ethylamine was used in the condensations of the 2'-cyanine type. In the preparation of V, a 100% excess of quinoline ethiodide and of potassium hydroxide was used, the yield being considerably higher (with respect to 2-methylthiazoline ethiodide) than when equimolecular proportions of the reactants were taken. The amount of solvent required for each reaction is shown as well as that required for the recrystallization of the product. The yield of crude washed dye is given, and also the yield after recrystallization.

In most cases the melting of a cyanine dye is accompanied by decomposition. However, it was noticed that II melted without decomposition. With III there was slight decomposition and IV melted with decomposition and gas evolution. Melting of the other dyes (Table I) was accompanied by more or less profound decomposition.

The appearance of the dyes was as follows: II, large pale yellow prisms; III, yellow-orange prisms; IV, scarlet needles; V, lustrous brown prisms; VI, orange powder; 3,3'-dimethylthiazolinocarbocyanine iodide, brownish amber prisms with blue reflex; VII, orange-brown needles with blue reflex; 7-ethyl-3,3'-dimethylthiazolinocarbocyanine iodide, brown needles with blue reflex; VIII, orange powder.

The dyes were compared photographically by incorporation in a chloride emulsion. A list of wave lengths follows giving the approximate position of maximum sensitivity conferred by each dye, the order being that used above and the maxima being read directly from the individual wedge spectrograms: 4250, 4600, 4750, 4800, 5300, 4750, 4750, 4830 and 4830 Å.

Summary

1. A base containing a partially saturated nucleus, 2-methylthiazoline, has been used for the preparation of cyanine dyes.

2. The new dyes are of special interest because their absorption bands lie at shorter wave lengths than those of corresponding derivatives of any other heterocyclic base thus far applied to cyanine dye formation.

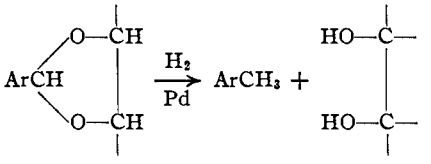
ROCHESTER, NEW YORK RECEIVED FEBRUARY 10, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE WASHINGTON SQUARE COLLEGE, NEW YORK UNIVERSITY]

Synthesis of 1,2-Monoacetone-5,6-benzophenone-α-*d*-glucofuranose. Catalytic Hydrogenation of Acetals of Aromatic Ketone Sugars

BY PHILIPPOS E. PAPADAKIS

It is known that acetals of aromatic aldehydes $ArCH(OR)_2$ on catalytic hydrogenation in the presence of palladium or platinum yield $ArCH_3$ and the respective alcohols.[1] The application of catalytic hydrogenation to acetals of aromatic aldehydes and sugars or other polyhydroxy compounds has attracted considerable interest in the last few years.[2] The hydrogenation reaction takes place as follows

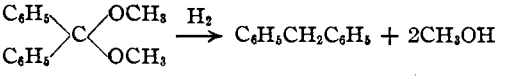


The splitting of the benzylidene residue by this method has been used advantageously, instead of acid hydrolysis, wherever the latter is objectionable. Thus sugars which have part of their hydroxyl groups blocked as above become convenient starting materials in synthetic work.

(1) T. Kariyone and Y. Kimura, *J. Pharm. Soc. Japan*, 51–52 (1923).

(2) K. Freudenberg, H. Toepffer and C. C. Andersen, *Ber.*, **61**, 1759 (1928); N. M. Carter, *ibid.*, **63**, 1684 (1930); M. Bergmann and N. M. Carter, *Z. physiol. Chem.*, **191**, 211 (1930); L. Zervas and P. Sessler, *Ber.*, **66**, 1326 (1933); L. Zervas, *ibid.*, **64**, 2289 (1931).

In the present work, it is shown that acetals of aromatic ketones are affected similarly; the dimethyl acetal of benzophenone for example, gives on catalytic hydrogenation[3] diphenylmethane and methyl alcohol as follows



The acetals of aliphatic ketones do not show such reactions.

Since the benzophenone residue can be split off easily in this way, it was thought that benzophenone derivatives of sugars could be prepared and tested as above. Benzophenone derivatives, as far as the present author is aware, are not known. The methods used for the preparation of acetone sugars are neither convenient nor easy to use for the preparation of benzophenone sugars. The preparation of the latter is accomplished by allowing benzophenone chloride to react with sugar in dry pyridine at 0°. Thus benzophenone acetone glucose was prepared from 1,2-monoacetone glucose and benzophenone chloride. It was expected that the benzophenone residue would

(3) It is expected that the splitting of the benzophenone residue may be accomplished with sodium amalgam.

enter in position, 5,6. Since the benzophenone acetone glucose prepared as above does not react with trityl chloride, it is concluded that position 6 is occupied.[4] Catalytic hydrogenation of 1,2-acetone-5,6-benzophenone glucose resulted in splitting of the benzophenone residue as diphenylmethane, and the regeneration of monoacetone glucose. Other experiments will show benzophenone derivatives of other sugars and their application in synthetic work. Particularly, investigation will be made to find whether benzophenone chloride will react with sugars which have only secondary hydroxyl groups free.

Experimental

Dimethyl Acetal of Benzophenone from Benzophenone Chloride and Methyl Alcohol in Pyridine.—Benzophenone chloride[5] (1 mol) was added with shaking to a solution of absolute methanol (3 mols) and anhydrous pyridine (3 mols), all reagents previously cooled to 0°. The reaction mixture was kept at 0° for five hours, precautions being taken to exclude moisture. Crystals of dimethyl acetal of benzophenone[6] were formed, filtered off and recrystallized twice from methanol, m. p. 107–108°. An additional quantity of the substance was obtained from the pyridine methanol filtrate by concentrating under vacuum, adding water and extracting with ether. The ether layer was evaporated and the crystals were recrystallized as above.

Catalytic Hydrogenation of Dimethyl Acetal of Benzophenone.—Dimethyl acetal of benzophenone 13.4 g. was mixed with 50 cc. of methyl alcohol and 5 cc. of glacial acetic acid and hydrogenated in the presence of 0.5 g. of palladium catalyst (prepared according to Wieland–Jausz–v. Putnoky[7]). The amount of hydrogen taken up in four hours, calculated at N. T. P., was 689 cc.; theoretical, 668 cc. The solution was concentrated under vacuum, ether was added and the ether solution was shaken with a solution of sodium bicarbonate. From the ether layer 2 g. of diphenylmethane was obtained, b. p. 140°, at 27 mm.

Anal. Calcd. C, 92.81; H, 7.19. Found: C, 92.84; H, 7.32.

Benzophenone Acetone Glucose.—Benzophenone chloride (24 g.) was added with shaking to a solution of monoacetone glucose (20 g.) in anhydrous pyridine, all reagents previously cooled to 0°. The reaction mixture was kept at 0° for five hours in a glass-stoppered bottle. By distilling part of the pyridine under vacuum, adding water to the remaining solution and extracting first with petroleum ether and second with diethyl ether, the benzophenone acetone glucose was separated from unreacted monoacetone glucose and a red material which has not yet been examined. From the diethyl ether extracts, 4 g. of the crude product was obtained. The benzophenone acetone glucose was washed with cold methanol and recrystallized successively by dissolving the crystals in boiling methanol and then cooling the solution to 0°. The compound melts at 147–148°; $[\alpha]^{22}D$ +21.70 (0.4727 g. in 10 cc. of pyridine in a 1-dm. tube rotates 1.02° to the right).

Anal. Calcd.: C, 68.70; H, 6.29. Found: C, 69.01; H, 6.34.

Position of Benzophenone Residue in the Benzophenone Acetone Glucose.—Triphenylchloromethane (0.330 g.) was added to a solution containing 0.4727 g. of benzophenone acetone glucose in 10 cc. of anhydrous pyridine. The rotation of the solution before the addition of the trityl chloride was +1.02 (one-dm. tube and sodium light) and twenty-four hours after the addition was the same. Since the trityl chloride did not react it seems that the hydroxyl of carbon six in the benzophenone acetone glucose was blocked. Further evidence has been obtained by adding 20 cc. of water to the pyridine solution (containing the benzophenone acetone glucose and the trityl chloride) and allowing it to stand for five hours. Two kinds of crystals, triphenylcarbinol and acetone glucose, were formed and filtered out. By recrystallizing twice from methanol crystals of triphenylcarbinol, m. p. 162°, were obtained. The filtrate was evaporated and the mixture of crystals from it was reserved for further work. On further addition of water to the mother liquor containing the pyridine, more crystals separated. These and the crystals recovered from the methyl alcohol above were dissolved in ether. The ether was allowed to evaporate at room temperature. The two kinds of crystals formed were separated mechanically under a lens and then recrystallized separately from methyl alcohol. In this way the benzophenone acetone glucose, m. p. 145°, was separated from the triphenylcarbinol, m. p. 162°.

Catalytic Hydrogenation of 1,2-Acetone 5,6-Benzophenone *α-d* Glucose.—Benzophenone acetone glucose (0.9 g.) was dissolved in methyl alcohol and 1 cc. of glacial acetic acid and the solution hydrogenated as above. The hydrogen taken up calculated at N. T. P. was 114 cc., theoretical, 104 cc. The solution was evaporated and then ether was added; 0.4 g. of crystals of monoacetone glucose was obtained, m. p. 160°.

The author wishes to express his thanks to Mr. D. Rigakos of the Rockefeller Institute for Medical Research for the microanalyses for carbon and hydrogen.

Summary

1. A study was made of the effect of catalytic hydrogenation upon acetals of aliphatic alcohols and aromatic ketones.

2. Dimethyl acetal of benzophenone was prepared by a new method.

3. 1,2-Monoacetone 5,6-benzophenone *α-d* glucofuranose was prepared.

4. It was found that the benzophenone residue of monoacetone benzophenone glucose is removed by hydrogenation in the presence of Pd catalyst and monoacetone glucose is regenerated.

NEW YORK, N. Y. RECEIVED JANUARY 31, 1936

(4) B. Helferich, L. Moog and Adolf Junger, *Ber.*, **58**, 872 (1925).

(5) A. Kekulé and A. Franchimont, *ibid.*, **5**, 908 (1872).

(6) J. E. Mackenzie, *J. Chem., Soc.*, **69**, 987 (1896); F. Straus and O. Eckner, *Ber.*, **39**, 3005 (1906); G. Schroeter, *ibid.*, **42**, 2342 (1909).

(7) H. Wieland, *ibid.*, **45**, 484, 2606 (1912); J. Jausz and N. von Putnoky, *ibid.*, **52**, 1576 (1919).