

their structural formulas, a relationship may be established between the number of stereoisomeric and non-stereoisomeric paraffins and the alkyl groups of which the former may be considered to be composed. Mathematical formulas of the recursion (finite) type are advanced which permit of the calculation, from their carbon content, of the number of stereoisomeric and non-stereoisomeric paraffins in each of these structural types. In using these recursion formulas to calculate the total of such isomers of any specified carbon content, the total number of stereoisomeric and non-stereoisomeric alkyl groups of $N/2$ and all lesser carbon contents must be known.

2. The total number of isomers so obtained agrees exactly through the tetradecanes with the numbers required by theory as tested by actually writing the structural formulas and counting the number of stereoisomers and non-stereoisomers.

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PREPARATION OF 1,2,3,4-TETRABROMOBUTANE

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One of the methods described in the literature for the laboratory preparation of 1,3-butadiene is that of Harries,¹ in which 2,3-dibromobutane is decomposed by soda lime at 600°. Although this method does not yield pure butadiene, the latter can be obtained by converting the impure product into 1,2,3,4-tetrabromobutane, and then reducing this compound with zinc and alcohol according to the method of Thiele.² The tetrabromo compound therefore represents a convenient source of pure butadiene. In connection with a problem requiring rather large amounts of butadiene, a modification of Harries' method was employed as a preparative procedure for 1,2,3,4-tetrabromobutane. As a result, considerable data were collected and several changes in the apparatus and procedure were made which render the method somewhat more reliable and convenient.³

The original Harries method involved dropping 2,3-dibromobutane upon soda-lime contained in an iron pot at 600°. The butadiene and

¹ Harries, *Ann.*, **383**, 176 and 181 (1911).

² Thiele, *ibid.*, **308**, 333 (1899); Birch, *Ind. Eng. Chem.*, **20**, 474 (1928); Farmer, Lawrence and Thorpe, *J. Chem. Soc.*, 729 (1928).

³ Recently Muskat and Northrup [*THIS JOURNAL*, **52**, 4050 (1930)], have described a laboratory method of preparing butadiene which involves the following operations: (1) converting butyl alcohol into butyl chloride, (2) chlorinating butyl chloride to dichlorobutane and (3) converting dichlorobutane into butadiene by passing it over heated soda-lime.

other gaseous products were passed through an ice condenser, after which the butadiene was absorbed in bromine yielding 1,2,3,4-tetrabromobutane. In place of the iron pot, a pipe furnace similar to that used by Adams, Kamm and Marvel⁴ for the preparation of amylene proved to be more convenient. Also, less charring occurred and somewhat better yields were obtained by carrying out the reaction at 530–550° instead of at 600°. Saturation of the soda-lime with carbon dioxide, as recommended by Harries, was found to be unnecessary since no improvement in the yield resulted. Purification of the crude 1,2,3,4-tetrabromobutane was effected by crystallization from alcohol. Among the by-products isolated in small amounts were *trans*-2-bromo-2-butene, 1,2-dibromobutane, 2,3-dibromobutane, 1,3-dibromobutane, 1,4-dibromobutane, isomeric 1,2,3,4-tetrabromobutane and 1,1,4,4-tetrabromobutane.

In two of the experiments, crotyl chloride⁵ was employed instead of 2,3-dibromobutane. The reaction between crotyl chloride and soda lime occurred at lower temperatures and with less charring than in the case of 2,3-dibromobutane. Since, also, both the theoretical and actual yields of 1,2,3,4-tetrabromobutane were in excess of those obtained with 2,3-dibromobutane, the use of crotyl chloride is to be recommended. While the yield of 1,2,3,4-tetrabromobutane from either 2,3-dibromobutane or crotyl chloride is not entirely satisfactory, the apparatus required is simple and the procedure can be carried out by a non-technical laboratory assistant.

Experimental

Apparatus.—The apparatus consisted of a horizontal iron pipe 5 cm. in diameter and 152 cm. in length, wound with 13.7 meters of number 18 nichrome wire, imbedded in alundum cement, and covered with magnesia. Near one end a vertical section of pipe 2.5 × 20 cm. was welded to the furnace. This end was closed by a screw cap to which was welded a 13-mm. thermocouple well extending inward to the center of the furnace. The other end was fitted with a screw cap to which was attached a section of iron pipe 2.5 × 20 cm. The furnace was connected to a train consisting of two vertical Liebig ice condensers attached to 1-liter flasks (A) and (B) packed in ice, two gas-washing bottles (C) and (D) containing bromine also surrounded by ice, and a trap (E) packed in carbon dioxide snow.

Procedure.—The furnace was used on a 220 d.c. line with suitable resistance in the circuit for regulating the temperature. Preliminary runs had shown that at temperatures of 600° and above large amounts of tarry products were formed. In a typical run the furnace was packed with 914 g. of soda lime and heated to 530–550°. By means of a separatory funnel inserted in the vertical section of pipe, 600 g. of 2,3-dibromobutane was dropped into the furnace at such a rate that the escaping gas passed into the bromine rapidly but not violently. A slight pressure of nitrogen was maintained on the liquid in the separatory funnel to avoid the escape of gas bubbles through the liquid.

⁴ Adams, Kamm and Marvel, "University of Illinois Bulletin," 16, No. 43, 13 (1919).

⁵ Charon [*Ann. chim. phys.* [7] 17, 234 (1899)], prepared 1,3-butadiene by heating crotyl bromide and potassium formate in a sealed tube.

Approximately two hours were required for the addition of the bromide and an additional half hour for sweeping out the apparatus with a slow stream of nitrogen. When the run was completed, the excess bromine was distilled from the crystals of 1,2,3,4-tetrabromobutane, the latter filtered from the small amount of accompanying products, and washed with alcohol. Crystallization of the product from alcohol gave white plates or needles melting at approximately 112°. A second crystallization from alcohol gave the pure product melting at 116–117°. The yield of pure 1,2,3,4-tetrabromobutane per 600-g. run varied from 140 to 150 g. (13.5 to 14.5% of the theoretical). In two experiments with crotyl chloride, the yields at 550° and at 400° were, respectively, 16.4 and 19.3% of the theoretical.

Examination of Condensates (A) and (B).—The condensates (A) and (B) from eleven runs with 2,3-dibromobutane were combined and distilled. The gas liberated upon gentle warming of the mixture was absorbed in bromine and yielded 50 g. of 1,2,3,4-tetrabromobutane. Following the separation of 545 g. of water, fractional distillation of the residue yielded 45 g. of a liquid boiling at 90.5–92.5°, which from its boiling point and analysis appeared to be *trans*-2-bromo-2-butene. In addition, 50 g. of 2,3-dibromobutane, b. p. 157.5–159°, was collected as well as several intermediate fractions containing unsaturated compounds that were not purified and identified.

ANALYSES			
	Bromine calcd.	Bromine found	
<i>Trans</i> -2-bromo-2-butene	59.24	59.07	58.89
2,3-Dibromobutane	74.04	73.83	74.05

Examination of By-products Accompanying 1,2,3,4-Tetrabromobutane.—The liquid residues (790 g.) from six runs after filtration of the crude 1,2,3,4-tetrabromobutane were combined and distilled at atmospheric pressure. Separation into a volatile portion (345 g.) and a non-volatile portion (440 g.) was thereby effected. Fractional distillation of the volatile portion yielded 1,2-dibromobutane, 1,3-dibromobutane, 2,3-dibromobutane and 1,4-dibromobutane.

The non-volatile portion (300 g.) upon cooling in ice deposited crystals of 1,2,3,4-tetrabromobutane (106 g.). Fractional distillation under reduced pressure of the remaining liquid portion yielded 40 g. of 1,1,4,4-tetrabromobutane, and 42 g. of a tetrabromide which was probably the isomeric 1,2,3,4-tetrabromobutane. The table summarizes the by-products obtained.

TABLE I
SUMMARY OF BY-PRODUCTS OBTAINED

Compound	B. p., °C.	B. p. "Int. Crit. Tables"	Yield, g.	Analyses, %			
				Br calcd.	Br found		
1,2-Dibromobutane	165–166	166	59	74.04	74.09	74.23	
2,3-Dibromobutane	158–159	158	71	74.04	73.83	74.05	
1,3-Dibromobutane	173–175	174	15	74.04	74.14	74.20	
1,4-Dibromobutane	197–198 (dec.)	198 (dec.)	20	74.04	74.27	74.53	
1,1,4,4-Tetrabromo- butane	133 (1 mm.)	145 (10 mm.)	40	85.55	85.55	85.57	
Isomeric 1,2,3,4- tetrabromobutane	M. p. 38	M. p. 39	42	85.55	84.30	84.44	

Summary

1. Directions are given for the preparation of 1,2,3,4-tetrabromobutane from 2,3-dibromobutane and from crotyl chloride by passing these over

soda lime at elevated temperatures and subsequently absorbing the gaseous products in bromine.

2. The use of crotyl chloride for this purpose represents a more convenient procedure. Its use in preference to 2,3-dibromobutane is recommended because less charring occurs, the yields of 1,2,3,4-tetrabromobutane are better, and the temperature required for reaction is lower.

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THE SURFACE TENSION OF VARIOUS ALIPHATIC ACIDS
PREVIOUSLY STUDIED FOR BACTERICIDAL ACTION
TO MYCOBACTERIUM LEPRAE. XX¹

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During a research on compounds possessing antileprocidal properties, a large number of aliphatic acids were prepared, many of which were found to be bactericidal *in vitro* toward *Mycobacterium leprae*. Since the effective acids differed from each other rather widely in chemical structure, it was concluded that their bactericidal effectiveness was due to a certain combination of physical properties common to all of these acids, rather than to any specific chemical structure as was at first thought probable. A study of the physical properties was undertaken to determine whether any correlation could be found between one or more of these and the bactericidal effectiveness of the acids.

During the bacteriological work the acids were usually tested for their effectiveness in the form of their soluble salts. It was noticed that, in general, the aqueous solutions of the sodium salts of the most effective acids were very soapy, whereas those of the ineffective acids were not. This suggested that the ability to form soapy solutions might be one of the important properties related to the bactericidal action of the acids, and hence that a correlation might exist between the bactericidal action and the surface tension of solutions of the acids in the form of their salts. A further indication of such a correlation was the fact that the acids were bactericidally effective *in vitro* only in a form in which the surface tension reducing action became effective, that is, in the form of the soluble salts. The free acids appeared to be effective only in so far as they were able to form soluble salts with the buffer of the media. The ethyl esters unable to form sodium salts were entirely ineffective *in vitro*.

¹ For the last papers in this field see Stanley, Jay and Adams, *THIS JOURNAL*, 51, 1261 (1929); Ford and Adams, *ibid.*, 52, 1259 (1930); Browning, Woodrow and Adams, *ibid.*, 52, 1281 (1930); Armentdt and Adams, *ibid.*, 52, 1289 (1930); Greer and Adams, *ibid.*, 52, 2540 (1930). In these and in previous papers the bactericidal action of these compounds may be found.