Tetraacetyl - β - benzylglucopyranoside.—Acetobromoglucose, 110 g., redistilled benzyl alcohol, 265 cc., dry ether, 250 cc., and dry silver oxide, 60 g., were shaken together till the liquid was bromide free.[9] After filtration and evaporation of ether, the excess benzyl alcohol was recovered for the next run by distillation, bath 95–100° (0.1 mm.). A still head lagged with asbestos tape and at least 1 cm. in diameter, together with efficient cooling (ice water) of condenser and receiver, was necessary. The slightly impure product (75%) after complete purification from alcohol had specific rotations of −53.2° in chloroform and −46.7° in dioxane (*c*, 4.0).

Deacetylation gave pure β-benzylglucopyranoside, m. p. 122° (corr.), with rotations of −56.3° in water, −59.5° in dioxane (*c*, 2.0) and −57.6° in methyl alcohol (*c*, 1.5).

Tetraacetyl-α-benzylglucopyranoside.—The β-isomer, 20 g., titanium tetrachloride, 9 g. (1 mole), and pure chloroform, 200 cc., were heated under reflux for seventy-five minutes and the crude product was isolated by Pacsu's methods.[2] Recrystallization from 100 cc. of hot alcohol gave a first fraction of 15 g. and a second fraction, after dilution of the mother liquors with water, of 5 g., the rotations in chloroform being 141.5 and 38.3°, respectively. As those of the pure α- and β-isomers were 144.8 and −53.2°, the α-contents of the two fractions were 99 and 47%, corresponding to an average of 86% for the α-isomer. In a duplicate rearrangement of 153 g. of the β-tetraacetate, the second fraction, 15 g., was twice recrystallized from alcohol and gave 5 g. of the pure starting material with the correct levorotation of −52.8°. Other experiments are summarized in Table I.

Pure tetraacetyl-α-benzylglucopyranoside, m. p. 111°, had rotations of 144.8° in chloroform and 146.0° in dioxane (*c*, 2.5). Deacetylation gave the pure α-benzyl glycoside with rotations of 133.5° in water, 152° in dioxane (*c*, 2.5) and 150.3° in methyl alcohol, m. p. 122° corr.

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[9] Such syntheses have been improved by the addition of Drierite [Kreider and Evans, THIS JOURNAL, **58**, 1661 (1936)].

CONTRIBUTION NO. 199 FROM THE
RESEARCH LABORATORY OF ORGANIC CHEMISTRY
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE, MASS. RECEIVED JULY 26, 1939

Benzoylformic Acid from Styrene

BY CHARLES D. HURD, R. W. MCNAMEE AND FRANK O. GREEN

Oxidation of mandelic acid with potassium permanganate is the usual method[1] of synthesizing benzoylformic acid. Yields of 50 to 72% are attained. In place of mandelic acid it has been found that styrene (phenylethylene) may be oxidized in satisfactory yields to benzoylformic acid according to the equation

$$3C_6H_5CH{=}CH_2 + 8KMnO_4 \longrightarrow 3C_6H_5COCOOK + 8MnO_2 + 5KOH + 2H_2O$$

The commercial availability of pure styrene makes this an economical source of benzoylformic acid, whereas mandelic acid is much more expensive. It was established also that crude styrene, which was obtainable from "Drip Oil"[2] by fractional distillation, might be used also in this synthesis.

For some of the work, styrene was prepared by pyrolysis of cinnamic acid.[3] In other experiments, technical styrene[4] was used. This was vacuum distilled before use to remove the inhibitor (*p*-*t*-butylcatechol) and the polymers. From 3.5 g. of this distilled styrene, 8 g. of styrene dibromide, m. p. 72°, was obtained by reaction with bromine in carbon tetrachloride. The purity of this styrene, therefore, was at least 90%, and probably higher.

Styrene was concentrated from "Drip Oil"[5] for the oxidation experiments by fractionation through an efficient column. The fraction taken, b. p. 141–142°, was about one-half styrene because 2.78 g. of it yielded 3.56 g. of styrene dibromide.

Oxidation of Styrene of 90–100% Purity.—Eighteen grams (0.173 mole) of styrene and 9 g. (0.225 mole) of sodium hydroxide were shaken with 100 cc. of water in a 2-liter flask fitted with an air condenser. To this mixture was added in six portions a hot (70°) solution of 75 g. (0.474 mole) of potassium permanganate in 1500 cc. of water. After each addition the mixture was shaken vigorously for two minutes and cooled under the water tap so that the reaction temperature was kept at about 70°. When all the permanganate had been introduced, the excess was reduced with about 100 cc. of alcohol and the manganese dioxide filtered off and washed with water. The filtrate and washings were combined and evaporated down to 400 cc., then acidified with concentrated hydrochloric acid. The 1.5 g. of benzoic acid which separated was removed by filtration. When the addition of hydrochloric acid failed to precipitate any more benzoic acid the solution was extracted several times with ether. On evaporation of the ether, 20.4 g. of a light yellow liquid remained. This crude benzoylformic acid contained 2 to 3 cc. of water which made it quite insoluble in carbon disulfide. The water was removed by distilling with 7 cc. of toluene. An alternative procedure for removing the water was to dry the ether solution with calcium chloride. The residual acid, 18 g. (0.120 mole) or 69% yield, was dissolved in 30 cc. of carbon disulfide and the solution cooled with ice and salt. About 10 g. of crystals came down in the first crop and 5–6 g. in subsequent crops. Recrystallization gave 14.5 g. (0.096 mole) or 55% yield, of benzoylformic acid which melted at 59–61°.

Oxidation of Styrene of about 50% Purity.—A 26.5-g. fraction, b. p. 141–142°, obtained from drip oil, contained 13.3 g. (0.128 mole) of styrene. The quantities of other reagents were based on the styrene content; hence, 55.5 g. (0.351 mole) of potassium permanganate was used. The experimental details were the same as those outlined previously, but this time no benzoic acid separated after

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[1] Acree, *Am. Chem. J.*, **50**, 389 (1913); Hurd and Raterink, THIS JOURNAL, **56**, 1349 (1934); Hurd and McNamee, *Org. Syntheses*, **16**, 89 (1936).

[2] Brown, *Ind. Eng. Chem.*, **20**, 1178 (1928).

[3] *Org. Syntheses*, **8**, 84 (1928).

[4] Grateful acknowledgment is made to the Dow Chemical Company for a generous supply of styrene.

[5] An abundant supply of drip oil was generously furnished by Mr. G. J. Hart, Norshore Gas Co., Waukegan, Ill.

concentration and acidification. The crude benzoylformic acid was a light yellow oil which weighed 12.6 g. It contained about 2 cc. of water which was removed as before. The crystalline benzoylformic acid obtained after purification weighed 7.5 g. (0.05 mole). This is a yield of 39%, based on the styrene content.

When drip oil fractions were taken which contained only 25% of styrene, oxidation to benzoylformic acid was not satisfactory.

CHEMICAL LABORATORY
NORTHWESTERN UNIVERSITY
EVANSTON, ILL.

RECEIVED AUGUST 9, 1939

COMMUNICATIONS TO THE EDITOR

THE ENTROPY AND HEAT CAPACITY OF PROPYLENE

Sir:

Recently[1] Powell and Giauque have published measurements of the heat capacity of solid and liquid propylene which enabled them to determine the entropy change from 0°K. to the boiling point. By comparing this result with an entropy value calculated statistically on the basis of certain assumptions, they concluded that in solid propylene there is random end for end orientation of the molecules. This does not seem very reasonable to us *a priori*, inasmuch as one end is flat (CH_2), the other round (CH_3); one leg is considerably longer than the other and less polarizable; and finally the molecule has an appreciable dipole moment.[2] Furthermore their statistical calculations were based on a set of frequencies and a potential barrier hindering rotation of the methyl group (700 cal), published by one of us,[3] which are no longer acceptable. These frequencies were estimates obtained by comparison with other molecules, but on carrying the heat capacity measurements to higher temperatures it is found that the original set of frequencies would require a contribution from the internal torsional motion of the methyl group less than the classical value $^1/_2 R$, which is not plausible. Furthermore, an experimental study of the infrared and Raman spectra and a normal coördinate analysis has since been carried out, which, although not yet complete, shows that the estimated frequencies were not satisfactory. The revised frequencies lower somewhat the vibrational entropy at the boiling point, but the main effect is to raise considerably the potential barrier necessary to account for the heat capacity of the gas.

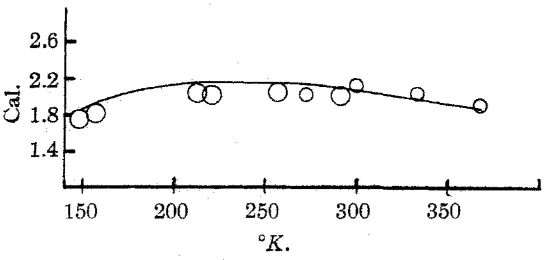

Fig. 1.—Calculated (solid line) and observed (circles) values of torsional heat capacity of propylene gas.

Before the publication of the entropy data we had reached the conclusion that a barrier of about 2000 cal. best fitted the heat capacity measurements when the revised frequencies were used. We have therefore calculated both the entropy at the boiling point and the gaseous heat capacity over a range of temperatures, using a barrier of 2119 cal. and the following frequencies: 432, 580, 921, 940, 1000, 1022, 1100, 1111, 1297, 1399, 1445, 1468(2), 1647, 3000(6) cm.$^{-1}$. Moreover, this calculation was carried out by a method which takes into account the complete dynamics of the molecule, including the coupling of the angular momentum of the top and of the whole molecule. This more complete calculation gave results differing from the values of Pitzer[4] by as much as 19% of the difference between free and hindered rotation. The heat capacities calculated are compared with those observed[5] in Fig. 1. The entropy of the ideal gas at the boiling point (225.35°K.) is calculated to be 59.87 cal., compared with the experimental value of 59.93 cal.

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[1] T. M. Powell and W. F. Giauque, THIS JOURNAL, **61**, 2366 (1939).

[2] H. E. Watson, C. G. Rao and K. K. Ramaswamy, *Proc. Roy. Soc.* (London), **143**, 558 (1934).

[3] G. B. Kistakowsky, J. R. Lacher and W. W. Ransom, THIS JOURNAL, **60**, 900 (1938).

[4] K. S. Pitzer, *J. Chem. Phys.*, **5**, 469 (1937).

[5] From ref. 3 and unpublished work.