801. *Isomerisation of Phenylpropargylidenemalonic Acid to γ-Benzylidene-α-carboxybutenolide.*

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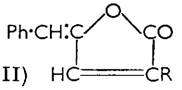
Phenylpropargylidenemalonic acid is converted into γ-benzylidene-α-carboxybutenolide by thermal isomerisation as well as through the silver salt. The structure of the product has been established by spectral and chemical evidence.

THE product of reaction of phenylpropargylaldehyde and malonic acid in acetic acid has been shown to be phenylpropargylidenemalonic acid (I; R = H).[1,2] The present work describes some properties of this substance.

The melting point 218° of this acid corresponds to that of an isomer formed during the heating (about 150—170°) and shown to be γ-benzylidene-α-carboxybutenolide * (II; R = CO_2H) by the following evidence:

$Ph{\cdot}C{\vdots}C{\cdot}CH{:}C(CO_2R)_2$

(I)



(II)

The acid (II; R = CO_2H), through its silver salt, gave a methyl ester (II; R = CO_2Me), which with hydrochloric acid in dioxan regenerated the acid (II; R = CO_2H). When this acid was heated at 250° *in vacuo* it yielded γ-benzylidenebutenolide (II; R = H), first prepared by H. Gilman and his co-workers.[3] Catalytic hydrogenation of the acid (II; R = CO_2H), followed by decarboxylation of the resulting gum, furnished a mixture from which were isolated δ-phenyl-*n*-valeric acid and γ-benzylbutanolide, characterised as γ-hydroxy-δ-phenyl-*n*-valero-*p*-toluidide and by reduction with hydriodic acid to δ-phenyl-*n*-valeric acid.

The ultraviolet spectra of compounds (I; R = H) $\lambda_{max.}$ 312 mμ (ε 20,000), (I; R = Me) [1]

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* Jacobs and his co-workers' assumption that the isomerisation product of m. p. 218° is 6-phenyl-α-pyrone-3-carboxylic acid is untenable because this substance has already been reported with different properties.[1]

[1] Castañer and Pascual, *Anales real. Soc. Españ. Fís. Quím.*, 1957, **53**, *B*, 651.

[2] Jacobs, Dankner, and Dankner, *J. Amer. Chem. Soc.*, 1958, **80**, 864.

[3] Gilman, Franz, Hewlett, and Wright, *J. Amer. Chem. Soc.*, 1950, **72**, 3.

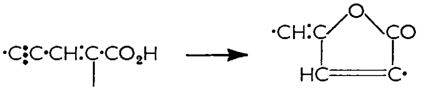
$\lambda_{max.}$ 316 mμ (ε 22,500), (II; R = H) $\lambda_{max.}$ 331 mμ (ε 26,050), (II; R = CO_2H) $\lambda_{max.}$ 358 mμ (ε 35,890), and (II; R = CO_2Me) $\lambda_{max.}$ 361 mμ (ε 29,270) are in good agreement with the accepted conjugation of the unsaturated bonds[4] and with the bathochromic effect due to cyclisation.[5]

In the infrared spectra of these substances and of phenylpropargylaldehyde (A) there are acetylenic bands at 2233—2183 (A), 2183 (I; R = H), and 2199 cm.$^{-1}$ (I; R = Me), that have disappeared in the spectra of the lactones (II). There are also bands at 1790 and 1750 cm.$^{-1}$ for the lactones (only a shoulder for II, R = CO_2H), that must be due to the γ-ylidenebut-αβ-enolide system (cf. the double band in Fig. 2 of ref. 6).

Addition of aqueous silver nitrate to an alcoholic solution of the acid (I; R = H) gave a precipitate which, on treatment with hydrogen sulphide afforded acid (II; R = CO_2H), and with methyl iodide gave the methyl ester (II; R = CO_2Me). The dimethyl ester (I; R = Me) was, however, obtained by treating the acid (I; R = H) with the theoretical amount of diazomethane.[1]

The acid (I; R = H) is probably also partially isomerised by alkali since the correct equivalent weight is obtained only from acid prepared in the cold and then only by titration (with sodium hydroxide) in the cold (cf. refs. 1 and 2).

The transformation:



is a nucleophilic addition of the carbonyloxy-group to the triple bond, and the resulting butenolide probably has a *trans*-ylidene bond. Recently, the same lactonisation, effected however under different conditions, has been reported in the polyacetylenic acid series.[6, 7]

EXPERIMENTAL

γ-Benzylidene-α-carboxybutenolide.—(*a*) Phenylpropargylidenemalonic acid (30 g.) was heated at 190° for 10—15 min. After cooling the product was washed with benzene. Recrystallisation from dioxan gave *γ-benzylidene-α-carboxybutenolide* (27 g.), as yellow rhombs, m. p. 218° (decomp.) (Found: C, 66·6; H, 3·8. $C_{12}H_8O_4$ requires C, 66·7; H, 3·7%).

(*b*) Silver nitrate (0·8 g.) in water (10 c.c.) was added to phenylpropargylidenemalonic acid (0·4 g.) in alcohol (6 c.c.). A brown precipitate appeared. More water (16 c.c.) was added. The precipitate became yellow after a few minutes and then was collected, suspended in water, and treated with hydrogen sulphide. The silver sulphide and free acid were filtered off and extracted with boiling dioxan. The yellow solution was concentrated to a small volume and water was added. The yellow precipitate was recrystallised from dioxan, to give γ-benzylidene-α-carboxybutenolide (0·35 g.) as yellow rhombs, m. p. 218° (decomp.).

γ-Benzylidene-α-methoxycarbonylbutenolide.—γ-Benzylidene-α-carboxybutenolide (1 g.) was treated with silver nitrate as above. The precipitate was collected and dried. The dry salt was ground and shaken for 24 hr. with methyl iodide. The precipitated silver iodide was filtered off and the solution was evaporated to dryness. Recrystallisation of the residue from ether gave the *ester* (0·72 g.), as yellow needles with a weak green fluorescence, m. p. 151—153° (Found: C, 67·9; H, 4·4. $C_{13}H_{10}O_4$ requires C, 67·8; H, 4·4%).

Phenylpropargylidenemalonic acid treated as above gave the same compound, m. p. 151—153°.

A solution of γ-benzylidene-α-methoxycarbonylbutenolide (0·2 g.) in dioxan (6 c.c.) and concentrated hydrochloric acid (8 c.c.) was refluxed for 5 hr. After cooling, more water (14 c.c.)

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[4] Houben-Weyl, "Methoden der Organischen Chemie," Georg Thieme Verlag, Stuttgart, 1955, Vol. B III, Part 2, p. 654.

[5] Braude and Nachod, "Determination of Organic Structures by Physical Methods," Academic Press Inc., New York, 1955, p. 154.

[6] Christensen, Sorensen, Bell, Jones, and Whiting, "Festschrift Arthur Stoll," Basel, 1957, p. 545.

[7] Bell, Jones, and Whiting, *J.*, 1958, 1313.

was added, whereupon a yellow precipitate was formed, which was collected and recrystallised from dioxan to give γ-benzylidene-α-carboxybutenolide, m. p. 218° (decomp.).

γ-Benzylidenebutenolide.—γ-Benzylidene-α-carboxybutenolide (3 g.) was heated *in vacuo* at 240—250°. A yellow oil, that solidified easily, distilled at 180°. This yellow solid recrystallised from ether to give γ-benzylidenebutenolide [3] (1·2 g.) as white prisms, m. p. 86—87° (Found: C, 76·6; H, 4·55. Calc. for $C_{11}H_8O_2$: C, 76·7; H, 4·7%), whose structure was confirmed by reduction with hydriodic acid to δ-phenyl-lævulic acid, as indicated by Gilman.[3]

Catalytic Hydrogenation of γ-Benzylidene-α-carboxybutenolide.—γ-Benzylidene-α-carboxybutenolide (4 g.) in alcohol (200 c.c.) was hydrogenated over Adams catalyst (0·15 g.) at 1 atm. (absorption 865 c.c.; theor., 861 c.c.). After filtration and evaporation the residue was a yellowish gum (3·95 g.) which was heated *in vacuo* at 140—150° for 15 min., then extracted with aqueous sodium hydroxide. The alkaline solution was acidified with hydrochloric acid and extracted with ether. Evaporation of the dried ethereal solution gave an oil which partially crystallised. Filtration of this material afforded a solid A (0·25 g.) and an oil B (1·6 g.). The solid A (0·25 g.), recrystallised from ether, gave δ-phenyl-*n*-valeric acid (0·20 g.), m. p. and mixed m. p. 58—59°. The liquid B (1·5 g.) in ether (20 c.c.) was added to a Grignard reagent prepared by adding *p*-toluidine to ethereal ethylmagnesium bromide. After 30 minutes' refluxing more ether (50 c.c.) was added and the cold solution was washed several times with 2N-hydrochloric acid, then with water. The dried ethereal solution was evaporated and the residue recrystallised from ether, to give *γ-hydroxy-δ-phenyl-*n*-valero-*p*-toluidide* (1·6 g.) as needles, m. p. 144—145° (Found: C, 76·15; H, 7·5; N, 5·0. $C_{18}H_{21}O_2N$ requires C, 76·3; H, 7·5; N, 4·9%).

The liquid B (1 g.), acetic acid (20 c.c.), and 40% hydriodic acid (20 c.c.) were heated at 160° during 6 hr. in a sealed tube, then diluted with water (100 c.c.), decolorised with a few drops of sodium hydrogen sulphite solution, and extracted with ether. The ethereal solution was extracted with aqueous sodium carbonate. The alkaline solution was acidified with hydrochloric acid and extracted with ether. This extract was dried and evaporated *in vacuo*. The residue, recrystallised from ether, gave δ-phenyl-*n*-valeric acid (0·8 g.), needles, m. p. 58—59°.

Titration of Phenylpropargylidenemalonic Acid.—The acid (11·06 mg.), prepared without heating,[1] was titrated in the cold (5·26 c.c. of 0·0196N-sodium hydroxide; equivalent, 107·3. Calc., 108·1). If the titration was carried out hot, or if heat was used in preparation of the acid, the values were about 120.

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