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Aryl-2,3-oxaphosphabicyclo[2.2.2]octene derivatives—the precursors of oxoarylphosphine oxides (aryl metaphosphonates)

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We would like to dedicate our paper in memory of Late Professor William E. McEven, distinguished chemist and founder editor of Heteroatom Chemistry

Abstract—The Baeyer–Villiger oxidation of 7-phosphanorbornene 7-oxides with sterically demanding substituents on the phosphorus atom (**4a–d**) by *m*-chloroperbenzoic acid afforded the title products (**5a–d**) as a mixture of two regioisomers (**A** and **B**). Isomer **A**, the result of thermodynamic control, was stable, while isomer **B**, the product of kinetic control, underwent decomposition and/or epoxidation. Single crystal X-ray analysis of *P*-(2,4,6-triisopropylphenyl) oxaphosphabicyclooctene (**5Ac**) was not only useful in the evaluation of its structure, but, for the first time in the literature, a low-coordinated arylmetaphosphonate (**15c**) formed by fragmentation on X-ray irradiation could also be detected. The precursors (**5Aa-c**) were utilized in the thermoinduced and UV light-mediated fragmentation-related phosphorylations of alcohols. Beside the well-known elimination-addition mechanism via the metaphosphonate intermediate (**15**), a novel addition-elimination route involving a species with a pentavalent pentacoordinated phosphorus atom (**16**) was also substantiated.

1. Introduction

The first synthesis of oxophenylphosphine oxide (phenyl metaphosphonate) Ph-PO_2 and its methyl derivatives $Me_nC_6H_{5-n}$-PO_2, (n=1–3) in the reaction of aryl phosphonic acids with aryl phosphonic dichloride was reported by Michaelis over hundred years ago.[1] Almost eighty years later it was shown that the trimers of oxoarylphosphine oxides were formed rather than monomers.[2] The intermediacy of metaphosphonate Ph-PO_2 was proposed in several reactions on the basis of the resulting oligometaphoshonates and the trapping products formed by reaction with the added nucleophiles,[3,4] as well as from kinetic experiments.[5]

Attempts to decrease the reactivity of phenyl metaphosphonate by the introduction of *t*-butyl groups in *ortho* positions of the phenyl ring were unsuccessful. Oxidation of diphosphene Ar-P=P-Ar (Ar=2,4,6-$^tBu_3C_6H_2$–) led to a polymer that was presumably $(Ar\text{-}PO_2)_n$.[6] The metaphosphonate Ar-PO_2 was formed as an intermediate during the flash vacuum pyrolysis of a cyclic phosphonite. Subsequent insertion of the PO_2 moiety into the neighboring methyl group led to a stable cyclic phosphinic acid.[7] *N*-*t*-Butyl-*P*-(2,4,6-tri-*t*-butylphenyl)phosphonamidic acid was reported to be an unstable precursor of 2,4,6-tri-*t*-butylphenylmetaphosphonate.[8]

Since 1985, the thermal or photochemical fragmentation of 2,3-oxaphosphabicyclo[2.2.2]octene ring systems has been widely used as a source of metaphosphoric (RO-PO_2) or metaphosphonic (R-PO_2) acid anhydride.[4] The intermediacy of *meta*(thio)phosphates Y-P(X)O (Y=RO, R′R′R″N; X=O, S) in the fragmentation of oxa(thia)phosphabicyclooctenes was confirmed by mechanistic studies.[9,10]

In this paper, we present the synthesis of *P*-aryl oxaphosphabicyclooctenes that are the precursors of metaphosphonates ArPO_2 with sterically demanding substituents on the phosphorus atom (Ar=2,4,6-$^iPr_3C_6H_2$, 2,4,6-$Me_3C_6H_2$, 4-MeC_6H_4).

Keywords: Phosphorus heterocycles; Baeyer–Villiger reactions; Fragmentation reactions; Metaphosphonate; Mechanisms; Phosphonylation.

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2. Results and discussion

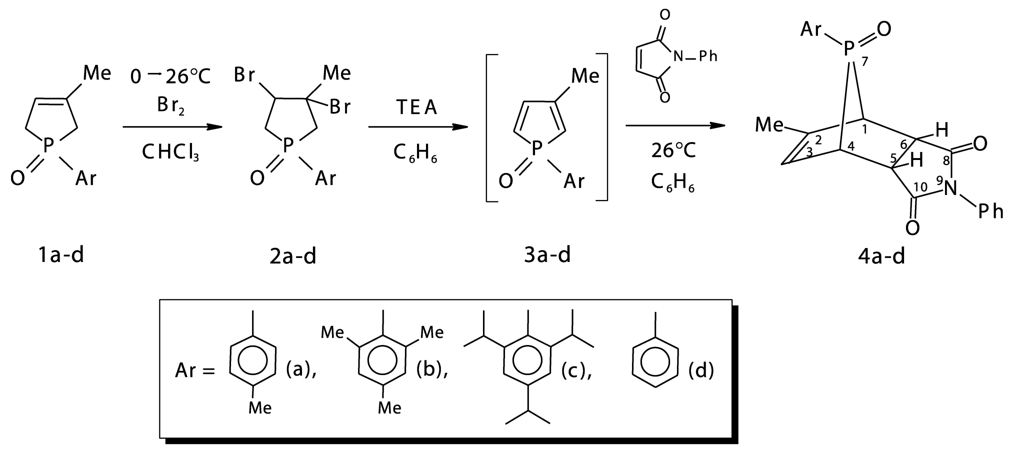
2.1. *O*-insertion into the 7-PNB framework

To investigate the effect of the P-substituent on the synthesis and fragmentation of 2,3-oxaphoshabicyclo[2.2.2]octenes, we utilized compounds **4a–c** that were prepared according to an earlier protocol (Scheme 1).[11]

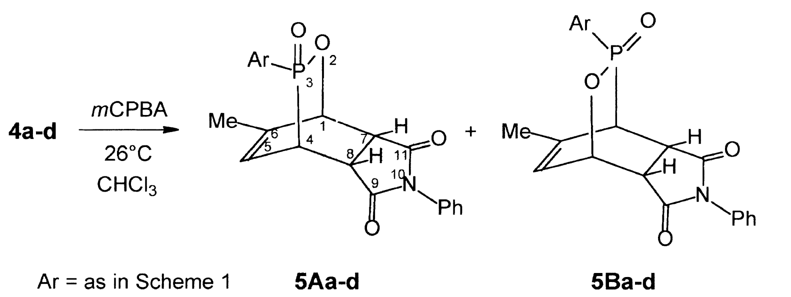
The *O*-insertion realized by *m*CPBA led to two regioisomers **5A** and **5B** (Scheme 2). Additional products were observed after a certain period of time, which depended on the substrate. As compared to phenyl derivative **4d**, the reaction was slower when electron donating 4-methylphenyl (**4a**) or bulky trialkylphenyl substituents (**4b** and **4c**) were present on the phosphorus atom. This is consistent with the associative $S_N2(P)$ or addition–elimination (AE) mechanisms. The formation of regioisomer **5A** (shifted downfield in the ^{31}P NMR spectrum at δ_P 41–37) was faster than that of **5B** (δ_P of 35–39). The ratio of regioisomers **5A** and **5B** also depended on the space requirement of the substituent and was constant up to the time shown in Scheme 2; then it was increasing. Simultaneously, new upfield signals at δ_P 20–26 appeared.

It is known from earlier work that regioisomers of type **5A** and **5B** have different stability, and usually the minor isomers were lost during the isolation procedures.[12,13] However, in the case of the *P*-ethoxy[12] and the *P*-mesitylamino[14] derivatives both regioisomers were isolated and characterized. The regioisomers could be distinguished by the ^{31}P NMR chemical shift and coupling constant between the carbon atom of the vinyl methyl group and the phosphorus atom. For the regioisomer of type **5B**, a coupling of 4–4.4 Hz with phosphorus was observed, while a value of 0–2.7 Hz was detected for regioisomers of type **5A**.[12–14] From the above data it was concluded that the isolated products of *O*-insertion into *P*-Aryl 7-PNB system were regioisomers **5Aa-d**. To prove this conclusion, the X-ray analysis of a **5Ac** crystal obtained by vapor diffusion was carried out. A sample dissolved in dichloromethane was equilibrated against hexane at 10 °C for several days. Due to the small size of the crystals obtained, a synchrotron source had to be used for data collection. Routine solution and refinement procedures[15,16] confirmed unambiguously the structure of the product from the *O*-insertion as **5Ac** (Fig. 1).

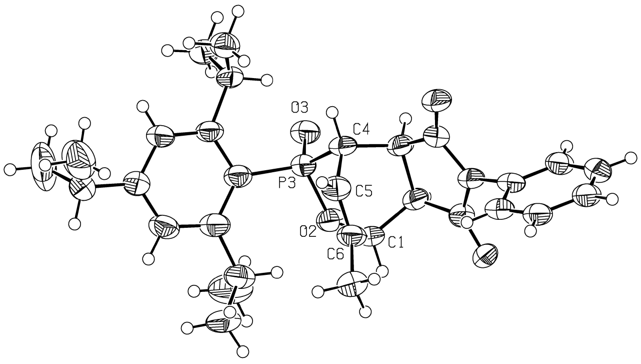
Though the geometry of **5Ac** is consistent with that of analogous derivatives[17,18] and anisotropic thermal parameters do not show any unusual features (Fig. 1), the *R* factor remained high (R_1=0.167) and several unexpected peaks (the highest one of 2.57 e A^{-3} was 1.2 Å from phosphorus) appeared on the final electron density map (Fig. 2(A)). A detailed analysis of the map suggested, however, the presence of a metaphosphonate group built of the two highest differential peaks, (Q_1 at 1.22 Å from P1 and Q_2 at 1.17 Å from O2) and the original atom O3. These two new P–O distances are 1.46 Å and the O–P–O angle is 114° (Fig. 2(B)). The three atoms Q_1, Q_2 and O3 lie in a plane parallel to that of *P*-aryl with a separation of 1.2 Å on the opposite side of the phosphonate group in



Scheme 1.



Scheme 2.



Selected bond lengths (Å)		Selected bond angles (deg)	
P3 –O2	1.608(2)	O2 –P3 –O3	109.7(2)
P3 –O3	1.476(3)	O2 –P3 –C4	98.4(2)
P3 –C4	1.853(3)	O2 –P3 –C01	109.7(2)
P3 –C01	1.816(3)	O3 –P3 –C4	117.7(2)
		O3 –P3 –C01	113.2(2)
		C4 –P3 –C01	107.1(2)

Figure 1. The view of molecular structure and selected geometric parameters of **5Ac** in solid state.

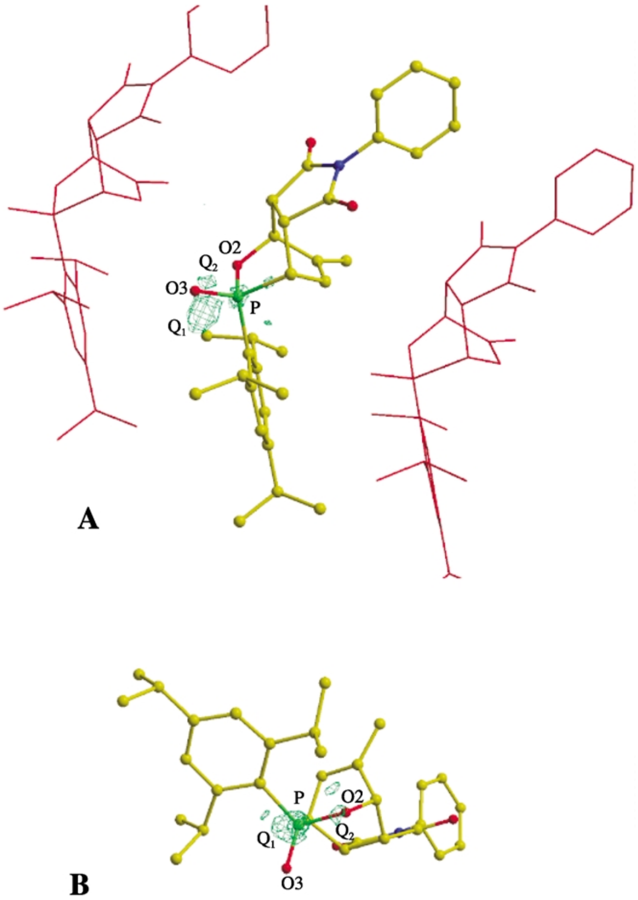


Figure 2. Residual peaks comprising metaphosphonate **15c** formed by fragmentation of **5Ac** on X-ray irradiation in the crystalline phase. (A) Viewed parallelly to the 2,4,6-triisopropylphenyl groups and showing their packing. (B) Viewed perpendicularly to the newly formed metaphosphonate moiety.

5Ac than the vinyl bridge. Hence, there is space for the planar diene system (**14**) emerging after the fragmentation (Scheme 5). It explains the shift of the *P*-aryl fragment, allowed by the loose packing in the crystal (Fig. 2(A)). The distance between the neighboring 2,4,6-isopropylphenyl groups equals 6.044 Å, that is the *b* dimension of the unit cell.

We suppose that powerful synchrotron X-rays could initiate the extrusion of metaphosphonate. Both products were observable in the same crystal by diffraction method due to their moderate amounts and fairly loose packing, which enabled the measured monocrystal to remain intact after the fragmentation. A decomposition degree of 10–15% was estimated from absolute electron densities of residual peaks corresponding to new P and O positions.

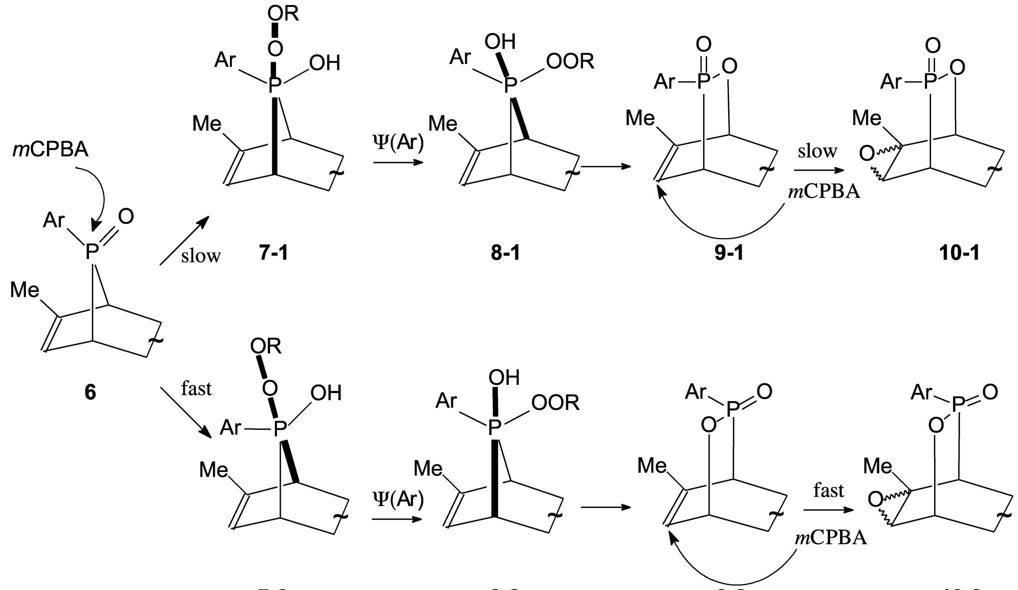
This is the first example of metaphosphonate Ar-PO_2 structure in the solid state. The X-ray structure was determined only for a more stable sulphur analogue.[19] Dithioxo(tri-*tert*-butylphenyl)phosphorane Ar-PS_2 (Ar=2,4,6-$^t Bu_3C_6H_2$–) was obtained by reaction of bis-(trimethylsilyl)(tri-*tert*-butylphenyl)phosphane with sulfur dichloride. The CPS_2 moiety was planar and the torsion angle of the aryl group to the PS_2 plane was ca. 80°.

The reaction of 7-phosphanorbornenes (7-PNB) with *m*-chloroperbenzoic acid (*m*CPBA) proceeds with retention of phosphorus configuration.[13] *m*CPBA attacks the phosphorus atom with the formation of P(V) intermediates **7-1** and **7-2**, possessing one of the P–C bonds in an apical, while the other in the equatorial position (Scheme 3). The pseudorotation places the peroxy group into the equatorial position necessary for the migration of the P–C bond (**8-1** and **8-2**). According to this mechanism, the phosphoryl oxygen should remain intact.

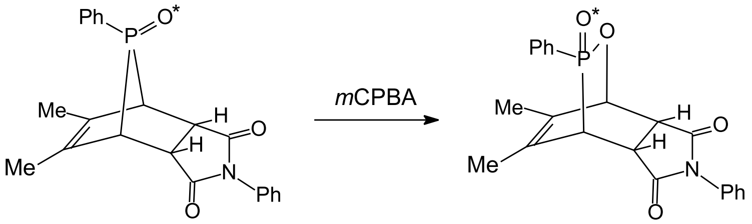
To investigate this problem, 7-phosphanorbornene **11*** labeled with O-18 in the phosphoryl group was treated with *m*CPBA. The product **12*** contained the same amount of heavy oxygen and its ^{31}P NMR spectrum showed the same $^{16}O/^{18}O$ splitting as in the substrate. This is an additional proof that reaction of 7-phosphanorbornenes with *m*CPBA follows a similar mechanism as the oxidation of ketones (Scheme 4).[20]

After the substrate **4a–c** was consumed, the excess of *m*CPBA and its reduction product *m*-chlorobenzoic acid were removed from the solution by complexation on the surface of anhydrous potassium fluoride. Phosphorus containing by-products were also adsorbed. We were successful in isolating the by-product from the synthesis of **5Ac** using the preparative TLC for the reaction mixture obtained without KF treatment. The major by-product was probably a product of double *O*-insertion **13**. The epoxidation of the double-bond for the phosphabicyclooctene system by *m*CPBA was observed previously by Kashman[21] and for 3,4-dimethyl-1-phenylphosphole oxide by Quin.[22]

The steric hindrance due to the substituents in 7-PNB system (**6**, Scheme 3) decreases the rate of *O*-insertion and prolongs the time of exposure to *m*CPBA. The oxygen is



Scheme 3.



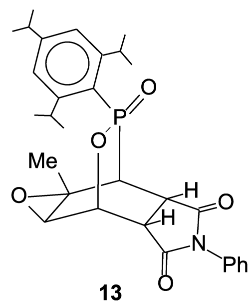
Scheme 4.

inserted easier into the P–C bond placed farther from the vinyl methyl group, than in the other case (**8-2** vs. **8-1**). The epoxidation of the double-bond is facilitated when the vinyl methyl group and the phosphorus atom are on the same side (**9-2** vs. **9-1**). The standard ab initio LCAO-SCF calculations[23] (STO-2G and STO-4G) evidenced that the unsymmetrical transition state is energetically favorable in the reaction of peroxy acids with olefins–the peroxyacid oxygen attacks one of the vinyl carbons.[24] Thus, the steric effect of the substituents at phosphorus is responsible for the kinetic control of the *O*-insertion and the consecutive epoxidation of the double bond.

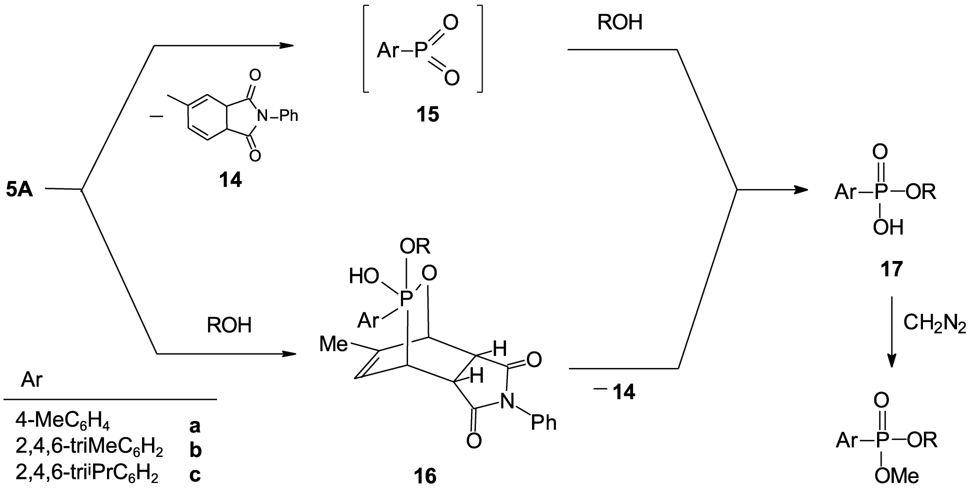
2.2. Fragmentation reaction of 2,3-oxaphospha-bicyclo[2.2.2]octenes 5A in the presence of alcohols

The fragmentation of 2,3-oxaphosphabicyclo[2.2.2]octenes can be achieved by thermolysis or photolysis.[4] The thermolysis of compounds **5Aa-c** in toluene at 110 °C in the presence of methanol or *tert*-butyl alcohol or irradiation at 254 nm in 1,2-dichloroethane in the presence of an alcohol, followed by reaction with diazomethane led to the corresponding phosphonates **18a–c** and **19a–c**, respectively (Scheme 5).

The necessary time for the consumption of the substrate increases with the steric hindrance of the *P*-aryl substituent (Scheme 5). Reaction with methanol is much faster than that with *tert*-butyl alcohol. For the thermal or photochemical fragmentation of 2,3-oxaphosphabicyclo[2.2.2]octene derivatives, a pure retrocycloaddition process was postulated.[9,10] The sensitivity to steric effects suggests the mixture of EA and $S_N(2)P$ (or AE) mechanisms, as for the EA mechanism no significant effect of the alcohol on the rate should be observed.[25] The pure $S_N(2)P$ or AE mechanism can also be excluded, as the phosphonylation of the sterically hindered and low nucleophilic *tert*-butyl alcohol evidences the intermediacy of **14a–c**.[26] The participation of $S_N2(P)$ or AE is reduced by the increase of steric hindrance of the reactants, or even eliminated in the case of reaction of **5Ac** with *tert*-butyl alcohol. The participation of **15c** was additionally proved by the result of the reaction with menthol or with a mixture of alcohols. When menthol was used, the (1:1) mixture of diastereoisomers of **20c** was found in the reaction mixture after the methylation of menthol phosphonate (**17**, R=menthyl) with diazomethane. The lack of stereoselectivity evidences the presence of planar 3-coordinated intermediate.[27] Competition experiment with different alcohols was also performed in order to check the selectivity. We found that **5Ac** reacts three times faster with methanol than with *tert*-butyl alcohol in toluene at 110 °C. A somewhat lower selectivity (2.1) was observed for the reaction of Et-P(S)O with ethanol and *tert*-butyl alcohol in chloroform.[9] The



13



Components		reaction time [min] Δ	hν
5Aa	MeOH	45	50
5Aa	^{t}BuOH	60	180
5Ab	MeOH	60	40
5Ab	^{t}BuOH	150	125
5Ac	MeOH	150	180
5Ac	^{t}BuOH	190	-

R	
Me	**18**
^{t}Bu	**19**
menthyl	**20**

Scheme 5.

systematic kinetic studies to establish the ratio of EA and $S_N2(P)$ or AE mechanisms will be continued.

3. Experimental

3.1. General

NMR spectra were recorded on Bruker Avance DPX 250 spectrometer at 250.13 MHz (^{1}H), 101.20 MHz (^{31}P) and 62.86 MHz (^{13}C) in $CDCl_3$, using tetramethylsilane as internal and 85% H_3PO_4 as external standard. Chemical shifts (*δ*) are indicated in ppm and coupling constants (*J*) in Hz. FAB/MS were recorded on a APO Electron (Ukraine) model MI 12001E mass spectrometer equipped with a FAB ion source (3-nitrobenzyl alcohol matrix). HRMS spectra were recorded on a Finnigan MAT 95 (Finnigan MAT GmbH, Germany) mass spectrometer. Column chromatography was performed with glass column packed with silica gel (0.063–0.2 mm) (Fluka). Eluents: $CHCl_3$ and $CHCl_3$/MeOH (95/5). Melting point was determined using Boetius apparatus. Alcohols (Aldrich, Fluka, P. O. Ch. Poland) were dried over CaH_2. L-Menthol (Fluka, pure) was used without additional purification. Chloroform and dichloromethane (P. O. Ch., Poland, analytical grade) were dried over P_2O_5. KF (Bruxelles-r.c.b. 85078 Belgium) was dried in a dryer at 100–110 °C. Diazomethane in ethyl ether was generated from Diazald (Aldrich) directly before use. Water with 79.3% enrichment of ^{18}O was supplied by Techsnabeksport (USSR).

3.2. 7-Phosphanorbornenes 4a–c and 11

Compounds **4a–d** and **11** were prepared following literature procedures.[11,22]

3.2.1. 2-Methyl-7-oxo-9-phenyl-7-*p*-tolyl-9-aza-7-phosphabicyclo[5.2.1.0^{2,6}]dec-2-ene-8,10-dione (4a). Colorless solid, mp 230–232 °C (ethyl acetate); ν_{max} (CCl_4) 1704, 1496, 1392, 1192, 1136, 784 cm^{-1}; δ_P (101.3 MHz, $CDCl_3$) 84.2; δ_H (250.1 MHz, $CDCl_3$) 7.42–7.58 (5H, m, Ph), 7.26–7.29 (2H, m, H_{Ar}), 7.12–7.16 (2H, m, H_{Ar}), 5.86 (1H, ddq, J=11.2 Hz, C_3H), 4.15 (2H, bd, J=1.8 Hz, C_5H, C_6H), 3.72–3.80 (m, 1H, C_4H), 3.57–3.63 (1H, m, C_1H), 2.40 (3H, s, $C_{4'}CH_3$), 1.81 (3H, dd, J=1.56 Hz, C_2CH_3); δ_C (125.7 MHz, $CDCl_3$) 174.4 (d, J=13.4 Hz), 174.1 (d, J=13.0 Hz), 142.1, 139.8 (d, J=10.3 Hz), 130.7, 128.5 (d, J=11.3 Hz), 128.2, 127.8, 125.5, 121.9 (d, J=97.0 Hz), 121.4 (d, J=7.9 Hz), 45.9 (d, J=64.1 Hz), 44.0 (d, J=13.3 Hz), 42.8 (d, J=11.5 Hz), 42.8 (d, J=64.7 Hz), 20.6, 18.3; m/z (FAB/NBA) 378 (100, MH^+), 286 (11), 240 (22); HRMS (FAB/NBA): MH^+, found 378.1254. $C_{22}H_{21}NO_3P$ requires 378.1259.

3.2.2. 2-Methyl-7-oxo-9-phenyl-7-(2,4,6-trimethylphenyl)-9-aza-7-phosphabicyclo[5.2.1.0^{2,6}]dec-2-ene-8,10-dione (4b). Colorless solid, mp 246–248 °C (ethyl acetate); ν_{max} (CCl_4) 2960, 1712, 1596, 1496, 1448, 1380, 1184, 1040, 880, 660; δ_P (101.3 MHz, $CDCl_3$) 84.2; δ_H (250.1 MHz, $CDCl_3$) 7.45–7.38 (3H, m, H_{Ar}), 7.15–7.11 (m, 2H, H_{Ar}), 6.88 (2H, d, H_{Ar}), 5.85 (ddtq, 1H, J=10.4, 3.1, 1.6 Hz, C_3H), 4.11–4.15 (2H, bd, J=1.7 Hz, C_5H, C_6H), 3.94–4.02 (1H, m, C_4H), 3.83–3.90 (1H, m, C_1H), 2.61 (3H, s, $C_{6'}CH_3$), 2.51 (3H, s, $C_{4'}CH_3$), 2.28 (3H, s, $C_{2'}CH_3$), 1.72 (3H, t, J=1.6 Hz, C_2CH_3); δ_C (62.9 MHz, $CDCl_3$) 18.2, 20.1, 21.9 (d, J=6.4 Hz), 22.2 (d, J=4.7 Hz), 42.3 (d, J=13.8 Hz), 43.7 (d, J=15.4 Hz), 46.3 (d, J=63.2 Hz), 48.8 (d, J=62.9 Hz), 119.6 (d, J=9.4 Hz), 122.0 (d, J=94.6 Hz), 125.0, 125.5, 128.0, 128.2, 130.7, 139.6 (d, J=8.9 Hz), 140.1 (d, J=9.4 Hz), 140.2 (d, J=11.5 Hz), 140.7 (d, J=2.2 Hz), 174.5 (d, J=14.0 Hz), 174.7 (d, J=15.9 Hz); m/z (FAB/NBA) 406 (100, MH^+), 167 (86, ArPOH); HRMS (FAB/NBA): MH^+, found 406.1561. $C_{24}H_{25}NO_3P$ requires 406.1572.

3.2.3. 2-Methyl-7-oxo-9-phenyl-7-phenyl-9-aza-7-phosphabicyclo[5.2.1.0^{2,6}]dec-2-ene-8,10-dione (4d). Colorless solid, mp 239–241 °C (ethyl acetate); δ_P (101.3 MHz, $CDCl_3$); ν_{max} (KBr) 1776, 1712, 1496, 1384, 1200, 752, 704 cm^{-1}; δ_H (250.1 MHz, $CDCl_3$) 7.76–7.55 (3H, m, H_{Ar}), 7.55–7.40 (5H, m, Ph), 7.22–7.13 (2H, m, H_{Ar}), 5.89 (1H, dddq, J=11.3, 5.0, 1.8, 1.7 Hz, C_3H), 4.20 (2H, ddd, J=2.3, 1.7, 04 Hz, C_5H, C_6H), 3.88–3.80 (1H, m, C_4H), 3.70–3.64 (1H, m, C_1H), 1.84 (t, 3H, J=1.8 Hz, C_2CH_3), δ_C (62.9 MHz, CDCl3) 175.2, (d, J=13.8 Hz), 175.0 (d, J=13.6 Hz), 140.9; 140.7, 132.4 (d, J=2.8 Hz), 131.4 (d, J=8.7 Hz), 129.2, 128.9, 128.3 (d, J=11.8 Hz), 126.5 (d, J=91.4 Hz), 126.4, 122.4 (d, J=8.8 Hz), 46.8 (d, J=64.0 Hz), 44.9 (d, J=14.2 Hz), 43.6 (d, J=64.2 Hz), 43.7 (d, J=12.6 Hz), 19.3 (d, J=3.3 Hz); HRMS (FAB/NBA): MH^+, found 364.1086. $C_{21}H_{19}NPO_3$ requires 364.1103.

3.3. Synthesis of 2,3-oxaphosphabicyclo[2.2.2]octenes (5Aa-c)

A solution of 0.20 mmol of 7-phosphanorbornene derivative **4a–c** in dry $CHCl_3$ (1 mL) was added to a solution of *m*CPBA/15% *m*CBA (202 mg, 1.02 mmol) in dry $CHCl_3$ (4 mL). The solution was stirred at room temperature and monitored by ^{31}P NMR. After the completion of reaction, the ^{31}P NMR spectra were complex (**4a**: δ (rel. int.)=36.6 (54), 34.8 (27), 21.2 (9), 12.8 (3), 12.4 (7); **4b**: 40.5 (29), 24.6 (65), −3.7 (6); **4c**: 40.3 (16), 27.3 (23), 26.2 (14), 23.1 (6), 21.6 (3), 18.9 (6), 14.5 (27), −2.4 (5). Then KF (202 mg, 3.5 mmol) was added and the mixture was stirred for 3 h at room temp. The suspension was filtered off (Celite 500) and the solvent evaporated. The crude product was subjected to column chromatography ($CHCl_3$/MeOH) and then crystallized from AcOEt to give analytically pure product in about 15–20% yield.

The reaction of **4d** with *m*CPBA was carried out in an NMR tube (10 mg of substrate) and monitored by ^{31}P NMR to examine the kinetics of *O*-insertion only, without isolation of the product. Attempts to isolate the by-products of *O*-insertion by column chromatography were unsuccessful. However, when preparative TLC chromatography (2 mm silica gel plates, Merck) was applied to the reaction mixture after the synthesis of **5Ac**, the component at R_F=0.88 (chloroform/methanol 5% as an eluent) was extracted with acetone to give **13**; δ_P (101.3 MHz, $CDCl_3$) 21.1; HRMS (ESI): MH^+, found 521.2326. $C_{30}H_{36}NO_5P$ requires 521.2322.

3.3.1. 5-Methyl-8-(4-methylphenyl)-2-phenyl-3a,4,7,7a-tetrahydro-1*H*-4,7-(epoxyphosphano)isoindole-1,3-dione 8-oxide (5Aa). Thick oil; δ_P (101.3 MHz, $CDCl_3$) 35.2; ν_{max} (neat) 2984, 1716, 1648, 1496, 1448, 1400, 1208, 1144, 792 cm^{-1}; δ_H (250.1 MHz, $CDCl_3$) 7.56–7.43 (5H, m, Ph) 7.31–7.26 (2H, m, H_{Ar}), 7.17–7.13 (2H, m, H_{Ar}), 5.95–5.85 (1H, m, C_5H), 5.36 (1H, ddd, J=21.9, 4.2, 2.0 Hz, C_4H), 4.18 (1H, dt, J=7.5, 4.2 Hz, C_8H), 4.02 (1H, dt, J=7.5, 2.6 Hz, C_7H), 3.67 (1H, dt, J=7.5, 7.3, 2.6 Hz, C_1H), 2.42 (3H, s, $C_{4'}CH_3$), 1.99 (3H, dd, J=5.2, 1.75 Hz C_6CH_3); δ_C (62.9 MHz, $CDCl_3$) 175.6 (d, J=15.1 Hz), 173.0, 143.9, 142.0 (d, J=10.7 Hz), 132.7 (d, J=10.7 Hz), 131.3, 129.2, 129.0, 126.1, 125.4 (d, J=90.0 Hz), 123.5 (d, J=8.2 Hz), 76.7 (d, J=9.4 Hz), 46.1 (d, J=12.0 Hz), 36.5 (d, J=79.6 Hz), 36.8 (d, J=6.8 Hz), 21.6, 19.8 (d, J=2.5 Hz); m/z (FAB/NBA) 394 (30, MH]$^+$), 240 (75, $[MH-ArPO_2]^+$,), 154 (15); HRMS (FAB/NBA): MH^+, found 394.1214. $C_{22}H_{21}NO_4P$ requires 394.1208.

3.3.2. 8-Mesityl-5-methyl-2-phenyl-3a,4,7,7a-tetrahydro-1*H*-4,7-(epoxyphosphano) isoindole-1,3-dione 8-oxide (5Ab). Thick oil; δ_P (101.3 MHz, $CDCl_3$) 38.97; ν_{max} (neat) 2976, 1716, 1604, 1380, 1188, 984, 760 cm^{-1}; δ_H (250.1 MHz $CDCl_3$) 7.47–7.42 (3H, m, H_{Ar}), 7.16–7.12 (2H, m, H_{Ar}), 6.88 (2H, d, J=5.0 Hz, $C_{3'}H$, $C_{5'}H$), 5.85–5.70 (1H, m, C_5H), 5.31 (1H, ddd, J=20.1, 4.0, 2.0 Hz, C_4H), 4.15 (1H, dt, J=7.9, 4.0 Hz, C_8H), 3.97 (1H, dt, J=2.5, 7.9 Hz, C_7H), 3.94 (1H, dt, J=7.5, 2.5 Hz, C_1H), 2.58 (6H, s, $C_{2'}CH_3$, $C_{6'}CH_3$), 2.28 (3H, s, $C_{4'}CH_3$), 1.90 (3H, dd, J=5.15, 1.75 Hz, C_6CH_3); m/z (FAB/NBA) 422 (60, MH^+), 240 (57, $[MH-ArPO_2]^+$,), 154 (100), 136 (82); HRMS (FAB/NBA): MH^+, found 422.1514. $C_{24}H_{25}NO_4P$ requires 422.1521.

3.3.3. 6-Methyl-2-phenyl-9-(2,4,6-triisopropylphenyl)-3a,4,7,7a-tetrahydro-1*H*-4,7 (phosphanomethano)isoindole-1,3-dione 9-oxide (5Ac). Colorless solid, mp 162–164 °C; δ_P (101.3 MHz $CDCl_3$) 39.0; ν_{max} (KBr) 2960, 1712, 1396, 1212, 1184, 1128, 984 cm^{-1}; δ_H (250.1 MHz,

$CDCl_3$) 7.39–7.35 (3H, m, H_{Ar}); 7.09–7.05 (2H, m, H_{Ar}), 7.00 (2H, d, J=5.0 Hz, $C_{3'}H$, $C_{5'}H$), 5.70 (1H, dddd, J=7.50, 7.25, 2.0, 1.50 Hz, C_5H), 5.21 (1H, ddd, J=22.0, 4.50, 2.00 Hz, C_4H), 1.17 (d, 12H, $^3J_{HH}$=6.75 Hz, $(CH_3)_2CH-C_{2'}$, $(CH_3)_2CH-C_{6'}$), 4.07 (1H, ddd, J=8.25, 7.25, 4.5 Hz, C_8H), 3.94 (1H, dt, J=2.5, 8.25 Hz, C_7H), 3.80 (1H, dt, J=7.25, 2.5 Hz, C_1H), 3.62 (2H, ht, J=6.75 Hz, $(CH_3)_2CHC_{2'}$, $CH_3)_2CHC_{6'}$), 2.80 (1H, ht, J=6.5 Hz, $(CH_3)_2CHC_{4'}$), 1.78 (3H, dd, J=6.75, 1.50 Hz, CH_3C_6), 1.19 (6H, d, 6.5, $(CH_3)_2CHC_{4'}$), δ_C (62.9 MHz, $CDCl_3$) 176.0 (d, J=15.1 Hz), 173.2, 152.9, 152.6 (d, J=12.6 Hz), 141.4 (d, J=11.7 Hz), 131.4, 129.3, 129.0, 126.2, 125.5 (d, 93.7 Hz), 122.8 (d, J=8.2 Hz), 76.1 (d, J=10.1 Hz), 46.3 (d, J=10.2 Hz), 38.9 (d, J=77.9 Hz), 36.7 (d, J=5.2 Hz), 34.3, 31.6 (d, J=4.2 Hz), 26.6, 24.9 (d, J=25.4 Hz), 20.0; m/z (FAB/NBA) 506 (22, MH^+), 240 (22, $[MH-ArPO_2]^+$), 154 (100), 136 (71); HRMS (FAB/NBA): MH^+, found 506.2466. $C_{30}H_{37}NO_4P$ requires 506.2460.

3.3.4. 5-Methyl-8-phenyl-2-phenyl-3a,4,7,7a-tetrahydro-1*H*-4,7-(epoxyphosphano)isoindole-1,3-dione 8-oxide (5Ad). Colorless solid, mp 132–134 °C; δ_P (101.3 MHz, $CDCl_3$) 34.7; ν_{max} (CCl_4) 2928, 1712, 1388, 1232, 1192, 984, 936, 784 cm^{-1}; δ_H (250.1 MHz, $CDCl_3$) 7.75–7.46 (8H, m, H_{Ar}) 7.17–7.13 (2H, m, H_{Ar}), 5.95–5.84 (1H, m, C_5H), 5.37 (1H, ddd, J=21.3, 4.3, 2.0 Hz, C_4H), 4.18 (1H, dd, J=7.3, 4.3 Hz, C_8H), 4.02 (1H, dt, J=7.3, 2.5 Hz, C_7H), 4.02 (1H, dt, J=7.3, 7.3, 2.5 Hz, C_1H), 2.00 (3H, dd, J=5.0, 1.75 Hz, C_6CH_3); δ_C (62.9 MHz, $CDCl_3$) 175.5 (d, J= 15.6 Hz), 173.0, 142.1 (d, J=10.6 Hz), 133.1 (d, J=2.5 Hz), 132.7 (d, J=9.4 Hz), 131.3, 129.3, 128.6 (d, J=10.9 Hz), 126.1, 123.5 (d, J=7.9 Hz), 46.2 (d, J=11.3 Hz), 36.8 (d, J=6.9 Hz), 36.5 (d, J=80.5 Hz), 19.8 (d, J=2.8 Hz); m/z (FAB/NBA) 380 (30, MH^+), 240 (40, $[MH-ArPO_2]^+$), 154 (75), 137 (90), 109 (100); HRMS (FAB/NBA): MH^+, found 380. 1044, $C_{21}H_{19}NO_4P$ requires 380. 1052.

3.4. Thermolysis of bicyclooctenes 5Aa-c

A solution (1 mL) of **5Aa-c** (0.02 mmol) and an alcohol (2 mmol) in dry toluene were placed into 5 mm NMR tube and sealed under argon. Sample was placed in thermostat at 110 °C and the reaction was monitored by ^{31}P NMR. When the signal of substrate diminished the solvent was evaporated and the excess of diazomethane in diethyl ether was added. The solution was again evaporated to dryness and phosphonate methyl esters **15** were purified by column chromatography ($CHCl_3$) with 90% yield.

3.5. Photolysis of bicyclooctenes 5Aa-c

A solution (1 mL) of **5Aa-c** (0.02 mmol) and an alcohol (2 mmol) in dry 1,2-dichloroethane in 5 mm quartz NMR tube was placed in the centre of Rayonet reactor fitted with 8 low-pressure mercury lamps (253.7 nm). The reaction was monitored by ^{31}P NMR. After the completion of reaction the same protocol as in case of thermolytic reaction was applied. The reaction of **5Aa** and **5Ab** with alcohols proceeded quantitatively and the corresponding methyl esters **17a** and **17b** obtained after treatment with diazomethane were isolated in about 90% yield. In case of reaction of **5Ac** with methanol the yield was only 29% and by-products were observed at 53.7, 36.3 and 35.0 ppm. When **5Ac** was irradiated in the presence of *tert*-butyl alcohol, the product of phosphonylation could not be detected.

3.5.1. Dimethyl 4-methylphenylphosphonate (18a). Thick oil; δ_P (101.3 MHz, $CDCl_3$) 22.7; ν_{max} (neat, NaCl) 2952, 1248, 1188, 1032 cm^{-1}; δ_H (250.1 MHz, $CDCl_3$) 2.41 (s, 3H, $CH_3-C_{4'}$), 3.75 (d, 6H, $^3J_{HP}$=11.0 Hz, CH_3O), 7.26–7.31 (m, 4H, Ar);); δ_C (62.9 MHz, $CDCl_3$) 132.0 (d, J=10.3 Hz), 129.3 (d, J=15.1 Hz), 129.2, 124.3 (d, J=94.4 Hz), 52.6 (d, J=5.4 Hz), 21.7; m/z (FAB/NBA) 201 (MH^+, 100), 91 (24), 77 (20); HRMS (EI): M^+, found 200.0595. $C_9H_{13}O_3P$ requires 200.0602.

3.5.2. *tert*-Butyl methyl 4-methylphenylphosphonate (19a). Thick oil; δ_P (101.3 MHz, $CDCl_3$) 16.8; ν_{max} (neat, NaCl) 2952, 1192, 1128, 1048 cm^{-1}; δ_H (250.1 MHz, $CDCl_3$) 1.51 (s, 9H, $(CH_3)3-C$), 2.40 (s, 3H, $CH_3-C_{4'}$), 3.65 (d, 3H, $^3J_{HP}$=10.0 Hz, CH_3O), 7.23–7.28 (m, 4H, Ar); δ_C (62.9 MHz, $CDCl_3$) 131.6 (d, J=10.1 Hz), 129.2, 129.0 (d, J=15.1 Hz), 124.4 (d, J=95.0 Hz), 83.2, 52.0, (d, J=5.4 Hz), 30.4 (d, J=3.8 Hz), 21.7; m/z (FAB/NBA) 243 (5, MH^+), 187 ([100), 173 (13), 91 (11), 57 (17); HRMS (EI): M^+, found 242.1077.$C_{12}H_{19}O_3P$ requires 242.1072.

3.5.3. Dimethyl mesitylphosphonate (18b). Thick oil; δ_P (101.3 MHz, $CDCl_3$) 23.9; ν_{max} (neat, NaCl) 2952, 1232, 1208, 1184, 1032 cm^{-1}; δ_H (250.1 MHz, $CDCl_3$) 2.27 (s, 3H, $CH_3-C_{4'}$), 2.58 (s, 6H, $CH_3-C_{2'}$, $CH_3-C_{6'}$), 3.73 (d, 6H, $^3J_{HP}$=11.5 Hz, CH_3O), 6.91 (d, 2H, $^4J_{HP}$=5.0 Hz, $H-C_{3'}$, $H-C_{5'}$); δ_C (62.9 MHz, CDCl3) 142.2, 129.2 (d, J=10.7 Hz), 130.4 (d, J=16.4 Hz), 120.9 (d, J=98.4 Hz) 51.7 (d, J=5.0 Hz), 23.0; m/z (FAB/NBA) 229 (100, MH^+), 197 (8), 119 (18), 91 (15), 77 (14); HRMS (EI): M^+, found 228.0919.$C_{11}H_{17}O_3P$ requires 228.0915.

3.5.4. *tert*-Butyl methyl mesitylphosphonate (19b). Thick oil; δ_P (101.3 MHz, $CDCl_3$) 17.7; ν_{max} (film, NaCl) 2976, 1256, 1212, 1168, 1040 cm^{-1}; δ_H (250.1 MHz, $CDCl_3$) 1.49 (s, 9H, $(CH_3)3-C$), 2.34 (s, 3H, CH_3-C4'), 2.59 (s, 6H, $CH_3-C_{2'}$, $CH_3-C_{6'}$), 3.62 (d, 3H, $^3J_{HP}$=11.5, CH_3O), 6.89 (d, 2H, $^4J_{HP}$=4.5, $H-C_{3'}$, $H-C_{5'}$); δ_C (62.9 MHz, $CDCl_3$) 142.0, 130.4 (d, J=15.7 Hz), 129.2 (d, J=9.4 Hz); 120.6 (d, J=97.0 Hz), 77.2 (d, J=1.8 Hz), 22.7, 21.1; m/z (FAB/NBA) 271 (5, MH^+), 215 (100), 197 (10), 119 (9); HRMS (EI): M^+, found 270.1389.$C_{14}H_{23}O_3P$ requires 270.1385.

3.5.5. Dimethyl 2,4,6-triisopropylphenylphosphonate (18c). Thick oil; δ_P (101.3 MHz, $CDCl_3$) 24.3; ν_{max} (film, NaCl) 2960, 1240, 1212, 1188, 1024 cm^{-1}; δ_H (250.1 MHz, $CDCl_3$) 1.24 (d, 12H, $^3J_{H-H4}$=5.50 Hz), 1.26 (d, 6H, $^3J_{H-H}$=5.75 Hz), 2.83 (ht, 1H, $^3J_{H-H}$=5.75 Hz), 3.75 (d, 6H, $^3J_{HP}$=11.26 Hz), 4.11 (ht, 2H, $^3J_{H-H}$=5.50 Hz), 7.14 (d, $2H_{ar}$, $^4J_{Har-P}$=5.28 Hz); δ_C (62.9 MHz, $CDCl_3$) 152.8, 155.2 (d, J=13.8 Hz), 121.6 (d, J=15.7 Hz), 52.0 (d, J=5.6 Hz), 34.3, 30.5 (d, J=2.5 Hz), 24.9, 23.6; HRMS (CI, isobutane): MH^+, found 313.1925. $C_{17}H_{30}O_3P$ requires 313.1933.

3.5.6. *tert*-Butyl methyl 2,4,6-triisopropylphenylphosphonate (19c). Thick oil; δ_P (101.3 MHz, $CDCl_3$) 18.4; ν_{max} (film, NaCl) 2960, 1256, 1240, 1168, 1044 cm^{-1};

δ_H (250.1 MHz, $CDCl_3$) 1.22 (d, 12H, $^3J_{H-H}$=6.75 Hz), 1.25 (d, 6H, $^3J_{H-H}$=6.75 Hz), 1.56 (s, 9H), 2.88 (ht, 1H, $^3J_{H-H}$=6.75 Hz), 3.64 (d, 3H, $^3J_{H-P}$=11.51 Hz), 4.24 (ht, 2H, $^3J_{H-H}$=6.75 Hz), 7.10 (d, $2H_{ar}$, $^4J_{H-P}$=5.00 Hz);); δ_C (62.9 MHz, $CDCl_3$) 151.9, 151.5 (d, J=13.8 Hz), 122.4 (d, J=15.7 Hz), 77.2 (d, J=1.8 Hz), 51.5 (d, J=5.7 Hz), 34.3, 30.5 (d, J=3.8 Hz), 30.1, 25.1; HRMS (CI, isobutane): MH^+, found 355.2399. $C_{20}H_{35}O_3P$ requires 355.2402.

3.6. Synthesis of 12* labeled with O-18

The solution of **11** (30 mg, 0.0796 mmol) and $H_2^{18}O$ (15 mg, 0.85 mmol) in dry acetonitrile was sealed in glass ampule under argon and kept at 100 °C for 45 h. Then the solution was evaporated to dryness under reduced pressure (0.5 mm Hg), dissolved in $CHCl_3$ and filtered through the silica gel layer. ^{31}P NMR spectrum showed broad resonances of **11** at 77.86 ppm and of **11*** at 77.82 ppm. The ^{18}O shift of 0.04 ppm is characteristic for the P=O group.[28] The isotopic ratios $[M^++3]/[M^++3]$ were determined by FAB/MS analysis and equal to 1.982±0.020 and 0.049±0.002 for **11*** and **11**, respectively. *m*CPBA (27 mg, 0.135 mmol) was added to the solution of **11*** (17 mg, 0.045 mmol) in chloroform (1 mL) and left with stirring for 3 h. Then KF (27 mg) was added and stirring was continued for next 90 min. After filtration and solvent evaporation the residue was crystallized from ethyl acetate. Yield of **12***: 10 mg (0.025 mmol) (55.6%). The product showed a pair of well resolved peaks at 34.66 and 34.62 (1:1.9) and mass spectrometric analysis gave the isotopic ratios 1.987±0.022 and 0.048±0.005 for **12*** and **12**, respectively.

3.7. Crystal data of 5Ac

Colorless prisms. Crystal size 0.10×0.05×0.03 mm, $C_{30}H_{36}NO_4P$, M=505.57, monoclinic, a=42.105(8) Å, b=6.044(1) Å, c=20.930(4) Å, $\alpha=\gamma=90°$, β=93.36(3)°, V=5317.17 Å^3, T=100 K, space group $C2/c$, Z=8, μ= 0.14 mm^{-1}, λ=0.7 Å, D(cal)=1.263 Mg/m^3, F(000)=2160, $R1$=0.167, for 4442 observed, $wR2$=0.559 for all 4594 reflections. Diffraction data were collected on the 5-ID beam line of the DND-CAT at the Advanced Photon Source, Argonne, IL, using a MARCCD detector.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC-226060. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax:+44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

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