iodite would consist of *d*-galacturonic acid combined with *l*-rhamnonic acid. Such a compound would give a high percentage of carbon dioxide when heated with 12% hydrochloric acid, a low percentage of furfural and a positive naphthoresorcinol test. These are the results obtained. On the other hand, if in the aldobionic acid the aldehyde group of the *d*-galacturonic acid is free while the aldehyde group of the *l*-rhamnose is combined, then the dibasic acid formed by oxidation would consist of mucic acid combined with *l*-rhamnose. Such a compound would give no carbon dioxide, a high percentage of furfural and a negative naphthoresorcinol test. These results were not obtained. These facts prove conclusively that in the aldobionic acid the linkage is from the aldehyde group of the *d*-galacturonic acid to one of the secondary alcohol group of the *l*-rhamnose.

Summary

Flaxseed mucilage yields on hydrolysis an aldobionic acid consisting of one molecule of *d*-galacturonic acid and one molecule of *l*-rhamnose. The molecule is joined together by a glucosidic linkage involving the aldehyde group of the *d*-galacturonic acid and an alcohol group of the *l*-rhamnose. This mucilage is similar in composition and structure to some of the plant gums.

Further work on the structure of the mucilage is in progress.

TUCSON, ARIZONA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MARYLAND]

PARA-PHENYLPHENACYL BROMIDE, A REAGENT FOR IDENTIFYING ORGANIC ACIDS[1]

BY NATHAN L. DRAKE AND JACK BRONITSKY

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Phenacyl bromide and the *p*-halogen substituted phenacyl bromides have been used with great success by Reid and his co-workers[2] for preparing esters which are excellently adapted for characterizing the organic acids therein combined. Such an ester may be prepared easily by the action of the bromide on the sodium salt of an acid in aqueous alcoholic solution; as a rule the ester crystallizes well and may be purified easily by a few crystallizations from aqueous alcohol. The reaction involved may be represented

$$p\text{-XC}_6\text{H}_4\text{COCH}_2\text{Br} + \text{NaOCOR} = p\text{-XC}_6\text{H}_4\text{COCH}_2\text{OCOR} + \text{NaBr}$$

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[1] From a thesis submitted to the Graduate School of the University of Maryland by Jack Bronitsky in partial fulfilment of the requirements for the degree of Master of Science.

[2] Reid and co-workers, THIS JOURNAL, **41**, 75 (1919); **42**, 1043 (1920); **52**, 818 (1930).

The melting points of the esters from a given acid increase as X varies from hydrogen to chlorine to bromine to iodine. The iodophenacyl ester has the highest melting point, but in certain cases the melting point of even this derivative is so low as to make purification by crystallization difficult, particularly when small quantities of material are involved. Furthermore, with several acids Reid was unable to obtain a satisfactory solid derivative with any of the above-mentioned reagents.

The authors appreciated the facility with which the phenacyl esters may be prepared, but they desired a reagent which would yield, with certain acids containing highly branched chains, esters of melting points sufficiently high that purification by crystallization would be easy. A few tenths of a gram of acid would then suffice for its identification.

p-Phenylphenacyl bromide was consequently prepared, in the hope that the phenylphenacyl esters which could be derived from it would satisfy these requirements. Inasmuch as diphenyl is today a readily obtainable substance[3] and all the reactions involved in the preparation of the bromide give good yields, phenylphenacyl bromide is inexpensive and easy to prepare. Furthermore, examination of the properties of the esters obtained from a number of representative organic acids listed in the table clearly shows that in every case they compare favorably in melting point with the corresponding *p*-halogenated phenacyl esters. Of the ten acids which admit of comparison, the melting points of the *p*-phenylphenacyl esters are higher than those of the *p*-iodophenacyl esters in five instances, and do not differ by more than three degrees in two others. With only three acids out of eighteen, *viz.*, succinic, citric and caproic, were esters obtained which melted lower than the corresponding *p*-bromophenacyl esters, and the maximum difference was 6.6°—the *p*-phenylphenacyl ester of caproic acid melted at 65°, and the *p*-bromophenacyl ester melted at 71.6°. In addition, the solubility behavior of the phenylphenacyl esters is such that purification by crystallization is easily accomplished.

A more significant advantage of the new reagent lies in the fact that no carboxylic acid which we have so far investigated has failed to give a solid derivative. Referring again to the table, it is seen that of the twenty-four acids selected from those with which Reid worked, but eighteen yielded crystalline derivatives. *p*-Phenylphenacyl bromide, however, yielded a solid derivative in every case. It was not found possible to prepare the *p*-phenylphenacyl ester of benzene sulfonic acid in the usual way.

The procedure adopted for the preparation of *p*-phenylphenacyl esters was as follows. A weighed amount of acid (0.005 mole) was added to 5 cc.

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[3] Technical diphenyl is quoted in *Ind. Eng. Chem.*, for May, 1930, at 40 cents per lb. This substance is obtainable from the Federal Phosphorus Company of Birmingham, Alabama. The authors wish to express their thanks to this organization, which kindly supplied some of the diphenyl used in this research.

of water in a small Erlenmeyer flask, and then 0.0025 mole of sodium carbonate. The mixture was tested for acidity, and just enough more acid was added to make the solution acid to litmus; 10 cc. of alcohol was then put in, and if the salt of the acid was not thrown out of solution, 0.005 mole of the bromide was added and the mixture refluxed for an hour or more, depending on the acid involved.[4] If the acid salt was thrown out by the alcohol, a bit more water was added until the salt dissolved. The amounts of material recommended above yielded a quantity of ester which was sufficient, after purification, for elementary analyses. If only sufficient ester was desired for melting point comparisons, half of the amounts mentioned above yielded equally good results.

Some of the esters prepared were sparingly soluble in the reaction mixture and crystallized from the boiling solution. In the majority of cases, however, crystal formation did not take place until the reaction mixture was cooled, and in a few instances it was necessary to concentrate the solution to obtain a sufficiently large crop of crystals.

In most cases the ester formed rapidly, and many times a period of heating as short as twenty minutes was sufficient to bring about practically complete conversion of the acid salt into ester.

Certain dibasic acids whose sodium or potassium salts were sparingly soluble in aqueous alcohol of the requisite strength caused difficulty, and ester formation could not be brought about in the usual way. However, substitution of the methyl ammonium salts for the alkali salts made it possible to operate in such a fashion that at the outset all the reactants were in solution. When an ester was prepared in this way, it was found particularly important to have present a very slight excess of acid so that the reaction of the medium was not basic to litmus. If this precaution was not taken, colored by-products were formed which were very difficult to remove from the ester by subsequent recrystallizations. The ester prepared in the proper way was colorless.

In almost every case two recrystallizations of the crude ester proved ample to yield a substance whose melting point did not change on further crystallizations.

Experimental

Adam,[5] who first prepared phenylacetophenone, described his product as the 3-phenyl derivative. Vorländer,[6] however, showed that the compound which Adam prepared was probably 4-phenylacetophenone, and

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[4] Reid recommends refluxing monobasic acids for one hour, dibasic acids for two hours and tribasic acids for three hours; in many cases it is certain that when using *p*-phenylphenacyl bromide refluxing for a shorter period would be equally satisfactory.

[5] Adam, *Ann. Chim.*, [6] **15**, 255 (1888).

[6] Vorländer, *Ber.*. **40**, 4535 (1907).

later work has confirmed Vorländer's contention. Dilthey,[7] by oxidation of the benzal derivative of Adam's phenylacetophenone, obtained a diphenyl carbonic acid whose melting point and properties proved it to be identical with an acid prepared by Schlenk,[8] whose carbonyl was in the 4-position.

p-Phenylphenacyl bromide is not mentioned in the literature, although the corresponding chloride was described by Collet,[9] who prepared it by the Friedel and Crafts synthesis

$$C_6H_5C_6H_5 + ClCH_2COCl \xrightarrow{AlCl_3} C_6H_5C_6H_4COCH_2Cl + HCl$$

He describes the substance as a crystalline yellowish powder, soluble in alcohol, and possessing a melting point of 122–123°. Collet proved the location of the substituting group by oxidizing the chloro ketone to the corresponding acid. Collet's chloride was undoubtedly impure and should have been colorless.

p-Phenylphenacyl bromide was prepared by a method illustrated by the reactions

$$C_6H_5C_6H_5 + (CH_3CO)_2O \xrightarrow{AlCl_3} C_6H_5C_6H_4COCH_3 + CH_3COOH$$

$$C_6H_5C_6H_4COCH_3 + Br_2 \xrightarrow{CH_3COOH} C_6H_5C_6H_4COCH_2Br + HBr$$

It crystallizes in long colorless needles and melts sharply at 125.5°.

Preparation of *p*-Phenylacetophenone.—The procedure used in preparing this substance was a modification of that for the synthesis of acetophenone;[10] 0.8 mole (120 g.) of diphenyl, 1.76 mole (236 g.) of anhydrous aluminum chloride and 700 cc. of anhydrous carbon disulfide were placed in a two-liter three-necked flask provided with a mechanical stirrer, a dropping funnel and a reflux condenser holding a tube to carry off the evolved hydrogen chloride. The mixture was heated on the steam-bath until gentle refluxing started, and then 0.8 mole (85 g.) of acetic anhydride (b. p. 136–137°) was added. The addition of the anhydride required about an hour and the reaction mixture was refluxed gently for one hour after all of the anhydride had been added. When about three-quarters of the anhydride had been added, the addition product began to separate from the solution in the form of a curdy mass. Decomposition of the addition product was effected in the usual way by pouring the reaction mixture over ice and hydrochloric acid. The precipitate of *p*-phenylacetophenone was filtered on a Büchner funnel, washed several times with water, dried and distilled *in vacuo*. The carbon disulfide contains considerable of the ketone which can be recovered by evaporating the solvent. With very little forerunnings, the product boiled from 195 to 210° at 18 mm. pressure. The yield of distillate was 131 g. with a melting point of 118°. Crystallization from alcohol yielded a product melting at 120–121° in an amount corresponding to 80% of that theoretically possible.

Preparation of *p*-Phenylphenacyl Bromide.—The procedure used was a modification of that described by Reid[11] for the preparation of the halogenated phenacyl bromides;

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[7] Dilthey, *J. prakt. Chem.*, [2] **101,** 194 (1920).

[8] Schlenk, *Ann.*, **368,** 304 (1909).

[9] Collet, *Bull. soc. chim.*, **17,** 510 (1897).

[10] "Organic Syntheses," John Wiley and Sons, Inc., New York, **1925,** Vol. V. p. 19.

[11] Reid, THIS JOURNAL, **41,** 77 (1919).

0.183 mole (36 g.) of *p*-phenylacetophenone was suspended in 200 cc. of glacial acetic acid, warmed gently on the steam-bath until a clear solution resulted, and then cooled as far as possible without the formation of crystals. To this solution was added slowly 0.183 mole (29.4 g.) of bromine. During the addition of the bromine, the temperature was not allowed to rise above 45°. When about three-quarters of the bromine had been added, the brominated product separated from the solution. After two hours, the flask was cooled in an ice- and salt-bath, the product filtered and washed with a bit of cold glacial acetic acid and two 50-cc. portions of cold water. The yield of crude material was 42 g., its melting point 124.5–125.5°. Recrystallization from hot 95% alcohol, with the addition of some activated charcoal to remove color, yielded a product melting at 125.5°. Approximately 6.7 g. of *p*-phenylphenacyl bromide dissolved in 100 cc. of boiling alcohol, and about 1.3 g. in 100 cc. of cold (25°) alcohol.

TABLE I

THE MELTING POINTS OF A FEW *p*-PHENYLPHENACYL ESTERS COMPARED WITH THOSE OF SOME RELATED ESTERS

Acid	Phenacyl ester	*p*-Chloro-phenacyl ester	*p*-Bromo-phenacyl ester	*p*-Iodo-phenacyl ester	*p*-Phenyl-phenacyl ester
Formic	oil	...	neg.	neg.	74
Acetic	40	67.2	85	114	111
Propionic	...	...	59	94.9	102
Butyric	oil	...	63.2	81.4	97
n-Valeric	oil	...	63.6	78.6	63.5
Isovaleric	...	...	68.0	78.8	76
Caproic	...	...	71.6	81.5	65
Dimethylethylacetic	...	...	...	...	86.5
Heptylic	...	...	...	...	62
Caprylic	...	...	65.5	77.0	67
Lauric	48.9	70	76.0	...	84
Stearic	69	86	90	90.5	91
Oleic	oil	...	neg.	neg.	60.5
Monochloro-acetic	...	...	neg.	neg.	116
Maleic	119	...	neg.	...	168
Oxalic	oil	...	neg.	neg.	165.5 dec.
Succinic	148	197.5	211	...	208
Lactic	96	...	112.8	139.8	145
Mucic	...	...	neg.	...	149.5 dec.
Citric	104	...	148	...	146
Benzoic	118.5	118.6	119	126.5	167
o-Toluic	...	...	56.9	...	94.5
m-Toluic	...	...	108	...	136.5
p-Toluic	...	...	153	...	165
Cinnamic	140.5	...	145.6	...	182.5
Hippuric	...	...	151	...	163

In the table neg. means that the reaction did not occur, or yielded products of no significance. The leaders signify that data are not available. Compiled from data given by Reid, THIS JOURNAL, **41,** 83 (1919); **42,** 1055 (1920); **52,** 818 (1930).

Summary

1. *p*-Phenylphenacyl bromide has been prepared.
2. This substance has shown itself to be well adapted for preparing

solid esters of organic acids. The properties of these esters render them useful in the identification of organic acids.

3. A number of representative esters have been prepared, and their melting points compared with those of the corresponding *p*-nitrobenzyl esters, phenacyl esters, and *p*-halogen phenacyl esters, where such comparison was possible.

College Park, Maryland

[A Contribution from the Laboratories of the University of Maryland and the U. S. Industrial Alcohol Company]

SOME REPRESENTATIVE CARBONATES AND CARBO-ETHOXY DERIVATIVES RELATED TO ETHYLENE GLYCOL[1]

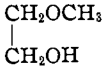
By Nathan L. Drake and Ray M. Carter

Received July 8, 1930 Published September 5, 1930

Certain derivatives of ethylene glycol, in particular its ethers and esters, have become important in industry by reason of their solvent power for the cellulose esters. It seems strange, therefore, that there appears in the published literature no information regarding either the preparation or the properties of the carbonates and the carbo-ethoxy derivatives of the mono ethers of ethylene glycol. Allpress[2] describes some carbonates and carbo-ethoxy derivatives of ethylene glycol, but the corresponding mono ethers have apparently not been made.

It was decided, therefore, to study certain of these substances, in the hope that they might prove of value in the lacquer industry as plasticizers. The raw materials were

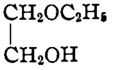
I



$$\begin{array}{l} CH_2OCH_3 \\ | \\ CH_2OH \end{array}$$

Methylcellosolve

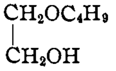
II



$$\begin{array}{l} CH_2OC_2H_5 \\ | \\ CH_2OH \end{array}$$

Cellosolve

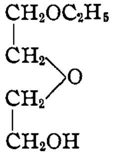
III



$$\begin{array}{l} CH_2OC_4H_9 \\ | \\ CH_2OH \end{array}$$

Butylcellosolve

IV



$$\begin{array}{l} CH_2OC_2H_5 \\ | \\ CH_2 \searrow \\ \qquad > O \\ CH_2 \nearrow \\ | \\ CH_2OH \end{array}$$

Carbitol

The carbonates were prepared by the reaction of phosgene and the glycol ether in a manner analogous to the preparation of alkyl carbonates. Phosgene was bubbled from a cylinder of the compressed gas into a weighed amount of the glycol ether in a tall narrow cylinder. The cylinder was immersed in a bucket of water in order that its temperature might be kept close to that of the laboratory, thus preventing the evolution of hydrogen chloride. At intervals the cylinder was removed and its increase in weight

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[1] From a thesis submitted to the Graduate School of the University of Maryland by Ray M. Carter in partial fulfilment of the requirements for the degree of Master of Science.

[2] Allpress, *J. Chem. Soc.*, **125**, 2259 (1924).