Acknowledgment.—The authors sincerely thank Dr. D. F. Blossey for proofreading the manuscript and for numerous helpful suggestions. Drs. J. B. Flannery, Jr., J. E. Kuder, and F. D. Saeva are also thanked for stimulating discussions.

Tautomeric Behavior Comparison of 4-Phenylazo-1-naphthol and 1-Phenylazo-2-naphthol Systems by Nuclear Magnetic Resonance

F. D. SAEVA

Xerox Corporation, Rochester Corporate Research Center, Webster, New York 14580

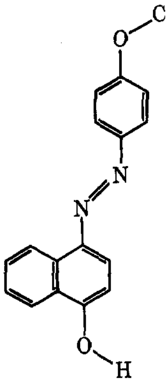
Received March 25, 1971

Azo–hydrazone tautomerism of arylazonaphthols has been the topic of many investigations[1-13] subsequent to Zincke's original observations in 1884.[14] However, to date the large difference between the tautomeric behavior of the 4-phenylazo-1-naphthol and 1-phenylazo-2-naphthol systems, which exist in solution predominantly as azo and hydrazone, respectively,[6,7,9,10,13] we believe has not been adequately explained. In this note we give the results of a thermodynamic study designed to provide an incisive explanation for this unusual difference in tautomeric behavior.

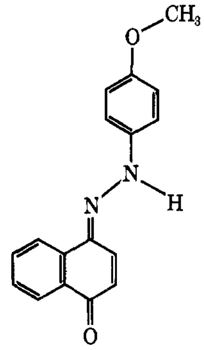
Since inter- and intramolecular proton exchange processes for 4-(*p*-methoxyphenylazo)-1-naphthol (1) and 1-(*p*-methoxyphenylazo)-2-naphthol (2) (in acetone-d_6) are sufficiently slow so that lifetimes of protons on oxygen and nitrogen are long compared to $1/(\nu_{OH} - \nu_{NH})$,[15] equilibrium constants, as a function of temperature, can be determined for the azo $\rightleftarrows$ hydrazone equilibrium process for these two compounds by nuclear magnetic resonance (nmr).

The proton nmr spectrum of 4-(*p*-methoxyphenylazo)-1-naphthol (1) at 10° (acetone-d_6) shows mobile proton resonances at δ 10.19 and 3.59 ppm downfield from tetramethylsilane. On the other hand, the nmr spectrum of 1-(*p*-methoxyphenylazo)-2-naphthol (2) at 38°, in the same solvent, shows a single acidic proton resonance at δ 16.2 ppm.

Assignment of the azo OH in **1a** and hydrazone NH in **1b** resonances were made on the basis of the temperature dependence[16] of the azo ($\sim$400 mμ) and hydrazone ($\sim$480 mμ) electronic transitions, which have been clearly established.[1,4] We found that the transition at $\sim$480 mμ increased in intensity relative to the band at $\sim$400 mμ (in acetone) with decreasing temperature. From this we conclude that the signals at δ 10.19 and 3.59 ppm are due to the hydrazone NH and azo OH protons, respectively.



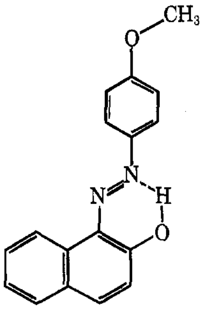
1a



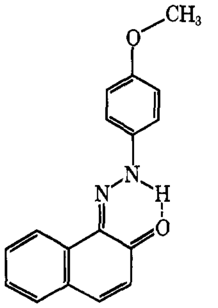
1b

The δ 16.2 ppm resonance in 2 possessed an integrated intensity considerably less than one proton using the time-averaged peri naphthalene proton as an internal standard. Assignment of this signal to the azo OH in **2a** was made on the basis of the visible spectrum temperature dependence using electronic transitions at $\sim$420 and $\sim$500 mμ for monitoring the relative concentrations of azo and hydrazone species,[3,4,11] respectively, as described for 1.

The intensity of the band at $\sim$500 mμ increased relative to that at $\sim$400 mμ as the temperature was decreased, confirming earlier observations.[10] This temperature-induced equilibrium change indicates the resonance at δ 16.2 ppm to be from the azo OH proton.



2a



2b

Integration of the NH and OH proton resonances in 1 allowed direct evaluation of equilibrium constants for the tautomerization process. In the case of the 1-phenylazo-2-naphthol derivative (2), the hydroxyl proton resonance was integrated with respect to the time-averaged peri naphthalene proton (δ 8.65 ppm) for equilibrium constant evaluation. Table I presents

---

(1) R. Kuhn and F. Bar, *Justus Liebigs Ann. Chem.*, **516**, 143 (1935).

(2) H. Shingu, *Sci. Pap. Inst. Phys. Chem. Res., Tokyo*, **35**, 78 (1938).

(3) A. Burawoy, A. G. Salem, and A. R. Thompson, *J. Chem. Soc.*, 4793 (1952).

(4) A. Burawoy and A. R. Thompson, *ibid.*, 1443 (1953).

(5) D. Hadzi, *ibid.*, 2143 (1956).

(6) G. Gabor, Y. Frei, D. Gegiou, M. Kaganowitch, and E. Fischer, *Israel J. Chem.*, **5**, 193 (1967).

(7) K. J. Morgan, *J. Chem. Soc.*, 2151 (1961).

(8) B. L. Kaul, P. Nair, A. V. Rama Rao, and K. Venkataraman, *Tetrahedron Lett.*, 3897 (1966).

(9) A. H. Berrie, P. Hampson, S. W. Longworth, and A. Mathias, *J. Chem. Soc. B*, 1308 (1968).

(10) V. Bekarek, K. Rothschein, P. Vetesnik, and M. Vecera, *Tetrahedron Lett.*, 3711 (1968).

(11) I. Saito, Y. Bansho, and M. Iwasaki, *Tokyo Kogyo Kagaku Zasshi*, **70**, 1725 (1967).

(12) V. Bekarek, J. Dobas, J. Socha, P. Vetesnik, and M. Vecera, *Collect. Czech. Chem. Commun.*, **35**, 1406 (1970).

(13) R. L. Reeves and R. S. Kaiser, *J. Org. Chem.*, **35**, 3670 (1970).

(14) T. Zincke and H. Bindewald, *Ber.*, **17**, 3026 (1884).

(15) J. Pople, H. Bernstein, and W. Schneider, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959, p 100.

(16) E. Fisher and Y. F. Frei, *J. Chem. Soc.*, 3159 (1959).

TABLE I

TAUTOMERIC EQUILIBRIUM CONSTANT TEMPERATURE DEPENDENCE

Compd	Temp, °K	K_{eq}[a]	Compd	Temp, °K	K_{eq}[a]
1	293	0.25	2	322	0.95
	283	0.34		311	1.13
	264	0.54		303	1.33
	252	0.84		293	1.54

[a] K_{eq} = [hydrazone]/[azo] or [b]/[a], determined from an average of four integrations, estimated error of ±5% in K_{eq}.

the calculated equilibrium constant temperature dependences for compounds **1** and **2** in acetone-d_6. The assignment of the δ 16.2 ppm signal in compound **2** is further substantiated by the fact that the experimental data in Table I are in general agreement with the work of Bekarek, *et al.*,[10] who used ^{15}N–H coupling constants to evaluate tautomer ratios for the parent phenylazo-2-naphthol. Thermodynamic parameters derived from the equilibrium constant (K_{eq} = [b]/[a]) temperature dependence data allow, for the first time, a quantitative comparison of the phenylazo-1- and -2-naphthol systems (see Table II).

TABLE II

TAUTOMERIC THERMODYNAMIC PARAMETERS

Compd	$\Delta G°_{293°}$, cal/mol	$\Delta H°$, kcal/mol[a]	$\Delta S°_{293°}$, cal/(mol deg)[a]
1	807	−4.5	−18.1
2	−250	−3.1	−9.7

[a] Estimated errors are *ca.* ±0.5 kcal/mol in $\Delta H°$ and *ca.* ±2.0 cal/mol deg in $\Delta S°$.

The thermodynamic data show the 2-naphthol derivative (at 293°K) to be mainly hydrazone **2b**, while the 1-naphthol analog, on the other hand, is predominantly azo **1a**. The enthalpy and entropy contributions to the thermodynamic free-energy difference between tautomers, for both systems, are of the same sign but differ in magnitude.

The enthalpy for the equilibrium process favors the hydrazone tautomer in both systems. The smaller $\Delta H°$ for system **2** is attributed to stabilization of the azo tautomer **2a** relative to the hydrazone species **2b** by intramolecular hydrogen bonding present only in system **2**.

The entropy term, however, favors the less polar azo species for both systems. The larger negative entropy term in system **1** is ascribed to the existence of a more polar hydrazone species **1b** relative to the azo tautomer **1a**, than is present in system **2**.

From the results which we have presented, it can be concluded that the difference in the tautomeric behavior between systems **1** and **2** is due to the fact that in system **1** the entropy term dominates and governs the free-energy difference between tautomers, while in system **2** the enthalpy contribution is the dominating factor (at 293°K in acetone solvent).

Experimental Section

Materials Characterization.—1-(*p*-Methoxyphenylazo)-2-naphthol (**2**) (mp 141–142°; lit.[17] mp 141°) and 4-(*p*-methoxyphenylazo)-1-naphthol (**1**) (mp 172–173°; lit.[18] mp 168°) were prepared from the corresponding substituted aniline by diazotization and coupling with 2- and 1-naphthol, respectively.

Spectroscopic Characterization.—A JEOL C-60-H nuclear magnetic resonance spectrometer equipped with a JES-VT-3 variable-temperature controller was employed for equilibrium constant determinations in acetone-d_6; the solutions were *ca.* 10% (w/v). The nmr probe temperature control was calibrated, with an estimated accuracy of ±1°, using anhydrous methanol and ethylene glycol solutions. The probe temperature accuracy was periodically checked by using a 5-mm probe thermometer supplied by JEOL.

Registry No.—**1a**, 3009-53-8; **1b**, 32159-06-1; **2a**, 13411-91-1; **2b**, 15096-03-4.

Acknowledgment.—Stimulating discussions with Lewis B. Leder, as well as the synthesis of 4-(*p*-methoxyphenylazo)-1-naphthol by Richard L. Schank, are gratefully acknowledged.

---

[17] J. M. Tedder, *J. Amer. Chem. Soc.*, **79**, 6090 (1957).

[18] L. N. Ogoleva and B. I. Stepanov, *Zh. Org. Khim.*, **1** (12), 2083 (1965).

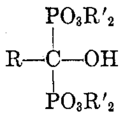
A General Method of Preparation of Tetramethyl Alkyl-1-hydroxy-1,1-diphosphonates

D. ALLAN NICHOLSON* AND HAROLD VAUGHN

The Procter & Gamble Company,
Miami Valley Laboratories, Cincinnati, Ohio 45239

Received June 8, 1971

We recently developed a need in our laboratories for a series of esterified alkyl-1-hydroxy-1,1-diphosphonic acids (I). Where the specific acid was available, esterification was accomplished by the published[1] orthoformate route. For most of the esters envisioned the corresponding acids were either difficult to synthesize or not previously reported in the chemical literature. Hence, a search was begun for a direct method of preparation of tetraalkyl alkyl-1-hydroxy-1,1-diphosphonates.

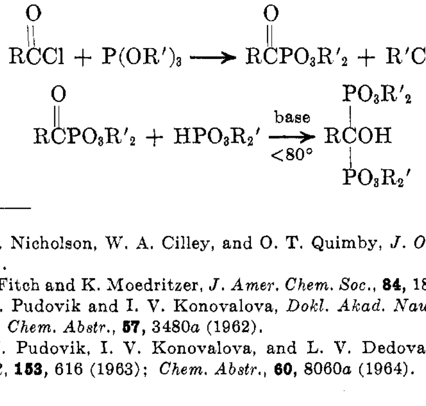


$$\mathrm{R{-}\overset{PO_3R'_2}{\underset{PO_3R'_2}{C}}{-}OH}$$

I

The chemical literature describing this class of compounds is very ambiguous. Fitch and Moedritzer[2] and Pudovik, *et al.*,[3,4] have described the synthesis of I, where R = CH_3 and R′ = C_2H_5, by the route shown in Scheme I. The reaction is complicated by rearrange-

SCHEME I



$$\mathrm{R\overset{O}{\overset{\|}{C}}Cl + P(OR')_3 \longrightarrow R\overset{O}{\overset{\|}{C}}PO_3R'_2 + R'Cl} \qquad (1)$$

$$\mathrm{R\overset{O}{\overset{\|}{C}}PO_3R'_2 + HPO_3R_2' \xrightarrow[<80^\circ]{base} R\overset{PO_3R'_2}{\underset{PO_3R_2'}{C}}OH} \qquad (2)$$

---

[1] D. A. Nicholson, W. A. Cilley, and O. T. Quimby, *J. Org. Chem.*, **35**, 3149 (1970).

[2] S. J. Fitch and K. Moedritzer, *J. Amer. Chem. Soc.*, **84**, 1876 (1962).

[3] A. N. Pudovik and I. V. Konovalova, *Dokl. Akad. Nauk SSSR*, **143**, 875 (1962); *Chem. Abstr.*, **57**, 3480*a* (1962).

[4] A. N. Pudovik, I. V. Konovalova, and L. V. Dedova, *Dokl. Akad. Nauk SSSR*, **153**, 616 (1963); *Chem. Abstr.*, **60**, 8060*a* (1964).