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Preparation of 2-Alkenonitrile by Means of the Pyrolysis of Diethyl 1-Cyanoalkyl Phosphate

Yoshiki OKAMOTO, Tsutomu NITTA and Hiroshi SAKURAI

The Institute of Scientific and Industrial Research, Osaka University, Yamada-kami, Suita-shi, Osaka

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In previous papers, it has been reported that the long-chain aliphatic aldehydes and α-hydroxycarboxylic acids were prepared from diethyl acylphosphonates by treatment with sodium borohydride or potassium cyanide *via* the following scheme:

$$\mathrm{RCOPO(OC_2H_5)_2} \xrightarrow{\mathrm{NaBH_4}} \mathrm{RCH(OH)PO(OC_2H_5)_2} \xrightarrow{\mathrm{OH^-}} \mathrm{RCHO} + \mathrm{HPO(OC_2H_5)_2} \quad (1)^{1)}$$

$$\mathrm{RCOPO(OC_2H_5)_2} \xrightarrow[2)\ \mathrm{KCN}]{1)\ \mathrm{NaHSO_3}} \mathrm{RCH(OH)PO(OC_2H_5)_2} \xrightarrow{\mathrm{OH^-}} \mathrm{RCH(CN)OPO(OC_2H_5)_2} \xrightarrow[\mathrm{H_2O}]{\mathrm{H^+}} \mathrm{RCH(OH)COOH} \quad (2)^{2)}$$

It has also been reported that 2-butenonitrile was synthesized by the pyrolysis of 1-cyanopropyl acetate, itself prepared by the acetylation of propionaldehyde cyanhydrin.[3] In order to get long-chain 2-alkenonitriles, the corresponding long-chain aliphatic aldehydes were necessary. The preparation of long-chain aldehyde is, however, generally troublesome, and, in addition, the cyanhydrin could not be acetylated in a good yield.

In this note, a convenient method for the preparation of 2-alkenonitrile by means of the pyrolysis of diethyl 1-cyanoalkyl phosphate will be reported.

1) Y. Okamoto and H. Sakurai, *Kogyo Kagaku Zasshi* (*J. Chem. Soc. Japan, Ind. Chem. Sect.*), **70**, 797 (1967).

2) Y. Okamoto, T. Nitta and H. Sakurai, *ibid.*, **71**, 187 (1968).

3) D. L. Macpeek, P. S. Strarcher and B. P. Benjamin, *J. Am. Chem. Soc.*, **81**, 680 (1959).

$$RCH_2\dot{C}H(OPO(OC_2H_5)_2)\dot{C}N \longrightarrow RHC{=}CHCN + HPO(OC_2H_5)_2 \quad (3)$$

Diethyl acylphosphonates were easily prepared in good yields by the reaction of the corresponding acid chloride and triethyl phosphite.[2] The properties and the yields are summarized in Table 1.

Table 1. Preparation of diethyl acylphosphonates ($RCH_2COPO(OC_2H_5)_2$)

R	Yield (%)	Bp (°C/mmHg)	n_D^{25}
CH_3	85	66—67/0.5	1.4245
C_2H_5	90	75—76/1	1.4273
C_4H_9	89	85—86/0.5	1.4326
C_8H_{17}	87	125—126/0.5	1.4392
$C_{10}H_{21}$	88	155—156/1	1.4407

Diethyl 1-cyanoalkyl phosphates could be obtained from the corresponding diethyl acylphosphonate and potassium cyanide in an aqueous solution, but the yields were reduced by the hydrolysis reaction of some of the diethyl acylphosphonates.

$$RCOPO(OC_2H_5)_2 + H_2O \xrightarrow{OH^-} RCOOH + HPO(OC_2H_5)_2 \quad (4)$$

On the other hand, when the sodium bisulfite adduct of diethyl acylphosphonate, which had been prepared by the addition of diethyl acylphosphonate to the saturated aqueous solution of sodium bisulfite, was treated with an aqueous solution of potassium cyanide at pH 8, the corresponding cyanhydrin derivative was obtained as crystals in high yields. The yields and the properties are listed in Table 2. The infrared spectra showed the absortption peak of the hydroxyl group at 3170 cm^{-1}.

Diethyl 1-cyano-1-hydroxyalkylphosphonate isomerized rapidly into diethyl 1-cyanoalkyl phosphate in a large excess of a saturated aqueous solution of potassium cyanide (pH>12). The reaction occurred exothermically, and the diethyl 1-cyanoalkyl phosphate was almost quantitatively separated in an oily layer. After having been washed with water, the phosphate was used for the pyrolysis without further purification. The infrared spectra showed no absorption peak of the hydroxyl group.

Table 2. Preparation of diethyl 1-cyano-1-hydroxyalkylphosphonate ($RCH_2C(OH)(CN)PO(OC_2H_5)_2$)

R	Yield (%)	Mp (°C)		Anal. (%) P	N	C	H
CH_3	85	—	Found	14.01	6.31	43.22	7.11
			Calcd	14.00	6.33	43.88	7.29
C_2H_5	88	68—69	Found	13.00	5.97	46.00	7.79
			Calcd	13.13	5.96	45.89	7.71
C_4H_9	89	25—26	Found	11.52	5.29	50.68	8.59
			Calcd	11.77	5.32	50.19	8.42
C_8H_{17}	87	42—43	Found	10.21	4.41	56.00	9.70
			Calcd	10.01	4.53	55.01	9.76
$C_{10}H_{25}$	90	45—46	Found	8.86	3.93	58.58	10.05
			Calcd	8.92	4.03	58.77	10.03

The pyrolysis was carried out under reduced pressure (2—3 mmHg) in a stainless steel tube (ϕ 3 cm×60 cm) heated at 400—600°C in an electric furnace. The thermal decomposition of diethyl 1-cyanoalkyl phosphate occurred thoroughly above 300°C. The pure 2-alkenonitriles were obtained by the fractional distillation of the pyrolysis products. The yields and the properties of 2-alkenonitriles are listed in Table 3.

Table 3. Preparation of 2-alkenonitrile obtained from 1-cyanoalkyl phosphate (RCH=CHCN)

R	Yield (%)	Bp (°C/mmHg)	n_D^{20}
CH_3	71	103—105	1.4195
C_2H_5	53	44—45/17	1.4301
C_4H_9	52	71—74/22	1.4399
C_8H_{17}	52	86—89/1.5	1.4507
$C_{10}H_{21}$	51	105—109/3.5	1.4549

The purities of the 2-alkenonitriles were checked by gas chromatography (>98%). The infrared spectra indicated that the double bond (C=C) was only in the trans form (965 cm^{-1}).

The yield of 2-butenonitrile from diethyl 1-cyanopropyl phosphate was almost equal to that from 1-cyanopropyl acetate.

Diethyl 1-cyano-2-phenylethyl phosphate gave 3-phenylpropenonitrile in a 76% yield, but diethyl 1-cyanobenzyl phosphate did not give the corresponding 2-alkenonitrile, but rather benzalaldehyde in a 51% yield.

Experimental

Diethyl Acylphosphonate. The diethyl acylphosphonates were prepared by the reaction of the corresponding acyl chlorides with triethyl phosphite according to a procedure described earlier.[2]

Diethyl 1-Cyano-1-hydroxyalkylphosphonate and Diethyl 1-Cyanoalkyl Phosphate. One hundred grams of diethyl acylphosphonate were stirred, drop by drop, into 400 ml of a saturated aqueous solution of sodium bisulfite at 30°C. The reaction mixture came to be viscous; then a saturated aqueous solution of potassium cyanide was stirred in over a period of 1 hr, until the pH of the mixture rose to 8. The oily layer separated was extracted with ether. After the evaporation of the solvent, diethyl 1-cyano-1-hydroxyalkylphosphonate solidified on cooling. It was then recrystallized

from acetone (see Table 2).

Eighty grams of diethyl 1-cyano-1-hydroxyalkylphosphonate were added slowly to 200 m*l* of a saturated aqueous solution of potassium cyanide cooled with ice water. The isomerization reaction occurred exothermically. Then the reaction mixture was stirred for 30 min, and the product was extracted with ether. The ethereal extract was washed with water. After the removal of the solvent under a vacuum, the residue, diethyl 1-cyanoalkyl phosphate, was obtained; it was used for pyrolysis without any further purification.

Pyrolysis of Diethyl 1-Cyanoalkyl Phosphate. Typical Procedure. Thirty grams of diethyl 1-cyanoalkyl phosphate were charged continuously, at the rate of 1 m*l*/min, into the top of a 60 cm stainless steel tube (dia. 3 cm), which was inclined at twenty degrees from the horizontal; the tube was then heated at 600°C under reduced pressure (3—5 mmHg). The products were trapped as solid materials in a tube cooled with liquid nitrogen. Pure 2-alkenonitrile was obtained by fractional distillation in the presence of a catalytic amount of hydroquinone (see Table 3).