time (possible oxidation of the phenol), and with Ag(I) a silver mirror. When the solutions containing the *o*-aminophenol and the metallic cations were made alkaline with sodium hydroxide the following precipitation reactions were noted: greenish-gray with copper(II), reddish-orange with nickel(II), green with cobalt(II), dark red-brown with iron(III), gray with bismuth(III), gray-black with mercury(II) (probably metallic mercury), white precipitates (indistinguishable from blanks) with aluminum(III), magnesium(II), zinc, manganese(II), lead(II) and cadmium(II). The alkaline earth ions and chromium(III) also gave tests similar to their blanks.

Reaction of *o*-Aminobenzenethiol with Metals.—The following metals in sodium acetate–acetic acid medium gave well-defined precipitation reactions with *o*-aminobenzenethiol: copper(II), greenish-yellow; nickel(II), green; cobalt(II), reddish-brown; bismuth(III), bright orange; zinc(II), white; mercury(II), yellowish-white; silver(I), yellowish-white; cadmium(II), white; iron(III), yellow. No reaction was observed under these conditions with aluminum(III), manganese(II), chromium(III), magnesium(II), or the alkaline earth ions. The bismuth salt was rather soluble in chloroform. The other precipitates formed were only slightly soluble in chloroform. *o*-Aminobenzenethiol may be a useful reagent for bismuth.

Discussion of Results

It is noteworthy that both zinc and lead, the only metals for which it was possible to determine *o*-aminobenzenethiol chelate formation constants, formed complexes which are significantly more stable than those with aminophenol. The fact that this latter reagent is both stronger as a base and weaker as an acid than the aminobenzenethiol would tend to increase chelate stability, according to Calvin.[2] This is a good indication of the possibility that the strength of the bond of metal with sulfur is greater than that with oxygen because of the lower electronegativity of the sulfur and consequent increase in covalent character of the bond. The chelates formed by *o*-aminophenol are more stable than those of the β-diketones and substituted salicylaldehydes.[2] The difference in chelate stability here may involve the questions of ring size (5 *vs.* 6-membered rings), the amount of unsaturation in the reactive groupings, and steric factors but, nevertheless, is what would be expected since the electronegativity of nitrogen is lower than that of oxygen.

The order of decreasing stability of the complexes of *o*-aminophenol with respect to K_{av} is (Cu, Ni), Zn, Co, Pb. This is in general agreement with the results reported for sodium 5-salicylaldehyde sulfonate[3] and for salicylaldehyde.[4] The most pronounced difference with respect to the latter is the position of lead which is relatively more stable with salicylaldehyde. It should be noted however that this is not the case when the two stability sequences with respect to K_1 are compared. Apparently there is some steric interference associated with the introduction of a second aminophenol anion about the lead atom. From the titration curves of Fig. 1, it is possible to approximate the stability order of the complexes of *o*-aminobenzenethiol. The order found is (Cu, Ni), Pb, Zn, Co with the position of Co not entirely certain. This order is again similar to that found for salicylaldehyde. It is significant that the titration curves obtained for the copper and nickel complexes of *o*-aminobenzenethiol are nearly identical, indicating that the two complexes may be of nearly the same stability. It is hoped that the measurement of the stabilities of chelates of reagents similar to the thiol, *e.g.*, 8-mercaptoquinoline, will reveal more concerning the order of metals found here.

Acknowledgment.—The authors are grateful for a research grant from the Atomic Energy Commission.

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[2] M. Calvin and K. W. Wilson, THIS JOURNAL, **67**, 2003 (1945).

[3] M. Calvin and N. C. Melchior, *ibid.*, **70**, 3270 (1948).

[4] L. E. Maley and D. P. Mellor, *Australian J. Sci. Research*, **2**, 92 (1949).

PITTSBURGH 13, PENNA. RECEIVED AUGUST 21, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND PURDUE RESEARCH FOUNDATION, PURDUE UNIVERSITY]

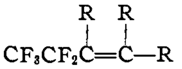
Alcohols and Olefins Containing the Pentafluoroethyl Group[1]

BY E. T. MCBEE, J. F. HIGGINS AND O. R. PIERCE

The reactions of pentafluoropropionaldehyde 3,3,4,4,4-pentafluoro-2-butanone and ethyl pentafluoropropionate with alkylmagnesium halides have been investigated as a means of preparing a series of pentafluoroethyl substituted ethylenes. Normal addition products were obtained as well as materials formed by the reduction of the aldehyde or ketone. Dehydration of the fluorinated alcohols produced was not accomplished with sulfuric acid, hot alumina or pyrolysis of the corresponding xanthate or acetate esters. However, phosphorus pentoxide was successfully employed.

Discussion

The preparation of a series of olefins containing the pentafluoroethyl group was undertaken because of interest in the effect of adjacent groups containing fluorine on the reactions of double bonds. It was planned to synthesize the six possible compounds of the type where R could be hydrogen or a methyl group.



$$\mathrm{CF_3CF_2\overset{R}{\overset{|}{C}}{=}\overset{R}{\overset{|}{C}}{-}R}$$

The reaction of pentafluoropropionaldehyde[2] with methyl, ethyl and isopropyl Grignard reagents and subsequent hydrolysis was expected to yield alcohols which on dehydration would give three of the desired olefins. Although methylmagnesium iodide gave the expected addition product, 3,3,4,4,4-pentafluoro-2-butanol, in 85% yield, ethylmagnesium iodide gave only 34% of the addition product, 1,1,1,2,2-pentafluoro-3-pentanol and 55% of the reduction product, pentafluoropropanol. When pentafluoropropionaldehyde was added to isopropylmagnesium iodide only the reduction product,

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[1] This paper represents part of a thesis submitted by J. F. Higgins to the Graduate School, Purdue University, in partial fulfillment of the requirements for the degree of Doctor of Philosophy. This work was supported by the Westinghouse Electric Corporation.

[2] D. R. Husted and A. H. Albrecht, 118th Meeting of The American Chemical Society, Chicago, Illinois, September, 1950.

pentafluoropropanol, was isolated. The occurrence of reduction, where very little steric effect exists, indicates that another factor, due to the presence of the fluorine, is operative.

Similar results were observed with ethyl and isopropyl Grignard reagents and 3,3,4,4,4-pentafluoro-2-butanone. With ethylmagnesium iodide, the addition product, 3-methyl-1,1,1,2,2-pentafluoro-3-pentanol, was obtained in 42% yield and the reduction product, 2,2,3,3,3-pentafluoropropanol, in 45% yield. Isopropyl Grignard yielded only the reduction product. Thus, only one of the desired alcohols, 3-methyl-1,1,1,2,2-pentafluoro-3-pentanol, could be obtained in this manner.

Since it appeared that extensive reduction could be postulated when the carbonyl compound contained several fluorine atoms adjacent to the carbonyl group, the ethyl ester of pentafluoropropionic acid was treated with isopropyl Grignard in the hope that the intermediate ketone would be reduced to the desired secondary alcohol, which could not be obtained from the same Grignard and pentafluoropropionaldehyde. This was achieved in 35% yield. Work by Campbell[3] has since shown that this reaction is general for esters of trifluoroacetic acid. The last alcohol necessary as an intermediate for the olefin series was easily prepared by the action of methylmagnesium iodide on ethyl 2,2,3,-3,3-pentafluoropropionate in 76% yield.

The difficulty of dehydration of these alcohols was such that only two olefins were actually prepared. 3,3,4,4,4-Pentafluoro-1-butene was formed by heating the secondary alcohol with phosphorus pentoxide at 275°. With the same reagent, 2-methyl-3,3,4,4,4-pentafluoro-1-butene was formed from the corresponding tertiary alcohol. The secondary alcohol, 3,3,4,4,4-pentafluoro-2-butanol, did not dehydrate when heated in concentrated sulfuric acid. Carbonization occurred when pyrolysis of its acetate was attempted at 450°, and no olefin was obtained. The methyl xanthate of the secondary alcohol did not decompose on refluxing at atmospheric pressure (b.p. 151–152°). Attempted dehydration of 3,3,4,4,4-pentafluoro-2-butanol over activated alumina at 300–500° failed to yield the olefin. Since products were formed which were not condensable in a Dry Ice cooled trap, it is probable that the molecule underwent cracking. The reaction tube was etched slightly in this experiment, indicating hydrogen fluoride formation. The strengthening of the carbon–oxygen bond in these fluorinated alcohols, as a result of the inductive effect of the fluorine atoms, is a possible explanation of the difficulty of dehydration. The dehydration of 1,1,-1,2,2-pentafluoro-3-pentanol gave an isomeric mixture of olefins, as shown by infrared spectra, which was difficultly separable. Consequently, dehydration of 4-methyl-1,1,1,2,2-pentafluoro-3-pentanol and 3-methyl-1,1,1,2,2-pentafluoro-3-pentanol was not conducted.

Addition of bromine to the olefins proceeded slowly. In the case of 2-methyl-3,3,4,4,4-pentafluoro-1-butene, only 43% of the theoretical amount of bromine was absorbed in 48 hours. After 20 days in a sealed tube, in the presence of light, 3,3,4,4,4-pentafluoro-1-butene absorbed only 50% of the theoretical amount of bromine.

Solid derivatives were prepared for the primary and secondary alcohols; however, none could be made from the tertiary alcohols. A modified procedure was necessary to obtain derivatives for the primary and secondary alcohols. A further investigation of the reducing action of Grignard reagents on fluorinated aldehydes is in progress.

Physical constants, analytical data and reaction yields are summarized in Table I.

Experimental

Equipment.—Rectification of liquids boiling above 20° was accomplished using a Todd Precise Fractionation apparatus rated at 30–50 theoretical plates depending on the type packing, glass helices or wire spiral, employed. Liquids boiling below room temperature were rectified using a vacuum-jacketed column packed with a Podbielniak-type wire spiral. The fractions collected as pure compounds possessed a boiling range of 0.0–0.2°.

Pentafluoropropionaldehyde.—The method used comprised the lithium aluminum hydride reduction of pentafluoropropionic acid.[4] Three-quarters of a mole of the hydride was used per mole of acid reduced and in general, two moles of acid were reduced in each preparation. The yields of aldehyde varied from 40–49% and that of the accompanying 2,2,3,3,3-pentafluoropropanol from 40–50%.

The Reaction of Pentafluoropropionaldehyde with Ethyl Grignard Reagent.—A Grignard reagent was prepared in ether solution from 28.8 g. (1.2 moles) of magnesium and 187.2 g. (1.2 moles) of ethyl iodide. The apparatus used was a three-necked flask equipped with stirrer, dropping funnel and reflux condenser. After the formation of the Grignard reagent appeared complete, as evidenced by solution of most of the magnesium used, 139 g. (0.93 mole) of pentafluoropropionaldehyde was passed into the flask by allowing the trap containing the aldehyde to warm up, and admitting it to the flask just over the surface of the ether by means of an inlet tube. This tube was attached in place of the dropping funnel after the Grignard reagent had formed. Before the aldehyde was admitted a Dry Ice cooled trap was attached to the condenser. When all the aldehyde had been added, the liquid in the flask was stirred an hour and then hydrolyzed by pouring over cracked ice and acidifying with 10% sulfuric acid. The ether layer was washed with a solution of sodium bisulfite to remove iodine and dried over Drierite. The ether layer was rectified to yield 2,2,3,3,3-pentafluoropropanol and 1,1,1,2,2-pentafluoro-3-pentanol.

The Reaction of Isopropyl Grignard with Pentafluoropropionaldehyde.—Eighty grams (0.54 mole) of pentafluoropropionaldehyde was passed into a solution of 0.7 mole of isopropylmagnesium bromide in ether. (The apparatus was the same as that used for the reaction of ethyl Grignard with the aldehyde.) When all the aldehyde had been added, stirring was continued for 30 minutes. Then the mixture was poured on ice, the precipitate hydrolyzed with 25% sulfuric acid, and the ether layer separated. After drying over Drierite the ether was removed and the remaining liquid rectified. The liquid collected was 2,2,3,3,3-pentafluoropropanol.

The Reaction of Pentafluoropropionaldehyde with Methyl Grignard.—Thirty-eight and one-half grams of aldehyde polymer (0.26 mole) was vaporized into an ether solution of methylmagnesium iodide (0.33 mole). The temperature rose until the ether refluxed for a short time. After refluxing the mixture for one hour, it was cooled to room temperature, poured on ice and the precipitate dissolved with 25% sulfuric acid. The ether layer was dried and rectified. Thirty-six grams of 3,3,4,4,4-pentafluoro-2-butanol was obtained.

Ethyl Pentafluoropropionate.—One mole (164 g.) of pentafluoropropionic acid was added to 110 g. (1.12 moles) of concentrated sulfuric acid in a 500-ml. flask. Fifty grams of ethanol (1.09 moles) was added through the condenser. Heat developed immediately and the mixture turned milky. Refluxing was continued by heating overnight. On cooling,

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(3) K. N. Campbell, J. O. Knobloch and B. K. Campbell, THIS JOURNAL, **72**, 4380 (1950).

(4) D. R. Husted and A. H. Albrecht, ref. 2.

TABLE I

NEW COMPOUNDS

Compound	Yield, %	B.p., °C.	$n^{20}D$	$d^{20}{}_4{}^b$	Analyses,[c] % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
$CF_3CF_2\underset{\mathrm{OH}}{\underset{\vert}{CH}}-CH_3$	85	85	1.3126	1.406	29.26	29.42	3.04	3.14
$CF_3CF_2\underset{\mathrm{OH}}{\underset{\vert}{CH}}CH_2-CH_3$	33.6	98	1.3280	1.329	33.70	33.82	3.93	4.19
$CF_3CF_2\underset{\mathrm{OH}}{\underset{\vert}{CH}}-\overset{\mathrm{CH_3}}{\overset{\vert}{CH}}-CH_3$	35	109	1.3425	1.289	37.50	37.20	4.52	4.68
$CF_3CF_2\underset{\mathrm{OH}}{\underset{\vert}{\overset{\mathrm{CH_3}}{\overset{\vert}{C}}}}-CH_2CH_3$	41.6	109	1.3460	1.251	37.50	37.30	4.58	4.84
$CF_3CF_2\underset{\mathrm{OH}}{\underset{\vert}{\overset{\mathrm{CH_3}}{\overset{\vert}{C}}}}-CH_3$	76	90	1.3292	1.240	33.70	33.58	3.85	3.93
$CF_3CF_2CO_2CH_2CH_3$	80	73	<1.3000	1.289	31.24	31.02	2.80	2.60
$CF_3CF_2\overset{\mathrm{O}}{\overset{\Vert}{C}}-CH_3$	67	40	<1.3000	1.284	29.62	29.55	1.85	1.87
$CF_3CF_2\underset{\mathrm{O_2CCH_3}}{\underset{\vert}{CH}}CH_3$	65	96	1.3220	1.299	34.95	34.72	3.39	3.55
$CF_3CF_2\underset{\mathrm{OCS_2CH_3}}{\underset{\vert}{CH}}CH_3$	50	41[a]	1.4157	1.387	28.34	28.50	2.75	2.74
$CF_3CF_2-\overset{\mathrm{CH_3}}{\overset{\vert}{C}}=CH_2$	65	30	<1.3000	1.184[d]	37.50	37.42	3.12	3.28
$CF_3CF_2\underset{\mathrm{Br}}{\underset{\vert}{CH}}-CH_2Br$	50	123	1.4060	1.1994	15.68	15.59	0.98	0.94
$CF_3CF_2-\overset{\mathrm{CH_3}}{\overset{\vert}{C}}BrCH_2Br$	43	135	1.4168	1.955	18.75	81.88	1.56	1.56

[a] 6 mm. [b] Densities by Mrs. Margaret Turner. [c] Analyses by Galbraith Laboratories. [d] At 3.0°.

TABLE II

DERIVATIVES

Compound	Derivative	M.p., °C.	Nitrogen,[a] % Calcd.	Nitrogen,[a] % Found
$CF_3C\ {}_2\underset{\mathrm{O}}{\underset{\Vert}{C}}\ H$	2,4-Dinitrophenylhydrazone	128.5–129.0	17.07	17.02
$CF_3CF_2\underset{\mathrm{O}}{\underset{\Vert}{C}}CH_3$	2,4-Dinitrophenylhydrazone	101-101.5	16.37	16.52
$CF_3CF_2CH_2OH$[b]	3,5-Dinitrobenzoate	96–96.5	8.13	8.28
$CF_3CF_2\underset{\mathrm{OH}}{\underset{\vert}{CH}}CH_3$	3,5-Dinitrobenzoate	61.5–62.0	7.82	7.87
$CF_3CF_2\underset{\mathrm{OH}}{\underset{\vert}{CH}}-CH_2-CH_3$	3,5-Dinitrobenzoate	65–65.5	7.58	7.73

[a] Nitrogen analyses by Miss H. D'Agostino. [b] This compound, b.p. 80°, has been prepared by Minnesota Mining and Manufacturing Company.

two layers appeared. The upper, clear organic layer was washed with water and sodium carbonate solution, dried for 24 hours, and rectified from phosphorus pentoxide.

2-Methyl-3,3,4,4,4-pentafluoro-2-butanol.—Ninety-six grams (0.5 mole) of ethyl pentafluoropropionate was added over a period of two hours to an ether solution of methyl Grignard reagent, prepared from 14.4 g. (0.6 mole) of magnesium and 85.2 g. (0.6 mole) of methyl iodide. The apparatus used was a three-necked 500-ml. flask equipped with stirrer, dropping funnel and reflux condenser. After the ester was added, the mixture was hydrolyzed with sulfuric acid (25%), the ether layer separated, dried over Drierite and rectified.

4-Methyl-1,1,1,2,2-pentafluoro-3-pentanol.—Isopropyl bromide (85 g., 0.7 mole), was added to 16.8 g. (0.7 mole) of magnesium in 125 ml. of anhydrous ether in a three-necked 500-ml. flask equipped with stirrer, dropping funnel and reflux condenser to which was attached a Dry Ice cooled trap. When all the magnesium had dissolved, 57.7 g. (0.3 mole) of ethyl pentafluoropropionate was added dropwise with stirring. After addition was completed (2 hr.), the mixture was stirred for three hours more. It was then hydrolyzed with a saturated solution of ammonium chloride. The aqueous layer was extracted with ether and the combined ether layers dried with Drierite. Rectification yielded 20 g. of 4-methyl-1,1,1,2,2-pentafluoro-3-pentanol. The material collected in the cooled trap during the reaction was identified as propylene.

3,3,4,4,4-Pentafluoro-2-butanone.—One hundred-eighty grams of sodium dichromate was dissolved in 300 ml. of water and 240 g. of concentrated sulfuric acid was added. This oxidizing mixture was added through a dropping funnel to 129 g. (0.78 mole) of 3,3,4,4,4-pentafluoro-2-butanol dissolved in 200 ml. of glacial acetic acid. Fifteen minutes was taken for the addition. The temperature rose to approximately 60° and the mixture was then allowed to cool to room temperature. The reaction mixture, now dark green in color, was then rectified to recover the ketone.

The Reaction of Ethyl Grignard with 3,3,4,4,4-Pentafluoro-2-butanone.—Eighty grams (0.49 mole) of 3,3,4,4,4-pentafluoro-2-butanone was added dropwise to an ether solution of ethyl Grignard reagent, prepared from 0.6 mole of ethyl iodide and 0.6 mole of magnesium. The reaction flask was cooled in an ice-bath. When all the ketone had been added the mixture was hydrolyzed by pouring over cracked ice and adding dilute (10%) sulfuric acid. After drying, the ether layer was rectified yielding 3-methyl-1,1,1,2,2-pentafluoro-3-pentanol and 3,3,4,4,4-pentafluoro-2-butanol.

The Reaction of Isopropyl Grignard with 3,3,4,4,4-Pentafluoro-2-butanone.—Twenty-four grams of 3,3,4,4,4-pentafluoro-2-butanone was added to an ether solution of isopropyl Grignard reagent, prepared from 0.2 mole of isopropyl iodide and 0.2 mole of magnesium. After addition was completed the hydrolysis was accomplished by pouring over cracked ice and dilute sulfuric acid (25%). The ether layer was dried and rectified. A yield of 54% of the reduction product 3,3,4,4,4-pentafluoro-2-butanol was obtained

2-Methyl-3,3,4,4,4-pentafluoro-1-butene.—Phosphorus pentoxide (15 g., 0.11 mole) was added to a three-necked 200-ml. flask with dropping funnel and a reflux condenser attached. Forty grams (0.22 mole) of 2-methyl-3,3,4,4,4-pentafluoro-2-butanol was added through the dropping funnel. Reaction was slow at first but vigorous when heating was begun. A liquid b.p. 30–70° was collected which smelled only slightly of the initial alcohol. Rectification yielded the desired olefin.

3,3,4,4,4-Pentafluoro-1-butene.—Twenty-five grams of 3,3,4,4,4-pentafluoro-2-butanol was added to 10 g. (0.07 mole) of phosphorus pentoxide in a 200-ml. flask with attached condenser and Dry Ice cooled trap.

The alcohol was added through the condenser. On addition the mixture sputtered and fumed and heat was evolved. Heating was continued for three hours and the material in the flask turned dark and viscous. Fifteen grams of material was collected in the Dry Ice cooled trap and rectified in a low temperature Podbielniak column to give the olefin.

1,2-Dibromo-2-methyl-3,3,4,4,4-pentafluorobutane.—Seventeen grams (0.10 mole) of 2-methyl-3,3,4,4,4-pentafluoro-1-butene was added slowly dropwise to 16 g. (0.10 mole) of bromine dissolved in 50 ml. of carbon tetrachloride. A three-necked flask, with dropping funnel and condenser attached, was used. At first the flask was cooled in ice, but since no decolorization of the bromine solution was apparent, the flask was allowed to warm up and illuminated by a 100-watt lamp bulb. After 24 hours the bromine color still remained. The solution was washed with sodium bisulfite solution and rectified to yield the dibromo derivative.

1,2-Dibromo-3,3,4,4,4-pentafluorobutane.—Twenty grams of 3,3,4,4,4-pentafluoro-1-butene (0.13 mole) was distilled into a cooled Carius tube containing a solution of 64 g. of bromine (0.4 mole) in 50 ml. of carbon tetrachloride. After sealing, the mixture was allowed to warm to room temperature and illuminated by a 100-watt lamp bulb for 20 days. The tube was opened and the excess bromine removed with sodium bisulfite. After drying over Drierite the solution was rectified to give the dibromo derivative.

3,3,4,4,4-Pentafluoro-2-butyl Acetate.—An excess of acetic anhydride was added to 46 g. (0.25 mole) of 3,3,4,4,4-pentafluoro-2-butanol and refluxed overnight. Water was added to separate the acetic acid and the alcohol. The mixture was warmed to destroy the excess of anhydride, and the lower organic layer was washed with water several times, dried and rectified to obtain the acetate.

Methyl Xanthate of 3,3,4,4,4-Pentafluoro-2-butanol.—Sixty-seven and one-half grams of 3,3,4,4,4-pentafluoro-2-butanol (0.4 mole) was added to 500 ml. of anhydrous diethyl ether and 50 ml. of carbon tetrachloride in a two-liter flask equipped with stirrer, dropping funnel and reflux condenser. Seventeen grams of sodium hydroxide (0.42 mole) was pulverized and added to the solution which was refluxed for three hours. Carbon disulfide (30.4 g., 0.4 mole) was then added and the mixture refluxed for four hours. Methyl iodide (56.8 g., 0.4 mole) was added dropwise and the mixture refluxed for 12 hours. The liquid was decanted from the solids, the low boiling constituents removed by distillation and the remaining liquid distilled under reduced pressure.

Preparation of Derivatives.—Known procedures were used for the preparation of the derivatives listed in Table II.

LAFAYETTE, INDIANA RECEIVED AUGUST 29, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF BIOCHEMISTRY, QUEEN'S UNIVERSITY]

2-Octadecenoic Acid. II. Preparation of the 2,3-Epoxystearic Acids and the Configurational Relationships between the 2,3-Epoxy-, Bromoacetoxy- and Dihydroxystearic Acids

BY GORDON S. MYERS[1]

The reaction scheme described by Swern, to correlate the configurations of the compounds formed in the conversion of oleic and elaidic acids (*cis*- and *trans*-9-octadecenoic acids, respectively) to the 9,10-dihydroxystearic acids, through the intermediate epoxy and chlorohydroxy compounds, has been used to correlate the stereochemical relationships involved in the conversion of *cis*- and *trans*-2-octadecenoic acids to the 2,3-dihydroxystearic acids, both by direct hydroxylation and by way of the intermediate bromoacetoxy and oxirane compounds. Positions have been assigned to the bromine and acetoxy groups in three 2,3(3,2)-bromoacetoxystearic acids, the preparations of which were recorded in a previous publication. The following new compounds have been described: 2,3-epoxystearic acid (m.p. 87.5–88°), 2,3-epoxystearic acid (m.p. 90.5–91°), 3,2-bromohydroxystearic acid (m.p. 83–83.3°) and its ethyl ester, and ethyl 3,2-bromoacetoxystearate (m.p. 40.5–41°).

The stereochemical relationships involved in the conversion of *cis*- and *trans*-9-octadecenoic acids to the 9,10-dihydroxystearic acids, by the way of the intermediate epoxy and chlorohydroxy compounds, have been studied by King[2] and also by Atherton and Hilditch.[3] More recently, Swern[4] has suggested a scheme, differing on several points with those proposed by the former, which correlates the configurational relationships involved. It was of interest to extend this mechanism scheme to correlate the stereochemical relationships of the 2,3-epoxy-, bromoacetoxy- and dihydroxystearic acid derivatives of the 2-octadecenoic acids; the latter, unlike oleic and elaidic acids, having the carbon–carbon unsaturation adjacent to the carboxyl group.

The 2,3(3,2)-bromoacetoxystearic acid melting at 57° (I), which was obtained by reaction of the high-melting 2,3-dihydroxystearic acid isomer (m.p. 126°) with hydrogen bromide in acetic acid,[5] has been converted with dilute alkali to 2,3-epoxystearic acid melting at 87.5° (II). Although this epoxide was difficult to hydrolyze in hot dilute sulfuric acid, the oxirane ring could be opened readily by acetylation with acetic acid containing a catalytic amount of sulfuric acid. The diacetoxystearic acid so obtained (not isolated) was saponified to the low-melting 2,3-dihydroxystearic acid isomer (m.p. 107°). Both the 2,3-bromoacetoxystearic acid

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[1] Ayerst, McKenna & Harrison Ltd., Montreal.

[2] G. King, *J. Chem. Soc.*, **387** (1942).

[3] D. Atherton and T. P. Hilditch, *ibid.*, 204 (1943).

[4] D. Swern, THIS JOURNAL, **70**, 1235 (1948).

[5] G. S. Myers, *ibid.*, **73**, 2100 (1951).