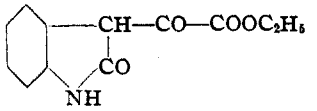
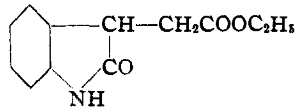


(V)



(VI)

oxindole. Horner reduced compound V with zinc amalgam and hydrochloric acid and obtained a product melting at 217° which he designated as "oxindoleacetic acid" (II). When the reduction was accomplished by the use of zinc amalgam and acetic acid the product was VI (the ethyl ester of I), m. p. 95°.

In view of the fact that Gränacher's "oxindoleacetic acid" and Horner's product had essentially the same melting point and that Gränacher's product had been shown by Aeschlimann to be III it was suspected that Horner's "oxindoleacetic acid" was also compound III.

To investigate this point the experimental work of Horner in preparing V and reducing it with zinc amalgam and hydrochloric acid was repeated. The product was found to be identical with a sample of compound III prepared according to the procedure of Aeschlimann. The identity was established by melting point methods and by the conversion of both samples to the ethyl ester of III (m. p. and mixed m. p. 155°).

Further the reduction of oxindole-3-glyoxylic ester (V) by zinc amalgam and acetic acid was repeated. It appeared that if the product of this reduction was the ethyl ester of oxindoleacetic acid (VI) compound III should result when VI was treated with hydrolytic agents through the opening of the five membered ring of the resulting oxindoleacetic acid and subsequent closure of the six membered ring giving III. It was found that VI is in fact converted into III by refluxing with aqueous hydrochloric acid.

It has been reported[8] that the reduction of α-keto acids and esters under Clemmensen conditions always results in the formation of α-hydroxy acids and esters. The reduction of ethyl oxindole-3-glyoxalate under Clemmensen conditions constitutes an exception to this rule since in both cases reported herein the carbonyl group of compound V is reduced to the methylene group in the formation of compounds III and VI.

Experimental

Ethyl Oxindole-3-glyoxalate (V).—This compound was prepared as described by Horner[7]; m. p. 187°.

2-Keto-1,2,3,4-tetrahydroquinoline-4-carboxylic Acid (III).—A. The compound was prepared by reducing V with zinc amalgam and hydrochloric acid as described by Horner[7]; colorless needles from water, m. p. 218°.

B. The compound was prepared by the procedure of Aeschlimann; colorless needles, m. p. 218°. A mixture of samples prepared by procedures A and B showed no depression in melting point.

Ethyl Ester of 2-Keto-1,2,3,4-tetrahydroquinoline-4-carboxylic Acid.—This compound was prepared by heating samples of III with absolute alcohol containing a few drops of sulfuric acid. Samples of III prepared by procedures A and B yielded identical samples of the ester; m. p. and mixed m. p., 155°.

Ethyl Ester of Oxindoleacetic Acid (VI).—2.5 grams of ethyl oxindole-3-glyoxalate (V) was refluxed with 10 g. of zinc amalgam and 50 cc. of 50% acetic acid until the resulting solution was decolorized. The solution was filtered and extracted with ether. The ether extract was shaken with saturated sodium carbonate solution until all acetic acid was neutralized. The ether extract was dried over sodium sulfate and the ether removed. The resinous residue was purified by crystallization from aqueous alcohol from which it separated as colorless needles; m. p. 95° as reported by Horner.

2-Keto-1,2,3,4-tetrahydro-quinoline-4-carboxylic Acid by the Hydrolysis of VI.—Three-tenths gram of compound VI was heated for one hour under reflux with a mixture of 6 cc. of concentrated hydrochloric acid and 30 cc. of water. The resulting solution was cooled, the precipitate collected and purified by crystallization from hot water. The product was obtained as colorless needles; m. p. 218°. The melting point of mixtures of this product with samples of III prepared by procedure B was also 218°.

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(8) Martin, "The Clemmensen Reduction," page 159 of "Organic Reactions," Vol. I, Roger Adams, Editor, John Wiley and Sons, New York, N. Y., 1942.

Methacrylic Esters of Glucose and Other Carbohydrates[1]

BY R. H. TREADWAY AND E. YANOVSKY

Recently methacrylic anhydride became available for research purposes. Although methacrylic esters of lower aliphatic alcohols have been of technical importance for some time, none has been prepared with methacrylic anhydride. Properties of methacrylic esters of the starch group of carbohydrates (glucose, maltose, dextrin, and starch) prepared by us are described here.

Preparation and Properties of Glucose Pentamethacrylate.—Thirty grams of glucose was stirred into 150 g. of pyridine at 65°. Methacrylic anhydride (192 g.) was added gradually. This amount is 50% more than that required for penta substitution. The sugar dissolved entirely in about three hours, but stirring and heating were continued for another half hour. The solution was then poured into stirred cold water. The sirup which separated was washed with water several times and then dissolved in warm alcohol. On cooling, twenty grams of fine needle-shaped white crystals of glucose pentamethacrylate separated. The substance was soluble in alcohol, acetone, benzene, chloroform, and other organic solvents, but insoluble in aliphatic hydrocarbons. After two recrystallizations, a constant melting point was attained, 115° (cor.). The specific rotation for a 4% solution in absolute alcohol was $[\alpha]^{25}\text{D}$ +87.3°.

Anal. Calcd. for $C_{26}H_{32}O_{11}$: C, 60.0; H, 6.2. Found: C, 59.8; H, 6.1. Calcd. for $C_6H_7O_6(CH_2{=}C(CH_3){-}CO{-})_5$: methacrylyl, 66.4. Found by saponification: methacrylyl, 66.4.

Solutions of glucose pentamethacrylate in chloro-

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[1] Not copyrighted.

form and other solvents gel in the presence of benzoyl peroxide or cobalt naphthenate. The fact that both these agents accelerate polymerization of glucose pentamethacrylate suggests that besides the addition polymerization, polymerization accompanied by oxidation takes place. This was further substantiated by the following experiments. After a month at room temperature, glucose pentamethacrylate crystals were still soluble in organic solvents, but combustion analysis showed only 57.8% carbon, which corresponds approximately to the original compound with one atom of oxygen added. After being heated for two hours at 100°, glucose pentamethacrylate became insoluble in all organic solvents. The carbon value was 54.2%, indicating the addition of approximately 3 atoms of oxygen.

Maltose octamethacrylate was prepared as an amorphous powder by the procedure used for glucose. It was soluble in the same solvents as glucose pentamethacrylate. Analysis showed 62.5% methacrylyl (calcd., 62.3%); specific rotation $[\alpha]^{25}\text{D}$ +81.4° in 4% solution in alcohol. A solution of maltose octamethacrylate (50% in chloroform) gelled in fifteen days at room temperature, in four in the presence of benzoyl peroxide, and in two in the presence of cobalt naphthenate. The amorphous powder became insoluble in one to two weeks at room temperature and in about two hours when heated at 100°.

Dextrin trimethacrylate was prepared in a similar manner (six hours at 95°). The amorphous powder was insoluble in alcohol and aliphatic hydrocarbons but soluble in most other usual solvents. It insolubilized on exposure to air.

Starch methacrylate (substitution 2.9) was prepared (seven hours at 95°) as an amorphous powder insoluble in most solvents but slightly soluble in pyridine and tetrachlorethane. It became entirely insoluble on exposure to air or after short heating.

EASTERN REGIONAL RESEARCH LABORATORY
PHILADELPHIA, PA. RECEIVED MARCH 26, 1945

Polarographic Reduction Potentials of Quaternary Ammonium Ions

BY PIERRE VAN RYSSELBERGHE AND J. M. MCGEE

The halides of tetra-substituted ammonium ions, particularly the tetramethylammonium ion, are used as supporting electrolytes in polarographic work whenever the reduction reactions to be studied occur at potentials more negative than those corresponding to the reduction of the ions of the alkali metals. In our polarographic researches[1] we have now been led to a study of the reduction of various quaternary ammonium ions in presence of the most difficultly reducible one of them all, the tetramethylammonium ion, $N(CH_3)_4^+$. A brief digest of the previous, and very fragmentary, work on some of these ions will be found in Kolthoff and Lingane's book.[2]

Materials.—Besides $N(CH_3)_4Br$, the other three tetraalkylammonium salts (tetraethylammonium bromide, tetra-*n*-propyl and *n*-butyl iodides) were also Eastman Kodak Co. white label products, ammonium chloride was Baker C. P. and trimethylammonium chloride was Kahlbaum C. P. Some of the choline hydrochloride used was Merck C. P. Choline isolated from the lecithin of egg yolks gave results identical with those obtained with the Merck product. The acetylcholine hydrochloride was Merck C. P. The two other unsymmetrical ions were prepared by us according to standard methods.

Procedure.—The instrument was a Heyrovsky polarograph of the Sargent Company. Polarographic reduction curves of the supporting electrolyte alone (Eastman Kodak Co. white label tetramethylammonium bromide, carefully recrystallized from water–ethanol mixtures) were recorded as blanks for each case. The average of a large number of limiting tangent potentials for the reduction of this ion is −2.93 ± 0.03 volt referred to the saturated calomel electrode. Varying amounts of each one of the other salts were then added to the solution of the supporting electrolyte and their reduction waves recorded. The half-wave potentials could, in all cases, be determined without ambiguity. Several of the diffusion currents (but not those of the symmetrical ions) exhibited maxima before merging into the reduction wave of the supporting ion, but these maxima were always exactly reproducible. The crests of these maxima were used to determine the half-wave potential, since, in the case of choline, a detailed analysis showed that the heights of these crests were closely proportional to the concentration. The uncertainty on the various half-wave potentials is well within the general upper limit ±0.03 volt. The temperature was not controlled but was in all cases close to 25°. No detectable variations could be observed in the reduction potentials for the cases which were repeated at intervals of several days.

Results.—In Table I we give for each quaternary ammonium ion the accompanying halide ion and the half-wave potential referred to the saturated calomel electrode. No striking regularity is apparent in Table I. It seems unlikely, however, that the reduction corresponding to the $N(CH_3)_4^+$ ion could be the decomposition of water,[2] since different potentials are observed with the other tetraalkylammonium ions. This is also indicated by some experiments in which these other tetraalkylammonium salts were used as supporting electrolytes. The inversion in the sequence $N(C_3H_7)_4^+$, $N(C_4H_9)_4^+$, $N(C_2H_5)_4^+$, $N(CH_3)_4^+$ is peculiar, but is again substantiated in the results obtained when using the corresponding salts as supporting electrolytes. In the case of the unsymmetrical ions it appears that the reduction potential of the most reducible group is affected by the nature of the other groups present, as is clear if one compares the relative positions of these ions in the table. In the only case where three different groups are present, $N(CH_3)_2C_2H_5C_6H_5^+$, it is impossible to decide whether the

TABLE I

POLAROGRAPHIC HALF-WAVE REDUCTION POTENTIALS OF QUATERNARY AMMONIUM IONS

Positive ion	Negative ion	Half-wave potential, volts
NH_4^+	Cl^-	−2.21
$N(CH_3)_3H^+$	Cl^-	2.23
$N(C_2H_4OH)_3C_2H_5^+$	Br^-	2.38
$N(C_3H_7)_4^+$	I^-	2.52
$N(C_4H_9)_4^+$	I^-	2.57
$N(CH_3)_3C_2H_4OCOCH_3^+$	Cl^-	2.64
$N(C_2H_5)_4^+$	Br^-	2.67
$N(CH_3)_2 \cdot C_2H_5 \cdot C_6H_5^+$	Br^-	2.71
$N(CH_3)_3C_2H_4OH^+$	Cl^-	2.72
$N(CH_3)_4^+$	Br^-	2.93 (tangent potential)

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[1] P. Van Rysselberghe and G. J. Alkire, THIS JOURNAL, **66**, 1801 (1944).

[2] I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941, p. 380.