successfully to certain secondary alkyl and aryl halides. It involves the preparation of the Grignard reagent and its treatment with the corresponding mercuric halide.

Experimental Part

Table I gives the melting points for several compounds of this class that are known, but which have not previously been identified by this method. It includes also the formulas and analytical data for new secondary alkyl and aryl mercuric halides prepared as indicated above.

Summary

The method already described for the identification of primary alkyl bromides and iodides may be applied with success to secondary alkyl and aryl bromides and iodides.

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THE ELECTRON-SHARING ABILITY OF ORGANIC RADICALS—GLUCOSE AND OTHER POLY-ALCOHOLS

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A preceding paper[1] pointed out that the physical properties of the polar groupings RNH_2, RCOOH, RCH_2COOH, RCH_2CH_2COOH and ROH could be expressed as an exponential function of "the electron-sharing ability" of "R." A strict interpretation of these data implies that the electron-sharing ability of the carbon radicals varies from a range more "positive" than hydrogen to a range more "negative" than chlorine, according to the substituents of the carbon under consideration. When the composition of the radicals is considered in the order of their "negativity," it is found that the typical aromatic groupings are intermediate to the most "positive" and most "negative" of the aliphatic radicals. In other words, we may expect to find carbons in "aliphatic" compounds with properties as negative, or even more negative, than those in "aromatic" structures.

In a previous paper[2] attention was called to the negative nature of the third carbon atom in diacetoneglucose on the following evidence.

1. The chlorine in 3-chlorodiacetoneglucose is relatively stable toward alkaline hydrolysis.

2. When diacetoneglucosetoluenesulfonate ester is treated with Grignard's reagent, *p*-tolylphenylsulfone is obtained in analogy with the aromatic sulfonate esters rather than the aliphatic esters.[3]

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[1] Hixon and Johns, This Journal, **49**, 1786 (1927).

[2] Allison and Hixon, *ibid.*, **48**, 406 (1926).

[3] Gilman, Robinson and Beaber, *ibid.*, **48**, 2715 (1926).

3. When the sulfonate ester of diacetoneglucose is treated with hydrazine, dehydration as well as substitution takes place, which is analogous to the terpene sulfonate reaction.

The physical data presented in the following paper have been assembled in order to substantiate these qualitative observations and to correlate the chemical properties of the carbohydrate carbons with the properties of the more familiar "aliphatic" and "aromatic" carbons. These data indicate that the "electron-sharing ability" of the carbons in the aliphatic polyalcohols is intermediate to that of the alkyl and phenyl radical. This paper also indicates an experimental method of approach for the study of the affinity of particular carbons in complex structures such as glucose.

Acid dissociation constants for the hexoses have been measured by Osaka,[4] Madsen[5], Euler[6] and Michaelis and Rona[7] by the cryoscopic, saponification and electrode methods. These authors all agree in reporting values of a magnitude of $Ka = 10^{-13}$ for fructose, glucose and sucrose. The dissociation constant for ethyl alcohol is less than 10^{-15} and for phenol 10^{-11}. Madsen by means of the van't Hoff equation calculates the heat of neutralization for these three sugars and finds them to be respectively about 50, 35 and 25% that of the strong acids.

While these measurements are indicative of the semi-phenolic, semi-aliphatic nature of the carbohydrates they must be considered with the following two reservations.

(*a*) Values of the same magnitude have been reported for some of the aliphatic aldehydes and accordingly these values might be assigned to the hexose aldehydic or ketonic group. Such an explanation could not, however, be applied to sucrose.

(*b*) Since there are a large number of hydroxy groups, these values might be considered as the sum of many weaker dissociations.

The heat of the replacement of hydrogen by sodium in the general reaction

$$\text{ROH} + \text{Na} \longrightarrow \text{RONa} + {}^1/_2\,\text{H}_2 + \text{heat}$$

may also be used as a comparative index of the degree of "acidity" of the hydrogen. Since R is the only variable in the reaction, this gradation must be explained as a function of the electron-sharing ability of R. A series of hydroxides is given in Table I in the order of the magnitude of the heat of this reaction, grading from the strong base sodium hydroxide to sulfuric acid. The values for the poly-alcohols have been taken from de Forcrand's[8] work; the other data are either taken directly or calculated from values given in Landolt-Börnstein.

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[4] Osaka, *Z. physik. Chem.*, **35**, 673 (1900).

[5] Madsen, *ibid.*, **36**, 290 (1901).

[6] Euler, *Ber.*, **39**, 344 (1906).

[7] Michaelis and Rona, *Biochem. Z.*, **49**, 248 (1913).

[8] De Forcrand, *Ann. chim. phys.*, [6] **30**, 56 (1893).

TABLE I

HEAT OF REPLACEMENT OF HYDROGEN BY SODIUM

Sodium hydroxide	2.0	Mannitol, average value	34.82
Aluminum hydroxide	27.0	Erythrite, average value	38.14
Tertiary alcohol, average value	27.89	Glycerol, average value	39.99
Secondary alcohol, average value	29.75	Phenol	39.10
Primary alcohol, average value	32.00	Acetic acid	50.17
Water	31.87	Sulfuric acid	68.00

Attention should be called to the fact that these values indicate that the sugar alcohol groups and other poly-alcohols are almost as negative as phenol itself.

Dissociation Constant of Glucosamine.—The values given above cannot be localized for any particular carbon. From the variation in the reactivity of the various halides, it seems probable that there is a marked difference in the affinity of the various carbons in the glucose chain. It should be possible to measure the electron-sharing ability of any of these carbons by replacing the particular hydroxy group by more polar groups such as the amino or carboxy group. The conductivity of the free hydroxy groups is so small (10^{-13}) that it can be ignored for values of strongly polar groups. If trouble is encountered due to the hydroxy groups, they can be easily muzzled by methylation.

Vellinger[9] has reported the value $pK_b = 6.34$ for glucosamine, which gives the value 4.6×10^{-7} for the basic dissociation constant. This value was obtained by potentiometric measurements in connection with a study of the relationship of rotation to acidity of the solution. This value has been confirmed by conductivity measurements in this Laboratory.

Glucosamine was prepared from the hydrochloride salt by the method of Breuer.[10] It was recrystallized several times from methyl alcohol and checked for purity by Dumas nitrogen analysis and by direct titration. The melting point was indefinite, as reported in the literature, depending upon rate of heating. As the amine was repeatedly recrystallized the melting point was raised from 105–110° as reported to 125–130°. Conductivities of three separate preparations are reported in Table II. The value of μ_0 has been obtained by Washburn's[11] method of extrapolation and is an approximation at best. A comparison of the basic properties of glucosamine with those of ammonia and hydrazine is shown graphically in Fig. I, data for the latter being taken from Bredig.[12]

When this value for the dissociation constant of glucosamine is compared with the list presented in the previous mathematical treatment,[1] it shows

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[9] Vellinger, *Compt. rend.*, **182**, 1625 (1926).

[10] Breuer, *Ber.*, 31, 2194 (1898).

[11] Washburn, THIS JOURNAL, **40**, 122 (1918).

[12] Bredig, *Z. physik. Chem.*, **13**, 308 (1894).

TABLE II

CONDUCTANCE OF GLUCOSAMINE

Temp., 25°. $\mu_0 = 200$. Average value of dissociation constant $= 6.5 \times 10^{-7}$. Specific conductance of water, 4.5×10^{-6}.

Concn., millimoles	Molecular conductance	Dissoc. const., $K \times 10^{-7}$
48.51	0.92	10.3
24.20	1.01	6.2
12.12	1.28	4.8
6.06	1.65	4.2
3.03	1.97	3.0
1.52	2.62	2.6
45.20	0.89	8.9
22.60	1.27	9.2
11.30	1.56	6.9
5.65	2.17	6.7
2.82	3.10	6.9
1.41	4.44	7.1
20.52	1.2	7.4
10.26	1.6	8.1
5.13	2.2	6.2
2.56	3.06	6.1
1.28	4.3	6.1

that the "electron-sharing ability" of this particular carbon in the glucose chain is almost exactly intermediate to that of the methyl and phenyl radicals, respectively. As in the previous paper mechanical concepts of valence have been intentionally avoided. The conclusions rest on the assumption that, whatever the mechanistic cause of the conductance, the

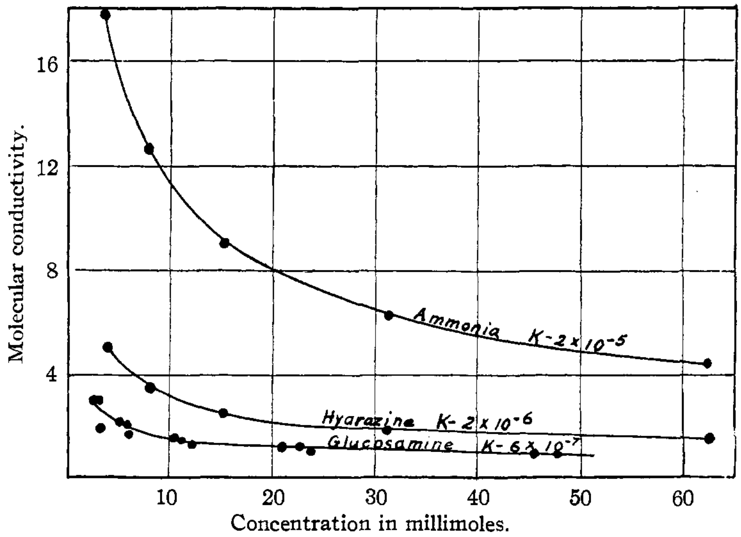

Fig. 1.—Molecular conductivities of ammonia, hydrazine and glucosamine.

magnitude is a function of the "electron-sharing ability" of the radical linked to the amine group.

Summary

It is pointed out that the electron-sharing ability of the aliphatic carbon radicals varies over a range extending from values more positive than hydrogen to values more negative than chlorine. The available physical data have been assembled to show the position of glucose (and other polyalcohols) among the more familiar aliphatic and aromatic radicals. These data agree in showing the intermediate position of this group of compounds as summarized in the following figures.

Nature of radical	Dissoc. const. of amine	Dissoc. of hydroxide	Heat replacement of H by Na
Methyl-	5×10^{-4}	10^{-15}	32
2-Glucosyl-	6×10^{-7}	10^{-13}	37
Phenyl-	4×10^{-10}	10^{-11}	39

AMES, IOWA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

STUDIES ON THE PREPARATION OF THE HIGHER ACETYLENES. I. (PRELIMINARY PAPER.) DEHALOGENATION OF 1,1-DICHLOROHEPTANE IN THE VAPOR PHASE

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Acetylenes, more particularly those of the normal, or alpha type, $RC\equiv CH$, are peculiarly reactive and in consequence may be used for the preparation of many interesting and important types of organic compounds. Unfortunately, however, their applicability in synthetic work is rather restricted because of the difficulty of preparing many of the α-acetylenes in quantity and in a state of purity. The usual methods of preparation involve dehalogenation of dihalides, or olefinic monohalides, with solid, aqueous or alcoholic alkalies, alcoholic sodium ethylate, metallic sodium, sodium amide and, in a few cases, soda lime,[1] magnesium,[2] zinc dust and alcohol[3a] and the Grignard Reagent.[3b]

Failure to obtain satisfactory yields, apart from incomplete removal of halogen, is usually due to one, at least, of the following causes, namely, (*a*) molecular rearrangement by aqueous or alcoholic alkaline reagents to diolefins and *iso*-acetylenes ($RC\equiv CR$); (*b*) ether formation, when alcoholic alkalies are employed; (*c*) polymerization. The use of sodium

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[1] Peratoner, *Chem. Zentr.*, **1892**, II, 737.

[2] Porcher, *Bull. soc. chim.*, [4] **31**, 334 (1922).

[3] (a) Lespieau, *Compt. rend.*, **170**, 1584 (1920); (b) **171**, 111 (1920).