[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DUKE UNIVERSITY]

Condensations. XVIII. The Acylation of the Anions of Certain Esters with Ethyl Carbonate

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The acylation of organic esters having two α-hydrogens with alkyl carbonates in the presence of sodium or potassium alkoxides has been developed by Wallingford and co-workers[1] for the convenient production of malonic esters. Esters having only one α-hydrogen failed to be acylated, and even with ethyl *t*-butyl acetate the yield was not reported. Moreover, the method does not appear to be applicable to the preparation of malonic esters with two different ester groups, that is, "mixed" malonic esters.

Although these acylations fail in the presence of metal alkoxides, they may be effected by means of the stronger base, sodium triphenylmethyl, which converts esters largely into their anions.[2] The acylation of the anions of esters with only one α-hydrogen, for example, ethyl isobutyrate, is probably best effected with ethyl chlorocarbonate, diethyl α,α-dimethylmalonate being obtained in this manner in 75% yield.[2] The anion of ethyl isovalerate (which has two α-hydrogens) with ethyl chlorocarbonate, however, gives only a low yield of the malonic ester, forming mainly the diacylated ester.[2] It is shown in the present investigation that the anions of certain esters having two or three α-hydrogens may be acylated satisfactorily with ethyl carbonate to produce malonic esters. With this acylating reagent, the anion of ethyl *t*-butylacetate gives diethyl *t*-butylmalonate in 47% yield, while the anions of *t*-butyl acetate and *t*-butyl propionate give the "mixed" malonic esters, *t*-butyl ethylmalonate and *t*-butyl ethyl-α-methylmalonate in yields of 54 and 72%, respectively. These acylations may be represented as follows.

$$C_2H_5OCO_2C_2H_5 + [(CH_3)_3CCHCO_2C_2H_5]^- \longrightarrow (CH_3)_3CCH(CO_2C_2H_5)_2 + {}^-OC_2H_5$$

$$C_2H_5OCO_2C_2H_5 + [CH_2CO_2C(CH_3)_3]^- \longrightarrow C_2H_5O_2CCH_2CO_2C(CH_3)_3 + {}^-OC_2H_5$$

$$C_2H_5OCO_2C_2H_5 + [CH(CH_3)CO_2C(CH_3)_3]^- \longrightarrow C_2H_5O_2CCH(CH_3)CO_2C(CH_3)_3 + {}^-OC_2H_5$$

In each of these reactions equivalent amounts of the ester having α-hydrogen, sodium triphenylmethyl and ethyl carbonate were used. The malonic ester formed was probably converted into its anion by means of the ester anion first prepared, and the corresponding amount of the ester was regenerated. The amount of ethyl carbonate used was twice that theoretically required but the excess seemed desirable in order to minimize the self-condensation of the ester having α-hydrogen. The yields of malonic esters reported above are based on the sodium triphenylmethyl used.

This method should be applicable to the acylation with ethyl carbonate of other esters that undergo self-condensation relatively slowly[3] (compared to ethyl acetate) to produce malonic esters in which the ester groups are the same or different.

Experimental

Ethyl *t*-Butyl Malonate.—Sodium triphenylmethyl[2] (1700 cc., 0.730 mole) was prepared in a 2-liter "Pyrex" bottle. The stopper was removed and the bottle quickly fitted with an efficient mechanical stirrer, dropping funnel, and bent tube delivering a slow stream of dry nitrogen. *t*-Butyl acetate (94.5 cc., 84.7 g., 0.73 mole) was added rapidly to the vigorously stirred solution (the red color being discharged immediately) and after one minute 88 cc. (86.1 g., 0.73 mole) of ethyl carbonate (b. p. 125.5–126.0°) was added during seven minutes, the bottle being cooled if the ether began to boil. Stirring was continued for two hours longer. Glacial acetic acid (60 cc.) dissolved in 300 cc. of ice-water was then added and the mixture transferred to a 2.5-liter separatory funnel. The mercury, aqueous solution, and sludge were then separated, the latter being washed with ether. The combined ether solutions were extracted with 10% sodium carbonate solution, and dried over anhydrous sodium sulfate followed by Drierite, and the solvent distilled. Distillation of the residue from a 1-liter Claisen flask yielded 41.0 g. of recovered esters (b. p. 45° at 60 mm. to 70° at 35 mm.) and 69.5 g., of material (b. p. 70° at 35 mm. to 150° at 18 mm.) which on fractionation through a twelve-inch Vigreux column at 17 mm., yielded 27.0 g. of a fore-fraction (b. p. 40–93°) and 36.0 g. (54% yield based on the sodium triphenylmethyl) of ethyl *t*-butyl malonate, b. p. 93–95°.

Anal.[4] Calcd. for $C_9H_{16}O_4$: C, 57.4; H, 8.57. Found: C, 57.4; H, 8.56.

Ethyl *t*-Butyl-α-methylmalonate.—*t*-Butyl propionate (b. p. 118.0–118.5°) was prepared in 63% yield from *t*-butyl

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(1) Wallingford, Homeyer and Jones, THIS JOURNAL, **63**, 2056 (1941).

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

(3) Results on the relative ease of self-condensations of esters in the presence of sodium triphenylmethyl will be published shortly.

(4) Analysis by Saul Gottlieb, Columbia University, New York, N. Y.

alcohol and propionyl chloride in the presence of dimethylaniline, essentially according to the procedure of Norris and Rigby[5] for the preparation of *t*-butyl acetate.

Anal.[4] Calcd. for $C_7H_{14}O_2$: C, 64.6; H, 10.84. Found: C, 65.1; H, 11.20.

t-Butyl propionate (107 cc., 92 g., 0.708 mole) was added to sodium triphenylmethyl[2] (1700 cc., 0.708 mole), the color being discharged within thirty seconds, and after two minutes 86 cc. (83.5 g., 0.708 mole) of ethyl carbonate was added. Stirring was continued for one and one-half hours longer. Glacial acetic acid (60 cc.) was added and the mixture worked up. After distilling off the solvent the residue gave 55.2 g. of a mixture (b. p. 35–77° at 40 mm.) of *t*-butyl propionate and ethyl carbonate, and 66.2 g. of material (b. p. 77° at 40 mm. to 150° at 12 mm.). Redistillation of the latter fraction through a twelve-inch Vigreux column at 14 mm., yielded 13.0 g. of a fore-fraction (b. p. 49–94°) and 48.7 g. (72% yield based on the sodium triphenylmethyl) of ethyl *t*-butyl-α-methylmalonate (b. p. 94–95°).

Anal.[4] Calcd. for $C_{10}H_{18}O_4$: C, 59.4; H, 8.97. Found: C, 60.0; H, 9.10.

Diethyl *t*-Butylmalonate.—Ethyl *t*-butyl acetate (38.2 g., 0.266 mole) prepared by the method of Homeyer, Whitmore and Wallingford,[6] was added with shaking to an ether solution of 0.266 mole of sodium triphenylmethyl and, after standing for ten minutes, 31.4 g. (0.266 mole) of ethyl carbonate was added. After twenty-four hours the reaction mixture was acidified with dilute acetic acid, the ether solution dried and the solvent distilled. The residue yielded 30 g. of recovered esters (b. p. 67–78° at 100 mm.) and 13.3 g. (47%) of diethyl *t*-butylmalonate (b. p. 102–104° at 11 mm.).

Anal.[7] Calcd. for $C_{11}H_{20}O_4$: C, 61.10; H, 9.32. Found: C, 61.24; H, 9.20.

Summary

The anions of ethyl *t*-butyl acetate, *t*-butyl acetate and *t*-butyl propionate (prepared by means of sodium triphenylmethyl) have been acylated with ethyl carbonate to form, respectively, diethyl *t*-butylmalonate and the "mixed" malonic esters, ethyl *t*-butylmalonate and ethyl *t*-butyl-α-methylmalonate.

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[5] Norris and Rigby, THIS JOURNAL, **54**, 2097 (1932).

[6] Homeyer, Whitmore, and Wallingford, *ibid.*, **55**, 4209 (1933).

[7] Analysis by William Saschek, 630 W. 168 St., New York, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI]

A Study of the Products Obtained by the Reducing Action of Metals upon Salts in Liquid Ammonia Solution. VIII. The Reduction of Complex Cyanides

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Introduction

The unusual result obtained by the action of alkali metals on the complex cyanides of nickel in liquid ammonia solution,[2] as contrasted to that obtained through the use of simple nickel salts,[3] prompted the examination of the behavior of the complex cyanides of other metals, some of whose simple salts are also known to give the free metal when reduced by alkali metals in liquid ammonia solution. For this purpose the complex cyanides of cadmium, copper, silver and zinc were chosen. Also the action of calcium on potassium cyanonickelate was investigated. The reactions were carried out as described in previous articles.[2]

Preparation of Complex Cyanides

The complex potassium cyanides of silver, copper and zinc were prepared in the way previously described for the nickel compound.[2] All were markedly more soluble in hot than cold water. Inasmuch as cadmium cyanide is soluble in water, the complex cyanide was prepared by crystallization from a solution containing the stoichiometric quantities of cadmium sulfate and potassium cyanide. The product was recrystallized until free of sulfate ion and then dried at 110°.

All of these complex cyanides were very soluble in liquid ammonia, giving clear colorless solutions.

Potassium Cyanocadmiumate, $K_2Cd(CN)_4$, and Potassium.—Pieces of potassium, when added to a liquid ammonia solution of potassium cyanocadmiumate (in excess), slowly react in such a way that each piece is replaced by a clump of metallic cadmium. No hydrogen gas is given off during the reaction. The black metallic cadmium is not reactive with water, but is highly pyrophoric.

Potassium Cyanocopperate, $K_3Cu(CN)_4$, and Potassium.—Potassium, when added to a solution of potassium cyanocopperate in liquid ammonia, reacts to give a finely divided black precipitate of pyrophoric copper. At the instant the solution turns blue, due to reaction of all of the complex cyanide and solution of the excess potassium, a beautiful copper mirror forms on the surface of the reaction tube in contact with the solution.

Potassium Cyanosilverate, $KAg(CN)_2$, and Potassium.—When pieces of potassium are added to a liquid ammonia

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[1] This article is based upon the thesis presented to the Faculty of the Graduate School, University of Cincinnati, by John W. Eastes in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1936.

[2] Eastes and Burgess, THIS JOURNAL, **64**, 1187 (1942).

[3] Burgess and Eastes, *ibid.*, **63**, 2674 (1941).