AN IMPROVED PREPARATION OF ω-HYDROXY ALIPHATIC ACIDS AND THEIR ESTERS¹

D. G. M. DIAPER AND D. L. MITCHELL²

ABSTRACT

Reductive cleavage of the ozonides of aliphatic acids and their esters by sodium borohydride or by hydrogenation produces ω -hydroxy aliphatic acids and ω -hydroxy aliphatic esters, respectively, in high yields.

INTRODUCTION

ω-Difunctional aliphatic compounds have found much employment in the synthesis of higher aliphatic compounds. Among these, substances having two different terminal functions are the most favored, and probably the most important reagents for chain extension are the esters of the ω -halogeno acids. These compounds, in various chainlengths, were required for condensation with malonic ester derivatives in the preparation of branched alkanedioic acids (1, 2, 3, 4) in this laboratory. With the exception of those members of the series of very short chain-length, only one ω -bromo acid, 11-bromoundecanoic, is easily available and this substance is best prepared by the peroxidecatalyzed addition of hydrogen bromide to 10-undecenoic acid (5). The latter compound is unique among the terminal unsaturated acids in that it is available in quantity and this method of preparation cannot be regarded as a method of general applicability. Use of the more common unsaturated acids with non-terminal olefinic linkages as starting materials for the preparation of ω -hydroxy acids and ω -bromo acids was first explored by Adams (6, 7), who ozonized the esters and isolated ω -aldehydo esters. These compounds were then reduced to give the esters of the ω -hydroxy acids. A practical difficulty in preparations of this type is the inevitable oxidation of a portion of the aldehydo ester to the half ester of the corresponding dicarboxylic acid. Contamination of intermediates with substances in the dicarboxylic acid series is undesirable as such compounds are usually high melting and insoluble and therefore difficult to remove. It is desirable, therefore, to obviate the sensitive aldehyde intermediate by exploitation of the new metal hydride reagents (8) and by selective reductive cleavage of the ozonide-ester prepare the hydroxy ester without isolation of the aldehyde. A similar observation on the preparation of primary alcohols by the borohydride cleavage of ozonides appeared while this work was in progress (9).

We have compared the high-pressure hydrogenolysis of certain ozonides with their reductive cleavage by sodium borohydride and the results are summarized in Table I. Yields of hydroxy ester were found to be superior when the borohydride was used and the products were also of higher purity as indicated by a narrow boiling range and ease of crystallization of the phenylurethane. When the scale of the preparation was increased, the yield by borohydride cleavage remained the same but the yield by high-pressure hydrogenation diminished. Sodium borohydride is still an expensive reagent and it may therefore be more economical to use the hydrogenation method on a large scale.

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Olefinic substrate	Product isolated	Yield	
		$\frac{-}{\text{Method } (a)^*}$	Method (b)
10-Undecenoic acid (undecylenic acid)	10-Hydroxydecanoic acid	91	56
Ethyl 10-undecenoate	Ethyl 10-hydroxydecanoate	94	71
9,12-Octadecadienoic acid (linoleic acid)	9-Hydroxynonanoic acid	42	_
cis-9-Octadecenoic acid (oleic acid)	9-Hydroxynonanoic acid	50	-
trans-9-Octadecenoic acid (elaidic acid)	9-Hydroxynonanoic acid	74	_
Methyl 9,12-octadecadienoate	Methyl 9-hydroxynonanoate	78	78
Ethyl 9.12-octadecadienoate	Ethyl 9-hydroxynonanoate	74	66
Methyl 9-octadecenoate (methyl oleate)	Methyl 9-hydroxynonanoate	88	66
Isopropyl 9-octadecenoate (+)-12-Hydroxy-9-octadecenoic acid	Isopropyl 9-hydroxynonanoate	70.5	
(ricinoleic acid)	(–)-Nonane-1,3-diol	72	

TABLE I

*Method (a) by sodium borohydride reduction, method (b) by Raney nickel catalyzed hydrogenation.

The working solvent employed for ozonizations has customarily been chloroform, carbon tetrachloride, acetic acid, ethyl acetate, or light petroleum. We have found absolute methanol, ethanol, and isopropanol to be convenient solvents and have used sodium borohydride in the same solvent, thus performing the ozonization and reductive cleavage in one sequence. The alcohol chosen as a solvent for the ozonolysis of an ester was that corresponding to its alkyl radical for it was found that transesterification took place if a different alcohol was employed. Presumably the basic environment of the borohydride reduction step made this transesterification possible.

A limitation on the use of methanol as a solvent is the rapid decomposition of sodium borohydride in this solvent. This can be obviated by reversing the usual order of addition and employing solid borohydride in place of an alcoholic solution.

It may be seen that 9-hydroxynonanoic acid may be obtained either from oleic acid or from linoleic acid. Using the former starting material, difficulties were encountered in freeing the hydroxy acid from the concomitant nonan-1-ol either by the method of Sousa and Bluhm (8) or by the steam-distillation method here described. When linoleic acid is the starting material, the other cleavage products are of lower molecular weight and therefore more easily removed.

10-Hydroxydecanoic acid was obtained in two ways from 10-undecenoic acid. The direct ozonization-borohydride method gives good yields and a high degree of purity. In the second method, undecenoic acid was esterified and reduced by the Bouveault-Blanc process, giving 10-undecen-1-ol without saturation or migration of the olefinic linkage. The acetate of the latter was then ozonized and the aldehyde thus obtained was oxidized to the corresponding acid, 10-acetoxydecanoic acid. This was then saponified. In the first method the carboxylic acid function of the starting material is retained and in the second it becomes the primary alcohol function of the end product.

The structure of (+)-ricinoleic acid as 12-hydroxy-9-octadecenoic acid (10) and most likely possessing the D-configuration (11) has been established by degradation studies (12, 13) and by synthesis (14, 15, 16). Early ozonolysis experiments performed on ricinoleic acid produced 3-hydroxy-nonanoic and nonanedioic acids and the corresponding aldehydes, which were characterized by the formation of crystalline derivatives (17, 18). These experiments supported the Goldsobel formula. We have found that sodium borohydride reduction of the ozonide of (+)-ricinoleic acid formed a hitherto unknown laevorotatory diol with boiling point, refractive index, and infrared spectrum very similar to those of racemic (\pm) -nonane-1,3-diol. The latter compound was synthesized by a

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Reformatsky condensation of *n*-heptanal and ethyl bromoacetate followed by lithium aluminum hydride reduction of the intermediate ethyl 3-hydroxynonanoate which was not isolated. Although racemic (\pm) -nonane-1,3-diol formed a crystalline mono-*N*-phenyl-carbamate and bis-*N*-phenylcarbamate, attempts to form these crystalline derivatives from the optically active isomer were unsuccessful.

EXPERIMENTAL

Melting points were uncorrected. Infrared spectra were determined on 5% solutions in chloroform. Hydrogenations were carried out in a high-pressure autoclave equipped with a stirrer.*

10-Hydroxydecanoic Acid by the Sodium Borohydride Reduction Method

A stream of ozonized oxygen was bubbled through a solution of 10-undecenoic acid (undecylenic acid, b.p. 176–178° C/23 mm, 39.7 g) in absolute methanol (40 ml) at 0° C until an aliquot test portion no longer decolorized a dilute solution of bromine in a glacial acetic acid. The ozonide solution was then added dropwise to an ice-cold solution of sodium hydroxide (12.5 g) and sodium borohydride (17g) in 50% aqueous ethanol (300 ml). A gentle evolution of hydrogen resulted and stirring was continued at room temperature for at least 10 hours. The methanol and ethanol were removed by distillation under reduced pressure and at a bath temperature of 40° C or less, and the alkaline aqueous solution was then added dropwise with stirring to an excess of ice-cold dilute hydrochloric acid (1.5 liters). The precipitated 10-hydroxydecanoic acid was collected by suction filtration, washed thoroughly with portions of ice-cold water, and dried under reduced pressure to constant weight (37.0 g, 91%). The yield was not reduced when the scale of the experiment was doubled. Recrystallization twice from benzene gave a product of constant melting point, 77° C, and mixed melting point 75.5–77° C (lit. 75.5–76.5° C (19)).

10-Hydroxydecanoic Acid by the Pressure Hydrogenolysis Method

A solution of the ozonide from 10-undecenoic acid (37.4 g) in ethanol was hydrogenated at room temperature and 2000 p.s.i. for 3 hours using Raney nickel W-2 catalyst (20). The temperature was increased to $130-150^{\circ}$ C and the hydrogenation was continued a further 5 hours. The product was isolated by solvent removal, conversion to the sodium salt, and precipitation by pouring the alkaline solution into ice-cold dilute hydrochloric acid. The slightly syrupy crude product (33.6 g) was recrystallized from benzene – light petroleum to give a product (21.4 g, 56%) with a melting point of 75° C.

Ethyl 10-Hydroxydecanoate

The ozonide from ethyl 10-undecenoate (ethyl undecylenate) (204 g) in absolute ethanol (200 ml) was prepared according to the above method. The solution was added to sodium borohydride (60 g) in absolute ethanol (300 ml) as before and allowed to stand for 24 hours in a loosely stoppered flask at 5° C. After removal of most of the ethanol under reduced pressure, the product was taken up in ether (1500 ml), washed with acid and alkali in the usual manner, and dried. The product (197 g, 94%) distilled at 114–115° C/0.07 mm and crystallized in the refrigerator (m.p. 15° C, thermometer immersed), $n_{\rm 24}^{24}$ 1.4460.

Reduction of the ozonide from methyl 10-undecenoate (24.9 g) with a cold (3%)

*Superpressure Division of American Instrument Company, Inc., Silver Springs, Maryland, U.S.A. †A test for ozonide (i.e. starch iodide paper) and a safety shield are recommended for this distillation. In a preliminary experiment, when the borohydride reduction step was acidified after 5 minutes of reduction, the isolated crude product decomposed explosively during distillation presumably due to unreduced ozonide present.

Can. J. Chem. Downloaded from www.nrcresearchpress.com by 141.114.238.19 on 11/09/14 For personal use only. ethanolic solution of sodium borohydride (9 g) for 30 hours produced ethyl 10-hydroxydecanoate (22.2 g, 82%). The derived N-phenylcarbamate had a melting point and a mixed melting point of $52-54^{\circ}$ C.

The derived *N*-phenylcarbamate of ethyl 10-hydroxydecanoate melted at $52-54^{\circ}$ C after two recrystallizations from heptane. The ethyl ester of 10-hydroxydecanoic acid was prepared; it formed a *N*-phenylcarbamate of melting point $52-54^{\circ}$ C and mixed melting point $52-54^{\circ}$ C. Both specimens gave an identical infrared absorption spectrum. Anal. Calc. for C₁₉H₂₉O₄N: C, 68.1; H, 8.7; N, 4.2. Found: C, 67.4; H, 8.8; N, 4.3.

Ethyl 10-hydroxydecanoate was also prepared from ethyl 10-undecenoate (25.2 g) by the ozonolysis-hydrogenation method described above. The product (18.4 g, 71%) was purified by two distillations and had a boiling point of 106–108° C/0.04 mm and $n_{\rm p}^{22}$ 1.4410.

Large-scale experiments (ca. 100 g of ozonide) produced a less pure product boiling over a 10° C range in yields of 40 to 66%.

The derived N-phenylcarbamate (m.p. $52-54^{\circ}$ C) was prepared but did not crystallize readily.

9-Hydroxynonanoic .1cid

The ozonide from linoleic acid* (50 g) in absolute ethanol (100 ml) was added dropwise to an aqueous alcoholic solution (1:1, 100 ml) of sodium hydroxide (20 g) and sodium borohydride (15 g). The solution was stirred for 48 hours, and it was acidified and extracted with ether (3×200 ml). The ethereal extracts were steam distilled until most of the alcohols had been removed. The product was recovered by ether extraction, was crystallized from benzene – light petroleum (13 g, 42%) and had a melting point of 43–45° C. Recrystallization from ethyl acetate raised the melting point to 50–51° C [lit. m.p. $53–54^{\circ}$ C (corr.) (6), and m.p. $51–51.5^{\circ}$ C (21)].

When the above procedure was carried out with oleic and elaidic acids, crude 9-hydroxynonanoic acid was obtained in 50% and 74% yields, respectively. The product obtained from oleic acid was difficult to purify by crystallization. Poor yields and resinous products in the ozonization of oleic acid and its esters have been attributed to excessive temperatures of ozonization (22).

Methyl 9-Hydroxynonanoate

Methyl oleate (20.6 g) in methanol (200 ml) was ozonized as described above. To minimize the borohydride-methanol reaction, however, the order of addition was reversed, the borohydride (9 g) being added in 0.5-g portions during 5 hours. Distillation at 0.1 mm produced two fractions: (a) b.p. 80–100° C (7.2 g) (72%), $n_{\rm D}^{22}$ 1.4340 (lit. for nonan-1-ol, $n_{\rm D}^{20}$ 1.4338 (23)); (b) b.p. 103–109° C/0.1 mm, 11.75 g (88%), $n_{\rm D}^{21}$ 1.4433. The derived *N*-phenylcarbamate melted at 53–54° C and had a mixed melting point of 53.5–55.5° C [lit. methyl 9-hydroxynonanoate *N*-phenylcarbamate 53–54° C (6)].

Methyl 9-hydroxynonanoate was also prepared from methyl oleate by the ozonizationhydrogenation technique and from methyl linoleate by the borohydride and catalytic hydrogenation methods. The yields are listed in Table I. Examination of the forerun (b.p. $80-105^{\circ}$ C/0.2 mm) from the latter preparation by gas-liquid chromatography indicated the presence of at least two components.

Ethyl 9-Hydroxynonanoate

The ozonide from ethyl linoleate (b.p. 148–153° C/0.4 mm, $n_{\rm D}^{20}$ 1.4573) (50.15 g) in absolute ethanol was divided equally into two parts. One part was reduced by the dropwise

*Nutritional Biochemicals Corporation, Cleveland 28, Ohio (linoleic acid, 75%).

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addition to sodium borohydride in absolute ethanol and gave a product (12.1 g, 73%) with a boiling point of 110-118° C/0.2 mm and $n_{\rm D}^{21}$ 1.4441. Anal. Calc. for C₁₁H₂₂O₃: C, 65.3; H, 11.0. Found: C, 65.6; H, 11.0. The second portion was reduced by the two-stage hydrogenation described above and gave a product (10.8 g, 65%) with a boiling point of 110-120° C/0.1 mm and $n_{\rm D}^{18}$ 1.4415.

When both specimens were warmed with one-half by weight of phenyl isocyanate, the derived N-phenylcarbamate was obtained (m.p. 59–60° C). Recrystallization from 2,2,4-trimethylpentane – benzene raised the melting point to 60–61.5° C. Anal. Calc. for $C_{18}H_{27}O_4N: C, 67.3; H, 8.5; N, 4.5$. Found: C, 67.5; H, 8.6; N, 4.7.

Isopropyl 9-Hydroxynonanoate

The ozonide from isopropyl oleate (b.p. $225-227^{\circ}$ C/22 mm, $n_{\rm D}^{22}$ 1.4491) (32 g) was reduced with sodium borohydride in isopropanol according to the above method. The product (15 g, 70.5%) had a boiling point of 116–120° C/0.4 mm and $n_{\rm D}^{25.5}$ 1.4399. Anal. Calc. for C₁₂H₂₄O₃: C, 66.6; H, 11.2. Found: C, 66.8; H, 11.3.

The derived N-phenylcarbamate was recrystallized from 2,2,4-trimethylpentane and had a melting point of 66.5–68° C. Anal. Calc. for $C_{19}H_{29}O_4N$: C, 68.1; H, 8.7; N, 4.2. Found: C, 68.3; H, 8.8; N, 4.1.

10-Hydroxydecanoic Acid by the Ozonization of the Acetate of 10-Undecen-1-ol

10-Undecen-1-ol (from ethyl undecylenate by Bouveault-Blanc reduction (24)) was acetylated by the acetic anhydride method of Chuit (25) in 83-86% yield. The acetate was ozonized in 20-g portions in acetic acid (40 cc) and the ozonide was reduced by the zinc dust – ether – water method of Adams (7). 10-Acetoxydecanal was obtained as a pungent oil, b.p. 113-118° C/0.3 mm, and was not purified before oxidation. Its oxime was obtained from ethanol as colorless prisms, m.p. 67.5-68° C. Anal. Calc. for $C_{12}H_{23}O_3N$: C, 63.0; H, 10.0; N, 6.1. Found: C, 63.0; H, 9.85; N, 5.7. Its *p*-nitrophenyl-hydrazone was obtained as yellow needles from aqueous acetic acid, m.p. 118° C. Anal. Calc. for $C_{18}H_{27}O_4N_3$: C, 61.9; H, 7.75; N, 12.0. Found: C, 61.8; H, 7.65; N, 11.5.

Oxidation of 10-acetoxydecanal (15 g) to the corresponding acid was performed in 65-68% yield by passing air through a rapidly stirred mixture of the aldehyde with 200 cc of 20% aqueous manganous chloride solution. The product, 10-acetoxydecanoic acid, isolated with the aid of ether and potassium carbonate, melted at $34.5-36^{\circ}$ C and a 15-30% recovery of unchanged aldehyde was effected. By saponification of 10-acetoxydecanoic acid in aqueous-ethanolic potassium hydroxide, 10-hydroxydecanoic acid, m.p. $74-74.5^{\circ}$, was obtained and found to be identical with the product described above.

(-)-Nonane-1,3-diol

After ozonolysis of ricinoleic acid (26 g, $[\alpha]_D^{22}$ 16.3°, c, 14.1, ethanol) and sodium borohydride reduction in aqueous alkaline methanol as described above, there was obtained an aqueous solution which was extracted with ether. From the extract of non-acidic products was obtained (-)-nonane-1,3-diol (10.0 g, 72%, b.p. 98–105°/0.1 mm). Two further distillations produced a colorless liquid with a boiling point of 97–99° C/0.1 mm, $n_D^{23.5}$ 1.4506, $[\alpha]_D^{22}$ -6.0° (neat liquid), and $[\alpha]_D^{22}$ -6.3° (c, 10, ethanol).

The product had an infrared absorption spectrum identical with that of (\pm) -nonane-1,3-diol prepared by the method described below. The infrared spectrum was also very similar to those of octan-1-ol and octan-2-ol with the major difference being a stronger absorption at the stretching frequency due to hydroxyl (3420 cm⁻¹).

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Examination of the product by gas-liquid chromatography indicated the presence of at least three impurities which constituted approximately 6% of the product. This material was fractionally distilled in a Piros-Glover microdistillation still* with seven fractions being collected with $n_{\rm D}^{25}$ 1.4483, 1.4490, 1.4495, 1.4500, 1.4500, 1.4500, 1.4500, respectively. Anal. Calc. for C₉H₂₀O₂: C, 67.45; H, 12.6. Found: C, 67.3; H, 12.6.

Attempts to prepare the N-phenylcarbamate from fractions 4, 5, 6, or 7 resulted in the formation of a gel. This phenomenon of gel formation was also observed on the slightly impure product.

(\pm) -Nonane-1,3-diol

n-Heptanal (57 g) and ethyl 1-bromoacetate (83.5 g) were condensed by a standard Reformatsky procedure. After the reaction was complete, the solution was filtered from the unreacted zinc granules and the volume of the filtrate was adjusted to 300 ml with dry ether. The ethereal solution was added dropwise to an ethereal suspension of excess lithium aluminum hydride at such a rate that a gentle reflux was maintained. After the solution had been heated under reflux for an additional 2 hours, the residual lithium aluminum hydride was decomposed by the addition of excess ethyl acetate (100 ml). After 0.5 hour, water was added and a voluminous froth developed. The froth was suspended in ether and cold dilute hydrochloric acid was added until the solution was strongly acidic. The ethereal layer was separated and washed successively with water, sodium hydrogen carbonate solution, and water. Evaporation of the ether left an oil which distilled at 97–99° C/0.04 mm (42 g, 52.5%). A second distillation gave a main fraction with a boiling point of 97–99° C/0.1 mm and $n_{\rm p}^{23}$ 1.4512. Anal. Calc. for $C_9H_{20}O_2$: C, 67.45; H, 12.6. Found: C, 67.4; H, 12.6.

Bis-N-phenylcarbamate of (\pm) -Nonane-1,3-diol

Equal weights of phenyl isocyanate and (\pm) -nonane-1,3-diol were warmed to 60° C for 8 hours. Upon cooling, the product crystallized and was recrystallized from 2,2,4-trimethylpentane, m.p. 85–85.5° C. Examination of the infrared spectrum indicated the absence of the hydroxyl band. Anal. Calc. for C₂₃H₃₀O₄N₂: C, 69.3; H, 7.6; N, 7.0. Found: C, 69.3; H, 7.7; N, 7.2.

N-Phenylcarbamate of (\pm) -Nonane-1,3-diol

(±)-Nonane-1,3-diol was mixed with one-half by weight of phenyl isocyanate and the solution was stored at room temperature for 6 hours, then gently warmed to 60° C for 0.5 hour. The crystalline product was recrystallized from 2,2,4-trimethylpentane and melted at 83–84.5° C. The melting point was depressed upon admixture with the above bis-*N*-phenylcarbamate. Examination of the infrared spectrum indicated the presence of bands due to OH and NH stretching frequencies in approximately equal intensity. Anal. Calc. for $C_{16}H_{25}O_3N$: C, 68.8; H, 9.0; N, 5.0. Found: C, 69.0; H, 9.1; N, 5.0.

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