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]

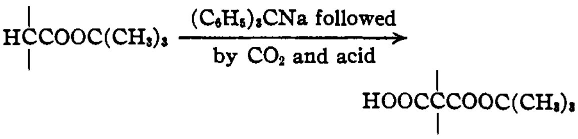
The Carbonation and Carbethoxylation of Certain Esters Using Sodium Triphenylmethide Reagent[1,2,3]

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.

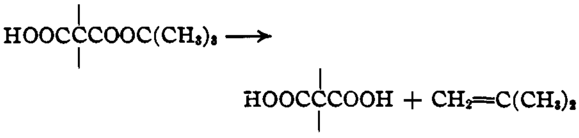
Carbonations.—The carbonation of esters to form half malonic acid esters has previously been carried out apparently only with methyl diphenylacetate,[4] the reaction being effected by means of sodium triphenylmethide. In the present investigation, four aliphatic esters have been carbonated using this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



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

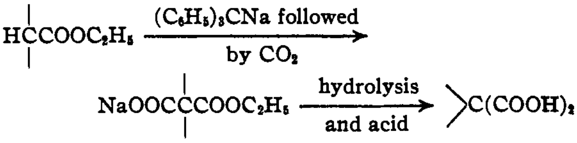
In contrast to malonic acids and their ethyl esters (which undergo decarboxylation when heated),[5] mono-*t*-butyl malonate and mono-*t*-butyl dimethylmalonate undergo mainly the elimination reaction to form isobutene and the corresponding malonic acid on pyrolysis.



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

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

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[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).

product. Analogous reactions have been observed previously.[8,9]

Experimental[11]

General Procedure.—Ester anions were prepared from equivalents (0.2 mole) of ester and sodium triphenylmethide reagent essentially as described for the preparation of ketone anions.[12] When formation of the anion was indicated by the disappearance of the characteristic color of the reagent, the anions were carbonated or carbethoxylated as described for these reactions with ketones.[12]

Dimethylmalonic Acid.—The anion of ethyl isobutyrate prepared at room temperature from 23.2 g. (0.2 mole) of ethyl isobutyrate was carbonated after fifteen minutes. After the Dry-Ice had evaporated, 400 ml. of water and 200 ml. of ether were added and the resulting ether phase extracted with 50 ml. of 10% sodium hydroxide solution. The combined aqueous phases (washed with ether) were left for twenty-four hours at room temperature (to permit hydrolysis of the half ester) prior to neutralization with dilute sulfuric acid. Extraction of the acidic solution with ether followed by evaporation of the solvent gave 19 g. (73%) of dimethylmalonic acid, m. p. 193–194° (dec.) (reported,[13] 192–193°).

Malonic Acid.—The anion of ethyl acetate prepared at 0° from 10.55 g. (0.12 mole) of ethyl acetate was carbonated immediately and the mixture worked up as in the preceding experiment. The aqueous solution of malonic acid was saturated with sodium chloride prior to the final ether extractions. There was obtained 4.3 g. (34%) of malonic acid, m. p. 131–133°. Recrystallization gave 3.4 g. of pure product, m. p. 133.5–134.5° (dec.) (reported,[14] 134.8–134.9°).

Mono-*t*-butyl Dimethylmalonate.—The anion of *t*-butyl isobutyrate prepared at room temperature from 28.8 g. (0.2 mole) of *t*-butyl isobutyrate[6] was carbonated after five hours. The alkaline solution of the reaction product, obtained as described above, was immediately acidified with iced sulfuric acid. Evaporation of the ether extract of the acidic solution yielded 30 g. (81%) of mono-*t*-butyl dimethylmalonate, m. p. 78–81°; from petroleum ether (b. p. 30–60°), m. p. 80.0–80.9°.

Anal. Calcd. for $C_9H_{16}O_4$: C, 57.43; H, 8.57; neut. eq., 188.2. Found: C, 57.64; H, 8.26; neut. eq., 188.5.

Mono-*t*-butyl Malonate.—The anion of *t*-butyl acetate prepared at 0° from 23.2 g. (0.2 mole) of *t*-butyl acetate[6] was carbonated immediately. After removal of low boiling impurities from the crude acidic material, 18 g. (57%) of slightly impure mono-*t*-butyl malonate was obtained. Neutral equivalent: calcd. for $C_6H_{12}O_4$: 160.2. Found: 154. The compound could not be distilled at a pressure below 1 mm.

Pyrolysis of Mono-*t*-butyl Malonates.—Pyrolysis of mono-*t*-butyl dimethylmalonate at 140–150° for two hours gave dimethylmalonic acid, m. p. 180–182.5°; from ether–petroleum ether, m. p. 190–192°.[13] The characteristic odor of isobutyric acid, arising from decarboxylation of dimethylmalonic acid, was observed after pyrolysis. A gas evolved during the pyrolysis and condensed in a Dry-Ice trap absorbed bromine in carbon tetrachloride solution. The gas was presumably isobutene.

The pyrolysis of mono-*t*-butyl malonate at 120° proceeded with the evolution of a gas. The residue was malonic acid, m. p. 133.5–134.5° (dec.).[14]

Diethyl Malonate.—The anion of ethyl acetate was prepared from 17.2 g. (0.2 mole) of ethyl acetate and carbethoxylated immediately with 23.6 g. (0.2 mole) of diethyl carbonate. A precipitate formed and after four hours 20 ml. of glacial acetic acid in 80 ml. of ice-water was added to the reaction mixture. The ether phase (extracted with iced sodium hydroxide solution) was dried (sodium sulfate followed by "Drierite") and distilled. The material, b. p. 40° (atm.) to 150° (15 mm.), was redistilled, yielding 6.6 g. (41%, based on sodium triphenylmethide) of diethyl malonate, b. p. 94–97° (19 mm.). From the alkaline extract of the original reaction mixture, 1.5 g. (12%) of ethyl acetoacetate, b. p. 76–79° (19 mm.), was isolated.

Diethyl Dimethylmalonate.—The anion of ethyl isobutyrate was prepared from 23.2 g. (0.2 mole) of ethyl isobutyrate and carbethoxylated with 36.3 g. (0.15 mole) of ethyl 4-phenylphenyl carbonate.[15] The mixture was worked up after one and one-half hours as in the preceding experiment (omitting alkali extraction of the ether phase), yielding 23 g. (83%, based on ethyl 4-phenylphenylcarbonate) of diethyl dimethylmalonate, b. p. 87–88° (15.5 mm.[9]). Diethyl dimethylmalonate did not absorb bromine in carbon tetrachloride solution and was hydrolyzed in 90% yield to dimethylmalonic acid, m. p. 193–194°.[13]

Ethyl *t*-Butyl Malonate.—The carbethoxylation of 0.2 mole of *t*-butyl acetate[6] with ethyl *p*-diphenylcarbonate[15] gave 4.4 g. (23%, based on sodium triphenylmethide) of ethyl *t*-butyl malonate, b. p. 100–101° (18.5 mm.[10]), after one and one-half hours. No ethyl *t*-butyl malonate could be isolated after twelve hours reaction time.

Summary

1. The carbonation of certain *t*-butyl esters has been effected by means of sodium triphenylmethide to form the corresponding mono-*t*-butyl esters of malonic acids. The carbonation of certain ethyl esters, followed by hydrolysis, has given the corresponding malonic acids.

2. The carbethoxylation of certain esters with diethyl carbonate has been effected using sodium triphenylmethide to form the corresponding malonic esters. Carbethoxylation with ethyl 4-phenylphenylcarbonate appears to give partly the dicarbethoxylation product.

3. Half *t*-butyl malonates on heating were found to undergo mainly the elimination reaction instead of the more common decarboxylation reaction.

DURHAM, N. C. RECEIVED FEBRUARY 29, 1944

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[11] Micro analyses by Dr. T. S. Ma, University of Chicago, Chicago, Illinois.

[12] Baumgarten, Levine and Hauser, THIS JOURNAL, **66**, 862 (1944).

[13] Koenigs and Hoerlin, *Ber.*, **26**, 2049 (1893).

[14] Serwy, *Bull. soc. chim. Belg.*, **42**, 483 (1933).

[15] Baumgarten, Walker and Hauser, THIS JOURNAL, **66**, 303 (1944).