Studies on Nitro Carboxylic Acids. III. The Reaction of α-Nitroolefins with Triethyl or Diethyl Phosphite[1)]

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The reaction of α-nitroolefins with triethyl or diethyl phosphite was studied and structural assignment of the products was made by spectroscopic analyses. Ethyl α,β-unsaturated α-nitrocarboxylates (IV) and 1-nitroalkenes (V) reacted with triethyl phosphite to afford ethyl β-diethoxyphosphinyl-α,β-unsaturated-carboxylates (IX) and 2-diethoxyphosphinyl-1-alkenes (X), respectively. Compound (IV) reacted with diethyl phosphite to give ethyl β-diethoxyphosphinyl-α-nitrocarboxylates (VI). The geometrical isomerism in IX and the reaction mechanism were discussed.

Numerous reports have appeared on the deoxygenation and intramolecular cyclization reaction of aromatic nitro and nitroso compounds with tervalent organophosphorus reagents,[3—7)] but little attention has been paid to that of aliphatic nitro compounds with the above reagents.[3)]

The reaction of ethyl α,β-unsaturated α-nitrocarboxylates (IV)[8,9)] with triethyl phosphite gives ethyl β-diethoxyphosphinyl-α,β-unsaturated-carboxylates (IX). Only two kinds of vinylphosphonates (IXa and IXb) have recently been prepared by nucleophilic substitution of the corresponding activated vinyl halides with triethyl phosphite, as useful intermediates (Arbuzov reaction).[10,11)]

In the present paper, detailed studies on the reaction of α-nitro-olefins (IV and V) with triethyl or diethyl phosphite and on the structural assignment of products are described.

Results and Discussion

Reactions of α-Nitroolefins with Triethyl Phosphite. When a benzene solution of IV and triethyl phosphite was refluxed for about 3 hr, evolution of a gaseous substance was observed. This was trapped and identified by gas chromatography to be ethyl nitrite. Fractional distillation of the reaction mixture gave ethyl β-diethoxyphosphinyl-α,β-unsaturated-carboxylates (IX) as a colorless oil in good yield.

Similar reaction of ethyl 3-hydroxy (Id)-, 3-acetoxy (IId)- and 3-methoxy-2-nitrohexanoates (IIId) with triethyl phosphite also gave IXd and ethyl nitrite, together with a small amount of water, acetic acid and methanol, respectively. It is well-known that hydroxy, acetoxy and methoxy groups in the 3-position of 2-nitrocarboxylic esters are easily eliminated in the persence of base to afford the corresponding nitroolefins.[1,8,12,13)] The reaction might thus be preceded by the elimination of the substituents in the presence of triethyl phosphite as Lewis base. In the cases of Id and IIId, the yield of IXd decreased a great deal.

Under similar experimental conditions, 1-nitroalkenes (V) also reacted with triethyl phosphite to afford 2-diethoxyphosphinyl-1-alkenes (X) as a colorless oil in good yield. The results are summarized in Table 1, 2, 3, and 4.

Structural Assignment of IX and X. The streeochemical assignment of IX and X was made on the basis of independent preparation from vinyl halides and triethyl phosphite,[11)] elementary and spectroscopic analyses. NMR spectra of IX (Table 2) showed two kinds of vinyl hydrogen signals, one with smaller coupling constants ($J_{\mathrm{P,H}}=23.5-28.4$ Hz) appearing in the lower magnetic field and the other in higher field with larger coupling constants ($J_{\mathrm{P,H}}=43.5-46.3$ Hz) and were assigned to *cis* and *trans* isomers,[14)] respectively.

Similarly, two vinyl hydrogen signals of *cis* and *trans* to the phosphorus atom appeared in lower and higher magnetic fields with smaller ($J_{\mathrm{P,H}}=22.5-23.8$ Hz) and larger ($J_{\mathrm{P,H}}=46.3-50.0$ Hz) coupling constants, respectively. The composition of *cis* and *trans* isomers in IX was evaluated from the intensity of the vinyl proton signals to be approximately 7/3.

The infrared spectra of IX showed a waek band of carbon-carbon double bond in the region 1615—1630 cm^{-1} and two strong bands of P=O and P–O–C groups at 1250 and 1020—1025 cm^{-1}, respectively (Table 2). The absorption pattern of X is essentially the same

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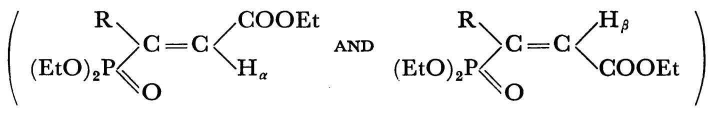
TABLE 1. PHYSICAL CONSTANTS, YIELDS, AND ELEMENTARY ANALYSES OF IX

Compound	Bp °C/mmHg	Yield (%)	Formula	Found (Calcd) C%	Found (Calcd) H%
IXb	118—121/2	72.4	$C_{10}H_{19}O_5P$	47.89 (48.00)	7.62 (7.60)
IXc	121—123/1.5	67.2	$C_{11}H_{21}O_5P$	49.78 (50.00)	8.19 (7.90)
IXd	117—122/1	77.3	$C_{12}H_{23}O_5P$	51.59 (51.79)	8.03 (8.27)
IXe	119—122/1.5	62.8	$C_{12}H_{23}O_5P$	51.56 (51.79)	8.66 (8.27)
IXf	150—152/0.5	65.6	$C_{15}H_{20}O_5P$	57.61 (57.69)	6.79 (6.73)

TABLE 2. NMR[a] AND IR[b] SPECTRA OF IX



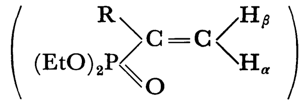
Compound	cis-H$_\alpha$ (τ)		trans-H$_\beta$ (τ)		J_{PH} (Hz) cis	J_{PH} (Hz) trans	COOEt (s)[c]	C=C (w)[d]	P=O (s)	P–O–C (s)	ratio cis	ratio trans
IXb	3.39	3.63	3.51	3.95	24.5	44.5	1723	1634	1250	1020	7	3
IXc	3.43	3.67	3.56	4.02	25.0	46.3	1725	1630	1250	1025	6	4
IXd	3.19	3.45	3.34	3.80	25.0	45.8	1727	1628	1250	1025	7	3
IXe	3.46	3.71	3.53	3.99	28.4	46.3	1722	1620	1250	1020	7	3
IXf	3.18	3.42	3.30	3.73	23.5	43.5	1730	1615	1250	1020	7	3

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

TABLE 3. PHYSICAL CONSTANTS, YIELDS, AND ELEMENTARY ANALYSES OF X

Compound	Bp °C/mmHg	Yield (%)	Formula	Found (Calcd) C%	Found (Calcd) H%
Xc	65—67/4	71	$C_8H_{17}O_3P$	50.28 (50.00)	9.01 (8.85)
Xd	77—80/2	47	$C_9H_{19}O_3P$	52.38 (52.42)	9.13 (9.22)
Xe	70—73/3	65	$C_9H_{19}O_3P$	52.31 (52.42)	9.29 (9.22)
Xf	120—125/0.35	31	$C_{12}H_{17}O_3P$	60.21 (60.00)	6.98 (7.09)

TABLE 4. NMR[a] AND IR[b] SPECTRA OF X



Compound	cis-H$_\alpha$ (τ)		trans-H$_\beta$ (τ)		J_{PH} (Hz) cis	J_{PH} (Hz) trans	C=C (w)[c]	P=O (s)[d]	P–O–C (s)[d]
Xc	3.89	4.10	4.00	4.50	22.5	49.0	1630	1245	1023
Xd	3.88	4.11	4.04	4.53	23.8	50.0	1640	1250	1030
Xe	3.85	4.08	3.94	4.45	23.0	48.0	1630	1240	1020
Xf	3.56	3.78	3.62	4.09	22.5	46.3	1680	1250	1025

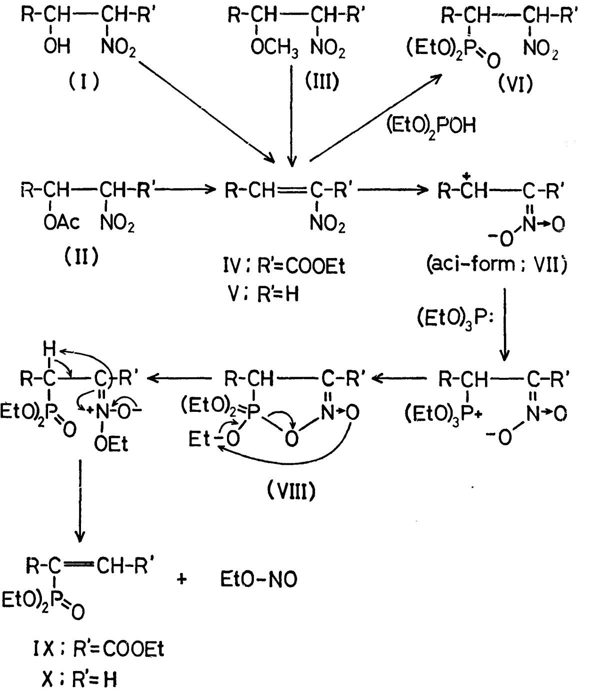
a ; 100 MHz, in $CDCl_3$. b ; cm^{-1}, in NaCl. c ; w=weak. d ; s=strong.

as that of IX except for the lack of ethoxycarbonyl band (Table 4).

Reaction of α-Nitroolefins with Diethyl Phosphite. In contrast to triethyl phosphite, diethyl phosphite can add to the olefinic bond of IV easily. When a mixture of IV and the phosphite was heated at 100 °C for 2 hr, the expected ethyl α-nitro-β-diethoxyphosphinylcarboxylates (VI) were obtained in about 50% yield. Compounds (VI) keep the nitro group, which showed stretching bands at *ca* 1565 and 1370 cm^{-1} in the infrared spectra. The disappearance of the stretching band of carbon-carbon double bond in the region 1640—1665 cm^{-1} and the appearance of P=O and P–O–C groups at 1250 and *ca* 1020 cm^{-1} seem to support the formation of VI.

Reaction Mechanism. From the results, it is postulated that the triethyl phosphite attacked nucleophilically on the β-position of the nitro-olefins (aci-form; VII) and cyclized to afford five-membered intermediates, 3-ethoxycarbonyl-Δ^2-1,2,5-oxazaphospholine-2-oxide derivatives (VIII), and the subsequent concerted reaction in VIII occurred to give IX and X together with ethyl nitrite (Scheme 1). In fact, in the case of isopropyl derivative (VIIIe, R'=COOEt), an unstable intermediate was obtained under mild conditions and decomposed to IXe and ethyl nitrite during the course of redistillation.

On the other hand, diethyl phosphite added nucleophilically to β-position of the nitroolefins (nitro-form; IV) affords VI.



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.

Experimental

All boiling points are uncorrected. The IR spectra were recorded on a Hitachi EPI-S2 spectrometer. The NMR spectra were measured with a JNM-4H-100 spectrometer (Japan Electron Optics Laboratory Co., Ltd.) at 100 MHz.

Materials. Ethyl α,β-unsaturated α-nitrocarboxylates were prepared by the reaction of ethyl α,β-unsaturated carboxylates with fuming nitric acid.[9] Ethyl α-nitrocinnamate was prepared according to the method of Dornow and Menzel.[15]

Reactions of IV with Triethyl Phosphite. A solution of IV (0.05 mol) in dry benzene (40 ml) was added dropwise, with stirring, to triethyl phosphite (0.05 mol) at a temperature below −5 °C. After being stirred for 3 hr at this temperature, the mixture was allowed to warm to room temperature, when stirring was continued for 1 hr. When the mixture was refluxed for about 3 hr, evolution of gaseous substance was observed. This was trapped in a U-tube fitted at the top of a condenser and cooled below −20 °C, and identified to be ethyl nitrite by gas chromatography. After concentration of the reaction solution, the residual oil was distilled under reduced pressure to afford a colorless oil, which was identified as ethyl β-diethoxyphosphinyl-α,β-unsaturated-carboxylates (IX). The results are summarized in Tables 1 and 2.

Reaction of IVe with Triethyl Phosphite below 30 °C. Ethyl 4-methyl-2-nitro-2-pentenoate (IVe; 5 g) was added dropwise, with stirring, to triethyl phosphite (10 g) at a temperature below −20 °C. After stirring for 2 hr, the mixture was allowed to warm slowly to room temperature and stirring was continued for 2 days at 30 °C. After concentration of the reaction mixture, the residual viscous oil was carefully distilled in a vacuum to afford 3-ethoxycarbonyl-4-isopropyl-Δ^2-1,2,5-oxazaphospholine-2-oxide (VIIIe) as yellow viscous oil (3.9 g, 41.5%), bp 95—105 °C/0.001 mmHg. IR (KBr disk): 1730 (-COOEt), 1625 (-C=N-), 1240 (-P-O-), and 1030 (P-O-C-) cm^{-1}.

Found: N, 4.14%. Calcd for $C_{14}H_{28}NO_7P$: N, 3.87%.

When a solution of VIIIe (2.8 g) in dry benzene (30 m*l*) was refluxed for 3 hr and the reaction solution was concentrated, residual oil was obtained accompanied by liberation of ethyl nitrite. The oil was distilled under reduced pressure to afford a colorless oil, which was identified as ethyl 3-diethoxyphosphinyl-4-methyl-2-pentenoate (IXe; 1.9 g, 74 %).

Reactions of V with Triethyl Phosphite. 1-Nitro-1-alkene (0.05 mol) was added dropwise, with stirring, to triethyl phosphite (0.07 mol) maintained below 15 °C. After stirring for 1 hr, the mixture was allowed to stand at 40 °C for about 2 hr when liberation of ethyl nitrite ceased. Concentration of the reaction mixture afforded residual oil, which was identified as 2-diethoxyphosphinyl-1-alkene (X). The results are summarized in Tables 3 and 4.

Reactions of Id-IIId with Triethyl Phosphite. Ethyl 3-acetoxy-2-nitrohexanoate[13] (IId; 0.03 mol) was added dropwise, with stirring, to a solution of triethyl phosphite (0.03 mol) in dry benzene (20 ml) cooled below 15 °C. After being stirred for 30 minutes at room temperature, the solution was refluxed for 1 hr. After concentration of the reaction solution, the residual oil was distilled under reduced pressure to afford a colorless oil, which was identified as ethyl 3-diethoxyphosphinyl-2-hexenoate (IXb). Yield 68.3%.

An analogous treatment of ethyl 3-hydroxy-2-nitrohexanoate (Id)[13] and ethyl 3-methoxy-2-nitrohexanoate (IIId)[9] with triethyl phosphite under reflux for 6 hr also afforded IXd, in 38.5 and 23.5% yields, respectively.

Reactions of IV with Diethyl Phosphite. Diethyl phosphite (0.03 mol) was added dropwise, with stirring, to ethyl 2-nitropentenoate (IVc; 0.03 mol) at room temperature, and the mixture was heated at 100 °C for 2 hr when it changed to brown. After concentration of the reaction mixture, the residual oil was distilled under reduced pressure to afford a colorless oil (68%, bp 130—135 °C/0.75 mmHg), which was identified as ethyl 3-diethoxyphosphinyl-2-nitropentanoate (VIc). IR(KBr disk): 1750 (-COOEt), 1565 and 1370 (-NO_2), 1250 (P=O), and 1020 (P-O-C) cm^{-1}. NMR ($CDCl_3$): 4.40—4.75 τ (double doublets, J=7.0 Hz) and 4.58 τ(doublet, J_{P-C-CH}=16.2 Hz).

Found: C, 42.84; H, 6.91; N. 4.33%. Calcd for $C_{11}H_{22}NO_7P$: C, 42.85; H, 7.07; N, 4.50%.

An analogous treatment of ethyl 2-nitrobutenoate (IVb) with diethyl phosphite also afforded ethyl 3-diethoxyphosphinyl-2-nitrobutanoate (VIb). Yield 41%, bp 126—128 °C/0.8 mmHg. IR: 1755 (-COOEt), 1565 and 1370 (-NO_2), 1250 (P=O), and 1020 (P-O-C) cm^{-1}. NMR: 4.60—4.73 τ(double doublets, J=6.8 Hz) and 4.66 τ(doublet, J_{P-C-CH}=12.5 Hz).

Found: C, 40.32; H, 6.83; N, 4.32%. Calcd for $C_{10}H_{20}NO_7P$: C, 40.40; H, 6.73; N, 4.71.%

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