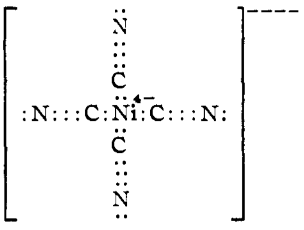
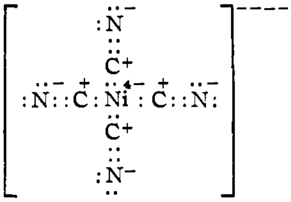
B



$$\left[\begin{array}{c} N \\ ::: \\ C \\ :N:::C:\overset{4-}{Ni}:C:::N: \\ C \\ ::: \\ N \end{array}\right]^{----}$$

C



$$\left[\begin{array}{c} :\ddot{N}^{-} \\ :: \\ C^{+} \\ :\ddot{N}^{-}::\overset{+}{C}:\overset{4-}{Ni}:\overset{+}{C}::\ddot{N}^{-}: \\ C^{+} \\ :: \\ :\ddot{N}^{-} \end{array}\right]^{----}$$

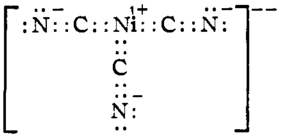
Structure A seems more satisfactory than the single-bonded structures since the nickel atom is neutral, rather than negative; and in its general behavior nickel is electropositive rather than electronegative. It also has a stable octet of electrons about the carbon atom; this is not shown by structure C, which has only a sextet of electrons. In A four of the 3*d* orbitals of nickel, as well as the 4*s* orbital and one 4*p* orbital, would be used in bond formation.

Probably, as in the case of nickel carbonyl, the molecule resonates between the double-bonded and single-bonded structures. A more detailed discussion of the nature of the bonds and of their spatial configuration must await the determination of physical data.

It may be noted that chemically nickel carbonyl and the $[Ni(CN)_4]^{----}$ ion show a similarity in properties. Both, for example, are oxidized by air or oxygen and are decomposed by water.[1,3]

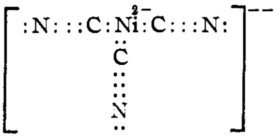
Two resonance structures are suggested for the $[Ni(CN)_3]^{--}$ ion:

D



$$\left[\begin{array}{c} :\ddot{N}^{-}::C::\overset{1+}{Ni}::C::\ddot{N}^{-}: \\ :: \\ C \\ :: \\ \ddot{N}^{-}: \end{array}\right]^{--}$$

E



$$\left[\begin{array}{c} :N:::C:\overset{2-}{Ni}:C:::N: \\ C \\ ::: \\ N \end{array}\right]^{--}$$

Formula D may make the greater contribution because here the nickel is electropositive. In this structure four 3*d* orbitals, the 4*s*, and one 4*p* orbital might be used in bond formation, with the unpaired electron in a second 4*p* orbital. A similar structure can be postulated for E, with one 3*d*, the 4*s*, and one 4*p* orbital used for bond formation, and the lone electron in a 4*p* orbital.

Either of these would be an electronic configuration similar to that of cobalt in the $[Co(CN)_6]^{----}$ ion, in which it is postulated that the unpaired electron of cobalt occupies the outer unstable 4*d* orbital. This outer lone electron is believed to account for the instability of the complex[4]; this instability is evidenced, for example, by the liberation of hydrogen from water by the ion. The $[Ni(CN)_3]^{--}$ ion also decomposes water, liberating hydrogen; this chemical behavior gives support to the above formulation.

Again physical data are needed for complete elucidation of the structure.

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(3) Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., London, 1924, p. 955.

(4) Pauling, ref. 2, p. 94.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF ILLINOIS
URBANA, ILL.

RECEIVED OCTOBER 30, 1944

Isolation of Mannitol from the Seeds of *Citrullus vulgaris*[1,2]

BY W. MAYO HIGGINS[3] AND MELVIN F. W. DUNKER

In a phytochemical study of the seeds of *Citrullus vulgaris* Schrader, the common watermelon, *d*-mannitol was isolated from the alcohol extract of the defatted whole seeds. Separate extractions of the shells and kernels of the seeds showed mannitol to be present only in the shells. No previous reference to the isolation of *d*-mannitol from *Citrullus vulgaris* was found in the literature.

Experimental

Twenty pounds (9080 g.) of seeds was ground to pass a 20-mesh screen and exhaustively extracted in a Soxhlet type, stainless steel extractor successively with petroleum ether (b. p. 60–70°) and 95% alcohol.

The alcohol extract, 409 g. (4.3%) of a viscous reddish-brown material containing suspended solid, was washed by decantation successively with boiling ether, alcohol at room temperature, and warm alcohol (45°) until the washings were colorless in each case. Finally the solid residue was dissolved in boiling alcohol from which fine white needles crystallized on cooling. About 6 g. (0.065%) of crude material was obtained and purified by crystallization from 95% alcohol to a constant m. p. of 164.6–166.5° (cor.).

Elementary analysis and classification tests indicated a polyhydroxy alcohol or sugar. The m. p. corresponded to that recorded for *d*-mannitol and mixed m. p. with a known sample of *d*-mannitol gave no depression. The optical rotation was $[\alpha]^{26}D$ $-0.86°$ (*c*, 1.6) in water and $[\alpha]^{22}D$ 27.75° (*c*, 3.03) in 7.4% aqueous solution of borax. The optical rotation of mannitol in water has been reported as levo,[4] $[\alpha]^{25}D$ $-0.49°$,[5] and $[\alpha]^{22}D$ -0.99,[6] and the rota-

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(1) Abstracted from a part of the thesis of W. Mayo Higgins presented to the Graduate School of the University of Wisconsin, in partial fulfillment of the requirements for the degree of Doctor of Philosophy, September, 1943.

(2) The investigation of *Citrullus vulgaris* was begun under the direction of Dr. Lloyd M. Parks, now on leave of absence to the Armed Forces.

(3) Present address: Burroughs Wellcome and Co., Tuckahoe, New York.

(4) H. Landolt, "The Optical Rotating Power of Organic Substances," The Chemical Publishing Co., Easton, Pa., 1902, 2nd ed., p. 511.

(5) A. Grun, I. Husman and H. Nossowitsch, *Monatsh.*, **37**, 215 (1916).

(6) A. A. Dodge, Thesis, University of Wisconsin, 1941.

tion in an aqueous 7.4% borax solution is given as [α]D 28.3°[7] and [α]^{26}D 28.5°.[5]

The acetyl derivative prepared by heating with acetic anhydride and sodium acetate had m. p. 123–123.5° (cor.) and [α]^{25}D 21.53° (*c*, 1.97) in chloroform. The hexaacetate of *d*-mannitol has been reported to have m. p. 122° [α]^{20}D 24.4° in chloroform[8] and m. p. 123.5–124.5°, [α]^{27}D 21.3° in chloroform.[5] A mixed m. p. with an authentic sample of mannitol hexaacetate gave no depression.

To determine in which part of the seed the mannitol was present, 680 g. of the whole seeds was separated into shells and kernels and each extracted as above. Mannitol could be isolated only from the shells.

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(7) E. Fischer, *Ber.*, **23**, 385 (1890).

(8) E. Pacsu and F. V. Rich, THIS JOURNAL, **55**, 2023 (1933).

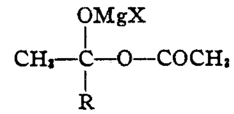
SCHOOL OF PHARMACY
UNIVERSITY OF WISCONSIN
MADISON, WISCONSIN
RECEIVED NOVEMBER 13, 1944

The Preparation of Ketones from Grignard Reagents

BY MELVIN S. NEWMAN AND WILLIAM T. BOOTH, JR.

We have found that excellent yields of methyl ketones may be obtained by the addition of Grignard reagents to an ether solution of acetic anhydride at about −70°. Primary, secondary, tertiary aliphatic, and aromatic Grignard reagents give 70–79% yields of the corresponding methyl ketones while the allyl and benzyl reagents give 42 and 52%, respectively.[1]

We attribute the success of these reactions at low temperature to the thermal stability of the complex, I, formed by the addition of one molecule



$$CH_3\text{—}\overset{\overset{\displaystyle OMgX}{|}}{\underset{\underset{\displaystyle R}{|}}{C}}\text{—}O\text{—}COCH_3$$

I

of Grignard reagent to one of the carbonyl groups of acetic anhydride, and to its decreased solubility. These factors both tend to reduce the further reaction of I with more Grignard reagent to form tertiary alcohol. At the low temperature involved there is probably no cleavage of this complex to form ketone which might further react.

The success of the above reactions led to the hope that good yields of ketones may be obtained also from acid chlorides and esters in a similar manner. These possibilities are being examined as well as the effect of low temperatures on other preferential Grignard reactions.

Experimental

In a typical experiment, 0.2 mole of a titrated Grignard reagent was added slowly during one hour to a stirred solution of 40 g. of acetic anhydride in 100 cc. of dry ether in a 500-cc. 3-necked flask cooled by a mixture of Dry Ice and acetone in a Dewar flask. The added reagent was cooled by dripping through a tube externally cooled with Dry Ice. After stirring for two to three hours the cooling bath was removed and the mixture was treated with ammonium chloride solution. After washing out the acetic anhydride and acid with alkali the ether was fractionated and the ketones distilled. For the most part the ketones were identified by boiling point and index of refraction, although a few derivatives were made. The following Grignard reagents gave the corresponding methyl ketones in the following yields: *n*-butylmagnesium chloride, 79%; *n*-butylmagnesium bromide, 79%; *s*-butylmagnesium bromide, 78%; *t*-butylmagnesium chloride; 77%; phenylmagnesium bromide, 70%; benzylmagnesium chloride, 52%; and allylmagnesium bromide, 42%. With phenylmagnesium bromide and propionic anhydride a 59% yield of propiophenone was obtained.

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(1) Fournier, *Bull. soc. chim.*, (3) **31**, 483 (1904); (3) **35**, 19 (1906); (4) **7**, 836 (1910), treated a series of primary halide Grignard reagents with a series of anhydrides at about −20° and reported general yields in the range 25–50%. We have found that on adding butylmagnesium bromide to acetic anhydride at −33° the yield of somewhat impure ketone is less than 40%.

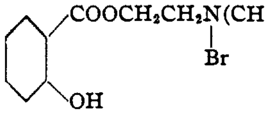
DEPARTMENT OF CHEMISTRY
OHIO STATE UNIVERSITY
COLUMBUS 10, OHIO
RECEIVED SEPTEMBER 20, 1944

Some New Esters of Choline

BY M. WEIZMANN AND E. BOGRACHOV

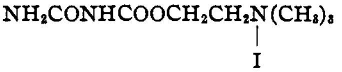
For a pharmacological and physiological study[1] esters of choline were required which were expected to be less easily saponified under biological conditions than acetyl-choline. To this end the derivatives of salicylic acid and of allophanic acid have been synthesized.

As the quaternary ammonium chlorides corresponding to acetyl-choline proved too hygroscopic, the bromides and iodides have been prepared. Salicyloyl chloride reacts with the hydroxyl group of trimethyl-(β-hydroxyethyl)-ammonium bromide and iodide in the normal way, and from the ester-bromide so obtained



the sulfate is prepared by interaction with silver sulfate.

For the preparation of the allophanic acid ester β-iodo-ethyl allophanate was prepared from ethylene iodohydrin and cyanic acid according to Béhal.[2] The halogenated ester was then treated with trimethylamine



$$NH_2CONHCOOCH_2CH_2\underset{\underset{\displaystyle I}{|}}{N}(CH_3)_3$$

Experimental

(1) Trimethyl-(β-hydroxy-ethyl)-ammonium Bromide (I).—Trimethylamine (75 g.) is added to a concentrated aqueous solution of ethylene bromohydrin (125 g.) at ice temperature. The mixture is kept overnight at below 5°, evaporated to dryness *in vacuo* and the residue recrystallized from alcohol; yield, 172 g. *Anal.* Calcd. for $C_5H_{14}ONBr$: C, 32.6; H, 7.6; N, 7.6. Found: C, 32.6; H, 7.6; N, 7.5.

The iodide (II) was prepared and recrystallized in the same way; yield, 94%. *Anal.* Calcd. for $C_5H_{14}ONI$: N, 6.1; I, 55.0. Found: N, 6.1; I, 54.9.

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(1) A. Schweitzer, M. Weizmann and S. Wright, *Cardiologia*, Vol. II, fasc. 4/5, 1938.

(2) Béhal, *Bull. soc. chim.*, [4] **25**, 477 (1919).