TABLE III

OXIDATION OF 1-BUTANOL WITH SULFUR AND AQUEOUS CAUSTIC

Reaction temperature, °C.	180	230	290
Butanol recovd., moles	1.66	1.25	0.61
Sulfur recovd., g. atoms	3.25	....	.0
Acetic acid, mole	0.056	0.10	.272
Propionic acid, mole		0.26	.228

acidified to *p*H 1 and extracted with ethyl ether. From the ether extract, 1.7 g. (0.03 mole) of acetic acid was recovered. The aqueous solution then was evaporated to dryness and extracted with hot ethanol from which was obtained 35.4 g. (0.30 mole) of succinic acid, neutral equivalent 59.

Succinic and Acetic Acids from Thiacyclopentane.—Reaction of 1.0 mole of thiacyclopentane (tetrahydrothiophene), 6 moles of ammonia, 128 g. (4 g. atoms) of sulfur and 1300 g. of water in a 4.5-liter autoclave at 232° for 3 hours gave a maximum pressure of 72 atm. Ether extraction of the condensate obtained by steam distilling the product gave 3.8 g. of thiacyclopentane. The liberated sulfur (11.3 g.) was filtered from the product, and the amide saponified by addition of sodium hydroxide and continued steam distillation. Ether extraction of the acidified product yielded 5.4 g. (0.09 mole) of acetic acid (Duclaux constant) plus some succinic acid, neutral equivalent 59. The aqueous solution was evaporated to dryness and extracted with acetone. Total yield of succinic acid was 23 g. (0.19 mole).

Acetic and Propionic Acids from Propylene.—Propylene (5 moles) was treated with 5.5 moles of potassium hydroxide, 396 g. (12.4 g. atoms) of sulfur and 810 cc. of water at 230° for 90 minutes in a 2.5-liter autoclave. Gases were withdrawn through a caustic scrubber which gained 210 g. The remaining gas (3410 cc.) contained 2.4 volume per cent. of propylene. The product was worked up by the same procedure as for acetone oxidation products. Steam distillation gave 203.9 g. of neutral organic oil, d_4^{20} 0.886, containing sulfides which were not further characterized. A crude sulfur cake of 384.6 g. was obtained at *p*H 7. Fractional distillation of ether extracts yielded a mixture of acids which analyzed as consisting of 0.361 mole of acetic and 0.630 mole of propionic acid.

RICHMOND 1, CALIF.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

Synthesis of Compounds Related to Segments of Synthetic Sulfhydryl Polymers[1]

BY C. G. OVERBERGER AND P. V. BONSIGNORE[2]

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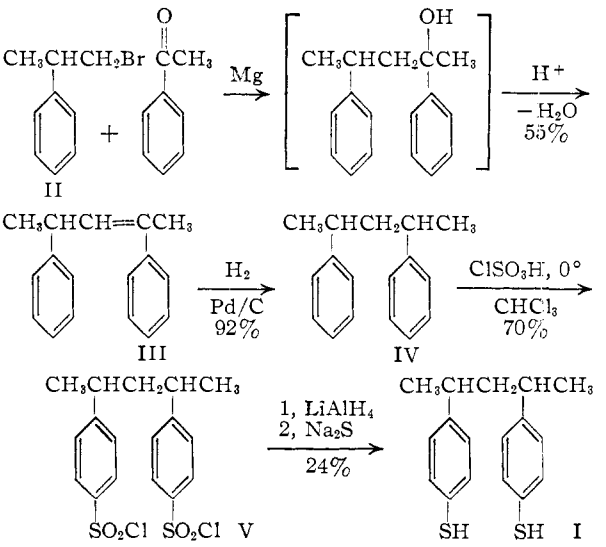
The synthesis of a 2,4-di-(*p*-mercaptophenyl)-pentane is described. This compound served as a model compound representing a segment of a hydrolyzed polymer of *p*-vinylphenyl thioacetate. The synthesis of methyl 2,2-dimethyl-4-phenylvaleric ester, a precursor of a model compound representing a segment of a hydrolyzed copolymer of *p*-vinylphenyl thioacetate and methyl methacrylate is also described. Pyrolytic cracking of the ethyl ester of 2,2-dimethyl-3-acetoxy-4-phenylvaleric acid, which was first investigated as an intermediate in the latter model compound, was found to undergo a facile cleavage of the carboxyethyl and acetate groups to give 2-methyl-4-phenylpentene-2. A mechanism for the latter is proposed. An improved procedure for the preparation of ethylene dithiocarbonate is also described.

Recently, Overberger and Lebovits have reported the synthesis of *p*-vinylphenyl thioacetate.[3] Free radical polymerization of this monomer alone and copolymerization with methyl methacrylate gave macromolecules which on saponification contained free sulfhydryl groups and were soluble in aqueous base. A solution of the hydrolyzed copolymer was found effective in reactivating urease, a natural sulfhydryl enzyme, which had been inactivated by oxidation with iodine.[4]

A study of the relative ease of oxidizability and the alkylation reactivity of the sulfhydryl groups of these hydrolyzed polymers of *p*-vinylphenyl thioacetate was undertaken in order to determine the effects imposed on the reactivity of the sulfhydryl group by the restraints of a polymeric carbon–carbon chain and the presence of various functional groups introduced by copolymerization, such as the carboxyl group of methyl methacrylate in the hydrolyzed copolymer. The results of the oxidation and alkylation studies will be reported separately; this paper is concerned with the synthesis of compounds related to the segments of the hydrolyzed homopolymer of *p*-vinylphenyl thioacetate and its copolymer with methyl methacrylate which were needed for comparison purposes.

The scheme adopted for the preparation of 2,4-di-(*p*-mercaprophenyl)-pentane, a representative segment of the hydrolyzed homopolymer of *p*-vinylphenyl thioacetate, is



2-Phenylpropyl bromide (II) was synthesized in 50–55% yield by reduction with lithium aluminum hydride in refluxing ether, of 1,2-dibromo-2-

(1) This is the 16th in a series of papers on new monomers and polymers. For the previous papers in this series see C. G. Overberger, H. Biletch and R. G. Nickerson, *J. Polymer Sci.*, **27**, 381 (1958).

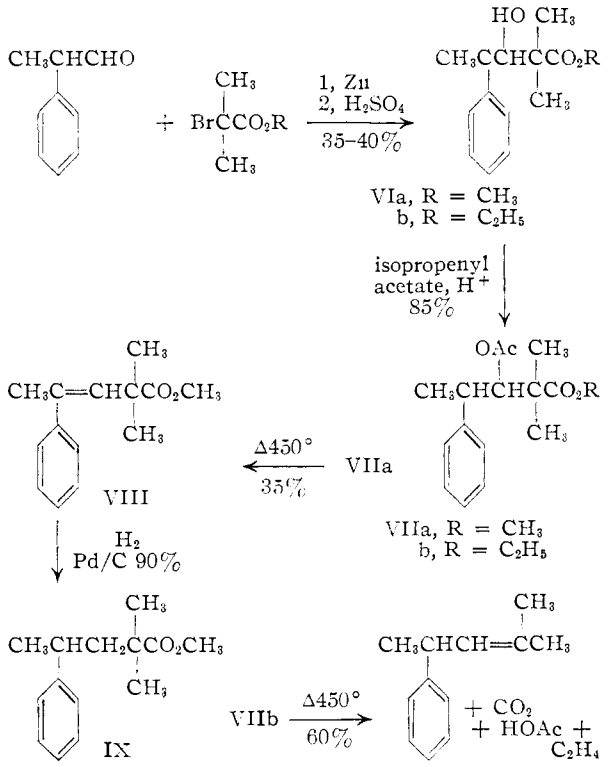
(2) This paper comprises a portion of a dissertation submitted by P. V. Bonsignore in partial fulfillment of the requirements of the degree of Doctor of Philosophy in the Graduate School of the Polytechnic Institute of Brooklyn.

(3) C. G. Overberger and A. Lebovits, THIS JOURNAL, **77**, 3675 (1955).

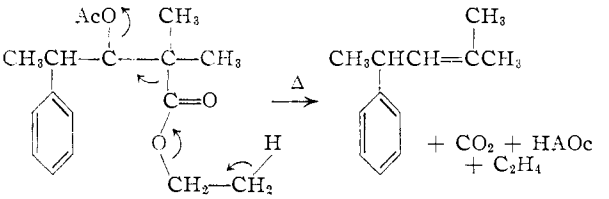
(4) C. G. Overberger and A. Lebovits, *ibid.*, **78**, 4792 (1956).

phenylpropane formed *in situ* from bromine and α-methylstyrene. Chlorosulfonation of IV in chloroform at 0° gave a 70% yield of 2,4-di-(*p*-chlorosulfophenyl)-pentane whose identity and configuration as the *p*-isomer was confirmed by the formation of the disulfonamide and its oxidation to the known *p*-sulfonamidobenzoic acid.[5] Reduction of V by stannous chloride in acetic–hydrochloric acid according to the method of Bogert and Bartlett[6] was unsatisfactory. Lithium aluminum hydride reduction in ether[7] followed by treatment with sodium sulfide to reduce any disulfide present gave the desired compound 2,4-di-(*p*-mercaptophenyl)-pentane (I) in 17% over-all yield based on IV.

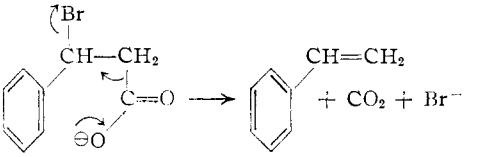
For the preparation of a model compound related to a segment of the hydrolyzed copolymer of *p*-vinylphenyl thioacetate and methyl methacrylate, the synthesis of a suitably substituted 2,2-dimethyl-4-phenylvaleric ester was undertaken. The reaction scheme adopted for the synthesis of methyl 2,2-dimethyl-4-phenylvaleric ester is outlined below. For other reasons, the synthesis of the sulfhydryl compound has been discontinued.



Removal of the 3-hydroxy group of VI by means of the pyrolytic cracking of the acetate was used to obviate the possibility of rearrangement of the phenyl group under the alternative method of dehydration by acid catalysts.[8] It is interesting that when the ethyl ester VIIb was subjected to pyrolytic cracking, a facile cleavage of the carboxyethyl and acetate groups took place with the formation of 2-methyl-4-phenylpentene-2, whose identity was confirmed by comparison of its physical properties and infrared spectrum with an authentic sample prepared by the method of Klages.[9] Confirmation of the structure was obtained by ozonolysis and identification of the fragments as α-phenylpropionaldehyde and acetone by comparison and mixed melting point of the 2,4-dinitrophenylhydrazones with authentic samples. A possible mechanism for this reaction is

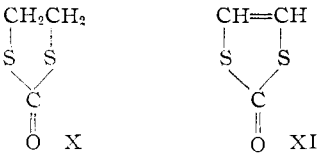


This reaction may be similar to the decarboxylation of the hydrogen bromide adduct of cinnamic acids by sodium carbonate to form olefins,[10] where the presence of an electron-withdrawing group in the β-position favors the decarboxylation.



The pyrolytic cleavage that occurs with the ethyl ester analog of VII is not possible with the methyl ester[11] and the carboxymethyl group remained intact when subjected to cracking conditions. Hydrogenation of the unsaturated ester VIII to the desired product methyl 2,2-di-methyl-4-phenylvaleric ester was realized in good yield with 10% palladium-on-carbon catalyst in methyl alcohol.

In connection with the preparation of sulfhydryl-containing polymers, the synthesis of vinylene dithiocarbonate (XI) was attempted.



The properties of "vinylene dithiocarbonate" were first reported by Challenger[12] who obtained it by the action of mercuric acetate on "vinylene trithiocarbonate," one of the reaction products of acetylene and boiling sulfur at 450° in low yield. Therefore the synthesis of ethylene dithiocarbonate (X), which could give XI on dehydrogenation was studied.

Ethylene dithiocarbonate has been prepared by the action of dilute nitric acid on ethylene trithiocarbonate,[13] the acid hydrolysis of the phenylhydrazone of ethylene trithiocarbonate[14] and the action of water on the addition product of aluminum tri-

(5) C. Palmer, *Am. Chem. J.*, **4**, 164 (1882).

(6) M. T. Bogert and J. H. Bartlett, THIS JOURNAL, **53**, 4046 (1931).

(7) N. G. Gaylord, "Reduction with Complex Metal Hydrides," Interscience Publishers, Inc., New York, N. Y., 1956, p. 852.

(8) R. L. Shriner, "The Reformatsky Reaction, Vol. I, Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1942, p. 1.

(9) A. Klages, *Ber.*, **37**, 2306 (1904).

(10) K. V. Auwers, *ibid.*, **45**, 2764 (1912).

(11) C. D. Hurd and F. H. Blunck, THIS JOURNAL, **60**, 2419 (1938).

(12) B. F. Challenger, E. A. Mason, E. C. Holdsworth and E. Emett, *J. Chem. Soc.*, 292 (1953).

(13) A. Husemann, *Ann.*, **126**, 269 (1863).

(14) M. Busch and E. Lingenbrink, *J. prakt. Chem.*, [2] **61**, 339 (1900).

bromide with carbon disulfide and ethylene dibromide.[15] The synthesis of X which was adopted was based on the observation of Challenger[12] that mercuric acetate converts the thione group of ethylene trithiocarbonate to the carbonyl group. Dehydrogenation of X was attempted with chloranil, selenium dioxide and lead tetraacetate but only starting material was recovered in each case.

Experimental[16]

2-Phenylpropyl Bromide (II).—α-Methylstyrene (236 g., 2.0 moles) in one liter of ether was kept at a temperature below 15°, while bromine (320 g., 2.0 moles) was dropped in slowly. After the addition was complete the reaction mixture was stirred an additional hour at room temperature and then lithium aluminum hydride (25 g., 0.67 mole), powdered below 30 mesh and dispersed in 300 ml. of anhydrous ether was added in small portions. The reaction mixture spontaneously warmed to a reflux during the addition of the hydride. Addition of the hydride was maintained at such a rate as to allow a gentle reflux; too fast an addition caused excessive foaming. The reaction was allowed to reflux for 16 hours and then poured into 2 l. of ice-water containing 100 ml. of concentrated hydrochloric acid (very lachrymatory side products). The ether layer was washed once with dilute hydrochloric acid, once with 5% sodium bicarbonate and dried over magnesium sulfate. After removal of the ether, distillation gave one main fraction b.p. 105–115° (18 mm.). Redistillation of this fraction yielded 218 g. (55%) of 2-phenylpropyl bromide, b.p. 115–116° (15 mm.), $n^{25}D$ 1.5453 (b.p. 117–118° (20 mm.),[17a] $n^{28}D$ 1.5448[17b]). *Anal.* Calcd. for $C_9H_{11}Br$: C, 54.21; H, 5.65; Br, 40.14. Found: C, 54.54; H, 5.36; Br, 40.42.

2,4-Diphenylpentene-2 (III).—To 8.90 g. (0.365 g. atom) of magnesium turnings in 300 ml. of ether was added 73 g. of II in 100 ml. of ether. The resultant Grignard solution was refluxed an additional hour, and then 44 g. (0.367 mole) of acetophenone in ether was added dropwise. The reaction was refluxed an additional two hours and then decomposed with 200 ml. of dilute sulfuric acid. The residual oil, after removal of the ether, consisting of 2,4-diphenylpentanol-2 and 2,4-diphenylpentene-2, was dehydrated directly with 0.5 g. of *p*-toluenesulfonic acid as catalyst. At 20 mm. vacuum, water vapor was removed for 4 hours while the contents of the reaction flask were held at 150°. The oil was then cooled and dissolved in ether, washed with water and sodium bicarbonate and dried over magnesium sulfate. Distillation of the residue gave three fractions: b.p. 67° (9 mm.), b.p. 89° (8 mm.) and a main fraction, b.p. 171–176° (8 mm.), 40 g. (59%). Redistillation of this third fraction gave 36 g. (53%) of 2,4-diphenylpentene-2, b.p. 163–165° (5 mm.), $n^{25}D$ 1.5665, d^{25}_4 0.9930.

Anal. Calcd. for $C_{17}H_{18}$: C, 91.84; H, 8.16. Found: C, 91.41; H, 8.27.

2,4-Diphenylpentane (IV).—2,4-Diphenylpentene-2 (55.6 g., 0.25 mole) and 1 g. of 10% palladium-on-charcoal catalyst in 200 ml. of ethanol were shaken in the Parr hydrogenation apparatus. The theoretical amount of hydrogen was absorbed in five hours. The catalyst was removed by filtration; distillation of the residue gave 51 g. (92%) of 2,4-diphenylpentane, b.p. 157–158° (4 mm.), $n^{25}D$ 1.5446, d^{25}_4 0.9677.

Anal. Calcd. for $C_{17}H_{20}$: C, 91.01; H, 8.99. Found: C, 90.97; H, 9.02.

2,4-Di-(*p*-chlorosulfophenyl)-pentane (V).—The technique of Huntress and Carten[18] was used. 2,4-Diphenylpentane (11.2 g., 0.05 mole) was dissolved in 150 ml. of chloroform, the solution was cooled in an ice–salt-bath and chlorosulfonic acid (93 g., 0.8 mole) was added dropwise over a 30-minute period. After the addition was complete, the reaction was stirred for one hour at room temperature and then poured onto cracked ice. The chloroform layer was washed once with ice-water and dried over magnesium sulfate. The residue after removal of the chloroform under vacuum was a viscous light tan oil which solidified on standing overnight; 15 g. (71%). A mixture of benzene and Skellysolve B (b.p. 40–60°) proved suitable for large scale recrystallization; 11.6 g. (55%), m.p. 116–117°. An analytical sample was recrystallized twice from Skellysolve B (b.p. 40–60°), m.p. 118–119°.

Anal. Calcd. for $C_{17}H_{18}Cl_2O_4S_2$: C, 48.46; H, 4.31; Cl, 16.82. Found: C, 48.65; H, 4.50; Cl, 16.34.

2,4-Di-(*p*-sulfonamidophenyl)-pentane.—2,4-Di-(*p*-chlorosulfophenyl)-pentane (0.2 g., m.p. 116–117°) was boiled with 5 ml. of concentrated ammonium hydroxide for 10 minutes. After cooling to room temperature and adding 10 ml. of cold water, the resultant solid sulfonamide was removed by filtration and thoroughly washed; 0.137 g. (75%) m.p. 135–136°. Recrystallization three times from dilute ethanol with the aid of Norite decolorizing charcoal gave 0.085 g. (47%) of the disulfonamide, m.p. 138° (cor.).

Anal. Calcd. for $C_{17}H_{22}N_2O_4S_2$: C, 53.38; H, 5.80; N, 7.32. Found: C, 53.62; H, 5.74; N, 7.12.

Evidence that the product obtained was the *p*-isomer was shown by oxidizing the disulfonamide with aqueous potassium permanganate. From 0.200 g. of the disulfonamide was obtained 0.118 g. (54%) of *p*-sulfonamidobenzoic acid, m.p. 275–276°. A mixed m.p. with an authentic sample of *p*-sulfonamidobenzoic acid, m.p. 280°,[5] melted at 274–276°.

2,4-Di-(*p*-mercaptophenyl)-pentane (I).—The recrystallized disulfonyl chloride V (16.8 g., 0.04 mole), m.p. 116–117°, was dissolved in 100 ml. of anhydrous ether and added slowly to a refluxing ether solution of lithium aluminum hydride (6.0 g., 0.159 mole). Refluxing was continued for 5 hours and the excess lithium aluminum hydride was decomposed by the cautious addition of 200 ml. of 5% hydrochloric acid. The ether solution was filtered through a glass wool plug to remove a waxy polymeric material which separated during the reaction, washed once with dilute hydrochloric acid and dried over calcium chloride. Removal of the ether gave 4.5 g. (35.5%) of a semi-solid waxy material. This product was dissolved in 20 ml. of dioxane and added slowly to a boiling solution of sodium sulfide (12 g., 0.05 mole) and 2 g. of sodium hydroxide in 200 ml. of water in order to reduce any disulfide present. After 20 minutes, the solution was cooled to 0° and acidified with dilute hydrochloric acid. Three extractions with 50-ml. portions of methylene chloride were made and the extracts combined, washed with dilute hydrochloric acid, sodium bicarbonate and then dried over magnesium sulfate. Removal of the solvent gave an oil which was distilled under nitrogen to give 2.8 g. (22.2%) of 2,4-di-(*p*-mercaptophenyl)-pentane, b.p. 188–190° (0.20 mm.), $n^{26.5}D$ 1.6156, d^{25}_4 1.0977. This compound gave a strong positive nitroprusside test for sulfhydryl groups. Its infrared absorption spectrum showed the characteristics S–H stretching frequency at 2570 cm.$^{-1}$.[19]

Ethyl 2,2-Dimethyl-3-hydroxy-4-phenylvaleric Ester (VIb).—The procedure for the Reformatzky reactions as given in ref. 8 was used. Ethyl α-bromoisobutyrate (200 g., 1.0 mole) and α-phenylpropionaldehyde (140 g., 1.05 moles) in 200 ml. of benzene were placed in a dropping funnel and added dropwise to 70 g. (1.0 g. atom) of 20 mesh zinc metal in 100 ml. of benzene. After starting the reaction by the addition of iodine crystals, the addition of the reagents was added at such a rate to maintain a gentle reflux. The reaction was completed by an additional hour reflux and then poured into one liter of 6 *N* sulfuric acid containing ice and stirred vigorously. The benzene layer was separated, washed once with 6 *N* sulfuric acid, once with sodium bicarbonate, then dried over magnesium sulfate. The residue was distilled through a packed column; the main fraction boiled at 160–163° (3 mm.). Redistillation gave ethyl 2,2-dimethyl-3-hydroxy-4-phenylvaleric ester as product; 90 g. (42%), b.p. 146° (1.25 mm.), $n^{25}D$ 1.5040, d^{25}_4 1.0426. An infrared spectrum showed strong hydroxyl bond absorption at 2.85 mμ.

Anal. Calcd. for $C_{15}H_{22}O_3$: C, 71.96; H, 8.86. Found: C, 71.60; H, 8.85.

(15) M. Konowolow, *J. Russ. Phys. Chem. Soc.*, **30**, 16 (1898); *Chem. Zentr.*, **69**, II, 362 (1898).

(16) Analyses by Dr. F. Schwarzkopf, New York, N. Y., and Dr. K. Ritter, Basel, Switzerland; melting points are uncorrected unless otherwise noted.

(17) (a) P. A. Magat, *Bull. soc. chim.*, **49**, 1411 (1931); (b) P. A. Levene, R. E. Marker and A. Rothen, *J. Biol. Chem.*, **100**, 598 (1933).

(18) E. H. Huntress and F. H. Carten, THIS JOURNAL, **62**, 511 (1940).

(19) N. F. Trotter and H. W. Thompson, *J. Chem. Soc.*, 481 (1946); N. Sheppard, *Trans. Faraday Soc.*, **46**, 429 (1950).

Ethyl 2,2-Dimethyl-3-acetoxy-4-phenylvaleric Ester (VIIb).—Acetylation of the 3-hydroxy group by acetyl chloride and pyridine in ether was not successful, probably because of the sterically hindered nature of the hydroxy group. Use of isopropenyl acetate and an acid catalyst gave a good yield of the acetylated product.

The ethyl hydroxy ester VIb (60 g., 0.24 mole) was mixed with 75 g. (0.75 mole) of isopropenyl acetate and 1 g. of *p*-toluenesulfonic acid. The reaction flask was fitted with a 10-inch Vigreux column and a distilling head. On heating the reactions mixture slowly, a temperature was reached where vigorous boiling took place and acetone distilled over at a temperature of 56–60°. Over a 3-hour period 13.5 g. of acetone was collected as compared to a theoretical amount of 14 g. The cooled solution was dissolved in ether, washed with water, three times with sodium bicarbonate and dried over magnesium sulfate. Distillation of the residue gave a single fraction, 56 g. (82%), of the pure ethylacetoxy ester (VIIb), b.p. 149° (1.15 mm.), $n^{25}D$ 1.4890, d^{25}_4 1.0443. An infrared spectrum showed the disappearance of the hydroxyl group absorption at 2.85 μ.

Anal. Calcd. for $C_{17}H_{24}O_4$: C, 69.84; H, 8.27. Found: C, 69.93; H, 8.15.

Pyrolysis of the Ethyl Acetoxy Ester VIIb.—The cracking procedure and apparatus used was the one described by Overberger and Tanner in the preparation of a series of alkyl styrenes by cracking of the suitably substituted acetoxy esters.[20] The cracking oven consisted of a Pyrex tube filled with 6 × 6 mm. Raschig rings mounted vertically in a furnace. The length of the reaction zone was 13 inches and the outside jacked temperature at a point halfway down the tube was measured by a thermocouple. A slow stream of nitrogen was passed through the tube from the top and the receiver at the bottom was cooled to Dry Ice temperatures. The oven was heated to 450° and 80 g. (0.27 mole) of the ethyl acetoxy ester was added dropwise at a rate of 30–40 drops per minute. The pyrolyzate was dissolved in ether and cautiously neutralized with 10% sodium bicarbonate, washed once with water and dried over magnesium sulfate. The ether was removed and the residue distilled through a packed column. One main fraction was collected, b.p. 87–88° (5 mm.), $n^{25}D$ 1.5138, 27 g. (61%), in addition to some uncracked starting material. This product was demonstrated to be 2-methyl-4-phenyl pentene-2 by the identity of its infrared spectrum with that of an authentic sample prepared according to the method of Klages.[8] Confirmation of the identity of the cracked product of VIIb as 2-methyl-4-phenylpentene-2 was obtained by ozonolysis in ethyl acetate solution. The 2,4-dinitrophenylhydrazone of the ethyl acetate-soluble product of the zinc reduction of the ozonides melted at 134°; a mixed melting point with an authentic sample of the 2,4-dinitrophenylhydrazone of α-phenylpropionaldehyde, m.p. 135°,[21] melted at 134–135°. The 2,4-dinitrophenylhydrazone of the water-soluble fragment melted at 125°; a mixed melting point with an authentic sample of the 2,4-dinitrophenylhydrazone of acetone, m.p. 125–126°,[22] melted at 124–125°.

Methyl 2,2-Dimethyl-3-hydroxy-4-phenylvaleric Ester (VIa).—The methyl hydroxy ester was prepared in an exactly analogous manner to that used for the ethyl acetoxy ester. From 270 g. (1.5 moles) of methyl α-bromoisobutyrate and 205 g. (1.5 moles) of α-phenylpropionaldehyde and 100 g. (1.5 g. atoms) of zinc metal were obtained 140 g. (40%) of the crude methyl hydroxy ester. Redistillation yielded 125 g. (35%) of methyl 2,2-dimethyl-3-hydroxy-4-phenylvaleric ester, b.p. 133° (1.2 mm.), $n^{25}D$ 1.5104, d^{25}_4 1.0675.

Anal. Calcd. for $C_{14}H_{20}O_3$: C, 71.17; H, 8.53. Found: C, 71.41; H, 8.23.

Methyl 2,2-Dimethyl-3-acetoxy-4-phenylvaleric Ester (VIIa).—The methyl acetoxy ester was prepared in an analogous manner to that used for the preparation of the ethyl acetoxy ester VIIb. From 130 g. (0.60 mole) of the methyl hydroxy ester, 150 g. (1.50 moles) of isopropenyl acetate and 1 g. of *p*-toluenesulfonic acid was obtained 130 g. (85%) of methyl 2,2-dimethyl-3-acetoxy-4-phenylvaleric ester, b.p. 135° (1.5 mm.), $n^{25}D$ 1.4933, d^{25}_4 1.0664.

Anal. Calcd. for $C_{16}H_{22}O_4$: C, 69.12; H, 7.97. Found: C, 69.04; H, 7.65.

Pyrolysis of the Methyl Acetoxy Ester VII.—While the cracking oven was maintained at 450°, the methyl acetoxy ester (130 g., 0.47 mole) was added dropwise at a rate of 35 drops per minute. The pyrolyzate was dissolved in ether and cautiously neutralized with sodium bicarbonate, washed well with water and finally dried over magnesium sulfate. After removal of the ether, the residue was distilled to give two main fractions: fraction A, b.p. 100–120° (1.5 mm.), 42 g., $n^{25}D$ 1.5125; fraction B, b.p. 130–135° (1.5 mm.), $n^{25}D$ 1.4948. Redistillation of fraction A gave 35 g. (33%) of methyl 2,2-dimethyl-4-phenylpentene-2-oic ester (VIII), b.p. 111° (2.7 mm.), $n^{26.5}D$ 1.5108, d^{25}_4 1.0050. An infrared spectrum showed the presence of the carbonyl ester group at 5.75 μ and the *gem* dimethyl bending band at 7.25 μ.

Anal. Calcd. for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 76.67; H, 8.57.

Methyl 2,2-Dimethyl-4-phenylvaleric Ester (IX).—The unsaturated methyl ester VIII (22 g. 0.1 mole) and 0.35 g. of 10% palladium-on-charcoal catalyst in 200 ml. of ethanol were shaken in the Parr hydrogenation apparatus. At the end of 6 hours the theoretical absorption of hydrogen was complete and the catalyst was removed by filtration. After removal of the alcohol, the residue was distilled to give 19.3 g. (88%) of the saturated ester, b.p. 119–123° (5 mm.). Redistillation gave 18 g. (82%) of pure methyl 2,2-dimethyl-4-phenylvaleric ester, b.p. 114° (4.5 mm.), $n^{25}D$ 1.4933, d^{25}_4 0.9856.

Anal. Calcd. for $C_{14}H_{20}O_2$: C, 76.32; H, 9.15; sapn. equiv., 220.3. Found: C, 76.56; H, 9.17; sapn. equiv., 223.

Preparation of Ethylene Dithiocarbonate.—To 86.4 g. (0.4 mole) of red mercuric oxide suspended by vigorous stirring in 300 ml. of water was added in one portion 30 g. (0.22 mole) of ethylene trithiocarbonate dissolved in 100 g. (1.0 mole) of acetic anhydride. Within five minutes, the temperature of the reaction mixture rose to 60–65° and a heavy white precipitate formed. Stirring, without the application of heat, was continued for one hour and then the reaction was subjected to steam distillation. The steam distillate, about 2 l. was extracted three times with 200 ml. of ether and the combined ether extract dried over anhydrous sodium sulfate. After removal of ether, the oily residue, 19.2 g. (72%), easily crystallized from ethyl alcohol to give white needles of ethylene dithiocarbonate, 14.5 g. (55%), m.p. 35° (reported 35°,[12] 31°,[13] 33–34°[15]).

Acknowledgment.—We wish to acknowledge gratefully the support of this work by Public Health Service Grant, G-4154.

BROOKLYN 1, N. Y.

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(21) "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 734.

(22) N. R. Campbell, *Anal.*, **61**, 391 (1936).