had all been added, during which time an appreciable quantity of the yellow 5′,8′-dinitro-1′-naphthoyl-2-benzoic acid precipitated and was filtered. The acetic anhydride filtrate was poured into a large volume of water and allowed to stand overnight to decompose the acetic anhydride. A yellow precipitate was produced which was filtered and dried at room temperature. The precipitate was then crystallized twice from boiling toluene; yield, 10 g. (32%) of yellow plates. If heated rapidly it melted sharply at 262–263° (decomp.).

Anal. Calcd. for $C_{18}H_{10}O_7N_2$: C, 59.0; H, 2.43. Found: C, 59.9; H, 2.52.

Summary

1. A study of the substitution of α-naphthoyl-*o*-benzoic acid has been made. By the action of chlorine or bromine, either the 5′- or 5′,8′-disubstitution derivatives are obtained which may readily be dehydrated to the corresponding benzanthraquinones.

2. Proof of the 5′-position of the monobromo derivative was established by oxidation of the bromobenzanthraquinone to anthraquinone-1,2-dicarboxylic acid and by fusion of the bromo-α-naphthoyl-*o*-benzoic acid with sodium and potassium hydroxide to yield 1-hydroxy-5-naphthoic acid.

3. Nitration of 5′-chloro- or bromo-1′-naphthoyl-2-benzoic acid gave the 8′-nitro derivative, as shown by the fact that on reduction a ring structure was produced characteristic of 1-keto-8-aminonaphthalenes. Further nitration gave a halogen-free dinitro compound, probably 5′,8′-dinitro-1′-naphthoyl-2-benzoic acid.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

THE DEAMINATION OF ETHYL BETA-METHYLAMINOPROPIONATE

BY W. B. THOMAS AND S. M. MCELVAIN

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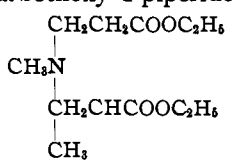
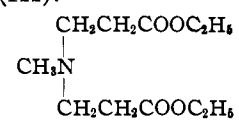
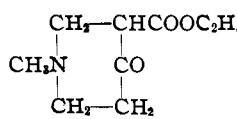
In an attempt to prepare β-carbethoxyethyl-β-carbethoxypropylmethylamine (I), ethyl β-methylaminopropionate was treated with ethyl β-bromoisobutyrate. Instead of the desired compound the product which was obtained was β,β′-dicarbethoxydiethylmethylamine[1] (II) as shown by the fact that it was converted by sodium ethoxide into 1-methyl-3-carbethoxy-4-piperidone[1] (III).



I



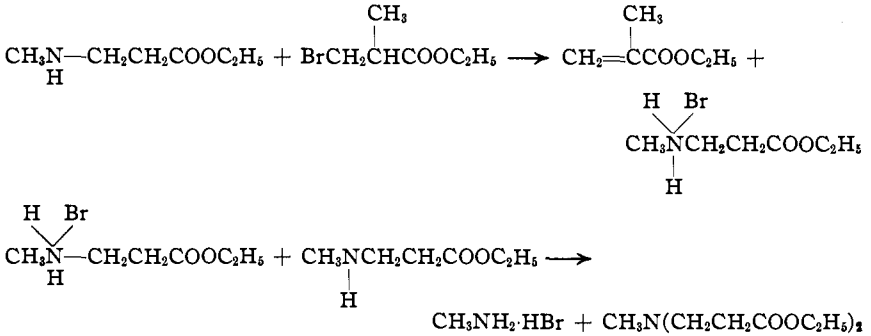
II



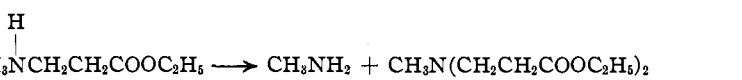
III

[1] McElvain, THIS JOURNAL, **46**, 1721 (1924).

The course which the reaction had taken may be shown, thus



Since ethyl β-methylaminopropionate readily adds to ethyl acrylate to give the amino ester (II) it is probable that ethyl acrylate is an intermediate in the second phase of the above reactions. For this reason it seemed likely that the unsymmetrical amino ester (I) might be obtained by the addition of ethyl β-methylaminopropionate to ethyl α-methylacrylate. However, this reaction also yielded the symmetrical amino ester (II). It is evident, therefore, that ethyl β-methylaminopropionate as well as its salt readily loses methylamine to form a tertiary amino ester, thus



Since it is probable that this reaction also involves the intermediate formation of ethyl acrylate[2] it is quite surprising that both the formation of this latter ester and the addition of a molecule of the secondary amino ester to it take place rather than the addition of any appreciable amount of the secondary amino ester to the ethyl α-methylacrylate.

Experimental

Ethyl β-Bromoisobutyrate.—This ester was prepared by the addition of hydrogen bromide to α-methyl acrylate.[3] The yield of ethyl α-methyl-β-bromopropionate was 76% of the theoretical, b. p. 68–72° (14 mm.), n_D^{25} 1.44506, d_{25}^{25} 1.3275. This ester distils with slight decomposition at 180–180.5° at atmospheric pressure. Calcd. for $C_6H_{11}O_2Br$, Br: 40.96. Found: 41.12. Recently Vocke[4] obtained methyl β-bromoisobutyrate by the action of hydrogen bromide on a methyl alcoholic solution of α-methylacrylic acid.

Ethyl β-Methylaminopropionate from Ethyl β-Benzoylmethylaminopropionate.—To a solution of 48 g. of ethyl β-methylaminopropionate[5] in 30 cc. of acetone was added 100 g. of anhydrous potassium carbonate. Then, during vigorous stirring, 66 g. of

[2] *Cf.* Abderhalden, *Z. physiol. Chem.*, **85**, 114 (1913); Fuson, THIS JOURNAL, **50**, 1448 (1928).

[3] Ruzicka, *Helv. Chim. Acta*, **2**, 152 (1919).

[4] Vocke, *Z. physiol. Chem.*, **191**, 83 (1930).

[5] McElvain, THIS JOURNAL, **46**, 1726 (1924).

benzoyl chloride was added from a dropping funnel at such a rate that the acetone did not reflux too vigorously. After this addition the acetone was refluxed and stirred for ten hours. The solid precipitate was then filtered off and the acetone removed by distillation. The residue was taken up in ether, washed with dilute hydrochloric acid and dilute sodium hydroxide and, after drying over anhydrous potassium carbonate, distilled. The yield of the benzoyl derivative was 86 g. (62%); b. p. 155–157° (3 mm.); n_D^{25} 1.51741; d_{25}^{25} 1.1076. Calcd. for $C_{13}H_{17}O_3N$: N, 5.96. Found: N, 6.31.

This benzoyl derivative was hydrolyzed by refluxing for eight hours with 20% hydrochloric acid. After cooling the precipitated benzoic acid was filtered off and any remaining in solution extracted with ether. The acid solution was evaporated to dryness and the residue esterified as previously described.[5] The yield of ethyl β-methylaminopropionate from 48 g. of the benzoyl derivative was 18 g. (67%). It boiled at 60.5–61° (10 mm.); n_D^{25} 1.41990; d_{25}^{25} 0.9502. Calcd. for $C_6H_{13}O_2N$: N, 10.7. Found: N, 11.1. The secondary amino ester obtained by the above procedure differs quite materially in physical properties from the product previously described.[5]

Reaction of Ethyl β-Methylaminopropionate and Ethyl β-Bromoisobutyrate.—A mixture of 70.1 g. (2 mols) of ethyl β-methylaminopropionate and 52.2 g. (1 mol) of ethyl β-bromoisobutyrate was heated in an oil-bath at 130–140° for two hours. After this time the reaction mixture was cooled, diluted with ether and the ethereal solution separated by decantation from the semi-crystalline precipitate. From an alkaline solution of this precipitate methylamine was distilled out and characterized as methyl benzamide, m. p. 79–80°. After removal of the ether from the ethereal extract the residue was fractionated and the following fractions collected: (1) 9.5 g. below 50° (25 mm.), (2) 8.9 g. at 40–50° (4 mm.) and (3) 37.5 g. at 116–117° (4 mm.). Fraction (1) was mainly ethyl α-methylacrylate, (2) unchanged secondary amine and (3) was a tertiary amino ester which gave 6.25% N on analysis. (Calcd. for symmetrical ester (II), 6.06% and unsymmetrical ester (I), 5.72%.) This tertiary amino ester was condensed by sodium ethoxide to 1-methyl-3-carbethoxy-4-piperidone (III).

Reaction of Ethyl β-Methylaminopropionate with Ethyl α-Methylacrylate.—A mixture of 12.4 g. (1 mol) of the secondary amino ester and 10.8 g. (1 mol) of the unsaturated ester was heated in an oil-bath at 130–140° for three hours. After this time the reaction mixture was fractionated and the following fractions obtained (1) 8.9 g. of ethyl α-methylacrylate, (2) 4.9 g. of secondary amino ester and (3) 6 g. of a tertiary amino ester. A residue of polymerized methylacrylate remained. Fraction (3) was shown to be the β,β′-dicarbethoxydiethylmethylamine (II) by analysis (found, 6.12 N) and by the fact that sodium ethoxide condensed it to 1-methyl-3-carbethoxy-4-piperidone as above.

Preparation of β,β′-Dicarbethoxydiethylmethylamine (I) from Ethyl β-Methylaminopropionate.—(1) To 8.4 g. (1 mol) of the secondary amino ester was added 13.5 g. (1 mol) of its hydrobromide and the mixture heated in an oil-bath at 130–140° for three hours. After cooling, ether was added and the ethereal solution decanted from the precipitated hydrobromide. On distillation of the ethereal extract, 1.5 g. of unreacted secondary amino ester and 5 g. (34%) of the tertiary amino ester (II) was obtained. To the hydrobromide residue left after the ether decantation 30 cc. of 20% sodium hydroxide was added. Then about half of the alkaline solution was carefully distilled into standard acid and the methylamine determined; 0.99 g. (51%) was found.

(2) A 25-g. sample of the secondary amino ester when heated under a reflux condenser at 130–140° for four hours evolved 0.445 g. (14.8%) of methylamine. Fractionation of the remaining ester yielded 18.9 g. of unchanged secondary amino ester and 3.4 g. (15%) of the tertiary amine (II).

(3) A mixture of 7 g. of ethyl acrylate and 9.2 g. of the secondary amino ester

was heated under reflux in an oil-bath at 110–120° for two hours. Distillation of the reaction mixture yielded small amounts of unreacted acrylic and secondary amino esters and 11.6 g. (80%) of tertiary amino ester (II).

Summary

It has been found that when ethyl β-methylaminopropionate is allowed to react with either ethyl β-bromoisobutyrate or ethyl α-methylacrylate the product obtained is not the expected β-carbethoxyethyl-β-carbethoxypropylmethylamine, but is β,β′-dicarbethoxyethylmethylamine which is formed by the elimination of methyl amine (or its salt) from two molecules of the secondary amino ester.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE LABORATORY OF FOODS AND SANITATION, UNIVERSITY OF WISCONSIN]

RYE GERM OIL

BY ALBERT W. STOUT AND H. A. SCHUETTE

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Little published information[1] on the composition of the oil in rye, *Secale cerealae* L., is available. That which has found its way into the literature is of European origin and is not pertinent to the same type of product in each instance inasmuch as the whole kernel,[1a,d,h] its bran,[1b] its embryo[1g] and its flour[1c,h] and breads[1h] baked therefrom have been used as the sources of the oil or "ether extract," under examination. The inevitable result of this diversity in selection of raw material has been a lack of correlation of data.[2] Furthermore, with one exception,[1h] all of the reports in question are incomplete when viewed in the light of the newer trends in the technique of fatty oil analysis.

Unlike the embryo oils of other cereals such as corn and wheat, rye oil finds at present no important technical or alimentary use. The facts that it is apparently rich in the carotinoid pigments, that it contains a high percentage of lecithin-bearing unsaponifiable matter, and that the antimony trichloride test which is presumed to be indicative of the presence of vitamin A is positive, suggest the thought that the clinical advantages of

[1] (a) König, *Landw. Vers. Sta.*, **17**, 1 (1874); (b) Stellwaag, *ibid.*, **37**, 135 (1890); (c) Spaeth, *Forschungsber. Lebensm.*, **3**, 251 (1896), through *Z. Nahr. Genussm.*, 11, 410 (1896); (d) Meyer, *Chem.-Ztg.*, **27**, 958 (1903); (e) Grimme, *Seifensieder-Ztg.*, **45**, 704 (1918); (f) Herbig, *Seifenfabrikant*, **38**, 497 (1918); (g) Alpers, *Chem.-Ztg.*, **42**, 37 (1918); (h) Croxford, *Analyst*, **55**, 735 (1930).

[2] This is particularly noticeable in the description of the color—it has been variously reported as being dark green to yellowish-brown—and other external characteristics of the oil and in the records of its simpler chemical constants. Iodine numbers, for example, have been reported as lying between 81.8 and 127.7; saponification numbers between 172.8 and 196.0; and the content of unsaponifiable matter to vary between 8.2 and 11.20%.