to decide whether the variation is due to a change of ϵ_{mol}, or of k, or of both. However, on comparing a homologous series, such as the compounds of quinone and, on the other hand, either hydroquinone or its ethers, in the same solvent, the values of ϵ_{st} are found to vary but little within this homologous series. It does not seem probable that the variation of ϵ_{mol} should be always just inversely proportional to the variation of k. It may rather be inferred from this fact, with high probability, that both ϵ_{mol} and k are approximately constant within the homologous series. For instance, both the molar absorption coefficients and hence the association constants are found to be almost alike for the compounds formed by quinone either with hydroquinone, its monoether, or its di-ethers, in alcohol. The substitution in the OH group is no steric hindrance to the formation of the molecular compound in solution.

In benzene the situation is slightly different. Quinone + hydroquinone cannot be compared with the other compounds of quinone because in benzene even at extremely low concentration precipitation of crystalline quinhydrone occurs. However, the compounds of quinone with the various ethers of hydroquinone can be mixed at proper concentration without any precipitation occurring. It can be seen that ϵ_{st} for the monomethyl ether compound is about twice that for a di-alkyl ether compound. In all probability this is due, not to any appreciable change of ϵ_{mol}, but to a slight change in the association constant, k, which in its turn is probably due to competition between the mutual affinity of the components and the affinity between components and solvent.

Summary

Highly colored molecular compounds of the quinhydrone type exist, not only in the crystalline state, but, to a slight extent, also in solution, in equilibrium with their free components. Because of their intense color such compounds lend themselves to a study by spectrophotometric methods. The compounds studied here consist usually of a quinone (Q) and another component of benzenoid structure (B), usually a phenolic compound. In the crystalline state the stoichiometric composition of the compound may vary, according to the particular phenolic compound used. It may be Q_1B_1, Q_1B_2, or Q_2B_1. No solid compound is formed when the OH group of phenol, or all OH groups in a poly-phenol, are alkylated. In the dissolved state, however, all of these compounds have the composition Q_1B_1, and molecular compounds exist just as well with unsubstituted as with alkylated phenols. This conclusion is based on the fact that the absorption of light due to the molecular compound is always proportional to the concentration of either component. It is furthermore shown that the affinity of quinone for a phenolic compound in solution is not essentially altered by alkylation of the phenolic OH groups. It is inferred from this that in the dissolved state the rings of the two components are superimposed upon each other and are not coplanar, and that no hydrogen bond plays any essential role in the establishment of these compounds. The crystalline compounds may differ from the dissolved ones, both in their stoichiometrical composition and in their spatial structure.

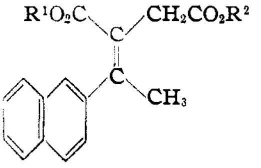
NEW YORK 21, N. Y. RECEIVED MARCH 1, 1944

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

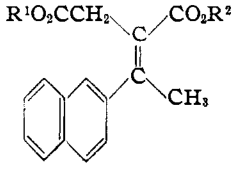
The Condensation of 2-Acetylnaphthalene with Diethyl Succinate[1]

BY WILLIAM S. JOHNSON AND ARTHUR GOLDMAN

In the course of certain synthetic work being carried out in this laboratory the occasion arose to investigate the condensation of 2-acetylnaphthalene with diethyl succinate. Through the efforts of Stobbe and his collaborators it has been well established that the alkoxide-catalyzed reaction of succinic ester with a ketone proceeds not by the acetoacetic ester type but mainly by an aldol type of condensation between the carbonyl group of the ketone and a methylene group of the ester. Stobbe and Lenzner[2] have reported that this condensation with 2-acetylnaphthalene gave a crystalline half-ester, m. p. 103–104° (yield unspecified). Saponification yielded a dicarboxylic acid, m. p. 165° (dec.), which they presumed to be an itaconic acid (formula I or II) by analogy with the products formed in similar condensations.[3]



I ($R^1 = R^2 = H$)
Ia ($R^1 = C_2H_5$, $R^2 = H$)
Ib ($R^1 = H$, $R^2 = C_2H_5$)
Ic ($R^1 = R^2 = C_2H_5$)



II ($R^1 = R^2 = H$)
IIa ($R^1 = H$, $R^2 = C_2H_5$)
IIb ($R^1 = C_2H_5$, $R^2 = H$)
IIc ($R^1 = R^2 = C_2H_5$)

In the present investigation when the condensation was conducted in ether solution with alcohol-free sodium ethoxide according to the reported

---

[1] This work was assisted in part by a grant from the Wisconsin Alumni Research Foundation.

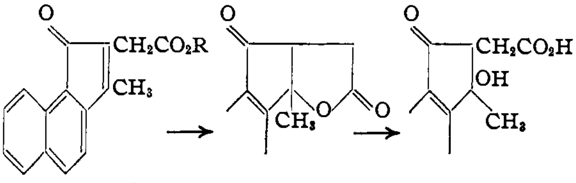
[2] Stobbe and Lenzner, *Ann.*, **380**, 93 (1911).

[3] *Cf.* the reaction with acetophenone: (a) Stobbe, *Ann.*, **308**, 114 (1899); (b) *Ber.*, **37**, 1619 (1904); (c) *Ann.*, **380**, 36 (1911).

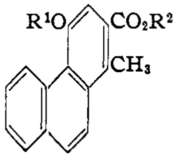
procedure,[2] an acidic mixture was produced from which a crystalline half-ester could be separated in 18% yield. This substance in contrast to that of Stobbe and Lenzner melted at 119–119.6° (pure). No other crystalline products could be isolated at this stage. The reaction proceeded similarly when carried out in ethanol with approximately one equivalent instead of excess sodium ethoxide. The latter procedure was easier and gave the 119° half-ester in 21% yield. Saponification yielded a dibasic acid, m. p. 179.5–180.5° (dec.), which gave an anhydride, m. p. 155.5–156°.

The oily mixture remaining after removal of the 119° half-ester was saponified with barium hydroxide, and the acidic material was treated with acetyl chloride. Fractional crystallization of the neutral material first gave a fraction which appeared to contain some of the previously mentioned 156° anhydride, followed by a more soluble fraction which consisted largely of a new isomer, m. p. 116°. This separation was inefficient, but did serve as a source of pure materials. From a study of the reactions, however, an indirect method was evolved for estimating the relative amounts of materials in the original mixture. This is described later.

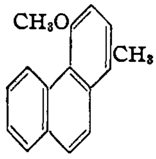
Hydrolysis of the 116° anhydride gave a dibasic acid, m. p. 167–168° (dec.). The position of the ethylenic bond in this and in the 180° acid was shown by ozonolysis of derivatives which gave 2-acetylnaphthalene in each case. This proves that these are the geometrically isomeric γ-methyl-γ-(2-naphthyl)-itaconic acids. Stobbe[3b] determined the configurations of the two corresponding γ-methyl-γ-phenylitaconic acids from their behavior with sulfuric acid. One of the acids was converted to its anhydride, while the other was cyclized to give 3-methyl-1-indone-2-acetic acid (and the corresponding lactone), indicating that it had the *allo*-cinnamic acid configuration. The method of Stobbe was not successful when applied to the present case, probably because the higher polycyclic nuclei are more susceptible to sulfonation by the reagent.[4] When hydrogen fluoride[5] was used instead of sulfuric acid satisfactory yields of cyclized products were obtained. The 180° acid gave a mixture of 3-methyl-6,7-benz-1-indone-2-acetic acid (III) and the corresponding lactone IV. It is therefore assigned the configuration shown in formula I. The 168° acid was converted to 4-hydroxy-1-methylphenanthrene-2-carboxylic acid (VI), and is therefore represented by formula II. The cyclization of II to form the phenanthrol instead of the anhydride (as with the phenylitaconic acid analog[3b]) may be explained by the greater reactivity of the naphthalene nucleus or/and a cyclizing action of hydrogen fluoride which is different from that of sulfuric acid. The proof of structure of the cyclization products III and VI is considered later.



III (R = H) IV V
IIIa (R = C_2H_5)



VI ($R^1 = R^2 = H$)
VIa ($R^1 = COCH_3$, $R^2 = C_2H_5$)
VIb ($R^1 = H$, $R^2 = C_2H_5$)
VIc ($R^1 = CH_3$, $R^2 = H$)
VId ($R^1 = CH_3$, $R^2 = C_2H_5$)



VII

When the anhydride of I was treated with ethanol containing a drop of sulfuric acid it was converted into a new half-ester, m. p. 118°, which was different from the 119° isomer as shown by the melting point depression of the mixture. The 118° half-ester could be prepared also in good yield by mild esterification of the dibasic acid (I). Exhaustive esterification of the 118° half-ester gave the di-ester (Ic) which on partial saponification with one equivalent of barium hydroxide yielded the 119° half-ester, thus completing the cycle (see Fig. 1). The mode of formation of the two half-esters suggests that the 119° substance has the structure Ia and that the 118° isomer is Ib.. These structures were substantiated by cyclization experiments. When heated with acetic anhydride and sodium acetate the 118° half-ester was converted into the red indoneacetic ester IIIa. Upon the same treatment the 119° isomer, in contrast, was recovered largely unchanged. The small neutral fraction contained the anhydride of I and none of the indone derivative. The above transformations are indicated in the accompanying chart (Fig. 1).

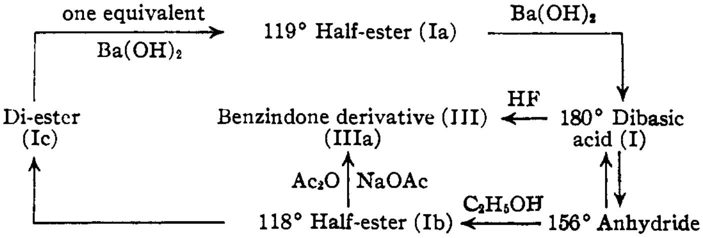


FIG. 1.

A sequence of transformations analogous to those described above for the dibasic acid I was developed from the stereoisomeric acid II (see

---

[4] *Cf.* how attempts to cyclize certain reactive γ-arylbutyric acids with sulfuric acid resulted in sulfonation: Krollpfeiffer and Schäfer, *Ber.*, **56**, 620 (1923).

[5] Fieser and Hershberg, THIS JOURNAL, **61**, 1272 (1939); **62**, 49 (1940).

Fig. 2). Although the half-ester IIb obtained by alcoholysis of the 116° anhydride melted at 102–102.5°, its mode of formation makes improbable its identity with the material of Stobbe and Lenzner. This same argument seems to rule out the 118° half-ester Ib, even though it has been obtained in a polymorphic modification melting at 105–105.5°. This leaves IIa as a possible structure for their half-ester; however, this also seems unlikely, for we have prepared IIa by partial saponification of the di-ester IIc, and have not been able to obtain it crystalline. The alternate possibility still remains that their substance actually was a lower-melting modification of Ia, and that coincidentally their dibasic acid was similar to a low-melting (163–165°) fraction of I isolated in the present work.

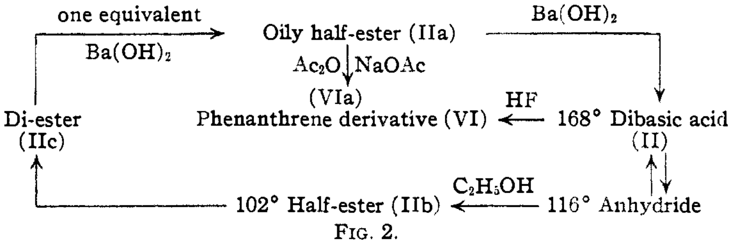


Fig. 2.

The structures of the half-esters IIa and IIb were assigned on the basis of their behavior toward acetic anhydride and sodium acetate. The former was cyclized to ethyl 4-acetoxy-1-methylphenanthrene-2-carboxylate (VIa), while the isomeric half-ester IIb was converted largely to the anhydride.

The structure of the red indoneacetic ester IIIa was assigned on the basis of the following transformations. Oxidation with nitric acid gave benzene-1,2,3,4-tetracarboxylic acid which proved that ring closure took place into the 1-position of the naphthalene nucleus. On acid hydrolysis of IIIa the color (which is characteristic of an indone) was dispelled and the colorless lactone IV was produced. This was identical with the material obtained by the cyclization of the itaconic acid I. Alkaline cleavage gave the hydroxy acid V which reverted easily to the lactone on heating. Hydrogenation of IIIa in the presence of palladium on charcoal gave the colorless ethyl 3-methyl-6,7-benz-1-hydrindone-2-acetate.

The structure of the phenanthrene derivative VIa follows from a consideration of the reactions described below. Acid alcoholysis gave the phenolic ester VIb. Methylation produced the ether VId which on hydrolysis to the acid VIc followed by decarboxylation yielded 4-methoxy-1-methylphenanthrene (VII). This substance has been prepared previously[6] by the Pschorr synthesis, and the reported melting points of VII and of the picrate are in agreement with those found in the current work. Alkaline hydrolysis of VIa produced 4-hydroxy-1-methylphenanthrene-2-carboxylic acid (VI) which was the product of cyclization of the itaconic acid II.

A rough estimation of the amounts of the itaconic half-esters present in the original reaction mixture was made by treating the crude oily fraction which remained after the separation of the half-ester Ia (in 21% yield), with acetic anhydride and sodium acetate. The half-ester IIa thus was cyclized to the phenanthrol acetate VIa which crystallized in 30%[7] yield from the neutral fraction. On working up the acidic residues additional half-ester Ia was accounted for, raising the amount of this isomer in the original mixture to 29% of the theoretical. The total amount of itaconic half-esters thus accounted for is 59% of the theoretical based upon 2-acetylnaphthalene. This is in fair agreement with the yield (65%) of the mixture of itaconic di-esters obtained from the crude reaction mixture by esterification and fractional distillation. Partial saponification of this product gave a mixture which was rich in respect to the itaconic half-esters as shown by analysis according to the procedure described above for the crude mixture. About 47% of Ia and 38% of IIa were accounted for in this way.

Experimental Part[8]

The Condensation of Diethyl Succinate with 2-Acetylnaphthalene

(*a*) *By the Procedure of Stobbe and Lenzner.*[2]—The reported procedure has been repeated several times, and the results of a typical run are given herewith. When 19.5 g. (0.112 mole) of diethyl succinate, 19.1 g. (0.112 mole) of 2-acetylnaphthalene and 0.20 mole of alcohol-free sodium ethoxide (from 4.6 g. of sodium) were used, all but about 10% of the product was alkali-soluble. The oily acidic fraction was dissolved in ether, petroleum ether[9] was added to the point of incipient cloudiness and crystallization was induced. The crude product was filtered and then recrystallized from ether–petroleum ether.[9] The first and second crops of colorless crystals both had the same m. p., 118–119°, and amounted to 6.0 g., a yield of 18%.

(*b*) *With Alcoholic Sodium Ethoxide.*—To a solution of 6.4 g. (0.28 mole) of sodium in 120 cc. of absolute alcohol were added 43.5 g. (0.25 mole) of diethyl succinate and 42.5 g. (0.25 mole) of 2-acetylnaphthalene. The mixture was refluxed on the steam-bath for fifteen hours during which the solution turned brown and a heavy precipitate formed. Water was added, and the alcohol removed by steam-distillation. Ether extraction of the alkaline solution gave 5.9 g. of dark neutral oil which was not further investigated. The aqueous layer was acidified, and the orange oil which separated was taken up in ether and washed with water followed by saturated salt solution. After drying over anhydrous sodium sulfate the solution was concentrated and treated with petroleum ether[9] to precipitate the crude half-ester Ia. By recrystallization from ether–petroleum ether[9] a total of 15.3 g. (21% yield) of colorless plates, m. p. 117.5–118.5°, was obtained. The nature of the residues is considered later.

---

(6) Higginbottom, Hill and Short, *J. Chem. Soc.*, 263 (1937).

(7) The amount of IIa in the original mixture is probably more than indicated by this yield, since the cyclization of relatively pure IIa to VIa was not quantitative. See experimental part.

(8) Unless otherwise stated, all melting points are corrected.

(9) Boiling range 60–68°.

3-Carbethoxy-4-(2-naphthyl)-*cis*-3-pentenoic Acid (Ia).—Material obtained in the preceding experiment was recrystallized to constant m. p. from ether–petroleum ether.[9] It formed colorless plates, m. p. 119–119.5°.

Anal. Calcd. for $C_{18}H_{18}O_4$: C, 72.47; H, 6.08. Found: C, 72.60; H, 5.82.

3-Carboxy-4-(2-naphthyl)-*cis*-3-pentenoic Acid (γ-Methyl-γ-(2-naphthyl)-isoitaconic Acid) (I).—A mixture of 9.10 g. of the above half-ester (m. p. 117–118°), 13 g. of barium hydroxide, 75 cc. of alcohol and 100 cc. of water was heated under reflux on the steam-bath for six hours. The colorless barium salt was filtered from the cooled solution, washed with water, then with alcohol. Treatment with dilute hydrochloric acid gave 8.10 g. of crude dibasic acid, m. p. 169–171° (dec.). The first crop obtained by recrystallization from dilute alcohol amounted to 5.40 g. of colorless crystals, m. p. 176.5–178.5° (dec.). Repeated recrystallization from acetone–petroleum ether[9] gave material of constant m. p., 179.5–180.5° (dec.).

Anal. Calcd. for $C_{16}H_{14}O_4$: C, 71.10; H, 5.22. Found: C, 71.40; H, 5.26.

The mother liquor from the dilute alcohol crystallization yielded an additional 2.50 g. of acid, m. p. 163–165° (dec.), which could not be purified readily. The m. p. of a mixture with the analytical sample was not depressed (165–167°). When mixed with the stereoisomeric acid II (m. p. 167–168°) the m. p. was depressed (150–155°). This second crop of the dibasic acid I corresponds in m. p. to the acid of Stobbe and Lenzner.[2] This suggests that their half-ester possibly could have been a lower-melting polymorphic modification of the 119° half-ester.

The **anhydride** of I was prepared by Stobbe's general procedure[3a] with acetyl chloride at room temperature. From 0.670 g. of I (m. p. 179–180°) was obtained 0.552 g. of bicarbonate-insoluble material, m. p. 153–154°. The pure anhydride was obtained as colorless blades, m. p. 155.5–156°, from chloroform–petroleum ether.[9]

Anal. Calcd. for $C_{16}H_{12}O_3$: C, 76.18; H, 4.80. Found: C, 76.30; H, 4.94.

Ethyl 3-Carboxy-4-(2-naphthyl)-*cis*-3-pentenoate (Ib). (*a*) *From the Anhydride of I.*—A mixture of 1.04 g. of the anhydride described in the preceding experiment and 20 cc. of ethanol containing one drop of concentrated sulfuric acid was warmed on the steam-bath until solution was nearly complete. After standing overnight the solution was evaporated in a stream of air, and the solid residue was taken up in ether. The solution was washed with water, and then extracted with portions of 5% sodium bicarbonate solution. Acidification of these extracts gave 1.17 g. (95% yield) of colorless half-ester, m. p. 117–118°.

(*b*) *From the Dibasic Acid I.*—A mixture of 4.90 g. of the itaconic acid I (m. p. 177–179°), 40 cc. of alcohol and 60 cc. of benzene containing three drops of sulfuric acid was allowed to reflux through a system which included a constant water separator of the type described by Cope, Hofmann, Wyckoff and Hardenbergh.[10] After nineteen hours water had ceased to separate. The solvent was removed, and the product worked up as in (*a*) above. The crude half-ester was colorless and amounted to 5.03 g. (93% yield), m. p. 116–117.5°. The pure substance, m. p. 118.5–119°, formed fine colorless needles from ether-petroleum ether.[9] When mixed with the half-ester Ia, it melted at 98–105°.

Anal. Calcd. for $C_{18}H_{18}O_4$: C, 72.47; H, 6.08. Found: C, 72.45; H, 6.03.

On slow crystallization from dilute solution the half-ester Ib sometimes formed prisms, m. p. 105–105.5°. The polymorphic nature of this product was established by adding to the clear melt at 110° a seed of the higher-melting modification. Solidification occurred immediately, and the material then melted at 116.5–117.5°.

In order to show that no structural or configurational change had occurred in the acid portion of the molecule during the above alcoholysis reactions, the half-ester Ib was saponified with barium hydroxide, and the dibasic acid (I) was reconverted to the original anhydride, m. p. 154.5–155°.

Ethyl 3-Carbethoxy-4-(2-naphthyl)-*cis*-3-pentenoate (Ic).—The diethyl ester Ic can be prepared from either half-ester Ia or Ib. From structural considerations it was expected that the former would be easier to esterify. This was borne out by the fact that Ia could be esterified under conditions to which Ib already has been shown to be stable.

(*a*) *From Half-ester Ia.*—To esterify 7.51 g. of Ia (m. p. 117–118°) the procedure described in the preceding experiment, part (*b*), was followed. The quantities of solvents and catalyst were the same as before. The di-ester Ic was obtained from the neutral fraction; yield 6.95 g. of material boiling at 184–186° (0.05–1 mm.), $n^{22}D$ 1.5667. Partial saponification with one equivalent of barium hydroxide according to the procedure described below part (*b*), regenerated the half-ester Ia.

Anal. Calcd. for $C_{20}H_{22}O_4$: C, 73.60; H, 6.80. Found: C, 73.87; H, 6.82.

(*b*) *From Half-ester Ib.*—A solution of 0.650 g. of the half-ester Ib in 15 cc. of ethanol was saturated with hydrogen chloride and heated under reflux for twenty-four hours. Only a trace of acidic material remained, and the crude di-ester amounted to 0.639 g. This was characterized by partial saponification (of the di-ester Ic) to the half-ester Ia with 0.32 g. of barium hydroxide octahydrate in 9 cc. of alcohol and 6 cc. of water. After refluxing for six hours the insoluble barium salt of the dibasic acid was filtered. Decomposition with hydrochloric acid gave 0.113 g. of crude I characterized by conversion to the anhydride, m. p. 152–153°. The alcoholic filtrate containing the half-ester was evaporated, and the residue was treated with dilute hydrochloric acid, taken up in ether, washed with water and finally extracted with 5% sodium bicarbonate solution. The colorless half-ester obtained on acidification amounted to 0.295 g., m. p. 117–118°, not depressed on mixing with authentic Ia. Unchanged diester amounting to 0.120 g. was recovered from the ether solution.

3-Carboxy-4-(2-naphthyl)-*trans*-3-pentenoic Acid (γ-Methyl-γ-(2-naphthyl)-itaconic Acid) (II).—A condensation of 2-acetylnaphthalene (68.0 g.) and diethyl succinate (69.6 g.) was carried out according to procedure (*b*) described above. The crude half-ester remaining after crystallization of about 16 g. of Ia was hydrolyzed for five hours with 135 g. of barium hydroxide in 800 cc. of alcohol and 700 cc. of water. The mixture of acids obtained by decomposing the barium salt with hydrochloric acid was dried and treated with excess acetyl chloride at room temperature. The bicarbonate-insoluble mixture of anhydrides amounted to 62.0 g. (59%) of dark-brown solid material. Eleven grams of this material was distilled rapidly in a two-bulb flask under reduced pressure. The red, viscous distillate (9.6 g.) was crystallized from chloroform–petroleum ether[9] to yield the following fractions: (a) 2.6 g. (m. p. 85–108°); (b) 1.1 g. (m. p. 90–113°); (c) 2.1 g. (113–115°). Only crude anhydride of I (m. p. 141–148°) could be isolated from fractions (a) and (b) by recrystallization. Fraction (c), however, consisted largely of the **anhydride of II**, which after several recrystallizations had the constant m. p. 116–116.5°; colorless prisms from chloroform–petroleum ether.[9]

Anal. Calcd. for $C_{16}H_{12}O_3$: C, 76.18; H, 4.80. Found: C, 76.05; H, 4.89.

Hydrolysis of the above anhydride (0.105 g.) with 5 cc. of 2% sodium hydroxide solution yielded on acidification 0.091 g. of the dibasic acid II, m. p. 165–167° (dec.). The pure substance forms colorless microscopic crystals from dilute alcohol and melts at 167–168° (dec.).

Anal. Calcd. for $C_{16}H_{14}O_4$: C, 71.10; H, 5.22. Found: C, 71.29; H, 5.03.

With acetyl chloride this acid could be reconverted to the anhydride in practically quantitative yield.

Ethyl 3-Carboxy-4-(2-naphthyl)-*trans*-3-pentenoate (IIb).—Alcoholysis of 3.88 g. of the anhydride of II (m. p.

---

[10] Cope, Hofmann, Wyckoff and Hardenbergh, THIS JOURNAL, 63, 3452 (1941).

115–116°) described in the preceding experiment was effected with 100 cc. of ethanol containing 4 drops of sulfuric acid. The procedure already described for the stereoisomer was followed, and 4.06 g. of colorless half-ester, m. p. 100–101.5° was obtained. Pure IIb crystallized from ether–petroleum ether[9] in colorless prisms, m. p. 102–102.5°.

Anal. Calcd. for $C_{18}H_{18}O_4$: C, 72.47; H, 6.08. Found: C, 72.54; H, 6.25.

This half-ester was reconverted to the anhydride, m. p. 115–116° (not depressed on mixing with anhydride of II prepared as above) in 77% yield by the usual saponification with barium hydroxide followed by dehydration of the dibasic acid with acetyl chloride.

Ethyl 3-Carbethoxy-4-(2-naphthyl)-*trans*-3-pentenoate (IIc).—Esterification of 3.09 g. of the above half-ester (IIb) was effected according to the procedure already described for the stereoisomer Ib. Thirty cubic centimeters of ethanol saturated with hydrogen chloride was used, and the yield of liquid di-ester IIc was 2.72 g. (81%) after a rough distillation in a two-bulb flask under reduced pressure; $n^{22}\text{D}$ 1.5670.

Anal. Calcd. for $C_{20}H_{22}O_4$: C, 73.60; H, 6.80. Found: C, 73.81; H, 6.77.

This ester gave a pale yellow color with concentrated sulfuric acid. In contrast the isomeric *cis* di-ester Ic gave a dark-red brown color. These observations are compatible with those of Stobbe[3c] regarding the color reactions and configurations of the methylphenylitaconic esters.

Partial saponification of IIc (1.52 g.) was effected with 0.76 g. of barium hydroxide octahydrate, 25 cc. of alcohol and 15 cc. of water. The procedure described above for the stereoisomer Ic was followed. Thus was obtained 0.30 g. of the dibasic acid II, m. p. 165–167°, which was converted to the anhydride, m. p. 113–115°, no depression on mixing with original anhydride of II. The neutral fraction amounted to 0.41 g. of unchanged di-ester, and the yield of oily **3-carbethoxy-4-(2-naphthyl)-*trans*-3-pentenoic acid** (IIa) was 0.64 g. All attempts thus far to crystallize this material have failed. It is easily characterized by conversion to ethyl 4-acetoxy-1-methylphenanthrene-2-carboxylate (VIa) which is described below, or by preparation of the crystalline anilide, m. p. 153–154°, which forms fine colorless needles from acetone–petroleum ether.[9]

Anal. Calcd. for $C_{24}H_{23}O_3N$: N, 3.75. Found: N, 4.06.

Ozonolysis. (*a*) *Of 3-Carbethoxy-4-(2-naphthyl)-cis-3-pentenoic Acid (Ia).*—A slight excess of ozone (detected by starch–iodide test), was introduced into a cold (ice-bath) solution of 1.00 g. of the pure half-ester Ia in 25 cc. of ethyl acetate. The ozonide was decomposed[11] by stirring with 1–2 g. of Raney nickel for two hours at room temperature, then at refluxing temperature for three hours. The filtered solution was extracted thoroughly with 5% sodium bicarbonate solution and dried over anhydrous potassium carbonate. The neutral oil obtained on evaporation was dissolved in 10 cc. of methanol and treated with 0.5 g. of semicarbazide hydrochloride and 0.42 cc. of pyridine by refluxing for twenty minutes. The semicarbazone was obtained as tan needles, m. p. 229–230° (dec.); yield 0.294 g. (39%). The mixed m. p. with authentic 2-acetylnaphthalene semicarbazone (m. p. 234–235° (dec.)) was not depressed. The above semicarbazone was cleaved by warming with 20% hydrochloric acid to give 0.201 g. of yellow ketone, m. p. 48.5–50°. Recrystallization from petroleum ether[9] containing a little benzene gave material having the m. p. 52–53° which was not depressed on mixing with authentic 2-acetylnaphthalene (m. p. 53–54°).

(*b*) *Of Ethyl 3-Carboxy-4-(2-naphthyl)-cis-3-pentenoate (Ib).*—One gram of the half-ester Ib was ozonized according to the preceding procedure. The semicarbazone amounted to 0.321 g., m. p. 228–230° (dec.). This and the ketone obtained by hydrolysis showed no depression of m. p. on mixing with authentic specimens.

(*c*) *Of Ethyl 3-Carboxy-4-(2-naphthyl)-trans-3-pentenoate (IIb).*—The results of ozonolysis of IIb were practically identical with those described in the preceding experiment. The yield of 2-acetylnaphthalene semicarbazone was 0.320 g. or 42%.

Cyclization of Ethyl 3-Carboxy-4-(2-naphthyl)-*cis*-3-pentenoate (Ib).—A solution of 0.800 g. of the half-ester and 0.2 g. of sodium acetate in 7 cc. each of acetic anhydride and acetic acid was boiled under reflux for three hours. The deep-red solution was evaporated in a current of air, and the residue (which was insoluble in cold bicarbonate) was boiled for thirty minutes with 25 cc. of 5% sodium bicarbonate solution to decompose the anhydride of I. The undissolved portion was filtered, dried, and crystallized from petroleum ether.[9] Thus was obtained 0.111 g. of **ethyl 3-methyl-6,7-benz-1-indone-2-acetate** (IIIa) m. p. 95.5–97°. An additional 0.023 g., m. p. 93–95° was obtained from the filtrate. A purified sample crystallized from dilute alcohol as orange needles, m. p. 96.5–97°.

Anal. Calcd. for $C_{18}H_{16}O_3$: C, 77.12; H, 5.75. Found: C, 77.15; H, 5.75.

Acidification of the sodium bicarbonate solution gave an oily acid which was converted to anhydride by the acetyl chloride treatment. Crystallization from chloroform–petroleum ether[9] yielded 0.120 g. of good material, m. p. 154–155°.

Oxidation of Ethyl 3-Methyl-6,7-benz-1-indone-2-acetate.—A mixture of 0.5 g. of the indoneacetic ester IIIa, 1.5 cc. of water and 2 cc. of concentrated nitric acid was heated in a sealed tube at 190–200° for sixteen hours. The crude product which was filtered on a sintered-glass plate amounted to 0.18 g., m. p. 229–236°. Once recrystallized from concentrated nitric acid, it melted at 232–237°. For benzene-1,2,3,4-tetracarboxylic acid the reported[12] m. p. is 238° with softening at 225°. The methyl ester was prepared with diazomethane. After sublimation and recrystallization twice from methanol, tetramethylbenzene-1,2,3,4-tetracarboxylate was obtained as colorless needles, m. p. 129.5–131° (reported[12] 133–135°).

For comparison a sample of 1-keto-1,2,3,4-tetrahydrophenanthrene kindly supplied by Dr. A. L. Wilds was oxidized in the same way. The crude acid produced therefrom melted at 228–231°, and the purified tetramethyl ester had the m. p. 130–131°. No depression of the m. p. of a mixture of the two samples was observed. When mixed with an authentic specimen of tetramethylbenzene-1,2,4,5-tetracarboxylate, m. p. 137–139°, each of the above products depressed the m. p. to 109–126°.

Lactone (IV) of 3-Methyl-3-hydroxy-6,7-benz-1-hydrindone-2-acetic Acid.—A solution of 1.84 g. of ethyl 3-methyl-6,7-benz-1-indone-2-acetate (IIIa) in 15 cc. of acetic acid and 10 cc. of concentrated hydrochloric acid was boiled under reflux overnight. The hot mixture which had turned from a deep red to a pale yellow color was diluted with water to the point of incipient cloudiness, and on cooling the lactone IV crystallized in straw-colored plates. It amounted to 1.35 g. (81% yield), m. p. 167–168°. An additional 0.14 g. of less pure material, m. p. 164–166°, was obtained from the filtrate. After three recrystallizations from benzene–petroleum ether[9] the lactone was obtained as thick, colorless plates, m. p. 168.5–169°. It is insoluble in, but is cleaved slowly by, dilute alkali.

Anal. Calcd. for $C_{16}H_{12}O_3$: C, 76.18; H, 4.80. Found: C, 76.36; H, 5.01.

An attempt to prepare the semicarbazone of the above lactone (IV) gave a product which after recrystallization from dilute alcohol melted at 244° (dec.) (introduced in bath at 239°). The analysis of this material is compatible with a hydrazide structure which could result from cleavage of the lactone ring by the semicarbazide.

Anal. Calcd. for $C_{17}H_{17}O_4N_3$: C, 62.37; H, 5.24. Found: C, 62.06; H, 5.15.

---

(11) Cook and Whitmore, THIS JOURNAL, 63, 3540 (1941).

(12) Bamford and Simonsen, *J. Chem. Soc.*, 1904 (1910)

3-Methyl-3-hydroxy-6,7-benz-1-hydrindone-2-acetic Acid (V).—A suspension of 2.02 g. of the above lactone IV (m. p. 167–168°) in 20 cc. of 5% sodium hydroxide was allowed to stand overnight at room temperature. The clear red solution was filtered, carefully acidified in the cold with dilute hydrochloric acid, and the gummy red precipitate was extracted with ether–ethyl acetate. The organic layer was washed with water, dried over anhydrous sodium sulfate and concentrated. The residue was treated with hot benzene which dissolved all but 0.27 g. of amorphous red material, m. p. 227–235° (dec.) which was not further investigated. The filtrate deposited 0.61 g. of orange microscopic crystals, m. p. 146–150° (dec.). Unlike the lactone this material was soluble in sodium bicarbonate solution. After one recrystallization from benzene it melted sharply at 148.5–150° (dec.). On a second recrystallization the m. p. jumped to 168–169° (dec.) (polymorphic form ?). The best sample was obtained as buff-colored, flat rods, m. p. 169–169.5° (dec.).

Anal. Calcd. for $C_{16}H_{14}O_4$: C, 71.10; H, 5.22. Found: C, 71.20; H, 5.42.

In the crystallizations described above it was necessary to use glassware which had been washed with alkali and thus rinsed free of traces of acid which catalyze the lactonization of the hydroxy acid V. Even with this precaution the dehydration was not eliminated completely, for the more soluble lactone was usually found in the mother liquors.

Ethyl 3-Methyl-6,7-benz-1-hydrindone-2-acetate.—A solution of 1.44 g. of the indoneacetic ester (IIIa) in 25 cc. of ethyl acetate was hydrogenated in the presence of 0.250 g. of 30% palladium-charcoal.[13] After shaking for one-half hour one molecular equivalent of hydrogen was absorbed. The residue obtained after filtration and evaporation was recrystallized from petroleum ether[9] giving 0.803 g. of colorless plates, m. p. 68.5–70°. A second crop obtained from the mother liquor amounted to 0.280 g., m. p. 66–68°, making the total yield 75%. The residue was oily and may have contained the diastereoisomer. Pure ethyl 3-methyl-6,7-benz-1-hydrindone-2-acetate was obtained by two recrystallizations from petroleum ether[9] from which it formed colorless plates, m. p. 70.2–70.6°.

Anal. Calcd. for $C_{18}H_{18}O_3$: C, 76.58; H, 6.42. Found: C, 76.63; H, 6.36.

Cyclization of 3-Carbethoxy-4-(2-naphthyl)-*cis*-3-pentenoic Acid (Ia). (*a*) *By the Acetic Anhydride–Sodium Acetate Method.*—The half-ester Ia (0.512 g.) was treated with 0.14 g. of sodium acetate in 3 cc. each of acetic anhydride and acetic acid just as described above for the stereoisomer Ib. In distinct contrast to the case of Ib, the reaction mixture of Ia, even after the heating was complete, was pale yellow. No trace of the red color which is characteristic of the indone derivative was detected. Acidification of the sodium bicarbonate extracts gave back 0.310 g. (61%) of unchanged half-ester, m. p. 117–118°. The neutral fraction was a yellow oil from which could be crystallized a small amount, 0.019 g., of crude anhydride of I, m. p. 135–142°. One recrystallization brought the m. p. to 149–151°, which was not depressed on mixing with authentic anhydride. No more crystalline material was obtained from the residues, but the lack of red color was considered sufficient evidence for the absence of the indone derivative.

(*b*) *With Hydrogen Fluoride.*—This reagent effects cleavage of the ester group, and therefore promotes cyclization to the expected (see later experiments on the dibasic acid I) lactone IV. Thus 0.44 g. of half-ester Ia after standing in about 20 g. of hydrogen fluoride at room temperature for five hours, yielded 0.291 g. of neutral crystalline material, m. p. 167–168.5°. The m. p. of a mixture with lactone IV was not depressed.

Cyclization of 3-Carbethoxy-4-(2-naphthyl)-*trans*-3-pentenoic Acid (IIa).—When 0.560 g. of the crude oily half-ester IIa was treated with 0.15 g. of sodium acetate in 5 cc. each of acetic acid and acetic anhydride according to cyclization procedures described above, very little (0.016 g.) acidic material remained. The neutral material consisted of **ethyl 4-acetoxy-1-methylphenanthrene-2-carboxylate (VIa)** obtained by crystallization from ethyl acetate–petroleum ether.[9] The first crop amounted to 0.339 g., m. p. 127–128°, and the second 0.133 g., m. p. 125.5–127°, making the total yield 78%. The analytical sample of VIa formed colorless prismatic rods from dilute alcohol and melted at 127.5–128°.

Anal. Calcd. for $C_{20}H_{18}O_4$: C, 74.52; H, 5.63. Found: C, 74.66; H, 5.72.

Ethyl 4-hydroxy-1-methylphenanthrene-2-carboxylate (VIb) was prepared by acid alcoholysis of 5.00 g. of the above acetoxy derivative (VIa) in 100 cc. of ethanol saturated with hydrogen chloride. After refluxing for five hours, the solution was concentrated, and water was added. The crystalline precipitate amounted to 4.00 g., m. p. 175–178°. An additional 0.21 g., m. p. 174–176°, was obtained by concentrating the filtrate. Recrystallization of the combined crops from dilute alcohol gave 4.01 g. (92% yield) of colorless blades, m. p. 177–179°. Material recrystallized three times from the same solvent had the constant m. p. 178.5–179°.

Anal. Calcd. for $C_{18}H_{16}O_3$: C, 77.12; H, 5.75. Found: C, 76.80; H, 5.76.

Ethyl 4-methoxy-1-methylphenanthrene-2-carboxylate (VId) was prepared in 95% yield by methylaton of the above phenolic ester (5.0 g.) with excess dimethyl sulfate in cold dilute sodium hydroxide. The crude product amounted to 5.0 g., m. p. 70–73°. The analytical sample crystallized from dilute alcohol in the form of colorless needles, m. p. 74–74.5°.

Anal. Calcd. for $C_{19}H_{18}O_3$: C, 77.53; H, 6.16. Found: C, 77.40; H, 5.76.

4-Methoxy-1-methylphenanthrene-2-carboxylic acid (VIc) was obtained by hydrolysis of 5.0 g. of crude VId with 100 cc. of 5% alcoholic potassium hydroxide. After refluxing for four hours the acidic material amounted to 4.29 g. (95% yield), m. p. 222–225.5°. After several recrystallizations from dilute alcohol a sample was obtained as colorless needles, m. p. 225–225.5°.

Anal. Calcd. for $C_{17}H_{14}O_3$: C, 76.67; H, 5.30. Found: C, 76.85; H, 5.33.

4-Methoxy-1-methylphenanthrene (VII).—Attempts to decarboxylate the free phenolic acid VI or the acetate (which are described below) were not successful, because these substances were too sensitive. The more stable methoxy derivative VIc, however, was quite suitable.

The decarboxylation of 1.20 g. of VIc was effected by heating in 5 cc. of quinoline with 0.60 g. of copper powder at 205–210° for one-half hour, then at 215–220° for twenty minutes. On working up the mixture 0.03 g. of unchanged acid was recovered. The neutral fraction was recrystallized from methanol (Norit) to give 0.71 g. of colorless needles, m. p. 76.5–78°. From the mother liquor was obtained an additional 0.09 g., m. p. 74–76°, making the total yield 80%. A sample of the methoxymethylphenanthrene VII after further recrystallizations from methanol melted at 78–79° (reported[6] 78.5–79°). The picrate was prepared in the customary way. It crystallized from the reaction mixture in the form of orange, microscopic crystals, m. p. 183–184° (reported[6] 182–183°).

4-Hydroxy-1-methylphenanthrene-2-carboxylic acid (VI) was obtained by the hydrolysis of VIa (3.00 g.) with 60 cc. of 5% alcoholic potassium hydroxide. The yield of material obtained after three hours of refluxing and recrystallization from dilute acetic acid was 2.25 g. (96%); slightly yellow rods, m. p. 249–251° (dec.) (uncor.). Material having the same appearance and melting at 253–254° (dec.) (uncor.) was obtained after several recrystallizations.

Anal. Calcd. for $C_{16}H_{12}O_3$: C, 76.18; H, 4.80. Found: C, 76.02; H, 5.01.

4-Acetoxy-1-methylphenanthrene-2-carboxylic acid was obtained in 94% yield by acetylation of the phenolic acid

---

[13] Zelinsky and Turowa-Pollak, *Ber.*, **58**, 1295 (1925).

VI with acetic anhydride and sulfuric acid. The best material formed almost colorless needles, m. p. 227.5–229°, from ethyl acetate.

Anal. Calcd. for $C_{18}H_{14}O_4$: C, 73.46; H, 4.79. Found: C, 73.48; H, 5.06.

Cyclization of Ethyl 3-Carboxy-4-(2-naphthyl)-*trans*-3-pentenoate (IIb).—The half-ester (0.530 g.) was treated with 0.14 g. of sodium acetate in 5 cc. each of acetic acid and acetic anhydride according to procedures described above. Only a trace of acidic material was recovered. The neutral fraction was crystallized from chloroform-petroleum ether.[9] The first crop amounted to 0.211 g., m. p. 112–115°; and the second 0.078 g., m. p. 108–112°. Both fractions were identified (by mixed m. p.) as the anhydride of II described above. The oily residue was almost all converted to bicarbonate-soluble material after treatment with 5 cc. of ethanol containing a drop of sulfuric acid. This indicated that litle, if any, of the phenanthrol derivative VIa could have been present.

Cyclization of 3-Carboxy-4-(2-naphthyl)-*cis*-3-pentenoic Acid (I).—A solution of 0.710 g. of the dibasic acid (I) in about 20 g. of anhydrous hydrogen fluoride was allowed to stand in a platinum vessel in an ice–salt bath for one and one-half hours. The reagent was evaporated in a current of air, and the residue taken up in ether and extracted with 5% sodium bicarbonate solution. Acidification of the latter gave 0.220 g. of crude **3-methyl-6,7-benz-1-indone-2-acetic acid (III)**, m. p. 198–211°. The best sample, obtained as flat, red rods after two recrystallizations from benzene–alcohol, melted at 215.5–219.5°. Attempts to prepare this acid by saponification of the ester IIIa failed.

Anal. Calcd. for $C_{16}H_{12}O_3$: C, 76.18; H, 4.80. Found: C, 75.87; H, 4.88.

The material which remained in the original ether layer amounted to 0.271 g., m. p. 164–166°. It was identified (by mixed m. p.) as the lactone (IV) of 3-methyl-3-hydroxy-6,7-benz-1-hydrindone-2-acetic acid described above.

Cyclization of 3-Carboxy-4-(2-naphthyl)-*trans*-3-pentenoic Acid (II).—The dibasic acid (0.321 g., m. p. 165–166°) was treated with hydrogen fluoride according to the procedure described for the stereoisomer I. The yield of material once recrystallized from ethyl acetate–petroleum ether[9] was 0.246 g. (82%), m. p. 251–253° (dec.) (uncor.). The mixed m. p. with 4-hydroxy-1-methylphenanthrene-2-carboxylic acid (VI) was not depressed.

Analysis of Original Reaction Mixture.—This is a continuation of the procedure described at the beginning of the experimental part for the condensation of diethyl succinate with 2-acetylnaphthalene (part b). The combined residues from the crystallization of the half-ester Ia were dissolved in 400 cc. of alcohol, and a concentrated aqueous solution of barium hydroxide was added with stirring until the mixture was basic to litmus. The crude insoluble barium salt of dibasic acid was filtered, washed with water, alcohol and finally with ether, and was then decomposed with dilute hydrochloric acid. After extraction and drying the crude oily acidic material amounted to 6.9 g. This could not be crystallized. With acetyl chloride at room temperature all but 0.8 g. was converted to neutral material, which also could not be crystallized readily and was not further investigated.

The solution and washings containing the barium salt of the half-ester mixture were combined, acidified with dilute hydrochloric acid, and the organic solvents removed under reduced pressure. The oily residue was extracted with ether and dried over anhydrous sodium sulfate. The ether was removed, and the residue was treated with 11 g. of sodium acetate in 100 cc. each of acetic acid and acetic anhydride. After refluxing for three hours the solvent was removed under reduced pressure and the residue was taken up in ethyl acetate where it was washed with sodium bicarbonate solution. Acidification gave 6.0 g. of crude half-ester. Crystallization from ether–petroleum ether[9] gave 2.2 g. of half-ester Ia, m. p. 116–117°. An additional 1.5 g. of good material was accounted for in the filtrate making the yield of Ia in this fraction 5%. If it is assumed that this represents three-fifths of the amount of Ia which was present before cyclization—the remaining two-fifths presumably having been converted to the anhydride as observed in the experiment described above with pure Ia—an additional 3% of Ia may be accounted for. The neutral fraction in the ethyl acetate solution was concentrated and crystallized by the addition of petroleum ether.[9] In this way 24.1 g. (30% yield) of ethyl 4-acetoxy-1-methylphenanthrene-2-carboxylate (VIa), m. p. 126.5–127.5°, was obtained. No more crystals could be obtained from the oily residue (12.1 g.) which was submitted to acid-catalyzed alcoholysis in order to convert any anhydride of I into the bicarbonate soluble half-ester Ib, and thus to separate any remaining phenanthrene derivative either in the neutral fraction as VIa or in the sodium hydroxide-soluble fraction as VIb. In this way a trace (0.2 g.) of additional VIa was obtained, and the presence of Ib was verified by cyclization of the crude acidic fraction to give the indoneacetic ester IIIa; a small yield of red needles, m. p. 94–96.5°, was obtained. The various oily residues have not been investigated further.

Mixture of Itaconic Di-esters.—The acidic portion of a condensation reaction in which 85 g. (0.5 mole) of 2-acetylnaphthalene was employed was exhaustively esterified with ethanol and hydrogen chloride. Only 2.5 g. of dark, oily acid material was recovered. The distilled yellow mixture of di-esters amounted to 106.7 g. (65% yield) boiling over a 10° range. The main fraction boiled at 203–206° (2–3 mm.).

Anal. Calcd. for $C_{20}H_{22}O_4$: C, 73.60; H, 6.80. Found: C, 73.66; H, 6.75.

The balance of material was accounted for as decomposed residue from the distillation. Since the itaconic di-esters are perfectly stable to distillation, the residue (which may correspond to the uncrystallizable fractions of the preceding experiment) probably contained little, if any, of the itaconic di-esters. The undistillable fraction may contain higher molecular weight substances possibly of the type produced by the condensation of two moles of ketone with one of succinic ester.[14]

Mixture of Itaconic Half-esters.—The partial saponification of 10.17 g. of the above di-ester mixture was effected with 5.10 g. of barium hydroxide octahydrate in 250 cc. of ethanol and 200 cc. of water. After refluxing for seven hours the dibasic acid fraction (1.38 g.) was obtained in the usual way via the insoluble barium salt. An equivalent amount (1.71 g.) of unchanged di-ester fraction was found in the neutral portion. The crude mixture of half-esters amounted to 6.64 g. of brown semi-crystalline material.

Analysis of Mixture of Half-esters.—Crystallization of the above half-ester fraction gave 2.66 g. (40% yield) of colorless half-ester Ia, m. p. 116.5–118.5°. The residues were cyclized with 1.5 g. of sodium acetate in 10 cc. each of acetic acid and anhydride. An additional 4% yield of Ia was accounted for in the small acidic portion which remained. The neutral fraction amounted to 2.97 g. (41% yield) of crude phenanthrene derivative VIa presumably containing about a 3% yield of anhydride of I estimated from the 4% of Ia accounted for above. Purification by distillation under reduced pressure gave 2.06 g. of VIa, m. p. 124–127°. The identity of all crystalline products isolated in the above analyses of mixtures was checked by mixed m. ps. with authentic samples.

Summary

1. The condensation of 2-acetylnaphthalene with diethyl succinate in the presence of sodium ethoxide has been studied.

2. Structures and configurations have been assigned to the resulting itaconic acid derivatives, in the course of which some interesting phenanthrene and 6,7-benzindone cyclization products were encountered.

---

(14) Stobbe, *Ann.*, **380**, 1–129 (1911).

3. A method has been described for the rough estimation of the itaconic acid derivatives present in the original reaction mixture.

MADISON 6, WISCONSIN RECEIVED MARCH 9, 1944

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DUKE UNIVERSITY]

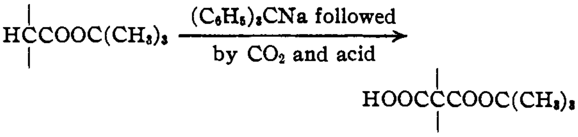
The Carbonation and Carbethoxylation of Certain Esters Using Sodium Triphenylmethide Reagent[1,2,3]

BY ERWIN BAUMGARTEN AND CHARLES R. HAUSER

In the present paper, the synthesis of certain malonic acid derivatives by means of the carbonation or carbethoxylation of the anions of esters (prepared by the action of sodium triphenylmethide) is reported.

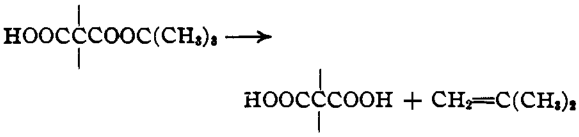
Carbonations.—The carbonation of esters to form half malonic acid esters has previously been carried out apparently only with methyl diphenylacetate,[4] the reaction being effected by means of sodium triphenylmethide. In the present investigation, four aliphatic esters have been carbonated using this reagent.

The carbonation of *t*-butyl acetate gave mono-*t*-butyl malonate as a slightly impure oil in 57% yield, while the carbonation of *t*-butyl isobutyrate gave mono-*t*-butyl dimethylmalonate as a crystalline solid in 81% yield. Such half *t*-butyl esters of malonic acids have apparently not been reported previously. The general reaction may be represented as



$$\mathrm{H\overset{|}{\underset{|}{C}}COOC(CH_3)_3} \xrightarrow[\text{by } \mathrm{CO_2} \text{ and acid}]{\mathrm{(C_6H_5)_3CNa}\text{ followed}} \mathrm{HOOC\overset{|}{\underset{|}{C}}COOC(CH_3)_3}$$

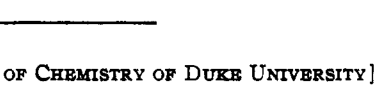
In contrast to malonic acids and their ethyl esters (which undergo decarboxylation when heated),[5] mono-*t*-butyl malonate and mono-*t*-butyl dimethylmalonate undergo mainly the elimination reaction to form isobutene and the corresponding malonic acid on pyrolysis.



$$\mathrm{HOOC\overset{|}{\underset{|}{C}}COOC(CH_3)_3} \longrightarrow \mathrm{HOOC\overset{|}{\underset{|}{C}}COOH + CH_2{=}C(CH_3)_2}$$

The ease with which this elimination reaction occurs is probably due to an acid catalysis, since ordinary *t*-butyl esters, such as *t*-butyl cinnamate and *t*-butyl isovalerate, are stable at these temperatures.[6] It should be pointed out, however, that *t*-butyl esters undergo the elimination reaction more readily[7] than the corresponding ethyl esters.

The carbonation of ethyl acetate and ethyl isobutyrate formed presumably the half-ethyl esters of the corresponding malonic acids (in the form of their sodium salts). In the present study, these intermediates were allowed to hydrolyze to the corresponding malonic acids; this reaction occurred readily. There were obtained from ethyl acetate, a 34% yield of malonic acid and from ethyl isobutyrate, a 73% yield of dimethylmalonic acid.



$$\mathrm{H\overset{|}{\underset{|}{C}}COOC_2H_5} \xrightarrow[\text{by } \mathrm{CO_2}]{\mathrm{(C_6H_5)_3CNa}\text{ followed}} \mathrm{NaOOC\overset{|}{\underset{|}{C}}COOC_2H_5} \xrightarrow[\text{and acid}]{\text{hydrolysis}} \mathrm{{>}C(COOH)_2}$$

The mechanism of the carbonation of esters by means of sodium triphenylmethide reagent is analogous to that for the carbonation of ketones reported in the preceding paper.[1]

Carbethoxylations.—The carbethoxylation of ethyl acetate with diethyl carbonate to form diethyl malonate has previously been effected with sodium ethoxide.[8] This reaction has now been effected by sodium triphenylmethide. The carbethoxylation of ethyl isobutyrate to form diethyl dimethylmalonate, which has been effected previously with ethyl chlorocarbonate[9] in high yield using sodium triphenylmethide, has now been effected in even higher yield with ethyl 4-phenylphenyl carbonate using the same base.

The carbethoxylation of *t*-butyl acetate with diethyl carbonate using sodium triphenylmethide, which has been carried out previously[10] and confirmed in the present investigation, gives ethyl *t*-butyl malonate in more than 50% yield. It has been found, however, that when ethyl 4-phenylphenyl carbonate is used instead of diethyl carbonate, the yield of ethyl *t*-butylmalonate is only 23% after one and one-half hours, and negligible after twelve hours. Apparently, in the presence of the reactive diphenyl ester, the ethyl *t*-butylmalonate first formed undergoes further carbethoxylation to give the di-carbethoxylation

---

(1) Paper XXV on "Condensations"; paper XXIV, THIS JOURNAL, **66**, 862 (1944).

(2) Presented at the Pittsburgh meeting of the A. C. S., Sept., 1943.

(3) Supported in part by a grant of the Duke University Research Council.

(4) Schlenk, Hillemann and Rodloff, *Ann.*, **487**, 135 (1931).

(5) Marguery, *Bull. Soc. Chim.*, [3] **33**, 541 (1905).

(6) Abramovitch, Shivers, Hudson and Hauser, THIS JOURNAL, **65**, 986 (1943).

(7) See for example, Norris and Rigby, *ibid.*, **54**, 2097 (1932).

(8) Wallingford, Homeyer and Jones, *ibid.*, **63**, 2056 (1941).

(9) Hudson and Hauser, *ibid.*, **63**, 3156 (1941).

(10) Hauser Abramovitch and Adams, *ibid.*, **64**, 2714 (1942).