cis- AND trans-4-AMINOCYCLOHEXYLACETIC ACIDS AND THEIR DIETHYLENIMIDO(THIO)PHOSPHORYL DERIVATIVES

K. I. Karpavichyus, A. I. Palaima, and I. L. Knunyants

UDC 542.91:541.634:547.466

The stereospecific synthesis of trans-4-aminocyclohexanecarboxylic acid, and also the preparation of the pure stereoisomeric ethyl esters of cis- and trans-4-aminocyclohexanecarboxylic acid by the hydrogenation of anesthesin on Pt–Rh catalyst, were described in [1, 2]. The insertion of N-diethylimido(thio)phosphoryl groups into the molecule of the indicated esters made it possible to create active antitumor [3] and chemosterilate [4] drugs.

In the present paper is described the preparation of the stereoisomeric 4-aminocyclohexylacetic acids (4-ACHAA) and their esters, and also the cis- and trans-N-diethylenimido-(thio)phosphoryl derivatives of 4-ACHAA. To study the PMR spectra of these derivatives we synthesized the cis- and trans-N-phthalyl-4-ACHAA and their methyl and ethyl esters, containing the AcOH moiety in either the axial or equatorial position.

In a previous paper [5] it was established that the hydrogenation of p-aminophenylacetic acid on Ru catalyst proceeds at 85-95°C to give chiefly cis-4-ACHAA, and at 130-160° in alkaline medium on Raney Ni catalyst to give chiefly trans-4-ACHAA. Analysis of the configurational isomers in the hydrogenation product of the p-nitro- or p-aminophenylacetic acid on Ru and Ni catalysts by the PMR method disclosed* that the reaction product on the Ru catalyst is a mixture of cis/trans 4-ACHAA (3:1), while on Raney Ni the ratio is 1:5.

When the hydrochlorides of cis- and trans-4-ACHAA (1:5), obtained by the hydrogenation of p-nitrophenylacetic acid on Raney Ni, were reprecipitated from aqueous acetone the hydrochloride of trans-ACHAA was isolated, which was converted to the hydrochloride of either the methyl or ethyl ester of trans-4-ACHAA. The free bases of the trans-4-ACHAA esters were obtained from the hydrochlorides by treatment with NH_3 in chloroform. The trans-4-ACHAA was synthesized by hydrolyzing the methyl or ethyl ester of trans-4-ACHAA in aqueous medium. The reprecitation of the cis/trans-4-ACHAA (3:1) from aqueous alcohol mixture (1:1) gave cis-4-ACHAA, which was converted to the methyl and ethyl esters of cis-4-ACHAA. The hydrochloride of trans-4-ACHAA was precipitated from the acidified mother liquor with acetone. When the Na salt of cis-4-ACHAA is heated in an H_2 atmosphere in the presence of Raney Ni it is isomerized to give trans-4-ACHAA; isomerization fails to occur without the catalyst.

The stereoisomeric ethyl esters of 4-ACHAA, by phosphorylation with either $POCl_3$ or $PSCl_3$ in ether in the presence of triethylamine, were converted to either the dichlorophosphoryl or dichlorothiophosphoryl ethyl esters of cis- and trans-4-ACHAA, which by reactions with ethylenimine were converted to either the N-diethylenimidophosphoryl or N-diethylenimidothiophosphoryl derivatives. The reaction of the ethyl esters of the dichlorophosphoryl- and dichlorothiophosphoryl-trans-4-ACHAA with dimethylamine gave the ethyl esters of tetramethyldiamido(thio)phosphoryl-trans-4-ACHAA. The insoluble thiophosphoryl derivatives were converted by alkaline hydrolysis to the soluble Na salts.

The properties of the obtained compounds are given in Tables 1 and 2.

EXPERIMENTAL

Hydrogenation of p-Nitrophenylacetic Acid on Raney Ni. A mixture of 18.2 g of p-nitrophenylacetic acid, 4 g of NaOH, 250 ml of water, and 7 g of Raney Ni (the Class W_6 catalyst was prepared as described in [6]) was hydrogenated in a rotated 0.5-liter autoclave for 8 h

*The configuration, as well as the qualitative and quantitative analysis of the stereoisomeric 4-ACHAA and their derivatives by the PMR method, will be reported separately.

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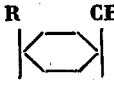
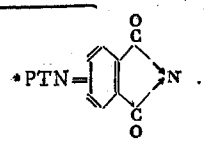
TABLE 1



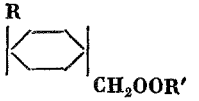
Compound	R	R′	Yield, %	mp, °C	Found, %						Empirical formula	Calculated, %					
					C	H	N	P	S	Cl		C	H	N	P	S	Cl
(I)	H_2N	H	60	287	60,86	10,23	8,66	–	–	–	$C_8H_{16}NO_2$	60,72	10,19	8,85	–	–	–
(II)	H_2N·HCl	H	60	188–190	49,55	8,57	7,22	–	–	18,38	$C_8H_{17}NO_2Cl$	49,35	8,80	7,19	–	–	18,21
(III)	H_2N·HCl	CH_3	62	138–140	51,99	8,74	6,47	–	–	17,56	$C_9H_{18}NO_2Cl$	52,04	8,73	6,74	–	–	17,07
(IV)	H_2N·HCl	C_2H_5	66	125–128	53,87	9,10	6,11	–	–	15,86	$C_{10}H_{20}NO_2Cl$	54,17	9,09	6,31	–	–	15,98
(V)	H_2N	CH_3	35	–	63,43	9,86	8,07	–	–	–	$C_9H_{17}NO_2$	63,13	10,00	8,18	–	–	–
(VI)	H_2N	C_2H_5	86	–	64,90	10,44	7,68	–	–	–	$C_{10}H_{19}NO_2$	64,83	10,34	7,56	–	–	–
(VII)	PTN *	H	95	181–182	66,74	6,04	4,61	–	–	–	$C_{16}H_{17}NO_4$	66,88	5,96	4,64	–	–	–
(VIII)	PTN	CH_3	87	94–96	67,81	6,47	4,53	–	–	–	$C_{17}H_{19}NO_4$	67,75	6,35	4,64	–	–	–
(IX)	PTN	C_2H_5	87	78–80	68,43	6,68	4,17	–	–	–	$C_{18}H_{21}NO_4$	68,55	6,71	4,44	–	–	–
(X)	$Cl_2P(O)NH$	C_2H_5	83	Oil	–	–	–	–	–	–	$C_{10}H_{18}NO_3PCl_2$	39,76	6,00	4,63	10,25	–	23,30
(XI)	$Cl_2P(S)NH$	C_2H_5	80	56–58	37,62	5,83	4,20	9,52	–	–	$C_{10}H_{18}NO_2PSCl_2$	37,74	5,70	4,40	9,73	10,07	22,39
(XII)	$[(CH_2)_2N]_2P(O)NH$	C_2H_5	60	70–72	53,14	8,49	13,21	9,18	–	–	$C_{14}H_{26}N_3O_3P$	53,33	8,30	13,32	9,82	–	–
(XIII)	$[(CH_2)_2N]_2P(S)NH$	C_2H_5	72	84–85	50,22	8,14	12,54	8,79	10,02	–	$C_{14}H_{26}N_3O_2PS$	50,75	7,90	12,68	9,34	9,67	–
(XIV)	$[(CH_2)_2N]_2P(O)NH$	Na†	80	180	46,71	6,62	13,60	9,23	–	–	$C_{12}H_{21}N_3O_3PNa$	46,61	6,84	13,58	10,02	–	–
(XV)	$[(CH_2)_2N]_2P(S)NH$	Na‡	89	210	44,07	6,70	13,05	9,42	10,41	–	$C_{12}H_{21}N_3O_2PSNa$	44,31	6,50	12,91	9,52	9,85	–



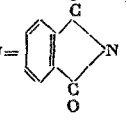
†Found Na 7.25%. Calculated: Na 7.43%.

‡Found Na 7.12%. Calculated: Na 7.06%.

TABLE 2



Compound	R	R′	Yield, %	mp, °C	Found, %						Empirical formula	Calculated, %					
					C	H	N	P	S	Cl		C	H	N	P	S	Cl
(XVI)	H_2N	H	91	310	60,47	10,06	8,74	–	–	–	$C_8H_{16}NO_2$	60,72	10,19	8,85	–	–	–
(XVII)	$H_2N \cdot HCl$	H	63	240–242	49,23	8,50	6,93	–	–	18,10	$C_8H_{17}NO_2Cl$	49,35	8,80	7,19	–	–	18,21
(XVIII)	$H_2N \cdot HCl$	CH_3	60	205–207	51,81	8,56	6,78	–	–	17,43	$C_9H_{18}NO_2Cl$	52,04	8,73	6,74	–	–	17,07
(XIX)	$H_2N \cdot HCl$	C_2H_5	61	174–176	53,84	9,18	6,07	–	–	15,60	$C_{10}H_{20}NO_2Cl$	54,17	9,09	6,31	–	–	16,98
(XX)	H_2N	CH_3	87	–	62,84	10,15	8,22	–	–	–	$C_9H_{17}NO_2$	63,13	10,00	8,18	–	–	–
(XXI)	H_2N	C_2H_5	90	–	64,88	10,12	7,30	–	–	–	$C_{10}H_{19}NO_2$	64,83	10,34	7,56	–	–	–
(XXII)	PTN *	H	95	154–156	67,03	5,71	4,56	–	–	–	$C_{16}H_{17}NO_4$	66,88	5,96	4,87	–	–	–
(XXIII)	PTN	CH_3	82	99–101	67,79	6,24	4,39	–	–	–	$C_{17}H_{19}NO_4$	67,75	6,35	4,64	–	–	–
(XXIV)	PTN	C_2H_5	78	98–100	68,25	6,97	4,05	–	–	–	$C_{18}H_{21}NO_4$	68,55	6,71	4,44	–	–	–
(XXV)	$Cl_2P(O)NH$	C_2H_5	68	59–61	39,91	6,00	4,40	9,12	–	23,34	$C_{10}H_{18}NO_3PCl_2$	39,76	6,00	4,63	10,25	–	23,50
(XXVI)	$Cl_2P(S)NH$	C_2H_5	84	115–117	38,02	5,60	4,18	9,42	–	–	$C_{10}H_{18}NO_2PSCl_2$	37,74	5,70	4,40	9,73	10,07	22,39
(XXVII)	$[(CH_2)_2N]_2P(O)NH$	C_2H_5	56	95–96	53,47	8,68	13,41	9,25	–	–	$C_{14}H_{26}N_3O_3P$	53,33	8,30	13,32	9,82	–	–
(XXVIII)	$[(CH_2)_2N]_2P(S)NH$	C_2H_5	75	87–89	50,28	7,98	12,52	8,79	–	–	$C_{14}H_{26}N_3O_2PS$	50,75	7,90	12,68	9,34	9,67	–
(XXIX)	$[(CH_2)_2N]_2P(O)NH$	Na†	81	245	46,32	7,03	13,39	10,50	–	–	$C_{12}H_{21}N_3O_3PNa$	46,61	6,84	13,58	10,02	–	–
(XXX)	$[(CH_2)_2N]_2P(S)NH$	Na‡	83	260	44,52	6,71	13,07	9,04	10,18	–	$C_{12}H_{21}N_3O_2PSNa$	44,31	6,50	12,91	9,52	9,85	–
(XXXI)	$[(CH_3)_2N]_2P(O)NH$	C_2H_5	52	116–118	52,07	9,71	13,40	8,89	–	–	$C_{14}H_{30}N_3O_3P$	52,66	9,47	13,16	9,70	–	–
(XXXII)	$[(CH_3)_2N]_2P(S)NH$	C_2H_5	65	70–72	50,27	9,00	12,61	9,07	10,06	–	$C_{14}H_{30}N_3O_2PS$	50,13	9,01	12,52	9,23	9,55	–

* PTN= 

†Found: Na 7.16%. Calculated: Na 7.43%.

‡Found: Na 6.94%. Calculated: Na 7.06%.

at 130°C and an initial H_2 pressure of 150 atm. The catalyst was filtered and the mixture was worked up by either method A or B.

A. The mixture was acidified with conc. HCl to pH 5, evaporated in vacuo to dryness, and the residue was rubbed in acetone, filtered, and dried at 100°. We obtained 21.4 g of a mixture of 4-ACHAA hydrochloride (15.6 g), with a 1:5 ratio of the cis/trans isomers, and NaCl.

B. The mixture was acidified with conc. HCl to pH 5, evaporated in vacuo to 50 ml, and 500 ml of acetone was added. The precipitate was filtered (filtrate 1) and refluxed with 500 ml of 95% ethanol. The hot solution was filtered from the NaCl. The filtrate on cooling deposited 12.3 g (63%) of (XVII). The evaporation of filtrate 1 to dryness gave 2 g of a stereoisomeric mixture of the 4-ACHAA hydrochlorides, with a 5:1 ratio of the cis/trans isomers.

Hydrochloride of Methyl Ester of trans-4-ACHAA (XVIII). The stereoisomeric mixture of 4-ACHAA hydrochlorides and NaCl (21.4 g), obtained by method A, was suspended in 200 ml of abs. methanol, saturated with dry HCl at 0°, and refluxed for 2 h. The mixture was cooled, the NaCl precipitate was filtered, and the filtrate was evaporated in vacuo. The residue was reprecipitated from ethanol solution with ether to give 12.4 g (60%) of (XVIII).

In a similar manner, the use of ethanol gave the hydrochloride of the ethyl ester of trans-4-ACHAA (XIX).

Separation of Isomeric Mixture of 4-ACHAA. The crude 4-ACHAA (100 g), obtained as described in [5], with a 3:1 ratio of the cis/trans isomers, was dissolved in 700 ml of water and treated with active charcoal (BAC). The filtrate was evaporated to 250 ml, 250 ml of 95% ethanol was added to the hot solution, and the mixture was left standing overnight. The precipitate was filtered and dried at 100° to give 40 g of cis-4-ACHAA (I). The filtrate was evaporated to dryness, and the residue (60 g) was subjected to repeated recrystallization. An additional 20 g of (I) was isolated, giving a total yield of 60 g (60%) of (I). The filtrate was used to obtain (XVII).

Hydrochloride of trans-4-ACHAA (XIII). The filtrate from the (I) separation was evaporated to 1/4 volume, acidified with conc. HCl to pH 5, and 500 ml of acetone was added. The precipitate was filtered and recrystallized from ethanol to give 24.5 g (20%) of (XVII).

Hydrochloride of cis-4-ACHAA (II). A solution of 5 g of (I) in 60 ml of 10% HCl solution was evaporated to dryness. The residue was recrystallized from acetone to give 3.5 g (57%) of (II).

Conversion of cis-4-ACHAA to trans-4-ACHAA. A mixture of 15.9 g of (I), 250 ml of 2% NaOH solution, and 7 g of Raney Ni was heated in a rotated 0.5-liter autoclave for 6 h at 130° and an initial H_2 pressure of 150 atm. Compound (XVII) was isolated by method B in 70% yield.

Methyl Ester of cis-4-ACHAA (V). A suspension of 15.9 g of (I) in 200 ml of abs. MeOH was saturated with dry HCl at 0° and then refluxed for 8 h, with the slow passage of HCl. The methanol was vacuum-distilled, and the solid residue was treated with 500 ml of a $CHCl_3$ solution of NH_3, saturated at 0°. The NH_4Cl was filtered, and the filtrate was evaporated in vacuo. Distillation gave 5.9 g of (V), bp 135-136° (10 mm), n_D^{20} 1.4715, d_4^{20} 1.0419.

The ethyl ester of cis-4-ACHAA (VI) was obtained in a similar manner, bp 125-126° (10 mm), n_D^{20} 1.4700, d_4^{20} 1.0029.

The treatment of (XVIII) and (XIX) with a $CHCl_3$ solution of NH_3 gave the methyl ester of trans-4-ACHAA (XX), bp 135-136° (12 mm), n_D^{20} 1.4745, d_4^{20} 1.0235, and the ethyl ester of trans-4-ACHAA (XXI), bp 132-134° (12 mm), n_D^{20} 1.4664, d_4^{20} 0.9971.

The hydrochlorides of the methyl and ethyl esters of cis-4-ACHAA (III) and (IV) were purified by reprecipitation from methanol or ethanol solution with abs. ether.

trans-4-ACHAA (XVI). A solution of 1.8 g of (XXI) in 20 ml of water was refluxed for 12 h, evaporated in vacuo, and the residue was reprecipitated from water solution with acetone to give 1.46 g of (XVI).

N-Phthalyl-cis-4-ACHAA (VII). A solution of 0.052 mole of phthalic anhydride and 0.05 mole of (I) or (II) in 80 ml of pyridine was refluxed for 5 h, the pyridine was vacuum-distilled on the steam bath, 11 ml of Ac_2O was added, and the mixture was refluxed for 10 min.

With stirring, the hot solution was poured into 80 ml of water. The precipitate was filtered, washed with water, and reprecipitated from ethanol solution with water to give 11.4 g of (VII).

In a similar manner, from (XVII), (XVIII), and (XIX) were respectively obtained N-phthalyl-trans-4-ACHAA (XXII), the methyl ester of N-phthalyl-trans-4-ACHAA (XXIII), and the ethyl ester of N-phthalyl-trans-4-ACHAA (XXIV).

Methyl and Ethyl Esters of cis-4-ACHAA (V) and (VI). A solution of 0.01 mole of (VII) in 40 ml of abs. methanol or abs. ethanol, saturated with dry HCl, was refluxed for 2 h, and then the solvent was distilled off. Recrystallization of the residue from aqueous alcohol respectively gave (V) and (VI).

Ethyl Ester of N-Dichlorophosphoryl-trans-4-ACHAA (XXV). With stirring, to a solution of 0.01 mole of freshly distilled $POCl_3$ in 50 ml of abs. ether at −5° was added a mixture of 0.01 mole of (XXI) and 0.01 mole of Et_3N in 60 ml of abs. ether. The mixture was stirred for another hour at 0°, for 3 h at 20°, left standing overnight at 0°, filtered, the filtrate was evaporated in vacuo, and the residue was recrystallized from abs. ether at −30° to give 2 g of (XXV).

In a similar manner we obtained the ethyl ester of N-dichlorophosphoryl-cis-4-ACHAA (X), which was isolated as the crude oil. The use of $PSCl_3$ gave the ethyl esters of N-dichlorothiophosphoryl-cis- and trans-4-ACHAA (XI) and (XXVI).

Ethyl Ester of N-Diethylenimidophosphoryl-trans-4-ACHAA (XXVII). With ice cooling and stirring, to a mixture of 0.2 mole of ethylenimine and 0.2 mole of Et_3N in 200 ml of abs. ether was added a solution of 0.1 mole of (XXV) in 400 ml of abs. ether, followed by the addition of 70 ml of CH_2Cl_2, and the mixture was left standing overnight. The $Et_3N \cdot HCl$ was filtered (27.3 g), the filtrate was evaporated in vacuo, and the residue was recrystallized from ether to give 17.6 g of (XXVII).

In a similar manner we obtained the ethyl ester of N-diethylenimidophosphoryl-cis-4-ACHAA (XII) and the ethyl esters of N-diethylenimidothiophosphoryl-cis- and trans-4-ACHAA (XIII) and (XXVIII) (from aqueous alcohol).

Ethyl Ester of N-Tetramethyldiamidophosphoryl-trans-4-ACHAA (XXXI). With stirring and ice cooling, the ether solution, obtained from 0.1 mole of $POCl_3$, 0.1 mole of (XXI), and 0.1 mole of Et_3N, was saturated with dry Me_2NH, filtered, the filtrate was evaporated in vacuo, and the residue was recrystallized twice from ether to give 16.7 g of (XXXI).

In a similar manner, by using $PSCl_3$ we obtained the ethyl ester of N-tetramethyldiamidothiophosphoryl-trans-4-ACHAA (XXXII) (from aqueous alcohol).

Na Salt of N-Diethylenimidophosphoryl-trans-4-ACHAA (XXIX). To a solution of 0.8 mole of (XXVII) in 100 ml of methanol were added 2 ml of H_2O and 80 ml of a 1 N solution of MeONa in methanol. The mixture was kept for 4 days at 20°, filtered, and evaporated in vacuo. The residue, which was dried by azeotropic distillation with abs. benzene, was rubbed in 100 ml of a 1:1 abs. ether—abs. acetone mixture to give 20 g of salt (XXIX).

We obtained the Na salts of N-diethylenimidophosphoryl-cis-4-ACHAA (XIV), and the N-diethylenimidothiophosphoryl-cis- and trans-4-ACHAA (XV) and (XXX), in a similar manner.

CONCLUSIONS

1. The stereospecific hydrogenation of p-nitrophenylacetic acid was run on Raney Ni catalyst to give chiefly the trans isomer of 4-aminocyclohexylacetic acid. The cis and trans isomers were separated as the hydrochlorides.

2. We synthesized the N-phthalyl, N-dichloro(thio)phosphoryl, N-diethylenimido(thio)-phosphoryl, and N-tetramethyldiamido(thio)phosphoryl derivatives of cis- and trans-4-aminocyclohexylacetic acid.

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REACTION OF DICHLOROPHOSPHORYLIMIDOPHOSPHORUS TRICHLORIDE WITH NUCLEOPHILIC REAGENTS

A. A. Khodak, V. A. Gilyarov, and M. I. Kabachnik

UDC 542.91:547.1'118

Dichlorophosphorylimidophosphorus trichloride ("pentachloride"), $Cl_3P{=}NP(O)Cl_2$ (I), is an intermediate for the synthesis of insecticides, oil additives, plasticizers, and corrosion inhibitors [1]. A systematic study of its chemical properties has not been made up to now. The products of replacing all of the chloride atoms by anilide [2], p-nitrophenoxyl [2], dimethylamido [3], and alkoxy [4] groups have been described. The monoalkoxy derivatives of the pentachloride were described in [6].

The reaction of pentachloride (I) with phenols, amines, and their derivatives, was studied in the present paper in order to expand the methods for the synthesis of phosphorylimidophosphorus compounds of general formula $R_3P{=}NP(O)R_2$, and also to determine the order of replacing the Cl atoms.

When (I) is heated with phenol, using a 1:1 ratio of the reactants, the monophenoxy derivative (II) is obtained in good yield:

$$\underset{(I)}{Cl_3P'{=}NP''(O)Cl_2} + C_6H_5OH \rightarrow \underset{(II)}{(C_6H_5O)Cl_4P_2NO} + HCl$$

It is possible to propose two structures for (II): $(C_6H_5O)Cl_2P{=}N{-}P(O)Cl_2$ (IIA) and $Cl_3P{=}NP(O)Cl(OC_6H_5)$ (IIB).

The IR spectral data (presence of absorption in the vicinity of 1350 and 1275 cm^{-1}, which is characteristic for the P=N and P=O groups of the conjugated P=N–P=O fragment) do not permit choosing between structures (IIA) and (IIb). The ^{31}P NMR spectrum of (II) consists of two doublets at −2.3 and −13.1 ppm (J_{PNP} = 51.3 Hz) and is in agreement with formula (IIA). The signals of the P atoms of the starting pentachloride are found in the vicinity of δP' 0.9 and δP'' − 12.5 ppm [7]. The decision in favor of structure (IIA) is also confirmed by the data of the ^{35}Cl NQR spectrum, which consits of three lines with the frequencies ν_1 26.758, ν_2 27.192, and ν_3 28.527 MHz, with the relative intensities equal to 1:1:2. The signals in the vicinity of 26.758 and 27.192 MHz are characteristic for Cl atoms on the phosphoryl P atom, while the signal at 28.527 MHz is characteristic for a Cl on an imido P atom. The average frequencies of the Cl atoms of (dichlorophosphorylimido)methyl dichlorophosphonate, $CH_3Cl_2P{=}N{-}P(O)Cl_2$, are found in the vicinity of ν_{av} 28.075 MHz for the Cl at P=N, and ν_{av} 26.343 MHz for the Cl at P=O [8].

Compound (I) reacts in a similar manner with halo-substituted phenols, but the yield of the corresponding monosubstituted derivatives is substantially lower:

$$(I) + XC_6H_4OH \rightarrow (XC_6H_4O)\,Cl_2P{=}N{-}P(O)Cl_2$$

Here X= o-, m-, p-Cl, o-, m-, p-Br, p-F. The yields, constants, and the IR and ^{31}P NMR spectral data for the obtained compounds are given in Table 1.

Compound (I) does not react with p-nitrophenol at 160°C, while the reaction mixture decomposes at a higher temperature.

The second Cl atom of pentachloride (I) can be replaced by the phenoxy group at 150–160°, and here O,O-diphenyl(N-dichlorophosphorylimido)chlorophosphate (III) is obtained in good yield, whose structure was proved via the IR and ^{31}P NMR spectral data (Table 2).

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