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REACTION OF ETHYL α,β-UNSATURATED β-NITROCARBOXYLATES WITH TRIETHYL PHOSPHITE

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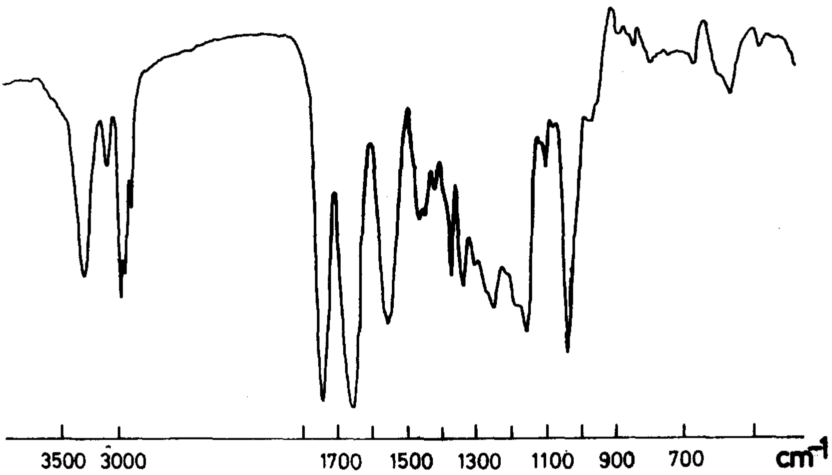
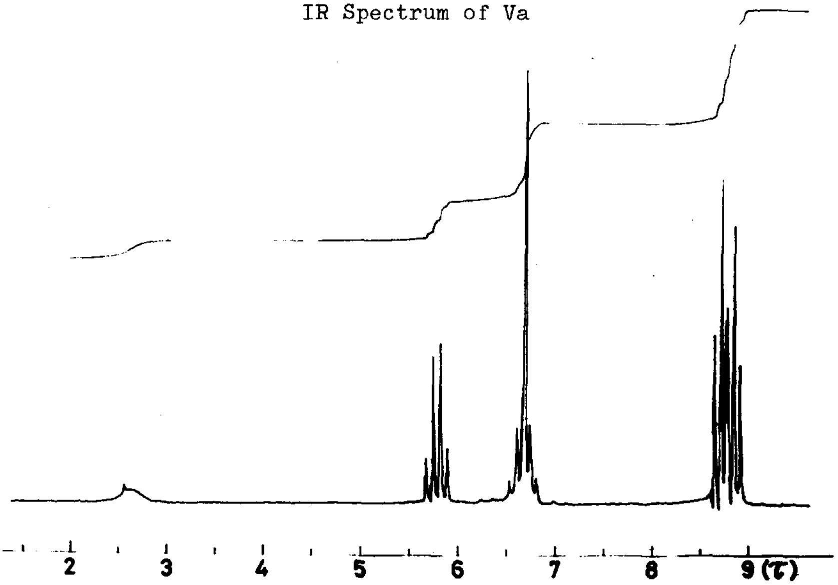
In a previous communication,$^{1)}$ we have reported that reaction of ethyl α,β-unsaturated α-nitrocarboxylates with triethyl phosphite afforded ethyl β-diethoxyphosphinyl-α,β-unsaturated-carboxylates via unstable five-membered intermediates, 4-alkyl-3-ethoxycarbonyl-1,2,5-oxazaphospholine-2-oxides.

Here, we found that the reaction of ethyl α,β-unsaturated β-nitrocarboxylates (I)$^{2)}$ with triethyl phosphite afforded a mixture of 3-alkyl-4-ethoxycarbonyl-1,2,5-oxazaphospholine-2-oxides (VII) and the 2-hydroxy isomers (VIII) in a stable state, together with 2-alkyl-3-ethoxycarbonyl-1-hydroxyaziridines (V), a new class compound. As a similar reaction, the formation of azirine and 1,2,5-oxazaphospholine derivatives by the reaction of phosphorane with nitrile oxide or nitrone$^{3,4)}$ is known.

A solution of I (0.058 mole) and triethyl phosphite (0.116 mole) in dry tetrahydrofuran (40 ml) was refluxed for 1 hr, and subsequently distilled to give two fractions. The absorption pattern and the boiling point (58-65°C/3mmHg) of the lower-boiling product was essentially identical with that of triethyl phosphate, except a sharp strong band at 2050 cm^{-1}, supposed to be attributable to $-\overset{|}{C}=\underset{+}{N}=O$ function (IV). It was found that the band gradually disappeared for a week, but didn't in a dark room. Irradiation of a solution of the product in cyclohexane at room temperature by an external low-pressure mercury lamp until the band had disappeared for a day, and fractional distillation of the resultant solution gave triethyl phsphate and V even in the absence of hydrogen donor.[5)] Va and Vb showed N-OH band at 3280 and characteristic band of aziridine ring at 3050 and <u>ca</u> 1650 cm^{-1} in IR spectra and a broad singlet at τ 2.68 (-OH), ring protons as a singlet at τ 6.70 (2H) and r-methylene protons as quintet (Va, τ



IR Spectrum of Va

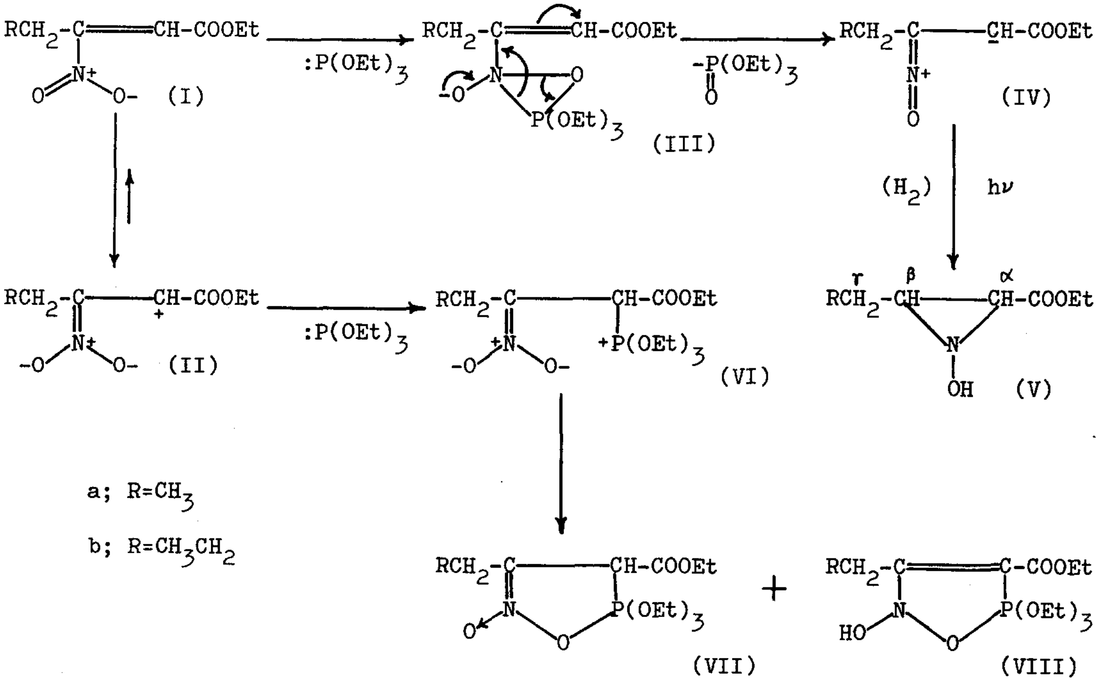


NMR Spectrum of Va

6.65) or quartet (Vb, τ 6.78) in NMR spectra, respectively. Other possible structures, the corresponding β-oximino esters and its cyclization product, isoxazolones were excluded from the above spectral data.

On the other hand, the IR spectrum of the higher-boiling product (VII and VIII) showed N-OH band at 3270, C=N at 1660 and C=C at 1590 cm^{-1}; the NMR spectrum showed a characteristic signals of a doublet at τ 4.82 (J_{P-CH} = 15.0 Hz) and two broad peaks at τ ca 1.55 and 2.00 (N-OH). The P^{31} signals appeared at ca +208 and +215 ppm ($CDCl_3$, 85 % phosphoric acid as external standard), indicating the presence of two chemical species of quinqecovalent phosphorous compounds. If the phosphonium betaines (VI) were present, then large negative chemical shifts should be observed.[3)] The ratio of VII and VIII in mixture was determined from the intensity of H-4, O$\underline{H}$-2 and that of two species in P^{31}(Table).

From the results it is supposed that the β-nitroolefin (I) exists pre nantly in aci-form (II) in the presence of triethyl phosphite, and then the phosphite reacted nucleophilically to α-position of II and cyclized to afforded VII



and VIII On the other hand, the phosphite attacked to nitro-form (I) to give IV *via* three-membered cyclic intermediate (III).[6)]

Table. The Physical Constants, Yields, IR and NMR Spectra of V, VII and VIII[a)]

Compound	Bp $^{\circ}$C/10^{-1}mmHg	Yield (%)	IR cm^{-1} in NaCl	NMR[c)], in $CDCl_3$ N-OH	α-H	β-H	r-H	P^{31} ppm
Va	80-81/3[b)]	18	3280, 3050, 1740, 1650	2.67		6.55-6.90		
Vb	85-86/2.5	12	3280, 3050, 1740, 1655	2.68		6.55-6.95		
VIIa	98-100/0.05	36	3270, 1740, 1660, 1590		4.82			208.0
VIIIa				1.68-2.00				214.9
VIIb	125-129/0.8	32	3270, 1740, 1660, 1590		4.82			207.9
VIIIb				1.55-1.90				214.8

a) All products were characterized by elementary and spectroscopic analyses. Ratio of VIIa and VIIIa is 1:1, and that of VIIb and VIIIb is 1:2.

b) Mp. 35-36°C, colorless needles from ethyl ether.

c) 100 Mc., τ -value.

References

1) C. Shin, Y. Yonezawa, and J. Yoshimura, *Bull. Chem. Soc. Japan*, **44**, 3488 (1971).

2) C. Shin, Y. Yonezawa, H. Narukawa, K. Nanjo, and J. Yoshimura, *ibid*., in press.

3) a) R. Huisgen and J. Wulff, *Tetrahedron Lett*., **1967**, 917. b) J. Wulff and R. Huisgen, *Angew. Chem*., **79**, 472 (1967).

4) a) H. J. Bestmann and R. Kunstmann, *Angew. Chem*., **78**, 1059 (1966); b) *Chem. Ber*., 102, 1816 (1969).

5) R. J. Sundberg and T. Yamazaki, *J. Org. Chem*., **32**, 290 (1967).

6) T. Nishiwaki and T. Saito, *J. Chem. Soc* , **1971**, 3021.