

that reactions proceed more smoothly and in better yield when conducted in dilute isopropyl alcohol in which I was soluble. Reaction of the amino group of I with isocyanate was very rapid, and carbamate formation by reaction with solvent or the hydroxymethyl groups of I was negligible.³ The urea derivatives listed in Table I ranged from colorless crystals in the case of the short-chain members to white waxy solids in the case of the long-chain compounds.

TABLE I

1-SUBSTITUTED-3-TRIS(HYDROXYMETHYL)METHYLUREAS
RNHCONHC(CH₂OH)₃

R	Yield, %	M.P., ⁴ °C.	Analysis	
			% N Calcd.	% N Found
Allyl	79	140	13.72	13.45
Isopropyl	75	165	13.59	13.49
<i>n</i> -Butyl	82	145	12.72	12.21
<i>n</i> -Amyl	81	162	11.96	11.77
Phenyl	85	196	11.66	11.86
Cyclohexyl	82	189	11.38	11.26
<i>n</i> -Octyl	79	140	10.14	9.87
1-Naphthyl	96	215	9.65	9.90
<i>n</i> -Dodecyl	89	141	8.43	8.37
2-Biphenyl	95	188	8.86	8.43
<i>n</i> -Octadecyl	97	64	6.73	6.38

EXPERIMENTAL

Materials. Isocyanates were supplied by the Monsanto Chemical Co., Anniston, Ala., and St. Louis, Mo. Tris-(hydroxymethyl)aminomethane was obtained from the Commercial Solvents Corp., New York, N. Y.

Anal. Calcd. for C₄H₁₁NO₃: N, 11.57. Found: N, 11.63.

Synthesis of 1-substituted-3-tris(hydroxymethyl)methylureas.
General procedure. Isopropyl alcohol (35 ml.) was added to a hot solution of tris(hydroxymethyl)aminomethane (I) (12.1 g., 0.10 mole) in water (25 ml.) and the mixture heated to gentle reflux. The isocyanate (0.10 mole), followed by isopropyl alcohol (15 ml.), was then added dropwise during a two-minute period and the mixture was refluxed for ten minutes. On cooling, the urea derivative was filtered and recrystallized twice from isopropyl alcohol.

Tolylene-2,4-bis[3'-tris(hydroxymethyl)methylurea]. This compound was prepared in 96% yield by the method described above, using tolylene-2,4-diisocyanate (17.5 g., 0.10 mole) and I (24.2 g., 0.20 mole) in isopropyl alcohol (75 ml.). Recrystallization twice from the same solvent yielded white needle-like crystals, m.p. 207-208°.

Anal. Calcd. for C₁₇H₂₈N₄O₈: N, 13.46. Found: N, 13.27.

4,4'-Bis[3'-tris(hydroxymethyl)methylureido]diphenylmethane. One-gram increments of diphenylmethane-4,4'-diisocyanate (25.0 g., 0.10 mole) were slowly added to I (24.2 g., 0.20 mole) dissolved in a hot mixture of water (20 ml.) and isopropyl alcohol (75 ml.). After the initial strongly exothermic reaction had subsided the mixture was refluxed for 15 min., then set aside to cool. White

(3) The amino group of I is much more basic than are the hydroxyl groups. The basic dissociation constant, *pK_b* 5.97, has been determined by S. Glasstone and A. F. Schram, *J. Am. Chem. Soc.*, **69**, 1213 (1947). When I is treated with RNCO the amino group apparently reacts at a greater rate than the hydroxyl groups.

(4) Melting points are uncorrected.

crystals, yield, 48.2 g. (98%). Two recrystallizations from isopropyl alcohol gave a product of m.p. 188°.

Anal. Calcd. for C₂₃H₃₂N₄O₈: N, 11.38. Found: N, 11.30.

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Intramolecular Hydrogen Bonding Involving π -Electrons in Phenethyl Alcohols

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That aromatic hydrocarbons can participate as weak electron donors in hydrogen bond formation has been shown conclusively in recent publications.¹⁻³ Of special interest is the intramolecular hydrogen bonding in a series of vinyl alcohols reported by Rodebush.⁴ Evidence is presented here for the presence of intramolecular hydrogen bonding in a series of phenethyl alcohols.

During the course of a spectral examination of phenethyl alcohol (I) (0.5% in carbon tetrachloride) it was observed that the first overtone of the fundamental stretching vibration of the hydroxyl group⁵ was not a single, sharp peak as would have been expected for a non-bonded hydroxyl group, but was a doublet with a strong peak at 1.4084 μ and a weaker peak at 1.4209 μ . The ratio of the intensities of these two peaks (as measured at maximum absorption) was independent of concentration at several low concentrations. Under the same conditions benzyl alcohol (II) and 3-phenyl-1-propanol (III) showed only sharp singlets at 1.4155 μ and 1.4067 μ , respectively.

From an examination of molecular models of I, II, and III it was apparent that the peak at 1.4209 μ in the spectrum of I could have resulted from an intramolecular hydrogen bond between the hydroxyl group and the π -electrons at the 1-position of

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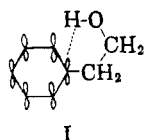
(2) M. Tamres, *J. Am. Chem. Soc.*, **74**, 3375 (1952).

(3) H. C. Brown and J. D. Brady, *J. Am. Chem. Soc.*, **74**, 3570 (1952).

(4) W. H. Rodebush and R. Feldman, *J. Am. Chem. Soc.*, **68**, 896 (1946); **69**, 770 (1947).

(5) The 1.4 μ region has been used extensively for the study of intramolecular hydrogen bonding in compounds containing a hydroxyl group. See L. Pauling, *The Nature of the Chemical Bond*, Cornell Univ. Press, Ithaca, N. Y., 1940, p. 316; also L. J. Bellamy, *The Infra-red Spectra of Complex Molecules*, John Wiley and Sons, Inc., New York, N. Y., 1954, p. 83.

the aromatic nucleus in those molecules having the conformation shown:



This interesting possibility was confirmed by examining the spectra of *p*-methoxyphenethyl alcohol (IV) and *p*-nitrophenethyl alcohol (V): IV showed the expected doublet; V showed only a singlet.⁶ Since compounds I to V all showed only one peak in the 1.417 to 1.424 μ region when the spectra were run in *benzene* solution, the peak at longer wave length for each doublet is assigned to the first overtone of the fundamental stretching vibration of the bonded hydroxyl group. The expected doublets were also observed in the spectra of 1,2-diphenyl ethanol (VI) and 1-phenyl-2-propanol (VII). All spectra are recorded in Table I.

TABLE I
ABSORPTION BANDS IN THE 1.4 μ REGION⁷

	0.5% CCl ₄ Soln.	Δ^8	0.5% Benzene Soln.
Phenethyl alcohol (I)	1.4084, 1.4209	0.0125	1.4235
Benzyl alcohol (II)	1.4155		1.4193
3-Phenyl-1-propanol (III)	1.4067		1.4170
<i>p</i> -Methoxyphenethyl alcohol (IV)	1.4085, 1.4223	0.0138	1.4220
<i>p</i> -Nitrophenethyl alcohol (V)	1.4088 ⁹		1.4220
1,2-Diphenyl ethanol (VI)	1.4161, 1.425 ¹⁰		
1-Phenyl-2-Propanol (VII)	1.4129, 1.4229		

That the above spectral data are compatible with the postulated intramolecular hydrogen bonding at the 1-position rather than at the 2,6-positions is shown by comparison of the Δ values above. The order $\Delta_{IV} > \Delta_I$ would be expected on the basis of Hammett's σ constants¹¹ for interaction at the 1-position. If, on the other hand, the interaction were at the 2,6-positions the reverse order $\Delta_I > \Delta_{IV}$ should have been observed.

(6) The absence of a second peak at longer wave length in the spectrum of V is attributed to the powerful electron-withdrawing ability of the *p*-nitro group.

(7) Spectra were measured on a Cary recording spectrophotometer, Model 14. Wave lengths, in microns, are accurate to ± 0.0003 micron.

(8) Δ = distance in microns between the peaks for I and IV.

(9) 0.15% solution.

(10) Shoulder.

(11) L. P. Hammett, *Physical Organic Chemistry*, McGraw-Hill Book Company, Inc., New York, N. Y., 1940, p. 188.

Using the value of 70 cm^{-1} for each kcal/mole of bond energy¹² the strengths of the hydrogen bonds in compounds I and IV are determined to be 0.88 and 0.98 kcal/mole, respectively.

EXPERIMENTAL

The phenethyl alcohol (Dow Chem. Co.) was purified by fractional distillation, n_D^{20} 1.5325 (lit.¹³ n_D^{20} 1.5310–1.5330). *p*-Methoxyphenylacetic acid (Aldrich Chem. Co.), m.p. 86–88° (lit.¹⁴ m.p. 85–87°), was reduced with lithium aluminum hydride to give IV, semicrystalline at 25° (lit.¹⁵ m.p. 24°). Nitration of I according to the published procedure¹⁶ yielded V, m.p. 61.5–62.5° (lit.¹⁶ m.p. 62°). A commercial sample of 1,2-diphenyl ethanol (VI), m.p. 66–67° (Eastman), was used without further purification. 1-Phenyl-2-propanone (Eastman) was reduced with lithium aluminum hydride to give VII, n_D^{20} 1.5217 (lit.¹⁷ n_D^{14-5} 1.5243).

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Carbonyl Reactions. III. The Formation of Aromatic Semicarbazones. A Nonlinear Rho-Sigma Correlation¹

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The formation of semicarbazones represents one of the important examples of general acid catalysis.²⁻⁴ The effect of structure upon reactivity has been studied by Price and Hammett³ who point out that the relative entropy of activation fluctuates in a series of aliphatic compounds. Cross and Fugassi⁵ have reported a satisfactory Hammett-type correlation for a limited number of *p*-substituted acetophenones. On the other hand, the report of

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(4) G. H. Stempel and G. S. Schaffel, *J. Am. Chem. Soc.*, **66**, 1158 (1944).

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