

An analytical sample, m.p. 174.5–175.5°, was prepared by crystallization from ethyl acetate.

*Anal.* Calcd. for  $C_{22}H_{16}$ : C, 94.25; H, 5.75. Found: C, 94.45; H, 5.64.

The hydrocarbon IV gave an unstable, purple picrate, m.p. 182–184°.

*Ultraviolet absorption spectrum.* The ultraviolet absorption spectrum of 9,10-dimethyl-3,4-benzopyrene in 95% ethanol was measured with a Model DU Beckman spectrophotometer. Maxima and ( $\log \epsilon$ ) values are: 260  $m\mu$  (4.59), 268  $m\mu$  (4.70), 288  $m\mu$  (4.63), 300  $m\mu$  (4.70), 372  $m\mu$  (4.40), and 392  $m\mu$  (4.48).

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### Vinyl-Alkali Metal Compounds<sup>1</sup>

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Reaction of vinyl chloride with alkali metals in tetrahydrofuran has yielded the vinyl-alkali metal compounds, as might be expected from recent success in making the vinyl-Grignard reagent in that solvent.<sup>2</sup> The simplicity of the procedure makes it preferable to the exchange reaction through which vinylsodium was first made.<sup>3</sup> Propenyllithium and several other alkenyllithium compounds have been made directly from the bromides in diethyl ether or petroleum ether,<sup>4</sup> but all attempts to similarly prepare vinyl compounds have failed.

The example given below concerns vinylpotassium prepared from liquid 90% potassium-sodium alloy,<sup>5</sup> but small-scale qualitative observations have shown that potassium, sodium, and lithium will each react.

Though the Grignard reagent is as easily made, vinylsodium or vinylpotassium may offer advantage on those occasions where the solid organometallic compound is needed, since they have little solubility and can be made solvent-free without decomposition by removal of solvent under reduced pressure. This operation leads to decomposition of the vinyl Grignard reagent.<sup>2</sup>

(1) This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command under Contract No. AF 18(600)-1541. Reproduction in whole or in part is permitted for any purpose of the United States Government.

(2) H. Normant, *Compt. rend.*, **239**, 1510 (1954). Ramsden *et al.* Abstracts, 130th Meeting, ACS, September 1956, p. 80–O.

(3) A. A. Morton, F. D. Marsh, R. D. Coombs, A. L. Lyons, S. E. Penner, H. E. Ramsden, V. B. Baker, E. L. Little, and R. L. Letsinger, *J. Am. Chem. Soc.*, **72**, 3785 (1950).

(4) E. A. Braude, J. A. Coles, and C. J. Timmons, *J. Chem. Soc.*, 2000, 2007, 2012, 2014 (1950).

(5) M. Sittig, Sodium, *ACS Monograph No. 133*, Reinhold, N. Y., 1956, p. 61.

As an example the reaction of vinyl Grignard solution with diethyl bromoborane gave only triethylborane, no trivinylborane, and evidence of polymers was seen. In contrast reaction of solid vinylpotassium gave some polymer, but trivinylborane and a mixture of ethylvinylboranes were obtained also.

The solvent should be removed from vinylpotassium (and presumably vinylsodium) as soon as possible because the solid reacts with the tetrahydrofuran. Were the solvent removed at once, the yield would probably be comparable with the best obtained by the exchange method.

### EXPERIMENTAL

The vinyl chloride solution (95 g. in 405 g. tetrahydrofuran) was prepared by passing the gas through sodium hydroxide solution and a drying train into the solvent cooled to 0°. This was added slowly to 50 g. 90% potassium-sodium alloy covered with 350 g. tetrahydrofuran cooled to 0° C. in a 3-neck flask fitted with a Hershberg stirrer. A blue precipitate formed which reached a viscous gel-like consistency as the reaction proceeded.

A day after completion the preparation was assayed using a 3/808 g. aliquot from the well stirred slurry. Treatment with isopropyl alcohol in the vacuum apparatus gave 1.8 mmoles of ethylene with the correct vapor pressure, corresponding to a total vinylpotassium content of 485 mmoles or a yield of 32%. Five days later the solvent was removed under reduced pressure, and a similar assay of a 1.81/90 g. aliquot of dry powder gave a yield of 7.4%. Apparently reaction with the solvent had occurred.

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### Reaction of Isocyanates with Tris(hydroxymethyl)aminomethane

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During the course of an investigation of certain urea derivatives it was necessary to prepare a series of 1-substituted-3-tris(hydroxymethyl)methylureas. Pierce *et al.*<sup>2</sup> described aromatic compounds of this type in which the substituents were phenyl, *o*- and *p*-tolyl, and 1- and 2-naphthyl. These compounds were prepared by reaction of equimolar quantities of isocyanate with tris(hydroxymethyl)aminomethane (I) in chloroform solution, but this method was disadvantageous in that I was insoluble in chloroform.

In addition to the phenyl and 1-naphthyl derivatives, made by the method of Pierce, a series of new derivatives has been prepared. It was found

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(2) J. S. Pierce, C. D. Lunsford, R. W. Raiford, J. L. Rush, and D. W. Riley, *J. Am. Chem. Soc.*, **73**, 2595 (1951).

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.<sup>3</sup> 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(CH<sub>2</sub>OH)<sub>3</sub>

R	Yield, %	M.P., <sup>4</sup> °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 C<sub>4</sub>H<sub>11</sub>NO<sub>3</sub>: 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 C<sub>17</sub>H<sub>28</sub>N<sub>4</sub>O<sub>8</sub>: 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<sub>b</sub>* 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 C<sub>23</sub>H<sub>32</sub>N<sub>4</sub>O<sub>8</sub>: N, 11.38. Found: N, 11.30.

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### Intramolecular Hydrogen Bonding Involving $\pi$ -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.<sup>1-3</sup> Of special interest is the intramolecular hydrogen bonding in a series of vinyl alcohols reported by Rodebush.<sup>4</sup> 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 group<sup>5</sup> 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  $\mu$  and a weaker peak at 1.4209  $\mu$ . 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  $\mu$  and 1.4067  $\mu$ , respectively.

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

(1) R. M. Badger, *J. Chem. Phys.*, **8**, 298 (1940); *J. Am. Chem. Soc.*, **73**, 3132 (1951).

(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 $\mu$  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.