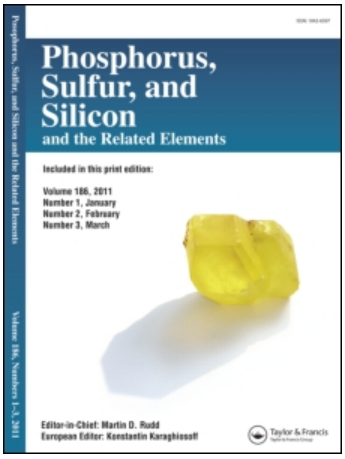

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SYNTHESIS AND STEREOCHEMISTRY OF α-ARYL-β-NITROALKYLPHOSPHINATES

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SYNTHESIS AND STEREOCHEMISTRY OF α-ARYL-β-NITROALKYLPHOSPHINATES

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An one-pot reaction of O-alkyl arylphosphonites **1** with α-aryl-β-nitroalkenes(β-nitrostyrenes) **2** in the presence of trimethylsilylchloride and triethylamine was studied. Twenty-three new α-aryl-β-nitroalkylphosphinates **3a–y** were synthesized in high yield under very mild condition. Compounds **3** consist of two pairs of diastereomeric isomers (A) and (B). The racemic pair (A) was separated by recrystallization and its structure was determined by X-ray diffraction on single crystal.

Key words: α-aryl-β-nitroalkenes; O-alkyl arylphosphonite; phosphinate; raceme; stereochemistry; one-pot reaction.

INTRODUCTION

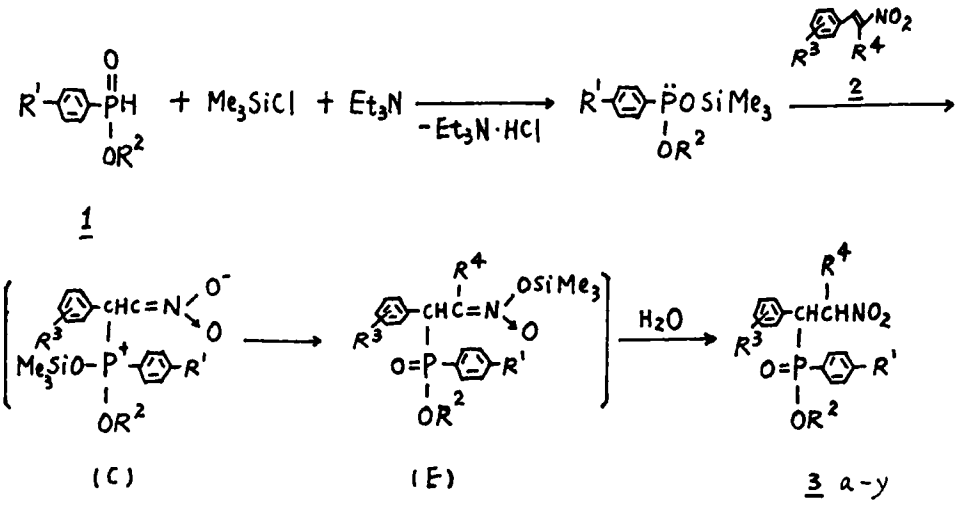
The synthesis of β-nitroalkylphosphinates has attracted attention for a long time.[1,2] In general, β-nitroalkylphosphinates were synthesized by the addition reaction of phosphites or phosphonites with derivatives of β-nitrostyrenes. However, the normal adducts (β-nitroalkylphosphinates) have hardly been obtained except a patent,[3] because the reaction is affected by many factors.[1] In the present paper, we report a very convenient method for the preparation of the title compounds **3** and their stereochemistry rarely studied before.

RESULTS AND DISCUSSION

Chemical Reactions

The one-pot reaction of O-alkyl arylphosphonites **1** with α-aryl-β-nitroalkenes **2** in DMF under excess Me_3SiCl/Et_3N gives twenty-three new compounds **3a–y** in

high yields (70–90%):



No.	R^1	R^2	R^3	R^4	No.	R^1	R^2	R^3	R^4
3a	H	Et	H	H	**3n**	H	Et	p-Me_2N	H
3b	H	Et	p-MeO	H	**3p**	H	n-Pr	p-Me_2N	H
3c	H	i-Pr	H	H	**3q**	H	i-Pr	p-Me_2N	H
3d	H	i-Pr	p-MeO	H	**3r**	H	n-Pr	H	Me
3e	H	Et	m-C_6H_5O	H	**3s**	H	n-Bu	p-MeO	H
3f	H	i-Pr	H	H	**3t**	H	i-Pr	3,4-CH_2(O–O)	H
3g	H	n-Pr	p-MeO	H	**3u**	H	Et	3,4-CH_2(O–O)	H
3h	H	i-Pr	m-C_6H_5O	H	**3v**	H	Et	H	Me
3i	H	Et	m-C_6H_5O	H	**3w**	H	n-Bu	H	Me
3j	H	Et	p-OH	H	**3x**	Me	i-Pr	3,4-CH_2(O–O)	H
3k	H	i-Pr	p-OH	H	**3y**	Me	i-Pr	p-MeO	H
3m	H	n-Pr	p-OH	H					

This one-pot reaction is very convenient. The procedure is carried out by adding nitroalkenes **2** to a solution of phosphonites **1**, Me_3SiCl and Et_3N in DMF, stirring the mixture at room temperature for several hours, then hydrolyzing the reaction mixture by adding excess of ice to afford products **3** almost without any side reaction.

1. The Michael–Arbuzov mechanism. The active nucelophiles, tricoordinate silylated phosphonites, formed initially by reacting phosphonites **1** with excess Me_3SiCl/Et_3N, attack the α-carbon of β-nitrostyrenes **2** to give dipolar form (C). (C) undergoes silyl migration to oxygen atom linking with nitrogen which possesses more electronic charge, and an Arbuzov rearrangement occurs at

TABLE I

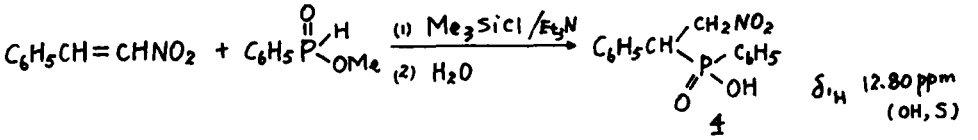
Conditions of preparation 3

Substituents \ Conditions	Mol ratio 1	2	Me_3SiCl	Et_3N	Reaction temp. (°C)	Time (h)	Solvent	Water†
R^3 = H	1.5–3.0	1	3	3	r.t.	6		
R^3 = p-OH	2–3	1	3–3.3	3	r.t.	10		
p-NMe_2							DMF	about 20 times as much as the amounts of the solution
m-C_6H_5O								
R^3 = p-MeO	2–3	1	3–3.3	3	below 5° for 0.5h then r.t.	8		
3,4-CH_2(O–)(O–)								

† For hydrolysis

phosphorus atom simultaneously[2] to form the stable intermediate (E). Hydrolysis of (E) (via elimination of silyl alcohol or disilyl ether once isolated) gives the products **3**. The whole process may be considered as a Michael-like addition accompanying an Arbuzov rearrangement at the phosphorus atom (see Figure 3).

2. Suitable reaction conditions. (1) Phosphonites **1**. It was found that phosphonites **1** should be excess (about as 1.5–3.0 times as that of nitroalkenes) in order to ensuring completion of the reaction (see Table I). α-phenyl-β-nitroethylphosphinic acid **4** is isolated when O-methyl phenylphosphonite is used to react with α-phenyl-β-nitrostyrene:



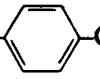
This may be due to the fact that O-methyl phosphinate is unstable in aqueous solution and the methyl group is easy to be hydrolysed or eliminated.[4]

(2) Solvents and Other Factors. We found that the reaction rate increases as the enhancement of the polarity of the solvents: DMF > THF ~ Et_2O > CH_2Cl_2 ~ C_6H_6. This fact corresponds with the mechanism proposed before, for polar solvents may stabilize the formed phosphonium intermediate. The DMF–H_2O solvent system only allows products **3** to precipitate in pure form and the other side products or unreacted reactants (such as the excess phosphonites, Me_3SiCl, Et_3N and the formed silyl alcohol etc.) still remain in the solution.

The suitable reaction temperature is at r.t. (Table I). Adding β-nitroalkenes **2** to the solution of silylated phosphonites prepared in advance (without separation) can ensure the existence of very dilute solution of β-nitroalkenes, which may prevent the occurring of self-polymerization of β-nitroalkenes. The suitable conditions for synthesis of **3** are listed in Table I.

Spectral Data

1. IR All products show two characteristic bands of nitroaliphatic compounds at the ranges of 1540–1560 (s) and 1370–1380 (m) cm^{-1}, respectively.

2. MS It was observed that almost all compounds **3** exhibit normal molecular ion peaks. Usually they have a fragment ion $PhP(O)OH^{1+}$ m/z 141 (no substituents at the benzene ring) or R^3–  –$CH{=}CH_2^{1+}$ (substituents at the benzene ring) as a base peak, the former comes from a McLafferty rearrangement and the latter from a heterolysis of P–C bond.

3. NMR All chemical shifts of ^1H corresponding to their structures are assigned well. The isopropoxy group linking directly with P atom shows a double-double peak due to the slight difference in chemical environment of the two methyl groups, this view has been confirmed by the analysis of X-ray crystal structure (see Crystal Structure on page 7).

The ^{13}C shift signals were characterized on the basis of the analysis of substituent effects, coupling constants (J_{P-C}) and the data of known analogues, the details will be reported in another article. The values of $\delta_{^{13}C}$ and J_{P-C} of compound **3n** are listed in Table II. The C^1 atom of **3n** shows a relatively long-range double peak ($^1J_{P-C}$ 96.4 Hz) due to the biggest coupling from P atom, but at the same time there is another considerable weak double peak with the same coupling constant ($^1J_{P-C}$) near to the "normal double peak" (Figure 1).

This phenomenon may be interpreted as a result of existing two pairs of

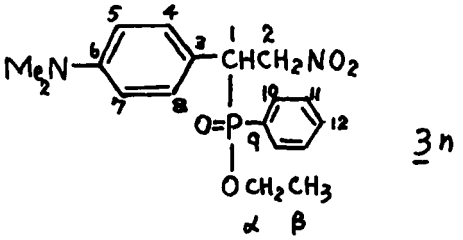
TABLE II

$\delta_{^{13}C}$ and J_{P-C} of compound **3n**

Carbon†	C^1	C^2	C^3	C^4	C^5	C^6	C^7	C^8	C^9
$\delta_{^{13}C}$ (ppm)	44.99	74.98	117.90	129.72	112.46	150.06	112.46	129.72	128.39
$^nJ_{P-C}$	^1J	^2J	^2J	^3J		^5J		^3J	^1J
(Hz)	96.4	4.8	3.6	6.1		2.4		6.1	129.4

Carbon†	C^{10}	C^{11}	C^{12}	C_α	C_β	Me_2N
$\delta_{^{13}C}$ (ppm)	132.19	128.45	132.67	61.67	16.44	40.30
$^nJ_{P-C}$	^2J	^3J	^4J	^2J	^3J	
(Hz)	5.8	8.5	4.8	6.1	6.1	

† Numbering as follows:



3n

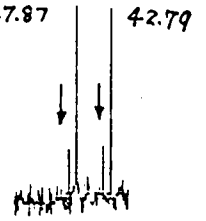


FIGURE 1 ^{13}C NMR of C^1 of **3n**.

diastereomeric (A) and (B) with different proportion (see Crystal Structure of (A) **3k** at Figure 2). In ^{31}P NMR all compounds **3** show a strong and a weak peaks at the range of 36–41 ppm which may also be interpreted as existence of two pairs of isomers (A) and (B), and there is about 2 ppm D-value ($\Delta\delta_{^{31}P}$) between (A) and (B) except **3e**. The D-value and $\delta_{^{31}P}$ of isomers (A) and (B) are listed in Table III.

TABLE III

$\delta_{^{31}P}$ and $\Delta\delta_{^{31}P}$† of compounds **3**

No.	Isomer A	Isomer B	Δδ	No.	Isomer A	Isomer B	Δδ	No.	Isomer A	Isomer B	Δδ
a	38.90	36.75	2.15	**i**	38.63	36.61	2.02	**s**	39.16	37.06	2.10
b	39.03	36.88	2.15	**j**	40.25	42.28	2.03	**t**	39.03	37.03	2.00
c	37.55	35.27	2.28	**k**	38.50	40.53	2.03	**u**	40.91	38.80	2.11
d	37.69	35.40	2.29	**m**	40.52	38.23	2.29	**v**	—	—	—
e	38.77	34.19	4.58	**n**	39.30	37.28	2.02	**w**	39.03	36.93	2.10
f	38.77	36.48	2.29	**p**	39.17	37.15	2.02	**x**	38.08	35.98	2.10
g	39.03	36.88	2.15	**q**	37.96	35.94	2.02	**y**	38.22	36.10	2.12
h	37.42	35.40	2.02	**r**	40.92	37.42	3.50				

† $\Delta\delta_{^{31}P} = \delta_{^{31}P(A)} - \delta_{^{31}P(B)}$.

Crystal Structure of Compound (A) **3k**

The colorless crystal of (A) **3k** was isolated by recrystallization from a mixed solution of compound **3k** in ethylacetate/petroleum ether (3:1). The structure was determined on an Enraf–Nonius CAD-4 diffractometer, using Mo–Kα radiation. 2176 independent reflections were measured by the $\omega/2\theta$ scan technique in the range of $2 \leq 2\theta \leq 50°$. The structure was solved by direct methods, refinement was based on full matrix least squares with anisotropic thermal parameters for non-H atoms and isotropic ones for H atoms, final $R = 0.058$, and final max. height in final difference Fourier synthesis was 0.68 e/Å^3. The parameters of the crystal cell are as follows: monoclinic, $P2_{1/c}$, $a = 11.512(1)$, $b = 9.432(1)$, $c = 16.604(2)$ Å, $\beta = 92.01(1)°$, $V = 1802.9$ Å^3, $D_c = 1.288$ g cm^{-3}. The fractional atomic coordinates and thermal parameters are listed in Table IV, bond distances and bond angles listed in Table V.

TABLE IV

Fractional atomic coordinates and thermal parameters of (A) **3k**

Atom	*X*	*Y*	*Z*	Beq. (Å × 10^3)
P(1)	0.7756(2)	0.1672(2)	0.4192(1)	3.15(3)
O(1)	0.8776(4)	0.0974(6)	0.3842(3)	4.5(1)
O(2)	0.6836(4)	0.0625(5)	0.4549(3)	3.5(1)
O(3)	0.9241(4)	0.6864(5)	0.1777(3)	4.9(1)
O(4)	0.5253(6)	0.204(1)	0.1678(4)	10.1(2)
O(5)	0.4700(5)	0.3227(8)	0.2704(5)	8.8(2)
N(1)	0.5318(5)	0.2370(9)	0.2386(4)	6.3(2)
C(1)	0.6806(5)	0.2637(8)	0.3470(4)	3.2(1)
C(2)	0.6209(6)	0.1561(8)	0.2901(4)	4.2(2)
C(3)	0.7220(7)	−0.0463(8)	0.5150(5)	4.5(2)
C(4)	0.736(1)	−0.1856(9)	0.4691(6)	8.0(3)
C(5)	0.6297(7)	−0.051(1)	0.5765(5)	7.0(2)
C(11)	0.8172(6)	0.2904(7)	0.4974(4)	3.8(2)
C(12)	0.9364(7)	0.3004(9)	0.5190(5)	5.8(2)
C(13)	0.9700(9)	0.395(1)	0.5814(6)	7.7(3)
C(14)	0.887(1)	0.4789(9)	0.6172(6)	7.8(3)
C(15)	0.769(1)	0.468(1)	0.5948(5)	7.5(3)
C(16)	0.7324(8)	0.3697(9)	0.5346(5)	5.6(2)
C(21)	0.7494(5)	0.3759(7)	0.3025(4)	3.1(1)
C(22)	0.8370(6)	0.3356(8)	0.2496(4)	3.5(1)
C(23)	0.8970(6)	0.4399(8)	0.2086(4)	3.5(2)
C(24)	0.8696(6)	0.5827(8)	0.2186(4)	3.5(2)
C(25)	0.7824(6)	0.6230(7)	0.2713(4)	3.5(2)
C(26)	0.7233(6)	0.5185(7)	0.3128(4)	3.4(2)

The perspective view of the molecular structure of (A) **3k** with numbering is shown in Figure 2. Obviously there are two chiral atoms, P(1) and C(1), in the (A) **3k**. The configuration shown in Figure 2 is R_PS_C,but since the synthesis of the compound was carried out under non-chiral condition, in fact, crystal (A) **3k** consists of two enantiomers with identical contents, R_PS_C and S_PR_C, or a pair of racemic modification. It is a tetrahedron around the P atom, but the bond angles involving P atom deviate much from the standard values (max. deviation is 10°) because of the significant differences in volume and polarity among the groups linked wth P atom. The two benzene rings are non-coparallel with a dihedral angle of 67° instead. The C(4) and C(5) atoms is isopropoxy group located slightly above the benzene ring linked with P atom, the distances between C(4), C(5) and the centre of the benzene ring are 5.72, 4.86 Å respectively, and this fact results in a measurable difference in the chemical shifts of ^{1}H NMR of the two methyl groups.

Stereochemistry of Products **3**

Gareev[5] once suggested that the reaction of phosphonites with α-alkyl-β-nitroalkenes would give two stereoisomers. As mentioned before, both ^{31}P and ^{13}C NMR of compounds **3** appear as two peaks with different intensity, and further studies indicated that the form, position and intensity of the signals of the temperature-dependent ^{1}H NMR spectrum (from 20°C to 120°C, measuring every

TABLE V

Bond distances (Å) and bond angles (°) of (A) **3k**

P(1)–O(1)	1.483(4)	C(11)–C(12)	1.409(8)
P(1)–O(2)	1.580(3)	C(11)–C(16)	1.393(9)
P(1)–C(1)	1.836(5)	C(12)–C(13)	1.409(10)
P(1)–C(11)	1.794(5)	C(13)–C(14)	1.390(12)
O(2)–C(3)	1.487(6)	C(14)–C(15)	1.405(12)
O(3)–C(24)	1.356(6)	C(15)–C(16)	1.416(10)
O(4)–N(1)	1.215(7)	C(21)–C(22)	1.413(7)
O(5)–N(1)	1.210(7)	C(21)–C(26)	1.391(7)
N(1)–C(2)	1.518(9)	C(22)–C(23)	1.394(8)
C(1)–C(2)	1.533(7)	C(23)–C(24)	1.395(7)
C(1)–C(21)	1.527(7)	C(24)–C(25)	1.407(7)
C(3)–C(4)	1.529(10)	C(25)–C(26)	1.393(7)
C(3)–C(5)	1.500(8)		
C(1)–P(1)–O(2)	114.8(2)	P(1)–C(11)–C(16)	119.7(5)
O(1)–P(1)–C(1)	115.2(3)	C(12)–C(11)–C(16)	122.8(7)
O(1)–P(1)–C(11)	112.1(3)	C(11)–C(12)–C(13)	118.0(8)
O(2)–P(1)–C(1)	99.4(2)	C(12)–C(13)–C(14)	120.0(9)
O(2)–P(1)–C(11)	107.4(2)	C(13)–C(14)–C(15)	121.3(9)
C(1)–P(1)–C(11)	106.8(3)	C(14)–C(15)–C(16)	119.5(9)
P(1)–O(2)–C(3)	119.7(3)	C(11)–C(16)–C(15)	118.2(8)
O(4)–N(1)–O(5)	125.1(8)	C(1)–C(21)–C(22)	120.5(5)
O(4)–N(1)–C(2)	115.8(8)	C(1)–C(21)–C(26)	119.6(5)
O(5)–N(1)–C(2)	119.1(7)	C(22)–C(21)–C(26)	119.9(5)
P(1)–C(1)–C(2)	108.6(4)	C(21)–C(22)–C(23)	119.5(6)
P(1)–C(1)–C(21)	110.6(3)	C(22)–C(23)–C(24)	120.4(6)
C(2)–C(1)–C(21)	113.0(5)	O(3)–C(24)–C(23)	121.7(5)
N(1)–C(2)–C(1)	107.1(5)	O(3)–C(24)–C(25)	118.0(5)
O(2)–C(3)–C(4)	107.0(5)	C(23)–C(24)–C(25)	120.3(5)
O(2)–C(3)–C(5)	106.0(5)	C(24)–C(25)–C(26)	119.2(5)
C(4)–C(3)–C(5)	113.7(7)	C(21)–C(26)–C(25)	120.8(5)
P(1)–C(11)–C(12)	117.4(5)		

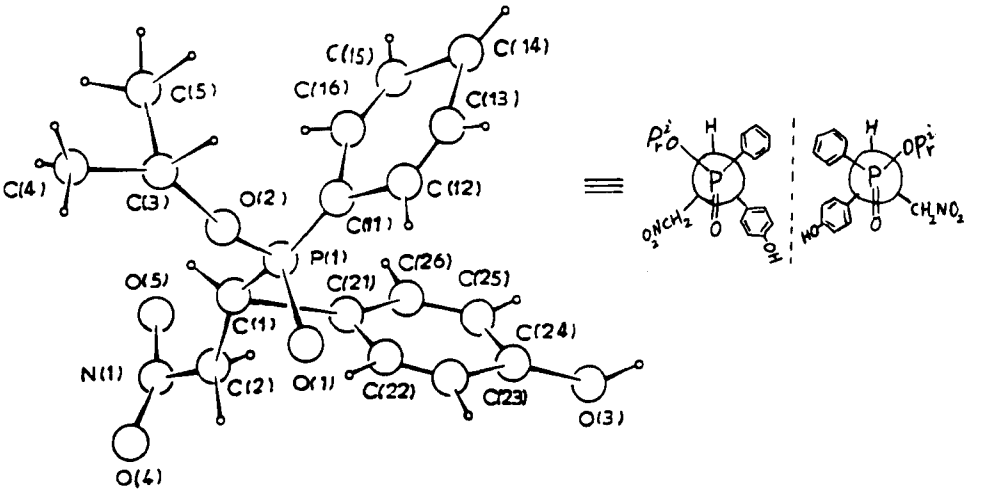


FIGURE 2 Perspective view of the molecular structure of (A) **3k** with numbering.

10°C) of **3** are constant. This fact indicates that the "abnormal" NMR signals not result from conformation factor. Theoretically there should be two pairs of diastereoisomers[4] (one pair is R_PS_C and S_PR_C, the other is R_PR_C and S_PS_C), because there are two chiral atoms, P and C, in compounds **3**. Since the synthesis is completed under non-chiral conditions, the suggestion that compound **3** may consist of two pairs of diastereomeric isomers (A) and (B) with differences in contents is reasonable. So there are two NMR peaks with different intensity resulted from the two pairs of racemic isomers. The possible mechanism for producing two pairs of diastereomeric isomers (A) and (B) is shown in Figure 3.

The pair of racemic silylated phosphonites can attack re- or si-face of nitroalkene with an equal chance in dynamics forming the two unstable racemic pairs (C) and (D) initially, following by silyl migration the two relatively stable

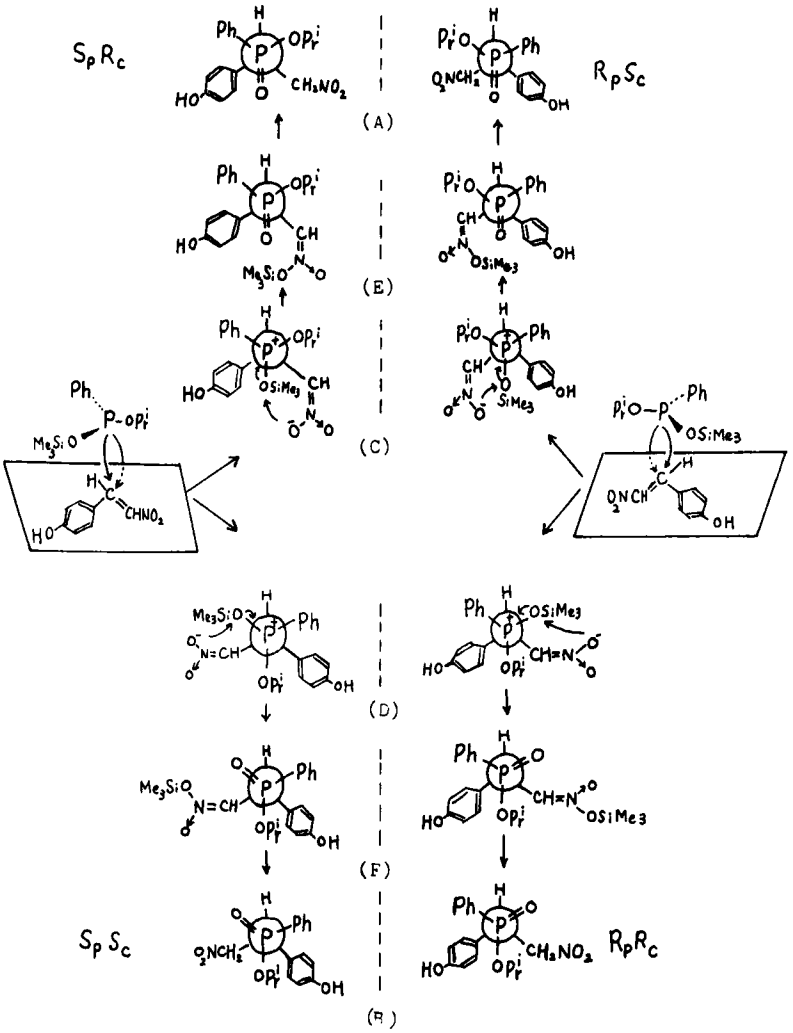


FIGURE 3 Possible mechanism for producing two pairs of diastereomeric isomers (A) and (B).

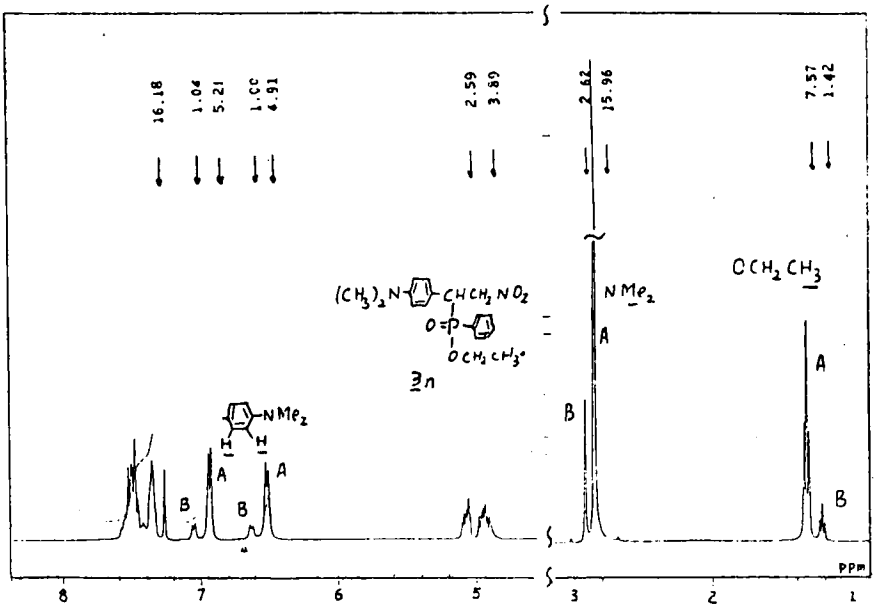


FIGURE 4 High resolution ^{1}H NMR (400 Hz) of **3n**.

pairs (E) and (F) are formed. (C) is more stable than (D) due to their difference in steric effects, so much more the racemic pair (A) is obtained finally.[6] Because of their difference in spacial connection of groups, the appearance of ^{1}H NMR of (A) differs slightly from that of (B). As shown in Figure 4, high resolution ^{1}H NMR (400 Hz) of compound **3n** gives different δ^1H for (A) and (B). The protons

TABLE VI

Contents of δ^1H NMR (400 Hz) of (A) and (B) of selected compounds **3**

No.	Content (%)	δ^1H NMR (ppm) OCHCH$_3$	OCH$_2$CH$_2$CH$_3$	R—	R— —CH (H, H)
3a	A 86	1.331–1.367(t)			
	B 14	1.192–1.227(t)			
3b	A 75			3.712(3H, s)	
	B 25			3.780(3H, s)	
3c	A	1.206–1.433(6H, dd)			
	B	1.346–1.198(6H, dd)			
3d	A 89	1.198–1.426(6H, dd)		3.713(3H, s)	6.673–7.018(4H, dd)
	B 11	1.138–1.224(6H, dd)		3.785(3H, s)	6.801–7.104(4H, dd)
3f	A 80	0.951–0.988(3H, t)	1.683–1.772(2H, m)		
	B 20		1.562–1.615(2H, m)		
3g	A 70	0.947–0.979(3H, t)	1.670–1.758(2H, m)	3.715(3H, s)	6.683–6.996(4H, dd)
	B 30	0.844–0.881(3H, t)	1.569–1.621(2H, m)	3.782(3H, s)	6.801–7.017(4H, dd)
3h	A 94	1.198–1.213(3H, dd)			
	B 6	1.139–1.154(3H, dd)			
3n	A 84 ± 1	1.305–1.344(3H, t)		2.853(6H, s)	6.495–6.966(4H, dd)
	16 ± 1	1.198–1.232(3H, t)		2.915(6H, s)	6.627–7.052(4H, dd)

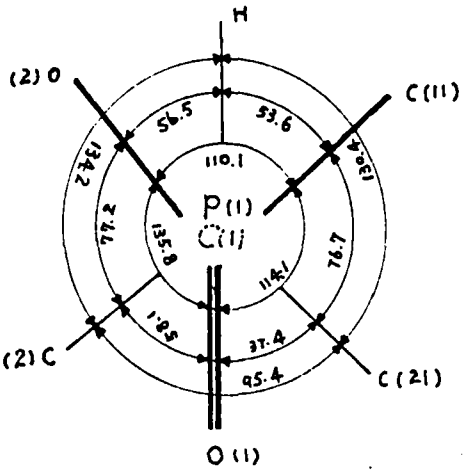


FIGURE 5 Newman's projective formula of (A) **3k**.

at methyl group in ethoxy appear at 1.308–1.344 (3H, t)ppm for (A) and 1.198–1.232 (3H, t) ppm for (B). The protons of substituent group $(CH_3)_2N$ at the benzene ring and that of para-disubstituted benzene ring Me_2N–C_6H_4– also show peaks likewise.

Contents of (A) and (B) can be calculated from the integral area (marked with ↓ in Figure 4) of high resolution ^1H NMR. Values of δ^1H and contents of (A) and (B) for part of compounds **3** are listed in Table VI. These isomers are stable and can be stored at r.t. with no decomposition, the isolation and resolution of them are expected to study further.

The torsion angles (56.5°, 53.6°, 76.7°, 37.4°, 58.1° and 77.2° respectively) of Newman's projective formula (Figure 5) of (A) **3k** (R_PS_C) have been calculated from X-ray crystal diffraction analysis, conformation of (A) **3k** can be considered as syn-clinal.

EXPERIMENTAL

Melting points were uncorrected and all compounds are colorless crystals. IR spectra were recorded on a JSCODS-301 IR spectrometer (KBr). NMR were obtained on a JEDL FX-90Q NMR spectrometer unless some ^1H NMR indicated on a JEDL-GX^{400} NMR spectrometer with TMS as internal standard (^1H, ^{13}C) or H_2PO_4 (85%) as a external standard (^{31}P) and $CDCl_3$ as solvent. MS were taken on a MAT-711 mass spectrometer. Elemental analyses were performed by the Analytical Laboratory, Institute of Elemento-Organic Chemistry, Nankai University, Tianjin, P.R. China.

O-alkyl arylphosphonites **1** were prepared from alcohol and dichloro arylphosphines[7] and α-aryl-β-nitroalkenes **2** from arylaldehydes and nitroalkanes[8] among which α-(m-phenoxy) phenyl-β-nitroethene is a new compound, yield 70%, m.p. 57–59°C, brown crystal, $\nu_{C=C}$1630 cm^{-1}(s), ν_{NO_2}1570, 1330 cm^{-1}(s), δ_{1H} 6.85–7.90 (m, 11H) ppm.

O-ethyl α-phenyl-β-nitroethyl phenylphosphinate **3a**, *typical procedure for synthesis of* **3**. To a stirred solution of O-ethyl phenylphosphonite (3.4 g, 0.02 mol) and triethyl amine (3.1 g, 0.03 mol) in dry DMF (20 ml) is added slowly (about 15 min.) a solution of trimethylchlorosilane (3.3 g, 0.03 mol) in dry DMF (5 ml) at 0°C, and stirring is continued for 15 min. at 0°C and then 1.5 h at r.t. After that, a solution of α-phenyl-β-nitroethene (β-nitrostyrene 1.5 g, 0.01 mol) in dry DMF (5 mL) is added below 20°C. The reaction is continued at r.t. for about 6–8 h until β-nitrostyrene completely disappeared (monitoring by TLC). The mixture is then poured to the surface of finely smashed ice

TABLE VII

Physical and spectral data of compound **3**

No.	Formula (M.W.)	Yield (%)	m.p. (°C)	Elemen. Anal. (%) Found (Calcd) C	H	N	P	IR ν(kBr) cm^{-1} NO_2	P-ph	P=C	P-O-(C)	^{1}H NMR δ($CDCl_3$, TMS) ppm CHRNO$_2$ P—OCH$_2$R	C$_6$H$_5$-R P—O—C—H	CHP	CHNO$_2$ C$_6$H$_5$-, P-C$_6$H$_5$		m/z (%) Base peak	M^+
3a	$C_{16}H_{18}NO_4P$ (319.29)	88	122–124	60.25 (60.18)	5.79 (5.68)	4.44 (4.39)		1540 1370	1435	1220	1025	1.33–1.36 (3H, t)	3.92–3.98 (2H, m)	4.05–4.20 (1H, m)	4.97–5.15 (2H, m)	7.08–7.56 (10H, m)	141 (100)	
3b	$C_{17}H_{20}NO_5P$ (349.32)	85	115–117	58.42 (58.45)	5.72 (5.77)	3.90 (4.00)		1545 1370	1434	1220	1020	1.31–1.41 (3H, t)	3.69 (3H, s)	3.89–4.22 (3H, m)	4.84–5.13 (2H, m)	6.64–7.56 (9H, m)	134 (100)	349.1 (8.12)
3c	$C_{17}H_{20}NO_4P$ (333.29)	95	135–136	61.63 (61.64)	6.16 (6.05)	4.09 (4.20)		1543 1370	1431	1220	980	1.15–1.44 (6H, dd)	3.96–4.26 (1H, m)	4.56–4.71 (1H, m)	4.96–5.14 (2H, m)	7.24–7.61 (10H, m)	141 (100)	
3d	$C_{18}H_{22}NO_5P$ (363.32)	90	144–146			3.46 (3.85)	8.88 (8.52)	1545 1370	1431	1220	975 995	1.15–1.44 (6H, dd)	3.66 (3H, s) 3.81–4.20 (1H, m)	4.40–4.78 (1H, m)	4.90–5.10 (2H, m)	6.61–7.63 (9H, m)	134 (100)	363.1 (8.80)
3e	$C_{22}H_{22}NO_5P$ (411.36)	91	138–140			3.30 (3.43)	7.38 (7.60)	1540 1370	1430	1220 1250	1020	1.24–1.39 (3H, t)		3.80–4.25 (3H, m)	4.93–5.10 (2H, m)	6.69–7.53 (14H, m)	141 (100)	411.2 (30.36)
3f	$C_{17}H_{20}NO_4P$ (333.31)	90	112–114	61.64 (61.26)	6.26 (6.05)	4.40 (4.20)		1550 1375	1440	1221	980	0.85–1.02 (3H, t) 1.44–1.90 (2H, m)		3.79–4.30 (3H, m)	4.88–5.15 (2H, m)	7.24–7.38 (10H, m)	141 (100)	333.2 (0.27)
3g	$C_{18}H_{22}NO_5P$ (363.32)	93	125–126			3.72 (3.85)	9.01 (8.52)	1555 1380	1440	1220	984	0.85–1.04 (3H, t) 1.50–1.84 (2H, m)	3.68 (3H, s)	3.78–4.24 (2H, m)	4.85–5.13 (2H, m)	6.63–7.60 (9H, m)	134 (100)	363.3 (14.45)
3h	$C_{23}H_{24}NO_5P$ (425.38)	92	132–133			3.31 (3.32)	6.90 (7.35)	1550 1365	1434	1220 1250	970	1.16–1.40 (6H, dd)	3.75–4.20 (1H, m)	4.40–4.70 (1H, m)	4.80–5.10 (2H, m)	6.69–7.64 (14H, m)	196 (100)	425.3 (30.26)
3i	$C_{23}H_{24}NO_5P$ (425.38)	94	124–126			3.20 (3.32)	6.99 (7.35)	1555 1375	1440	1220 1240	980	0.85–1.00 (3H, t) 1.50–1.80 (2H, m)		3.70–4.20 (3H, m)	4.84–5.10 (2H, m)	6.69–7.56 (14H, m)	196 (100)	425.3 (25.96)
3j	$C_{16}H_{18}NO_5P$ (335.28)	75	165–167	57.67 (57.31)	5.65 (5.41)	4.35 (4.18)		1560 1380	1440	1201	1020 920	1.24–1.38 (3H, t)	8.30 (1H, s)	3.70–4.30 (3H, m)	4.90–5.10 (2H, m)	6.60–7.53 (9H, m)	141 (100)	335.3 (14.04)
3k	$C_{17}H_{20}NO_5P$ (349.32)	78	187–189	58.58 (58.45)	5.84 (5.78)	3.99 (4.01)		1550 1370	1440	1190 1205	970	1.18–1.43 (6H, dd)	3.80–4.20 (1H, m)	4.40–4.76 (1H, m)	4.92–5.10 (2H, m)	6.50–7.60 (9H, m)	120 (100)	349.2 (8.78)

TABLE VII (*Continued*)

Physical and spectral data of compound **3**

No.	Formula (M.W.)	Yield (%)	m.p. (°C)	Elemen. Anal. (%) Found (Calcd) C	H	N	P	IR ν(kBr) cm^{-1} NO_2	P-ph	P=C	P-O-(C)	^{1}H NMR δ($CDCl_3$, TMS) ppm CHRNO$_2$ P—OCH$_2$R	R P—O—C—H	CHP	CHNO$_2$	, P-	*m/z* (%) Base peak	M^+
3m	$C_{17}H_{20}NO_5P$ (349.32)	76	161–163			3.61 (4.01)	8.42 (8.86)	1545 1370	1430	1195	995	0.60–1.00 (3H, t) 1.50–1.80 (2H, m)	7.70 (1H, s)	3.60–4.24 (3H, m)	4.90–5.08 (2H, m)	6.59–7.53 (9H, m)	141 (100)	349.2 (9.13)
3n	$C_{18}H_{23}N_2O_4P$ (362.35)	87	140–142	59.64 (59.66)	6.54 (6.44)	7.53 (7.73)		1554 1330	1440	1220	1026	1.20–1.34 (3H, t)	2.85 (6H, s)	3.86–4.17 (3H, m)	4.88–5.08 (2H, m)	6.50–7.53 (9H, m)	147 (100)	362.2 (26.01)
3p	$C_{19}H_{25}N_2O_4P$ (376.37)	86	138–140	60.66 (60.63)	6.80 (6.70)	7.40 (7.44)		1555 1380	1440	1222	990 1002	0.87–1.04 (3H, t) 1.55–1.90 (2H, m)	3.00 (6H, s)	3.65–4.20 (3H, m)	4.90–5.15 (2H, m)	7.10–7.60 (9H, m)	147 (100)	376.1 (22.78)
3q	$C_{19}H_{25}N_2O_4P$ (376.37)	88	159–161	60.18 (60.63)	6.71 (6.70)	7.18 (7.44)		1560 1380	1440	1220	980	1.16–1.44 (6H, dd)	2.96 (6H, s)	3.70–4.25 (3H, m)	4.85–5.10 (1H, m)	7.15–7.65 (9H, m)	147 (100)	376.2 (21.27)
3r	$C_{18}H_{22}NO_4P$ (347.33)	68	123–125	62.47 (62.24)	6.70 (6.38)	4.01 (4.03)		1560 1380	1440	1220	990	0.88–1.04 (3H, t) 1.22–1.50 (2H, m)	1.85–2.04 (3H, d)	3.60–4.10 (3H, m)	4.20–4.30 (1H, m)	7.00–7.60 (10H, m)	141 (100)	347.2 (0.75)
3s	$C_{19}H_{24}NO_5P$ (377.33)	90	121–123			3.75 (3.71)	8.72 (8.21)	1540 1375	1440	1220	1020	0.85–1.00 (3H, t) 1.20–1.80 (4H, m)	3.70 (3H, s)	3.80–4.30 (3H, m)	4.76–5.20 (2H, m)	6.64–7.60 (9H, m)	134 (100)	377 (8.0)

3t	$C_{18}H_{20}NO_6P$ (377.31)	50	145–147			3.69 (3.71)	8.61 (8.21)	1550 1375	1435	1220 1240	980	1.16–1.44 (6H, dd)	3.80–4.06 (1H, m) 5.84 (2H, s)	4.40–4.80 (1H, m)	4.88–5.08 (2H, m)	6.54–7.70 (8H, m)	148 (100)	377 (22.0)
3u	$C_{17}H_{18}NO_6P$ (363.30)	52	90–93	56.95 (56.20)	5.04 (4.99)	3.90 (3.85)		1545 1375	1438	1220 1245	1030	1.24–1.42 (3H, t)	5.88 (2H, s)	3.75–4.30 (3H, m)	4.80–5.10 (2H, m)	6.56–7.70 (8H, m)		
3v	$C_{17}H_{20}NO_4P$ (333.29)	50	93–94	61.56 (61.26)	6.17 (6.05)	4.27 (4.20)		1540 1380	1440	1210	1020	1.20–1.50 (3H, m) 1.80–2.04 (3H, dd)		3.60–4.30 (3H, m)	5.30–5.50 (1H, m)	7.16–7.50 (10H, m)	141 (100)	
3w	$C_{18}H_{22}NO_4P$ (347.32)	85	92–95	62.66 (62.24)	6.56 (6.38)	4.05 (4.03)		1545 1370	1440	1220	1020	0.80–1.00 (3H, t) 1.20–1.90 (4H, m)		3.70–4.30 (3H, m)	4.80–5.20 (2H, m)	7.00–7.60 (10H, m)	141 (100)	
3x	$C_{19}H_{22}NO_6P$ (391.32)	55	136–138	57.00 (57.30)	5.78 (5.34)	3.72 (3.70)		1545 1370	1440	1220 1245	980	1.14–1.40 (6H, dd)	2.45 (3H, s) 5.82 (2H, s) 3.76–4.12 (1H, m)	4.40–4.58 (1H, m)	4.84–5.10 (2H, m)	6.52–7.60 (7H, m)		
3y	$C_{19}H_{24}NO_5P$ (377.33)	70	124–127	60.48 (60.47)	6.60 (6.41)	3.84 (3.71)		1545 1370	1438	1220	980	1.16–1.44 (6H, dd)	2.32 (3H, s) 3.70 (3H, s) 3.80–4.10 (1H, m)	4.40–4.70 (1H, m)	4.80–5.10 (2H, m)	6.60–7.50 (8H, m)		

(about 200 g) in a glass and allowed to stand overnight, the appeared white precipitate is filtered, followed by washing with water (3 × 10 ml) and dried, then recrystallized from a mix-solvent, petroleum ether/ethyl acetate (5:1), to give a colorless crystal, **3a**, 2.8 g, yield 88%, m.p. 122–124°C.

In a similar procedure $\mathbf{3}_{b-y}$ were obtained. The physical constants and spectral data of product **3** are listed in Table VII.

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