give 20 g. of crude, yellow product. This was purified by two crystallizations (Darco) from 50% ethanol followed by three crystallizations from 95% ethanol to give 5.2 g. (25%) of product as colorless crystals, m.p. 261–263°.

Anal. Calcd. for $C_{11}H_{12}N_2O_2$: C, 64.7; H, 5.93; N, 13.7. Found: C, 64.9; H, 5.95; N, 13.5.

5-(α-Bromobutyryl)-benzimidazolone-2.—A 22.5-g. (0.11 mole) sample of VIII was dissolved with warming in 300 cc. of glacial acetic acid and a solution of 17.6 g. (0.11 mole) of bromine in 50 cc. of glacial acetic acid was added dropwise at 50–60° over a 20-minute period. The reaction mixture was then concentrated by vacuum distillation to leave the product as a light tan, crystalline residue. This was recrystallized from a mixture of 350 cc. of ethyl acetate and 150 cc. of ethanol to give 20.1 g. (65%) of product as colorless crystals, m.p. 233–234° dec. Concentration of the filtrate until crystallization began and recooling yielded an additional 8.7 g. (28%) of product also melting at 233–234° dec. These crops were combined and recrystallized as above to give 22.7 g. (73%) of product melting at 235–236° dec.

Anal. Calcd. for $C_{11}H_{11}BrN_2O_2$: C, 46.7; N, 9.9. Found: C, 46.5; N, 10.2.

5-[α-(N-Benzohydrylamino)-butyryl]-benzimidazolone-2 Hydrochloride (IX).—A 2.8-g. (0.01 mole) sample of 5-(α-bromobutyryl)-benzimidazolone-2 and 3.6 g. (0.02 mole) of benzohydrylamine[9] were dissolved in 25 cc. of absolute ethanol and the solution heated under reflux for 3 hours. The ethanol was then removed by distillation and the light yellow residue was triturated with ether to dissolve the product and leave benzohydrylamine hydrobromide as a colorless residue. The ether solution was shaken with 75 cc. of 10% hydrochloric acid to precipitate an oil phase which slowly crystallized on standing for several hours; wt. 3.9 g. (93%), m.p. 180–200°. Two recrystallizations from ethanol–isopropyl alcohol (1:1) gave 2.9 g. (69%) of product as colorless needles, m.p. 182–184°.

Anal.[10] Calcd. for $C_{24}H_{23}N_3O_2 \cdot HCl$: C, 68.3; H, 5.73. Found: C, 68.2; H, 5.99.

1-(3,4-Ureidophenyl)-2-aminobutanol Hydrochloride (X).—A 2.8-g. (0.007 mole) sample of IX and 0.3 g. of 10% palladium-on-carbon catalyst[5] were placed in 30 cc. of absolute alcohol and shaken at room temperature under 50 lb./in.^{2} of hydrogen pressure for 7 hours. The theoretical amount of hydrogen was absorbed. The hydrogenation mixture was diluted with 50 cc. of alcohol, heated to boiling, and filtered to remove the catalyst. Dilution of the filtrate with 1 liter of acetone caused the product to precipitate as a colorless, crystalline powder, wt. 1.1 g. (65%). Concentration of the filtrate gave an additional 0.35 g. (21%) of crystalline solid. Both solids darkened above 200° and charred without melting between 215–250°. The first crop was recrystallized by dissolving it in 75 cc. of absolute ethanol and diluting the solution with 500 cc. of acetone and 250 cc. of ether. The product separated as a colorless crystalline powder, wt. 0.90 g. (82% recovery), having the same decomposition characteristics as described above.

Anal. Calcd. for $C_{11}H_{15}N_3O_2 \cdot HCl$: C, 51.3; H, 6.26; N, 16.3. Found: C, 51.7; H, 6.20; N, 16.2.

This product was further characterized by acetylation using acetic anhydride in the presence of sodium acetate to give **1-(3,4-ureidophenyl)-2-acetylaminobutyl acetate (XI).** This derivative was obtained as colorless needles by crystallization from 50% ethanol; m.p. 183–184°.

Anal.[10] Calcd. for $C_{15}H_{19}N_3O_4$: C, 59.0; H, 6.27. Found: C, 59.0; H, 5.90.

2-Methyl-5-(ω-bromoacetyl)-benzimidazole (XII).—A solution of 11.5 g. (0.066 mole) of 2-methyl-5-acetylbenzimidazole[6] in 100 cc. of glacial acetic acid at 70° was irradiated with an 100-watt light bulb and treated dropwise with a solution of 10.6 g. (0.066 mole) of bromine in 25 cc. of glacial acetic acid. The reaction required 4 hours. The excess acetic acid was removed by distillation and the tarry residue was converted to a white solid by stirring for several hours with two 300-cc. portions of 30–70° petroleum ether. Crystallization of the material from 100 cc. of 1:1 ethanol–isopropyl alcohol gave 6.1 g. (36.5%) of product as colorless granules. On rapid heating the material melts with decomposition at approximately 180°, but on slow heating it darkens above 250° but does not melt below 300°. This material was used in the next step without further purification.

2-Methyl-5-(N-benzyl-N-methylaminoacetyl)-benzimidazole (XIII).—A 3.8-g. (0.015 mole) sample of crude XII and 3.6 g. (0.03 mole) of benzylmethylamine were placed together in 25 cc. of ethanol. An exothermic reaction occurred and rapidly subsided. The mixture was refluxed for 1 hour and then concentrated to a red oil. This was triturated with ether to cause solidification and the solid was taken up in alcoholic hydrogen chloride and precipitated with ether. This process was repeated from isopropyl alcohol–ether to give a solid which, after crystallization from ethanol–ether, melted at 238–240° dec., yield 1.0 g. (25%). The material was not purified further.

2-Methyl-5-methylaminoacetylbenzimidazole Dihydrochloride (XIV) and 1-(2-Methyl-5-benzimidazolyl)-2-methylaminoethanol Dihydrochloride (XV).—A 1.0-g. (0.0033 mole) sample of crude XIII was placed in 30 cc. of water with 0.2 g. of 10% palladium-on-charcoal[5] and the mixture shaken at room temperature under a hydrogen pressure of 40 lb./in.^{2}. Two equivalents of hydrogen were absorbed in 2 hours. The solution was filtered, treated with Darco and concentrated to yield 0.50 g. (63%) of a crystalline solid. This was recrystallized from 40 cc. of 85% ethanol (Darco) to give 0.11 g. of colorless crystalline needles which darken above 240° and decompose above 275°. Recrystallization of this from 30 cc. of 95% alcohol gave 0.08 g. of colorless needles melting in the same fashion. Analysis of this material indicates that it is XIV.

Anal. Calcd. for $C_{11}H_{13}N_3O \cdot 2HCl$: C, 47.8; H, 5.48; N, 15.2; Cl^-, 25.7. Found: C, 47.6; H, 5.31; N, 15.2; Cl^-, 25.4.

On dilution of the original alcoholic mother liquor (40 cc. of 85% alcohol) with 5–6 cc. of ether, 0.2 g. of a colorless, crystalline product separated. This was recrystallized from 50 cc. of 95% alcohol as colorless needles which decompose above 275°.

Anal. Calcd. for XV, $C_{11}H_{15}N_3O \cdot 2HCl$: C, 47.5; H, 6.16; N, 15.1. Found: C, 47.1; H, 5.78; N, 15.1.

MEDICINAL CHEMICAL SECTION
RESEARCH DIVISION
AMERICAN CYANAMID COMPANY
STAMFORD, CONNECTICUT

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[9] C. F. Winans and H. Adkins, THIS JOURNAL, **55**, 2051 (1933).

[10] A satisfactory nitrogen value was not obtained on this compound.

Formation of Neopentyl Alcohol from Isobutylene in the Hydroformylation Reaction

BY IRVING WENDER, JULIAN FELDMAN, SOL METLIN, BERNARD H. GWYNN AND MILTON ORCHIN

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Considerations of the mechanism of the hydroformylation reaction have been influenced by the rule formulated by Keulemans, Kwantes and van Bavel which states that "addition of the formyl group to a tertiary carbon atom does not occur, so that no quaternary carbon atoms are formed."[1] During an investigation of the cobalt carbonyl catalyzed reaction of *t*-butyl alcohol with carbon monoxide and hydrogen in a continuous unit, a large amount of product was obtained. A distillation of this material after hydrogenation resulted in the isolation of a solid product which was shown to be neopentyl alcohol. Previous work has shown that *t*-butyl alcohol reacts rapidly at 150° to give isoamyl alcohol in good yield[2]; presumably the alcohol is dehydrated[2-4] to isobutylene which then undergoes the hydroformylation reaction.

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(1) A. I. M. Keulemans, A. Kwantes and Th. van Bavel, *Rec. trav. chim.*, **67**, 298 (1948).

(2) I. Wender, R. Levine and M. Orchin, THIS JOURNAL, **71**, 4160 (1949).

(3) K.-H. Ziesecke, *Brennstoff-Chem.*, **33**, 385 (1952).

(4) R. C. Anderson, Abstracts of the 123rd Meeting of the American Chemical Society, Chicago, Ill., Sept., 1953.

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]	Yield, % 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.

BRANCH OF COAL-TO-OIL RESEARCH
DIVISION OF SOLID FUELS TECHNOLOGY
BUREAU OF MINES, REGION V
BRUCETON, PENNSYLVANIA

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 $[\alpha]^{25}\mathrm{D}$ +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).