A Novel Synthesis of Ethyl β-Diethoxyphosphinyl-α,β-unsaturated-carboxylates

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(Received August 28, 1971)

Although there have been numerous reports on the reaction of aromatic nitro and nitroso compounds with tervalent organophosphorus reagents,[1–5] little attention has been paid to that of aliphatic nitro compound.

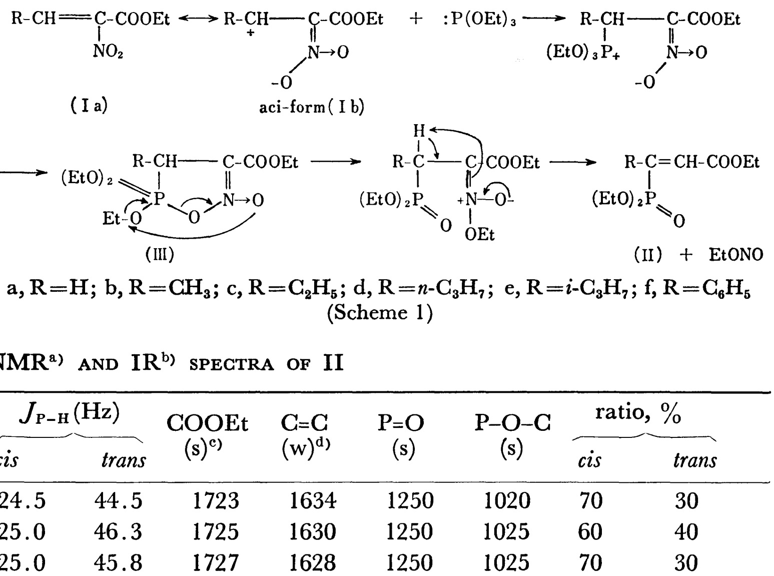
In the course of studies on the reaction of ethyl α,β-unsaturated α-nitrocarboxylates (I),[6] we have found that the reaction of I with triethyl phosphite gave ethyl β-diethoxyphosphinyl-α,β-unsaturated-carboxylates (II) in good yield, accompanied by liberation of ethyl nitrite. Only two kinds of vinylphosphonates (IIa and IIb) have recently been prepared by nucleophilic substitution of the corresponding activated vinyl halides with triethyl phosphite as useful synthetic intermediates (Arbusov reaction).[7,8]

When a solution of I (0.1 mol) and triethyl phosphite (0.1 mol) in dry benzene (30 m*l*) was refluxed for about 3 hr, evolution of gaseous substance took place. Fractional distillation of the reaction mixture gave colorless oil (Table 1). The gaseous substance trapped was identified to be ethyl nitrite by gas chromatography. The stereochemical assignments of II were made on the basis of independent preparation from vinyl halides and phosphite, and spectroscopic analysis. The vinyl hydrogen signal with $J_{P-H}=23.5$—28.4 Hz appearing in a lower magnetic field, and that with $J_{P-H}=43.5$—46.3 Hz in a higher field were assinged to *cis* and *trans*, respectively[9] (Table 2). Consequently, the composition of *cis* and *trans* isomers in II was evaluated from the intensity of the vinyl protons.

From the results it is postulated that the triethyl phosphite reacted nucleophilically to β-position of the nitrocarboxylic esters (aci-form; Ib) and cyclized to afford five membered intermediates (III), and the subsequent concerted reaction in III occurred to give II and ethyl nitrite (Scheme 1). In fact, in the case of isopropyl derivative, an unstable intermediate (bp 95—105°C/0.001 mmHg. Found: N, 4.14%. Calcd for $C_{14}H_{28}NO_7P$: N, 3.97%) was obtained under mild conditions and was decomposed to IIe and ethyl nitrite during the course of redistillation.

Table 1. Boiling points and yields of II

Compound	bp °C/mmHg	Yield(%)
IIb	118—121/2	75.2
IIc	121—123/1.5	67.2
IId	117—122/1	82.0
IIe	119—122/1.5	62.8
IIf	150—152/0.5	65.6



a, R=H; b, R=CH_3; c, R=C_2H_5; d, R=*n*-C_3H_7; e, R=*i*-C_3H_7; f, R=C_6H_5
(Scheme 1)

Table 2. NMR[a] and IR[b] spectra of II

Compound	α-H (τ)		β-H (τ)		J_{P-H}(Hz)		COOEt (s)[c]	C=C (w)[d]	P=O (s)	P–O–C (s)	ratio, %	
	cis	*trans*	*cis*	*trans*	*cis*	*trans*					*cis*	*trans*
IIb	3.39	3.51	3.63	3.39	24.5	44.5	1723	1634	1250	1020	70	30
IIc	3.43	3.56	3.67	4.02	25.0	46.3	1725	1630	1250	1025	60	40
IId	3.19	3.34	3.45	3.80	25.0	45.8	1727	1628	1250	1025	70	30
IIe	3.46	3.53	3.71	3.99	28.4	46.3	1722	1620	1250	1020	70	30
IIf	3.18	3.30	3.42	3.73	23.5	43.5	1730	1615	1250	1020	70	30

a; 100 Mc., in CCl_4. b; cm^{-1}, in NaCl. c; s=strong. d; w=weak.

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