Standardization of the Method of Analysis.—As a means of standardizing and testing the analytical method described above, runs were made using weighed amounts of phenylacetic acid and sodium acetate in various proportions as shown in Table I. Columns 2 and 3 list the moles of phenylacetic acid and sodium acetate subjected to the oxidation and isolation process, while column 4 gives the percentage of phenylacetic acid in the mixture. Column 5 shows the total volatile acids isolated and column 6 gives the percentage difference between the moles of volatile acids isolated and those calculated for each mixture examined. Column 7 contains the number of moles of benzoic acid isolated and column 8 gives the percentage difference between the moles of benzoic acid isolated and the number of moles calculated from the phenylacetic acid used. In runs 1–5 it became evident that approximately 3% of the benzoic acid was lost during the analysis. This was at first thought to be due to incomplete oxidation of the phenylacetic acid. However, when benzoic acid was substituted for the phenylacetic acid (run 6) the same loss was recorded. In runs 8, 9 and 10 solutions of benzoic acid were subjected to the standard extraction process with the same loss occurring as in the entire analytical procedure. Since the loss was proportional to the amount of phenylacetic acid present even though the percentage of this acid in the mixture was varied from 40–100% it was concluded that a 3% correction could be applied to the amount of benzoic acid isolated from the oxidation of the hydrocarbon mixture provided the moles of hydrocarbon taken corresponded to moles of phenylacetic and acetic acids used in the test runs. Run 7 was a blank made to show that no volatile acid is produced by oxidation of the pyridine under the conditions used in the analytical method. Run 11 using allylbenzene shows that no acetic acid is produced by the oxidation of this hydrocarbon. Propenylbenzene was not used in the standardization process since there is no agreement in the literature with respect to the physical properties of this compound. Hence no guaranteed criterion of purity was available.

Summary

An allylic rearrangement producing a mixture of 27% cinnamyl and 73% phenylvinylmagnesium chlorides has been shown to occur when cinnamyl chloride is converted into the Grignard reagent. The composition of the Grignard reagent has been estimated by measuring the composition of the hydrocarbon mixture obtained on hydrolysis of the Grignard reagent. The hydrocarbon mixture has been analyzed by quantitative oxidation with potassium permanganate in pyridine at 40° to a mixture of benzoic acid and acetic acid.

LOS ANGELES, CALIF. RECEIVED JULY 25, 1938

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WAYNE UNIVERSITY]

Sodium Saccharin as a Reagent for the Identification of Alkyl Halides

BY LYNNE L. MERRITT, JR., STANLEY LEVEY AND HAROLD B. CUTTER

Many reagents have been suggested for the identification of alkyl halides None are entirely satisfactory, either because of the experimental difficulties involved or because their application is not general. The most satisfactory are the N-alkyl-*p*-bromobenzenesulfon-*p*-anisides,[1] and the S-alkyl thiourea picrates.[2]

Sodium saccharin, as has long been known, reacts with alkyl halides to give N-alkyl saccharins.[3–5]

When the reaction is carried out in butyl carbitol–water solution, well crystallized derivatives are formed. The reaction does not take place with tertiary compounds nor with branched chain chlorides.

Experimental Part

Preparation of N-Alkyl Saccharins.—A mixture of 6 g. of sodium saccharin, 1 cc. of the alkyl halide, 25 cc. of butyl carbitol and 4 cc. of water is refluxed for thirty minutes. If the halide is a chloride, or methyl bromide, 3.5 g. of potassium iodide is added to the mixture. After refluxing, the mixture is poured into 300 cc. of water and the resulting suspension cooled in an ice-bath. The N-alkyl saccharin usually crystallizes. If an oil is obtained, it is separated and warmed in a small beaker until no odor of alkyl halide can be detected. It is then dissolved in a little hot alcohol, and water added until a slight cloudiness results. On cooling the material crystallizes. The derivatives are recrystallized from aqueous alcohol.

The yield of N-alkyl saccharin varies from 0.5 to 0.8 g., except in the case of *i*-butyl, where only about 0.25 g. is obtained and crystallization is difficult.

n-Propyl- and *i*-butylsaccharin have melting points differing by only 1°, but a mixture of the two shows a depression of from 8 to 10°. The same is true of allyl saccharin and bromoethyl saccharin.

Ethylene dibromide requires refluxing for one hour. The yield is about 0.5 g. of bromoethyl saccharin, very little of the disaccharide compound being formed. Longer refluxing—three hours—yields about 20% of a compound melting at 253–254°, presumably the disaccharinoethane.

No derivatives could be obtained with methyl, ethyl, isopropyl, secondary butyl chlo-

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[1] H. B. Gillespie, THIS JOURNAL, **56**, 2740 (1934).

[2] Brown and Campbell, *J. Chem. Soc.*, 1699 (1937).

[3] Eckenroth, Hugo and Koerppen, *Ber.*, **29**, 1048 (1896).

[4] C. Fahlberg and R. List, *ibid.*, **20**, 1596 (1887).

[5] Eckenroth, Hugo and Klein, *ibid.*, **29**, 329 (1896).

N-ALKYL SACCHARINS

Alkyl group	Melting point of derivs. Iodide	Bromide	Chloride	Formula	Analyses % N Found	% N Calcd.	% C and H Found	% C and H Calcd.
CH_3	132	132		$C_8H_7O_3SN$	7.23	7.11		
CH_3CH_2	94	94		$C_9H_9O_3SN$			C, 50.93	51.18
							H, 4.64	4.26
n-C_3H_7	74	74	74	$C_0H_{11}O_3SN$			C, 52.89	53.33
							H, 5.45	4.89
i-C_3H_7[a]	134	134		$C_{10}H_{11}O_3SN$			C, 53.21	53.33
							H, 5.17	4.89
n-C_4H_9[a]	38–39.5	38	38	$C_{11}H_{13}O_3SN$	5.81	5.85		
i-C_4H_9[a]	75	75		$C_{11}H_{13}O_3SN$	5.84	5.85		
s-C_4H_9[a]	81	81		$C_{11}H_{13}O_3SN$			C, 54.80	55.23
							H, 5.72	5.44
n-C_5H_{11}[a]	58	58	58	$C_{12}H_{15}O_3SN$	S 12.50	12.60		
$CH_2{=}CHCH_2$[a]		98	98	$C_{10}H_{10}O_3SN$	6.34	6.28		
$BrCH_2CH_2$		99		$C_9H_8O_3SNBr$			C, 37.78	37.25
							H, 3.08	2.76
$C_6H_5CH_2$			110.111	$C_{14}H_{11}O_3SN$			C, 61.57	61.54
							H, 4.11	4.06
p-$O_2NC_6H_4CH_2$		175.5		$C_{14}H_{10}O_5SN_2$			C, 52.90	52.83
							H, 3.52	3.17

[a] Compounds not previously described. The melting points were taken with a calibrated thermometer.

rides, nor with ethylene dichloride.

Summary

Sodium saccharin reacts with alkyl halides to give N-alkyl saccharins which are useful for the purposes of identification.

DETROIT, MICHIGAN RECEIVED JUNE 20, 1938

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE INSTITUTE OF TECHNOLOGY OF THE UNIVERSITY OF MINNESOTA]

Acid–Base Indicators in Methanol. II. The Dissociation of Triphenylcarbinols in Methanol

BY I. M. KOLTHOFF AND L. S. GUSS[1]

A number of methoxytriphenylcarbinols were prepared by Lund.[2] He investigated their properties, while Kolthoff[3] studied and advocated the use of the penta-, hexa- and heptamethoxy derivatives as acid–base indicators. The acid forms of these indicators are red, the alkaline forms colorless. In aqueous medium the indicator equilibrium is represented by the following equation

$$\underset{\text{colorless}}{ROH} + H^+ \rightleftarrows \underset{\text{red}}{R^+} + H_2O \qquad (1)$$

In methanol as a solvent, there is the establishment of an equilibrium between the two basic forms of the indicator

$$ROH + CH_3OH \rightleftarrows ROCH_3 + H_2O \qquad (2)$$

with the equilibrium constant

$$k = \frac{a_{ROH}}{a_{ROCH_3}\, a_{H_2O}} \qquad (3)$$

In this equation, a stands for activity. The activity of methanol in the presence of small amounts of water, as well as in anhydrous solutions, can be considered constant. From the above, it follows that the indicator equilibrium of the methoxytriphenylcarbinols in methanol is determined by equations (1) and (4)

$$ROCH_3 + H^+ \rightleftarrows R^+ + CH_3OH \qquad (4)$$

When the indicator constant is determined in the usual way,[4] we measure

$$K_I = \frac{a_{H^+}\,(a_{ROH} + a_{ROCH_3})}{a_{R^+}} \qquad (5)$$

which will greatly depend on the water content of the methanol. According to equation (1)

$$K_{ROH} = \frac{a_{H^+}\, a_{ROH}}{a_{R^+}\, a_{H_2O}} \qquad (6)$$

and, according to (4)

$$K_{ROCH_3} = \frac{a_{H^+}\, a_{ROCH_3}}{a_{R^+}} \qquad (7)$$

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(1) From a thesis submitted by L. S. Guss to the Graduate School of the University of Minnesota in partial fulfilment of the requirements for the degree of Doctor of Philosophy, May, 1938.

(2) H. Lund, THIS JOURNAL, **49**, 1346 (1927).

(3) I. M. Kolthoff, *ibid.*, **49**, 1218 (1927).

(4) I. M. Kolthoff and L. S. Guss, *ibid.*, **60**, 2516 (1938).