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Regiochemistry of Cleavage of Monosubstituted Oxiranes by Phosphorochloridites. Enantiomeric Composition of Oxiranes by ^{31}P NMR Spectral Data

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Abstract — The regioisomeric composition of the adducts of unsymmetrical oxiranes with achiral and chiral phosphorochloridites was studied. Factors allowing enantiomeric assessment of chiral oxiranes with the aid of chiral derivatizing organophosphorus reagents were revealed.

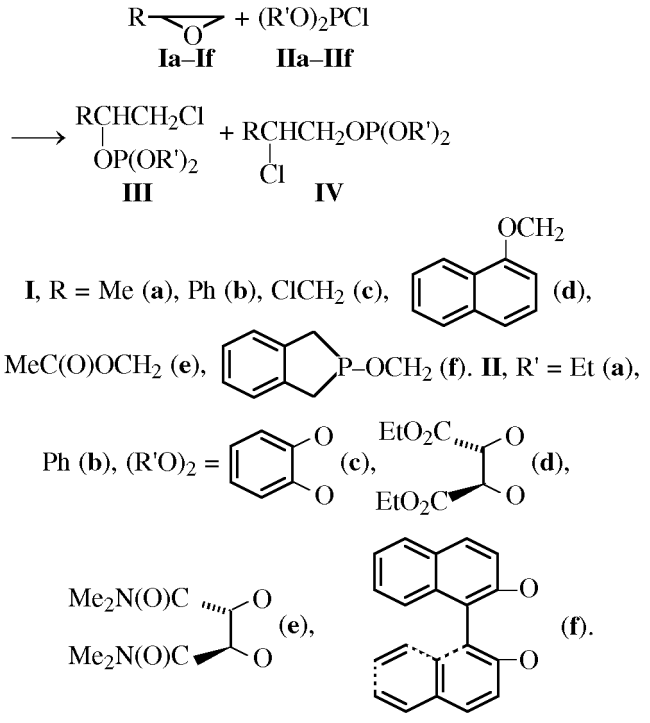
One of the most promising applications of organophosphorus compounds is their use as reagents for enantiomeric assessment of chiral organic compounds [1]. Chiral phosphorus(III) chlorides have most frequently been employed as such reagents, and active compounds with an X–H function (X = O, N, S), as substrates. Along with reactions with alcohols, amines, and thiols, P^{III} chlorides characteristically enter reactions with oxiranes [2–4], leading to β-chloroalkyl phosphites. It can be assumed that were the phosphorus component chiral, the resulting diastereomeric phosphites would have different ^{31}P NMR spectra, and these differences could be used for enantiomeric assessment of chiral epoxides. In the present work we examined this possibility. As chiral substrates we took monosubstituted oxiranes.

Additions of P^{III} monochloro derivatives can give two regioisomers. Certain aspects of the regiochemistry of such reactions have first been discussed in [5–8] as far back as 1960s. We considered it necessary to touch upon this problem.

Addition of P^{III} chlorides to monosubstituted oxiranes most frequently [3] involves epoxide ring cleavage by the C–O bond at a primary carbon atom. However, Pudovik and Faizullin [6] reported the additions of ethyl phosphorochloridite to styrene and divinyl oxides, occurring in preference to cleavage of the C–O bond at a secondary carbon atom.

The weakness of preceding works concerned with the regiochemistry of oxirane ring cleavage is that they all contain no quantitative data on the isomeric composition of the resulting products and no direct evidence for the structure of the isomers. Obereigner *et al.* [9, 10] performed quantitative GLC analysis in their studies on reactions of polychlorides (PCl_3, $PhPCl_2$, Et_2NPCl_2, etc.) with propylene oxide. However, they, too, did not directly analyze reaction mixtures. Assuming complex reaction patterns of polychlorides with oxiranes, we restricted ourselves to phosphorous ester monochlorides.

First we reacted racemic oxiranes **Ia**–**Ie** with achiral phosphorochloridites **IIa**–**IIc**.



The reactions were performed in methylene chloride with cooling. Immediately after reaction completion, the reaction mixtures were analyzed by ^{31}P NMR

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Table 1. Chemical shifts in the ^{31}P NMR spectra and relative contents [δ_P, ppm (%)] of regioisomeric phosphites **III** and **IV**, obtained by reaction of oxiranes **Ia**–**Ie** with achiral phosphorochloridites **IIa**–**IIc**

Oxirane	IIa		IIb		IIc	
	III	**IV**	**III**	**IV**	**III**	**IV**
Ia	138.55 (87)	138.28 (13)	129.18 (86)	127.16 (14)	130.06 (81)	127.31 (19)
Ib	137.91 (7)	138.01 (93)	127.14 (5)	127.27 (95)	121.25 (~0)	127.45 (~100)
Ic	139.29 (~100)	–	126.65 (76)	128.34 (24)	131.17 (97)	128.67 (3)
Id	138.51 (82)	139.29 (18)	129.33 (75)	126.64 (25)	131.47 (92)	127.09 (8)
Ie	139.11 (77)	138.44 (23)	129.02 (70)	126.85 (30)	128.69 (76)	132.08 (24)

Table 2. Chemical shifts in the ^{31}P NMR spectra, diastereomeric dispersions of chemical shifts, and relative contents of regioisomeric phosphites [δ_P, ppm, $\Delta\delta_P$, ppm (%)] obtained by reaction of chiral phosphorochloridites **IId**–**IIf** and oxiranes **Ia**–**Ie**

Oxirane	IId		IIe		IIf	
	III	**IV**	**III**	**IV**	**III**	**IV**
Ia	143.32, 143.43, 0.11 (73)	142.50, 142.64, 0.14 (27)	137.66, 138.35, 0.69 (89)	136.88, ~0 (11)	141.24, 142.58, 1.34 (80)	137.17, 137.28, 0.11 (20)
Ib	142.18, 142.52, 0.34 (3)	141.99, 142.34, 0.35 (97)	131.26, 138.00, 6.74 (3)	136.22, 136.43, 0.21 (97)	140.49, 147.08, 6.59 (~0)	137.36, 138.38, 1.02 (~100)
Ic	142.70 (94)	142.51, 0.00 (6)	138.39 (~100)	–	141.31 (~100)	–
Id	142.99, 143.10, 0.11 (93)	142.29, 142.40, 0.11 (7)	139.17, 139.69, 0.52 (78)	141.17, 0.00 (22)	144.36, 146.27, 1.91 (87)	137.75, 0.00 (13)
Ie	143.01, 143.30, 0.29 (74)	142.89, 143.25, 0.44 (26)	138.39, 138.99, 0.60 (97)	135.44, 135.52, 0.08 (3)	144.25, 144.90, 0.65 (93)	135.17, 0.00 (7)

spectroscopy. Except for the ^{31}P NMR spectra of the reaction mixtures of oxide **Ic** with phosphorochloridite **IIa** and of oxide **Ib** with phosphorochloridite **IIc**, which contain a single phosphite signal (Table 1), the other spectra contain two signals whose integral intensity ratio was used for isomeric assessment of the reaction products.

Assignment of signals to one or another regioisomer is difficult without additional evidence, since even within one series the signals of the major and minor components can trade places. The regioisomers were identified by the following procedure.

In separate experiments we reacted phosphorochloridites **IIa**–**IIc** with alcohols $RCH(OH)CH_2Cl$ (R = Me, Ph, $ClCH_2$). Thus obtained solution of phosphites **III** was added to a corresponding reaction mixture, and its ^{31}P NMR spectrum was measured again. The signal whose intensity had increased was assigned to isomer **III**. Upon addition of phosphite **III** to the reaction mixture of oxide **Ib** with 2-chloro-4,5-benzo-1,3,2-dioxaphospholane (**IIc**), we observed in the spectrum a new signal at δ_P 121.25 ppm, along with the signal at δ_P 127.45 ppm. To obtain conclusive evidence for the structure of the major isomer resulting from reactions of phosphorochloridites with oxide **Ib**, the latter was reacted with phosphorochloridite **IIc** on a preparative scale to isolate an individual reaction product. Simultaneously, from 2-chloroethanol and the same phosphorochloridite **IIc** we prepared isomer **III**. The aliphatic fragment of isomer **III** gives a triplet at δ_C 48.4 (CH_2Cl) and a doublet at δ_C 61.9 ppm (OCH) in the ^{13}C NMR spectrum. The same fragment of the styrene oxide adduct gives a doublet at δ_C 60.8 (CHCl) and a triplet at δ_C 67.8 ppm (OCH_2). These spectral data provide unambiguous evidence showing that the latter reaction product has structure **IV**.

Regioisomeric assessment of the phosphites obtained from epoxides **Id** and **Ie** was perfomed, first, by analogy with other reaction products and, second,

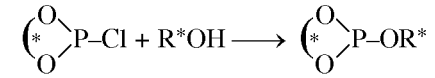
relying on the results of their reactions with chiral phosphorochloridites (see below).

As seen from Table 1, reactions of unsymmetrical epoxides with phosphorous ester monochlorides yield a mixture of two regioisomers. One of the isomers is always preferred, but its structure and relative content are strongly dependent on the nature of the reagents.

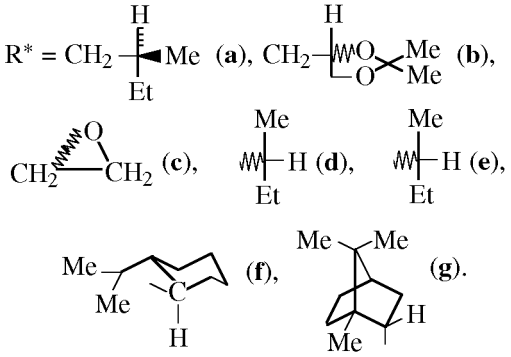
Irrespective of the mechanism of addition of phosphorus chlorides to epoxides, cleavage of the C–O bond with a terminal (primary) carbon atoms remains the initial conformation of the carbon chiral center intact, while the resulting phosphite **III** proves to be homochiral to the parent epoxide and preserves its enantiomeric composition. By contrast, the absolute configuration amd enantiomeric purity of regioisomeric phosphites **IV** depend on the mechanism of C–O bond cleavage with a central (secondary) carbon atom. Therefore, the enantiomeric composition of the alcohol fragment in phosphites **IV** is unsuitable for enantiomeric assessment of the parent epoxide. As noted above, regioisomeric phosphites **III** and **IV** are impossible to identify by their ^{31}P NMR chemical shifts. Other spectral methods, too, are hardly suitable for this purpose, because the resulting spectra are quite complex; in any case, invoking other techniques is time-consuming. Note that the adducts of phosphorochloridites with epoxides are not too stable and undergo rearrangements with time [5–8]. Staying in the framework of ^{31}P NMR, one can try to make use of chiral characteristic of regioisomers for their identification.

Regioisomers **III** and **IV** formed by reactions of chiral racemic epoxides **I** with chiral phosphorochloridites with a single chirality element (or with a group of chirality elements related by axial symmetry) each should be a mixture of diastereomers, and, therefore, the ^{31}P NMR spectrum should contain up to four signals. The difference in the chemical shifts of diastereomers ($\Delta\delta_P$) is called diastereomeric dispersion of chemical shift [1, 11]. The value of $\Delta\delta_P$ depends on the distance between chiral fragments and an indicator atom (here ^{31}P nucleus). In regioisomers **III**, the indicator atom is separated from the chirality center by two bonds, and in regioisomers **IV**, by three. Expected $\Delta\delta_P$ values for these two cases can be estimated by comparing the $\Delta\delta_P$ values of phosphites obtained from chiral phosphorus and alcohol components.

Chirality analysis by means of organophosphorus compounds is most conveniently performed with cyclic molecules whose chiral organic fragment possesses axial symmetry, since here the indicator phosphorus atom remains achiral and creates no additional problems associated with configurational changes in the course of reaction. Earlier we brought in reactions with achiral alcohols cyclic phosphorochloridites **IId**–**IIf** obtained from L-tartaric acid [12] and (*R*)-2,2'-dihydroxy-1,1'-binaphthyl [13]. Reagent **IId** was first proposed in [14].



IId–IIf **V** **VI**



As primary alcohols **V** we used (*S*)-(–)-2-methyl-1-butanol (**Va**), *rac*-4-hydroxymethyl-2,2-dimehyl-1,3-dioxalane (**Vb**), and *rac*-2,3-epoxy-1-propanol (**Vc**) and as secondary alcohols, *rac*-2-butanol (**Vd**), *rac*-1-phenylethanol (**Ve**), *l*-menthol (**Vf**), and *d*-borneol (**Vg**). Unfortunately, with enantiomerically pure phosphorochloridites **IId**–**IIf** we failed to determine $\Delta\delta_P$ for enantiomerically pure **Va**, **Vf**, and **Vg** in the cited works, which makes the selection even poorer. Therefore, here we additionally synthesized racemic phosphorochloridites from racemic tartaric acid and (*R*)-2,2'-dihydroxy-1,1'-binaphthyl. Table 3 lists the resulting $\Delta\delta_P$ values, as well as the mean $\Delta\delta_P$ values for primary and secondary alcohols reacted with each chiral phoshorus reagent.

It should be noted that $\Delta\delta_P$ depends on many factors, including solvent. According to [15], the $\Delta\delta_P$ of the adduct of methylene phosphorochloridite and *rac*-2,2'-dihydroxy-1,1'-binaphthyl in THF is 14.03 ppm. The adduct obtained in [15] is fully identical to adduct **VI** of phoshorochloridite *rac*-**IIf** and menthol **Ve**, whose $\Delta\delta_P$ in toluene is 5.54 ppm. Such a radical difference prompted us to repeat the experiment in THF. The chemical shifts of diastereomeric phosphites **VI** proved to be 149.74 and 155.22 ppm ($\Delta\delta_P$ 5.48 ppm). The respective values for the adduct of phosphite **IIf** with glycidol **Vc** in THF were found to be 136.71 and 138.59 ppm ($\Delta\delta_P$ 1.88 ppm). Both $\Delta\delta_P$ values we obtained in THF are close to those in toluene (Table 3). Thus, the $\Delta\delta_P$ values of 14.03 ppm is obviously errorneus. As a rule, solvent much less affects $\Delta\delta_P$

Table 3. Diiastereomeric dispersions of chemical shift ($\Delta\delta_P$, ppm) in the ^{31}P NMR spectra of diastereomeric phosphites obtained by reactions of primary (**Va**–**Vc**) and secondary (**Vd**–**Vg**) alcohols with chiral phosphorochloridites **IId**–**IIf**[a]

Alcohol	**IId**	**IIe**	**IIf**
Va	0.02	0.00	0.08
Vb	0.42	0.00	0.88
Vc	1.16	0.20	2.04
$\Delta\delta_{mean}$	0.53	0.07	1.00
Vd	0.25	0.81	0.06
Ve	1.05	7.84	7.07
Vf	0.08	2.60	5.54
Vg	1.09	3.32	3.02
$\Delta\delta_{mean}$	0.62	3.64	3.92

[a] For reagents **IId** and **IIe** in THF and for reagent **IIf** in toluene.

that the character of chiral environment of the indicator atom.

As seen from Table 3, the mean $\Delta\delta_P$ value for each reagent **IId**–**IIf** in the group of primary alcohols is lower than in the group of secondary alcohols. Consequently, the distance of the chiral center from the indicator atom is a factor useful for regioisomeric assessment of β-chloroalkyl phosphites **III** and **IV**. However, one should exercise caution in each case and take account of dissymmetry features of substrates. Whereas the dissymmetry degree is difficult to estimate quantitatively, it is intuitively obvious that the more similar the chemical environments of the chiral centers, the closer the quantitative manifestations of the chirality phenomenon. The $\Delta\delta_P$ values can be estimated using data in Table 3.

Table 2 lists the ^{31}P NMR data for the reaction mixtures of racemic oxiranes **Ia**–**Ie** with chiral cyclic phosphorochloridites **IId**–**IIf**. The reactions with compounds **IId** and **IIe** were performed in THF, and the reactions with compound **IIf**, in toluene. The pairs of signals of diastereomers of each regioisomer are readily identified by their close intensities. In Table 2, the regioselectivities of the reactions (percentages of isomers **III** and **IV**) are characterized by the integrated intensities of signals of both diastereomers. The regioisomeric adducts of phosphorochloridites **IId**–**IIf** with oxiranes **Ia**–**Ic** were identified in the same way as with dialkyl phosphorochloridites **IIa**–**IIc**, i.e. by addition to the mixtures of a known isomer. Identification of the adducts of epichlorohydrin (**Ic**) with chiral phosphorochloridites is facilitated by the fact that the central atom in isomers **III** loses chirality. As a result, their isomers are no longer subject to diastereomerism and give a single, nonsplit signal in the ^{31}P NMR spectrum.

As follows from Table 2, the $\Delta\delta_P$ values for the diastereomeric pairs of isomers **III** and **IV** of the adducts of oxiranes **Ia**–**Ic** with phosphorochloridites (Table 2) are either comparable for both regioisomers or, as would be expected, those for regioisomer **III** are much higher. Therefore, we can assign with assurance the signals at δ_P 144.36 and 146.27 ppm ($\Delta\delta_P$ 1.91 ppm) and the signals at δ_P 144.25 and 144.90 ppm ($\Delta\delta_P$ 0.65 ppm) in the spectra of the adducts of **IIf** with oxiranes **Id** and **Ie** to regioisomers **III**. The signals of regioisomers **IV** at δ_P 137.75 ($\Delta\delta_P$ ~0) and 135.17 ppm ($\Delta\delta_P$ ~0) are almost nonsplit. In both cases, isomer **III** with a largest $\Delta\delta_P$ value prevails. The same is true of the adducts of oxirane **Id** and phosphorochloridite **IIe** and of oxirane **Ie** and phosphorochloridite **IIe**. We suppose these fundings give sufficient grounds to state that all reactions of glycidyl ethers and esters with phosphorochloridites occur in preference to cleavage of the C–O bond with a terminal (primary) carbon atom.

Together data in Tables 1 and 2 enable us to answer most questions as to the possibility and reliability of enantiomeric assessment of chiral epoxides by means of ^{31}P NMR spectroscopy with use of chiral derivatizing organophosphorus reagents like **IId**–**IIf**. As seen from these data, the regiochemistry of phosphorochloridite addition to monosubstituted oxiranes generally follows common regularities of electrophilic additions (if, at least formally, one considers the phosphorus atom as electrophile). The overall reliability of the analysis is increased with increasing intensity of signals to be analyzed. In view of the above statement that one should take account of the characteristics of regioisomers **III** only, we are skeptical in advance of the attempts to analyze oxiranes with substituents efficiently stabilizing a neighboring cation (like Ph, CH_2=CH, etc.), since here the fraction of the required regioisomer is too small. On the contrary, strong σ- and/or π-acceptor substituents ensure preferential formation of the required regioisomer, thus giving stronger grounds for achieving success.

As seen from Table 2, the $\Delta\delta_P$ values sometimes vary in parallel with the difference in the chemical shifts of regioisomeric phosphites **III** and **IV**, which may result in overlap of signals, as, for instance, in Fig. 1a. The signals of racemic oxirans (and/or racemic phosphorochloridites) are easier to identify relying on the close intensities of signals in either diastereomeric pair. Thus, as seen from Fig. 1a, the pair of lower intensity signals with a larger $\Delta\delta_P$ relates

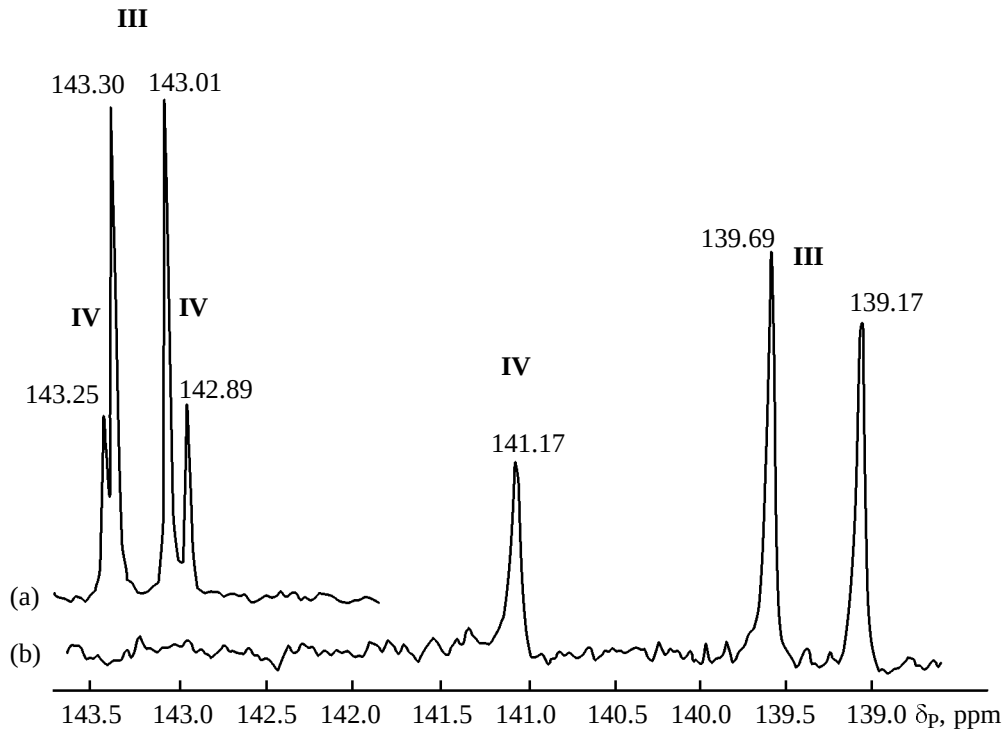
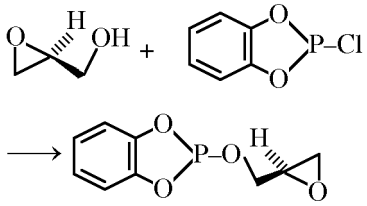


Fig. 1. ^{31}P NMR spectra of the reaction mixtures of (a) glycidyl acetate (**Ie**) and 2-chloro-(4*R*, 5*R*)-diethoxycarbonyl-1,3,2-dioxaphospholane (**IId**) and (b) glycidyl 1-naphthyl ether (**Ie**) and 2-chloro-(4*R*, 5*R*)-bis(*N*,*N*-dimethylaminocarbonyl)-1,3,2-dioxaphospholane (**IIe**).

to isomer **IV**, while the pair of strong signals relates to the major isomer **III**. When both components, oxirane and phosphorochloridite, are scalemic (i.e. enriched with one of the enantiomers or enantiomerically pure), the theoretically possible four signals will have different intensities, thus complicating interpretation. Therefore, even if the signals of regioisomers do not overlap (Fig. 1b), preliminary analysis of racemic samples makes sence, facilitating interpretation of the spectra of scalemic adducts.

Note that the difference in the δ_P values of the regioisomers of the cyclic phosphorochloridite obtained from diol **IIf** is larger than $\Delta\delta_P$. The case in point is that this $\Delta\delta_P$ value is larger in absolute value than all respective values for reagents derived from tartaric acid. Earlier [13] we revealed a pronounced diastereoselectivity of reaction of diol **IIf** with chiral alcohols. The adverse effect of the latter factor is readily bypassed by using excess phosphorochloridite, which ensures complete reaction of the substrate.

The procedure of enantiomeric assessment can be exemplified by a scalemic oxirane *o*-phenylene glycidyl phosphite (**If**). This oxirane was prepared from (*S*)-glycidol (*ee* 90.0%) and *o*-phenylene phosphorochloridite.



R-**If**

The synthesis remains the chiral center intact, and, therefore, oxirane *R*-**If** should preserve the enantiomeric composition of the parent alcohol. From a racemic starting material, a racemic glycidyl phosphite was obtained.

The spectrum of the reaction mixture of *rac*-**If** and (4*R*,5*R*)-**IId** is given in Fig. 2a. The diastereomers of the major regioisomer give signals at δ_P 143.03, 142.61 ($\Delta\delta_P$ 0.42 ppm, phosphorus atom in a chiral heterocycle) and 127.56, 127.46 ppm ($\Delta\delta_P$ 0.10 ppm, phosphorus atom in the pyrocatechol fragment). The respective signals of the minor (~12%) regioisomer are at δ_P 142.03, 141.83 ($\Delta\delta_P$ 0.20 ppm) and 130.77, 130.64 ppm ($\Delta\delta_P$ 0.13 ppm).

We showed above that glycidol ethers take up phosphorochloridites to give regioisomers **III** as

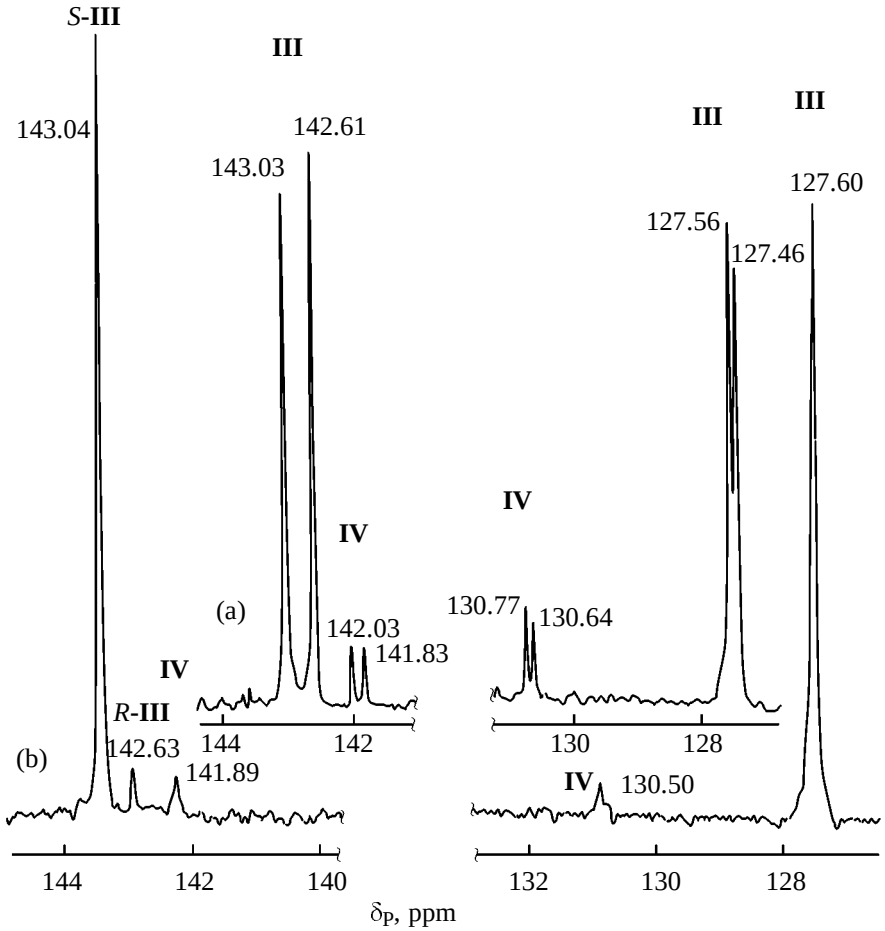


Fig. 2. ^{31}P NMR spectra of the adducts of (a) 2-chloro-(4*R*,5*R*)-diethoxycarbonyl-1,3,2-dioxaphospholane (**IId**) with *rac*-2-(2,3-epoxypropoxy)-4,5-benzo-1,2,3-dioxaphospholane (*rac*-**If**) and (b) of chlorophosholane **IId** and epoxyphospholane *R*-**If**.

major products; therefore, the stronger signals we assigned to these isomers. Further evidence for such assignment comes from the fact that the major isomer has a larger $\Delta\delta_P$ of the phosphorus atom in the chiral cycle.

The spectrum of the scalemic sample (Fig. 2b) contains only five defined peaks, since the signals of the minor diastereomers of the minor regioisomer **IV** are on the background level, while the signal of the minor diastereomer at δ_P ~127.6 ppm overlaps with the signal of the major isomer because of the small $\Delta\delta_P$ value. At the same time, the pair of downfield signals assignable to the phosphorus atom in a chiral heterocycle of diastereomeric phosphites **III** can be integrated. The relative integral intensities of these pair of signals are I_1 18.02 and I_2 1.00. From here, the enantiomeric purity of the oxirane in question can be estimated at 89.5% [*ee* = $(I_1 - I_2)/(I_1 + I_2)$].

Thus, the regiochemistry of addition of phosphorochloridites to unsymmetrical oxiranes follows general rules of electrophilic addition. In the case of chiral phosphorochloridites, the ^{31}P NMR signals of the regioisomeric phosphites resulting from these reactions can be differentiated by the regioisomeric dispersion of chemical shifts, which most frequently is larger for the isomers formed by C–O bond clevage at a primary carbon atom in the parent oxirane. The preferential formation of such regioisomers from monosubstituted epoxides makes favorable prerequisites for enantiomeric assessment of the latter by means of ^{31}P NMR spectroscopy with use of chiral derivatizing organophosphorus reagents.

EXPERIMENTAL

The NMR spectra were measured on Varian T-60 (^{1}H, 60 MHz) and Bruker MSL-400 (^{13}C, 100.6 MHz; ^{31}P, 161.92 MHz) spectrometers against internal TMS (^{1}H, ^{13}C) and external H_3PO_4 (^{31}P) in $CDCl_3$ (^{1}H, ^{13}C), CH_2Cl_2, THF, or toluene (^{31}P).

The optical rotation was measured on a Polamat A polarimeter.

Commercial chemical grade propylene oxide (**Ia**) and epichlorohydrin (**Ic**) were distilled before use.

Styrene oxide (**Ib**) was obtained from styrene according to [16], 1-naphthyl glycidyl ether (**Id**), from epichlorohydrin according to [17], and glycidyl acetate (**Ie**), from glycidyl mesylate according to [18]. 2-(2,3-Epoxypropoxy)-4,5-benzo-1,3,2-dioxaphospholane (**If**) were obtained according to [19]; compound (*R*)-**Ie**, bp 85–90°C (0.07 mm), n_D^{20} 1.5405, d_4^{20} 1.3022, $[\alpha]_D^{20}$ –2.47 (without solvent), was obtained in a similar way from (*S*)-glycidol (*ee* 90.0 %) which we obtained earlier [20].

1-Chloro-2-propanol was prepared from allyl chloride [21]. 2-Chloro-1-phenylethanol was prepared from styrene [22] and contained up to 10% of 2-chloro-2-phenylethanol. 1,3-Dichloro-2-propanol was prepared according to [23].

Reaction of oxiranes Ia–If with phosphorochloridites **IIa–IIf**. Oxirane **Ia–If**, 2 mmol, was added with shaking under dry argon at 5–10°C to a solution of 2.2 mmol of freshly distilled phosphorochloridite **Ia–Ic** in 2 ml of CH_2Cl_2 or to a solution of phosphorochloridite **Id**, **If** (prepared by the procedure in [12]) in 5 ml of THF, or to a solution of 2.2 mmol of phosphorochloridite **If** (prepared by the procedure in [13]) in 6 ml of toluene. The reaction mixture was left to stand for 30 min at room temperature and placed into an ampule for measuring its ^{31}P NMR spectrum.

Reaction of 2-chloro-4,5-benzo-1,3,2-dioxaphospholane (IIc) with styrene oxide (Ib). A solution of 1.11 g of oxide **Ib** in 4 ml of CH_2Cl_2 was added dropwise under dry argon with stirring (5°C) to a solution of 1.62 g of acid chloride **IIc** in 8 ml of CH_2Cl_2. The mixture was left to stand at room temperature for 1 h, the solvent was removed, and the residue was fractionated in a vacuum to isolate 1.7 g (62%) of 2-(2-chloro-2-phenylethoxy)-4,5-benzo-1,3,2-dioxaphospholane, bp 141–145°C (0.01 mm), n_D^{20} 1.5810. ^1H NMR spectrum, δ, ppm: 3.87 p. t (2H, $POCH_2$, $^3J_{PH}$ ~7.0, $^3J_{HH}$ ~7.0 Hz), 4.82 t (1H, CHCl, $^3J_{HH}$ 7.0 Hz), 6.83–7.08 m (4H, C_6H_4), 7.31 br.s (5H, C_6H_5). ^{13}C NMR spectrum, δ_C, ppm: 60.85 (CHCl), 67.76 (OCH_2), 112.14 (*o*-CH), 122.95 (*p*-CH), 145.48 (C_{ipso}), (C_6H_4), 127.45 (*o*-CH), 128.68 (*m*-CH), 128.86 (*p*-CH), 137.44 (C_{ipso}, Ph).

Reaction of 2-chloro-4,5-benzo-1,3,2-dioxaphospholane (IIc) with 2-chloro-1-phenylethanol. A solution of 0.67 g of acid chloride **IIc** in 2 ml of diethyl ether was slowly added under dry argon at 5°C to a mixture of 0.46 g of 2-chloro-1-phenylethanol and 0.39 g of triethylamine in 8 ml of diethyl ether. The mixture was left to stand at room temperature for ~1 h. The precipitate of triethylamine hydrochloride was filtered off, the solvent was removed, and the residue was fractionated in a vacuum to isolate 0.72 g (64%) of 2-(2-chloro-1-phenylethoxy)-4,5-benzo-1,3,2-dioxaphospholane, bp 170–171°C (0.2 mm), n_D^{20} 1.5770. ^1H NMR spectrum, δ, ppm: 3.92 d (1H, CH_2Cl, $^3J_{HH}$ 6.0 Hz), 3.95 d (1H, CH_2Cl, $^3J_{HH}$ 7.4 Hz), 5.00 d.d (1H, OCH, $^3J_{HH}$ 6.0, $^3J_{HH}$ 7.4 Hz), 7.00–7.20 m (4H, C_6H_4), 7.36 br.s (5H, Ph). ^{13}C NMR spectrum, δ_C, ppm: 48.42 (CH_2Cl), 61.87 (OCH); 113.22 (*o*-CH), 123.50 (*p*-CH), 144.21 (C_{ipso}) (C_6H_4), 127.43 (*o*-CH), 128.81 (*m*-CH), 129.14 (*p*-CH), 138.17 (C_{ipso}, Ph).

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