To show that neopentyl alcohol may be formed directly from the reaction of isobutylene with carbon monoxide and hydrogen, this olefin was treated with synthesis gas in an autoclave under hydroformylation conditions. The products were hydrogenated and then distilled in a column of high efficiency. Neopentyl alcohol was shown definitely to be present in the reaction products. The failure of other investigators to isolate or identify neopentyl alcohol is probably owing to the difficulty of isolating a pure compound which is present in minor quantities in a small sample.

The formation of neopentyl alcohol from isobutylene indicates that the widely accepted[5,6] rule of Keulemans, *et al.*, is incorrect. Any proposed mechanism for the hydroformylation reaction must be consistent with the new finding. Thus it is not possible to produce a compound with a quaternary carbon atom from a ketene[7] intermediate.

The distribution of products formed in the reactions of *t*-butyl alcohol and isobutylene with synthesis gas is shown in Table I.

TABLE I

DISTRIBUTION OF HYDROGENATED PRODUCTS FROM THE COBALT CARBONYL CATALYZED REACTION OF ISOBUTYLENE AND *t*-BUTYL ALCOHOL WITH SYNTHESIS GAS

Product	Yield, % From isobutylene[a]	From *t*-butyl alcohol[b]
Isobutylene	..	3.0
Isobutane	..	3.2
Neopentyl alcohol	1.2	4.1
Isoamyl alcohol	46.8	60.0
Higher boiling material calcd. as isovaleraldehyde polymer	29.7	26.3
	77.7	96.6

[a] Based on starting isobutylene. Some isobutylene was lost on flushing the autoclave. [b] Based on converted *t*-butyl alcohol. Reaction run in a flow system.

Experimental

Reaction of *t*-Butyl Alcohol.—*t*-Butyl alcohol was homologated in a small continuous unit under the conditions shown in Table II. The reaction vessel was partly filled with a cobalt–thoria–magnesia–kieselguhr catalyst. Twenty grams per liter of dicobalt octacarbonyl was added with the liquid feed which consisted of equal volumes of *t*-butyl alcohol (1 liter, 789 g., 10.7 moles) and solvent (2-ethylhexanol) corresponding to a mole ratio of 1.66. Tail gas samples were taken periodically. Water was separated mechanically from the product.

TABLE II

REACTION DATA FOR HOMOLOGATION OF *t*-BUTYL ALCOHOL

Pressure: 267 atm.
Volume of reactor: 295 ml.
Volume of catalyst: 106 ml.
Free space: 189 ml.
Temperature: 200°
Gas feed rate ($1H_2:1CO$): 102 l./hr.
Liquid feed rate: 200 ml./hr.
Residence time: 1.1 hr.

The product was hydrogenated in a batch autoclave at 160 to 180° using Raney nickel and 200 atm. of hydrogen. The hydrogenated material was dried over Drierite and distilled at atmospheric pressure in a 6-foot Heli-grid column at an efficiency of approximately 30 theoretical plates. A substance boiling at 113° was obtained that was identified as neopentyl alcohol (m.p. 52–53°) by its infrared and mass spectrum; this alcohol was obtained in sufficient amount (7 g., 4.1%) and purity to plug up the take-off condenser. Essentially all of the solvent was recovered unchanged. Only 1.19 moles (11.2%) of the 10.6 moles of *t*-butyl alcohol charged was recovered unchanged. The yield of products listed in Table I is based on reacted *t*-butyl alcohol.

Hydroformylation of Isobutylene.—To a one-liter autoclave, cooled in solid Dry Ice, 300 ml. (189 g., 3.3 moles) of liquid isobutylene, 200 ml. of *n*-hexane and 10 g. of cobalt carbonyl were added. The bomb was pressured to 250 atmospheres with 2:1 synthesis gas and heated to 121°. The reaction took place rapidly at this temperature, and fresh gas was added in batches as the pressure dropped. The autoclave was finally heated to 185°, kept at this temperature for 2 hours and then cooled. The liquid product, which was a mixture of aldehydes and alcohols dissolved in *n*-hexane, was hydrogenated in a batch autoclave at 160 to 180°, using Raney nickel and 200 atmospheres of hydrogen. The hydrogenated material was dried over Drierite and distilled at atmospheric pressure in a 6-foot Heli-grid column at an efficiency of approximately 30 theoretical plates.

Although no solid neopentyl alcohol was obtained, several fractions rich in this alcohol were isolated. Mass spectrometric analysis of the various fractions showed that neopentyl alcohol was present in fractions distilling over as low as 90° and as high as 131°.[8] The fraction collected at 110–112° (1.48 g.) was richest in neopentyl alcohol (59.9%); the remainder of this fraction consisted of isoamyl alcohol, isovaleraldehyde and probably traces of trimethylacetaldehyde. The yield of products listed in Table I is based on starting isobutylene.

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[5] J. W. Cook, "Progress in Organic Chemistry," Academic Press, Inc., New York, N. Y., 1952, p. 108.

[6] P. W. Sherwood, *Pet. Processing*, **8**, 241 (1953).

[7] M. Orchin and W. C. Schroeder, "Unit Processes in Organic Synthesis," edited by P. H. Groggins, McGraw-Hill Book Co., Inc., New York, N. Y., 1952, p. 589.

[8] We wish to thank Dr. R. A. Friedel for the spectrometric analyses.

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Isolation of Maltohexaose[1]

BY ROY L. WHISTLER AND BEN F. MOY

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Because of the chemical and biochemical importance of the maltoöligosaccharides, the isolation and characterization of individual members were undertaken in this Laboratory. The abundance of maltoöligosaccharides in commercial corn sirup makes this source a convenient starting material. Maltotetraose[2] and maltopentaose[3] have previously been isolated from corn sirup. Analysis shows that maltohexaose is present[4] in corn sirup of 42 dextrose equivalent to the extent of 6.2%. Isolation of the carbohydrate from this source is described here. Initial separation is accomplished on carbon columns[5] and final purification obtained by cellulose column chromatography.[6] The optical rotation $[\alpha]^{25}\text{D}$ +182° compares with the value reported for the oligosaccharide obtained from the partial acid hydrolysis of potato amylose.[7]

The presence of repeating α-D-1→4-links is evidenced by information obtained from periodate

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[1] Journal Paper No. 882 of the Purdue University Agricultural Experiment Station.

[2] R. L. Whistler and J. L. Hickson, THIS JOURNAL, **76**, 1671 (1954).

[3] R. L. Whistler and J. H. Duffy, *ibid.*, **77**, 1017 (1955).

[4] R. L. Whistler and J. L. Hickson, *Anal. Chem.*, in press (1955).

[5] R. L. Whistler and D. F. Durso, THIS JOURNAL, **72**, 677 (1950).

[6] L. Hough, J. K. N. Jones and W. H. Wadman, *J. Chem. Soc.*, 2511 (1949).

[7] W. J. Whelan, J. M. Bailey and P. J. P. Roberts, *ibid.*, 1293 (1955).

oxidation and from by-products obtained on hydrolysis with crystalline β-amylase. Though it has not been possible to crystallize higher members of the maltoöligosaccharide series, the acetylated glycitols have been obtained crystalline. However, reduction of maltohexaose followed by acetylation failed to yield a crystalline glycitol acetate.

Experimental

Isolation of Maltohexaose.—Approximately 20 g. of corn sirup[8] was placed on a carbon column[5] 75 × 750 mm. and eluted with 4 l. of 16% aqueous ethanol to remove D-glucose and malto-homologs below D.P. 6. Subsequent elution with 4 l. of 20% aqueous ethanol removed maltohexaose contaminated with homologs of similar D.P. On evaporation of this eluate approximately 2 g. of sirup was obtained. This residue with others similarly obtained to make 7 g. was placed on a cellulose[6] (Whatman Standard Grade W) column, 75 × 1050 mm., and the column eluted successively with 8 l. of 85% ethanol, 8 l. of 82% ethanol and finally with 80.5% ethanol. The 80.5% ethanol eluate was collected in a fraction collector[9] and fractions were tested by paper chromatography to determine which principally contained maltohexaose. These fractions were combined, concentrated to a sirup and again chromatographed on a cellulose column as described. The eluate containing maltohexaose from this column was free from other carbohydrates as evidenced by paper chromatography using ethyl acetate, pyridine and water (10:4:3 v./v.). Evaporation gave a white amorphous powder, $[\alpha]^{25}\text{D}$ +182° (*c* 1.0, water).

Anal. Calcd. for $C_{36}H_{62}O_{31}$: C, 43.6; H, 6.3. Found: C, 43.6; H, 6.5.

Characterization of Maltohexaose.—Reducing power was determined before and after hydrolysis according to the procedure previously used.[2] Hydrolysis caused the reducing power to be increased by a factor of 5.84 which is near the expected factor of 6. Under similar conditions hydrolysis increased the reducing power of maltose by a factor of 1.87.

Periodate oxidation by the method previously described[2] gave the results shown in Table I.

TABLE I

PERIODATE OXIDATION OF MALTOHEXAOSE

Determination	Mole equiv. of substance Calcd.	Found
Periodate consumed	9	8.78
Formic acid produced	3	2.92
Formaldehyde produced	1	1.15

β-Amylolysis of maltohexaose was performed as described by Whistler and Hickson[2] for maltotetraose. The products from cellulose column separation are given in Table II.

TABLE II

Fraction	Mg.	Yield, %	Substance by paper chromatography
A	510	76	Maltose
B	80	12	Maltotetraose
C	50	7.5	Maltohexaose

Maltose from the β-amylolysis was acetylated to produce crystalline octa-*O*-acetyl-β-maltose, m.p. 159°.

Maltohexaitol.—Two grams of maltohexaose in 75 ml. of water was hydrogenated at 50 lb. pressure with 0.7 g. of platinum oxide as catalyst.[10] After 7 days 0.3 g. of fresh catalyst was added and the hydrogenation continued for a further 4 days. At the end of this time the solution had no reducing power.

The catalyst was filtered off and the solution was evaporated under reduced pressure at 50° to a white amorphous powder; yield 1.95 g., $[\alpha]^{25}\text{D}$ +163° (*c* 1.0, water).

One-half gram of maltohexaitol was acetylated with 5.0 ml. of acetic anhydride and 0.2 g. of sodium acetate by the previously used procedure. Evaporation of the chloroform extract under reduced pressure gave a pale yellow solid. The crude maltohexaitol acetate, obtained in 0.7 g. yield, was dissolved in 30 ml. of benzene and placed on a silene EF column.[11] The column was developed with 12 l. of a mixture of benzene and *t*-butyl alcohol (75:1 v./v.). The extruded column was streaked with alkaline potassium permanganate. The acetate zone which was in the middle section of the column was extracted with acetone. On evaporation of the acetone there was obtained a pale yellow powder. The acetate was dissolved in 99.5% ethanol and purified with charcoal, $[\alpha]^{25}\text{D}$ +133.4° (*c* 0.9, chloroform). The maltohexaitol acetate did not crystallize.

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(8) Corn sirup unmixed, 42 D. E., Corn Products Refining Company, Argo, Ill.

(9) J. L. Hickson and R. L. Whistler, *Anal. Chem.*, **25**, 1425 (1953).

(10) V. Voorhees, R. Adams and R. L. Shriner, "Organic Syntheses," H. Gilman, Editor, Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1932, p. 452.

(11) A. Thompson and M. L. Wolfrom, THIS JOURNAL, **73**, 5849 (1951).

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COMMUNICATIONS TO THE EDITOR

THE BONDING OF THE HYDROGEN ATOM IN $Co(CO)_4H$[1]

Sir:

Cobalt carbonyl hydride is perhaps the best known example of an unusual class of substances. Its intriguing chemical and physical properties have led to much speculation about its structure, particularly in the location and the nature of the bonding of the hydrogen atom. Edgell, Magee and Gallup[2] have shown that their infrared spectra are consistent with the following structure: the four CO groups tetrahedrally arranged about the cobalt atom with the hydrogen atom embedded in one face of the tetrahedron (on the figure axis) to form a *bridge between the three CO groups*. We have examined such a structure with the aid of molecular orbital theory and find that it is plausible. Moreover the details of the bonding give a picture of the molecule which is in agreement with the substantiated experimental facts.

The starting point of the analysis is the assumed C_{3v} symmetry of the molecule which, while not proven by the infrared[2–4] and electron diffraction[5] data, is in harmony with them. With the localiza-

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(1) This work was sponsored by the Atomic Energy Commission.

(2) Walter F. Edgell, C. Magee and G. Gallup, to be published; presented before the 127th meeting of the American Chemical Society, Cincinnati April, 1955.

(3) H. W. Sternberg, I. Wender, R. A. Friedel and M. Orchin, THIS JOURNAL, **75**, 2717 (1953).

(4) R. A. Friedel, I. Wender, S. L. Shufler and H. W. Sternberg, *ibid.*, **77**, 3951 (1955).

(5) R. V. G. Ewens and M. W. Lister, *Trans. Faraday Soc.*, **35**, 681 (1939).