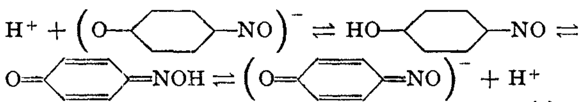
decrease in ionization as the water concentration in the dioxane–water mixture used as solvent was decreased below 25%; at 5% the specific conductance was no greater than of the solvent alone. The sodium salt precipitated in mixtures of dioxane containing less than 5% of water.

If the quinonoid form predominates in acid solution, as our absorption spectra data indicate, then the above conductivity data may be used to demonstrate that the quinonoid form probably predominates in alkaline solution also. The equation indicates that the only factor that would shift the equilibrium from one form to the other would be a difference in the degree of ionization of the two isomeric forms. The practically equal conductances of the two forms of the chloronitrosophenols indicate that there is no marked difference in their ionization and therefore one would expect little change in the equilibrium on changing from acid to alkaline solutions. It should be noted, however, that the experimental error in determining the conductances of these solutions is rather large, due to the low solubility of the substances and high resistance of the solutions, and it is not possible to say that there is absolutely no change in the ratio of the two forms present in the two media.



(1)

The absorption spectra data were obtained by methods which have been described.[6] The compounds used in these investigations were prepared by methods which have been published and each substance was carefully purified. All solvents were optically clear within the range of the spectrum under investigation.

Summary

1. Absorption spectra data indicate that the equilibrium mixture of quinonemonoxime and *p*-nitrosophenol exists largely in the quinonoid modification in dioxane, chloroform, absolute alcohol and aqueous acid solutions.

2. The absorption spectrum of 3-chloroquinone-4-oxime is very similar to that of its methyl ether while the absorption spectrum of 3-chloro-4-nitrosophenol is unlike that of its ether or isomeric quinonoid modification. This difference is not due to ionization nor to association of the nitrosophenol form.

3. The absorption spectra of alkaline solutions of the quinoneoximes are due to a highly ionized form and it appears probable that they are also due mostly to the ion from the quinonoid modification.

[6] Anderson and Gomberg, THIS JOURNAL, **50**, 203 (1928).

ANN ARBOR, MICHIGAN RECEIVED DECEMBER 21, 1933

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ARKANSAS]

d-Ethoxybutyl Urea[1]

BY E. WERTHEIM

In attempting to view the sweet taste of organic compounds from the standpoint which has proved successful in dealing with dyes, we may consider each compound the possessor of certain groups which have specific taste effects. In Dulcin the taste groups would be carbamido and ethoxy. These are held in a fixed position by the benzene ring. This paper reports the preparation of *d*-ethoxybutyl urea, in which the ring effect is absent but the identical groups are so held that they may assume the space arrangement found in Dulcin.[2]

The series of reactions used to prepare *d*-ethoxybutyl urea is sufficiently indicated by the following succession of formulas: $HOC_3H_6OH \longrightarrow EtOC_3H_6OH \longrightarrow EtOC_3H_6Br \longrightarrow EtOC_3H_6CN \longrightarrow EtOC_4H_8NH_2 \longrightarrow EtOC_4H_8NHCONH_2$.

The compound was found to be slightly bitter, resembling in this respect other aliphatic ureas which have been reported. It is thus established that while the relative position of the taste groups in Dulcin cannot be altered without destroying the sweetness, the ring framework must also be retained.[3] Work on the subject of taste *vs.* structure in Dulcin will be continued in this Laboratory.

[1] Paper No. 338, Journal Series, University of Arkansas.

[2] *Cf.* previous discussion, Wertheim, THIS JOURNAL, **55**, 2540 (1933).

[3] Similarly, *b*-hydroxyethyl urea recently has been prepared in this Laboratory and found to be practically tasteless. *o*-Hydroxyphenyl urea, on the other hand, is very sweet.

Experimental Part

γ-Ethoxybutyronitrile, $EtOC_3H_6CN$.—γ-Ethoxypropyl alcohol and γ-ethoxypropyl bromide were made essentially as described by Noyes.[4] Forty grams of ethoxypropyl bromide was refluxed for three and one-half hours on a water-bath with 28 g. of potassium cyanide, 6 cc. of water and 40 cc. of alcohol. The liquid was then decanted from the precipitated salts, which were washed with ether. The combined solution was diluted with water and extracted several times with ether. After removal of the solvent from the dried ether extract, the product was fractionated under reduced pressure: wt., about 16 g.; b. p. (716 mm.) 175°. The reported b. p. (750 mm.) is 181.2–181.5°.

δ-Ethoxybutylamine, $EtOC_4H_8NH_2$.—Ten grams of ethoxybutyronitrile and 200 cc. of absolute methanol were placed in a flask under an efficient reflux condenser. Twenty-six grams of sodium, cut into small pieces, was added as rapidly as possible through the condenser. When all the sodium had reacted, steam was passed through the mixture, the distillate being caught in a receiver containing 8 cc. of concd. hydrochloric acid. At the conclusion of the steam distillation the slightly acid distillate was evaporated to a small volume, first over a free flame, finally under reduced pressure using an oil-bath. The evaporation was interrupted upon appearance of a solid residue. This residue was treated with 60% potassium hydroxide solution and extracted with ether. The extract was dried with solid potassium hydroxide, the ether removed by distillation, and the resulting oil again dried with solid potassium hydroxide: yield, about 7 g.; b. p. (730 mm.) 155–156°. The recorded b. p. (746 mm.) is 153–154°.

δ-Ethoxybutyl Urea, $EtOC_4H_8NHCONH_2$.—Two grams of ethoxybutylamine was mixed with 1.5 g. of potassium cyanate in 3 cc. of water. The solution was cooled with ice and stirred while 0.95 cc. of a 1:1 solution of concd. sulfuric acid in water was added in small drops from a capillary pipet. When all the acid had been added the mixture was warmed to 55–60° for five minutes, then 25 cc. of acetone was added. After being cooled in an ice-bath the mixture was filtered by suction. The filtrate was warmed to 55–60° until the odor of acetone was lost, then for one hour to 60–65°. Upon cooling a solid was obtained. This was treated with 6 cc. of acetone; the mixture was filtered, 6 cc. of dry ether added, and the solution placed in ice. The urea soon appeared as a heavy precipitate of oblong microscopic platelets: weight, 1.0 g. of m. p. 68–69°.

The compound is freely soluble in water, ethanol, acetone, chloroform and benzene and practically insoluble in ether. When the compound is tasted a cooling sensation is felt on the tip of the tongue, followed (with most observers) by a faint bitter taste. A 2% water solution was faintly bitter (one observer reported a slight sweet taste).

Anal. Calcd. for $C_7H_{16}N_2O_2$: C, 52.50; H, 10.0; N, 17.50. Found: C, 52.92, 52.35; H, 10.28, 9.61; N, 17.52, 17.71.

Summary

The preparation of *d*-ethoxybutyl urea is described. The compound is faintly bitter, showing that the sweet taste of Dulcin depends upon the presence of the benzene ring. β-Hydroxyethyl urea is also not sweet, while *o*-hydroxyphenyl urea is very sweet.

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[4] Noyes, *Am. Chem. J.*, **19**, 767 (1897).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ILLINOIS]

Trihalomethylketonic Acids of the Naphthalene Series

BY BENTON A. BULL AND REYNOLD C. FUSON

The retardation of the cleavage phase of the haloform reaction in the case of diortho substituted aryl methyl ketones appears to depend partly on the steric hindrance involved and partly on the solubility of the trihalomethyl ketone in the alkaline medium employed for the cleavage.[1] The separate influence of each of these factors would be clearly demonstrated by a comparison of the reactions of methyl aryl ketones in which (1) the *solubility factor* was changed while the steric factor remained constant, and (2) the *steric factor* was changed while the solubility factor remained constant.

Such a comparison is satisfactorily afforded by a study of the three ketones 1-aceto-2-naphthyl methyl ether (I), 1-aceto-2-naphthoxyacetic acid (II) and 2-aceto-1-naphthoxyacetic acid (III).

Both I and II gave trihalomethyl ketones when treated with hypohalites, but the trihalomethyl ketones from II were cleaved by alkalies (to V) in approximately one-eighth of the time required for the cleavage of the trihalomethyl ketones from I.[2] Hence the cleavage of these two types of trihalomethyl ketones possessing approximately equal steric factors[3] indicates that the introduction of a solubilizing group leads to an increase in the ease of cleavage.

On the other hand, II and its position isomer, III, have approximately the same solubility. The

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[1] Bull and Fuson, THIS JOURNAL, **55**, 3424 (1933).

[2] See Fuson, Farlow and Stehman, *ibid.*, **53**, 4097 (1931).

[3] The molecular volume of the acetoxy group, while unknown, would certainly not be less than that of the methoxyl group.