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STUDIES ON PEROXYCOMPOUNDS—XXVI†
“$\text{S}_\text{N}2$”-TYPE DECARBETHOXYLATION OF O-BENZOYLTARTRONATES AND BENZOYLOXYCYANOACETATES. NEW SYNTHONS FOR 2-HYDROXYCARBOXYLIC ESTERS AND ALDEHYDES

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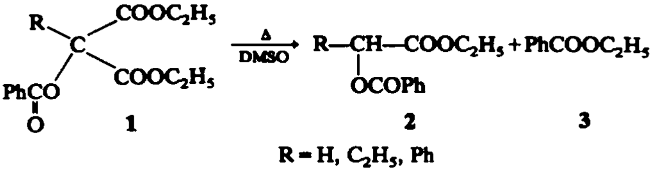
Abstract—Diethyl O-benzoyl-R-tartronates **1**; R = H, C_2H_5, Ph undergo $\text{S}_\text{N}2$-type dealkylation and subsequent CO_2 elimination at 175–190°C in anhydrous or wet DMSO, with or without inorganic salts as catalysts giving the corresponding 2-benzoyloxyesters **2**. Ethyl 2-benzoyloxy-2-benzylcyanoacetate **4** also undergoes decarbethoxylation (140°C, DMSO or wet DMSO) giving **6** in small yields (1–6%). The best yields of **6** (82%) were found when pyridine was the solvent and LiI the catalyst.

The reaction of sodium salts of malonates with benzoyl peroxide in an inert solvent like benzene produces the corresponding O-benzoyltartronates smoothly.[1,2] Other so called active methylene compounds (as Na-salt[3]) and also enamines[4,5] undergo the same reaction. Extension of these reactions has shown that, among others, 2-hydroxycarboxylic esters easily can be prepared after ethanolysis of suitable benzoyloxyderivatives.[1,6]

As esters can undergo $\text{S}_\text{N}2$-type dealkylation[7–9] decarbethoxylation of a few O-benzoyltartronates **1** under different conditions have been investigated. Dimethylsulfoxide (anhydrous or wet) was used as solvent without any catalyst present. Also anhydrous DMSO with salts (NaCl, NaN_3, Na_3PO_4) and wet DMSO with salts (NaCl, LiCl, KF, NaBr, Na_3PO_4) were tried and in most cases the two main products were the corresponding 2-benzoylesters **2** and ethyl benzoate.

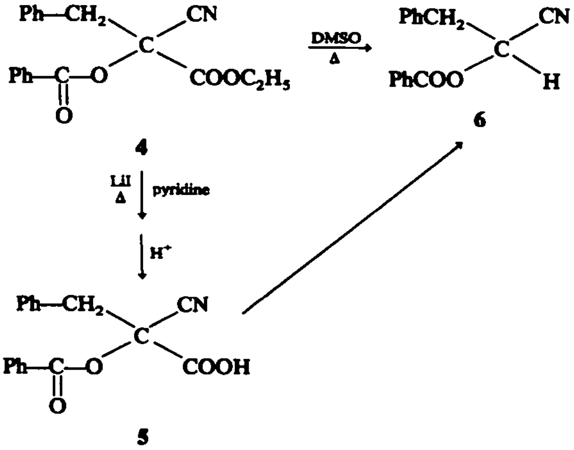
Relative yields, calculated from GLC measurements, and absolute yields (see Experimental) show, that the highest yields of **2** (≈50%) are obtained when anhydrous DMSO without catalyst is used. From the reaction of **1** in DMSO/sodium cyanide only ethyl benzoate was isolated in 42% yield. Attempts to decarbethoxylate **1** (R = H) by use of LiI in refluxing pyridine[8] resulted in the formation of **2** in 47% yield. It can thus be concluded that even if selective dealkylation of an ester containing a benzoyloxy group is known,[9] substrates of type **1** seem to give a more complex reaction mixture. In spite of these somewhat discouraging results, it was tempting to investigate if an easily available substrate **4** could be transformed into a synthon of an aldehyde **6**.



Many attempts were made to eliminate the ethoxycarbonyl group by refluxing **4** in DMSO with a catalyst present. Most experiments were unsuccessful. However, refluxing **4** in wet DMSO with NaCl as catalyst (175–200°C, ½ h) gave 1–6% of **6** and a number of unidentified products. At 133°C no reaction took place.

Using pyridine as solvent and LiI as catalyst (reflux, 12 h) and subsequent acidification, produced 82% yield of the free carboxylic acid **5** which spontaneously lost CO_2 under formation of **6**. The same treatment of ethyl 2-benzoyloxy-3-oxobutanoate with LiI in refluxing pyridine gave only quantitative yields of benzoic acid.

Although no attempts have been made to find optimal conditions a conclusion of this investigation is that O-benzoyltartronates on heating in pyridine



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† Part XXIV, see ref. 4.

with LiI present produces reasonable (∼50%) yields of 2-benzoyloxy esters. O-Benzoylcyanhydrins, synthrons of aldehydes, are prepared similarly in almost quantitative yields (90–100%) from benzoyloxycyanoacetates.

EXPERIMENTAL

^{1}H NMR spectra were recorded at 60 MHz on a Varian A-60 spectrometer and ^{13}C NMR spectra were recorded at 20 MHz on a Varian CFT-20 spectrometer. TMS was used as internal reference standard and chemical shifts are expressed in δ-values. $CDCl_3$ was used as solvent. IR spectra were recorded on a Beckman IR-18 spectrometer. Mass spectra were recorded on a CEC 21–104 Mass spectrometer operating at 70 eV using direct inlet. Elementary analyses were carried out by NOVO Microanalytical Laboratory, Novo Industri A/S, Novo Allé, DK-2880 Bagsvaerd, supervised by Dr R. E. Amsler. Silica gel 60 (Merck) was used for column chromatography. M.p.'s and b.p.s are uncorrected.

Ethyl 2-benzoyloxyethanoate (**2**, R = H). 2.74 g (0.01 mole) of diethyl-O-benzoyltartronate[1] were refluxed in 10 ml DMSO with 0.01 mole (1.64 g) Na_3PO_4 and 0.02 mole (0.36 g) water for 4 h in oil bath at 200°C. After cooling the reaction mixture was treated with the same volume of water to remove most of the DMSO and remaining salts. This mixture was extracted some times with ether. The combined ether phases were dried (Na_2SO_4), concentrated and separated on silica gel (ether/light petroleum, 20% v/v). Yield 0.80 g (40%) of **2** and 0.16 g (11%) of **3**. Anal.: Found: C 63.27, H 5.77, O 30.77. Calc.: C 63.46, H 5.77, O 30.77%. ^{1}H NMR ($CDCl_3$): 1.29 (t, 3H), 4.28 (q, 2H), 4.84 (s, 2H), 7.5–8.3 (m, 5H). MS: *m/e* 208 (M^+), 180, 163, 135, 105, 77. When NaCl, LiCl and NaBr were used as catalysts, the yields of **2** were 22%, 7% and 13% and the yields of **3** were 27%, 6% and 2%, respectively. Using anhydrous DMSO with no salt, the yields were 50% of **2** and 0% of **3**.

6.7 g (0.05 mole) LiI and 1.40 g (0.005 mole) of **1** (R = H) in 125 ml pyridine were refluxed for 12 h under N_2. After cooling the reaction mixture was poured into ice-water and acidified with hydrochloric acid. The mixture was extracted with 3 × 100 ml of ether, and the combined ether phases dried ($MgSO_4$) concentrated and separated on silicagel eluted with 5% (v/v) ether/light petroleum yielding 47% of **2** and benzoic acid in 29% yield.

Ethyl 2-benzoyloxybutanoate (**2**, R = C_2H_5). 3.02 g (0.01 mole) of diethyl-O-benzoyl ethyltartronate[1] were refluxed in 10 ml DMSO with 0.01 mole (0.58 g) NaCl and 0.02 mole (0.36 g) water for 3½ h in oil-bath at 200°C. Work up as above. Yield: 0.40 g (30%) of **3**, 1.11 g (50%) of **2** and 0.22 g of *I*. B.p. 96–100°C/0.25 Torr, n_D^{23} = 1.4899. Anal.: Found: C 66.26, H 6.85, O 26.51. Calc.: C 66.10, H 6.78, O 27.12%. ^{1}H NMR ($CDCl_3$): 1.08 (t, 3H), 1.25 (t, 3H), 2.02 (m, 2H), 4.25 (q, 2H), 5.2 (t, 1H), 7.5–8.3 (m, 5H). MS: *m/e* 236 (M^+), 191, 163, 150, 122, 114, 105, 77.

Ethyl 2-benzoyloxy-2-phenylethanoate (**2** R = Ph). 3.56 g (0.01 mole) diethyl-O-benzoyl phenyltartronate[1] were refluxed in 10 ml DMSO with 0.01 mole (0.58 g) NaCl and 0.02 mole (0.36 g) water for 3 h in oil-bath at 200°C. Work up as above. Yield: 0.66 g (44%) of **3** and 0.87 g (31%) of **2**. Anal.: Found: C 71.58, H 5.55. Calc.: C 71.83, H 5.63%. ^{1}H NMR ($CDCl_3$): 1.23 (t, 3H), 4.25 (q, 3H), 6.2 (s, 1H), 7.4–8.3 (m, 10H, Ar). MS: *m/e* 284 (M^+), 238, 211, 105, 77.

2-Benzoyloxy-3-phenyl propanitrile **6**. 3.23 g (0.01 mole) of **4**[10] were refluxed at 175°C in anhydrous DMSO for 2 h. After cooling the same volume of water was added and the products were extracted with ether. The combined ether phases were dried (Na_2SO_4), concentrated and purified on silica gel eluted with 50% ether/light petroleum yielding about 6% of **5** (calculated on basis of ^{1}H NMR spectrum) and 1.39 g (43%) of **4**. ^{1}H NMR ($CDCl_3$): δ 3.3 (d, J = 7 Hz, —CH_2—), 5.7 (t, J = 7 Hz, —CH—), 7.2–8.2 (m, Ar).

3.23 g (0.01 mole) of **4** (13.4 g; 0.1 mole) LiI in 150 ml pyridine were refluxed for 12 h. After cooling the reaction mixture was acidified with HCl in water and extracted with ether. The combined ether phases were washed once with water, dried ($MgSO_4$), concentrated and purified on silicagel eluted with ether/light petroleum (50% v/v) yielding 2.32 g (92%) of **5**. M.p. 33°C (d). Anal.: Found: C 76.21, H 5.08, N 5.64, O 12.62. Calc. ($C_{16}H_{13}NO_2$): C 76.49, H 5.18, N 5.58, O 12.75%.

After standing, CO_2 was expelled from **5** giving **6** in quantitative yields, m.p. 35.9°C. Anal.: Found: C 69.23, H 4.76, N 4.63. Calc. ($C_{17}H_{13}NO_4$): C 69.15, H 4.41, N 4.75%). ^{1}H NMR ($CDCl_3$): δ 3.29 (d, J = 7 Hz, CH_2), 5.73 (t, J = 7 Hz, CH), 7.2–8.2 (m, Ar). MS: 252 (M^+ + 1), 129, 105, 91, 77.

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