[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Investigations on the Stereoisomerism of Unsaturated Compounds. III. The Preparation of the *cis* and *trans* 4-Octenes[1]

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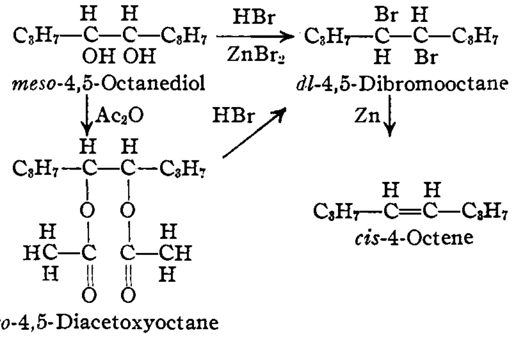
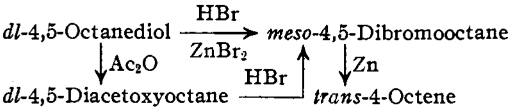
The *cis* and *trans* 4-octenes were prepared from the *dl*- and *meso*-4,5-dibromooctanes by the method of Gladstone and Tribe as modified by Wilkinson.[2] The 4,5-dibromooctanes were obtained from the *meso*- and *dl*-4,5-octanediols in two ways: (a) by the direct action of a reagent made by saturating an aqueous solution of zinc bromide with hydrogen bromide at 20° and (b) by the action of hydrobromic acid (saturated at 0°) on the diacetates of the *dl*- and *meso*-4,5-octanediols. The reactions involved are as follows





The dibromooctane derived from the meso glycol by the HBr–ZnBr$_2$ method was first throught to be a mixture of both *meso* and *dl* modifications since it boiled over a considerable range (83–98° at 4.5 mm.) and contained the correct quantity of bromine by Carius analysis. The fact that this bromide gave a mixture of octane and octene when treated with zinc and alcohol brought still more concern for it indicated that this reagent had caused a partial replacement of bromine by hydrogen. A reduction of this type had never been observed by the authors in dealing with similar dibromo compounds. However, when the dibromooctanes, prepared from the 4,5-diacetoxyoctanes, were treated with zinc in alcohol they produced only 4-octene. It was therefore considered unlikely that the octane mentioned above was formed by the reduction of the 4,5-dibromooctane in the previous sample. A discussion of these results with Professor H. J. Lucas of the California Institute of Technology brought out the fact that the HBr–ZnBr$_2$ treatment of the 2,3-butanediols gave very poor yields of dibromide. On the other hand, a ketone was formed as the result of a pinacolone rearrangement. In our case the rearrangement undoubtedly was followed by replacement of hydroxyl by bromine before ketone formation occurred, thus giving rise to 4,4-dibromooctane. In order to separate the mixture of 4,4- and 4,5-dibromooctanes the material was converted into a mixture of octene and octane which was then treated with bromine. The dibromide thus formed was separated from the octane by distillation. The product collected was identical with the *dl*-4,5-dibromooctane obtained from *meso*-4,5-octanediol by the diacetate method. The HBr–ZnBr$_2$ method proved to be the most satisfactory for the preparation of the dibromide from the *meso*-glycol and the HBr–diacetate method was best for the dibromide from the *dl*-glycol.[3]

The Configuration of Compounds Involved in the Synthesis of the *cis* and *trans*-4-Octenes.— Since previous work[4] on the reaction of stereoisomeric dibromides with potassium iodide in ethyl or methyl alcohols has shown that the meso isomer has the higher reaction rate, we have concluded from the specific second order reaction rate constants, k_2, for the 4,5-dibromooctanes,[5] that the value of $k_2 = 0.0996$ for the dibromide from the *meso*-4,5-octanediol shows that it is the *dl*-modification while the value of $k_2 = 0.1268$ for the dibromide from the *dl*-4,5-

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[2] Wilkinson, *J. Chem. Soc.*, 3057–62 (1931).

[3] This procedure was tried at the suggestion of Professor H. J. Lucas who had found that the 2,3-dibromobutanes could not be prepared by the HBr–ZnBr$_2$ method, Wilson and Lucas, THIS JOURNAL, **58**, 2396 (1936).

[4] (a) Van Duin, *Rec. trav. chim.*, **45**, 345–62 (1926); (b) Dillon, Young and Lucas, THIS JOURNAL, **52**, 1953–64 (1930).

[5] The details of this work, together with that on other dibromides, will be published elsewhere.

octanediol shows that it is the *meso* isomer. Obviously, a change in configuration has taken place in going from the glycols to the dibromides. A similar change in configuration has been observed in the case of the 2,3-butanediols by Lucas and Wilson.[3] It should be noted that only one of the asymmetric carbon atoms is involved in the inversion. If both asymmetric carbons were involved, the configuration change would not be apparent.

Fortunately, it is possible to confirm the conclusion that the *dl*-glycol gives the *meso*-dibromide. The *meso*-4,5-dibromooctane having the higher reaction rate should give the higher melting *trans*-4-octene and the *dl*-4,5-dibromooctane should give the lower melting *cis*-4-octene. The melting points of the octenes were found to be in agreement with the prediction.

Since the formation of the *meso*-4,5-dibromooctane from the *dl*-glycol involves two steps the question naturally arises: At which step does the change of configuration take place? A comparison of physical properties such as density and refractive index of the 4,5-diacetoxyoctanes with those of other known *meso*- and *dl*-stereoisomers leads to the conclusion that the *meso*-glycol gives the *meso*-diacetate. Work is now in progress in this Laboratory in which the dextrorotatory 4,5-octanediol is being converted into the diacetate and thence into the dibromooctane. The optical rotation is being followed at each step.

The Synthesis of Normal cis-trans-Alkenes

Although the preparation of alkene hydrocarbons has received much attention in the literature, it has been recognized only in recent years that the usual methods of preparation of olefins give rise to mixtures of structural as well as geometrical isomers.[6] In spite of the fact that this problem of dealing with mixtures has been partially solved by the development of (a) high precision fractionating columns and (b) synthetic methods which give rise to pure products, nevertheless, only the pure *cis*- and *trans*-butenes and pentenes are known.[7] Although several *cis*-isomers of the higher molecular weight normal alkenes have been prepared,[8] no pure *trans*-isomers have been obtained. Both the bromo-ether method[9] and the unsaturated acid method[7] of preparing alkenes give rise to pure structural isomers, but, unfortunately, fractionation of the intermediate or final products into their geometrical isomers becomes more difficult as the molecular weight increases in the homologous series. Schmitt and Boord[6a] have pointed out the fact that the apparent nonexistence of *cis–trans* isomerism in the case of 2-hexene and 3-hexene is due to the similarity in boiling point of the isomers. In the present paper it may be noted that the isomeric 4-octenes also have identical boiling points. The work of Lucas and Prater[7d] indicates that the unsaturated acid method has another disadvantage. The α-ethylcrotonic acids were prone to form equilibrium mixtures readily, a difficulty which was not encountered with the α-methylcrotonic acids.[7b] If this tendency to undergo stereomutation increased with molecular weight, it would be very difficult to isolate and keep the *cis* and *trans* acids necessary in the preparation of the isomeric normal hexenes and heptenes.

Although the action of zinc on dibromoalkanes has been used frequently in the purification of alkenes,[10] this procedure ordinarily has not been used in the preparation of pure *cis* and *trans* isomers since the usual source of the pure isomeric dibromides has been the hydrocarbons themselves. However, the method has been used in the synthesis of the polyene hydrocarbons[11] and now that it is feasible to obtain the pure *meso*- and *dl*-glycols[3,12] required for the preparation of the pure isomeric dibromides, this method should prove invaluable in synthesizing the *cis*- and *trans*-hexenes, heptenes, etc.

Work is now under way in this Laboratory on the preparation of the 3-hexenes and 3-heptenes from the corresponding glycols.

Experimental Part

***meso*- and *dl*-4,5-Octanediols.**—The pure *meso*- and *dl*-4,5-octanediols used in this work were prepared according to the method recently described.[12] The isomers had the

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(6) For a partial list of recent references on the preparation of olefins see: (a) Schmitt and Boord, This Journal, **54,** 753 (1932); (b) Young and Lucas, *ibid.*, **52,** 1964 (1930); (c) Weston and Hass, *ibid.*, **54,** 3337 (1932); (d) Young and Winstein, *ibid.*, **58,** 102 (1936); (e) Whitmore and co-workers, *ibid.*, (1932–1933).

(7) (a) Wislicenus, Talbot, Henze and Schmidt, *Ann.*, **313,** 207 (1900); (b) Young, Dillon, Lucas, This Journal, **51,** 2528 (1929); (c) Lauer and Stodola, *ibid.*, **56,** 1216 (1934); (d) Lucas and Prater, to be published soon.

(8) (a) Bourguel, *Bull. soc. chim.*, [4] **45,** 1067 (1929); (b) Bourguel and Gredy, *Compt. rend.*, **189,** 757 (1929); (c) Bourguel, Gredy and Piaux, *ibid.*, **195,** 129 (1932); (d) Gredy, *Bull. soc. chim.*, [5] **2,** 1029 (1935).

(9) Boord and co-workers, several papers in This Journal (1930–1933).

(10) For example, see Soday and Boord, *ibid.*, **55,** 3293 (1933).

(11) (a) Farmer, Laroia, Switz and Thorpe, *J. Chem. Soc.*, 2937 (1927); (b) Kuhn and Winterstein, *Helv. Chim. Acta*, **9,** 87 (1928).

(12) Young, Levanas and Jasaitis, This Journal, **58,** 2274 (1936).

following properties: *meso*-isomer, m. p. 123.5–124.5°; *dl*-isomer, m. p. 28°; b. p. (8 mm.) 109.8–110.0°; $n^{24.5}_{D}$ 1.4419.

The Reaction of Phosphorus Tribromide with the 4,5-Octanediols.—The most promising method of preparing the 4,5-dibromooctanes appeared to be the reaction of phosphorus tribromide on the dipropylglycols. However, when the general procedure described by Farmer and coworkers[11a] for the preparation of dibromohexadiene from divinylglycol was applied to the 4,5-octanediols, the yields were unsatisfactory.

Preparation of 4,5-Dibromooctanes, HBr–ZnBr$_2$ Method.—A mixture of 44 g. (0.3 mole) of *meso*-4,5-octanediol, 270 g. of 40% hydrobromic acid and 270 g. (1.2 moles) of zinc bromide contained in a 500-ml. round-bottomed flask was saturated with hydrogen bromide at 20°. The reaction mixture was allowed to stand overnight at this temperature. The flask was then attached to a reflux condenser and gradually warmed to 40° in a water-bath. This temperature was maintained during the day time over the next forty-eight to fifty-four hours but the flask was allowed to return to room temperature during the night. The dibromooctane, which gradually separated as an oil phase, amounted to 65–75% of the theoretical yield. At temperatures higher than 40° the reaction mixture had a tendency to become so dark that it was difficult to see the boundary between the dibromide and aqueous phases. The crude dibromide was then separated and washed several times with dilute sodium bicarbonate solution to neutralize the acid. The last washing was made with the bicarbonate solution since water occasionally formed a stable emulsion with the dibromide. The crude dibromide was then diluted with twice its volume of carbon tetrachloride and dried with anhydrous calcium chloride in the dark. Distillation of the dried solution through a 60-cm. Vigreux column gave 50 g. of dibromide, b. p. (4.5 mm.) 83–98°, n^{20}_{D} 1.4945. Per cent. bromine by Carius method, found: 58.24, 58.43; calcd.: for $C_8H_{16}Br_2$, 58.77. When the above method was used in preparing the dibromide from *dl*-4,5-octanediol, the reaction mixture became excessively colored and the yield of dibromooctane was less than half that obtained from the *meso*-glycol. Consequently, another procedure was adopted for preparing the dibromide from the *dl*-glycol (see HBr–diacetate method below).

Purification of *dl*-4,5-Dibromooctane from *meso*-4,5-Octanediol by the HBr–ZnBr$_2$ Method.—Since the dibromide obtained from the *meso*-4,5-octanediol described above had a boiling range of 15° and yet contained the required quantity of bromine for dibromooctane, it was at first thought to be a mixture of both the *dl*- and *meso*-dibromides. However, when it was treated with zinc in alcohol it gave a product which was approximately 50% unsaturated. (See discussion for explanation.) Consequently, several dibromide preparations were combined and purified as follows. The dibromide mixture was converted into a hydrocarbon mixture by the method of Gladstone and Tribe as modified by Wilkinson.[2] This hydrocarbon mixture was then placed in an all glass reaction flask kept at −15° and brominated by adding small amounts of bromine from time to time. At the end of the reaction, a slight excess of bromine was added to remove the last trace of unsaturated hydrocarbon. The product was washed immediately with dilute sodium bisulfite solution, sodium bicarbonate solution, and water, and then dried with anhydrous calcium chloride. Fractional distillation of the product at reduced pressures through a 70-cm. lagged, Vigreux column equipped with a Hopkins condenser in the Claisen-head gave crude octane, b. p. 123–125.5°, and *dl*-dibromooctane, b. p. (4.3 mm.) 84.3–85.8°. After further fractionation the *dl*-dibromooctane possessed the following properties: b. p. (4.3 mm.) 84.0–84.5°; d^{20}_{4} 1.4569; n^{20}_{D} 1.4981; MR found, 54.72; calcd. for $C_8H_{16}Br_2$, 54.38. Specific second order reaction rate constant with potassium iodide in methyl alcohol at 75°, $k_2 = 0.0996$. Per cent. bromine by Carius method, found, 58.46; calcd., 58.77.

Preparation of *meso*- and *dl*-Diacetoxyoctanes from *meso* and *dl*-4,5-Octanediols.—One-half mole quantities (73.0 g.) of either *meso*- or *dl*-4,5-octanediol, 2.5 moles (237 ml.) of acetic anhydride, and 1.5 moles (120 ml.) of pyridine were heated together under a reflux condenser at 85–95° for seven hours.[13] The mixture was then cooled, diluted with 600 ml. of water and saturated with sodium chloride. The upper layer which contained the diacetate was separated, diluted with an equal volume of ether and dried over anhydrous calcium chloride. After removal of the solvent the diacetate was fractionally distilled at reduced pressure through the column used in the distillation of the dibromooctanes. The yields of diacetates from both glycols averaged 75% of the theoretical. The products had the following properties: diacetate from *meso*-4,5-octanediol, b. p. (5.0 mm.) 100°; n^{20}_{D} 1.4252; d^{20}_{4} 0.9686; MR found, 60.89; calcd. for $C_{12}H_{22}O_4$, 60.84; equivalent weight, found: 114.5; calcd., 115.1; diacetate from *dl*-4,5-octanediol, b. p. (5.5 mm.) 110°; m. p. 26°; n^{20}_{D} 1.4283; d^{20}_{4} 0.9732; MR found, 60.88; calcd., 60.84; equivalent weight, found, 115.6; calcd., 115.1.

Preparation of 4,5-Dibromooctanes, HBr–Diacetate Method.—Three-tenths of a mole (69.0 g.) of the diacetate from either *meso*- or *dl*-4,5-octanediol and 210 g. of 48%, hydrobromic acid were placed in a 500-ml. glass-stoppered bottle and the mixture was saturated with hydrogen bromide at 0°. After the glass stopper was wired on, the bottle was placed in an ice box. After ten days the oil phase which formed was separated, washed, dried, distilled and purified as described above for the dibromide from the HBr–ZnBr$_2$ method. The yields of dibromooctanes from both of the diacetates averaged 55% of the theoretical before the final purification, in which there was usually a 90–95% recovery. The properties of the *meso*-4,5-dibromooctane obtained from the diacetate from the *dl*-4,5-octanediol are as follows: b. p. (4.3 mm.) 79–80.0°; n^{24}_{D} 1.4967; d^{20}_{4} 1.4525; MR found, 54.94; calcd. for $C_8H_{16}Br_2$, 54.38. Specific second order reaction rate constant with potassium iodide in methyl alcohol at 75°, $k_2 = 0.127$. Bromine by Carius method, found, 58.64; calcd., 58.77%.

Preparation of the *cis*- and *trans*-4-Octenes

(a) The Reaction of Phosphorus Triiodide with *meso*-4,5-octanediol.—Since phosphorus triiodide was used ef-

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[13] This procedure was adopted with the idea of obtaining good yields of a product free from the mono-acetate. Since the results were entirely satisfactory it was used throughout the work. It is possible that smaller quantities of acetic anhydride and a shorter period of heating would be just as acceptable.

fectively in the preparation of the diphenyl polyenes by Kuhn and Winterstein,[11b] this reagent, prepared from yellow phosphorus and iodine in carbon disulfide, was allowed to react with *meso*-4,5-octanediol (0.1 mole) according to their directions. The reaction mixture was then poured onto ice and the carbon disulfide layer was washed with dilute sodium thiosulfate solution, dilute sodium bicarbonate solution, and water, and dried over anhydrous calcium chloride. Distillation of the dried solution through a 60-cm. Vigreux column gave 6.3 g. of product, b. p. (47 mm.) 112–114°. This product did not react with bromine. It evolved iodine, however, when exposed to the light but not when heated at 75° for several hours. Molecular weight by Beckmann method in benzene, found, 240; calcd. for $C_8H_{17}I$, 240.1. It was therefore concluded that the product was probably 4-iodooctane formed by partial reduction. No further identification was made. There was no evidence for the formation of 4-octene by this method.

(b) **The Reaction of 4,5-Dibromooctane with Potassium Iodide in Aqueous Acetone at 75°.**—A mixture of 27.2 g. (0.1 mole) of dibromooctane from the HBr–$ZnBr_2$ method, and 40 ml. of saturated potassium iodide solution was made up to a volume of 250 ml. with acetone and sealed in a 500-ml. glass bulb. The bulb was placed in a thermostat at 75°. Every twelve hours the bulb was cooled rapidly to room temperature and opened. A 5-ml. portion of the reaction mixture was titrated against standard sodium thiosulfate solution and the bulb was resealed and placed in the thermostat again. After forty-eight hours the iodine concentration became constant. The yield of octene based on the iodine liberated was calculated to be 55.5%. It was concluded that this poor yield resulted from the establishment of an equilibrium between diiodooctane, iodine and octene and the method was discarded in favor of the zinc–copper couple method of preparing octene. However, since it was found later that the dibromooctane used in this work was actually a mixture of approximately equal quantities of 4,5-dibromooctane and of 4,4-dibromooctane which would not be expected to liberate iodine with potassium iodide, it is evident that the reaction to form octene actually went to completion and the method described above would be just as acceptable for the preparation of octene as the zinc–copper couple method.

(c) **The Reaction of *meso*- and *dl*-4,5-Dibromooctane with Zinc–Copper Couple in Alcohol.**—*cis* and *trans*-4-octenes were prepared from the pure *dl*- and *meso*-4,5-dibromooctanes by the method of Gladstone and Tribe as modified by Wilkinson.[9] After distillation at reduced pressure the octenes possessed the following properties:[14] *cis*-4-octene from *dl*-dibromooctane, m. p., approx. −115°; b. p. (97.4 mm.) 61.9°; b. p. (760 mm.) 20–20.5°; $n^{24.2}_D$ 1.4111; d^{20}_4 0.7186; MR found, 38.92; calcd., 38.46. Analysis for unsaturation, 100.5% *trans*-4-octene from *meso*-dibromooctane, m. p. approx. −105°; b. p. (103 mm.) 62.9 mm.; b. p. (760 mm.) 20–20.5°; $n^{24.2}_D$ 1.4110; d^{20}_4 0.7165; MR found, 39.03_4; calcd., 38.46. Analysis for unsaturation, 99.7%.

The authors are indebted to Dr. G. Ross Robertson of this Laboratory and Professor H. J. Lucas of the California Institute of Technology for their helpful suggestions.

Summary

1. *cis* and *trans*-4-octenes have been prepared from *dl*- and *meso*-4,5-dibromooctanes by the action of zinc–copper couple in alcohol. The direct action of phosphorus triiodide on *meso*-4,5-octanediol gives a monoiodooctane instead of the expected octene.

2. *meso*- and *dl*-4,5-dibromooctanes have been prepared: (a) from *meso*- and *dl*-4,5-octanediols by the action of a solution of zinc bromide, saturated with hydrogen bromide at 20°, on the glycols and (b) by the action of hydrobromic acid, saturated at 0°, on the 4,5-diacetoxyoctanes from the *meso*- and *dl*-4,5-octanediols.

3. A change of configuration occurs during the conversion of the glycols into the dibromooctanes. The *meso*-4,5-octanediol gives *dl*-4,5-dibromooctane and the *dl*-4,5-octanediol gives *meso*-4,5-dibromooctane.

4. 4,4-Dibromooctane is also formed from the *meso*-4,5-octanediol by the HBr–$ZnBr_2$ reagent, due to a pinacolone rearrangement.

5. The synthesis of the normal *cis–trans*-alkenes has been discussed.

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[14] The approximate melting points of the 4-octenes were obtained through the kindness of Mr. Saul Winstein, a graduate student at the California Institute of Technology. Due to the fact that the necessary equipment was not available, the exact melting points of the octenes have not yet been determined.