108.5°, mixed with the chromic acid (*or* permanganate) oxidation product of the dimer (*vide supra*), m. p. 107–108°.

6-Methoxy-3,4-dihydronaphthalene.—In the course of the above work, this material was obtained occasionally during distillation of 6-methoxy-α-tetralol, from hydrogenation of 6-methoxy-α-tetralone. The observation that the material in the pot was deep green when the decomposition occurred suggests that the irregularity was caused by the presence of a small amount of chromium salts in the ketone.

6-Methoxy-α-tetralone (9.0 g.) was hydrogenated in the usual way (*vide supra*). During distillation, decomposition occurred, and water appeared in the condenser: Fraction 1; 5.8 g., b. p. 110–118° (3 mm.); Fraction 2: 2.6 g. crystalline solid, m. p. 77–78°, b. p. 130–135° (3 mm.), mixed with 6-methoxy-α-tetralone, m. p. 77–78°. The low-boiling material was redistilled, 3.0 g., b. p. 107–111° (2.5 mm.); d^{30} 1.068; $n^{21}D$ 1.5825; M_R, 50.5. Calcd. for $C_{11}H_{12}O$, $4|^-$, 48.3, $\Delta M_R = 2.2$.

Anal. Calcd. for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 81.82; H, 7.53.

The physical constants may be compared with those of 6-methoxy-1,2,3,4-tetrahydronaphthalene [b. p. 105–106° (4 mm.), d^{19} 1.039, $n^{26.5}D$ 1.5441]. The absorption spectrum of the dihydro compound was measured in ethanol (Fig. 3), $\lambda_{max.} = 269$ mμ, log $\epsilon = 4.00$.

After shaking 2.8 g. of the material with 46% hydrobromic acid for twelve hours, a crystalline solid was obtained, which on crystallization from alcohol separated in lustrous white needles (1.72 g.), m. p. 70–72°. Recrystallized from alcohol, the m. p. was 75°; mixed with the dimer, m. p. 75°.

The dihydro compound also was obtained by the hydrolysis of 6-methoxy-1-acetoxytetralin with alcoholic sodium hydroxide.

Summary

The acid-catalyzed dehydration of 6-methoxy-1,2,3,4-tetrahydro-1-naphthol gives 6,6′-dimethoxy-1,2,3,3′,4,4′-hexahydro-1,2′-binaphthyl.

CAMBRIDGE, MASSACHUSETTS RECEIVED JANUARY 31, 1944

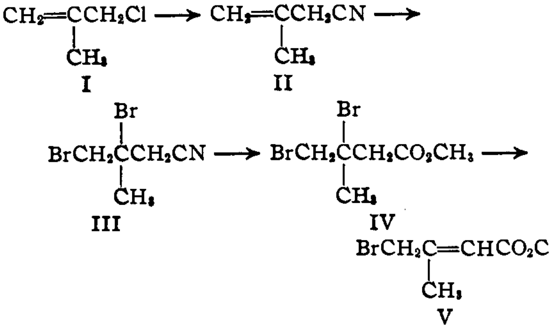
[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Reformatsky Condensations Involving Vinylogs of Haloacetic Esters. II.[1] Methyl γ-Bromosenecioate

BY REYNOLD C. FUSON AND PHILIP L. SOUTHWICK[2]

By the use of γ-halocrotonates in the Reformatsky reaction a synthetic route was found to polyene acids.[1] This method has now been extended to a β-methyl-γ-halocrotonate, methyl γ-bromosenecioate (V). The use of this new ester makes possible the extension of a carbon chain by an isoprene unit and thus opens the way for the synthesis of truly carotenoid chains.

After this work had been completed it was discovered that very similar results had been obtained by Ziegler, Schumann and Winkelmann.[3] One of the chief differences between our work and that of the German writers lies in the method of synthesis of the bromoester (V). The direct bromination of the senecioic ester[4] appears to be more convenient than our method which involved the conversion of methallyl chloride into methyl γ-bromosenecioate by the following scheme.



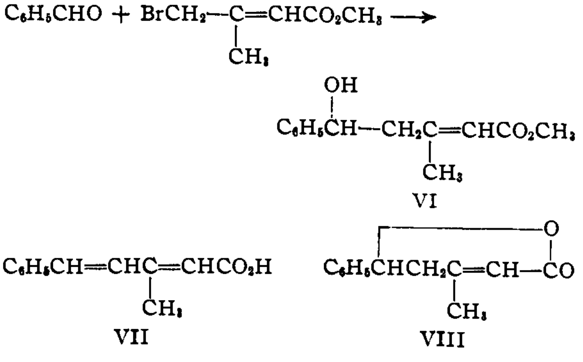
$$\underset{\text{I}}{CH_2{=}\underset{CH_3}{\underset{|}{C}}CH_2Cl} \longrightarrow \underset{\text{II}}{CH_2{=}\underset{CH_3}{\underset{|}{C}}CH_2CN} \longrightarrow$$

$$\underset{\text{III}}{BrCH_2\overset{Br}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}CH_2CN} \longrightarrow \underset{\text{IV}}{BrCH_2\overset{Br}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}CH_2CO_2CH_3} \longrightarrow$$

$$\underset{\text{V}}{BrCH_2\underset{CH_3}{\underset{|}{C}}{=}CHCO_2CH_3}$$

It was found that attempts to purify the ester obtained by this method were attended by very serious losses. For this reason the ester was used in a somewhat impure condition.

To determine whether the methyl γ-bromosenecioate could be condensed with carbonyl compounds by the Reformatsky method, a test run was made with benzaldehyde. The results were similar to those of Ziegler, Schumann and Winkelmann. The isolation and purification of the products presented difficulties. During the distillation and hydrolysis of the expected hydroxy ester (VI), decomposition occurred giving rise to a mixture of compounds. Chief of these were two isomeric unsaturated acids, evidently *cis-trans* forms of β-styrylcrotonic acid (VII). It is not clear which of these isomers corresponds to the product (m. p. 157°) described by Ziegler, Schumann and Winkelmann.



$$C_6H_5CHO + BrCH_2{-}\underset{CH_3}{\underset{|}{C}}{=}CHCO_2CH_3 \longrightarrow$$

$$\underset{\text{VI}}{C_6H_5\overset{OH}{\overset{|}{C}}H{-}CH_2\underset{CH_3}{\underset{|}{C}}{=}CHCO_2CH_3}$$

$$\underset{\text{VII}}{C_6H_5CH{=}CH\underset{CH_3}{\underset{|}{C}}{=}CHCO_2H}$$

VIII

A third product isomeric with the two acids appeared to be the corresponding lactone (VIII).

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[1] For the preceding paper see Fuson, Arnold and Cooke, THIS JOURNAL, **60**, 2272 (1938).

[2] Abbott Fellow, 1942–1943.

[3] Ziegler, Schumann and Winkelmann, *Ann.*, **551**, 120 (1942).

[4] Ziegler, Späth, Schaaf, Schumann and Winkelmann, *ibid.*, **551**, 80 (1942).

Experimental

Methallyl Cyanide.—The method of Tamele, Ott, Marple and Hearne[5] was used. From 422 g. of commercial cuprous cyanide and 418 g. of methallyl chloride there was obtained 285 g. (76%) of a water-white liquid boiling at 134.5–136.5°; n^{20}_{D} 1.4180.

Anal. Calcd. for C_5H_7N: C, 74.03; H, 8.70. Found: C, 74.28; H, 8.97.

In another run using 456 g. of cuprous cyanide and an initial 454 g. of methallyl chloride, more methallyl chloride was added until it no longer continued to react, as evidenced by vigorous refluxing of the mixture. An additional 160 cc. was required. By this means 349 g. of methallyl cyanide was obtained (an 86% yield based on the cuprous cyanide).

β,γ-Dibromoisovaleronitrile.—A solution of 200 g. of bromine in 200 cc. of dry chloroform was added dropwise to a stirred solution of 100 g. of methallyl cyanide in 400 cc. of dry chloroform. The mixture was cooled in a water-bath during the addition. When the solution ceased to absorb bromine, shortly before all of it had been added, the addition was stopped.

Removal of the solvent at temperatures not above 60° left 297 g. of crude dibromo nitrile. A portion of the heavy, yellow oil was distilled twice at reduced pressure. Distillation was accompanied by the evolution of hydrogen bromide, even when conducted at relatively low pressures. The product was a colorless oil, b. p. 89° (2–3 mm.), n^{20}_{D} 1.5308.

Anal. Calcd. for $C_5H_7NBr_2$: C, 24.92; H, 2.93; N, 5.81; Br, 66.33. Found: C, 25.62; H, 3.32; N, 6.33; Br, 65.79.

γ-Bromosenecionitrile.—Eighty-nine grams of the crude dibromonitrile was dissolved in 200 cc. of methyl ethyl ketone, and 92 g. of anhydrous potassium carbonate was added. The mixture was refluxed on a steam cone and stirred overnight. The product was a nearly colorless, lachrymatory liquid, boiling at 84° (8 mm.); n^{20}_{D} 1.5175. The yield was nearly 50%.

Anal. Calcd. for C_5H_6NBr: C, 37.55; H, 3.78; N, 8.75; Br, 49.94. Found: C, 38.09, 37.90; H, 3.98, 3.96; N, 8.76; Br, 49.37.

Methyl β,γ-Dibromoisovalerate.—To 200 g. of crude β,γ-dibromoisovaleronitrile was added a solution of 250 cc. of concentrated sulfuric acid in 400 cc. of methanol, and the mixture was stirred vigorously at the reflux temperature. More methanol was added from time to time to replace that which escaped from the condenser. Heating and stirring were discontinued after nine hours, and the mixture was allowed to stand overnight.

The crude product (124 g.), together with 20 g. of a similar crude product from a trial run, was distilled at reduced pressure through a carborundum-packed column. The major fraction, a colorless liquid boiling at 80–83° (2–3 mm.), weighed 104 g. Redistillation of a portion of this product gave a sample boiling at 84–85° (3 mm.); n^{20}_{D} 1.5078.

Anal. Calcd. for $C_6H_{10}O_2Br_2$: C, 26.30; H, 3.68; Br, 58.34. Found: C, 26.94; H, 4.25; Br, 56.32.

Methyl γ-Bromosenecioate.—To a solution of 80.6 g. of methyl β,γ-dibromoisovalerate in 170 cc. of methyl ethyl ketone (previously dried over calcium chloride) was added 80 g. of anhydrous potassium carbonate, and the mixture was stirred vigorously while it was refluxed on a steam cone. At the end of eight hours an additional 25 g. of potassium carbonate was added, and heating and stirring were continued overnight. Distillation of the product yielded a 20.2-g. fraction boiling at 73–76° (6–7 mm.); n^{20}_{D} 1.5003, and a 15.2-g. fraction boiling at 76–78° (6–7 mm.); n^{20}_{D} 1.5023. The combined weight of the two fractions was 35.4 g. (a 62% yield of the crude product). A portion of the lower-boiling fraction was redistilled to obtain an analytical sample. Three fractions were collected, the first boiling at 63° (3 mm.); n^{20}_{D} 1.5002, the second at 63–66° (3 mm.), and the third at 66° (3 mm.); n^{20}_{D} 1.5010. A Kjeldahl determination showed the presence of 0.1% of nitrogen in the first fraction, from which the following analytical results were obtained:

Anal. Calcd. for $C_6H_9O_2Br$: C, 37.33; H, 4.70; Br, 41.40. Found: C, 38.26; H, 5.13; Br, 39.28.

The remainder of the crude product was redistilled at a higher pressure. A large part of it boiled at 98–100° (24 mm.), although the last distillate from the higher-boiling crude fraction came over at 107°. The compound was highly lachrymatory.

Condensation of Methyl γ-Bromosenecioate with Benzaldehyde.—The procedure was similar to that described by Ziegler, Schumann and Winkelmann. A mixture of 24.6 g. of methyl γ-bromosenecioate, 16 g. of purified benzaldehyde, 25 cc. of dry benzene and 6 cc. of dry ether was placed in the dropping funnel, and 10.5 g. of 20-mesh granulated zinc (freshly cleaned with hydrochloric acid and dried with absolute alcohol and dry ether) was placed in the flask.

Approximately one-tenth of the mixture was run into the flask, and a crystal of iodine was added. When the flask was warmed over a low flame, the reaction began almost immediately. Stirring was then begun, and the mixture was added rapidly enough to maintain gentle refluxing of the solvents. The addition required about twenty-five minutes. Stirring was continued, and the mixture was maintained at the reflux temperature over a low flame for an additional two and one-half hours. Distillation of the product at a pressure of 2–3 mm. yielded a 3-g. fraction boiling at 146–148°, a 2.6-g. fraction at 148–152°, and a 9.2-g. fraction at 152–176°.

β-Styrylcrotonic Acid (Form A).—When 1 g. of the fraction boiling at 146–148° (2–3 mm.) was dissolved in 10 cc. of saturated alcoholic potassium hydroxide solution, a voluminous precipitate formed in a few minutes. The mixture was allowed to stand overnight, then diluted with water, and acidified. The precipitated acid was crystallized successively from benzene, alcohol and water, and benzene. White needles, melting at 158.5–159.5°, were obtained.

Anal. Calcd. for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43; neut. equiv., 188. Found: C, 76.76; H, 6.56; neut. equiv., 190.

This acid is probably identical with the high-melting form reported by Kuhn and Hoffer.[6]

β-Styrylcrotonic Acid (Form B).—The high-boiling fraction from the condensation (b. p. 152–176° (2–3 mm.)) was redistilled in the presence of a few crystals of iodine[7] in the hope of dehydrating the hydroxy ester which it was believed to contain. No water distilled from the mixture, however. A fore-run boiling at 146–155° (2–3 mm.) and a 3.9-g. fraction boiling at 172–178° (2–3 mm.) were collected. To the latter fraction 50 cc. of saturated alcoholic potassium hydroxide was added, and the mixture was allowed to stand overnight. Only a small precipitate formed in this time. When the solution was diluted with water, a small quantity of oily material was precipitated, and was removed by extracting the suspension twice with ether. A yellow oil as well as a solid acid was precipitated when the aqueous solution was acidified with hydrochloric acid. The solid (1.5 g.) was removed by filtration and crystallized twice from an alcohol-water solution to give needles, m. p. 156.5–157.5°. The melting point was not changed by a third crystallization from the same solvent, or by the final crystallization from a solution of benzene and low-boiling petroleum ether. A mixed melting point with acid A was depressed to 120°.

Anal. Calcd. for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43; neut. equiv., 188. Found: C, 76.36; H, 6.66; neut. equiv., 190.

Lactone of β-Styrylcrotonic Acid (IX).—After acid B had been removed by filtration, as described above, the oil

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[5] Tamele, Ott, Marple and Hearne, *Ind. Eng. Chem.*, **33**, 115 (1941).

[6] Kuhn and Hoffer, *Ber.*, **65**, 651 (1932).

[7] Hibbert, THIS JOURNAL, **37**, 1748 (1915).

which was precipitated at the same time was extracted from the filtrate with ether. The ethereal extract evaporated to leave a residual oil and several large crystals. The crystals dissolved when the mixture was stirred with 10% potassium carbonate solution, but the oil did not, and was removed from the suspension by ether extraction. Acidification of the bicarbonate solution precipitated an additional 0.3 g. of acid, and evaporation of the ether extract left 0.8 g. of an oil which solidified completely after standing for two days. This material melted at 55–57°, and crystallized in the form of needles or plates from mixtures of ether and low-boiling petroleum ether. After two crystallizations from these solvents it melted at 61–62°.

Anal. Calcd. for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.46; H, 6.66.

The compound dissolved slowly in cold aqueous potassium hydroxide solution and could be recovered by acidification of this solution. It dissolved more rapidly in saturated alcoholic potassium hydroxide solution and was not precipitated by dilution of the solution with water. When the diluted solution was acidified with hydrochloric acid a solid product, m. p. 155–157°, was precipitated. This compound was found by the mixed melting point method to be identical with acid B. It seems probable that the compound melting at 61–62° is the lactone of δ-hydroxy-β-methyl-δ-phenyl-α-pentenoic acid.

β-Styrylcrotonic Acid (Form A) from Benzalacetone and Ethyl Bromoacetate.—The procedure employed was essentially that of Kohler and Heritage.[8] These investigators, however, distilled the hydroxy ester which they obtained and subsequently dehydrated it by heating with hydrochloric acid, whereas in the present instance it was more convenient to dehydrate the crude ester directly by distillation in the presence of a few crystals of iodine. To the product obtained from the Reformatsky condensation of 61 g. of benzalacetone with 70 g. of ethyl bromoacetate, 0.1 g. of iodine was added and distillation was carried out under reduced pressure. After the water had been removed, three fractions were collected; a 14.5-g. fraction at 141–145° (2 mm.), a 20-g. fraction at 145–147° (2 mm.) and a 3-g. fraction at 147–149° (2 mm.).

To 1 g. of the middle fraction was added 25 cc. of saturated alcoholic potassium hydroxide solution, and the mixture, in which a precipitate quickly formed, was allowed to stand for two days. The precipitate dissolved when the solution was diluted with water, and a crude acid, m. p. 120–140°, was precipitated when the solution was acidified with hydrochloric acid. White needles melting at 158–159° were obtained after three crystallizations from benzene. No depression of the melting point was observed when this product was mixed with acid A from condensation of benzaldehyde with methyl γ-bromosenecioate.

The melting point reported by Kohler and Heritage[8] was 153°. von Auwers and Müller,[9] using the same method, obtained a product melting at 156–157°. Kuhn and Hoffer reported a melting point of 160°. It seems probable that all the samples made by this method are identical, and different from form B.

Summary

A method has been developed for the preparation of methyl γ-bromosenecioate from methallyl chloride.

Methyl γ-bromosenecioate has been condensed with benzaldehyde to yield two forms of β-styrylcrotonic acid and a third compound thought to be the lactone corresponding to the expected hydroxy acid.

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[8] Kohler and Heritage, *Am. Chem. J.*, **43**, 475 (1909).

[9] von Auwers and Müller, *J. prakt. Chem.*, [2] **105**, 379 (1932).

URBANA, ILLINOIS RECEIVED JANUARY 20, 1944

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

1,2-Addition of Methylmagnesium Iodide to Mesityl Ketones

BY REYNOLD C. FUSON, M. D. ARMSTRONG, WM. E. WALLACE[1] AND J. WAYNE KNEISLEY[2]

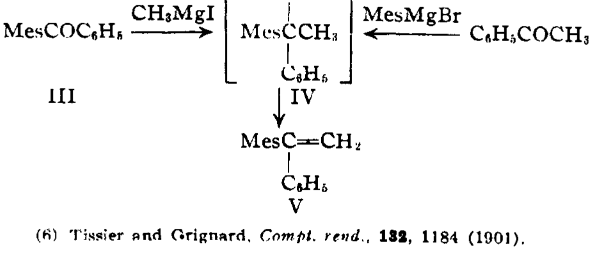
The carbonyl group of simple mesityl ketones has been known to react additively only with hydrogen. In particular, normal or 1,2 addition of a Grignard reagent has never been observed.[3] Recently mesityl *t*-butyl diketone (I) was found to undergo 1,2 addition of methylmagnesium iodide to each of the carbonyl groups.[4] Also the conversion of certain mesitoic esters to ketones by the action of Grignard reagents[5] may be explained by assuming 1,2 addition of the reagent to the ester carbonyl group.

These results led to a reëxamination of the behavior of simple mesityl ketones toward the Grignard reagent. The most favorable structure appeared to be that in which the mesitoyl radical was joined to the smallest possible group that possessed no *alpha* hydrogen atom. Among aliphatic radicals *t*-butyl was the logical choice. However, pivalylmesitylene (II) could not be induced to react with methylmagnesium iodide.[4] In the aromatic series benzoylmesitylene (III) appeared to offer the best chance of realizing 1,2 addition.

$\mathrm{MesCOCOC(CH_3)_3}$ I

$\mathrm{MesCOC(CH_3)_3}$ II

When benzoylmesitylene was treated with methylmagnesium iodide it was converted in 64% yield to 1-mesityl-1-phenylethylene (V), the dehydration product of the carbinol (IV) that would have resulted from 1,2 addition. The direct production of the olefin rather than the carbinol is similar to results obtained by others.[6]



$$\begin{array}{ccccc}\mathrm{MesCOC_6H_5} & \xrightarrow{\mathrm{CH_3MgI}} & \left[\begin{array}{c}\mathrm{OH}\\ |\\ \mathrm{MesCCH_3}\\ |\\ \mathrm{C_6H_5}\end{array}\right] & \xleftarrow{\mathrm{MesMgBr}} & \mathrm{C_6H_5COCH_3}\\ \mathrm{III} & & \downarrow\ \mathrm{IV} & & \\ & & \begin{array}{c}\mathrm{MesC{=}CH_2}\\ |\\ \mathrm{C_6H_5}\\ \mathrm{V}\end{array} & & \end{array}$$

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[1] Present address: General Aniline and Film Corporation, Easton, Pennsylvania.

[2] Present address: Hercules Powder Company, Wilmington, Delaware.

[3] Kohler and Baltzly, THIS JOURNAL, **54**, 4015 (1932).

[4] Fuson and Robertson, *J. Org. Chem.*, **7**, 466 (1942).

[5] Fuson, Bottorff and Speck, THIS JOURNAL, **64**, 1450 (1942).

[6] Tissier and Grignard, *Compt. rend.*, **132**, 1184 (1901).