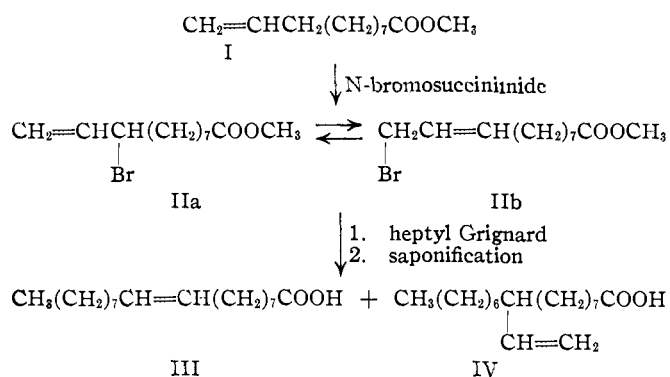


[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF HARVARD UNIVERSITY AND BOSTON UNIVERSITY]

Preparation of Unsaturated Fatty Acids

BY WALTER J. GENSLER, ELEANOR M. BEHRMANN AND GEORGE R. THOMAS

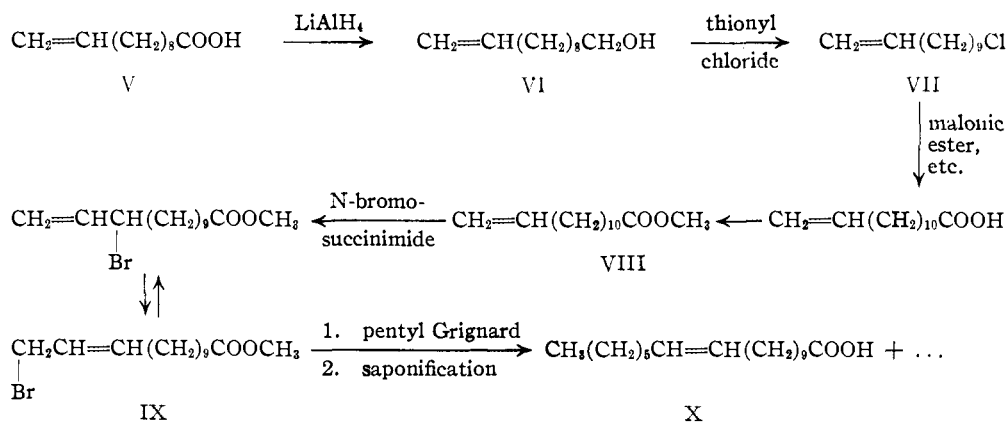
Bromination of terminally unsaturated straight-chain compounds with N-bromosuccinimide leads to monosubstituted allyl bromides.¹ Such compounds, on coupling with Grignard reagents, furnish either normal or branched-chain coupling products, or mixtures of both forms.² In the present work, the Grignard coupling of two allylic bromination products, methyl 9(11)-bromo-10(9)-undecenoate (II, a and b), and methyl 11(13)-bromo-12(11)-tridecenoate (IX), has been in-



vestigated. Interest in these compounds lies in the possibility that, if linear coupling were to predominate, a convenient method for the synthesis of long-chain unsaturated fatty acids would be at hand. The subject of this paper is the preparation, by this method, of elaidic (III, *trans*) and of vaccenic acid (X).

The starting materials for the two syntheses are, respectively, methyl 10-undecenoate (I), which is available, and methyl 12-tridecenoate (VIII), which was prepared in 60% over-all yield from 10-undecenoic acid (V) by modifying a series of reactions (V-VIII) previously reported.³

Bromination of the terminally unsaturated esters was carried out essentially according to the



directions of Ziegler and co-workers.⁴ The use of benzoyl peroxide⁵ offered no advantage. Much difficulty was encountered in the purification of the brominated products—particularly because of evolution of hydrogen bromide during the distillations. After many trials, procedures were developed which enabled bromoester II to be obtained in approximately 40% yield and bromoester IX to be obtained in 25–35% yield. The infrared absorption curves for the pure bromoester, II, showed maxima at 10.05 and 10.95 μ and at 10.3 μ . Inasmuch as absorption at these points is characteristic of mono and *sym*-disubstituted ethylenes, respectively,⁶ both the primary allylic bromide, IIb (a disubstituted ethylene), and the secondary allylic bromide, IIa (a monosubstituted ethylene), were present.

In the coupling of methyl bromoundecenoate with heptylmagnesium bromide, the Grignard reagent was added to the bromo compound. The coupling product was saponified, and elaidic acid (III, *trans*) was isolated from the alkali-soluble fraction by low-temperature crystallization from acetone.^{7,8}

Recovery of elaidic acid was considered to be substantially complete inasmuch as the material remaining in the acetone mother-liquor showed no sign of the characteristic elaidic acid absorption-

peak at 10.3 μ .⁶ The elaidic acid was hydrogenated to stearic acid, and also was hydroxylated to the "high melting" 9,10-dihydroxystearic acid.

Attempts at purification of the acetone-soluble acids revealed the presence of a persistent bromine-

(1) See Djerassi, *Chem. Revs.*, **43**, 271 (1948).

(2) For examples see Prévost and Daujat, *Bull. soc. chim.*, [4] **47**, 588 (1930); v. Braun and Schirmacher, *Ber.*, **56**, 538 (1923); Henne, Chanan and Turk, *This Journal*, **63**, 3474 (1941); Bateman and Cuneen, *J. Chem. Soc.*, 941 (1950).

(3) Chuit, *et al.*, *Helv. Chim. Acta*, **9**, 1074 (1926); **10**, 113 (1927); Tomecko and Adams, *This Journal*, **49**, 522 (1927); Buu-Hof and Cagniant, *Bull. soc. chim.*, [5] **9**, 107 (1942). In these papers the over-all yields from the eleven-carbon ester to the thirteen-carbon acid are given as no more than 40%.

(4) Ziegler, *et al.*, *Ann.*, **551**, 80 (1942).

(5) Schmid and Karrer, *Helv. Chim. Acta*, **29**, 573 (1946).

(6) The 10.3 μ peak is prominent in infrared absorption curves for *trans*-1,2-dialkylethylenes, but is absent in *cis*-1,2-dialkylethylenes and in vinyl compound. The vinyl compounds absorb strongly at 10.05 and 10.95 μ . See Thompson, *J. Chem. Soc.*, 328 (1948); VanZandt Williams, *Rev. Sci. Instruments*, **19**, 135 (1948).

(7) Brown, *Chem. Revs.*, **29**, 333 (1941).

(8) The lead salt procedure also was used, but was found to be far less satisfactory. See Cocks, Christian and Harding, *Analyst*, **56**, 368 (1931); Steger and Scheffers, *Rec. trav. chim.*, **46**, 492 (1927); Griffiths and Hilditch, *J. Chem. Soc.*, 2315 (1932).

containing compound⁹ which could be removed only after treatment with a solution of sodium in liquid ammonia.¹⁰ The halogen-free product finally obtained was a liquid mixture of octadecenoic acids. This was shown by the correct analysis and neutralization equivalent, as well as by the absorption of one mole of hydrogen. Separation of the components (IV, and *cis*-III or oleic acid) by low-temperature crystallization, by chromatography,¹¹ or by fractionation of the lithium salts¹² did not succeed, and accordingly the mixture itself was investigated.

That a vinyl compound was present in the mixture was indicated by strong absorption at 10.05 and 10.95 μ .⁶ This was confirmed by the formation of formaldehyde on ozonolysis. From the mode of synthesis the vinyl compound is considered to be 9-vinylpalmitic acid (IV). Evidence for the presence of oleic acid (III, *cis*) was obtained by hydrogenating the elaidic-free acids to a mixture of saturated acids from which stearic acid could be isolated. The liquid acid, which remained after all the stearic acid had been removed and which could be characterized as the *p*-bromoanilide, was taken as 9-ethylpalmitic acid. The weights of elaidic, stearic and 9-ethylpalmitic acid enabled the yield and composition of the coupling product to be estimated. It was found in this way that elaidic, oleic and 9-vinylpalmitic acids were present in the coupling product in the approximate ratio of 1:1:4, and that the total yield was 34%.

From the reaction of pentylmagnesium bromide and methyl bromotridecenoate (IX) there was obtained a mixture of unsaturated acids, from which vaccenic acid (X) could be isolated. This material was identical with vaccenic acid synthesized according to Ahmad, Bumpus and Strong.¹³ The infrared absorption curve was virtually identical with the curves reported for natural¹⁴ and for synthetic vaccenic acid.¹³

It is evident from the results obtained in the coupling reactions of the two bromoesters that, as a synthesis of straight-chain unsaturated fatty acids, the method leaves much to be desired. It is possible that the low over-all yield of coupling product is due to attack of the Grignard reagent on the ester grouping. In an attempt to eliminate this complication, brominated 11-chloro-1-undecene was used in place of the bromoester. The results of this work will be reported shortly.

Acknowledgment.—The authors wish to express their appreciation and thanks to Research Corporation for financial support in the form of Special Grants.

(9) Probably this is undecenoic acid carrying bromine at a vinyl position.

(10) Foster and Schreiber *THIS JOURNAL*, **70**, 2303 (1948); Cope and Bailey, *ibid.*, **70**, 2305 (1948); Hoff, Greenlee and Boord, Abstracts of Papers Presented at the American Chemical Society Meeting in San Francisco, March, 1949, page 7L.

(11) For references see Markley, "Fatty Acids," Interscience Publishers, Inc., New York, N. Y., 1947, p. 615.

(12) Armstrong and Hilditch, *J. Soc. Chem. Ind.*, **44**, 43T (1925); Griffiths and Hilditch, *ref. 8*; Noller and Bannerot, *THIS JOURNAL*, **56**, 1563 (1934).

(13) Ahmad, Bumpus and Strong, *ibid.*, **70**, 3391 (1948). We are indebted to Dr. Strong for the mixed melting point determination of the two synthetic acids.

(14) Rao and Daubert, *ibid.*, **70**, 1102 (1948).

Experimental

Bromination of Methyl 10-Undecenoate.⁴—A mixture of 119.0 g. (0.60 mole) of methyl 10-undecenoate (b.p. 91–92° (2 mm.); n_D^{25} 1.4372), 37.0 g. of 96.3% N-bromosuccinimide (0.20 mole) and 150 ml. of dry carbon tetrachloride was boiled under reflux for 1 hour. The tan-colored crystalline precipitate of succinimide was removed from the cooled reaction mixture by filtration, and was washed on the funnel with carbon tetrachloride. The recovery was 15.2 g. or 77% of the theoretical amount. After the solvent had been stripped from the filtrate, the residual material was diluted with 30–60° petroleum ether (200 ml.) and was held at 5° overnight.

The amber-colored liquid could be decanted from the mixture of crystalline and oily material (2.4 g.) which had separated. Removal of the petroleum ether solvent left an oily residue (167.4 g.) which, on distillation from a short-path, wide-bore still, was separated into a high and low-boiling fraction: (a) 81.9 g., b.p. 69–75° (0.2–0.35 mm.), n_D^{25} 1.4385; (b) 36.9 g., b.p. 86–108° (0.003–0.07 mm.), n_D^{25} 1.4715. Due to the evolution of hydrogen bromide, especially toward the end of the distillation, the pressure was observed to increase steadily. The material remaining in the distillation flask was a dark red oil (17.2 g.).

Fraction (b) was distilled through a short column until 7.4 g. of distillate (b.p. 79–119° (0.8–0.9 mm.), n_D^{25} 1.4493) had been collected. This low boiling fraction was combined with fraction (a). Petroleum ether was added, the resulting turbid solution was washed thoroughly with water, and was dried over magnesium sulfate. After removal of solvent, fractionation of the residual material afforded 80.1 g. of methyl 10-undecenoate (b.p. 79–83° (0.9–1.0 mm.), n_D^{25} 1.4373), and 3.9 g. of still-residue.

The carbon tetrachloride solution of this residue together with the remainder of fraction (b) was washed thoroughly with water to remove all traces of acid and of succinimide. Removal of carbon tetrachloride from the dry solution, and distillation of the residue through a short packed column afforded 23.6 g. of the desired product (b.p. 118–128° (0.7 mm.), n_D^{25} 1.4790) as a somewhat viscous straw-colored liquid. The percentage yield calculated either from the amount of methyl 10-undecenoate unrecovered, or from the amount of N-bromosuccinimide used, was 43%.

Anal. Calcd. for $C_{22}H_{42}O_2Br$: C, 51.99; H, 7.64. Found: C, 51.89; H, 7.59.

The index of refraction of the freshly distilled bromoester and that of the same material after it had been allowed to stand at room temperature for over 2 weeks were the same. Also, after the bromoester had been kept for three days, the infrared absorption curve was taken and was found to be identical with that of the freshly distilled material.

Coupling Reaction with Methyl Bromoundecenoate.—To a boiling solution of 12.0 g. (0.0433 mole) of bromoester in 40 ml. of dry ether was added 73.6 ml. of a 0.679-molar ethereal solution of heptylmagnesium bromide (0.050 mole).¹⁵ The addition required 30 minutes, after which time boiling was continued for another hour. The reaction mixture was then hydrolyzed with ice-water containing sulfuric acid, and the ethereal layer, after through washing with water, was dried over magnesium sulfate. Complete removal of solvent left a yellow oil.

In order to decompose unreacted allylic bromide, the oil was treated with 15 ml. of pyridine and heated on the steam-bath for 1 hour. The cooled pyridine solution was acidified with dilute sulfuric acid and extracted with 30–60° petroleum ether. Repeated washing of the petroleum ether solution with dilute sulfuric acid insured the removal of all acid-soluble material. Finally the solution was washed carefully with water, and dried over magnesium sulfate. The oil which remained after removal of the solvent was light amber in color and weighed 9.5 g.

Saponification of the ester coupling product was effected by boiling this oily fraction for 1 hour with sodium hydroxide in aqueous methyl alcohol. After separation of the non-saponifiable material by extracting the alkaline mixture with low-boiling petroleum ether, the aqueous methanolic solution was acidified with sulfuric acid and extracted

(15) The filtered Grignard solution was standardized by acid titration according to the directions of Gilman and co-workers, *ibid.*, **45**, 150 (1923).

thoroughly with low-boiling petroleum ether. The extract was washed free of mineral acid and was dried over sodium sulfate. The yellow oil (5.5 g.) obtained on removal of all solvent was partially solid at room temperature. It showed a positive Beilstein test for halogen, but gave no precipitate with silver nitrate-nitric acid in methanol.

Elaidic Acid.—Crystallization of this mixture from 55 ml. of absolute acetone at -20° afforded elaidic acid (0.95 g.) as a white powder melting (with faint preliminary sintering) at $42-44.5^{\circ}$. Attempts to obtain further quantities of elaidic acid from the material in the mother liquors failed. Recrystallization of the crude acid from 10 ml. of acetone produced a pure white crystalline powder (0.80 g.) melting sharply at $45-45.5^{\circ}$. Further crystallization did not change the melting point.

Anal. Calcd. for $C_{18}H_{34}O_2$: C, 76.54; H, 12.13; neut. equiv., 282.5. Found: C, 76.55; H, 12.02; neut. equiv., 282.

A mixture of this material with elaidic acid prepared from natural oleic acid¹⁶ melted at $45-45.5^{\circ}$. The infrared absorption curves for the two acids were identical. Quantitative hydrogenation of the synthetic acid resulted in the absorption of 1.01 moles of hydrogen, and gave rise to stearic acid (m.p. $69-71^{\circ}$) in near quantitative yield. Recrystallization brought the melting point to $70.5-71^{\circ}$; the melting point, on admixture of authentic stearic acid, was unchanged.

Hydroxylation of the synthetic elaidic acid with acetic acid-hydrogen peroxide according to the method of Scanlan and Swern¹⁷ converted the material to dihydroxystearic acid, m.p. $127-129^{\circ}$ (with preliminary sintering at 124°), in 80% yield. Purification by crystallization in 95% alcohol afforded a product which melted alone, or admixed with the dihydroxy acid obtained from natural oleic acid by permanganate hydroxylation,¹⁸ at $130-130.5^{\circ}$. The infrared absorption of the two samples of dihydroxystearic acids (taken as suspensions in mineral oil) differed slightly in intensity but was otherwise identical.

Low Melting Acids.—Removal of all acetone solvent from the elaidic acid mother liquors left an oily residue which showed a positive Beilstein test for halogen. Distillation failed to separate the halogen-containing contaminant, and analysis furnished carbon and hydrogen figures which were low. Further, the halogen could not be eliminated by treatment with the following reagents: hot aqueous alcoholic alkali, pyridine at 100° , zinc dust in boiling alcohol, or zinc dust in boiling acetic acid. Treatment with sodium in liquid ammonia,¹⁰ however, proved to be effective.

An ether solution of the liquid acids was added to a well-stirred solution of sodium in liquid ammonia (1.0 g. in 150 ml.). Stirring was continued for approximately 3 hours, during which time most of the ammonia evaporated. Fifty ml. of 95% alcohol followed by a portion of aqueous alcohol was then carefully added to the cooled mixture.

The resulting solution was warmed on the steam-bath to drive off the residual ammonia, and, after acidification with sulfuric acid, was extracted repeatedly with $30-60^{\circ}$ petroleum ether. The extract was washed free of sulfuric acid and then dried over sodium sulfate. Removal of all solvent furnished an oil which was distilled through a 2-inch Vigreux column. The fraction (3.3 g.) boiling at $154-157^{\circ}$ (0.22 mm.) was taken as the desired product. The water-white liquid (n_D^{25} 1.4560) showed a negative Beilstein test for halogen.

Anal. Calcd. for $C_{18}H_{34}O_2$: C, 76.54; H, 12.13; neut. equiv., 282.5. Found: C, 76.39; H, 12.12; neut. equiv., 282.

This material showed no sign of the characteristic elaidic acid absorption at 10.3μ , but did absorb strongly at 10.05μ and 10.95μ .

Ozonolysis of Low Melting Acids.—A stream of ozone in oxygen was bubbled through a solution of 0.38 g. of the liquid acids in 10 ml. of carbon tetrachloride held at 0° . The solvent was removed at room temperature first by distillation under reduced pressure and then by blowing a cur-

rent of air into the flask. The ozonide was reductively decomposed according to the method of Whitmore and Church,¹⁹ and the steam-volatile cleavage products were collected by distilling the aqueous mixture almost to dryness. After a small amount of insoluble oil had been removed from the distillate, the dihydromethylresorcinol derivative of formaldehyde was formed in the usual manner. The crystalline derivative weighed 0.09 g. and melted at $170-187^{\circ}$. Two crystallizations from methanol brought the melting point to $188-189^{\circ}$; the mixed melting point with an authentic sample was not depressed.

Hydrogenation of the Low-Melting Acids.—Quantitative hydrogenation resulted in the absorption of 1.01 moles of hydrogen. A larger run was made by hydrogenating 1.00 g. of the mixture in 25 ml. of glacial acetic acid over platinum until the absorption of hydrogen had ceased. The acetic acid was removed by distillation to yield a semi-solid residue. Two crops of stearic acid were obtained by cooling an alcoholic solution and then a methanolic solution of this material at ice-bath temperatures. After removal of non-volatile material by distillation in a notched test-tube, the stearic acid weighed 0.19 g. and melted (preliminary sintering) at $57-70^{\circ}$. Crystallization from absolute methanol afforded pure stearic acid (0.16 g.) in the form of thin platelets which melted alone or together with authentic stearic acid at $70-71^{\circ}$.

The material remaining in the mother liquors after separation of the two crops of stearic acid was distilled in a notched test-tube. The water-white product (0.70 g.) was converted directly to its *p*-bromoanilide derivative by way of the acid chloride.²⁰ The crude dry product weighed 1.05 g. (96%) and melted at $51-58^{\circ}$. The analytical sample, prepared by crystallizing the solid from acetone and from methanol, showed m.p. $58-59^{\circ}$.

Anal. Calcd. for $C_{24}H_{40}NOBr$: C, 65.73; H, 9.19. Found: C, 65.58; H, 8.81.

Methyl 12-Tridecenoate (VIII) from 10-Undecenoic Acid (V).—The lithium aluminum reduction of 10-undecenoic acid to 10-undecen-1-ol (VI) was carried out essentially according to the general procedure of Nystrom and Brown.²¹ The yield of undecenol, b.p. $140-142^{\circ}$ (18 mm.), was 95%. The alcohol was transformed (93% yield) to 11-chloro-1-undecene (VII), b.p. $105-107^{\circ}$ (6 mm.), by allowing the alcohol to react with warm thionyl chloride in the presence of small amounts of pyridine.²²

Anal. Calcd. for $C_{11}H_{21}Cl$: C, 70.2; H, 11.2. Found: C, 70.0; H, 11.2.

Boiling 11-chloro-1-undecene with sodiomalonic ester in alcohol containing 20 mole per cent. of potassium iodide afforded undecenylmalonic ester, b.p. $163-165^{\circ}$ (1.5-1.8 mm.), in 75% yield. The malonic acid, prepared from the ester in the usual manner, was decarboxylated at 170° , and the resulting 12-tridecenoic acid was converted first to the acid chloride and then to the methyl ester (VIII), b.p. $109-110^{\circ}$ (0.6-1.0 mm.).³

Bromination of Methyl 12-Tridecenoate.—A mixture of 19.95 g. (0.0883 mole) of methyl 12-tridecenoate, 16.4 g. of 96% N-bromosuccinimide and 100 ml. of carbon tetrachloride was boiled for 5.5 hours. Solids were removed from the cooled mixture by filtration and were washed on the funnel with carbon tetrachloride. After removal of solvent from the combined filtrates by distillation under reduced pressure, approximately 200 ml. of petroleum ether ($30-60^{\circ}$) was added, and the resulting turbid solution allowed to stand at room temperature.

The petroleum ether solution was decanted from the layer of oil and solids which had separated, and the oil-solid mixture rinsed with petroleum ether. The combined petroleum ether solutions were shaken with three portions of water, and then dried over magnesium sulfate. Removal of solvent left an oil which was distilled in a wide-bore short-path still. All material boiling below 173° (0.1-3.5 mm.) was collected. Toward the end of the distillation, the distillate, at first water-white, became slightly cloudy. Also vapors were noted in the still, and it was found impossible to keep the pressure down.

(16) The method of Griffiths and Hilditch (ref. 8) was employed in the conversion of methyl oleate to elaidic acid.

(17) Scanlan and Swern, *THIS JOURNAL*, **62**, 2305 (1940).

(18) See Hilditch, *J. Chem. Soc.*, 1828 (1926). We wish to thank Drs. A. F. McKay and Alfred R. Bader for their kindness in furnishing a sample of pure dihydroxystearic acid.

(19) Whitmore and Church, *THIS JOURNAL*, **54**, 3710 (1932).

(20) Cheronis and Entrikin, "Semimicro Qualitative Organic Analysis," Thomas Y. Crowell Co., New York, N. Y., 1947, p. 210.

(21) Nystrom and Brown, *THIS JOURNAL*, **69**, 2548 (1947).

(22) See Darzens, *Compt. rend.*, **152**, 1314 (1911).

The distillate was diluted with petroleum ether (30–60°), the solution washed with three portions of water, dried over magnesium sulfate, and distilled to remove solvent. The residual oil was fractionated using a short packed column. A fraction (6.7 g.) with b.p. 96–140° (0.5–0.8 mm.) was collected as crude recovered starting material, and two fractions (total of 12.5 g.) with b.p. 140–146° (0.8–0.9 mm.) and 126–130° (0.3 mm.) were taken as crude product. Fractionation of the recovered starting material afforded 5.4 g. of water-white methyl 12-tridecenoate, b.p. 99–100° (0.4 mm.) which showed an infrared absorption curve identical with that of the starting material. Fractionation of the higher boiling material through a 2-inch Vigreux column yielded (a) 2.5 g. of a straw-yellow liquid, b.p. 92–133° (0.25–0.35 mm.), n_D^{20} 1.4790, and (b) 6.8 g. (25%; corrected for recovered starting material, 35%) of yellow liquid, b.p. 133–136° (0.35–0.45 mm.), n_D^{20} 1.4804.

Anal. Calcd. for $C_{14}H_{24}O_2$: C, 55.08; H, 8.26. Found: (a) C, 62.32; H, 9.14; (b) C, 56.10; H, 8.21.

Further fractional distillation of these and other samples of brominated tridecenoic ester afforded no analytically pure product. Analysis of various fractions, with n_D^{20} ranging from 1.4796 to 1.4805, yielded C and H values of 55.52–56.63 and 7.97–8.42, respectively.

In every distillation, considerable amounts of non-volatile tar were left in the still. The distillates, originally yellow in color, gradually became darker and finally black. It was also noted that a petroleum ether insoluble oil developed on standing at room temperature.

Coupling Reaction with Methyl Bromotridecenoate.—Over a period of one hour, 42.4 ml. of 0.524 *N* ethereal pentylmagnesium bromide (0.0222 mole) was added to a boiling solution of 5.63 g. (0.0185 mole) of freshly distilled methyl bromotridecenoate in 20 ml. of absolute ether. After warming the mixture for an additional hour, it was poured over ice and dilute sulfuric acid. The organic material was taken up in ether, the ether extracts were washed with water and dried. Removal of ether solvent left 5.8 g. of residual oil.

This material was heated on the steam-bath with 6 ml. of pyridine for 1.5 hours. To the cooled deep-red mixture was added 100 ml. of ether followed by dilute sulfuric acid. The acid mixture was extracted thoroughly with ether, and the extract was washed first with dilute acid and then with water until neutral. After drying the solution (magnesium sulfate), it was boiled to remove solvent. The amber-col-

ored residue was then distilled in a small Claisen flask under reduced pressure.

To saponify the ester product, the distillate (3.0 g.) was boiled for one hour with a solution of 3 g. of sodium hydroxide in 45 ml. of 60% alcohol. The clear amber solution, after dilution with water and extraction with two portions of petroleum ether (30–60°), was acidified with dilute sulfuric acid and the organic acids extracted with petroleum ether. The petroleum ether solution was shaken with water until free of sulfuric acid and then dried with magnesium sulfate. Removal of solvent left 2.2 g. of a yellow oil.

Crystallization of this material from acetone at –15 to –20° afforded 0.43 g. of a white crystalline solid, m.p. 38–43.5° (preliminary sintering). Two further crystallizations from 5-ml. portions of acetone at –20° yielded 0.23 g. of vaccenic acid, m.p. 45–45.5° (sintering at 44°). A third crystallization brought the melting point to 45–45.5° (sintering at 44.5°).

Anal. Calcd. for $C_{18}H_{34}O_2$: C, 76.5; H, 12.1. Found: C, 76.7; H, 12.1.

A mixed melting point determination of this material with the synthetic vaccenic acid (m.p. 43–44°) prepared according to Ahmad, Bumpus and Strong¹² was carried out by Dr. Strong, who reported the first appearance of oily drops at 42.5°, and the sample completely liquid at 44°.

Infrared Absorption.—The infrared absorption curves were taken on a Baird infrared recording spectrophotometer which covered the range from 2–16 μ . Carbon tetrachloride solutions of approximately 2.5% by weight were used in a 0.1-mm. rock-salt cell.

Summary

Directions are given for the preparation of methyl bromoundecenoate and methyl bromotridecenoate by allylic bromination of the terminally unsaturated eleven-carbon and thirteen-carbon esters. The coupling of methyl bromoundecenoate with heptylmagnesium bromide yields a 1:1:4 mixture of elaidic, oleic and 9-vinylpalmitic acids. Coupling of methyl bromotridecenoate with pentylmagnesium bromide yields a mixture from which vaccenic acid may be isolated.

BOSTON, MASSACHUSETTS

RECEIVED JUNE 12, 1950

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF IOWA STATE COLLEGE]

Some Addition Reactions of Chalcones. II. The Preparation of Some γ -Ketosenelides

BY HENRY GILMAN AND LOUIS F. CASON

Incidental to some studies carried out in these laboratories¹ on the addition of unsymmetrical reagents to α,β -unsaturated ketones the reactions of selenols and benzeneseleninic acid with chalcones were investigated.

The addition of thiols and sulfinic acids to α,β -unsaturated compounds is well established.² However, similar reactions involving the selenium analogs have not been reported. By reason of the location of selenium and sulfur in the same periodic family it seemed probable that the course of addition of the selenols to chalcones would closely parallel that described for the corresponding sulfur compounds. In addition, it was of interest to explore the possibility of masking the extreme toxicity of the selenium atom in the effort to synthesize products of pharmacological value.

(1) Gilman and Cason, *THIS JOURNAL*, **72**, 3469 (1950).

(2) (a) Posner, *Ber.*, **34**, 1395 (1901); *ibid.*, **35**, 799 (1902); (b) Ruhemann, *J. Chem. Soc.*, **87**, 17, 461 (1905); (c) Nicolet, *THIS JOURNAL*, **53**, 3066 (1931); (d) *ibid.*, **57**, 1098 (1935); (e) Gilman and King, *ibid.*, **47**, 1136 (1935).

We found that aryl selenols add readily to chalcones in ethanol without the aid of a catalyst. The products were well-defined, sharp melting crystalline compounds which were obtained in yields varying from 44 to 80% (see Table I). No product resulted when the addition of benzeneselenol to an *o*-substituted chalcone, 2-chloro-4'-methoxychalcone, was attempted.

There is little doubt that the formation of these γ -ketosenelides takes place by the mechanism of 1,4-addition to the conjugated system as in the case of the formation of the corresponding ketosulfides.² However, in order to establish the conclusive proof of their structure, β -phenyl- β -(4-chlorobenzeneseleno)-propiofenone was prepared by an alternate method involving the alkylation of sodium *p*-chlorobenzeneselenoxide with β -phenyl- β -bromopropiofenone. The product obtained in this manner was identical (mixed m. p.) with that resulting from the addition of *p*-chlorobenzeneselenol to benzalacetophenone.