2. Dimeric ester mixture A apparently has the normal non-conjugated structure expected as a result of dimerization by way of a Diels–Alder reaction, with α-β double bond acting as dieneophile, resulting in structures III and IV.

A crystalline dimeric methyl ester has been isolated from A by refractionation and crystallization. It is nonconjugated, but gives the conjugated acid, m. p. 216°, of Farmer upon alkaline saponification. The probable structure of this ester is discussed and is believed to be III.

3. Dimer ester B apparently has a double bond α-β or conjugated to a carbomethoxy group. To a large extent this is apparently due to the γ-δ double bond in the sorbic ester acting as the dieneophile, resulting in structures V and VI, with various *cis–trans* isomers possible.

MINNEAPOLIS, MINNESOTA RECEIVED MARCH 29, 1948

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES, GENERAL MILLS, INC.]

1,4-Addition Reactions. II. Addition of Ethyl Malonate to Acrolein[1]

BY DONALD T. WARNER AND OWEN A. MOE

In a previous publication,[2] the 1,4-addition of ethyl acetamidomalonate and other closely related compounds to acrolein was reported. This is the first instance of a successful 1,4-addition between a malonate system and an α,β-unsaturated aldehyde. The present report is concerned with the extension of this reaction to other mono-substituted malonic esters. However, this type of reaction is not limited to mono-substituted malonates possessing only one α-hydrogen atom. Either ethyl malonate or ethyl cyanoacetate readily yields a 1,4-addition product with acrolein.

The 1,4-addition involving ethyl malonate and acrolein proceeded smoothly in the presence of an alkaline catalyst. The product, γ,γ-dicarbethoxybutyraldehyde I, was obtained in 50% yield. When I was separated from the crude reaction product by distillation under reduced pressure, a considerable quantity of a nearly colorless, viscous residue remained. This residue, probably the di-substitution product, is now being investigated further.

The structure of compound I was proved by an unequivocal synthesis involving the alkylation of ethyl malonate with β-chloropropionaldehyde diethylacetal.

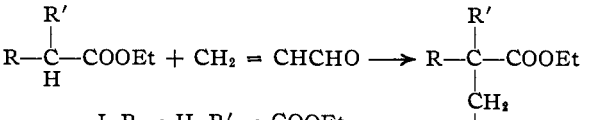
Reduction of the aldehydo compound I in the presence of Raney nickel catalyst yielded ethyl α-carbethoxy-δ-hydroxyvalerate which was characterized as the 3,5-dinitrobenzoate. The ethyl α-carbethoxy-δ-hydroxyvalerate was converted by the action of ammonia into α-carbamyl-δ-hydroxyvaleramide which in turn yielded a 3,5-dinitrobenzoate.

Addition of ethyl cyanoacetate to acrolein yielded the aldehydo compound II which was characterized as the 2,4-dinitrophenylhydrazone.

The 1,4-addition reactions of ethyl alkylmalonates gave the aldehydo compounds III, IV and V, where the alkyl groups were ethyl, hexyl and decyl, respectively. The aldehydo compound V was not purified by distillation under reduced pressure and the crude product yielded an oily 2,4-dinitrophenylhydrazone. However, this crude product V, when subjected to catalytic reduction in the presence of Raney nickel, yielded a carbinol which formed a crystalline 3,5-dinitrobenzoate. The aldehydo compounds III and IV yielded crystalline 2,4-dinitrophenylhydrazones.

γ-Acetoxy-γ,γ-dicarbethoxybutyraldehyde, VI, was prepared by the 1,4-addition of ethyl acetoxymalonate to acrolein. It was characterized as the 2,4-dinitrophenylhydrazone.

Certain features of the reaction between ethyl bromomalonate and acrolein are noteworthy. When the reaction was carried out in the presence of sodium ethoxide, difficulty was encountered in maintaining the alkalinity of the reaction mixture. In order to maintain alkalinity it was necessary to add a molar equivalent of the base. The product



I, R = H, R′ = COOEt
II, R = H, R′ = CN
III, R = Et, R′ = COOEt
IV, R = *n*-C_6H_{13}, R′ = COOEt
V, R = *n*-$C_{10}H_{21}$, R′ = COOEt
VI, R = CH_3COO, R′ = COOEt
VII, R = Br, R′ = COOEt

formed a 2,4-dinitrophenylhydrazone (m. p. 142–142.5°). However, this 2,4-dinitrophenylhydrazone did not contain bromine. Elementary analysis of the 2,4-dinitrophenylhydrazone indicated that the aldehydo compound was 4,4-dicarbethoxy-3-butenal which could arise from the dehydrohalogenation of the normal 1,4-addition product, VII. The occurrence of the dehydrobromination was not too surprising in view of the fact that a molar equivalent of the base had been employed. Supporting evidence for this structure was obtained by catalytic reduction of this product in the presence of 5% palladium-on-charcoal. The reduction product was γ,γ-dicarbethoxybutyraldehyde, I, identical with a specimen synthesized in another manner.

(1) Paper No. 92, Journal Series, Research Laboratories, General Mills, Inc.

(2) Moe and Warner, THIS JOURNAL, **70**, 2763 (1948).

When ethyl bromomalonate was added to acrolein in the presence of tributylamine as the catalyst, γ-bromo-γ,γ-dicarbethoxybutyraldehyde, VII, was obtained. The 2,4-dinitrophenylhydrazone melted at 82.5–83.5°.

Experimental

γ,γ-Dicarbethoxybutyraldehyde, I.—**A.** Ethyl malonate (400 g.) was added to a solution of sodium (0.3 g.) in absolute ethanol (1000 cc.). This solution was cooled to 0° and acrolein (168 g.) was added dropwise. The reaction temperature was maintained at approximately 5°. After the addition was complete the reaction mixture was stirred for two hours and neutralized with acetic acid. The solvent was removed by distillation under reduced pressure and the yellow oil was dissolved in benzene and extracted with three 500-cc. portions of water. The organic solution was dried over anhydrous sodium sulfate and the solvent was removed by distillation under reduced pressure. The viscous, nearly water-white residue was subjected to distillation under diminished pressure. The first fraction (78 g.) consisted predominantly of ethyl malonate. A large fraction (316 g.) was collected over the range of 80–120° at 0.4–1.5 mm. An appreciable amount of decomposition occurred during the collection of the latter part of this fraction. An appreciable quantity of a nearly colorless viscous residue remained. The large second fraction (316 g.) was redistilled. The first fraction (28 g.) was predominantly ethyl malonate. The second fraction (13.7 g.) was collected at 71–75.5° at 0.8 mm. and was probably a mixture of ethyl malonate and the aldehydo compound. The third fraction (266 g.) collected at 76–79° at 0.04–0.07 mm., $n^{25}D$ 1.4340, was γ,γ-dicarbethoxybutyraldehyde.

Anal. Calcd. for $C_{10}H_{16}O_5$: C, 55.52; H, 7.45. Found: C, 55.15; H, 7.33.

The 2,4-dinitrophenylhydrazone prepared in the conventional manner melted at 75–76° after recrystallization from ethanol.

Anal. Calcd. for $C_{16}H_{20}O_8N_4$: C, 48.46; H, 5.09; N, 14.14. Found: C, 48.83; H, 5.01; N, 14.23.

B. Ethyl malonate was alkylated with β-chloropropionaldehyde diethylacetal[3] as follows: Ethyl malonate (16.3 g.) was dissolved in absolute ethanol (50 cc.). The diethylacetal of β-chloropropionaldehyde (16 g.) was added and the solution was refluxed while a solution of sodium ethoxide (2.3 g. of sodium and 75 cc. of absolute ethanol) was added dropwise. The refluxing was continued for twenty-four hours. Sodium chloride was removed by filtration. The filtrate was concentrated under reduced pressure and diluted with water. The oily layer was extracted with ether and the extract was dried over anhydrous sodium sulfate. Evaporation under reduced pressure yielded a residual oil which was distilled. The product (8.6 g.) was collected at 165–175° at 17 mm. One gram of the product was warmed with hydrochloric acid (8 cc., 2%) on the steam-bath for five minutes. The aldehyde without isolation was then directly converted to the 2,4-dinitrophenylhydrazone which after recrystallization from ethanol melted at 75–76° alone or when mixed with the 2,4-dinitrophenylhydrazone obtained under A.

Anal. Calcd. for $C_{16}H_{20}O_8N_4$: N, 14.14. Found: N, 14.13.

Ethyl α-Carbethoxy-δ-hydroxyvalerate.—Distilled γ,γ-dicarbethoxybutyraldehyde (18.8 g.) was dissolved in absolute ethanol (100 cc.) and subjected to the action of hydrogen in the presence of Raney nickel catalyst at 80° and under an initial pressure of 1500 pounds. The catalyst was removed and the water-white filtrate was concentrated under reduced pressure. Benzene (100 cc.) was added and the reaction mixture was again concentrated under reduced pressure. A portion (0.7 g.) of the residual oil was converted into the 3,5-dinitrobenzoate which melted at 69.5–70.5° after crystallization from absolute ethanol.

Anal. Calcd. for $C_{17}H_{20}O_{10}N_2$: C, 49.49; H, 4.89; N, 6.79. Found: C, 49.60; H, 4.78; N, 6.87.

Another portion (7.5 g.) of the above residual oil was added to aqueous ammonia (32 g., saturated at 0°) and the mixture allowed to stand at room temperature for sixty hours. The solution was filtered and the filtrate was concentrated under reduced pressure. The crude diamido compound melted at 161–163°. After crystallization from 90% ethanol it melted at 164–165°.

Anal. Calcd. for $C_6H_{12}O_3N_2$: C, 44.97; H, 7.56; N, 17.49. Found: C, 45.10; H, 7.28; N, 17.76.

The 3,5-dinitrobenzoate of the diamido compound, crystallized from aqueous ethanol (60%), melted at 221–222° with decomposition.

Anal. Calcd. for $C_{13}H_{14}O_8N_4$: C, 44.05; H, 3.98; N, 15.83. Found: C, 44.36; H, 4.02; N, 15.60.

γ-Carbethoxy-γ-cyanobutyraldehyde, II.—A solution of sodium (50 mg.) in absolute ethanol (3 cc.) was diluted with dry benzene (72 cc.); ethyl cyanoacetate (28.4 g.) was added and the mixture was cooled to 6°. Acrolein (13.5 g.) was added dropwise while the temperature was maintained at 12°. The mixture was placed in the refrigerator overnight and then acidified with glacial acetic acid (0.5 cc.) and extracted with four 30-cc. portions of dilute aqueous sodium chloride. After drying over anhydrous sodium sulfate, the benzene was removed under reduced pressure, and the residual oil was subjected to distillation. The main fraction (8.9 g.) was collected at 106–115° (0.6 mm.). Redistillation yielded 5 g. of product which boiled at 90–93° (0.2 mm.).

Anal. Calcd. for $C_8H_{11}O_3N$: C, 56.78; H, 6.55; N, 8.26. Found: C, 56.30; H, 6.40; N, 8.65.

The 2,4-dinitrophenylhydrazone prepared in the usual way melted at 111–112° after recrystallization from ethanol.

Anal. Calcd. for $C_{14}H_{15}O_6N_5$: C, 48.13; H, 4.33; N, 20.05. Found: C, 48.14; H, 4.21; N, 20.05.

γ,γ-Dicarbethoxy-γ-ethylbutyraldehyde, III.—A solution of sodium (40 mg.) in absolute ethanol (200 cc.) was mixed with ethyl ethylmalonate (75 g.). Acrolein (23.5 g.) was added to the cooled (0°) solution. The mixture was placed in the refrigerator overnight. After acidification (acetic acid 1 g.) and concentration, the residual oil was dissolved in benzene (200 cc.), extracted with water (200 cc.) and dried over anhydrous sodium sulfate. The solvent was removed by distillation and the residual oil (91.5 g.) was distilled. The product (50 g.) was collected at 90–108° (0.25 mm.), most of it at 100–102°. A portion of this aldehyde was redistilled to give an analytical sample collected at 75–75.5° (0.07 mm.) ($n^{25}D$ 1.4386).

Anal. Calcd. for $C_{12}H_{20}O_5$: C, 58.96; H, 8.27. Found: C, 59.30; H, 8.53.

The 2,4-dinitrophenylhydrazone melted at 100–101° after recrystallization from ethanol.

Anal. Calcd. for $C_{18}H_{24}O_8N_4$: C, 50.95; H, 5.70; N, 13.20. Found: C, 50.74; H, 5.80; N, 13.16.

γ,γ-Dicarbethoxy-γ-hexylbutyraldehyde, IV.—The preparation of this aldehydo compound was carried out essentially as that described in the example above. The crude product was distilled under reduced pressure and the aldehydo compound IV was collected at 132–137° (0.3 mm.) ($n^{25}D$ 1.4478). The 2,4-dinitrophenylhydrazone melted at 86–87° after crystallization from ethanol.

Anal. Calcd. for $C_{22}H_{32}O_8N_4$: C, 54.96; H, 6.70; N, 11.66. Found: C, 55.07; H, 6.77; N, 11.73.

γ-Decyl-γ,γ-dicarbethoxybutyraldehyde, V.—This reaction was carried out essentially as described previously and the product was an oil which did not yield a crystalline 2,4-dinitrophenylhydrazone; hence, the crude γ-decyl-γ,γ-dicarbethoxybutyraldehyde was reduced in the presence of Raney nickel essentially as described above for γ,γ-dicarbethoxybutyraldehyde I. The resulting oil was

(3) Ellinger, *Ber.*, **38**, 2886 (1905).

converted into the 3,5-dinitrobenzoate which melted at 78.5–79.5° after crystallization from ethanol.

Anal. Calcd. for $C_{27}H_{40}O_{10}N_2$: C, 58.66; H, 7.30; N, 5.07. Found: C, 58.61; H, 7.27; N, 5.22.

γ-Acetoxy-γ,γ-dicarbethoxybutyraldehyde, VI.—This reaction was carried out essentially as described for compound III. The crude product was not distilled. However, it formed a 2,4-dinitrophenylhydrazone which melted at 114–115° after crystallization from ethanol.

Anal. Calcd. for $C_{18}H_{22}O_{10}N_4$: C, 47.55; H, 4.89; N, 12.33. Found: C, 47.69; H, 4.86; N, 12.33.

The Addition of Ethyl Bromomalonate to Acrolein: A. In the Presence of Sodium Ethoxide.—Ethyl bromomalonate (47.6 g.) was added to an alcoholic solution containing 200 cc. of absolute ethanol and 80 mg. of sodium. The resulting alcoholic solution was cooled to 0° and 11.5 g. of acrolein was added dropwise. After the acrolein had been added it was observed that the reaction mixture was acidic. Hence, an additional 0.5 g. of metallic sodium dissolved in ethanol was added. The reaction mixture was still acidic and an additional 4 g. of metallic sodium dissolved in approximately 100 cc. of absolute ethanol was added. The reaction mixture was permitted to stand in the refrigerator overnight. A considerable quantity of precipitate was noted, and it was removed by filtration. The resulting light brown filtrate was evaporated *in vacuo*. The residual oil was diluted with benzene and an additional quantity of the inorganic precipitate was removed by filtration. The benzene solution was extracted with three 70-cc. portions of water and then dried over anhydrous sodium sulfate. After filtration the benzene was removed by distillation *in vacuo* yielding a residual light yellow oil. The treatment of a portion of this residual oil with 2,4-dinitrophenylhydrazine yielded a crystalline derivative which melted at 137–139°. Recrystallization from absolute ethanol increased the melting point to 141.5–142.5°. However, this 2,4-dinitrophenylhydrazone did not contain bromine. Elementary analysis indicated that it was the 2,4-dinitrophenylhydrazone of 4,4-dicarbethoxy-3-butenal.

Anal. Calcd. for $C_{16}H_{18}O_8N_4$: C, 48.75; H, 4.61; N, 14.21. Found: C, 48.61; H, 4.60; N, 13.81.

A portion of the above residual light yellow oil (29 g.) was distilled *in vacuo*. The main fraction (13 g.) was collected at 78–85° (0.05–0.06 mm.). A portion (4.4 g.) of the distilled product was dissolved in 25 cc. of absolute ethanol, and 0.4 g. of 5% palladium-on-charcoal was added. The reduction was carried out at an initial pressure of 27 pounds of hydrogen and after twenty minutes the reduction was complete. The catalyst was removed by filtration and a portion of the alcoholic filtrate was employed in the preparation of the 2,4-dinitrophenylhydrazone which melted at 75–76° after crystallization from ethanol. There was no depression in the melting point when mixed with the 2,4-dinitrophenylhydrazone of γ,γ-dicarbethoxybutyraldehyde.

B. In the Presence of Tributylamine.—Ethyl bromomalonate (43.2 g.) was dissolved in 220 cc. of absolute ethanol and the solution was cooled to 2°. Tributylamine (0.5 g.) was added. Acrolein (10.5 g.) was added over a fifteen-minute period. No appreciable increase in the temperature of the reaction mixture was observed. After ninety minutes an additional quantity (0.15 g.) of tributylamine was added. The resulting reaction mixture was placed in the refrigerator overnight and then acidified with 5 cc. of glacial acetic acid. After filtration the filtrate was concentrated *in vacuo* to yield a brown oil. The residual oil was dissolved in 200 cc. of benzene and the benzene solution was washed with four 60-cc. portions of water. After drying over anhydrous sodium sulfate the benzene was removed by distillation *in vacuo* yielding 40.4 g. of a light yellow oil. The resulting oil was subjected to distillation under diminished pressure, and the desired fraction was collected at 97–100° (0.12 mm.), $n^{25}D$ 1.4665. A portion of the distilled product was treated with 2,4-dinitrophenylhydrazine and the resulting 2,4-dinitrophenylhydrazone was obtained in the form of light yellow platelets melting at 81–82.5°. After purification by recrystallization from absolute ethanol, the product melted at 82.5–83.5°.

Anal. Calcd. for $C_{16}H_{19}O_8N_4Br$: C, 40.42; H, 4.02; N, 11.79; Br, 16.82. Found: C, 40.82; H, 4.16; N, 11.75; Br, 16.82.

Summary

1. The 1,4-addition reaction involving malonate systems and acrolein has been extended to ethyl malonate and ethyl cyanoacetate which possess two α-hydrogen atoms and the resulting aldehydo compounds have been characterized.

2. The addition reactions of ethyl hexylmalonate, ethyl decylmalonate, ethyl acetoxymalonate and ethyl bromomalonate to acrolein have been described.

3. The structure of γ,γ-dicarbethoxybutyraldehyde, resulting from the 1,4-addition of ethyl malonate to acrolein, has been proved by an unequivocal synthesis.

MINNEAPOLIS, MINNESOTA RECEIVED JUNE 19, 1948

[CONTRIBUTION FROM THE DIVISION OF CHEMISTRY OF THE NATIONAL RESEARCH COUNCIL]

The Papilionaceous Alkaloids. V. *Baptisia minor*, Lehm.[1]

BY LÉO MARION AND W. F. COCKBURN

Baptisia minor, Lehm., is blue-flowered like *B. australis*, but smaller-leaved and it has for many years been taken as identical with the latter although it had originally been considered as specifically distinct. Recently it has again been claimed to be a species (*B. vespertina*),[2] still more recently a variety of *B. australis*[3] and, finally, it has been restored to specific rank.[4] It was, therefore, of interest to investigate the alkaloids of this plant. The results of the chemical study now reported support the more recent taxonomical evidence that the plant is specifically distinct from *B. australis*.

In common with *B. australis*,[5] *B. minor* contains *d*-sparteine, cytisine and N-methylcytisine, but it also contains anagyrine, baptifoline and alkaloid P4, all three of which are absent in the former. While alkaloid P4 is present in insufficient amount to permit satisfactory characterization, baptifoline, which is also present in *B. per-*

(1) Published as National Research Council Bull. No. 1732.

(2) P. A. Rydberg, "Flora of the Prairies and Plains of Central North America," The New York Botanical Garden, 1938, p. 456.

(3) M. L. Fernald, *Rhodora*, **39**, 312 (1937).

(4) Mary M. Larisey, *Ann. of the Missouri Botan. Garden*, **27**, 119 (1940).

(5) L. Marion and J. Ouellet, THIS JOURNAL, **70**, 691 (1948).