Acknowledgment.—We wish to thank Dr. F. C. Whitmore and J. D. Surmatis for supplying us with large quantities of methyl neopentyl ketone. Mr. David Jenkins kindly carried out the semimicro carbon and hydrogen determinations and Mr. A. A. Sacks performed the work on the identification of the α-methoxyisobutyrophenone.

Summary

1. The action of alcohol free sodium methylate or isopropylate on 3-bromo-2-butanone yields the product of normal metathesis.

2. The action of alcohol free sodium methylate on 4,4-dimethyl-3-bromo-2-pentanone gives a 73% yield of the pure methyl ester of methyl-*t*-butylacetic acid.

3. Under similar conditions 3-bromo-3-methyl-4-heptanone yields a mixture of methylethylpropylacetic acid and 3-methoxy-3-methyl-4-heptanone while α-bromoisobutyrophenone yields only α-methoxyisobutyrophenone.

4. It is hypothesized that when normal replacement is hindered, rearrangement occurs through an ethylene oxide intermediate. The rearranging group is the alkyl group if this is sufficiently small and the final product is the ester. Otherwise the alkoxyl group rearranges to give a product identical with that of normal metathesis.

STATE COLLEGE, PA. RECEIVED SEPTEMBER 24, 1941

[CONTRIBUTION FROM THE WOOD CONVERSION LABORATORY OF THE UNIVERSITY OF IDAHO]

The Constitution of Arabo-galactan. II. The Isolation of Heptamethyl- and Octamethyl-6-galactosidogalactose through Partial Hydrolysis of Methylated Arabogalactan[1]

BY E. V. WHITE

The water-soluble gum of the western larch, *Larix occidentalis*, has been shown to contain *d*-galactose and *l*-arabinose as monosaccharide components in 6:1 molecular ratio[2a,b,c,d] and was tentatively assumed to be a homogeneous polysaccharide, although more recent studies[3a,b,c] tend to discredit this hypothesis. In the first communication[4] of the present series it was shown that the methyl derivative of the polysaccharide, when subjected to complete hydrolysis and simultaneous glycoside formation, yielded the glycosides of 2,4-dimethyl-*d*-galactose, 2,3,4-trimethyl-*d*-galactose, 2,3,4,6-tetramethyl-*d*-galactose, and 2,3,5-trimethyl-*l*-arabinose in the approximate molecular ratio 3:1:2:1, respectively. Furthermore, the isolation of a relatively large proportion of the terminal arabo-furanose unit as the crystalline amide of the corresponding acid strongly suggested a direct linkage of the arabinose fraction to the galactose units of the polysaccharide.

The validity of this assumption might be established by the preferential hydrolysis of the furanopentose unit under mild conditions leaving a galactan residue of unchanged structure. The technique has been employed successfully in the case of xylan,[5] and Hirst, Jones and Campbell[3c] report its application to arabo-galactan, although the latter authors have not given the experimental details of their method. In the present experiments a successful partial hydrolysis of larch gum to arabinose and unchanged galactan has not been achieved as yet despite numerous attempts under a variety of conditions. The furanopentose unit is undoubtedly removed more rapidly than the galactopyranose residues but the preferential character of the hydrolysis has not been established. Similarly, the preferential aqueous hydrolysis of the methyl ether derivative was not successful and was complicated by precipitation of the ether in the hot aqueous acid solution unless alcohol or other diluent was used as solvent. On the other hand, hydrolysis of the methyl ether in methanol solution with anhydrous hydrochloric acid proceeded smoothly and in a regular manner. The reaction products were separable sharply into two fractions. One of these, soluble in hot petroleum ether (A), increased gradually in yield ap-

(1) Presented in part before the Pacific Intersectional Division of the American Chemical Society meeting with the American Association for the Advancement of Science, Pasadena, California, June 16–21, 1941.

(2) (a) Wise and Peterson, *Ind. Eng. Chem.*, **22**, 362 (1930); (b) Wise, Hamer and Peterson, *ibid.*, **25**, 184 (1933); (c) Wise and Unkauf, *Cellulosechem.*, **14**, 20 (1933); (d) Peterson, Maugham and Wise, *ibid.*, **15**, 109 (1934).

(3) (a) Peterson, Barry, Unkauf and Wise, THIS JOURNAL, **62**, 2361 (1940); (b) Husemann, *J. prakt. Chem.*, **155**, 13 (1940); (c) Hirst, Jones and Campbell, *Nature*, **147**, 25 (1941).

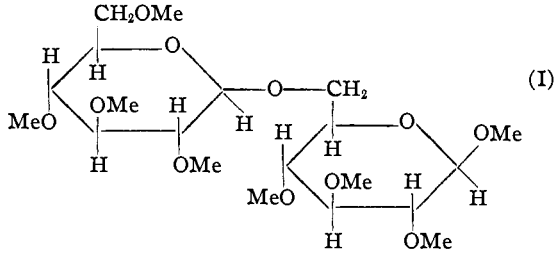
(4) White, THIS JOURNAL, **63**, 2871 (1941).

(5) Bywater, Haworth, Hirst and Peat, *J. Chem. Soc.*, 1983 (1937).

proaching a constant value, while a second, insoluble fraction (B), decreased in yield and in methoxyl content as hydrolysis proceeded until a constant value was obtained. The change in methoxyl content of the petroleum ether insoluble fraction is graphically illustrated in Fig. 1.

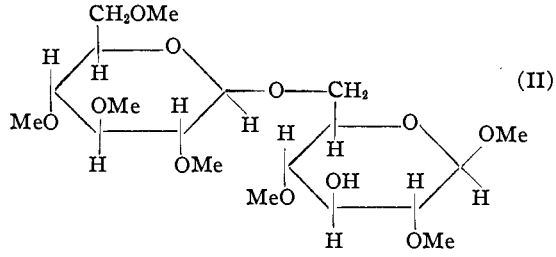
The fractionation does not, of course, provide any homogeneous substance but merely effects a separation of the higher methoxylated hydrolytic products from other polymeric, variously methoxylated, residues. Complete hydrolysis yields the products as described in Part I.[4] Under the conditions of hydrolysis employed in the present experiments, fractional distillation of the petroleum ether soluble extract (A) yielded the previously characterized 2,3,5-trimethyl-*l*-arabinoside, 2,3,4,6-tetramethyl-*d*-galactoside, and 2,-3,4-trimethyl-*d*-galactoside together with two high boiling disaccharide components.

One of these was shown to be octamethyl-6-*d*-galactosidogalactose (I) by hydrolysis of the com-



(I)

pound to 2,3,4,6-tetramethyl-*d*-galactose and 2,3,4-trimethyl-*d*-galactose. The second disaccharide component yielded 2,3,4,6-tetramethyl-*d*-galactose and 2,4-dimethyl-*d*-galactose upon hydrolysis. It proved to be heptamethyl-6-*d*-galactosidogalactose (II) since methylation gave



(II)

the above octamethyl derivative, and this, upon hydrolysis, again yielded tetramethylgalactopyranose and 2,3,4-trimethyl-*d*-galactose. The low positive rotation of both disaccharides suggests that the biose link is of the beta type.

The petroleum ether insoluble residue (B) from the partial hydrolysis of arabo-galactan methyl ether gave a large percentage of 2,4-dimethyl-*d*-

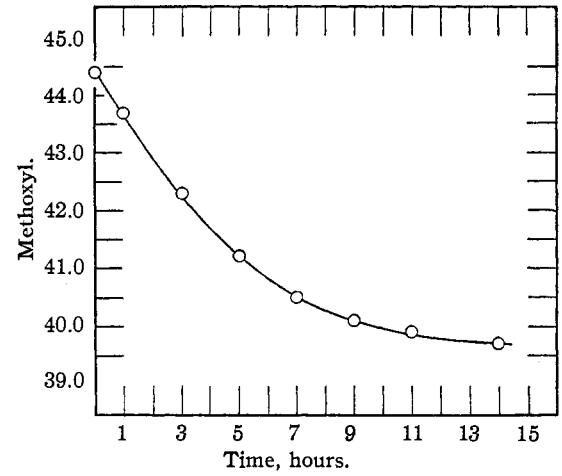


Fig. 1.—Methanolysis of arabo-galactan methyl ether.

galactoside and a relatively small proportion of 2,3,4,6-tetramethyl-*d*-galactoside upon complete alcoholysis. No trimethylated galactose component could be detected in the alcoholysis products. However, upon complete methylation of fraction (B) followed by hydrolysis, trimethylgalactose was obtained in addition to the above dimethyl- and tetramethylgalactose derivatives. This proved to be a mixture of 2,3,4-trimethyl-*d*-galactose and 2,4,6-trimethyl-*d*-galactose, identified through the corresponding crystalline anilides.

As a result of these experiments further information is gained as to the structural arrangement of the galactose residues in arabo-galactan. The isolation of octamethyl-6-*d*-galactosidogalactose demonstrates the linkage of a terminal galactose unit to the 6 position of an otherwise unsubstituted galactose residue in the original gum. This residue must, in turn, be joined through its reducing group to either the 3 or 6 position of a third galactose anhydride.

Similarly, the formation of heptamethyl-6-*d*-galactosidogalactose must have arisen through hydrolytic fission of a 2,4-dimethyl-6-tetramethyl-galactosidogalactosan at the 3 and 1 positions, respectively. The doubly linked dimethyl galactose unit illustrates the branched chain structure of arabogalactan. Apparently, the terminal galactose residues, and by analogy the terminal arabofuranose unit, are joined to the remainder of the polysaccharide through oxygen linkage at the 6 position of adjacent galactose units. However, the corollary of this conclusion, namely, that the dimethylated galactose residues of arabo-galactan methyl ether are linked to each other

through the 3 position, is not entirely valid. Certain of these units are undoubtedly joined 1–3 as evidenced by the isolation of 2,4,6-trimethyl-*d*-galactose from the partially hydrolyzed, remethylated and hydrolyzed fraction (B). The remaining disubstituted residues must be linked 1–6 as demonstrated by the separation of 2,3,4-trimethyl-*d*-galactose from the remethylated and hydrolyzed fraction (B). The conclusion is reached, therefore, that the structure of arabo-galactan is represented by a highly branched chain of galactose residues joined by oxygen linkage through both the 1–3 and 1–6 positions and that the terminal residues of arabofuranose and galactopyranose are linked to the 6 position of adjacent galactose anhydride units.

Experimental

Isolation, Purification, and Methylation of Arabo-galactan.—Larch sawdust, 1000 g. (20–30 mesh, prepared from the butt log of a mature tree) was steeped in 8 liters distilled water for twenty-four hours at room temperature. The aqueous extract with washings (8 liters) was then added to a fresh 1000-g. portion of sawdust. After a total of five similar extractions a concentrated aqueous solution of larch gum was obtained, and this, after clarification and filtration through norite, was fractionally precipitated with ethyl alcohol as described previously.[4]

A portion (100 g. solid) of the purified sirupy extract was methylated at 25° under nitrogen using 285 cc. of methyl sulfate and 855 cc. of 30% sodium hydroxide. The reagents were added dropwise and simultaneously with vigorous stirring over a period of five hours; 200 cc. of acetone was added over the interval to reduce foaming. After complete hydrolysis of the methyl sulfate, the product was freed from salt by dialysis and the liquor concentrated to a sirup under reduced pressure at 60°. The latter was then remethylated under similar conditions and the inorganic reaction products removed from the now insoluble sirup by decantation. After four methylations, the product was separated by shaking the methylation liquors with chloroform. The chloroform extract, dried over sodium sulfate and filtered, was evaporated to a sirup and exhaustively extracted with warm petroleum ether. The residue, evaporated under reduced pressure from acetone solution, was a light yellow friable glass, soluble in all solvents except petroleum ether; yield, 98 g. (Found: MeO, 44.4. Calcd. for $(C_5H_{10}O_5)_5(C_5HgO_4)(CH_2)_{30}$: MeO, 44.8).

Partial Methanolysis of Arabo-galactan Methyl Ether.—Twenty-five grams of arabo-galactan methyl ether was dissolved in anhydrous methyl alcohol and methanol-hydrogen chloride added together with fresh alcohol such that the total volume was 250 cc., 0.125 *N* in hydrochloric acid. The reaction was heated under reflux in a round bottom 2-neck flask and 20-cc. samples were removed at intervals. The samples were neutralized immediately with silver carbonate, decolorized with norite, filtered, and evaporated to a thin sirup. The latter was dropped into vigorously stirred light petroleum and the residue, taken up in chloroform, was reprecipitated into new solvent. After drying the precipitate at 35° a white powder was obtained. In the latter stages of the methanolysis reaction the product was isolated as a friable glassy solid. The analysis of the samples is given in Table I. During the course of the reaction the concentration of hydrogen chloride decreased in a regular manner as indicated.

TABLE I

PARTIAL METHANOLYSIS OF ARABO-GALACTAN METHYL ETHER

Sample	Time, hours	MeO	Acidity, *N*
1	0	44.4	0.125
2	1	43.7	
3	3	42.3	
4	5	41.2	
5	7	40.5	0.105
6	9	40.1	
7	11	39.9	
8	14	39.7	0.082

In a similar experiment 185 g. of arabo-galactan methyl ether was heated under reflux in 1850 cc. of methanol-hydrogen chloride, 0.125 *N*, for fourteen and one-half hours. The reaction was then neutralized with silver carbonate, decolorized with norite, filtered, evaporated to a sirup, and extracted five times with hot petroleum ether. The extract, freed from petroleum ether by distillation, gave a sirup (A); yield, 66.7 g. (Found: MeO, 53.8.) The residue (B), taken up in acetone, was evaporated under reduced pressure to a solid; yield, 122.0 g. (Found: MeO, 39.8.)

Examination of Petroleum Ether Soluble Fraction (A).—The petroleum ether soluble fraction (60.0 g.) was fractionally distilled slowly under high vacuum (0.1 mm.). The fractions taken and their respective methoxyl content are shown in Table II.

TABLE II

FRACTIONAL DISTILLATION OF PETROLEUM ETHER SOLUBLE FRACTION

Fraction	Temp., °C.	Yield, %	MeO
1	80–95	45.0	54.6
2	95–115	2.7	51.0
3	115–125	0.9	51.5
4	185–195	6.0	53.2
5	240–250	2.7	49.0
Residue	.....	2.7	45.5

Identification of Octamethyl-6-*d*-galactosidogalactose.—Fraction 4 (5.0 g.) from Table II, ref. index 1.4652 (25°), spec. rot. +49.0 (25° in methanol, *c*, 20) was dissolved in 50 cc. of methyl alcohol containing 2% dry hydrogen chloride. After reaction in a sealed tube maintained at 110° for six hours excess acidity was neutralized with silver carbonate. The filtered solution was decolorized with norite, evaporated to a sirup, and fractionally distilled under high vacuum. Fraction I: (2,3,4,6-tetramethyl-methyl-galactoside) 2.6 g., b. p. 90° (0.1 mm.). (Found: MeO, 61.0. Calcd. for $C_{11}H_{22}O_6$: MeO, 61.9.) Fraction II: (trimethyl-methyl-galactoside) 2.3 g., b. p. 115° (0.1 mm.). (Found: MeO, 52.1. Calcd. for $C_{12}H_{20}O_6$: MeO, 52.6.)

Fraction II (2.0 g.) was heated on a boiling water-bath with 25 cc. of 1.25 *N* sulfuric acid for eight hours. Excess acidity was then neutralized with barium carbonate, and, after filtering, the decolorized solution was evaporated to a sirup and dried by successive distillations with methyl alcohol. Vacuum distillation gave a sirup, b. p. 147° (0.1 mm.), which upon treatment with aniline in the usual manner gave the crystalline anilide (from ether) of 2,3,4-trimethyl-*d*-galactose m. p. 162°.[6] (Found: MeO, 31.4. Calcd. for $C_{15}H_{23}O_5N$: MeO, 31.4.)

Upon standing, fraction 4 from Table II crystallized and after recrystallization from acetone gave octamethyl-6-*d*-galactoside galactose; m. p. 101°, $[\alpha]^{25}$ +42.9° (*c*, 0.466, in methyl alcohol).

Anal. Calcd. for $C_{20}H_{38}O_{11}$: OMe, 54.6; C, 52.8; H, 8.44. Found: OMe, 54.7; C, 53.0; H, 8.38.

Identification of Heptamethyl-6-*d*-galactosidogalactose.—Fraction 5 (2.7 g.) from Table II, ref. index 1.4766 (25°), spec. rot. +36.4 (25° in acetone, *c*, 4) was dissolved in 25 cc. of acetone and methylated under nitrogen in the usual manner at 35° using 50 cc. methyl sulfate and 150 cc. of 30% sodium hydroxide. The product was removed from the reaction mixture by shaking the methylation liquors with chloroform. The chloroform extract, dried over magnesium sulfate, was evaporated to a sirup and the product purified by ether extraction. Vacuum distillation of the sirup gave (Fraction I: 1.3 g., b. p. 190° (0.1 mm.), ref. index 1.4660 (25°) spec. rot. +47.0 (25° in methanol c, 4). (Found: MeO, 52.9. Calcd. for $C_{20}H_{38}O_{11}$: MeO, 54.6.) Fraction II: 1.0 g., b. p. 250° (0.1 mm.), ref. index 1.4760 (25°), spec. rot. +38.0 (25° in methanol *c*, 4). (Found: MeO, 49.4. Calcd. for $C_{19}H_{36}O_{11}$: MeO, 49.3.)

Fraction I, treated in the manner described in the identification of octamethyl-6-*d*-galactosidogalactose, gave upon methanolysis and fractional distillation 2,3,4,6-tetramethyl-methyl-galactoside and trimethyl-methyl-galactoside. The latter was identified as the 2,3,4-trimethyl derivative by hydrolysis and treatment with aniline whereupon 2,3,4-trimethyl-*d*-galactose anilide was obtained m. p. 162°.[6] (Found: MeO, 31.4. Calcd. for $C_{16}H_{23}O_6N$: MeO, 31.4.)

Fraction II, treated in a similar manner, gave 2,3,4,6-tetramethyl-methyl-galactoside and 2,4-dimethyl-methyl-galactoside, the latter being identified as the corresponding anilide, m. p. 215°.[7] (Found: MeO, 21.9. Calcd. for $C_{14}H_{21}O_5N$: MeO, 21.9.)

Upon standing fraction 5 from Table II crystallized, and after recrystallization from acetone–light petroleum gave heptamethyl-6-*d*-galactosido galactose; m. p. 141°.

Anal. Calcd. for $C_{19}H_{36}O_{11}$: OMe, 49.4; C, 51.8; H, 8.25. Found: OMe, 49.6; C, 51.9; H, 8.42.

Examination of the Petroleum Ether Insoluble Fraction (B).—A portion (18.8 g.) of fraction (B) was subjected to complete alcoholysis using 100 cc. of 2% methanolic hydrogen chloride at 110° for six hours. The product was isolated in the usual manner and upon extraction with hot petroleum ether gave a residue (14.5 g.) which crystallized completely as the α- and β-methyl-2,4-dimethyl-*d*-galactosides. The extract, evaporated to a sirup (5.4 g.), gave 2,3,4,6-tetramethyl-methyl-*d*-galactoside upon distillation.

A second portion of fraction (B) (25 g.) was methylated under nitrogen in the usual manner at 35° using 250 cc. of methyl sulfate and 750 cc. of 30% sodium hydroxide. The product, extracted with chloroform, dried, and decolorized with norite was obtained as a sirup upon evaporation of the solvent; yield, 23.0 g. Extraction of the sirup with hot petroleum ether gave Fraction I: (petroleum ether soluble) 9.0 g. (Found: MeO, 44.8.) Fraction II: (petroleum ether insoluble) 14.0 g. (Found: MeO, 43.2.)

Fraction I was distilled fractionally and separated into three parts: (a) 1.1 g., b. p. 95–160° (found MeO, 53.6); (b) 1.0 g., b. p. 185–190° (found: MeO, 52.2); (c) residue 6.2 g. Fraction I was not investigated further.

Fraction II (14 g.) was subjected to complete alcoholysis using 65 cc. of 2% methanolic hydrogen chloride at 110° for six hours. The product was isolated in the usual manner, and upon extraction with hot petroleum gave a residue (7.0 g.) which crystallized completely as the α- and β-methyl-2,4-dimethyl-*d*-galactosides. The extract, evaporated to a sirup (6.3 g.) and distilled fractionally, gave fraction A: (2,3,4,6-tetramethyl-methyl-galactoside) 4.0 g., b. p. 95° (0.1 mm.) (Found: MeO, 61.0. Calcd. for $C_{11}H_{22}O_6$: MeO, 61.9.) Fraction B: (trimethyl-methyl-galactoside) 2.0 g., b. p. 115° (0.1 mm.). (Found: MeO, 51.7. Calcd. for $C_{10}H_{20}O_6$: MeO, 52.6.)

Identification of 2,3,4-Trimethyl-*d*-galactose and 2,4,6-Trimethyl-*d*-galactose.—Fraction B (2.0 g.) was heated on a boiling water-bath with 25 cc. of 125 *N* sulfuric acid for eight hours. The product was isolated in the usual manner and distilled yielding trimethyl-galactose, 1.7 g., b. p. 147° (0.1 mm.). (Found: MeO, 41.8. Calcd. for $C_9H_8O_6$: MeO, 41.9.)

The trimethyl-galactose thus obtained (1.7 g.) was dissolved in 25 cc. of absolute ethanol and heated under reflux with 0.75 g. of aniline for three hours. Excess solvent was removed by vacuum distillation and the sirup taken up in ether–alcohol. After two days in the ice-box the crystals were filtered and recrystallized from ether–alcohol giving the anilide of 2,4,6-trimethyl-*d*-galactose; yield, 0.6 g., m. p. 178°.[8]

The mother liquors, upon evaporation, deposited crystals and after recrystallization gave the anilide of 2,3,4-trimethyl-*d*-galactose; yield, 0.5 g., m. p. 162°.[6]

Summary

1. Octamethyl-6-*d*-galactosidogalactose has been isolated from the partial hydrolysis products of arabo-galactan methyl ether, demonstrating the 1–6 linkage of terminal galactose residues in larch gum. Structural proof of the identity of the new compound is given.

2. Heptamethyl-6-*d*-galactosidogalactose, isolated from the partial hydrolysis products of arabo-galactan methyl ether, is shown to be the 2,4-dimethyl-6-tetramethyl-galactosidogalactose derivative. The formation of this compound illustrates further the 1–6 linkage of terminal galac-

(6) McCreath and Smith, *J. Chem. Soc.*, 390 (1939).

(7) Smith, *ibid.*, 1736 (1939).

(8) Percival and Somerville, *ibid.*, 1615 (1937).

tose residues in larch gum and demonstrates the branched chain linkage thereof.

3. The galactose residues of arabo-galactan occurring as 2,4-dimethyl galactose in the hydrolysis products of arabo-galactan methyl ether are shown to be joined to one another in the original gum through the 1–6 position in some cases and through the 1–3 position in other instances.

MOSCOW, IDAHO RECEIVED OCTOBER 24, 1941

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

The Action of Ketene on 5,5-Dibromoxyhydrouracil[1]

BY MILTON FYTELSON[2] AND TREAT B. JOHNSON

It has been the experience of workers in this Laboratory that acetyl derivatives of cyclic ureides of the uracil type are difficult to prepare. In fact, very few acyl pyrimidine compounds in general have been described in the chemical literature. Some special citations, for example, from the literature of uracil derivatives are as follows. Ethyl 3-acetyluracil-4-carboxylate[3] is formed by the action of acetic anhydride on ethyl uracil-4-carboxylate. This compound is unstable and undergoes hydrolysis immediately when warmed with water. The corresponding 4-methyl- and 4-phenylpyrimidine carboxylates, uracil, 5-bromouracil, 4-methyluracil and thymine undergo no reaction when warmed with acetic anhydride. Hydrouracil, however, interacts to form 3-acetylhydrouracil, thereby illustrating the influence of saturation of the 4,5-position of the pyrimidine cycle on the reactivity of the uracil molecule.[4] On the other hand, in order to acetylate 1-phenylhydrouracil it is necessary to heat this pyrimidine with acetyl chloride under pressure. Acetic anhydride effects no change.[5] Like difficulties also arise when attempts are made to acetylate uric acid and its derivatives by the action of acetic anhydride.

So far as the authors are aware, the action of *ketene* on any pyrimidine structure has not been investigated. Our interest in the fundamental reactions of ureides of the uracil type called, therefore, for an examination of the reactivity of this reagent. The experimental evidence thus far obtained indicates no greater reactivity of this substance as an acetylating reagent than that exhibited by acetic anhydride, and we have had little success in adding the unsaturated *ketene* molecule to any ureide of the uracil type. Hydrouracil also failed to interact with ketene.

The most interesting experimental result to be reported by the author to date is the unexpected reactivity of *ketene* toward 5,5-dibromoxyhydrouracil (II).[6] It might be predicted that this hexahydropyrimidine (II) would interact with *ketene* to form the acetate expressed structurally by formula (V). Only one representative of this class has been described in the literature, namely: the acetate of 5,5-dichloroxyhydrouracil (VII). This was synthesized by Johnson and Sprague[7] (1) by the chlorination of uracil (I) in acetic anhydride solution and (2) by the direct action of acetic anhydride on 5,5-dichloroxyhydrouracil (IV). Acetic anhydride also reacts with 5,5-dibromoxyhydrouracil (II) to form the corresponding acetate (V) (see experimental part).

The authors now find that acetylation of the pyrimidine (II) with ketene is not accomplished without the use of a catalyst. Interaction with ketene alone leads only to the degradation of the hydrouracil molecule (II), giving 5-bromouracil (III). Interaction of ketene in the presence of silica gel, however, leads to only partial degradation of the hydrouracil (II), but is productive of a good yield of 3-acetyl-5-bromouracil (VIII). This new pyrimidine is easily converted into 5-bromouracil (III) by hydrolysis with formation of acetic acid.

As the pyrimidine (VIII) is not formed by the direct treatment of 5-bromouracil (III) with ketene, it is the conclusion of the authors that ketene first adds, in the presence of the catalyst, at position-3 of the pyrimidine (II) giving the acetyl

(1) Researches on Pyrimidines CLXXVI.

(2) (a) This paper was constructed from a dissertation presented by Milton Fytelson in June, 1941 to the Graduate Faculty of Yale University in partial fulfillment of the requirements for the degree of Doctor of Philosophy. (b) Present address: Department of Chemistry, Columbia University, New York, N. Y.

(3) Müller, *J. prakt. Chem.*, **56**, 492 (1897).

(4) Weidel and Roithner, *Monatsh.*, **17**, 176 (1896).

(5) Hoogewerf and Van Dorp, *Rec. trav. chim.*, **9**, 59 (1890).

(6) Wheeler and Johnson, *J. Biol. Chem.*, **3**, 187 (1907).

(7) Johnson and Sprague, THIS JOURNAL, **59**, 2437 (1937).