steam cone. The pink colored solid was digested in 40 ml. of water for one-half hour and filtered to give a crude yield of 4.45 g. (98.3%), m. p. 192–193°. The pink colored product was recrystallized three times from benzene to yield 3 g. (66.2%) of pure white crystalline material; m. p. 195–196°.

Anal. Calcd. for $C_{16}H_{29}N_7O$: N, 29.22; Found: N, 28.72.

8-Bromotheobromine.—Theobromine, 7.5 g. (0.0414 mole), was added to 42 g. (0.252 mole) of bromine and 25 ml. of chloroform with stirring. The mixture was allowed to stand at room temperature for one hour and then heated on a steam cone until all the bromine and chloroform had been expelled. The yellow solid was decolorized by digestion with acidified bisulfite solution, and washed with water. The crude product was dissolved in 5 *N* potassium hydroxide solution and the clear solution acidified with glacial acetic acid. The precipitated white product was removed by filtration, washed with water and dried in the air; yield 6.7 g. (62.1%), m. p. over 235°.

3,7-Dimethyl-2,6-dioxy-8-(γ-diethylaminopropylamino)-purine.—A mixture consisting 5.0 g. (0.019 mole) of 8-bromotheobromine and 7.5 g. (0.057 mole) of γ-diethylaminopropylamine was heated in a bomb tube at 165° for eight hours with no apparent change. The mixture was then heated first at 190° for six hours and finally at 200° for sixteen hours. In spite of the fact that the material appeared to be unchanged the contents of the tube were found to give a positive silver nitrate test for halogen. The white solid was boiled with 150 ml. of water, cooled, and the white crystalline product (2.8 g.) removed by filtration and washed with water. The combined filtrates were made exactly neutral with acetic acid and a second crop (1.17 g.) of the product separated; yield 3.97 g. (67%), m. p. 306°.

Anal. Calcd. for $C_{14}H_{24}O_2N_6$: N, 27.25. Found: N, 27.14.

The picrate was prepared in ethanol and after recrystallization the ruby red needles melted at 210–211°.

In a similar manner 1,3,7-trimethyl-2,6-dihydroxy-8-(γ-diethylaminopropylamino)-purine is obtained by the reaction of 8-chlorocaffeine and γ-diethylaminopropylamine;[11] m. p. of monohydrochloride 229–231°.

Anal. Calcd. for $C_{15}H_{26}O_2N_6 \cdot HCl$: N, 23.31. Found: N, 23.34, 23.37.

Summary

The synthesis of eleven new basically-substituted purine derivatives and their intermediates has been described.

[11] Walter F. Holcomb, private communication from the Research Laboratories of Parke, Davis and Company.

STATE COLLEGE, PA. RECEIVED APRIL 16, 1945

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Synthesis of β-Keto Esters by the Decomposition of Acylated Malonic Esters

BY BYRON RIEGEL AND W. M. LILIENFELD[1]

For many types of synthetic problems, β-keto esters have been used as intermediates. For instance, in the Bardhan synthesis of polycyclic compounds β-ketoadipic ester is the most suitable starting material for the preparation of certain substituted 1,2-cyclopentenophenanthrenes. The original method[2] for the preparation of this ester was to acylate acetoacetic ester with the half ester acid chloride of succinic acid and then ammonolyze the resulting compound to remove the acetyl group. The yield is low and the method is difficult and tedious. To facilitate further studies in this field a better method for the preparation of β-ketoadipic ester was developed.

This new method involves the use of malonic ester in place of the acetoacetic ester. Lund and co-workers[3] reported that the magnesium enolate derivative of malonic ester, in an ether solution, is acylated very readily and in excellent yields. However, with β-carbethoxypropionyl chloride the acylation did not proceed as well as that reported by Lund for the simpler acid chlorides. The excess alcohol in the solution of the magnesium enolate interferes with the acylation and must be removed before adding the acid chloride.

The tricarboxylic ester thus obtained was converted into β-ketoadipic ester by heating it with β-naphthalenesulfonic acid. The mechanism of this reaction is not clearly understood and will require further study. Willstätter[4] found accidentally that a lower homolog, namely, acetone-1,1,3-tricarboxylic ester, underwent thermal decomposition quite readily to give the ester of acetone-1,3-dicarboxylic acid. More recently Breslow, Baumgarten and Hauser[5] have reported a new synthesis of β-keto esters by the thermal decomposition of the acylated ethyl *t*-butylmalonates using *p*-toluenesulfonic acid as a catalyst. The remarkable ease with which these esters gave off isobutylene and decarboxylated, presumably due to the acid catalyst, led to the development of their new method. Our method[6] is very similar to theirs except that it does not require the initial preparation of ethyl *t*-butylmalonate and thus can be carried out in much less time. Preliminary experiments were then made to see if our method could be used for the preparation of ethyl propionylacetate and ethyl benzoxylacetate which were successful.

For the preparation of β-ketoadipic ester, β-

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[1] Anna Fuller Fund Research Associate, 1943–1944.

[2] J. C. Bardhan, *J. Chem. Soc.*, 1848 (1936); P. Ruggli and A. Maeder, *Helv. Chim. Acta*, **25**, 936 (1942).

[3] H. Lund, *Ber.*, **67**, 935 (1934); "Organic Syntheses," Coll. Vol. II, p. 594; H. Lund, A. U. Hasnen and A. F. Voigt, *Kgl. Danske Videnskab, Selskab, Math.-fys. Medd.*, **12**, 1 (1933).

[4] R. Willstätter, *Ber.*, **32**, 1272 (1899).

[5] D. S. Breslow, E. Baumgarten and C. R. Hauser, THIS JOURNAL, **66**, 1286 (1944).

[6] At the time that the method described here was being developed we noted in an O.S.R.D. report that Dr. C. R. Hauser was also studying a similar method. We wish to thank him for sending to us portions of the experimental part of the manuscript he was submitting for publication. However, we did not know, until after publication, that they had tried an acid-catalyzed decomposition (steam distillation) of an acylated diethyl malonate with negative results.

naphthalenesulfonic acid was added to the tricarboxylic ester and the decomposition was carried out by gradually raising the temperature to 190–200°. At 130–140° there was a vigorous evolution of gas. This gas consisted of carbon dioxide, ether and other organic vapors which were not investigated. The gas mixture did not decolorize a permanganate solution, hence the presence of ethylene and ethyl alcohol seemed unlikely. During the reaction the acid catalyst is partially esterified. Ethyl *p*-toluenesulfonate and diethyl β-ketoadipate boil at almost the same temperature which complicates their separation. To avoid this trouble β-naphthalenesulfonic acid was chosen for the catalyst and found to be highly satisfactory. The yield was 40% of β-ketoadipic ester which was shown to be at least 95% pure.

The magnesium derivative of malonic ester was treated with propionyl chloride. The resulting ester was thermally decomposed with β-naphthalenesulfonic acid and then distilled. A similar reaction using benzoyl chloride in place of the propionyl chloride was also carried out. Due to the lack of time further study of these reactions was not made but we believe the yields could be greatly improved. This method appears to be general and, in view of the convenience with which the reactions can be carried out, it should have wide application.

Experimental[7]

Diethyl β-Ketoadipate.—Magnesium malonic ester[3] was prepared by adding a solution of 160 g. (151 ml., 1 mole) of redistilled diethyl malonate in 80 ml. of absolute ethanol to a suspension of 25 g. of aluminum-free magnesium in 25 ml. of absolute alcohol and 1 ml. of carbon tetrachloride. To this mixture was added 300 ml. of dry ether and then it was refluxed until all of the magnesium had dissolved, which required about six hours. The ether and most of the alcohol were removed by distillation first under atmospheric pressure and then under reduced pressure. About 300 ml. of dry benzene was added to the partially crystalline sirupy residue. After the residue had dissolved in the benzene the solvent was again removed at atmospheric pressure and finally under reduced pressure. The residual sirup was then dissolved in 300 ml. of dry ether.

A solution of 130 g. of succinic anhydride in 150 ml. of absolute ethanol was heated on a steam-bath until the alcohol ceased to reflux. The excess alcohol was removed by distillation under reduced pressure and the residue of ethyl hydrogen succinate was refluxed for one hour with 150 ml. of thionyl chloride. The excess thionyl chloride was removed and the residue consisting chiefly of β-carbethoxypropionyl chloride was distilled under reduced pressure giving 190 g. (94%, 1.15 moles), b. p. 110–115° at 30 mm.

The acid chloride thus prepared was dissolved in 150 ml. of dry ether and this ether solution was added to the solution of magnesium malonic ester at such a rate that a vigorous reflux was maintained. After all of the acid chloride had been added the reaction mixture was refluxed for about two hours. After some time the magnesium complex separated as a brown, ether insoluble viscous mass. The reaction mixture was then hydrolyzed very carefully by the slow addition of a solution of 30 ml. of concentrated sulfuric acid in 600 ml. of water. The organic layer was separated, the aqueous solution extracted once with ether, and the combined ethereal solutions were washed once with dilute sulfuric or phosphoric acid and then twice with water. The ether solution was dried with anhydrous sodium sulfate and the ether evaporated. To the residue was added 14 g. (0.062 mole) of β-naphthalenesulfonic acid monohydrate and the reaction mixture was heated slowly up to a temperature of 190–200°. At 130–140° there was a vigorous evolution of gas. After the gas evolution had ceased the mixture was allowed to cool and was diluted with 100 ml. of ether. The ether solution was shaken vigorously with four portions of a strong, cold sodium carbonate solution. The combined carbonate solutions were back extracted once with ether. The combined ether solutions were washed with water, dilute acid and finally with water and then dried.

The carbonate solution was acidified and the organic matter which separated was extracted with ether. About 60 g. of the tricarboxylic ester could thus be recovered. The recovered material was treated with 5 g. of β-naphthalenesulfonic acid, and the reaction mixture was heated and then worked up as described above. The two alkali-insoluble fractions were combined. After drying and removing the ether the residue was fractionated through a 12-inch Vigreux column at a pressure of about 0.5 mm. The considerable forerun boiling chiefly at 80–90° and consisting mostly of diethyl succinate and diethyl malonate was discarded. The main fraction (86 g., 40%) distilled at 122–126° at 0.5 mm. and was practically pure diethyl β-ketoadipate. The residue consisted of some ethyl β-naphthalenesulfonate and tar.

Anal. Calcd. for $C_{12}H_{16}O_5$: C, 55.54; H, 7.46. Found: C, 55.52; H, 7.54.

The Knoevenagel condensation of the ester with isobutyraldehyde served as an excellent index of its purity. A mixture of 43.2 g. (39 ml., 0.2 mole) of the diethyl β-ketoadipate, 18 g. (22.6 ml., 0.25 mole) of redistilled isobutyraldehyde, 50 ml. of benzene, 3 ml. of glacial acetic acid and 1 ml. of piperidine was refluxed for two hours through a water trap. About 3.5 ml. (0.195 mole) of water separated. The isolation of the isobutylidene-β-ketoadipic ester from the benzene solution will be described in a later publication. To further identify the β-ketoadipic ester it was hydrolyzed, by the use of hydrochloric acid, according to the method described by Bardhan.[2] The white crusts which remained after concentration in a vacuum desiccator were crystallized from a mixture of acetone and petroleum ether (Skellysolve B, b. p. 60–70°). The crystalline β-ketoadipic acid melted at 121–123° with decomposition, whereas Bardhan reports a decomposition point of 125–126°.

Anal. Calcd. for $C_6H_8O_5$: C, 45.00; H, 5.0. Found: C, 44.93; H, 5.12.

The β-ketoadipic acid was decarboxylated to levulinic acid by heating it above its m. p. until the evolution of carbon dioxide ceased. The oil thus obtained was converted into its 2,4-dinitrophenylhydrazone which melted at 92–94°. Allen[8] reported the m. p. of the 2,4-dinitrophenylhydrazone of levulinic acid to be 92°.

Ethyl Propionylacetate.—To one-half of a mole of the magnesium enolate of malonic ester[3] from which the excess alcohol had not been removed was added 49 g. (46 ml., 0.53 mole) of propionyl chloride dissolved in 50 ml. of dry ether. The reaction mixture was refluxed for thirty minutes and then decomposed with dilute sulfuric acid. The ether layer was washed first with dilute sulfuric acid, then with water, dried over anhydrous sodium sulfate and the ether was removed. To the residue was added 8 g. of β-naphthalenesulfonic acid monohydrate and the reaction mixture was heated slowly to 200°. At about 120° a vigorous evolution of gas set in. When the gas evolution subsided the reaction mixture was cooled, diluted with ether and washed repeatedly with a dilute solution of sodium carbonate and finally with water. The aqueous washings were back extracted with ether, the combined ethereal solutions were dried and the ether was removed.

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(7) All melting points are corrected. Analyses by Dr. T. S. Ma, University of Chicago.

(8) C. F. H. Allen, THIS JOURNAL, 52, 2938 (1930).

The residue was distilled under reduced pressure and the fraction boiling between 100–105° at 22 mm. was collected. By acidifying the carbonate extracts 18 g. of propionylmalonic ester was recovered. Correcting for this recovery the yield was 57% (34 g.) of propionylacetic ester.

In order to prove the identity of the ester it was converted into the corresponding bis-pyrazolone by heating the compound overnight with a slight excess of phenylhydrazine. Ether was then added to the reaction mixture and the white crystalline pyrazolone was separated by filtration and thoroughly washed with ether. The bis-(1-phenyl-3-ethyl-5-pyrazolone) melted with decomposition at 331°, whereas Blaise[9] reports a m. p. of 335°.

Ethyl Benzoylacetate.—The benzoylacetic ester was obtained in a manner analogous to that of ethyl propionylacetate. To a solution of one-half mole of the magnesium enolate of malonic ester there was added 75 g. (62 ml., 0.53 mole) of benzoyl chloride dissolved in 75 ml. of dry ether. The reaction mixture was again refluxed for thirty minutes and then worked up and decarboxylated in the same way as described above. From the alkaline washings obtained after the decarboxylation was recovered 25 g. of benzoylmalonic ester. A yield of 34 g. or 44%, after correcting for the recovered benzoylmalonic ester, of ethyl benzoylacetate boiling at 140–145° at 3 mm. was obtained. To prove the identity of the ethyl benzoylacetate it was converted into its copper salt by shaking an ether solution of the ester with a saturated solution of cupric acetate. The copper salt which separated was filtered, washed with water and recrystallized from hot benzene. It melted sharply at 182° which agreed with the m. p. reported by Wislicenus[10] for this compound.

Summary

1. A method is described for the synthesis of β-keto esters. It consists in heating acylated malonic esters in the presence of arylsulfonic acids.

2. This desired decomposition takes place if malonic ester is acylated with an aliphatic, aromatic or a half ester acid chloride.

3. It is the most convenient and general method for the production of β-keto esters.

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[9] E. E. Blaise, *Compt. rend.*, **132**, 979 (1901).

[10] W. Wislicenus, *Ber.*, **31**, 3151 (1898).

EVANSTON, ILLINOIS

RECEIVED MARCH 3, 1945

[CONTRIBUTION FROM THE COLGATE-PALMOLIVE-PEET CO., JERSEY CITY, N. J.]

The Polymerization of Undecylenic Acid

BY JOHN ROSS, ARTHUR I. GEBHART AND J. FRED GERECHT

Low molecular weight vinyl compounds give high molecular weight polymers in which the ascertaining of the structural relationships and mode of combination of the individual polymer units presents peculiar difficulties. The polymerization of undecylenic acid is an interesting example of the reactivity of an olefinic group in the long chain fatty acid series and the degree of polymerization is sufficiently low to permit the isolation and examination of the structure of the dimeric stage of polymerization.

In 1877 Krafft isolated undecylenic acid from the products of distillation of castor oil. Later, Krafft and Brunner[1] found a solid acid in the distillation residues from castor oil, which was identical with a product they obtained by slow distillation of undecylenic acid. Taking into account the origin of this solid acid, m. p. 29°, and its analysis by combustion, they assigned it the structure $CH_2{=}CH(CH_2)_8COO(CH_2)_{10}COOH$ and called it di-undecylenic acid.

Cann and Amstutz[2] noted that undecylenic acid polymerizes under the influence of boron fluoride and their analytical data indicated that a product with some structural similarities to that postulated by Krafft and Brunner was formed.

We have examined the products of thermal polymerization of undecylenic acid and undecylenic methyl ester and in the dimeric fraction have found no material having the ester structure suggested by Krafft and Brunner. Instead we have found that polymerization proceeds linearly by the direct addition at terminal methylene groups.

Undecylenic acid in the form of the acid, anhydride, methyl ester, or sodium salt,[3] will polymerize at temperatures of 250–325°, to form dimers and higher polymers. When the reaction is allowed to proceed to the point where almost half of the monomer is polymerized, then the approximate composition of the polymerized material is one part of dimer to 2.5 parts of trimer and higher polymer. When polymerization is allowed to proceed further, the yield of dimeric material still remains about the same while the yield of the higher polymer increases.

For convenience, batches of methyl undecylenate were 50% polymerized under pressure of nitrogen gas in a steel bomb at 325° and the product separated by fractional distillation. The dimeric fraction was then further separated into solid and liquid portions by fractional crystallization from methanol.

The solid dimeric ester was shown to be a mixture of an unsaturated and a saturated dicarboxylic ester. The unsaturated dicarboxylic ester proved to be the dimethyl ester of 8-eicosene-1,20-dicarboxylic acid. Upon hydrogenation the latter gave the dimethyl ester of phellogenic acid (eicosane-1,20-dicarboxylic acid) and through periodic acid oxidation of the corresponding dihydroxy derivative, azelaic and brassylic acids were obtained, thus determining the position of the ethylenic linkage. The saturated dicarboxylic ester was not identified, but it appears probable

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[1] Krafft and Brunner, *Ber.*, **17**, 2985 (1884).

[2] Cann and Amstutz, THIS JOURNAL, **66**, 839 (1944).

[3] J. H. Percy and J. Ross, U. S. Patent 2,341,239 (1944).