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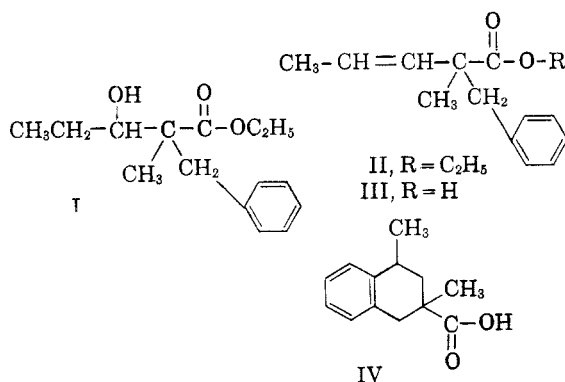
Dehydration of Ethyl 2-Benzyl-3-hydroxy-2-methylpentanoate

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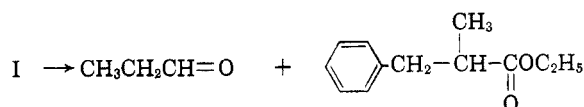
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An α -benzyl- β -hydroxy- α -methyl ester was dehydrated by pyrolysis of the crude phosphate ester to give the corresponding olefin. Phosphoric anhydride, on the other hand, produced, in addition, cyclized products.

As part of a program concerned with compounds having quaternary asymmetric carbon atoms, the dehydration of ethyl 2-benzyl-3-hydroxy-2-methylpentanoate, I, was studied with the production of the corresponding olefin, II, as the principal objective.



An outstanding feature of the chemistry of I is its facile cleavage in the reverse aldol manner to give propionaldehyde and ethyl α -benzylpropionate.



This occurred (a) after successful reduction of the corresponding ketone with sodium borohydride if, upon distillation of crude I, it was not washed until completely free of alkali, (b) in sodium borohydride reductions which involved both warming and an excess of borohydride, and (c) in attempted pyrolytic dehydration with boric acid.³

Pyrolysis of the acetate of I at 530°⁴ gave acetic acid and dibenzyl, presumably through the intermediate, II. This decomposition is similar to

that described for α -allyltoluene and allyl chloride.⁵ (A detailed study of the thermal stability of II will be described in a subsequent publication.)

Prolonged refluxing of a benzene solution of I with an excess of phosphoric anhydride gave a mixture of esters. Saponification gave the corresponding acids from which IV_a, m.p. 136°, crystallized in part. Acid IV_b, m.p. 72–74°, was isolated as the *p*-bromoanilide from a slightly higher boiling fraction of the esters. Accompanying IV_a was acid III, m.p. 53°, isolable as crystals in one experiment but only as the *p*-bromoanilide in others. The amounts of IV_a and IV_b could be increased by further heating of the phosphoric anhydride-phosphoric acid-ester mixture. It is presumed, therefore, that as I was slowly dehydrated, the II produced underwent a somewhat slower acid catalyzed cyclization. The formation of the six-membered ring (tetralin) instead of the five-membered (indane) is not surprising since Roblin, Davidson, and Bogert⁶ showed that indanes are obtained in such cyclizations only when the potential carbonium ion is *tertiary* and γ to phenyl. Thus, in perfect analogy to the present case, when 1-phenylpentanol-3 was cyclized,⁶ only 1-methyltetraline was formed.

The proof of the structures of the isomeric acids III (m.p. 53°), IV_a (m.p. 136°) and IV_b (m.p. 72–74°) should be mentioned. Both IV_a and IV_b gave, upon prolonged heating with an excess of potassium permanganate, phthalic acid and, upon treatment with *N*-bromosuccinimide,⁷ 1,3-dimethyl-naphthalene. III, in harmony with work of other authors,⁸ underwent decarboxylation at 250° to give the expected 2-methyl-1-phenyl-2-pentene. Ozonolysis of the sodium salt of III gave an aldehyde which was converted to the semicarbazone, m.p. 124°.⁹

Analysis supported the assumption that the semicarbazone was that of α -benzylpropionaldehyde. All of the properties of the acid melting at 53° are therefore in accord with structure III.

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TABLE I
 ACID DERIVATIVES

Acid	Deriv.	M.p., °C.	Carbon		Hydrogen		Nitrogen		Neut. Equiv.		Recrystal- lization Solvent
			Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	
α -Benzyl- propionic,	Glycine amide	112-113	65.14	65.37	6.83	6.96	6.33	5.97	221	221 222	20% HOAc
	<i>p</i> -bromo- anilide	128-130	60.39	60.76	5.07	5.14					EtOH
Methylbenzyl- pentenoic, III		53	76.44	76.32	7.90	7.90			204	202 204	Ligroin or 80% HOAc
	Glycine amide	107-109	68.94	69.02	7.33	7.47	5.36	5.36	261	262 264	50% HOAc
IV _a	<i>p</i> -bromo- anilide	126-127	63.69	63.57	5.63	5.67					EtOH
	<i>p</i> -benzene- azoanilide	146-148	78.29	78.56	6.52	6.66	10.96	11.04			EtOH
		136	76.44	76.31	7.90	7.88			204	197	80% HOAc 40% HOAc
IV _b	Glycine amide	156-158	68.94	68.99	7.33	7.39	5.36	5.41			
	<i>p</i> -bromo- anilide	155-156	63.69	63.59	5.63	5.54	3.91	4.22			80% EtOH
IV _b		72-74	76.44	76.30	7.90	7.85			204	204 208	80% HOAc
	<i>p</i> -bromo- anilide	133-134	63.69	63.84	5.63	5.68	3.91	4.23			EtOH

EXPERIMENTAL

All analyses for C, H, and N were carried out by Microtech Laboratories, 8000 Lincoln Avenue, Skokie, Ill. Melting points are not corrected but those at elevated temperatures were taken using a total immersion thermometer.

Ethyl α -propionylpropionate. A 1-l. three-necked flask equipped with a sealed stirrer, a reflux condenser of efficient type, and a thermometer which dipped to the bottom of the flask was heated while a stream of dry nitrogen was passed. Ethyl propionate (350 ml., 2.7 moles) was added and then, with stirring, 24 g. (1.0 mole) of sodium hydride. The mixture was slowly heated, the temperature never being allowed to rise above 75°. Above this temperature, substantial ethyl propionate was lost by volatilization. After all of the hydride had dissolved (about 4 hr.), heating at 70° was continued for an additional 18 hr. The solution was cooled with an ice-salt bath and a small amount of ethanol was added to decompose any remaining hydride. The contents were then poured into a beaker containing 400 ml. of 3*N* hydrochloric acid and 500 g. of cracked ice. A bit more hydrochloric acid was added until an acid reaction was obtained. Extraction with four 250 ml. portions of ether followed separation of the ester layer and the combined organic materials were dried over anhydrous magnesium sulfate. After removal of the solvent and excess ethyl propionate, the product was collected by fractional distillation under reduced pressure.

(9) G. Darzens, *Compt. rend.*, **139**, 1214 (1904), reported the semicarbazone of 2-methyl-4-phenylbutanal (this structure by our inference since it was made from benzylacetone) to melt at 70-72°. However, in D.R.P. 174239 (*Chem. Zentr.*, 1906, II, 1297), 70-72° is given by him as the melting point of "Methylphenylbutylaldehyde, C₆H₅CH₂(CH₂)CHCHO," this work duplicating to a large extent that of the previous publication. B. Prager, P. Jacobson, P. Schmidt, and D. Stern, *Beilsteins Handbuch der Organischen Chemie*, Julius Springer, Berlin, 1925, Band VII, p. 316, recorded 70-72° as the melting point of α -benzylpropionaldehyde. The present work supports the suggestion that 70-72° is the melting point of the semicarbazone of 2-methyl-4-phenylbutanal as was to be inferred from the earliest report.

The yield of colorless liquid, b.p. 89-91°, 14 mm., n_D^{25} 1.4189, was 94.8 g. (40% based on total ethyl propionate, 60% based on sodium hydride, or 63% based on consumed ethyl propionate). In our hands, the above method was superior to one previously described.¹⁰

Ethyl α -benzyl- α -propionylpropionate. No advantage of benzyl bromide over benzyl chloride was noted. The physical properties of material used in this work (b.p. 126-127°, 1 mm., n_D^{25} 1.4940) appeared to be in reasonable agreement with the boiling range reported by Dieckmann and Kron.¹¹

The pyrazolone, m.p. 116-117°, from the ester and hydrazine, was recrystallized from dilute ethanol.

Anal. Calcd. for C₁₃H₁₅N₂O: C, 72.19; H, 7.46; N, 12.95. Found: C, 72.46; H, 7.44; N, 13.39.

Ethyl 2-benzyl-3-hydroxy-2-methylpentanoate. To a stirred, ice cold solution of 50 g. (0.2 mole) of the ketoester in 200 ml. of methanol, 7.6 g. (0.2 mole) of solid sodium borohydride was added all at once. The solution became warm but did not reflux. It was allowed to stand in the cold for 2 hr. and then permitted to warm up to room temperature. The contents of the flask were poured into water and the mixture was extracted three times with petroleum ether. The combined organic layers were dried with anhydrous sodium sulfate and the solvents were removed. Distillation of the residue gave colorless, viscous liquid, b.p. 108-110°, 0.2 mm., n_D^{25} 1.4963; the yield was 43 g. or 85%. The ultraviolet absorption spectrum was that of toluene.

Anal. Calcd. for C₁₅H₂₂O₃: C, 71.96; H, 8.86. Found: C, 71.66; H, 8.91.

In subsequent runs, the amount of borohydride was reduced to 0.05 mole and the solvent changed to ethanol with, apparently, equally good results. When, however solutions at room temperature were used with an excess of borohydride, substantial ethyl α -benzylpropionate was formed.

The acetate, b.p. 107-110°, 0.1 mm., n_D^{25} 1.4870, was formed in 92% yield by boiling the ester with a large excess of acetic anhydride for 5 hr. without addition of catalyst.

(10) C. R. Hauser and B. E. Hudson, Jr., *Org. Reactions*, **I**, 280 (1942).

(11) W. Dieckmann and A. Kron, *Ber.*, **41**, 1269 (1908).

Anal. Calcd. for $C_{12}H_{16}O_4$: C, 69.83; H, 8.27. Found: C, 69.61; H, 8.17.

Dehydration of ethyl 2-benzyl-3-hydroxy-2-methylpentanoate.

(a) *Acetate pyrolysis.* Into a 13 inch column packed with glass beads and heated to a temperature of 555° was dropped 69 g. of the acetate at a rate of one drop per second. A slow stream of nitrogen carried the material through the column. The products were collected in an iced flask. Distillation of the neutral portion through a 10 inch Vigreux column gave three fractions: 7.5 g., b.p. 33–39° (0.5 mm.), n_D^{25} 1.4800; 7.0 g., b.p. 70–75° (0.3 mm.), n_D^{25} 1.4870; 5.0 g., b.p. 86–93° (1.3 mm.), n_D^{25} 1.5180. Upon being seeded with dibenzyl, m.p. 52°, the second fraction solidified and was recrystallized from ethanol. Colorless crystals, m.p. 46–47°, resulted. A mixture melting point with dibenzyl was not depressed. The yield of crude dibenzyl was 29%. The other two fractions were not further investigated.

(b) *Boric acid pyrolysis.* Into a 100 ml. Claisen flask equipped with a thermometer reaching the flask bottom and water cooler receiver was placed 25 g. (0.1 mole) of hydroxyester and 6.2 g. (0.1 mole) of solid boric acid. The contents were heated gradually to 200° with a Bunsen burner. A water aspirator was then attached and the contents were boiled over using the free flame. The boric acid dissolved and the vapor temperature rose to about 210° and the pot temperature to about 260°. After the addition of 25 ml. of benzene, the organic material was washed with water and dried. The benzene was removed by distillation and the residue fractionated under reduced pressure. The only fraction investigated boiled at 60° (0.5 mm.) and weighed 5.7 g. (30%). The colorless liquid, n_D^{25} 1.4853, was ethyl α -benzylpropionate¹¹ (sapon. equiv. calcd. 192; found, 196, 197). Derivatives are described in Table I.

(c) *Phosphoric anhydride.* In a 1-l. round-bottomed flask which was filled to 1/4 of its capacity with glass wool were placed 126 g. (0.5 mole) of hydroxyester, I, and 300 ml. of anhydrous benzene. The refluxing of this solution was interrupted hourly with the addition of 10 g. of phosphoric anhydride until a total of 90 g. (0.63 mole) had been added. Upon each addition, the glass wool was rotated so that fresh anhydride was submerged. The final mixture was refluxed an additional 15 hr. After removal of the benzene, the liquid residue was fractionated through a 10 inch Vigreux column under reduced pressure (0.3–0.6 mm.). Although the boiling points of 15 small fractions were rather constant, increasing from 94° (0.4 mm.) to 105° (0.3 mm.) only toward the end of the distillation, the indices of refraction decreased from 1.5150 to 1.5017 and then increased again to 1.5105. The total distillate was combined into two main fractions: 69.8 g. and 18.5 g. (total 88.3 g.; 75%). Each of these fractions was saponified with potassium hydroxide (1*N* in ethylene glycol), non-ester material being removed by extraction with benzene. The two fractions of crude acid (52.0 g.; 85% and 15.8 g.; 97%) were not distilled. From the first of these, there crystallized over a period of weeks about 26 g. of solid acid, which, after a series of recrystallizations from 80% acetic acid, melted at 136° and weighed 7.35 g. The thick acid in the filtrate again began to crystallize, this time much more slowly, depositing 8.75 g. of solid. This, recrystallized from 80% acetic acid with cooling below 0°, yielded 2.75 g. of acid, m.p. 52°. In another run, this second acid failed to appear but was isolated as the *p*-bromoanilide, m.p. 126–127° (Table I).

One gram of the second fraction of crude acid (15.8 g.) was converted to the *p*-bromoanilide in the usual way. The yield of pure material, m.p. 133–134°, was 36%. To 9.0 g. of this derivative was added 120 ml. of 1*N* potassium hydroxide in ethylene glycol. The solution was heated slowly to 175°, allowed to cool slowly over a period of 1 hr., heated again to 175°, and allowed to stand 3 hr. Poured into 200 ml. of water, it was extracted three times with benzene, acidified, and extracted three times again. The crude liquid acid remaining after the removal of the solvent was crystallized from 5 ml. of 80% acetic acid. The final

yield of purified material was 3.62 g. or 70%. This acid tended to retain solvent somewhat and melt low (61–63°) unless well dried (72–74°).

(d) *Pyrolysis of the crude phosphate.* To a mechanically stirred solution of 102.8 g. (0.411 mole) of hydroxyester, I, in 200 ml. of anhydrous pyridine and 200 ml. of benzene (dried over phosphoric anhydride) was added 23.2 g. (0.151 mole) of phosphorus oxychloride, the ester solution being cooled in ice the while. The mixture was allowed to stand for five days (coincidentally) and then filtered. The solvents were removed under reduced pressure (20 mm.). The liquid residue was then distilled rapidly under reduced pressure (20 mm.), heating being done with the free flame of a Bunsen burner. The liquid distillate containing much white solid was mixed with 50 ml. of benzene, washed with water, dried over anhydrous magnesium sulfate, and distilled through a 10 inch Vigreux column. During the very slow distillation (at about 85°, 0.1 mm.), fractions of about 5 ml. were taken. Those having index of refraction 1.4993 to 1.5029 (a total of 58.35 g.) were recombined and fractionated a second time, fractions having index of refraction 1.5010 to 1.5020 being recombined (48.4 g., 51%). Saponification gave 38.9 g. (91%) of crude acid which was not distilled. It slowly solidified. It was recrystallized first from petroleum ether and then from 80% acetic acid, substantial loss accompanying each purification. The melting point increased from 46–49° to 52–53°.

2-Benzyl-2-methyl-3-pentenoyl chloride. Obtained after refluxing the acid (17.1 g.) with 50 ml. of thionyl chloride for 1 hr., the colorless liquid, n_D^{25} 1.5262, was collected at 94–95° (0.9 mm.). The yield was 89%.

Anal. Calcd. for $C_{12}H_{15}ClO$: C, 70.10; H, 6.79; Cl, 15.92. Found: C, 70.37; H, 6.87; Cl, 15.46.

Ozonolysis of 2-benzyl-2-methyl-3-pentenoic acid, III. Through a solution of 2.95 g. (0.0145 mole) of the acid in a mixture of 85 g. of cracked ice and 35 ml. of water containing 8 ml. of 10% potassium hydroxide, there was passed at a rate of 0.01 c.f.m. ozonized oxygen until the equivalent of 0.72 g. (0.015 mole) of ozone was used. Additional ice (150 g.) and 10% potassium hydroxide (8 ml.) were added during this period, the latter as needed to maintain a clear solution. After the addition of 5 ml. of sulfuric acid, the clear solution, which became cloudy on heating, was steam distilled. The water insoluble oil was collected with benzene which was washed with sodium hydroxide, water, and dried. Removal of the solvent under reduced pressure (20 mm.) gave 1.1 ml. of residual oil which gave positive tests with Fehling's solution and with 2,4-dinitrophenylhydrazine.

From 1.0 ml. the *semicarbazone* was prepared. Recrystallization from 50% ethanol gave the colorless substance, m.p. 123–124.5°. The yield, based upon III, was 13% of purified substance.

Anal. Calcd. for $C_{11}H_{15}N_3O$: C, 64.37; H, 7.37; N, 20.47. Found: C, 64.42; H, 7.13; N, 20.39.

Decarboxylation of 2-benzyl-2-methyl-3-pentenoic acid, III. A sealed tube containing 6.45 g. of III, m.p. 52–53°, was heated over a period of 14 hr. to 255° and maintained at this temperature for an additional 10 hr. The liquid product was taken up in 30 ml. of benzene, washed twice with 10% potassium carbonate, washed with water, and dried. Distillation gave 4.0 g. (80%) of colorless material, b.p. 93–95° (20 mm.), n_D^{25} 1.5073.

Anal. Calcd. for $C_{12}H_{16}$: C, 89.94; H, 10.06. Found: C, 89.85; H, 9.82.

Ozonolysis of 2-methyl-1-phenyl-2-pentene. The above olefin (1.6 g., 0.01 mole) was dissolved in a solution of 20 ml. of acetic acid and 2 ml. of water. Ozonized oxygen equivalent to 0.01 mole of ozone was passed through the solution which was cooled in ice. At the conclusion of the ozone treatment, the solution was added to 600 ml. of water and the whole steam distilled. The distillate was made just basic to phenolphthalein and extracted three times with ether which was washed with dilute ferrous sulfate solution. Removal of the ether gave 1.0 ml. of residual oil. From 0.1

ml. of this there was obtained 0.13 g. of the 2,4-dinitrophenylhydrazone, m.p. 153.5–154.5°. From 0.5 ml. of the liquid residue was obtained 0.33 g. of semicarbazone, m.p. 188–192° (total immersion thermometer). Literature values are 156° and 198°. The yield of phenylacetone from the olefin, based upon the 2,4-dinitrophenylhydrazone, was 41%.

Reaction of IV_a with potassium permanganate. There was added to an alkaline solution of 0.7 g. (0.0034 mole) of IV_a, m.p. 136°, a solution of 5.4 g. (0.034 mole) of potassium permanganate in 300 ml. of water. The resulting mixture was stirred for 24 hr., being heated to boiling four times during this period. After the mixture was heated to boiling a final time, decolorized with a few drops of formic acid and filtered, it was extracted four times with ether which was discarded. The water layer was evaporated to a volume of 50 ml., acidified, and extracted continuously with ether for 24 hr. The solid material remaining after removal of the ether (0.16 g.) was recrystallized from water several times. The final material melted at 208–211° (block). A mixture melting point with phthalic acid was not depressed. Acid IV_b was converted to phthalic acid similarly.

Reaction of IV_a with N-bromosuccinimide. In a 100 ml. round-bottomed flask were placed 1.0 g. (0.005 mole) of acid IV_a, m.p. 136°, 1.78 g. (0.01 mole) of N-bromosuccinimide, 50 ml. of carbon tetrachloride and about 0.01 g. of benzoyl peroxide. The contents were heated slowly to boiling and then refluxed 2.5 hr. As the contents reached the boil, there was a sharp increase in boiling rate and the solution became red, and then again colorless, rapidly. The cooled mixture was washed twice with sodium bicarbonate, twice with 5% sodium hydroxide, once with water and dried. A pale orange oil remained after removal of the

solvent. The oil was heated to boiling momentarily with one gram of pyridine, diluted to 50 ml. with benzene, washed with 5% hydrochloric acid and water, and again freed from solvent. At this point, the crude oil was collected with 20 ml. of methanol which was then reduced, after the addition of 1.0 g. of picric acid, to 5 ml. by boiling. The first crop of crystals, yellow plates, identified as picric acid, was discarded. Later crops consisted of yellow-orange needles. After two recrystallizations from methanol these melted at 115–116°, a value which did not change on further recrystallization.¹² A confirmatory analysis was desired.

Anal. Calcd. for C₁₅H₁₅N₃O₇: C, 56.10; H, 3.92. Found: C, 56.03; H, 4.51.

Acid IV_b, when treated similarly, gave the same picrate (a mixture melting point was not depressed) and also the styphnate, m.p. 114–115°.¹²

Use of one molar equivalent of N-bromosuccinimide did not produce a bromoacid intermediate but a mixture of starting material and naphthalenic hydrocarbon.

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(12) M. C. Kloetzel, *J. Am. Chem. Soc.*, **62**, 1708 (1940), reported 117–118° as the melting point of the picrate of 1,3-dimethylnaphthalene and 116–118° as the melting point of the styphnate.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF DELAWARE]

Effect of Cobaltous 2-Ethylhexanoate and Other Salts on the Decomposition of Tetralin Hydroperoxide

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The decomposition of tetralin hydroperoxide, when catalyzed by cobaltous 2-ethylhexanoate in xylene was of apparent first order in hydroperoxide and second order in catalyst. However, the rate constants varied with the initial concentration of hydroperoxide and decreased with time under some conditions. The decomposition was retarded by acetic acid, chloroform, carbon tetrachloride, water, α -tetralone, and hydroquinone. The amount of α -tetralone produced at 100% decomposition was not markedly affected by changes in temperature, catalyst concentration, and solvents.

Manganous 3-cyclohexane propionate, suspended in benzene at 25°, was four times as active a catalyst as cobaltous 2-ethylhexanoate. Lead cyclohexane carboxylate, in tetralin solution at 80°, was much less active than the cobalt catalyst at 25°.

Relatively few detailed kinetic studies have been made on the metal-catalyzed decomposition of hydroperoxides, a reaction of importance in the polymerization of drying oils. The rate of decomposition of tetralin hydroperoxide with cobaltous naphthenate in tetralin was studied by Robertson and Waters,² and the decomposition with cobaltous acetate in glacial acetic acid–benzene solution was studied by Woodward and Mesrobian.³ The cleavage

of hydroperoxides in the presence of various metal salts was studied by Williams and coworkers⁴ and by Kharasch and coworkers.⁵

The present report deals chiefly with the effect of cobaltous 2-ethylhexanoate on the rate of breakdown of tetralin hydroperoxide in xylene and other solvents. Some data are also given on the decomposition of this hydroperoxide in the presence of lead cyclohexane-carboxylate and manganous 3-

(1) From the Ph.D. theses of Kenneth R. Carle (1955) and Donald E. Weiman (1953); Armstrong Cork Company Research Fellows.

(2) A. Robertson and W. A. Waters, *J. Chem. Soc.*, 1578 (1948); *Trans. Faraday Soc.*, **42**, 201 (1946).

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