

with a 10-cc. calibrated pipet and decomposed with 20 cc. of sodium acetate-potassium iodide buffer (250 g. of acetate and 20 g. of iodide in 1 liter of water) and the iodine titrated with thiosulfate with starch as indicator. A blank determination in which the hydrocarbon was omitted was conducted simultaneously with every oxidation experiment and a correction applied for any lead tetraacetate consumed by the solvent.

Summary of Results.—The results are reported in terms of the moles of lead tetraacetate consumed per mole of hydrocarbon. The results of the experiments with anthracene in different solvents are recorded only in the graphs of Fig. 1. The results for the other hydrocarbons are given in Table III. In the case of the hydrocarbons listed in Table II as showing "no reaction," the observation extended over periods of fifty to sixty hours.

Summary

The oxidation of anthracene by lead tetraacetate in acetic acid solution is accelerated enormously by water, methanol or potassium acetate, but is retarded by benzene. A study has been made of the rate of oxidation of several polynuclear aromatic hydrocarbons by excess lead tetraacetate in 99% acetic acid. Some correlation between rate of oxidation and carcinogenic activity is discernible in specific, limited series of compounds, but no general correlation exists.

CONVERSE MEMORIAL LABORATORY

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE OHIO STATE UNIVERSITY]

A New Method of Esterification¹

BY MELVIN S. NEWMAN AND WILLIAM S. FONES

Carre and Libermann reported the formation of butyl benzoate by pyrolysis of an intermediate formed from the reaction of butyl chlorosulfite with benzoic acid in the presence of pyridine.² We became interested in exploring the potentialities of this little known reaction. A few experiments showed that this scheme was not very promising because the yields were mediocre. However, we found that sodium benzoate reacts readily with butyl chlorosulfite to produce an intermediate which produced butyl benzoate in good yield on pyrolysis. This method likewise gave good yields when applied to butyric, tributylacetic, 2,4,6-trimethylbenzoic and 2,4,6-triethylbenzoic acids, but failed with 2,4,6-tribromobenzoic acid. It is thus a valuable new method for the esterification of aliphatic, aromatic and certain sterically hindered acids. It should prove useful in the esterification of acids containing an acid-unstable function.

This method failed to give appreciable amounts of the desired butyl ester when applied to α -hydroxy-*i*-butyric and *p*-acetylamino benzoic acids. Quantities of *n*-butyl sulfite were isolated from these reaction mixtures but no attempts to secure maximum yields of this by-product were made.

One attempt to use a secondary alkyl chlorosulfite, namely, *i*-propyl chlorosulfite, resulted in the formation of a much smaller yield of desired ester. Accordingly no further work was done in this direction.

Experimental³

Alkyl Chlorosulfites.—To 280 g. (2.34 moles) of purified thionyl chloride, cooled to 0°, was added dropwise with stirring 148 g. (2.0 moles) of anhydrous *n*-butyl alcohol, the temperature being maintained below 15°. The solution was then allowed to stand at room temperature for

three days (we did not investigate the effect of time and temperature on yield). The excess thionyl chloride was removed under reduced pressure and the residue on distillation yielded 295 g. (94%) of butyl chlorosulfite, b. p. 72–74° at 28 mm.² In a similar way, *i*-propyl chlorosulfite, b. p. 63–65° at 80 mm., was obtained in 28% yield. No attempt to find better conditions was made.

General Procedure.—To 0.1 mole of the dried sodium salt of the acid with or without benzene as a solvent was added 30 g. (0.19 mole) of butyl chlorosulfite. A vigorous exothermic reaction always occurred, even in those cases where the desired ester was not obtained. After a few minutes the reaction mixture was slowly heated until pyrolytic decomposition set in as indicated by the evolution of sulfur dioxide. The pyrolysis usually took place in the range of 100–150° and was maintained as long as any appreciable gas evolution took place. This usually required one to two hours. The mixture was then treated with water and the organic product isolated by suitable means. There was usually from 10 to 20% of unreacted acid which was recovered. By this procedure pure butyl benzoate and butyl butyrate were prepared in 81 and 61% yields.

Butyl 2,4,6-Trimethylbenzoate.—This compound, reported previously⁴ but not analyzed, was prepared in 71% yield by the above method. The reaction was carried out on a 0.01 molar scale and the ester boiled at 147.5–149° at 12 mm.

*Anal.*³ Calcd. for C₁₄H₂₀O₂: C, 76.3; H, 9.1. Found: C, 76.1, 76.3; H, 9.2, 9.5.

Butyl 2,4,6-Triethylbenzoate.—From 2.57 g. of 2,4,6-triethylbenzoic acid⁶ there was obtained 2.41 g. (74%) of butyl 2,4,6-triethylbenzoate, b. p. 136–140° at 3 mm.

*Anal.*³ Calcd. for C₁₇H₂₄O₂: C, 77.8; H, 10.0. Found: C, 77.6, 77.4; H, 10.2, 9.8.

Butyl Tributylacetate.—A sample of 11.2 g. of tributylacetic acid, prepared by alkylation of acetonitrile⁶ followed by hydrolysis, was converted into the sodium salt and gave in 82% yield the butyl ester, b. p. 148–153° at 9 mm., by the above method.

*Anal.*³ Calcd. for C₁₈H₃₀O₂: C, 76.0; H, 12.7. Found: C, 76.5, 76.3; H, 12.6, 12.7.

Isolation and Identification of Butyl Sulfite.—The dry salt obtained by the saponification of 13.2 g. of ethyl α -hydroxy-*i*-butyrate was treated as above with 45 g. of

(1) The material herein reported is from the thesis presented by W. S. Fones to the Graduate School in partial fulfillment of the requirements for the Ph.D. degree, December, 1946.

(2) Carre and Libermann, *Bull. soc. chim.*, [4] **53**, 1062 (1933).

(3) All microanalyses by the Arlington Laboratories, Fairfax, Va.

(4) Fuson and Bottorf, *This Journal*, **64**, 1451 (1942).

(5) We wish to thank Prof. R. C. Fuson, University of Illinois, for the sample of 2,4,6-triethylbenzoic acid.

(6) Ziegler and Ohlinger, *Ann.*, **495**, 84 (1932).

butyl chlorosulfite. After treating the reaction mixture with water, extraction with ether, and vacuum distillation, there was obtained 17.2 g. of dibutyl sulfite, b. p. 107-109° at 12 mm., n_D^{20} 1.4308.⁷ On saponification the butyl alcohol was identified as the normal isomer by conversion to the crystalline 3,5-dinitrobenzoate, m. p. and mixed m. p. 62.5-63.5°.

Summary

A new method for the conversion of an acid into

(7) Vogel and Cowan, *J. Chem. Soc.*, 22 (1943), give b. p. 90-95 at 5 mm., and n_D^{20} 1.43098.

its *n*-butyl ester is described. The method involves formation of the sodium salt, reaction of the sodium salt with butyl chlorosulfite, and pyrolysis of the intermediate thus obtained to yield the desired ester. This method appears to be general for primary alkyl chlorosulfites and applicable to aliphatic, aromatic and certain sterically hindered acids.

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The Nomenclature of Certain Sugar Derivatives

BY JOHN C. SOWDEN

The present nomenclature used for certain classes of compounds in the sugar group is based on their sources of preparation rather than on their actual structures. When such nomenclature is applied to substances possessing fewer asymmetric centers than the parent compounds for which they are named, it may be found that more than one name can be correctly applied to a single chemical substance. At present, this is true of the sugar osazones, osones, osotriazoles, the non-terminal desoxy sugars, the glycals and glycoseens. It is proposed that a single, systematic name can be devised readily to describe accurately any single substance in these classes of sugar derivatives.

The phenylosazone that arises in common from D-glucose, D-fructose and D-mannose is usually called D-glucose phenylosazone, but D-fructose phenylosazone and D-mannose phenylosazone must be accepted as alternate names under the present system of nomenclature. A faulty implication contained in any of these three names is that the phenylosazone has the configuration of the particular sugar from which it arose, whereas only the *D-arabo* fragment of the configuration of the three parent hexoses is retained. It is proposed that this osazone is fully and accurately described by the single name *D-arabo*-hexose phenylosazone.¹

The osone resulting from the hydrolysis of this

(1) A similar name, "*D*-mannoheptosazone," was used by E. Fischer and Passmore, *Ber.*, 23, 2226 (1890), for the phenylosazone common to the two *D*-mannoheptoses. Only one of these two heptoses was known at the time and it had been named simply "*D*-mannoheptose," a name now regarded as incomplete for the single, epimeric sugar. Thus, it is probably coincidental that the name *D*-mannoheptosazone, which conforms with the presently proposed nomenclature, was employed.

phenylosazone would then be named *D-arabo*-hexosone.

The proposed nomenclature can also be applied to the osotriazoles. These substances are closely related to and easily prepared from the osazones.² Thus, the phenylosotriazole derived from L-sorbose² would also arise from L-gulose and L-idose and would be named *L-xylo*-hexose phenylosotriazole.

The first synthetic 2-desoxyhexose was prepared from D-glucose and was named 2-desoxy-D-glucose.³ This substance could also be prepared from D-mannose by the same series of reactions used in preparing it from D-glucose and, thus, 2-desoxy-D-mannose is an alternate name. Recently⁴ this same desoxyhexose has been prepared starting from D-arabinose and without using either D-glucose or D-mannose as intermediates. The name proposed for this sugar derivative is *D-arabo*-2-desoxyhexose. As other examples, the natural desoxy sugar thymine would be named *D-erythro*-2-desoxypentose, while the naturally occurring digitoxose would be *D-ribo*-2,6-didesoxyhexose.

In extending the proposed nomenclature to the unsaturated sugar derivatives, "*D*-glucal" ("*D*-mannal") would be named *D-arabo*-hexal. Similarly, "*5,6*-D-glucoseen" ("*5,6*-L-idoseen") would become *D-xylo*-5,6-hexoseen.

A similar type of nomenclature to that proposed here has recently been advanced by Wolfrom, Thompson and Evans⁵ to replace the present trivial or non-systematic names for the ketose sugars.

DEPARTMENT OF CHEMISTRY
BANTING INSTITUTE
UNIVERSITY OF TORONTO
TORONTO, CANADA

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(2) Hann and Hudson, *This Journal*, 66, 735 (1944).

(3) Fischer, Bergmann and Schotte, *Ber.*, 55, 509 (1920).

(4) Sowden and Fischer, *This Journal*, 69, 1048 (1947).

(5) Wolfrom, Thompson and Evans, *ibid.*, 67, 1793 (1945).