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α,β-Unsaturated Carboxylic Acid Derivatives. VII. Reaction of Ethyl α,β-Unsaturated α-Cyanocarboxylates with Triethyl or Diethyl Phosphonate[1]

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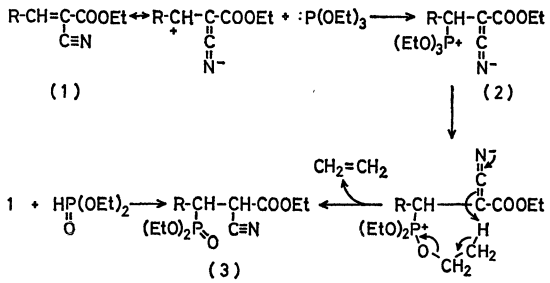
Synopsis. The reaction of ethyl α,β-unsaturated α-cyanocarboxylates with triethyl phosphonate gave ethyl α-cyano-β-diethoxyphosphinyl-carboxylates in about 50% yields.

In a previous paper,[2] we reported that the reaction of ethyl α,β-unsaturated α-nitrocarboxylates with triethyl phosphonate gave ethyl α,β-unsaturated β-diethoxyphosphinyl-carboxylates *via* unstable 3-ethoxycarbonyl-1,2,5-oxazaphospholine derivatives.

In this paper, we wish to report the reaction of ethyl α,β-unsaturated α-cyanocarboxylates (**1**) with triethyl or diethyl phosphonate.

Results and Discussion

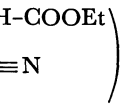
When compound **1a**—**d** (**a**; R=methyl, **b**; R=ethyl, **c**; R=*n*-propyl, **d**; R=*i*-propyl) was treated with triethyl phosphonate at room temperature for 30 min and then the mixture was heated at *ca.* 120 °C for 2 hr with continuous stirring, ethyl α-cyano-β-diethoxyphosphinyl-carboxylate (**3a**—**d**) was obtained in about 50% yield as a colorless oil. In the reaction of ethyl 2-cyanocinnamate (**1e**) with triethyl phosphonate, an adduct (**2e**) was obtained in a good yield. The IR spectrum of **2e** showed a strong absorption of C=C=N⁻ at 2050 cm^{-1} (Fig. 1). The compound **2e** can be repeatedly distilled (bp 152—155 °C/0.25 mmHg), but it changed gradually into **3e** at room temperature over 6 months. The stability of the intermediate, **2e**, is probably due to the resonance stabilization between its intramolecular phosphonium salt and phenyl group attached to the carbon atom at the 3-position. However, when a solution of **2e** in cyclohexane was irradiated at room temperature for 24 hr by using an external high-pressure mercury lamp, ethyl 2-cyano-3-diethoxyphosphinyl-3-phenylpropanoate (**3e**) was obtained in a good yield and ethylene was liberated. The reaction seems to proceed through the compound **2** which in turn decomposes to the compound **3** and ethylene as shown in Scheme 1. The structure of **3** was confirmed by IR spectra and an independent preparation from diethyl phosphonate and **1**. The physical properties of **3** were summarized in Table 1.



a: R=CH_3 b: R=C_2H_5 c: R=n-C_3H_7 d: R=i-C_3H_7 e: R=C_6H_5

Scheme 1.

TABLE 1. ETHYL 2-CYANO-3-DIETHOXYPHOSPHINYL-ALKANOATES (3)



Compound	R	Yield (%) A[a]	Yield (%) B[b]	bp °C/mmHg	Formula	Found (Calcd), % C	H	N	cm⁻¹, IR in KBr -C≡N (w)[c]	-COOEt (s)[d]	P=O (s)	P-O-C (s)	¹H (δ) NMR[e] α-H	β-H
3a	CH_3	49	65	118—120/0.25	$C_{11}H_{20}NO_5P$	47.83 (47.69)	7.75 (7.22)	5.39 (5.05)	2200	1745	1240	1020	3.77	2.65
3b	C_2H_5	35	—	118—120/0.18	$C_{12}H_{22}NO_5P$	49.19 (49.14)	7.75 (7.76)	4.64 (4.81)	2200	1745	1245	1020	3.76	2.63
3c	*n*-C_3H_7	36	58	120—125/0.18	$C_{13}H_{24}NO_5P$	51.08 (51.12)	7.77 (7.87)	4.50 (4.54)	2200	1745	1245	1020	3.76	2.60
3d	*i*-C_3H_7	58	—	124—127/0.18	$C_{13}H_{24}NO_5P$	51.08 (51.12)	7.75 (7.87)	4.49 (4.54)	2200	1740	1240	1020	3.75	2.62
3e	C_6H_5	66	—	148—152/0.25	$C_{15}H_{22}NO_5P$	54.92 (55.05)	6.95 (6.73)	4.11 (4.28)	2250	1750	1240	1020	3.55	2.39

a) From the reaction of **1** with triethyl phosphonate. b) From the reaction of **1** with diethyl phosphonate. c) w=Weak. d) s=Strong. e) Measured in $CDCl_3$.

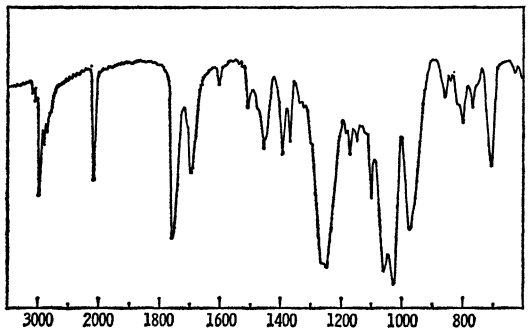


Fig. 1. IR absorption spectrum of **2e**.

Experimental

All boiling points are uncorrected. The IR spectra were recorded with a Hitachi EPI-S2 Spectrometer. The NMR spectra were measured with a JNM-4H-100 Spectrometer using tetramethylsilane as an internal standard.

Material. Compound **1** was prepared by the reaction of appropriate aldehyde with ethyl cyanoacetate.[3,4]

*Reaction of **1a–d** with Triethyl Phosphonate.* A mixture of **1a–d** (0.05 mol) and triethyl phosphonate (0.06 mol) was stirred at room temperature for 30 min and then heated at 120—130 °C for 2 hr. The corresponding ethyl α-cyano-β-diethoxyphosphinyl-β-alkylpropanoate was obtained by distillation under reduced pressure. The physical properties are listed in Table 1.

*Reaction of **1e** with Triethyl Phosphonate.* A mixture of **1e** (0.05 mol) and triethyl phosphonate (0.1 mol) was refluxed for 5 hr. After removal of excess triethyl phosphonate, the residual syrup was distilled under reduced pressure to give an adduct (**2e**) (70.5%) as a colorless oil, bp 152—155 °C/0.25 mmHg. IR (KBr disk); 2050 (–C=C=N–), 1740 (–COOEt) and 1020 ($\geqslant$P–O–C$\langle$)cm^{-1}. NMR (CDCl$_3$); δ 2.40 (1H, s, C_6H_5–CH–C–).

Found: C, 58.47; H, 7.67; N, 4.12%. Calcd for $C_{18}H_{26}NO_5P$: C, 58.85; H, 7.08; N, 3.81%.

*Irradiation of **2e**.* A solution of **2e** (7 g) in dry cyclohexane (90 ml) was irradiated at room temperature for 24 hr by an external high-pressure mercury lamp. After removal of cyclohexane, the residue was purified on a silica gel column using benzene-acetone (10 : 1 V/V). After removal of the solvent, the residual oil was distilled under reduced pressure to give a colorless oil (**3e**).

*Reaction of **1a** or **1c** with Diethyl Phosphonate.* A mixture of **1a** (0.05 ml) and diethyl phosphonate (0.1 mol) was refluxed for about 5 hr. After removal of the excess diethyl phosphonate, the residual oil was distilled under reduced pressure to give a colorless oil (**3a**).

In a similar manner, **3c** was obtained as a colorless oil starting from **1c** with diethyl phosphonate.

References

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4) F. D. Popp, *ibid.*, **25**, 646 (1960).