Substance + xH_2	°K.	ΔH, cal./mole	Deviation, cal.	Over-all accuracy, cal.	$\Delta H_{355°}$ 82° C., cal./mole
Ethylbenzene + $3H_2$	381	−49,235	±17	±100	−48,920
o-Xylene + $3H_2$	373	−47,466	±26	±200	−47,250
Mesitylene + $3H_2$	381	−47,930	±57	±200	−47,620
Styrene + $4H_2$	381	−77,893	±61	±200	−77,480
Hydrindene + $3H_2$	373	−45,987	±71	±250	−45,800
Indene + $4H_2$	373	−70,199	±194	±500	−69,910
Cyclopentene + $1H_2$	355	−26,915	±5	±60	−26,915
α-Phellandrene + $2H_2$	381	−53,622	±3	±300	−53,410
α-Terpinene + $2H_2$	355	−50,705	±12	±300	−50,705
Limonene + $2H_2$	373	−54,259	±24	±300	−54,110
Isopropylethylene + $1H_2$	355	−30,336	±15	±60	−30,336
Neo-amylethylene + $1H_2$	355	−29,532	±5	±60	−29,532
t-Butylethylene + $1H_2$	355	−30,341	±22	±150	−30,341
2,4,4-Trimethylpentene-1 + $1H_2$	355	−27,236	±7	±60	−27,236
2,4,4-Trimethylpentene-2 + $1H_2$	355	−28,392	±8	?	−28,392
Pentadiene-1,3 + $2H_2$	355	−54,112	±101	±150	−54,112
2,3-Dimethylbutadiene-1,3 + $2H_2$	355	−53,872	±13	±150	−53,872

1. The previously discussed rules correlating the heat of hydrogenation with the structure of unsaturated hydrocarbons have been extended. It has been found that branched-chain substituents do not follow the rules as well as do the straight chains.
2. The evidence of the heats of hydrogenation of the five-membered carbon ring systems points to a strain which decreases as unsaturation increases. This is quite contrary to conclusions which may be drawn from tetrahedral angle carbon atom models. The implications of these results are discussed.

CAMBRIDGE, MASS. RECEIVED JANUARY 28, 1937

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

Dibenzylideneglucose and Dibenzylideneglucuronic Acid from 6-Benzoyldiethylmercaptoglucose. Synthesis of Another Dibenzylideneglucose from 4,6-Benzylideneglucose

BY PHILIPPOS E. PAPADAKIS

It is known that acetals of aromatic aldehydes and sugars are obtainable in pure crystalline form. Benzylidene derivatives of sugars which have part of their hydroxyl groups blocked are convenient starting materials in synthetic work.[1] The application of catalytic hydrogenation to such acetals of aromatic aldehydes and sugars for the splitting of the benzylidene residue, wherever the acid hydrolysis is objectionable, constitutes another advantage in favor of their use.

The present author had occasion in the past to prepare 6-benzoyldiethylmercaptoglucose in pyridine solution at 0°. This was used as a starting material for the preparation of a dibenzylidene derivative of glucose. The method adopted was similar to that used by L. Zervas[1] in the preparation of 4,6-benzylideneglucose. In the course of the experimental work it was found that the ethyl mercaptal groups were split off and a monobenzoyl dibenzylidene derivative of glucose resulted which does not reduce Fehling's solution. It is thought that the compound may be 1,2,3,5-dibenzylidene-6-benzoyl-α-*d*-glucofuranose. If that be the case then by hydrolyzing the benzoyl group one may obtain 1,2,3,5-dibenzylidene-α-*d*-glucofuranose. The latter by subsequent oxidation should yield 1,2,3,5-dibenzylideneglucuronic acid which could be changed into glucuronic acid. The benzoyl residue of the monobenzoyldibenzylideneglucose was split off by means of either alcoholic potassium hydroxide solution and heat or by means of the calculated amount of sodium methoxide in chloroform at 0°. The resulting

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[1] L. Zervas, *Ber.*, **64**, 2289 (1931); P. Brigl and R. Schinle, *ibid.*, **66**, 325–30 (1933); P. Brigl and H. Grüner, *ibid.*, **65**, 1428 (1932); P. Brigl and O. Widmaier, *ibid.*, **69**, 1219 (1936); P. A. Levene and G. M. Meyer, *J. Biol. Chem.*, **53**, 431 (1922); *ibid.*, **57**, 319 (1923).

dibenzylideneglucose does not reduce Fehling's solution. On oxidation it yielded dibenzylideneglucuronic acid, m. p. 175°. The oxidation under the conditions of the experiment described later was difficult because of the low solubility of the substance in the presence of water. Attempts to oxidize the substance with alkaline permanganate in acetone–water solution or in dioxane were given up temporarily because the permanganate was reduced by the solvents.

At this point it was thought that if part of the benzoylmercaptoglucose had its benzoyl group located on some other carbon than the sixth, then the benzylidene group would block carbon no. 6 and the resulting monobenzoyldibenzilideneglucose would not oxidize. Since Zervas obtained a 4,6 - monobenzylideneglucose by treating glucose in the benzaldehyde with zinc chloride, it seemed plausible that if the hydroxyls of carbons 4 and 6 of the monobenzoylmercaptoglucose were free, then when the latter is treated with benzaldehyde and anhydrous zinc chloride the benzaldehyde group may go into acetal formation with them. In that case a 3-benzoyl-1,2,4,6-dibenzylideneglucose would be a possibility and hence a 1,2,4,6-dibenzylideneglucose would result from the hydrolysis of the benzoyl group. Zervas' work on 4,6-benzylideneglucose[1] and on 1,2-acetone-5,6-benzylidene-*α*-*d*-glucofuranose[2] suggests that by treating 4,6-benzylideneglucose with benzaldehyde in the presence of phosphorus pentoxide, one may obtain a 1,2,4,6-dibenzylideneglucose. As is shown later, a dibenzylideneglucose derivative was obtained by this method, m. p. 163°. Mixed melting points with this substance were tried with dibenzylideneglucose from the mercaptoglucose method before the oxidation to dibenzylideneglucuronic acid, and with the residue which had not oxidized. In both cases the melting point was depressed to the same extent. Further work is contemplated for the elucidation of the structure of these compounds.

Experimental

6-Benzoyldiethylmercaptoglucose.—The method used for the preparation of 6-benzoyldiethylmercaptoglucose is essentially the same as that of Lieser and Schweitzer[3] with some modifications.

Benzoyl chloride (1 mole) was added slowly with stirring to a saturated solution of diethylmercaptoglucose (1 mole) and anhydrous pyridine. The latter was cooled previously to 0°. The reaction mixture was kept at 0° for three hours; then the pyridine was extracted with petroleum ether and the residue was poured into ice water. Crystals of monobenzoyldiethylmercaptoglucose, m. p. 112°, were separated, washed with water, filtered and recrystallized by dissolving the crystals in boiling methanol and then cooling the solution to 0°. The compound melted at 114°; $[\alpha]^{23}\mathrm{D} + 47.23°$ (0.4393 g. in 25 cc. of chloroform solution in a 1-dm. tube rotates 0.83° to the right). Lieser and Schweizer did not give specific rotation while Brigl and Grüner[3] reported m. p. 111–112° and $[\alpha]\mathrm{D} + 45.82°$.

Anal. Calcd. for $C_{17}H_{26}O_6S_2$: C, 52.30; H, 6.66. Found: C, 52.23; H, 6.70.

The 6-benzoyldiethylmercaptoglucose prepared as above was dissolved in pyridine and boiled under a reflux condenser for three hours. Afterward it was reclaimed from pyridine and recrystallized as above. The specific rotation did not change.

6-Benzoyldibenzylideneglucose.—Anhydrous zinc chloride (6.5 g.) was added in small portions with shaking to a mixture of 4.9 g. of 6-benzoyldiethylmercaptoglucose and 30 cc. of benzaldehyde. The bottle containing the reaction mixture was kept in an ice-bath during the mixing period and later was placed on a shaking machine for fifteen minutes. The resulting solution was allowed to stand at room temperature for two hours. The benzaldehyde was extracted with petroleum ether and the glucose derivative with ethyl acetate. The latter solution was shaken with a saturated solution of sodium chloride and separated. From the ethyl acetate solution 2.2 g. of 6-benzoyldibenzylideneglucose, m. p. 156°, was obtained. It does not reduce Fehling's solution.

Anal. Calcd. for $C_{27}H_{24}O_7$: C, 70.40; H, 5.25. Found: C, 70.35; H, 5.21.

Dibenzylideneglucose.—6 - Benzoyldibenzylideneglucose (2.5 g.) was boiled for three hours under a reflux condenser with an alcoholic solution of potassium hydroxide (1 g.). Then the solution was diluted to five times its volume with water. The crystals separating melted at 161°. They were recrystallized from ether and then from methanol, m. p. 163°; yield 1.5 g.

Anal. Calcd. for $C_{20}H_{20}O_6$: C, 67.38; H, 5.66. Found: C, 67.07; H, 5.49. Calcd. for $C_{20}H_{20}O_6$: C, 67.38; H, 5.66. Found: C, 66.97; H, 5.68.

Dibenzylideneglucuronic Acid.—Twenty-five cc. of 2 *N* sodium hydroxide and 0.5 cc. of bromine were added with shaking to a solution of 1.4 g. of dibenzylideneglucose (m. p. 161°) and 20 cc. of pyridine at 0°. After five minutes the reaction mixture was placed on a shaking machine for fifteen hours. Only part of the substance dissolved and the remaining material was filtered off. The filtrate was cooled to 0° and titrated with concd. hydrochloric acid until Congo red paper changed to blue. Needle-like crystals were formed which were dissolved immediately in ethyl acetate. The ethyl acetate solution was shaken with potassium bicarbonate solution until it showed an alkaline reaction and was then separated from the water solution. The latter was cooled to 0° and titrated with concd. hydrochloric acid as before. The crystals were filtered off, redissolved in potassium bicarbonate, the solution cooled and

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[2] L. Zervas and P. Sessler, *Ber.*, **66**, 1328 (1933).

[3] P. Brigl and H. Grüner, *Ann.*, **495**, 60–83 (1932); Th. Lieser and Richard Schweitzer, *ibid.*, **519**, 271–278 (1935).

retitrated as before. This process was repeated three more times; 200 mg. of crystals was obtained. They were dissolved in alcohol and reprecipitated with distilled water, m. p. 175°.

Anal. Calcd. for $C_{20}H_{18}O_7$: C, 64.83; H, 4.9. Found: C, 64.93; H, 5.08.

Dibenzylideneglucose from 4,6-Benzylideneglucose.—4,6-Benzylideneglucose (2.1 g.) previously dried over phosphorus pentoxide was mixed with phosphorus pentoxide (2 g.) in a dry Erlenmeyer flask. All precautions were taken to avoid moisture. To this mixture was added freshly distilled benzaldehyde (7 cc.), previously cooled to 0°. The reaction flask was stoppered quickly and shaken in an ice-water-bath for ten minutes. Then it was taken out of the ice-bath and shaken twenty minutes at room temperature. Dry ether was added to extract the substance and the ether solution was washed with saturated sodium chloride solution made alkaline with a little ammonium hydroxide. The ether layer was separated and, after partially evaporating the ether, petroleum ether was added. The crystals formed were separated, boiled with water, filtered off from the hot water and then recrystallized from ether and finally from methanol, m. p. 163°. It does not reduce Fehling's solution. Mixed melting points of this substance were tried (a) with dibenzylideneglucose from the mercaptoglucose method before the oxidation to dibenzylideneglucuronic acid, m. p. 143–148°, and (b) with the residue which had not oxidized, m. p. 142–148°; mixed melting points of dibenzylideneglucose from (a) with residue from (b), m. p. 163°.

Anal. Calcd. for $C_{20}H_{20}O_6$: C, 67.38; H, 5.66. Found: C, 67.39; H, 5.92.

The author wishes to express his appreciation to Dr. L. Zervas for the interest which he has shown in this work, and to Mr. D. Rigakos of the Rockefeller Institute for Medical Research for the microanalyses for carbon and hydrogen.

Summary

1. 6-Monobenzoyldibenzylideneglucose was prepared by treating 6-monobenzoyldiethylmercaptoglucose with benzaldehyde and anhydrous zinc chloride. It does not reduce Fehling's solution.

2. Dibenzylideneglucose was prepared from 6-monobenzoyldibenzylideneglucose. The compound does not reduce Fehling's solution.

3. Dibenzylidene glucose was oxidized to dibenzylideneglucuronic acid.

4. Dibenzylideneglucose was prepared from 4,6-benzylideneglucose. It does not reduce Fehling's solution. It was found to differ from the dibenzylideneglucose prepared from 6-benzoyldiethylmercaptoglucose.

NEW YORK, N. Y. RECEIVED FEBRUARY 11, 1937

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

On 1,2- and 1,4-Addition.[1] II. Nitrogen Tetroxide and Trimethylethylene

BY ARTHUR MICHAEL AND G. H. CARLSON

Probably no other reagents act so diversely upon ethylenic hydrocarbons as the higher oxides of nitrogen and the reactions, although repeatedly investigated, are still understood very incompletely. The relative negativity of the possible addenda components, formed by intramolecular fission of nitrogen tetroxide, should decrease in the order. $ONO_2 > ONO > NO_2 > NO$ and, correspondingly, the polarity differences between the paired addendum groups of the following combinations should decrease as follows: $ONO_2 + NO > ONO + NO_2$. Alkenes in which the polarities of the Δ-carbons differ considerably should, therefore, add the tetroxide to form the nitroso-nitrate and less of the nitro-nitrite. This relationship has not been realized experimentally with alkylenes owing, largely, to the protean chemical character of the addendum. It may function not only as the balanced system $2NO \rightleftarrows O_2N—O—NO$, but as a powerful oxidant upon the alkene; further, as a polymerizing reagent upon alkenes easily susceptible to that process and the polymers may be reacted upon by the tetroxide.

Schmidt[2] passed the gas formed by heating lead nitrate into a cooled, ether solution of trimethylethylene until "saturated" and obtained mainly a greenish-blue oil with a varying yield (maximum 25%) of crystalline trimethylethylene nitrosate.[3] This compound was shown

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[1] For a previous paper in this series see, THIS JOURNAL, **59**, 744 (1937).

[2] Schmidt, *Ber.*, **35**, 2336 (1902). Guthrie [*J. Chem. Soc.*, **13**, 35, 129 (1861)] by the action of nitric acid, or of nitrogen tetroxide, upon trimethylethylene obtained, besides unidentified oily products, a colorless crystalline compound $C_5H_{10}N_2O_4$. This substance was prepared by Wallach [*Ann.*, **262**, 324 (1891)] by the action of nitric acid upon a solution of the alkene and isoamyl nitrite in acetic acid. From its chemical behavior, Wallach concluded the product is $C_5H_{10}(NO)(ONO_2)$ or $C_5H_9(=NOH)(ONO_2)$.

[3] The strongly oxidative, undried gas was used in a large excess and the solution stood at room temperature for a long time. Besides oxygen, nitrous and nitric acids were introduced into the reaction