressed as eq. 10, since the reaction of eq. 8 is negligible in the following kinetic equation.

$$v = k_5K_4\frac{(a - x)[Cu^{+2}]p}{1 + K_4[Cu^{+2}]} + k_9\frac{(a - x)p}{1 + K_4[Cu^{+2}]} \tag{10}$$

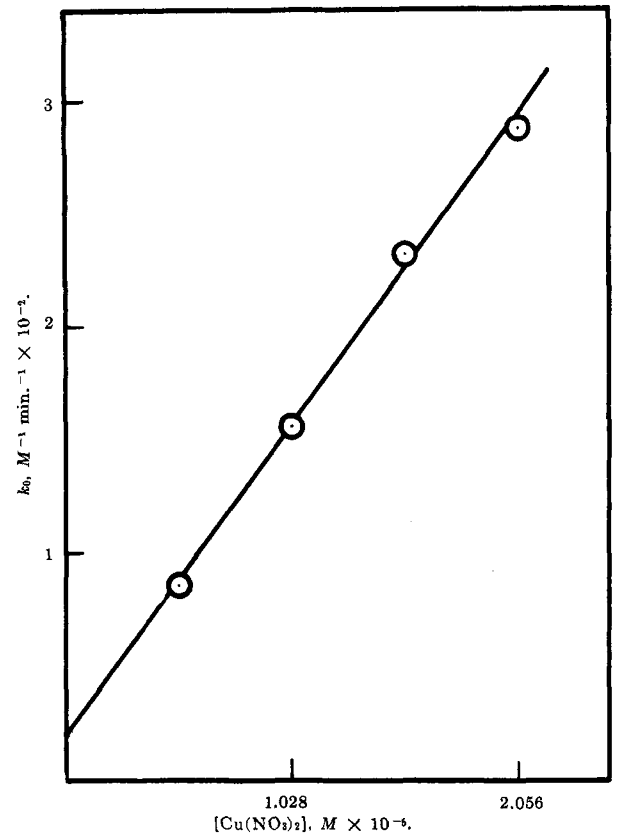

Figure 2.—The plot of rate constant k_0 *vs.* concentration of cupric nitrate.

Equation 10 may be simplified, if $K_4[Cu^{+2}]$ is much smaller than unity, or the concentration of complex I is much smaller than that of cupric ion and $[Cu^{+2}] \cong [Cu^{+2}]_s$.

$$v = (k_5K_4[Cu^{+2}]_s + k_9)(a - x)p \tag{11}$$

Equation 11 coincides with eq. 3 and supports the mechanism. If most of cupric ion were complexed with phenylhydroxylamine, the rate should be independent of the concentration of phenylhydroxylamine.

The retarding effect of styrene or methyl methacrylate seems to be a so-called solvent effect, since the effect is appreciable only in considerably high concentration of the olefinic compounds. Hydroquinone or diphenylamine have no influence because of their low ability for complex formation and also because of the short kinetic radical chain of this reaction.

The retardation by hydrochloric acid is peculiar in that the rate constant does not vary even with a tenfold increase of the acid concentration; this behavior is different from the acidity effect observed in the absence of cupric salt, where the rate decreases with increasing acidity.[1] The retardation may be due to the formation of less active and less soluble cuprous chloride from cuprous–phenylhydroxylamine complex which may be mostly removed from the solution. This assumption is supported by the fact that added lithium chloride showed an analogous retardation to hydrochloric acid.

Experimental

Materials.—Phenylhydroxylamine was prepared by the same way previously reported,[1] m.p. 82–83° (lit.[8] m.p. 82°). Sol-

---

[8] R. Willstätter and H. Kubli, *Ber.*, **41**, 1936 (1908).

vent methanol was redistilled, b.p. 64.7°. Inorganic chemicals including cupric nitrate were used without further purification of the commercial chemicals of guaranteed grade.

Stoichiometry.—The same procedure previously reported[1] was employed for the examination of the stoichiometry of the reaction in the presence of cupric salts. Phenylhydroxylamine (1.2200 g., 0.01118 mole) with 0.001028 *M* cupric nitrate (20 ml.) gave azoxybenzene (1.0514 g., 0.00531 mole, m.p. 35.8°) on exposure to air for 29 hr. at room temperature. Hence, 0.475 mole of azoxybenzene was obtained from 1 mole of phenylhydroxylamine. The result was confirmed by spectrophotometric estimation of azoxybenzene using λ_{max} at 322 mμ (0.475 mole of azoxybenzene from 1 mole of phenylhydroxylamine).

A methanolic solution (10 ml.) of *ca.* 0.2 *M* phenylhydroxylamine and 1.028×10^{-4} *M* cupric nitrate consumed 4.32×10^{-4} mole of oxygen at 35°, giving in average 8.68×10^{-4} mole of azoxybenzene after 30 min.; hence, *ca.* 0.5 mole of oxygen/mole of azoxybenzene was absorbed.

Kinetics.—The same apparatus and procedure[1] were used for the rate measurements. The reaction temperature was 35 ±0.1°.

Acknowledgment.—The authors are grateful to the Japanese Ministry of Education for their grant-in-aid and to Mr. Y. Sawaki for his aid in performing these experiments.

The Stereochemistry of Sulfinamides. Magnetic Nonequivalence of Protons in the Vicinity of the Asymmetric Sulfinamido Group

ROBERT M. MORIARTY

Department of Chemistry, The Catholic University of America, Washington 17, District of Columbia

Received July 8, 1964

The n.m.r. spectra of several N,N′-dialkylsulfinamides have been determined. Geminal protons adjacent the sulfinamido group are magnetically nonequivalent and display an AB rather than A_2 behavior. For example, the methylene protons of N,N′-diethylmethanesulfinamide(IV) in 50% benzene solution give rise to a 16-line spectrum rather than a simple four-line pattern. The observed spectrum has been compared with computed spectra. The methyl protons of the isopropyl group in N,N′-dimethylisopropanesulfinamide (III) appear as a quartet owing to their magnetic nonequivalence. This nonequivalence is a consequence of asymmetry at sulfur which causes adjacent nuclei to assume a mutually diastereomeric relationship. Additional conclusions are presented and discussed concerning rotation about the N–S bond and the configuration at nitrogen in the sulfinamido group. Relative comparisons are also drawn between the sulfinamido group and the sulfonamido group.

Magnetic nonequivalence of geminal protons in substituted ethanes of the general formula RCH_2-$CR_1R_2R_3$ is frequently observed and fairly well understood.[1] Waugh and Cotton[2a] have interpreted such nonequivalence in terms of symmetry arguments alone. Roberts, *et. al.*,[2b] recently have emphasized the importance of conformational preference among rotamers with respect to the asymmetric center as making the major contribution to the magnetic nonequivalence. Geminal nuclei such as protons of a methylene group adjacent an asymmetric center are diastereomeric.[3] Similarly, the methyl groups of an isopropyl group in a dissymmetric molecule are also diastereomeric. Furthermore, an asymmetric center need not be involved. For example, nondissymmetric molecules such as cyclopropylcarbinyl ethyl ether[4] and acetaldehyde diethyl acetal[4] display nonequivalence of the methylene protons. If the equilibrium populations of rotamers are temperature independent, variations in temperature cause no change in the appearance of the AB quartet. Such temperature independence serves as a useful means for distinguishing between slow exchange among nonequivalent sites and nonequivalence due to diastereomeric protons.

Somewhat less familiar is the related phenomenon due to low symmetry at atoms other than carbon. Complex methylene multiplets for ethyl groups, *i.e.*, splitting beyond a quartet, involving asymmetry at sulfur have been reported for diethyl sulfite,[5] for ethyl phenylsulfinate,[2] and for the methylene and methyl protons in ethylene sulfite,[5] *p*-tolyl isopropyl sulfoxide,[6] and diethyl sulfide–borane,[7] respectively. For phosphorus, nonequivalent methylene protons have been reported for O,O-diethyl methylphosphonothioate.[8] Recently a similar effect was demonstrated for nitrogen in dibenzylmethylammonium chloride[9] and diethylmethylammonium iodide[7] and also for silicon in tetramethyldisilane.[10]

Since the sulfinamido group appeared to possess the requisite elements of low symmetry, we decided to study the n.m.r. spectra of suitably substituted derivatives in order to gain further knowledge about the stereochemical details of these compounds and also about possible conformational consequences of N–S $p\pi$–$d\pi$ delocalization.[11] Comparison of the sulfinamido group with the related but symmetrical sulfonamido group seemed potentially instructive.

The n.m.r. absorption bands of interest for N,N′-dimethylmethanesulfonamide (II), N,N′-dimethyliso-

---

[1] (a) P. M. Nair and J. D. Roberts, *J. Am. Chem. Soc.*, **79**, 4565 (1957); (b) J. A. Pople, W. G. Schneider, and H. Bernstein, "High-Resolution Nuclear Magnetic Resonance Spectra," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, pp. 98, 119-123; (c) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press Ltd., London, 1959, pp. 99-103.

[2] (a) J. S. Waugh and F. A. Cotton, *J. Phys. Chem.*, **65**, 562 (1961); (b) G. M. Whitesides, D. Holz, and J. D. Roberts, *J. Am. Chem. Soc.*, **86**, 2628 (1964).

[3] K. Mislow, M. A. W. Glass, H. B. Hopps, E. Simon, and G. H. Wahl, Jr, *ibid.* **86**, 1710 (1964); these authors have introduced the nomenclature, "diastereomeric protons." A discussion of the implications of the term may also be found in this reference.

[4] P. R. Shafer, D. R. Davis, M. Vogel, K. Nagarajan, and J. D. Roberts, *Proc. Natl. Acad. Sci. U. S.*, **47**, 49 (1961).

[5] J. G. Pritchard and P. C. Lauterbur, *J. Am. Chem. Soc.*, **83**, 2105 (1961).

[6] K. Mislow, A. L. Ternay, Jr., J. T. Meillillo, *ibid.*, **85**, 2329 (1963).

[7] T. D. Coyle and F. G. A. Stone, *ibid.*, **83**, 4138 (1961).

[8] H. Finegold, *ibid.*, **82**, 2641 (1960).

[9] M. Saunders and F. Yamada, *ibid.*, **85**, 1882 (1963).

[10] R. West, private communication, University of Wisconsin.

[11] (a) R. M. Moriarty, *Tetrahedron Letters*, **No. 10**, 509 (1964); (b) R. M. Moriarty, *J. Org. Chem.*, **28**, 1296 (1963).