came evident that they were not correct. We do not know if the table of Giauque and Overstreet[4] was used as a basis for the recalculation but in any case it appears that the values are approximately those which would result if the presence of hydrogen chloride resulting from chlorine mass 37 had been overlooked. The corrections which should be applied to the table of Giauque and Overstreet are given in Table I. The correction can be applied to any of the isotopic species or their mixture. The effect of deuterium is not appreciable.

Chlorine.—Correction of the tables of Giauque and Overstreet for chlorine to the new natural constants gave results which differed from the retabulation in the Bureau of Standards Tables[5] by appreciable amounts which increased with temperature. No reason for this is evident since no revision of the molecular data has appeared. The corrections found are given in Table I.

TABLE I

CORRECTIONS TO BE ADDED TO TABLES OF $(F^0 - H_0^0)/T$ REFERRED TO ABOVE

Note: Values in tables are for $-(F^\circ - H_0^0)/T$; thus the additive correction reduces the numerical values

Correction cal. deg.$^{-1}$ mole^{-1}	H_2	Cl_2	HCl
0.018	298–450°K.	250–400°K.	250–700°K.
.019	500–1300	450–750	750–1600
.020	1400–2200	800–1400	1700–2700
.021	2300–2700	1500–2400	2800–3000
.022	2800–3700	2500–2900	
.023	3800–4300	3000	
.024	4400–5000		

Hydrogen.—The $(F^0 - H_0^0)/T$ function was tabulated to 5000°K. by Giauque.[6] Davis and Johnston[7] called attention to errors at 3000 and 4000°K. in the calculations of Giauque and showed that values used for interpolation above 2000°K. were affected. They published a corrected table above 2000°K. The above calculations on hydrogen were made in terms of natural constants given in the "I.C.T."[8] Davis and Johnston had sent details from their calculation sheets to Giauque and comparison with his calculation sheets disclosed the two basic arithmetical errors involved in Giauque's table. Thus the two pieces of work are now in agreement with respect to the details which determine the free energy function.

Wagman, Kilpatrick, Taylor, Pitzer and Rossini[9] have corrected the data of Giauque and of Davis and Johnston to constants available in 1945. They do not differ much from the present constants but as there is a small effect we have included corrections in Table I which should be applied to the table of Giauque up to 2000°K. and to the table of Davis and Johnston in the range 2000–5000°K. In addition the amount $R \ln 4 = 2.754$ cal. deg.$^{-1}$ mole^{-1} should be added to the absolute values of $(F^0 - H_0^0)/T$ given by Giauque and by Davis and Johnston to eliminate the contribution of nuclear spin as is customary. The value 2.754 is in terms of "I.C.T." constants to correspond to the original table. Wagman, *et al.*,[9] have also corrected the values of $(H^0 - H_0^0)/T$ given by Davis and Johnston. The correction to the new natural constants is trivial amounting to a maximum of -0.0002 at 5000°K. Thus corrected values of the entropy of hydrogen can be obtained by combining the values of $(F^0 - H_0^0)/T$ resulting from Table I with the $(H^0 - H_0^0)/T$ values of Wagman, *et al.* The corrected values of C_p for hydrogen given by Wagman, *et al.*, are also not changed by the newer constants.

The values of the entropies at a fugacity of one atmosphere and 298.16°K. for H_2, Cl_2 and HCl are 31.208, 53.290 and 44.645 cal. deg.$^{-1}$ mole^{-1}, respectively.

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[6] W. F. Giauque, THIS JOURNAL, **52**, 4816 (1930).

[7] C. O. Davis and H. L. Johnston, *ibid.*, **56**, 1045 (1934).

[8] "International Critical Tables," McGraw-Hill Book Co., Inc., New York, N. Y., 1926.

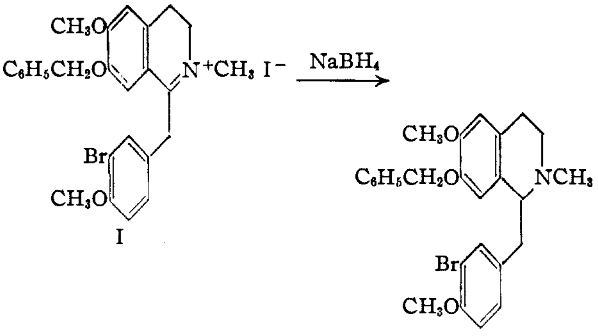
[9] D. D. Wagman, J. E. Kilpatrick W. J. Taylor, K. S. Pitzer, and F. D. Rossini, *J. Res. Nat. Bur. Sta.*, **34**, 143 (1945).

Sodium Borohydride Reduction of N-Alkyl-3,4-dihydroisoquinolinium Iodides[1]

BY WILSON M. WHALEY AND CHARLES N. ROBINSON

RECEIVED DECEMBER 22, 1952

The reduction of isoquinolinium salts with lithium aluminum hydride to the corresponding N-alkyl-1,2-dihydro- compounds[2] and of pyridinium salts with potassium borohydride to the N-alkyl-1,2-dihydro- and 1,2,3,4-tetrahydro- compounds[3,4] has been reported in the literature. Since the reduction of N-alkyl-3,4-dihydroisoquinolinium iodides containing other functional groups which are also reduced by lithium aluminum hydride is often of considerable importance in the synthesis of isoquinoline alkaloids, it seemed desirable to find a more specific reagent. Sodium borohydride is such a reagent. The present paper shows that N-alkyl-3,4-dihydroisoquinolinium iodides can also be reduced in very good yields to the corresponding N-alkyl-1,2,3,4-tetrahydroisoquinolines. Chaikin and Brown[5] have reported that, although this reagent reduces aldehydes, ketones and acid chlorides



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II

[1] The authors wish to express their appreciation to the Tennessee Eastman Corporation for a Grant-in aid to the University of Tennessee which made this work possible.

[2] H. Schmid and P. Karrer, *Helv. Chim. Acta*, **32**, 960 (1949).

[3] J. J. Panouse, *Compt. rend.*, **233**, 260 (1951); *C. A.*, **46**, 2542 (1952).

[4] J. J. Panouse, *Compt. rend.*, **233**, 1200 (1951); *C. A.*, **46**, 6643 (1952).

[5] S. W. Chaikin and W. G. Brown, THIS JOURNAL, **71**, 122 (1949).

in good yields, its effect on acids, esters,[6] anhydrides and nitriles is negligible; they have also reduced the carbonyl function in the presence of side-chain halogens and aromatic nitro groups.

Experimental[7]

Reduction of 2-Methyl-6,7-dimethoxy-3,4-dihydroisoquinolinium Iodide to 2-Methyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline.—To a solution of 10 g. (0.03 mole) of the methiodide in 200 ml. of absolute methanol was added 4 g. (0.105 mole) of solid sodium borohydride in small portions. The reaction was exothermic, hydrogen was evolved, and a clear, colorless solution was obtained at the end of the addition. It was evaporated to 25 ml., poured into 300 ml. of 2% sodium hydroxide, extracted with ether, and the combined ethereal extracts dried over anhydrous magnesium sulfate. The solution was then filtered and the ether removed by distillation to leave 5.5 g. (89% of the theoretical amount) of a light-yellow oil which quickly hardened to a white solid. This crude product melted at 55–57° and, on dissolving in a hot solution of picric acid in absolute ethanol and allowing to cool, formed a picrate (needles) of m.p. 157–158°.[8] Further recrystallization did not raise this melting point.

Reduction of 1-(3-Bromo-4-methoxybenzyl)-2-methyl-6-methoxy-7-benzyloxy-3,4-dihydroisoquinolinium Iodide (I) to 1-(3-Bromo-4-methoxybenzyl)-2-methyl-6-methoxy-7-benzyloxy-1,2,3,4-tetrahydroisoquinoline (II).—To a slurry of 0.5 g. (0.0133 mole) of sodium borohydride in 85 ml. of absolute methanol was added, as quickly as foaming would allow, 0.5 g. (0.00082 mole) of the methiodide. The clear, colorless solution was then concentrated to 15 ml. and poured into 300 ml. of 1% sodium hydroxide. It was extracted three times with ether, the ether was dried over anhydrous magnesium sulfate and filtered, and hydrogen chloride gas was passed into the filtrate. A light-yellow oil separated. The ether was removed on the steam-cone and 30 ml. of benzene was added to the residual oil. On evaporation white crystals separated slowly. The last of the benzene was removed in a stream of dry air to give 0.35 g. (82% of the theoretical amount) of the hydrochloride. An analytical sample prepared by recrystallization from 2-propanol consisted of white needles which melted first at 104–105°, resolidified at 127–130°, and remelted at 202–204°. The sample was dried *in vacuo* at 64°.

Anal. Calcd. for $C_{26}H_{29}O_3NBrCl$: C, 60.17; H, 5.63; N, 2.70. Found: C, 60.01; H, 5.74; N, 2.83.

The first procedure outlined above, which involves the solution of the methiodide in the solvent and subsequent addition of borohydride, is preferable, since it allows the use of a much smaller molar ratio of the reducing agent. In the second procedure a large excess of sodium borohydride must be used in order to get all of the methiodide in before the heat of reaction causes complete destruction of the hydride by the solvent.

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[6] M. L. Wolfrom and K. Anno, THIS JOURNAL, **74**, 5583 (1952), have reported that the esters and sodium salts of acids of sugars are reduced to alcohols.

[7] All melting points were obtained on a calibrated apparatus. Analysis by Galbraith Laboratories, Knoxville, Tenn.

[8] F. L. Pyman, *J. Chem. Soc.*, **95**, 1274 (1909), reports a melting point of 159–160° (cor.).

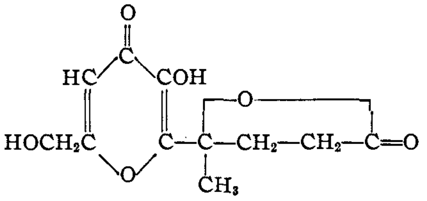
The Reaction of Kojic Acid with Ethyl Levulinate

BY L. L. WOODS[1]

RECEIVED DECEMBER 6, 1952

During the course of investigating the reactivity of kojic acid, many attempts have been made by the author to condense the pyrone with ketones, all unsuccessful except the one described in this report.

The compound produced as a result of the condensation of kojic acid with ethyl levulinate in mildly alkaline media is shown to be 3-(2-hydroxymethyl-5-hydroxy-4-pyrone-6)-3-valerolactone (I).



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The derivatives of this compound were nearly all as expected; however, the reaction with 2,4-dinitrophenylhydrazine was unusual. Repeated experiments reveal that the compound reacts with two molecules of the hydrazine to form an addition compound of the pyridazinone.

Experimental[2]

Four grams of sodium bicarbonate, 28.4 g. of kojic acid, 28.8 g. of ethyl levulinate and 100 ml. of absolute ethanol were mixed together and refluxed vigorously for about 20 hours. The mixture was then acidified with hydrochloric acid, treated with a small amount of charcoal, and filtered while hot. The solution slowly deposited soft brown crystals as the alcohol was removed by surface evaporation, yield 39 g. Two recrystallizations from hot benzene, in which the compound is only fairly soluble, gave light tan crystals, m.p. 153.5°.

Anal. Calcd. for $C_{11}H_{12}O_6$: C, 55.00; H, 4.58. Found: C, 54.78; H, 4.16.

The acetylated derivative was made in the usual manner using acetic anhydride; the excess anhydride was decomposed with water and the ester extracted with benzene. The ester was recrystallized twice from benzene and once from a 1–4 mixture of benzene and ligroin. The compound produced rosettes of white prisms, m.p. 98–100°.

Anal. Calcd. for $C_{17}H_{20}O_{10}$: C, 53.12; H, 5.20. Found: C, 53.35; H, 5.18.

Treating compound (I) with an excess of thionyl chloride followed by recrystallization from hot water and then from absolute ethanol gave the expected 2-chloromethyl derivative of (I) which easily sublimed to give white needles, m.p. 167–169°. The compound gave a red color with dilute ferric chloride solutions.

Anal. Calcd. for $C_{11}H_{11}ClO_5$: C, 51.06; H, 4.25. Found: C, 51.30; H, 4.09.

The *p*-bromophenacyl derivative was prepared from (I) and *p*-bromophenacyl bromide in essentially the manner as before,[3] but in this instance 1.5 g. of the phenacyl halide was used for each gram of (I).

However, the bisphenacyl derivative was formed. The compound was of a very light texture resembling white wool after having been recrystallized three times from ethanol, m.p. 180°. It had no acidic character and gave negative results with dilute solutions of ferric chloride.

Anal. Calcd. for $C_{27}H_{24}Br_2O_9$: C, 49.69; H, 3.68. Found: C, 49.87, 49.83; H, 3.32, 3.26.

When equal weights of (I) and 2,4-dinitrophenylhydrazine were refluxed for 15 minutes in ethanol, an orange compound was obtained upon cooling and filtering. The substance was purified by washing with water followed by two recrystallizations from ethanol, an orange-yellow powder was obtained, m.p. 100–102°.

Anal. Calcd. for $C_{17}H_{16}N_4O_9 \cdot C_6H_6N_4O_4$: N, 18.12. Found: N, 18.05.

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[1] The author wishes to acknowledge, with thanks, the financial support of the Research Corporation in this project. The kojic acid used in these experiments was furnished by the Corn Products Company.

[2] Analyses were performed by Dr. Carl Tiedcke, Teaneck, N. J., and Clark Microchemical Laboratory, Urbana, Ill. All melting points were determined on a Fisher–Johns melting point assembly.

[3] L. L. Woods, THIS JOURNAL, **74**, 3959 (1952).