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CHIRAL BICYCLIC SPIROPHOSPHORANES IN AN ARBUZOV-TYPE REACTION

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Summary : The reaction of 2-hydroxy-5-nitro-benzyl halides with three chiral five-or six-membered oxaphosphacycloalkanes has been studied. In each case, a ^{31}P NMR analysis shows the formation of resonance signals in the phosphorane region but these phosphoranes are usually unstable. However both enantiomers of the 2-phenyl-1,3,2-oxazaphospholidine give chiral bicyclic spirophosphoranes which have been characterized by ^{31}P and ^{1}H NMR and high resolution mass spectroscopies.

Halo-phosphoranes have been postulated but never observed as intermediates in the reaction of tricoordinated phosphorus esters and alkyl halides (Arbuzov reaction)[1]. In a related reaction, the alkylation by a phenolic Mannich base[2], (*vide infra*), a phenoxyphosphorane was isolated[6a]. We have now found evidence for the formation of chiral bicyclic phosphoranes from Koshland reagent I (1a)[7].

The thermal condensation of the triethyl phosphite with a sterically hindered *ortho* - hydroxy-benzylamine led to a triethoxyphosphorane [6a]. Use of a cyclic tricoordinated phosphorus compound, and particularly a five-membered oxaphosphacycloalkane, instead of the triethyl phosphite could also stabilize the phosphorane intermediate in which each five-membered ring occupies one apical and one equatorial position[8]. Moreover much milder reaction conditions are expected using the very reactive hydroxybenzyl halides 1a or 1b rather than the sluggish hydroxybenzyl amines [3,9]. When the starting P^{III} compound is chiral, an enantiospecific synthesis of the spirophosphorane 3' may occur[10] (fig.1).

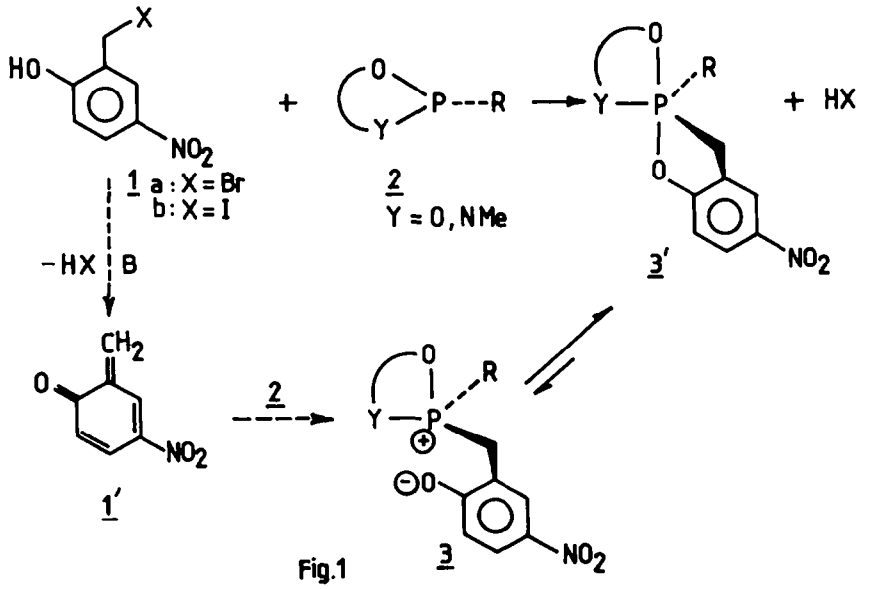


Fig.1

The first step of the reaction should be the formation of the quinone methide 1' by elimination[2,3] of HX from 1. Condensation[2,4] of 1' with the cyclic P^{III} compound 2 should lead to a phosphonium salt 3 in equilibrium with the phosphorane 3' which should be stabilized by the spiro effect[11].

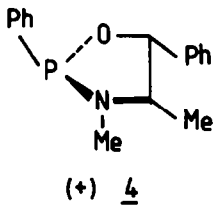
Following the classical rules[8], the most stable trigonal bipyramidal structure of the spirophosphorane should be 3'. Any pseudoration belonging to mode P1[8e], would put either the alkyl group R or the benzyl one in an unfavorable position.

Therefore the reaction of bromide 1a or the corresponding iodide 1b with the diastereomerically pure cyclic tricoordinated phosphorus compounds (+)4, (-)4, (-)9 and (-)15 has been studied. The starting P^{III} compounds have been respectively obtained from phenylphosphonous diamides and (+) or (-)-ephedrine or from phenylphosphonous dichloride and (+)-2-methyl-2,3-butanediol or (+)-chloramphenicol[12]

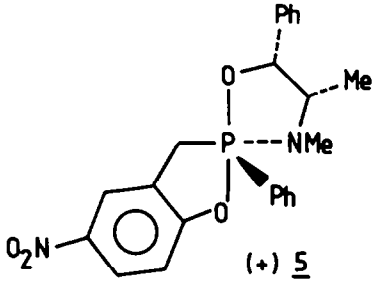
I-1,3,2-oxazaphospholidines (+)4 and (-)4:

Each enantiomer of the chiral 1,3,2-oxazaphospholidine was treated with one equivalent of the bromide 1a in toluene. The ^{31}P NMR spectra of the reaction mixtures showed two signals at -28.9 (10-20%) and -29.5 ppm (80-90%) in the region of the pentaccordinated phosphorus compounds[13,14]. The minor signal probably arises from inversion at phosphorus[15] as previously observed in the reaction of the benzyl bromide with (+)4[12a-c]. Flash chromatography on a short Florisil column gave colourless oils.

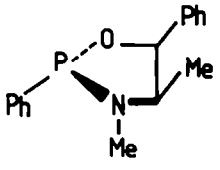
High resolution mass and ^1H NMR spectroscopies of these products supported the spirophosphorane structures (+)5 and (-)5. As for the starting compound 4[16], the absence of the ^3J (POCH) coupling constant shows that the oxazaphospholidine ring of 5 has an ^1E envelope conformation. The absolute configurations of compounds 5 shown on Fig.2 are attributed according to the absolute configuration[12] of the starting compounds 4 and to the rules[8] setting the oxygen atoms in apical positions. This attribution is supported by the shift at higher field of the signal of the 5-H of the major product[14]. This shift is probably due to the anisotropic effect of the phenyl group situated on the same side of the molecule. Moreover, optical rotations were observed for both isomers ; (+)5 was obtained from (+)4 and (-)5 from (-)4 : $[\alpha]_D^{20}$ (-)5 = -81.5° (c 1.57, CH_2Cl_2) $[\alpha]_D^{20}$ (+)5 = +81.3° (c 1.53, CH_2Cl_2).



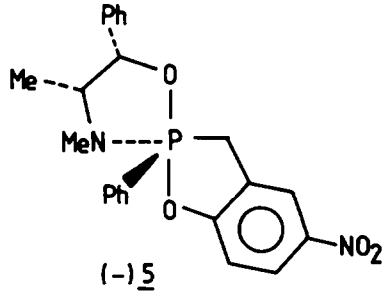
(+) 4



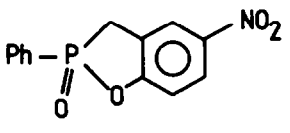
(+) 5



(-) 4



(-) 5



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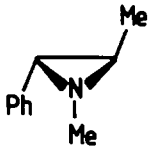

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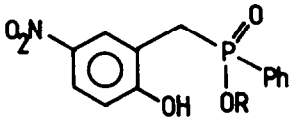


8 a: R = Et
b: R = Me

Fig. 2

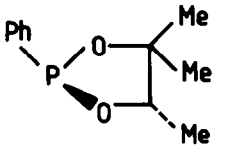
These spirophosphoranes were stable in the presence of sodium iodide. The thermolysis[11,17] of (+)5 led to a mixture of the racemic cyclic phosphinate 6[6c] and *trans*-aziridine 7[18]. The alcoholysis of crude (+)5 gave the racemic ethyl phosphinate 8a. Treatment of crude (+)5 with an excess of methyl trifluoromethylsulfonate afforded the analogous methyl phosphinate 8b.

II - 1,3,2-dioxaphospholane (-)9 :

In toluene at 25°C, a slow reaction of the bromide 1a with the dioxaphospholane (-)9 led mainly to the diastereoisomeric mixture of the phosphonates 10a and 10b ($\delta^{31}P$ = +29.1 and +28.5 ppm) formed by oxidation of (-)9.[19]

In the ^{31}P NMR spectrum of the reaction mixture, the appearance of two other signals at - 5.8 and - 7.8 ppm increased from 8 to 69 %(with a 15:85 ratio) in the presence of triethylamine in toluene or acetonitrile. These signals may be attributed[13] to the isomeric spirophosphoranes for which structures 11 and 12 are proposed. However they were unstable and could not be purified by chromatography on Florosil. Addition of sodium iodide induced the disappearance of the signals at - 5.8 and - 7.8 ppm and the formation of new signal at + 44.4 and + 41.3 ppm. Mass, ^1H and (DEPT ; off-resonance) ^{13}C NMR spectra of the products isolated by flash chromatography were in agreement with structure 13 and 14, the phosphinates formed by hydrolysis of the spirophosphoranes.[20]

The reaction of the iodide 1b was faster than that of the corresponding bromide 1a and led also to the spirophosphorane 11 and 12.



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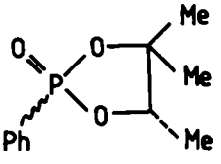
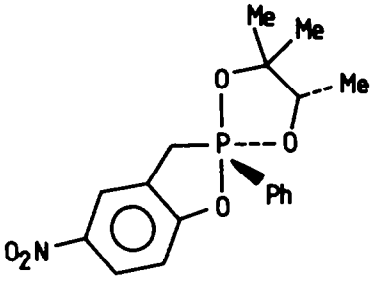


10 a,b



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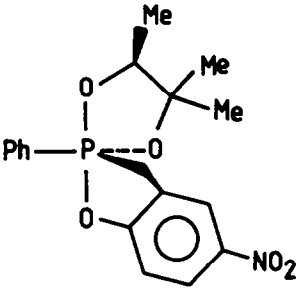

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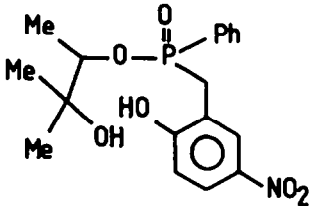

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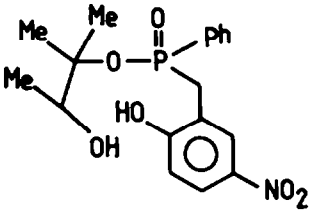

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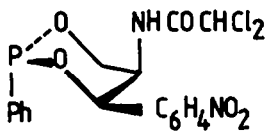
Fig. 3

III - 1,3,2-dioxaphosphorinane (-)15 :

Reactions of bromide 1a and iodide 1b with the six-membered dioxaphosphorinane (-)15 in acetonitrile were followed by ^{31}P NMR, the spectra showed the slow formation of signals in the phosphinate region : $\delta\,^{31}P$ = +42.7 (19 %), +42.2 (29 %), +41.8 (9 %), +41.4 ppm (12 %).

However these tetracoordinated phosphorus esters decomposed on silicagel and could not be purified by chromatography. After acetylation the less polar product 16 was isolated by preparative layer chromatography. This bromide probably results from the hydrolysis of the Arbuzov reaction product which is very sensitive to hydrolysis because of the assistance of the neighbouring hydroxyl group.



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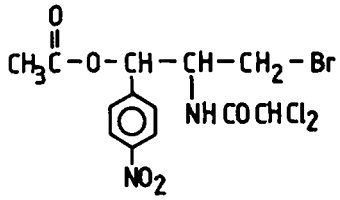

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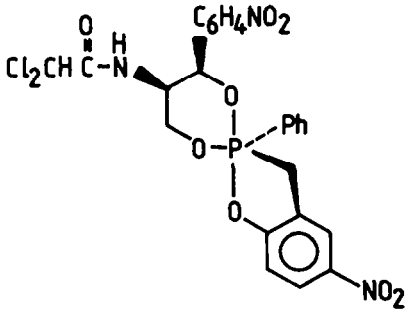

17

Fig.4

In the presence of triethylamine a signal at - 9.9 ppm (66%) was observed. However the spirophosphorane 17 was too unstable to be isolated by chromatography on silicagel or aluminium oxide. Addition of one equivalent of trifluoromethanesulfonic acid induced the disappearance of the signal at - 9.9 and the appearance of a signal in the phosphonium region at + 76.3 ppm[13] on the ^{31}P NMR spectrum.

Conclusion : The starting tricoordinated phosphorus compounds, in particular the dioxaphosphacycloalkanes (-)9 and (-)15 decompose in the presence of hydracids[12e,19]. Moreover they are oxidized readily. Therefore the condensation with *ortho* - hydroxyl-benzyl halides 1a or 1b has to be done under argon and is better achieved in the presence of an acid scavenger such as triethylamine.

For the three cyclic chiral P^{III} compounds studied, ^{31}P NMR spectroscopy[13] shows the formation of spirophosphoranes. The resonance occurs in the range - 29.5 to - 5.8 ppm depending on the structure of the starting P^{III} compounds. However these phosphoranes are not very stable. Only in the case of 5 they have been fully characterized by high resolution mass spectroscopy and ^{1}H NMR spectroscopy. Each enantiomer of the starting P^{III} compound 4 leads to a chiral spirophosphorane 5 having the same absolute optical rotation value but opposite sign of rotation.

We thank Dr. P. Savignac whose contribution was essential to the ^{31}P NMR study and the Elf Aquitaine Company for a financial support.

EXPERIMENTAL PART

Starting P^{III} compounds : The oxazaphospholidines (+) and (-)4 were purified by crystallization from toluene. The dioxaphospholane (-)9 was distilled. The dioxaphosphorinane (-)15 was obtained from (+) chloramphenicol (c 5,EtOH). The diastereoisomeric purity of all these P^{III} compounds was checked by ^{31}P NMR [12b,c].

2-hydroxy-5-nitrobenzyl iodide 1b : A solution of dry sodium iodide (0.330 g, 2.2 mmoles) in 5 ml of acetone was added dropwise to a stirred solution of bromide 1a (Fluka ; 0.465 g, 2 mmoles) in 5 ml of acetone. After 30 minutes, the solution was diluted with 30 ml of dichloromethane and filtrated. Evaporation of the filtrate yielded a pale yellow oil (0.500 g, 90 %) which crystallized in benzene (0.373 g, 67 %, m.p. 168°C, lit.[21] m.p. 169° C).

(+)-(2R, 3S) and (-)-(2S, 3R)-3,4-dimethyl-2,5-diphenyl-nitrobenzo [4,3-g]1,6-dioxa -4-aza-5-phospha (5-P^{V}) spiro [4.4] nonane (+)5 and (-)5 : A mixture of 0.232 g (1 mmole) of 2-hydroxy-5-nitrobenzyl bromide and 0.290 g (1.07 mmole) of optically pure (+)4 or (-)4 in 5 ml of dry toluene was stirred for 15 minutes under argon. Chromatography (elution with toluene or ethyl acetate/hexane) on a short Florisil column yielded 0.126 g of a colorless unstable oil (30 % yield).

^{1}H NMR ($CDCl_3$) δ = 8.3-7.4 (12, m), 6.88 (1, d, J=9), 4.96 (1, d, J=5.5), 3.8-3.35 (3, m), 3.25 (3, d, J=9), 0.81 (3,d, J=6) ppm. The integration show, that the purest sample used for the optical rotation determination contain, less than 5 % of the minor isomer[14].

^{31}P NMR ($CDCl_3$) δ = - 28.9 (10-15 %) and - 29.5 (90-85 %) ppm.

MS (EI) m/z : 423 (M+1 ,19 %), 422 (M, 8 %), 205 (20 %), 276 (55 %), 275 (73 %), 229 (49 %), 148 (45 %), 147 (56 %, 146 (70 %), 120 (20 %), 118 (27 %), 105 (38 %), 91 (28 %), 77 (100 %).

(+)5 : $[\alpha]_D^{20}$ =-81.5° (c 1.57, CH_2Cl_2)

(-)5 : $[\alpha]_D^{20}$ =+81.3° (c 1.53, CH_2Cl_2)

Anal. Calcd for $C_{23}H_{23}N_2O_4P$: 422.13955 ; Found (EI MS) : 422.13659.

Thermolysis of 5 : formation of 2-phenyl-nitrobenz [3, 4-d] 1, 2-oxaphospholane-2-oxide 6 and 1, 2-dimethyl-3-phenyl-aziridine 7 : The spirophosphorane (+) 5 was heated in a Büchi GKR (bulb to bulb) apparatus at 100°C for 1 h or at 150°C for 10 minutes under 0.05 torr, and the cyclic phosphonate 6 distilled at 240°C. During the heating, the aziridine was condensed in a dry ice/acetone bath. The ^{1}H NMR spectrum of 6 in $CDCl_3$ was identical to the one previously described (ref. 6c).

^{31}P NMR ($CDCl_3$) δ =+57.0 ppm.

7 : ^{1}H NMR ($CDCl_3$) δ = 7.35 (5, s), 2.5 (3, s), 2.0 (2, m), 1.35 (3, d) (identical to the spectrum of the *trans*-isomer in ref. 18).

O-ethyl and O-methyl (2-hydroxy-5-nitrophenyl) methyl-phenyl-phosphinate 8a and 8b : To a crude solution of spirophosphorane (+)5 prepared as previously mentioned, 0.4 ml of absolute ethanol was added. The solution was allowed to stand at room temperature for a few days. Crystalline salts of ephedrine derivatives were filtered, the filtrate evaporated and the residue recrystallized from acetone.

^{1}H NMR ($CDCl_3$) and m.p. identical to ref. 6c.

^{31}P NMR ($CDCl_3$/EtOH 10 %) δ = + 40.2 ppm.

Spirophosphorane (+)5 was prepared in 1.5 ml of dichloromethane from 0.172 g of (+)4 (0.63 mmole) and 0.147 g of 1a (0.63 mmole). One equivalent (90 µl) of triethylamine was added, the 3.4 equivalents (245 µl) of methyl triflate. The solution was stirred for 5 h, then evaporated. Purification on a silica column (elution with ethyl acetate) yielded 0.136 g of an oil (8b).

^{1}H NMR ($CDCl_3$) δ = 8.09-7.41 (7, m), 7.02 (1, d, J=9), 3.71 (3, d, J=11), 3.40 (2, m, J_{HaHb}=15, J_{HaP}=20, J_{HbP}=14).

(2S, 5S) and (2R, 5S)-2-phenyl-4, 4, 5-trimethyl-1, 3, 2-dioxaphospholane-2-oxides 10a and 10b : A mixture of 2-hydroxy-5-nitrobenzyl bromide (0.260 g, 1.12 mmoles) and (-)9 (0.210 g, 1 mmole) in 5 ml of dry toluene was stirred overnight under argon. The major products 10a and 10b (about 17 and 21 % estimated from the ^{31}P NMR spectrum) were purified by flash chromatography (ethyl acetate/cyclohexane 3 :1).

Less polar isomer : Rf = 0.31 (ethyl acetate/cyclohexane 3 :1). ^1H NMR ($CDCl_3$) δ = 7.9-7.41 (5, m), 4.38 (1, dq, J_{POCH}=1.5, J_{HCCH3}=6), 1.57 and 1.49 (6, 2s), 1.40 (3, d; J=6) ppm. ^{31}P NMR ($CDCl_3$) δ = +28.48 ppm.
Anal. Calcd for $C_{11}H_{15}O_3P$: 226.07587 ; Found (EIMS) : 226.0756.

More polar isomer : Rf = 0.22 (ethyl acetate/cyclohexane 3.1). ^1H NMR ($CDCl_3$) δ = 7.98-7.41 (5, m), 4.70 (1, dq, J_{POCH}=2, J_{HCCH3}=6.5), 1.57 (3, s), 1.38 (3, d, J=6.5), 1.31 (3, s) ppm. ^{31}P NMR ($CDCl_3$) δ =+29.1 ppm.

(3S)-5-phenyl-2,2,3-trimethyl-nitrobenzo [4, 3-g]1, 4, 6-trioxa-5 - phospha (5-P^V) spiro[4.4] nonanes 11 and 12, 0-2-(3-hydroxy-3-methyl-butyl) (2-hydroxy-5-nitro-phenyl) methyl -phenyl-phosphinate 13 and 0-2 (3-hydroxy-2-methyl-butyl) (2-hydroxy-5-nitro-phenyl) methyl-phenyl-phosphinate 14 : To one mmole of (-)9 in 5 ml of toluene or acetonitrile was added one equivalent of triethylamine, then one equivalent of 1a or 1b. The solution was stirred under argon overnight. The ^{31}P NMR spectrum of the crude solution showed two major signals (75 % estimated yield) at -5.8 (15 %) and -7.8 (85 %) ppm, and was found unchanged after four days. Although stable in solution, the phosphoranes 11 and 12 could not be purified by chromatography. Overnight reaction with 1.1 equivalent of dry sodium iodide and flash chromatography (CH_2Cl_2/MeOH 5 %) yielded a mixture of the isomeric phosphinates 13 and 14 (60 % yield).

^1H NMR ($CDCl_3$) δ = 8.0-7.5 (7, m), 6.99 and 6.97 (1, 2d, J=8), 6.4 (1.5, m), 4.27 (1, 2q), 3.80-3.22 (2, m), 1.34-1.12 (9, m) ppm.

^{31}P NMR ($CDCl_3$) δ =+41.4 and +38.4 ppm.

^{13}C NMR ($CDCl_3$) δ = 80.8 (13 C_2, J_{PC} = 7) 74.2 ppm (14 C_2)

MS (CI NH_3) m/z : 397 ($M+NH_4^+$, 36 %), 380 ($M+H^+$, 100 %), 362 (27 %).
Anal.Calcd For $C_{18}H_{22}NO_6P$: 379.11847 ; Found (EIMS) : 379.1187.

(7R,8R)-8-dichloroacetamido-7-(4-nitrophenyl)-5-phenyl-nitrobenzo [4,3 -b]1,6,10-trioxa-5-phospha (5-P^V) spiro [4.5] decane 17 : A solution of the dioxaphosphorinane (-)15 (0.215 g, 0.5 mmole) and bromide 1a (0.150 g, 0.65 mmole, 1.3 eq) in 1.5 ml of dry acetonitrile was prepared in a ^{31}P NMR tube. After 25 h the ^{31}P NMR spectrum showed several signals in the phosphinate region δ =+42.7 (19 %), +42.2 (29 %), + 41.8 (9 %), + 41.4 (12 %), + 41.0 (5 %) + 40.7 ppm (6 %) but the corresponding compounds could not be purified by chromatography.
When the same solution was prepared and 90 µl (0.65 mmole, 1.3 eq.) of triethylamine added just afterwards, the ^{31}P NMR spectrum showed an hour later, a major signal at -9.9 ppm (66 %); This signal, that stayed, for several days, disappeared upon addition of one equivalent of trifluoromethanesulfonic acid (45µl) and was replaced by a new peak at + 76.3 ppm. The latter gave in turn various peaks in the phosphinate region.

1-acetoxy-1-bromo-2-dichloroacetamido-3-(4-nitrophenyl)-propane(-)16 :Dioxaphosphorinane (-) 15 and bromide 1a were allowed to react overnight in acetonitrile as previously described. A mixture of acetic anhydride and pyridine (3 eq.) was added and the solution stirred for 2 days. The less polar product 16 was purified by thick layer chromatography. Rf 0.56 (ether/acetone 9:1).

IR (CH_2Cl_2) 3410, 1745, 1700, 1605, 1530, 1350 cm^{-1}.

^1H NMR ($CDCl_3$) δ= 8.33 (2, d, J=9), 7.68 (2, d, J=9), 6.97 (1, d, J=9), 6.25 (1, d, J=7), 5.95 (1, s), 4.65 (1, m), 3.57 (1, dd, J_1=11, J_2=5), 3.18 (1, dd, J_1=11, J_2=4), 2.17 (3, s).

$[\alpha]_D^{20}$ =-27.8° (c 3.2, $CHCl_3$).

MS (CI NH_3) m/z : 448 (29 %), 447 (28 %) ; 446 (77 %), 445 (38 %), 444 (50 %), 443 (32 %), 402 (28 %), 279 (25 %), 231 (100 %)
Anal. Calcd For $C_{13}H_{13}Cl_2N_2O_5$ (M-Br) : 347.0201 ; Found (EIMS) : 347.0199.

References and notes

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2 Owing to the strong electrondonating effect of OH and O^- substituents which stabilize an incipient benzyl cation in the transition state some *ortho*- or *para* -hydroxybenzyl compounds are very reactive and the substitution generally occurs by an elimination-addition mechanism with a quinone methide intermediate[3]. Condensations of phosphites with *ortho*- and *para* -quinone methides[4], hydroxybenzyl alcohols[5], hydroxybenzyl amines[6a,b] and hydroxybenzyl halides to give the corresponding tetracoordinated phosphorus esters have been described.

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21) Bayer and Co DRP 132475 (Beilstein Handbuch Org. Chemie 4 th Ed. VI, 368).