Abstract

In the present study of the ethylene molecule there has been made a complete reinvestigation of the Raman spectrum and of the infra-red absorption spectrum in the photographic region. Three new Raman lines have been found and eleven new infra-red absorption bands. Using these new data it has been possible to assign reasonable frequency values to all the twelve fundamental vibration modes of the ethylene molecule. From these frequency values, and the necessary formulas, eight of the force constants of the molecule have been obtained.

Ring Closure Studies in the Sugar Benzoates

BY M. L. WOLFROM AND CLARENCE C. CHRISTMAN

The work herein reported is a continuation of the ring closure studies in acylated sugar derivatives previously reported from this Laboratory.[1] The general procedure used in these studies is to treat a sugar mercaptal with trityl (triphenylmethyl) chloride. The extensive investigations of Helferich and co-workers[2] have shown that this reagent reacts preferentially with primary alcohol groups and the resultant ether is readily split with halogen acids to regenerate the original hydroxyl group. The tritylated mercaptal is then acylated. On removal of the trityl group and hydrolysis of the mercapto groups with mercuric chloride and moist acetone in the presence of cadmium carbonate,[3] ring closure on the open hydroxyl group may be effected. It was hoped that this ring closure would be on the terminal hydroxyl group, thus producing a <1,6> ring in the hexose series and the normal or <1,5> ring in the pentose series. Definite evidence that the trityl group had entered the terminal position was available for the glucose benzoate and galactose acetate series.

The work of Micheel and co-workers,[4] first performed through reactions not involving tritylation, has shown that a <1,6> or septanose structure is obtained in the galactose acetate series on further acetylation of the resultant tetraacetate. We found it necessary to leave the acetate series and enter the benzoate series in order to obtain crystalline derivatives. With glucose, the series of reactions described above resulted in the formation of the normal or pyranose ring as the end-product and a benzoyl shift had thus occurred. The tetrabenzoate obtained was identical with the ordinary form of glucose tetrabenzoate, which is generally assigned to the pyranose series, although in the case of this particular substance, this assignment cannot be considered as absolutely proved.

In the work herein reported the series of reactions described above has been extended to the galactose benzoate series. In the glucose benzoate compounds,[1] detritylation was always accompanied by halogenation of the terminal hydroxyl group and subsequent hydrolytic reactions were required to remove this halogen atom. With the galactose benzoates, conditions for detritylation unaccompanied by halogenation could be found although by changing these conditions, halogenation could be likewise readily effected. The final compound was a galactose tetrabenzoate which crystallized with one mole of methanol and like the corresponding acetate was probably an *aldehydo*-form. Due to the lack of known isomers in the sugar benzoate series, this structure could not be definitely determined. Further benzoylation of this tetrabenzoate did not produce a crystalline product, although benzoylation of α-galactose yielded a readily crystallizable α-galactose pentabenzoate.

Application of the same series of reactions to *d*-mannose diethyl mercaptal produced a crystalline diethyl mercaptal tetrabenzoate. Removal of the mercapto groups yielded a mannose tetrabenzoate obtained in the form of a colorless powder that was analytically pure. Provided no benzoate shift had occurred, this substance may be

(1) M. L. Wolfrom, J. L. Quinn and C. C. Christman, THIS JOURNAL, **56**, 2789 (1934); *ibid.*, **57**, 713 (1935).

(2) B. Helferich and J. Becker, *Ann.*, **440**, 1 (1924); B. Helferich, *Z. angew. Chem.*, **41**, 871 (1928).

(3) M. L. Wolfrom, THIS JOURNAL, **51**, 2188 (1929).

(4) F. Micheel and F. Suckfüll, *Ann.*, **502**, 85 (1933); *ibid.*, **507**, 138 (1933); *Ber.*, **66**, 1957 (1933); F. Micheel and W. Spruck, *ibid.*, **67**, 1665 (1934).
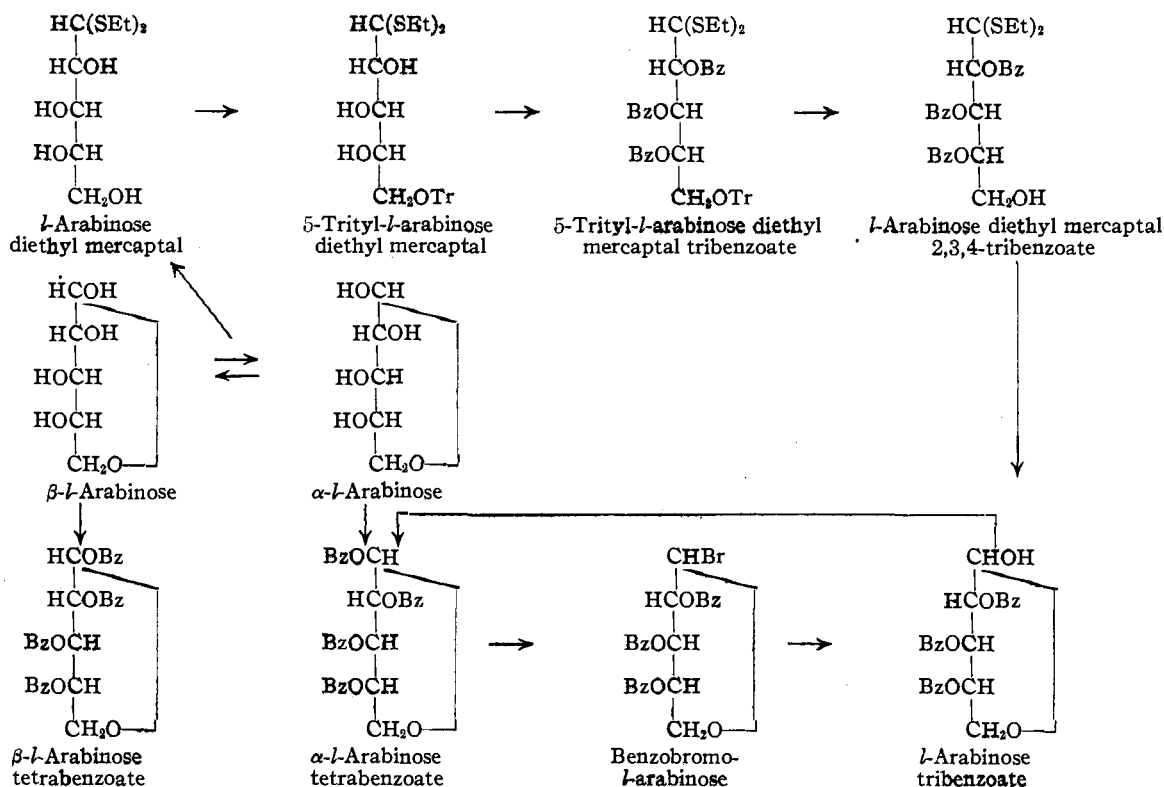
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HC(SEt)₂          HC(SEt)₂          HC(SEt)₂          HC(SEt)₂
   |                 |                 |                 |
 HCOH              HCOH              HCOBz             HCOBz
   |         →       |         →       |         →       |
 HOCH              HOCH              BzOCH             BzOCH
   |                 |                 |                 |
 HOCH              HOCH              BzOCH             BzOCH
   |                 |                 |                 |
 CH₂OH             CH₂OTr            CH₂OTr            CH₂OH
l-Arabinose       5-Trityl-l-arabinose   5-Trityl-l-arabinose diethyl   l-Arabinose diethyl mercaptal
diethyl mercaptal  diethyl mercaptal     mercaptal tribenzoate          2,3,4-tribenzoate
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 HCOH              HOCH
   |                 |
 HCOH              HCOH
   |       ⇌         |
 HOCH              HOCH
   |                 |
 HOCH              HOCH
   |                 |
 CH₂O—┘            CH₂O—┘
β-l-Arabinose     α-l-Arabinose
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 HCOBz             BzOCH             CHBr              CHOH
   |                 |                 |                 |
 HCOBz             HCOBz             HCOBz             HCOBz
   |                 |         →       |         →       |
 BzOCH             BzOCH             BzOCH             BzOCH
   |                 |                 |                 |
 BzOCH             BzOCH             BzOCH             BzOCH
   |                 |                 |                 |
 CH₂O—┘            CH₂O—┘            CH₂O—┘            CH₂O—┘
β-l-Arabinose     α-l-Arabinose     Benzobromo-       l-Arabinose
tetrabenzoate     tetrabenzoate     l-arabinose       tribenzoate
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Fig. 1.—Reaction series in the l-arabinose benzoate structures: Bz = C₆H₅CO—; Tr = (C₆H₅)₃C—.

characterized as d-mannose 2,3,4,5-tetrabenzoate, No other tetrabenzoate of mannose is at present available for comparative purposes.

In the l-arabinose benzoate series, the expected ordinary forms were obtained and all products were isolated in pure crystalline condition. The reactions involved are illustrated in Fig. 1. Gehrke and Aichner[5] have recorded a tetrabenzoate of l-arabinose (m. p. 153°; $[\alpha]_D$ + 301°, CHCl₃) prepared by the cold benzoylation of l-arabinose. On further purification of this substance we obtained the constants: m. p. 173–174°; $[\alpha]_D$ + 325°, CHCl₃. We have synthesized an isomeric tetrabenzoate (m. p. 160–161°; $[\alpha]_D$ + 112.5°, CHCl₃) through benzoylation of an equilibrated solution of l-arabinose in pyridine. The latter substance was also the form produced on further benzoylation of the tribenzoate obtained through the tritylation procedure. Furthermore, this tribenzoate was the one obtained from benzo-bromo-arabinose. We believe that the two tetrabenzoates above described represent an α,β-pair. According to the Hudson[6] nomenclature the more dextrorotatory derivative of this l-sugar would be designated as the β-isomer. On the

other hand, Isbell[7] reverses these designations for l-arabinose on the basis of his extensive experiments on the rates of oxidation of sugars. For the present, we will adhere to the Hudson nomenclature. The series of reactions shown in Fig. 1 may be considered as supporting evidence for the pyranose, <1,5>, structure of α-l-arabinose tetrabenzoate.

Brigl and Muehlschlegel[8] have stated that mercuric chloride would not remove the ethyl-mercapto groups from glucose diethyl mercaptal pentabenzoate. We have experienced no difficulty in applying this reagent to various benzoylated sugar mercaptals and find that the ethylmercapto groups are smoothly hydrolyzed from glucose diethyl mercaptal pentabenzoate when a sufficient excess of mercuric chloride is employed.

We have found that the Kunz[9] saponification procedure is applicable to a sugar benzoate provided the substance has an appreciable water solubility and we were able to use this excellent analytical procedure to estimate the benzoyl content of a number of the compounds now reported.

(5) M. Gehrke and F. X. Aichner, Ber., 60, 918 (1927).
(6) C. S. Hudson, THIS JOURNAL, 31, 66 (1909).
(7) H. S. Isbell, J. Chem. Ed., 12, 96 (1935).
(8) P. Brigl and H. Muehlschlegel. Ber., 63, 1551 (1930).
(9) A. Kunz and C. S. Hudson. THIS JOURNAL, 48, 1982 (1926).

Experimental

α-l-Arabinose Tetrabenzoate.—Ten grams of l-arabinose was dissolved in 75 cc. of hot, dry pyridine and the solution kept at room temperature for twenty-four hours. Benzoyl chloride (35 cc.) was added to the clear, colorless solution and the whole kept at room temperature for another twenty-four hours. The solution was then poured into one liter of ice and water and the precipitated sirup dissolved in chloroform and washed with aqueous solutions of sodium bisulfate, sodium bicarbonate and finally with water. The extract was dried with sodium sulfate and the chloroform removed under reduced pressure. The residual sirup crystallized on stirring with methanol and was purified by recrystallization from methanol to constancy; m. p. 160–161°; $[\alpha]^{29}_D$ +112.5° (c, 4; CHCl₃). The substance was moderately soluble in alcohol, practically insoluble in petroleum ether and water, and was soluble in other common organic solvents. The other benzoylated sugar derivatives herein reported exhibited similar solubilities.

Anal. Calcd. for C₃₃H₂₆O₉: C, 69.94; H, 4.62. Found: C, 69.86; H, 4.74.

Preparation and Purification of β-l-Arabinose Tetrabenzoate.—β-l-Arabinose (2.5 g.) was benzoylated at ice-box temperature with pyridine (15 cc.) and benzoyl chloride (12 cc.), the time of standing being thirty hours. After pouring into ice and water the product was crystallized from methanol; yield, 4.5 g.; m. p. 168–171°; $[\alpha]_D$ +317.5° (CHCl₃). Pure material was obtained on further recrystallization from methanol; m. p. 173–174°; $[\alpha]^{28}_D$ +325° (c, 4; CHCl₃). These constants were unchanged on further recrystallization. Gehrke and Aichner[5] give no details for the preparation of this substance and record the constants: m. p. 153°; $[\alpha]^{20}_D$ +301° (CHCl₃). The crystals of this substance have a characteristic pearly luster.

Benzobromo-l-arabinose.—Twenty-five grams of l-arabinose tetrabenzoate (m. p. 160–161°; $[\alpha]_D$ +112.5°, CHCl₃) was dissolved in a cold mixture of 200 g. of glacial acetic acid and 100 g. of dry hydrogen bromide and the whole allowed to stand overnight, during which time the benzobromoarabinose crystallized out of the reaction mixture. The product was removed by filtration and washed with cold glacial acetic acid; yield 10.5 g. After three recrystallizations from methanol the substance showed the constants: m. p. 144–145°; $[\alpha]^{26}_D$ +203° (c, 2; CHCl₃). Two further recrystallizations did not alter these constants.

Anal. Calcd. for C₂₆H₂₁O₇Br: Br, 15.22. Found: Br, 15.01.

Trityl-l-arabinose Diethyl Mercaptal Tribenzoate.—Seventeen grams (1 mol) of well-dried l-arabinose diethyl mercaptal[10] was dissolved in 70 cc. of dry pyridine, 18.4 g. (1 mol.) of dried triphenylchloromethane added, and the solution kept at room temperature for thirty hours. It was then treated with 70 cc. of dry pyridine and 50 cc. of benzoyl chloride, kept at room temperature for another thirty hours and poured into one liter of ice and water. The gummy mass that formed was separated by decantation, dissolved in chloroform and washed with aqueous solutions of sodium bisulfate, sodium bicarbonate and finally with water. The extract was dried with sodium sulfate and the chloroform removed under reduced pressure. The residual sirup was crystallized from methanol by the addition of water; yield 35 g.; m. p. 109–110°. Pure material was obtained on further recrystallization from methanol; m. p. 111–112°; $[\alpha]^{29}_D$ −25° (c, 4; CHCl₃).

Anal. Calcd. for C₄₉H₄₆O₇S₂: S, 7.91. Found: S, 7.80.

l-Arabinose Tribenzoate.—Trityl l-arabinose diethyl mercaptal tribenzoate (55 g.) was dissolved in 200 cc. of warm, anhydrous acetic acid, cooled to 12° and 10 cc. of a solution of anhydrous acetic acid containing 10 g. of dry hydrogen bromide was added with stirring. After three minutes of standing, the separated trityl bromide was removed by filtration and the filtrate poured into ice and water. The precipitated sirup was dissolved in chloroform and this solution was washed with a cold aqueous sodium bicarbonate solution, finally with water and dried with sodium sulfate. The chloroform solution was concentrated under reduced pressure to a volume of approximately 100 cc. and petroleum ether added until no more sirup separated. This sirup was again precipitated from chloroform–petroleum ether and dried in a vacuum desiccator. An amount of 25 g. of this sirup was dissolved in 150 cc. of acetone and 25 cc. of water and 50 g. of cadmium carbonate added. A solution of 50 g. of mercuric chloride in 100 cc. of acetone was then added under vigorous mechanical stirring and the stirring continued for twenty-four hours. The mixture was then refluxed for two hours, cooled and filtered into a flask containing 5 g. of cadmium carbonate. The filtrate was concentrated to dryness at 35° in the presence of 25 g. of cadmium carbonate. The residue was extracted with warm chloroform and the dried extract concentrated to a thick sirup under reduced pressure. The substance crystallized on the addition of a mixture of equal parts of ether and petroleum ether. Pure material was obtained after three recrystallizations from methanol and further recrystallization did not alter the constants; m. p. 162–163°; $[\alpha]^{30}_D$ +236° (c, 4; CHCl₃). The substance exhibited mutarotation in dry pyridine; $[\alpha]^{30}_D$ +143° ⟶ +196° (constant at twelve hours c, 4). The compound exhibited solubilities similar to those of the previously described α-l-arabinose tetrabenzoate except that it exhibited a certain amount of water solubility.

Anal. Calcd. for C₅H₇O₅(COC₆H₅)₃: C, 67.50; H, 4.80; benzoyl, 6.5 cc. 0.1 N NaOH per 100 mg. Found: C, 67.72; H, 4.88; benzoyl (Kunz method), 6.4 cc.; OMe, negative.

The same tribenzoate was obtained on hydrolysis of the bromine atom of the previously described benzo-bromo-arabinose. The procedure used was that described by Fischer and Noth[11] for the preparation of glucose tetrabenzoate methyl alcoholate. The product showed the constants: m. p. 162–163° (mixed m. p. unchanged); $[\alpha]^{28}_D$ +237° (c, 2.3; CHCl₃).

The above tribenzoate (5 g.) was further benzoylated at room temperature with pyridine (20 cc.) and benzoyl chloride (5 cc.) and the product isolated and purified as

(10) E. Fischer, *Ber.*, **27**, 673 (1894).

(11) E. Fischer and H. Noth, *ibid.*, **51**, 321 (1918).

previously described for the preparation of α-l-arabinose tetrabenzoate. The product showed the constants: m. p. 160–161°; $[\alpha]^{28}_D$ +113° (c, 4; CHCl$_3$). It was thus identical with the α-tetrabenzoate obtained directly from the free sugar and the mixed melting point showed no depression.

d-Galactose Diethyl Mercaptal Tetrabenzoate.—6-Trityl d-galactose diethyl mercaptal tetrabenzoate[1] (25 g.) was dissolved in 50 cc. of anhydrous acetic acid and detritylated as described for trityl l-arabinose diethyl mercaptal tribenzoate. The product crystallized from the concentrated chloroform extract upon the addition of petroleum ether; yield 13 g.; m. p. 123–125°. Pure material was obtained after repeated recrystallizations from chloroform–petroleum ether and finally from methanol; m. p. 127–128°; $[\alpha]^{25}_D$ −16.5° (c, 4; CHCl$_3$).

Anal. Calcd. for $C_{38}H_{38}O_9S_2$: S, 9.10. Found: S, 9.15.

6-Bromo d-Galactose Diethyl Mercaptal Tetrabenzoate.—6-Trityl d-galactose diethyl mercaptal tetrabenzoate (10 g.) was dissolved in 30 cc. of chloroform and dry hydrogen bromide passed into the solution for fifteen minutes. The chloroform was removed under reduced pressure and the residue extracted with warm petroleum ether to remove the trityl bromide. The crystalline residue was recrystallized several times from chloroform–petroleum ether; m. p. 103–104°; $[\alpha]^{25}_D$ −1.4° (c, 4; CHCl$_3$).

Anal. Calcd. for $C_{38}H_{37}O_8S_2Br$: S, 8.38; Br, 10.43. Found: S, 8.35; Br, 10.22.

d-Galactose Tetrabenzoate Methyl Alcoholate.—d-Galactose diethyl mercaptal tetrabenzoate (25 g.) was dissolved in 100 cc. of acetone in a three-necked flask fitted with a reflux condenser, mechanical stirrer and dropping funnel. Cadmium carbonate (75 g.) and water (25 cc.) were added, followed by the slow addition, under vigorous mechanical stirring, of a solution of 75 g. of mercuric chloride in 200 cc. of acetone. The mixture was refluxed for one hour and was then kept at room temperature for twenty-four hours, vigorous mechanical stirring being maintained throughout. The mixture was then filtered and the solids washed with warm acetone. The filtrate and washings were concentrated under reduced pressure in the presence of excess cadmium carbonate and the residue extracted with warm chloroform. The residual sirup obtained on chloroform removal was obtained crystalline from methanol by the addition of water and was recrystallized from chloroform–petroleum ether; yield 10.1 g.; m. p. 110–112°. Further recrystallization yielded a pure product; m. p. 112–113°; $[\alpha]^{26}_D$ −10° $\longrightarrow$ +6.5° (c, 4; alcohol-free CHCl$_3$; constant after about twelve hours).

Anal. Calcd. for $C_6H_8O_6(COC_6H_5)_4\cdot CH_3OH$: OMe, 4.93; benzoyl, 6.37 cc. 0.1 N NaOH per 100 mg. Found: OMe, 4.6; benzoyl (Kunz method), 6.45 cc.

α-d-Galactose Pentabenzoate.—This substance was synthesized from α-galactose according to the directions cited by Levene and Meyer[12] for the preparation of α-glucopyranose pentabenzoate. The resultant sirup crystallized after standing in methanol for three days and recrystallization was effected from methanol and chloroform–petroleum

ether; m. p. 128–129°; $[\alpha]^{23}_D$ +187° (c, 4; CHCl$_3$). Further recrystallization did not alter these constants.

Anal. Calcd. for $C_{41}H_{32}O_{11}$: C, 70.26; H, 4.61. Found: C, 70.00; H, 4.80.

Skraup[13] used the Schotten–Baumann procedure and obtained a crystalline pentabenzoate of galactose with a melting point of 165° but recorded no rotation for the substance.

Trityl d-Mannose Diethyl Mercaptal Tetrabenzoate.—This substance was synthesized from mannose diethyl mercaptal[14] according to the procedure previously described for the synthesis of trityl l-arabinose diethyl mercaptal tribenzoate. The resultant sirup was crystallized by repeated precipitations from methanol, effected by dissolving in the hot solvent and cooling. Pure material was obtained by recrystallization from the same solvent: m. p. 105–106°; $[\alpha]^{23}_D$ 0, $[\alpha]^{29}_{5461, Hg}$ −10.5° (c, 3.5; CHCl$_3$).

Anal. Calcd. for $C_{57}H_{52}O_9S_2$: S, 6.79. Found: S, 6.84.

Trityl d-Mannose Diethyl Mercaptal Tetraacetate.—This substance was synthesized from mannose diethyl mercaptal (24 g.) according to the procedure described by Wolfrom, Quinn and Christman[1] for the corresponding compound of galactose. The sirup was obtained crystalline from ethanol; yield 50 g. (2 crops); m. p. 120–122°. Pure material was obtained on further recrystallization from ethanol; m. p. 133.5–134.5°; $[\alpha]^{26}_D$ +36° (c, 4; CHCl$_3$).

Anal. Calcd. for $C_{37}H_{44}O_9S_2$: S, 9.21. Found: S, 9.22.

d-Mannose Diethyl Mercaptal Tetrabenzoate.—This substance was synthesized from trityl mannose diethyl mercaptal tetrabenzoate according to the procedure previously described for the corresponding galactose compound. The sirup obtained by the addition of petroleum ether to the chloroform solution was obtained crystalline from methanol after standing three weeks. Pure material was obtained on further recrystallization from methanol; m. p. 116–117°; $[\alpha]^{28}_D$ −5° (c, 2; CHCl$_3$).

Anal. Calcd. for $C_{38}H_{38}O_9S_2$: S, 9.10. Found: S, 8.88.

d-Mannose Tetrabenzoate.—This substance was synthesized from mannose diethyl mercaptal tetrabenzoate according to the procedure previously described for the corresponding l-arabinose compound. The substance was obtained as a sirup from the chloroform extract by the addition of petroleum ether and was purified by repeated precipitation effected from the same solvents and also from methanol–water. It was obtained in the form of an amorphous powder by drying in a vacuum oven at 50° for two days; $[\alpha]^{29}_D$ −115° (c, 2.3; CHCl$_3$).

Anal. Calcd. for $C_6H_8O_6(COC_6H_5)_4$: C, 68.43; H, 4.73; benzoyl, 6.71 cc. 0.1 N NaOH per 100 mg. Found: C, 68.20; H, 4.85; benzoyl (Kunz method), 6.75 cc.

Preparation of $aldehydo$-d-Glucose Pentabenzoate.—The ethylmercapto groups were removed from glucose diethyl mercaptal pentabenzoate[8] (25 g., 1 mol.) as previously described for the synthesis of galactose tetrabenzoate except that 100 g. (12 mols.) of mercuric chloride dis-

(12) P. A. Levene and G. M. Meyer, *J. Biol. Chem.*, **76**, 513 (1928).

(13) Z. H. Skraup, *Monatsh.*, **10**, 389 (1889).

(14) Ref. 10. *Cf.* P. A. Levene and G. M. Meyer, *J. Biol. Chem.*, **74**, 695 (1927).

solved in 200 cc. of acetone was employed and after the addition of this solution the mixture was refluxed for thirty minutes and immediately filtered. The residue obtained on concentration under reduced pressure in the presence of excess cadmium carbonate was treated with absolute ethanol and the solvent removed under reduced pressure, this process being repeated several times. The sirup obtained after chloroform removal was crystallized from 70% ethanol as described by Brigl and Muehlschlegel[8] and crystallized after standing in the ice box for one week. Pure material was obtained after several recrystallizations from absolute ethanol; m. p. 81–82°; $[\alpha]^{24}_D$ +40° (*c*, 3; abs. EtOH). The constants given by Brigl and Muehlschlegel were: m. p. 76–82°; $[\alpha]_D$ +37° (EtOH).

Summary

1. α-*d*-Galactose pentabenzoate and α-*l*-arabinose tetrabenzoate have been synthesized. New constants for β-*l*-arabinose tetrabenzoate have been reported.

2. Benzobromo-*l*-arabinose has been synthesized.

3. The benzoates of trityl-*l*-arabinose diethyl mercaptal and trityl-*d*-mannose diethyl mercaptal and the acetate of the latter have been synthesized.

4. 6-Bromo-*d*-galactose diethyl mercaptal tetrabenzoate has been synthesized.

5. The diethyl mercaptal tetrabenzoates of *d*-galactose and *d*-mannose have been synthesized through the tritylation reaction of Helferich. Hydrolysis of the ethylmercapto groups from the former produced a crystalline *d*-galactose tetrabenzoate methyl alcoholate, and from the latter an amorphous *d*-mannose tetrabenzoate.

6. Hydrolysis of the trityl and ethylmercapto groups of trityl-*l*-arabinose tribenzoate produced an *l*-arabinose tribenzoate identical with that obtained from benzobromo-*l*-arabinose. Further benzoylation of this tribenzoate produced α-*l*-arabinose-tetrabenzoate.

The Thermal Decomposition of Tertiary Butyl and Tertiary Amyl Chlorides, Gaseous Homogeneous Unimolecular Reactions
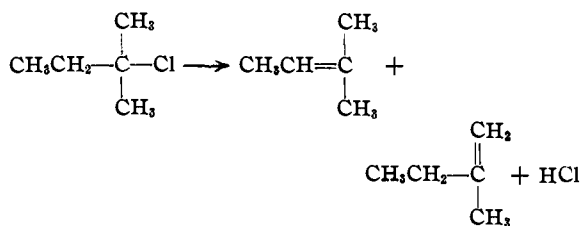
BY D. BREARLEY, G. B. KISTIAKOWSKY AND C. H. STAUFFER

Most unimolecular reactions which have been studied[1] have the disadvantage that the decomposition is quite complex and involves the breaking down of the entire molecule or various complicated secondary reactions. It was, therefore, the purpose of this study to add to the increasing list of unimolecular reactions two more reactions involving the rupture of only two bonds, the C–H and the C–Cl bonds. Also it was for the purpose of correlating the dehydration of *t*-butyl and *t*-amyl alcohols[2] with the elimination of hydrogen chloride from *t*-butyl and *t*-amyl chlorides.

The main reactions occurring may be written as follows

$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-Cl \longrightarrow CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_2}{\|}}{C}} + HCl$$

and

(1) A general review of existing data, Kistiakowsky, *Chem. Rev.*, **17**, 47 (1935).

(2) Schultz and Kistiakowsky, THIS JOURNAL, **56**, 395 (1934).

$$CH_3CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-Cl \longrightarrow CH_3CH=\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} +$$

$$CH_3CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_2}{\|}}{C}} + HCl$$
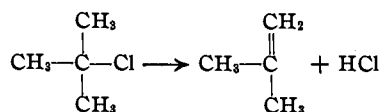
For the study of the thermal decomposition of these tertiary chlorides a static method was used, and the *t*-butyl chloride was studied over the temperature range 547–645°K. while the *t*-amyl chloride was studied over range 543–600°K.

The previous work of Schultz and Kistiakowsky[2] on the two tertiary alcohols was also done using a static method, but in a temperature range of 760 to 830°K., so that any close similarity between these two types of reactions should indicate quite definitely the absence of any chain mechanism, and classify them as true unimolecular reactions.