equiv., 218.6. Found: Cl, 16.41, 16.61; neut. equiv., 212, 219.

That the two acids were identical was shown by a mixed melting of the oximes (synthetic aldoxime, m. p. 202°; oxidation aldoxime, m. p., 199.5–200.5°).

(3) **2-Hydroxy-5-chloroisophthalic Acid.**—To a solution of 1.2 g. of synthetic 2-hydroxy-3-aldo-5-chlorobenzoic acid in 40 cc. of glacial acetic acid, 64 cc. of distilled water and 4 g. of potassium permanganate were added. The mixture was stirred about a minute, until a noticeable reaction began, and then it was allowed to stand for two hours. After clarification with sulfur dioxide, evaporation to about half its volume, and then cooling, the crude 2-hydroxy-5-chloroisophthalic acid, which had separated, was removed. Upon purifying and heating as before, the anhydrous synthetic dicarboxylic acid melted at 245–246°. The analysis, as given below, indicated that the compound was isomeric with the anhydrous oxidation dicarboxylic acid whose hydrate melted at 238–240°.[7]

Anal. Calcd. for $C_8H_5ClO_5$: Cl, 16.37; neut. equiv., 108.3. Found: Cl, 16.48, 16.17; neut. equiv., 113, 113.

That the two dicarboxylic acids were identical was shown by a mixed melting point of the two diethyl esters (synthetic ester, m. p. 50°; oxidation ester, m. p. 50–51°).

(7) For both 2-hydroxy-3-aldo-5-chlorobenzoic and 2-hydroxy-5-chloroisophthalic acids the melting points of the hydrates do not differ appreciably from those of the anhydrous forms.

Summary

1. 6-Chloro-8-chloromethyl-1,3-benzodioxane has been obtained by the action of formaldehyde on *p*-chlorophenol in the presence of hydrochloric acid.

2. Oxidizing the above dioxane with potassium permanganate in acetic acid gave five products: 6-chloro-8-chloromethyl-1,3-benzodioxane-4-one, 6-chloro-8-aldo-1,3-benzodioxane, 6-chloro-8-aldo-1,3-benzodioxane-4-one, 2-hydroxy-3-aldo-5-chlorobenzoic acid and 2-hydroxy-5-chloroisophthalic acid.

3. The structure of 6-chloro-8-chloromethyl-1,3-benzodioxane was established through the identity of 2-hydroxy-3-aldo-5-chlorobenzoic and 2-hydroxy-5-chloroisophthalic acids with two isomeric acids synthesized from salicylic acid.

KNOXVILLE, TENN. RECEIVED FEBRUARY 1, 1940

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, HOWARD UNIVERSITY]

The Acetylation of alpha-Bromo Ketones and their Derivatives

BY R. P. BARNES AND VICTOR J. TULANE

In an attempt to obviate certain difficulties experienced with glacial acetic acid solutions of freshly fused potassium acetate as an acetylating agent for alpha haloketones, we turned to acetic anhydride solutions of the acetate instead. The results were so surprising that we decided to test further the power of this acetylating combination. Thus the following compounds were investigated: phenyl bromobenzyl diketone (I), bromodibenzoylmethane (II), desyl bromide (III), acetylbenzoin (IV) and benzoin (V).

$C_6H_5CHBrCOCOC_6H_5$ (I)

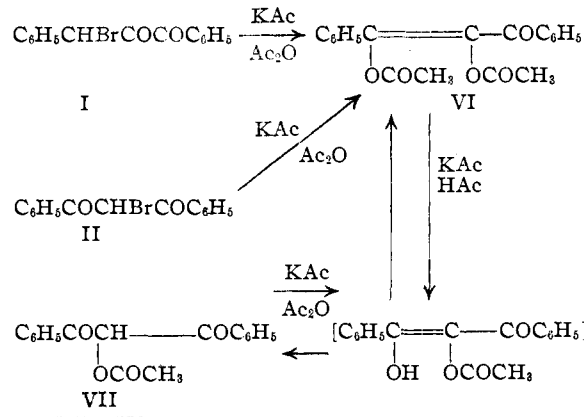
$C_6H_5COCHBrCOC_6H_5$ (II)

$C_6H_5CHBrCOC_6H_5$ (III)

$C_6H_5CH(OCOCH_3)COC_6H_5$ (IV)

$C_6H_5CHOHCOC_6H_5$ (V)

We have found that both bromo ketones (I) and (II) upon refluxing with a solution of freshly fused potassium acetate in acetic anhydride lead to the diacetate of phenylbenzoyl acetyleneglycol (VI). This diacetate, upon treatment with a solution of freshly fused potassium acetate in glacial acetic acid with subsequent distribution of the acetic acid by pouring into a large volume of water, is changed quantitatively into dibenzoylcarbinol acetate (VII). While other methods of acetylation fail,[1] dibenzoylcarbinol acetate is acetylated quantitatively by means of acetic anhydride–fused potassium acetate, giving the diacetate (VI).



(1) A. H. Blatt and W. Lincoln Hawkins, THIS JOURNAL, 58, 81 (1936).

Neither phenyl bromobenzyl diketone (I) nor bromodibenzoylmethane (II) is enolic as indicated by alcoholic ferric chloride, and both are unaffected by acetic anhydride and by acetyl chloride. It is our experience that unless an alpha-bromo diketone is enolic, it is not acetylated by either of these reagents. It seems reasonable therefore that in these acetylations, bromine is first split out by metathesis with subsequent enolization and acetylation to the diacetate, since we have found[2] that compounds of the type $R-C(OCOCH_3)=C(Br)-COR$, which result from the acetylation of enolic bromo diketones, do not acetylate further under any known conditions.

We believe that these reactions give a feasible explanation of the behavior of the bromo diketones (I) and (II) on treatment with a solution of freshly fused potassium acetate in glacial acetic acid.[3]

The diacetate (VI) when dissolved in cold concd. sulfuric acid and poured onto finely crushed ice, gives the separation of a pale yellow solid. This solid oils out so rapidly that its melting point cannot be determined. However, its alcoholic solution gives with ferric chloride solution a deep greenish-blue color which fades rapidly, decolorizes iodine solution, and bleaches indophenol. These properties are characteristic of ene–diols. Thus the mesityl group in phenylmesitoylacetyleneglycol[4] and other ene–diols[4] does exert a stabilizing influence upon the ene–diol. On exposure to atmospheric oxygen the ene–diol (VIII) is changed to diphenyl triketone (IX).

$$C_6H_5C(OCOCH_3)=C(OCOCH_3)-COC_6H_5 \xrightarrow{H_2SO_4}$$

VI

$$C_6H_5C(OH)=C(OH)-COC_6H_5 \xrightarrow{O_2} C_6H_5COCOCOC_6H_5 + H_2O_2$$

VIII IX

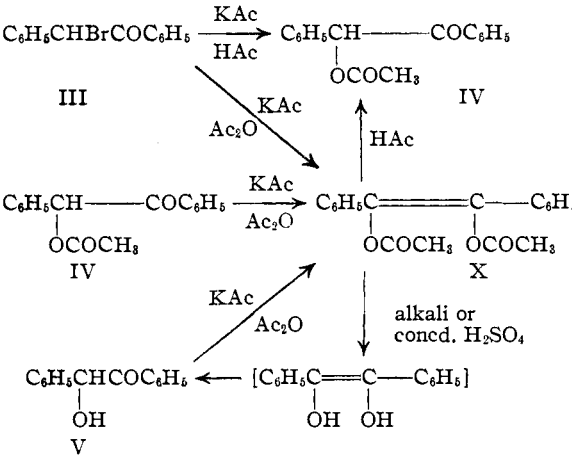
In a similar manner, desyl bromide (III), acetyl benzoin (IV), and benzoin (V), are acetylated by acetic anhydride–fused potassium acetate to the alpha-diacetate of diphenyl acetyleneglycol[5] (X), whereas potassium acetate and acetic acid convert desyl bromide into acetyl benzoin.

(2) Unpublished graduate thesis.

(3) A. H. Blatt, *J. Wash. Acad. Sci.*, **28**, 1 (1938).

(4) R. P. Barnes and Leila S. Green, THIS JOURNAL, **60**, 1549 (1938); R. B. Thompson, *ibid.*, **61**, 1283 (1939); Reynold C. Fuson and Joseph Corse, *ibid.*, **61**, 975 (1939).

(5) Johannes Thiele, *Ann.*, **306**, 142 (1899).



The driving power in these reactions seems to be the concentration of potassium acetate. The diacetate (X) is hydrolyzed to acetylbenzoin by boiling acetic acid, and either aqueous alkali or concd. sulfuric acid converts the diacetate (X) to benzoin. Thus again the stabilizing effect of the mesityl group is manifested, since Thompson[4] and Fuson[4] have found that the two geometrically isomeric ene–diols resulting from the reduction of dimesitoyl are quite stable.

Experimental

Phenylbenzoylacetyleneglycol Diacetate (VI).—A solution of 10 g. of either phenyl bromobenzyl diketone or bromodibenzoylmethane in 50 cc. of acetic anhydride is refluxed gently for thirty minutes with 5 g. of freshly fused potassium acetate, after which it is poured into 500 cc. of cold water and stirred vigorously until the acetic anhydride is decomposed. The resulting yellow oil solidifies. It is filtered immediately, washed with water and dried, yielding a practically quantitative amount of crude material. It is recrystallized from hot methyl alcohol, and melts at 133°.

Anal. Calcd. for $C_{19}H_{16}O_5$: C, 70.3; H, 4.9. Found: C, 70.0; H, 4.8.

A solution of 10 g. of dibenzoylcarbinol acetate in 50 cc. of acetic anhydride with 5 g. of freshly fused potassium acetate is treated as described above, yielding a practically quantitative yield of phenylbenzoylacetyleneglycol diacetate, melting and mix-melting at 133°.

The Action of Glacial Acetic Acid on Phenylbenzoylacetyleneglycol Diacetate.—A solution of 5 g. of the diacetate in 25 cc. of glacial acetic acid is refluxed gently for thirty minutes with 2.5 g. of freshly fused potassium acetate and worked up as above. The product is recrystallized from methyl alcohol, melting and mix-melting with pure dibenzoylcarbinol acetate at 94°.

Phenyl bromobenzyl diketone and bromodibenzoylmethane are both recovered unchanged after refluxing for four hours with either acetyl chloride or acetic anhydride Neither gives any color with alcoholic ferric chloride.

Hydrolysis of Phenylbenzoylacetyleneglycol Diacetate.—Solution of 2.0 g. of the diacetate in 10 cc. of cold concd.

sulfuric acid produces a deep orange color. This solution is poured with stirring onto crushed ice. A light yellow solid separates out which soon becomes sticky. It cannot be crystallized from alcohol. Its alcoholic solution gives a deep greenish-blue color with ferric chloride, which color fades rapidly; it bleaches iodine and indophenol solutions instantly. On exposure to atmospheric oxygen, it changes to a yellow solid which is identified as diphenyltriketone, melting and mix-melting with an authentic sample at 70°.

Diphenylacetyleneglycol Diacetate (X).—Separate solutions of 10.0 g. each of desyl bromide, acetylbenzoin and benzoin in 50 cc. of acetic anhydride are refluxed gently with equal weights of freshly fused potassium acetate for thirty minutes. Each solution turns yellow to light brown. After cooling, they are poured into large volumes of cold water and stirred vigorously until the acetic anhydride is decomposed. A cream-colored granular solid separates out. The solid is filtered, washed with water, and dried over solid potassium hydroxide. It is then crystallized from methyl alcohol, yielding 3.0 g. of a crystalline solid, melting at 153° and 6.0 g. of material melting at 70°. The material melting at 70° mix-melts with acetylbenzoin at 70°, and is hydrolyzed quantitatively by alkali to benzoin. Repeated recrystallizations do not change the melting point of 70°. When refluxed with acetic anhydride and potassium acetate, it yields the 153° substance. It is a mixture of acetylbenzoin and diphenylacetyleneglycol diacetate. The diacetate, melting at 153°, is hydrolyzed quantitatively by both alkali and cold concd. sulfuric acid to benzoin, identified by its melting point and mixed-melting point. Hot glacial acetic acid converts the diacetate to acetylbenzoin.

Acetylbenzoin (IV).—A solution of 10.0 g. of desyl bromide in 50 cc. of glacial acetic acid is refluxed with 10.0 g. of freshly fused potassium acetate for thirty minutes, cooled and poured into a large volume of water. An oily solid separates, which is crystallized from methyl alcohol, melting and mix-melting with acetylbenzoin at 84°.

Summary

Herein is reported the use of an acetylating combination which seems to be more powerful than acetic anhydride in the presence of concd. sulfuric acid, converting certain compounds which have the group —CH(Br)— or —CH(OCOCH$_3$)— or —CH(OH)— adjacent to a >C=O group, into diacetates of acetyleneglycol.

The properties of the ene-diol, phenylbenzoylacetyleneglycol, resulting from the hydrolysis of its diacetate are given.

Further possibilities of this acetylating combination are now under investigation.

WASHINGTON, D. C. RECEIVED JANUARY 22, 1940

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Sterols. XCV. Acid Isomerization of Pseudosapogenins to Sapogenins

BY RUSSELL E. MARKER AND EWALD ROHRMANN

The reaction of the sapogenins with acetic anhydride to yield the isomeric pseudosapogenins is now a well-established reaction which has been applied to sarsasapogenin,[1] *epi*-sarsasapogenin,[2] sarsasapogenone,[2] isosarsasapogenin,[2] tigogenin[3] and chlorogenin.[2] Although there may be some question concerning the structure of the pseudosapogenins all of the available evidence indicates the presence of an ethylenic linkage at C-16, C-17 and a reactive grouping at C-22 possibly as in I.[4]

In studying the reduction of pseudosarsasapogenone[2] by the Clemmensen method, it was observed that the essential reaction product was desoxysarsasapogenin and not desoxypseudosarsasapogenin. That this isomerization of the pseudosapogenin side chain to the sapogenin side chain is due to the presence of hydrochloric acid is clearly shown in succeeding experiments.

Pseudosarsasapogenin upon standing with aqueous ethanolic hydrochloric acid at 25° for one day is almost quantitatively converted into sarsasapogenin. Pseudotigogenin and pseudochlorogenin readily were converted into the corresponding sapogenins by short refluxing with aqueous ethanolic hydrochloric acid. It seems probable that this reaction involves the addition of hydrogen chloride to ethylenic linkages followed by elimination of hydrogen chloride and subsequent ring closure to yield the spiro ketal system. It is significant that dihydropseudosarsasapogenin[4] is unaffected by similar treatment.

In previous work we have shown that the side chains of tigogenin, chlorogenin and diosgenin and probably of gitogenin and digitogen differ in

(1) Marker and Rohrmann, THIS JOURNAL, **62**, 518 (1940).
(2) Marker, Rohrmann and Jones, *ibid.*, **62**, 648 (1940).
(3) Marker and Rohrmann, *ibid.*, **62**, 898 (1940).
(4) Marker and Rohrmann, *ibid.*, **62**, 521 (1940).