

we may calculate the rotation of the non-hydrolyzed moiety.

$$\text{For glucose, } (0.671)52.2 + (0.329)x = +40.9^\circ \\ x = +18^\circ$$

$$\text{For galactose, } (0.244)80.5 + (0.756)x = +74.1^\circ \\ x = +72^\circ$$

The above figures are within the range of a pyranoside mixture which is probably present.

### Experimental

Conversion of *d*-Glucose Dimethyl Acetal into  $\alpha$ -Methyl *d*-Glucopyranoside.<sup>9</sup>—*d*-Glucose dimethyl acetal (1.8 g.) was dissolved in 10 cc. of methanol containing 1.0% of dry hydrogen chloride and the solution was heated in a sealed tube at 80° for three days.  $\alpha$ -Methyl-*d*-glucopyranoside crystallized on concentration of the solution; yield 0.9 g., m. p. 162–163°. Pure material was obtained on one recrystallization from methanol; m. p. 165–166°

(9) Experiment performed by Mr. Robert L. Brown.

(mixed m. p. unchanged),  $[\alpha]_D^{25} +159^\circ$  (c, 2.1 g. per 100 cc. of water solution).

### Summary

1. The mutarotation of the dimethyl acetals of *d*-glucose and *d*-galactose at 25° and in the presence of 0.05% hydrogen chloride has been observed in aqueous and in methanol solutions.

2. The amount of material readily hydrolyzable by mild aqueous acidity has been determined at various significant points during the above mutarotations.

3. It is shown that the data obtained in (1) and (2) are interpretable on the basis of a very rapid initial reaction due to hydrolysis of the acetal followed by the formation of unstable, non-pyranoid glycosides which in turn are slowly converted into the stable pyranosides.

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\* [CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

## The Rearrangement of 1,3-Dimethyl-4-*t*-butylbenzene with Aluminum Chloride

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The reaction between *t*-butyl chloride and *m*-xylene in the presence of anhydrous aluminum chloride was carried out first by Bauer.<sup>1</sup> The product obtained by him was 1,3-dimethyl-5-*t*-butylbenzene, for on oxidation it gave 3,5-dimethylbenzoic acid. This hydrocarbon also has been prepared by the action of isobutyl alcohol and sulfuric acid upon *m*-xylene,<sup>2</sup> and commercially by the action of isobutylene on *m*-xylene in the presence of aluminum chloride,<sup>3</sup> while recently a synthesis from *m*-xylene, triisobutyl borate and aluminum chloride has been reported.<sup>4</sup>

The yields in these syntheses are reported to be very high, and the product appears to be a single substance. The two methyl groups would be expected to direct a new substituent mainly into the 4-position; thus *m*-xylene and acetyl chloride, in the Friedel-Crafts reaction, give exclusively 2,4-dimethylacetophenone.<sup>5</sup> The fact that the 1,3,5-compound is practically the only product when *t*-butyl chloride is used must mean that

either the methyl groups do not exert their usual directing effects in this synthesis, or the 1,3,4-compound is the primary product and this is rearranged to the 1,3,5-compound by the aluminum chloride. If the second of these alternatives should be true, it would be of interest, for although aluminum chloride is known to bring about rearrangements of alkyl groups in alkyl benzenes, it is rare that the final product is a single substance.

We therefore undertook an investigation of this reaction, and of the effect of aluminum chloride on 1,3-dimethyl-4-*t*-butylbenzene. We prepared the symmetrical compound from *m*-xylene,<sup>6</sup> *t*-butyl chloride and aluminum chloride. Although we did not obtain particularly good yields, the product contained no other dimethylbutylbenzene and it had the 1,3,5-orientation for it gave trimelic acid on oxidation.

The 1,3,4-isomer was prepared from 2,4-dimethylphenylmagnesium iodide and *t*-butyl chloride. The yield of pure product was poor, but it showed a constant boiling point and on oxidation gave trimellitic acid. When this hydrocarbon was heated on the steam-bath for two hours with

(1) Bauer, *Ber.*, **24**, 2840 (1891).  
 (2) Noelting, *ibid.*, **25**, 791 (1892).  
 (3) German Patent 184,230, *Chem. Centr.*, **78**, II, 366 (1907).  
 (4) French Patent 720,034 (1932).  
 (5) Claus, *Ber.*, **19**, 230 (1886); Frey and Horowitz, *J. prakt. Chem.*, [2] **43**, 120 (1891); Verley, *Bull. soc. chim.*, [3] **17**, 910 (1897); Bouveault, *ibid.*, [3] **17**, 1021 (1897); Meissel, *Ber.*, **32**, 2420 (1899).

(6) The *m*-xylene used in this work was supplied to us by E. I. du Pont de Nemours and Co., whom we wish to thank for this courtesy.

aluminum chloride, it was converted into 1,3-dimethyl-5-*t*-butylbenzene, identical with the product obtained from *m*-xylene and *t*-butyl chloride by the Friedel-Crafts reaction. Although the losses were high and the rearranged hydrocarbon was obtained only in 45% yield, no 1,3-dimethyl-4-*t*-butylbenzene could be detected in the product.

While these results do not prove that the 1,3,5-compound obtained in the Friedel-Crafts synthesis is derived entirely from the 1,3,4-compound, they do show that none of the 1,3,4-compound would survive the action of aluminum chloride, and this, together with the orienting effects of the two methyl groups, makes it seem quite likely that when *m*-xylene and *t*-butyl chloride react in the presence of aluminum chloride, the first product has the orientation 1,3,4 and subsequently is rearranged rapidly into the 1,3,5-compound by the catalyst.<sup>7</sup>

### Experimental

**1,3-Dimethyl-5-*t*-butylbenzene.**—*t*-Butyl chloride (83 g., 1 mole) was dropped slowly into a mixture of *m*-xylene (106 g., 1 mole) and aluminum chloride (50 g.) in an apparatus provided with a stirrer and condenser. After the addition, the mixture was refluxed until the evolution of hydrochloric acid ceased. The product was poured onto iced hydrochloric acid and worked up in the usual way. The hydrocarbon boiled at 103–105° under 29 mm., yield (two runs) 37 g. (23%) and 43 g. (26%); b. p. (760 mm.) 200–202°;  $n_D^{20}$  1.4890;  $d_4^{20}$  0.8619.

**Nitration.**—With nitric acid and sulfuric acid, the hydrocarbon gave 2-nitro-1,3-dimethyl-5-*t*-butylbenzene, m. p. 84°, as reported by Bauer.<sup>8</sup>

**Oxidation.**—Refluxing with aqueous permanganate for four to five hours converted the hydrocarbon completely into trimesic acid, m. p. 330–340°; the mixed m. p. with an authentic specimen prepared from mesitylene (345–350°) showed no depression.

(7) Shortly after we finished this work, a paper by Baddeley and Kenner [*J. Chem. Soc.*, 303 (1935), see also Kirmann and Graves, *Bull. soc. chim.*, [5] 1, 1494 (1934)] appeared, which deals with the meta alkylation of aromatic hydrocarbons by the Friedel-Crafts reaction. These authors showed, among other things, that 1,2,4-tripropylbenzene was largely converted by aluminum chloride into the 1,3,5-isomer, together with lower and higher alkylated products.

(8) Bauer, *Ber.*, **24**, 2840 (1891); **31**, 1345 (1898); **33**, 2564 (1900).

**1,3-Dimethyl-4-*t*-butylbenzene.**—A Grignard reagent was prepared from 1,3-dimethyl-4-iodobenzene (53 g., 0.25 mole) and magnesium (6 g.). To this was added an excess (40 g.) of *t*-butyl chloride. After refluxing for about an hour, the product was decomposed and worked up in the usual way. The ether and excess butyl chloride were removed by distillation at atmospheric pressure, and the residue then fractionated under reduced pressure. The portions boiling at 100–120 at 28 mm. from three runs were combined, washed with bisulfite, dried, and heated for a short time with metallic sodium. The product was halogen free, and boiled at 113–114° under 28 mm.; yield 7.5 g.; b. p. (760 mm.) 210–214°;  $n_D^{20}$  1.5030;  $d_4^{20}$  0.9372.<sup>9</sup>

**Oxidation** with permanganate gave trimellitic acid, m. p. 217–218°; mixed m. p. with an authentic specimen (215–217°), 215–218°.

**Rearrangement.**—Three grams of 1,3-dimethyl-4-*t*-butylbenzene was mixed with 0.5 g. of aluminum chloride and heated on the steam-bath for two hours. The reaction mixture was decomposed in the usual way, and the products from three such runs were combined and fractionated at 30 mm. The fractions were I, b. p. 40–100°, less than 0.5 g.; II, b. p. 100–105°, 4 g.; III, b. p. 105–115°, less than 0.5 g.; IV residue, 1 g. The total recovery was thus about 65%; yield of fraction II, 45%. Fraction II was 1,3-dimethyl-5-*t*-butylbenzene, b. p. 202–203° at 760 mm., 102–104° at 30 mm.,  $n_D^{20}$  1.4903,  $d_4^{20}$  0.8720. On oxidation it gave trimesic acid, m. p. 322–325°, mixed m. p. 320–325°.

### Summary

1. 1,3-Dimethyl-4-*t*-butylbenzene has been prepared and characterized.

2. This hydrocarbon, when treated with aluminum chloride, rearranges into the 1,3,5-isomer, which is the only one of the isomers obtained from *m*-xylene, *t*-butyl chloride and aluminum chloride.

3. In view of the orienting effects of the two methyl groups in *m*-xylene, and the rearrangement described in this paper, it is suggested that in the Friedel-Crafts synthesis of 1,3-dimethyl-5-*t*-butylbenzene, the *t*-butyl group first enters the 4-position, giving the 1,3,4-isomer, which is then rapidly rearranged by the catalyst to the 1,3,5-compound.

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(9) Two runs were made giving practically the same yields; of the remainder of the product, about 25% was identified as *m*-xylene.