2.   A study of the reaction between isomeric phenols and sulfur dichloride has been made.

3.   It has been found that linking two phenol molecules by means of a sulfur atom results in a relatively constant factorial enhancement of their respective bactericidal properties.

4.   Studies similar to this are now in progress and other series will be reported on later.

BALTIMORE, MARYLAND

THE STRUCTURE OF ENOL-ACETATES AND THE CORRESPONDING VINYLAMINES[1,2]

BY L. J. ROLL AND ROGER ADAMS

At present there has been only one method devised for the determination of the structure of enols where two or more structures are possible.   This is the ozonization method of Scheiber,[3] which consists merely in ozonizing any particular enol or equilibrium mixture of a keto and enol, and, after decomposing in the usual way, determining the structure of the products. There are in many instances, difficulties in the application of this method since it is frequently necessary to isolate and prove the constitution of secondary degradation products even if it is assumed that ozone during the course of the reaction does not cause any change in the equilibrium of the original mixture.

It has been the purpose of this investigation to determine the structure of some stable enol derivatives.   This, of course, might be done merely by ozonization and isolation of the products, but many of the same difficulties would occur as in the ozonization of the enols themselves.   Enol-acetates were selected for study.   Although two possible enol-acetates of each 1,3-dicarbonyl compound may exist, in each instance studied, only a single compound was isolated.   On the assumption that 1,3-dicarbonyl compounds in solution exist as equilibrium mixtures of the two enol and

[1] This communication was in completed manuscript form when a paper by Michael and Ross, THIS JOURNAL, 53, 2394 (1931), appeared.   During the course of this investigation the authors used a similar procedure to the one described in the Michael and Ross article for determining the structure of an enol ester.   The compounds used in this research are different from those studied by Michael and Ross.
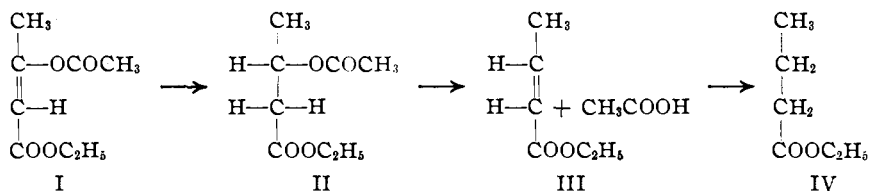
[2] This contribution is an abstract of a portion of a thesis submitted by L. J. Roll in partial fulfilment of the requirements for the Degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[3] (a) Scheiber and Herold, Ber., 46, 1105 (1913); Ann., 405, 295 (1914); (b) Lublin, Chem.-Ztg., 39, 433 (1915); (c) Scheiber and Hopfer, Ber., 47, 2704 (1914); ibid., 53, 697 (1920); (d) Weygand and Baumgärtel, ibid., 62, 574 (1929).
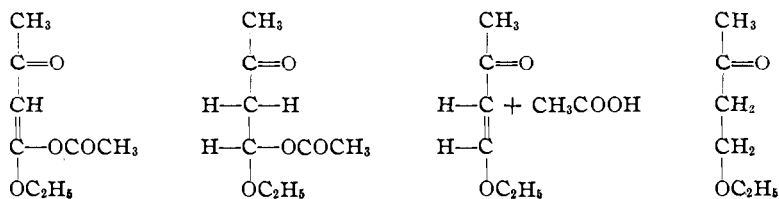
the dicarbonyl forms, or as Sidgwick[4] has suggested as chelate rings, it is open to discussion whether the enol-acetates have the analogous structure to the more easily formed enol. It would be a logical conclusion, however, that the acetate produced from such a mixture would probably be the derivative of the more active enol or of the less stable chelate and that by disturbing the equilibrium essentially a pure acetate might be obtained.

The enol-acetates were prepared by a method previously described in the literature,[5] the action of pyridine and acetyl chloride on the equilibrium mixture.

Preliminary experiments were made on acetoacetic ester. It was found that by the catalytic reduction with platinum-oxide platinum black in glacial acetic acid as a solvent, of the enol-acetate of acetoacetic ester (ethyl p-acetoxycrotonate) (I) that not one but two moles of hydrogen were readily absorbed and a very satisfactory yield of ethyl butyrate was thus obtained. Apparently the intermediate ethyl β-acetoxybutyrate (II) is unstable under the conditions of the reaction, acetic acid is eliminated and the ethyl crotonate (III) thus produced is reduced to ethyl butyrate (IV). There is the possibility of direct reduction of the ethyl β-acetoxybutyrate to ethyl butyrate but this seems unlikely.

$$
\begin{array}{cccc}
CH_3 & CH_3 & CH_3 & CH_3 \\
| & | & | & | \\
C\text{—}OCOCH_3 & H\text{—}C\text{—}OCOCH_3 & H\text{—}C & CH_2 \\
\| & | & \| & | \\
C\text{—}H & H\text{—}C\text{—}H & H\text{—}C + CH_3COOH & CH_2 \\
| & | & | & | \\
COOC_2H_5 & COOC_2H_5 & COOC_2H_5 & COOC_2H_5 \\
I & II & III & IV
\end{array}
$$

It is obvious that if the enol-acetate had formed in the other direction there would most probably have resulted ethoxy-1-butanone-3 (V) or possibly a reduction product of this compound.

$$
\begin{array}{cccc}
CH_3 & CH_3 & CH_3 & CH_3 \\
| & | & | & | \\
C=O & C=O & C=O & C=O \\
| & | & | & | \\
CH & H\text{—}C\text{—}H & H\text{—}C + CH_3COOH & CH_2 \\
\| & | & \| & | \\
C\text{—}OCOCH_3 & H\text{—}C\text{—}OCOCH_3 & H\text{—}C & CH_2 \\
| & | & | & | \\
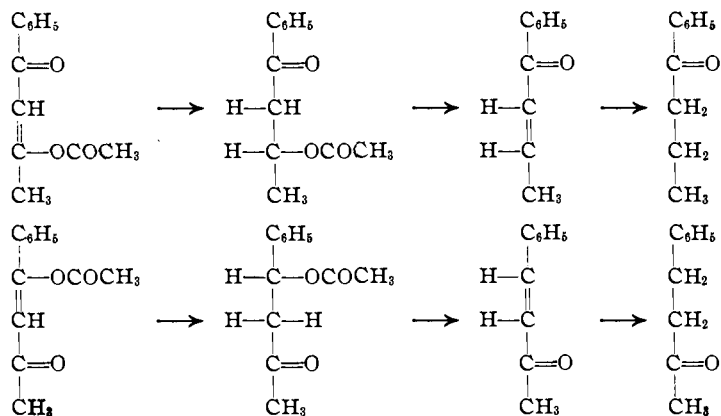OC_2H_5 & OC_2H_5 & OC_2H_5 & OC_2H_5
\end{array}
$$

The method was next applied to the enol-acetate of benzoylacetone, as there is marked disagreement as to the structure of the benzoylacetone. On the one hand, evidence seems in favor of the enol form from the carbonyl

4 Sidgwick, *J. Chem. Soc.*, **127**, 907 (1925).

5 Claisen, *Ann.*, **297**, 2 (1900); Claisen and Haase, *Ber.*, **33**, 1244 (1900).

attached to the phenyl group,[3a,6] on the other hand, from the carbonyl attached to the methyl group.[7]

By the reduction of the enol-acetate of benzoylacetone a very satisfactory yield of butyrophenone[1] was obtained, thus indicating without a doubt that it was formed from the enol of the carbonyl attached to the methyl group. If enolization had taken place on the benzoyl group, methyl phenethyl ketone would have been expected.

$$
\begin{array}{ccccc}
C_6H_5 & C_6H_5 & C_6H_5 & C_6H_5 \\
| & | & | & | \\
C{=}O & C{=}O & C{=}O & C{=}O \\
| & & | & | & | \\
CH & \longrightarrow H{-}CH & \longrightarrow H{-}C & \longrightarrow CH_2 \\
\| & | & \| & | \\
C{-}OCOCH_3 & H{-}C{-}OCOCH_3 & H{-}C & CH_2 \\
| & | & | & | \\
CH_3 & CH_3 & CH_3 & CH_3 \\
\end{array}
$$

$$
\begin{array}{ccccc}
C_6H_5 & C_6H_5 & C_6H_5 & C_6H_5 \\
| & | & | & | \\
C{-}OCOCH_3 & H{-}C{-}OCOCH_3 & H{-}C & CH_2 \\
\| & | & \| & | \\
CH & \longrightarrow H{-}C{-}H & \longrightarrow H{-}C & \longrightarrow CH_2 \\
| & | & | & | \\
C{=}O & C{=}O & C{=}O & C{=}O \\
| & | & | & | \\
CH_3 & CH_3 & CH_3 & CH_3 \\
\end{array}
$$

The wide application of this procedure is not so simple as might at first appear. Thus in the study of homologs of benzoylacetone, 1-phenylpentadione-1,3 and 1-phenylhexadione-1,3, preliminary experiments showed that the ketones expected, namely, valerophenone and caprophenone, could not be isolated. At first it was thought that in these instances the enol-acetates from the carbonyls next to the benzene ring were in hand, but later this proved not to be the case. The complication which entered the experiments was apparently due to the fact that in these latter compounds the rate of reduction of the initial olefin linkage was much slower than in the acetate of benzoylacetone and as a consequence the carbonyl next to the benzene ring was reduced simultaneously to the carbinol, which then acetylated to a certain extent, as shown by saponification equivalents. A mixture which appeared to be alkyl phenyl carbinols and their acetates was thus obtained as final products. Saponification and oxidation led to the expected ketones. Butyrophenone and valerophenone were reduced with platinum-oxide platinum black in glacial acetic acid and exactly the same type of mixtures was obtained.

[6] Smedley, *J. Chem. Soc.*, **97**, 1485 (1910). See also Dufraisse, *Bull. soc. chim.*, **41**, 843 (1927); Perkin, *J. Chem. Soc.*, **61**, 832 (1892); Meyer, *Ber.*, **45**, 2843 (1912).

[7] Claisen, *Ann.*, **277**, 184 (1893); **291**, 25 (1896); Fischer and Kuzel, *Ber.*, **16**, 2240 (1883); Claisen, *ibid.*, **29**, 1005 (1896); **40**, 3909 (1907); Auwers and Stuhlman, *ibid.*, **59**, 1043 (1926). See also Claisen, *ibid.*, **59**, 144 (1926), and Weygand, *ibid.*, **58**, 1473 (1925).

There is also a second complicating factor in attempting to apply this method. There are many ketones which are difficult to convert to their enol-acetates. It is noticeable, however, from the results of previous investigations, that in many instances where the enol-acetates are not readily produced, the corresponding vinylamines are frequently formed with ease, merely by the action of ammonia. This is true, for example, in the alkylated acetoacetic esters. As the size of the alkyl group is increased, the tendency to enolize is cut down enormously[8] and with this much difficulty in producing the enol-acetate is encountered. On the other hand, the corresponding vinylamines, in this case a substituted ethyl β-aminocrotonate, can be made almost as readily as ethyl β-aminocrotonate from ethyl acetoacetate. In the study of ethyl β-aminocrotonate it was discovered that reduction with platinum-oxide platinum black and hydrogen in glacial acetic acid gave essentially a quantitative yield of ethyl β-acetamidobutyrate. Previous investigators using colloidal platinum and ethyl alcohol as a solvent obtained the ethyl β-aminobutyrate.[9] The ethyl β-acetamidobutyrate, upon partial hydrolysis with alcoholic hydrochloric acid, and then distillation, decomposed to ammonia and ethyl crotonate. The intermediate which was presumably ethyl β-aminobutyrate was not isolated.
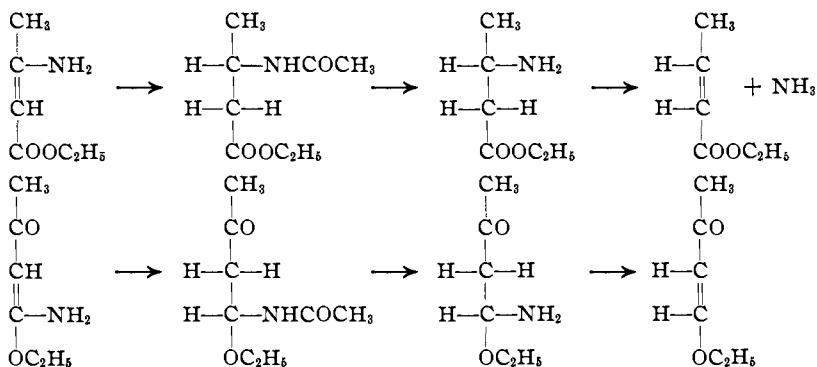
The ethyl β-amino-α-butylcrotonate formed by the action of ammonia on butyl acetoacetic ester also reduced readily with the formation of ethyl β-acetamido α-butylbutyrate. This ester was hydrolyzed to the corresponding β-amino α-butylbutyric acid, which readily decomposed on distillation to α-butylcrotonic acid. The enol-acetate of the original butylacetoacetic ester was therefore from the carbonyl of the acetyl group.

Experimental

Reduction of Ethyl-β-acetoxycrotonate.—A solution of 27.5 g. of ethyl-β-acetoxycrotonate[5] in 25 cc. of glacial acetic acid was reduced with 0.2 g. of platinum-oxide plati-

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[8] Auwers and Jacobsen, *Ann.*, **426**, 161 (1921).

[9] Skita and Wulff, *ibid.*, **453**, 190 (1927).

num black catalyst and hydrogen at 35 lb. pressure.   Two equivalents of hydrogen were absorbed in ninety minutes.   The catalyst was filtered and the solvent neutralized with a saturated sodium carbonate solution.   The ethyl butyrate was separated, dried with anhydrous magnesium sulfate and distilled.   Twelve grams (65.5%) was obtained; b. p. 118–121°; α_{20}^{20} 0.8803, n_D^{20} 1.3977: Butyramide prepared from the above ester melted at 114–115°.   The effect of the amount of the catalyst on this reaction was studied by reducing 0.1 mole portions of ethyl β-acetoxycrotonate dissolved in 25 cc. of acetic acid using 0.05-g., 0.1-g., 0.2-g. portions of catalyst.   The time for complete reduction (two mole equivalents of hydrogen) was thirty minutes, forty-five minutes and sixty minutes, respectively, and the yields were approximately 75% in each case.

Enol-acetate of Benzoylacetone.—A mixture of 50 g. of benzoylacetone,[10] 70 g. of pyridine, and 35 g. of acetyl chloride was allowed to stand at room temperature for three days with occasional shaking.   The solid reaction mixture was extracted with three 100-cc. portions of anhydrous ether.   This ether solution was washed with two 50-cc. portions of cold water, two 50-cc. portions of 10% hydrochloric acid solution, one 50-cc. portion of 10% sodium carbonate solution, and dried over anhydrous magnesium sulfate.   On distillation 43 g. (70%) of product was obtained, b. p. 120–122° at 2 mm.; d_{20}^{20} 1.123, n_D^{20} 1.5437.   Nef[11] obtained this product by the action of acetic anhydride on benzoylacetone and reported b. p. 170° at 22 mm. with slight decomposition.

Anal.   Calcd. for $C_{12}H_{12}O_3$: C, 70.59; H, 5.88.   Found: C, 70.77; H, 6.08.

Reduction of the Enol-acetate of Benzoylacetone.—A solution of 20 g. (0.1 mole) of the enol-acetate of benzoylacetone in 25 cc. of glacial acetic acid was reduced with 0.1 g. of platinum-oxide platinum black and hydrogen at 35 lb. pressure.   Two mole equivalents were absorbed in six hours.   The catalyst was removed by filtration, the solvent by neutralization and the product distilled.   After four distillations 10.8 g. of a product was obtained, b. p. 80–81° at 2 mm., 230–232° at 760 mm., n_D^{20} 1.5193; d_{20}^{20} 0.991. This corresponds to 73% of the theoretical calculated as butyrophenone.

Anal.   Calcd. for $C_{10}H_{12}O$: C, 81.08; H, 8.11.   Found: C, 79.44, 79.26, 79.75, 79.43; H, 8.69, 8.58, 8.78, 8.60.

The analyses were consistently too far away from the calculated values to indicate a pure product.   The butyrophenone was probably contaminated with a little phenyl-propylcarbinol and phenylpropylcarbinyl acetate as indicated by the experiments on 1-phenylpentadione-1,3 and 1-phenylhexadione-1,3.

From 1 g. of the above product 1 g. of a semicarbazone was formed, m. p. 188–189°. A mixed melting point with the semicarbazone of a sample of authentic butyrophenone showed no depression.

Anal.   Calcd. for $C_{11}H_{15}N_3O$: C, 64.39; H, 7.31.   Found: C, 63.98; H, 7.20.

1-Phenylpentadione-1,3.—The same method was used as for benzoylacetone except that the sodium salt was not isolated as an intermediate product.   From 30 g. of sodium, 250 g. of ethyl propionate and 80 g. of acetophenone, 58 g. of 1-phenylpenta-dione-1,3 boiling at 120–122° at 3 mm. was obtained.

1-Phenylhexadione-1,3.—In the same manner as above 28 g. of sodium, 180 g. of ethyl butyrate and 72 g. of acetophenone were used to prepare 39 g. of 1-phenylhexa-dione-1,3, b. p. 122–125° at 2 mm.

Enol-acetate of 1-Phenylpentadione-1,3.[12]—A mixture of 54 g. of 1-phenylpenta-dione-1,3, 50 g. of dry pyridine and 35 g. of acetyl chloride was allowed to stand in a stoppered flask for three days and the product isolated in the same way as the enol-

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[10] Adkins, Kutz and Coffman, THIS JOURNAL, **52**, 3213 (1930).

[11] Nef, *Ann.*, **227**, 60 (1893).

[12] Stylos and Beyer, *Ber.*, **20**, 2181 (1887).

acetate of benzoylacetone. The yield was 43 g. (64%), b. p. 130–133° at 2 mm., d_{20}^{20} 1.1023; n_D^{20} 1.5513.

Anal. Calcd. for $C_{13}H_{14}O_3$: C, 71.56; H, 6.42. Found: C, 71.21; H, 6.36.

Enol-acetate of 1-Phenylhexadione-1,3.—By a similar procedure 28 g. (60%) of product was obtained, b. p. 136–139° at 2 mm.; n_D^{20} 1.5460; d_{20}^{20} 1.093.

Anal. Calcd. for $C_{14}H_{16}O_3$: C, 71.98; H, 6.90. Found: C, 72.11; H, 7.06.

Reduction of the Enol-acetate of 1-Phenylpentadione-1,3.—A solution of 22 g. of the enol-acetate of 1-phenylpentadione-1,3 dissolved in 25 cc. of glacial acetic acid was reduced with 0.2 g. of platinum-oxide platinum black. Two mole equivalents of hydrogen were absorbed in four hours. Ten grams of a product was isolated, b. p. 147–150° at 25 mm.

Saponification Equivalent. Calcd. for $C_{13}H_{18}O_2$: 206. Found: 259. This indicates a high percentage of phenylbutylcarbinyl acetate in the product.

Ten grams of the reduced product was saponified with 100 cc. of 5% sodium hydroxide solution to give an oil, b. p. 143–145° at 23 mm. To 5.7 g. of potassium dichromate and 5 g. of concentrated sulfuric acid in 20 cc. of water, 3.2 g. of the oil was added. Oxidation was completed by warming on the steam-bath. The product was extracted with ether and condensed directly with semicarbazide. The semicarbazone melted at 165–166°. A mixed melting point with the semicarbazone of authentic valerophenone (m. p. 165–166°)[13] also melted at 165–166°.

Reduction of the Enol-acetate of 1-Phenylhexadione-1,3.—As in the previous experiment, a mixture was obtained, b. p. 145–147° at 18 mm., which was saponified and oxidized. There was thus obtained *n*-caprophenone, the semicarbazone of which melted at 131–132°.[13]

Reduction of Butyrophenone and of Valerophenone.—A solution of 14.8 g. (0.1 mole) of butyrophenone in 25 cc. of acetic acid was reduced with 0.1 g. of platinum-oxide platinum black and hydrogen at 35 lb. pressure. Somewhat more than one mole equivalent of hydrogen was absorbed. The product was isolated by neutralizing the acetic acid with sodium carbonate solution and drying the product over anhydrous potassium carbonate. Ten grams of material, b. p. 110–118° at 20 mm., was obtained.

In the same manner 2.8 g. of product, b. p. 120–130° at 20 mm., was obtained after the reduction of 5 g. of valerophenone. The products consisted of phenylpropylcarbinol, phenylbutylcarbinol and their acetates as shown by their saponification equivalents.

Saponification Equivalent.

Butyrophenone Product. Calcd. for $C_{12}H_{16}O_2$: 192. Found: 1306. This corresponds to 14% of the ester.

Valerophenone Product. Calcd. for $C_{13}H_{18}O_2$: 206. Found: 343. This indicates 60% of the ester.

Reduction of Ethyl β-Aminocrotonate. Preparation of Ethyl β-Acetamidobutyrate.—A solution of 39 g. of ethyl β-aminocrotonate[14] in 50 cc. of acetic acid was reduced with 0.1 g. of platinum-oxide platinum black and hydrogen at 35 lb. pressure. About one mole equivalent of hydrogen was absorbed in ten hours. The catalyst was removed by filtration and the solvent by neutralization with 20% sodium hydroxide solution. The ester on distillation gave 30 g. (57%) of a product insoluble in dilute hydrochloric acid, b. p. 117–120° at 4 mm.; d_{20}^{20} 1.0026; n_D^{20} 1.4440. This product was ethyl β-acetamidobutyrate,[15] identified by hydrolyzing with dilute hydrochloric acid and add-

[13] Tiffeneau and Levy, *Compt. rend.*, **183**, 969 (1926).

[14] Michaelis, *Ann.*, **366**, 337 (1909).

[15] Fischer and Roeder, *Ber.*, **34**, 3755 (1901).

ing benzoyl chloride and sodium bicarbonate in order to produce the benzoyl derivative of β-aminocrotonic acid, m. p. 153–154°.[16]

Conversion of Ethyl β-Acetamidobutyrate to Ethyl Crotonate.—A partial hydrolysis was effected by refluxing a solution of 15 g. of ethyl β-acetamidocrotonate in 20 cc. of ethyl alcohol and 15 cc. of concentrated hydrochloric acid for five hours. The mixture was then neutralized with sodium carbonate solution and extracted with ether. This ether solution was dried with anhydrous magnesium sulfate and distilled. At a bath temperature of 180–220°, decomposition occurred and the distillate of ethyl crotonate was redistilled; b. p. 141–143°, d_{20}^{20} 0.9189; n_D^{20} 1.4256. The yield was 5 g.

The ethyl crotonate was further identified by saponifying 4 g. with an excess of alcoholic sodium hydroxide. The mixture was evaporated almost to dryness, acidified with hydrochloric acid and extracted with ether. The ether solution was distilled and the crotonic acid which distilled at 100–105° at 18 mm. solidified, m. p. 70–71°.

Neutral Equivalent. Calcd. for $C_4H_6O_2$: 86. Found: 87.

Ethyl β-Amino-α-butylcrotonate.[17]—Ammonia gas was passed into a solution of 37 g. of ethyl n-butylacetoacetate in 50 cc. of absolute alcohol until the solution became saturated. It was allowed to stand for two days and distilled; b. p. 102–109° at 3 mm. This fraction solidified. It was purified by melting, allowing to solidify partially and then pouring off or filtering the supernatant liquid. The product formed large white needles solidifying at 31°. They decomposed on standing to an oily product and ammonia.

Anal. Calcd. for $C_{10}H_{19}NO_2$: C, 64.81; H, 10.27. Found: C, 64.39; H, 10.25.

Ethyl β-Acetamido-α-butylbutyrate.—A solution of 18.5 g. of ethyl β-amino-α-butylcrotonate in 20 cc. of glacial acetic acid was reduced in the usual manner with hydrogen and 0.2 g. of platinum-oxide platinum black catalyst in twelve hours. The catalyst was removed and the filtrate neutralized with sodium hydroxide. The ethyl β-acetamido-α-butylbutyrate was separated, dried over anhydrous magnesium sulfate and distilled; b. p. 158–160° at 3 mm.; n_D^{20} 1.4538; d_{20}^{20} 0.9591. The yield was 13 g. (59%).

Anal. Calcd. for $C_{12}H_{23}NO_3$: C, 62.88; H, 10.04. Found: C, 63.20; H, 10.20.

Hydrolysis of Ethyl β-Acetamido-α-butylbutyrate.—A mixture of 15 g. of ethyl β-acetamido-α-butylbutyrate and 100 cc. of 20% potassium hydroxide solution was refluxed for eight hours. The mixture was allowed to cool, extracted with ether, and the aqueous solution concentrated by evaporating to about 25 cc. The top layer solidified on cooling and the lower aqueous layer was removed by decantation. The solid was dissolved in 50 cc. of water, cooled to 0°, and neutralized with hydrochloric acid. A white precipitate of β-amino-α-butylbutyric acid formed. This was very hygroscopic and was kept dry in a vacuum desiccator.

The hydrochloride was formed by adding concentrated hydrochloric acid and evaporating the mixture to dryness. It was purified by crystallization from 95% alcohol; m. p. 87–88°.

Anal. Calcd. for $C_8H_{18}ClNO_2$: Cl, 17.95. Found: Cl, 17.61.

Conversion of β-Amino-α-butylbutyric Acid to α-Butylcrotonic Acid.—On heating the β-amino-α-butylbutyric acid to 220° and then distilling under reduced pressure, the β-butylcrotonic acid was obtained, boiling at 160–163° at 23 mm.; n_D^{20} 1.4550; d_{20}^{20} 0.9524.

Neutral Equivalent. Calcd. for $C_8H_{14}O_2$: 142. Found: 144.

Anal. Calcd. for $C_8H_{14}O_2$: C, 67.61; H, 9.86. Found: C, 67.13; H, 9.81.

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[16] Skita and Wulff, *Ann.*, **455**, 190 (1927), prepared this compound by the reduction of the corresponding crotonate and report a boiling point of 158° at 12 mm.

[17] Guareschi, *Chem. Zentr.* (5), **76**, II, 683 (1905).

Summary

1.   The enol-acetates of ethyl acetoacetate and benzoylacetone were prepared and reduced with hydrogen and platinum-oxide platinum black in glacial acetic acid.   Two mole equivalents of hydrogen were absorbed and there resulted ethyl butyrate and butyrophenone, respectively.

2.   The enol-acetates of 1-phenylpentadione-1,3 and 1-phenylhexadione-1,3 were also reduced in a similar manner.   A mixture of phenylbutylcarbinol and its acetate was obtained in the first case and phenylamylcarbinol and its acetate in the second.

3.   Butyrophenone and valerophenone when reduced catalytically with platinum-oxide platinum black in glacial acetic acid yielded similar mixtures.

4.   Ethyl β-aminocrotonate upon catalytic reduction with platinum-oxide platinum black and hydrogen in glacial acetic acid gave ethyl β-acetamidobutyrate.   This latter substance upon partial hydrolysis and decomposition by heating gave ethyl crotonate.

5.   A similar experiment with ethyl β-amino-α-butylcrotonate gave ethyl β-acetamido-α-butylbutyrate.   This product was completely hydrolyzed and the β-amino-α-butylbutyric acid distilled. α-Butylcrotonic acid resulted.

6.   These procedures were developed for determining the constitution of the enol-acetates and vinylamine products formed from 1,3-dicarbonyl compounds.

URBANA, ILLINOIS

THE ACTION OF ALIPHATIC OXIDES ON AROMATIC COMPOUNDS.   THE PREPARATION OF SUBSTITUTED DIBENZYLS

BY RICHARD A. SMITH AND SAMUEL NATELSON

Because of the occurrence of the dibenzyl residue in many of the isoquinoline alkaloids, such as narcotine,[1] hydrastine,[2] berberine,[3] corydaline,[4] papavarine,[5] laudanosine,[6] morphine[7] and probably emetine, research was undertaken with the intent of finding a general method for the syn-

[1] Perkin and Robinson, J. Chem. Soc., 99, 776 (1911).

[2] Freund, Ber., 20, 2403 (1889).

[3] Pictet and Gams, Compt. rend., 153, 386 (1911).

[4] Dobbie and Lauder, J. Chem. Soc., 83, 605 (1903).

[5] Pictet and Gams, Compt. rend., 149, 210 (1909).

[6] Pictet and Finkelstein, ibid., 148, 295 (1909).

[7] Faltis, Arch. Pharm., 255, 85 (1917).