Organophosphorus Compounds, 145[+]
Synthesis and Reactivity of a Polycyclic, Oxa-Bridged Phosphaalkene

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Dedicated to Professor A. Schmidpeter on the occasion of his 70th birthday

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Thermolysis of 2,3-diphenylindenone 2,3-epoxide **(1)** in the presence of *tert*-butylphosphaalkyne **(3)** proceeds through a regiospecific 1,3-dipolar cycloaddition of the phosphaalkyne to the carbonyl ylide intermediate to furnish the polycyclic phosphaalkene derivative **4**. Compound **4** exhibits a remarkable –– and for phosphaalkenes unusual –– stability: thus, it can be stored for several days and no decomposition can be observed even in the absence of inert gas protection. The phosphaalkene **4** reacts with 1,3-dipoles such as ethyl diazoacetate **(8)** by formal transfer of its phosphaalkene unit to afford the 1,2,4-diazaphosphole **10**. Addition of lithium alkoxides to the phosphaalkene unit of the polycyclic compound **4** occurs diastereoselectively to give the novel phosphinites **13** and **14**. In this context it should be mentioned that the choice of the lithium alkoxide has a decisive influence on the preferred formation of one diastereomer of the phosphinite.

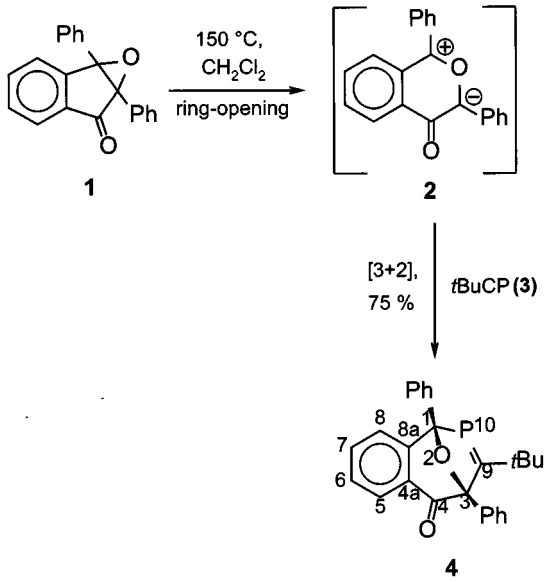
Introduction

Carbonyl ylide dipoles have proved to be important building blocks for the preparation of oxygen-containing heterocyclic systems.[1–4] The reactive carbonyl ylide is usually generated in situ in the presence of a suitable dipolarophile.[5] The elimination of nitrogen from suitable diazocarbonyl precursors with transition metal, especially rhodium, catalysis is a useful method for the generation of the carbonyl ylides.[6] The incorporation of the carbonyl ylide structure in a delocalized six π-electron system provides sufficient stabilization so that isolation of the dipolar species becomes possible.[7] The resultant mesoionic compounds are known as the isomünchnones. It was recently demonstrated that various isomünchnone derivatives also react readily with phosphaalkynes.[8] This provided a simple access to the poorly investigated class of the 1,3-oxaphospholes.[9] On the basis of this work, further investigations on the cycloaddition behavior of carbonyl ylides with phosphaalkynes have been performed in our laboratories.

Results and Discussion

Synthesis of the Oxo-Bridged Phosphaalkene 4

On warming, many acceptor-substituted oxiranes undergo cleavage of their C–C single bonds to generate carbonyl ylide intermediates.[10] For example, warming of the



Scheme 1. Cycloaddition of carbonyl ylide **2** with phosphaalkyne **3**

2,3-diphenylindenone epoxide **1** leads to the pyrylium 4-olate intermediate **2** with a carbonyl ylide structure.[11] When oxirane **1** is heated in dichloromethane solution in the presence of the phosphaalkyne **3**, the intermediate **2** reacts regiospecifically with **3** to furnish a novel, oxa-bridged phosphaalkene derivative **4** (Scheme 1). Product **4** is easily purified by flash chromatography,[12] and is thus obtained as pale yellow crystals that are stable for several days even in the absence of inert gas protection. This high stability to atmospheric moisture and oxygen is most unusual for a phosphaalkene derivative[13] and can be rationalized in terms of a high steric shielding of the reactive phosphaalkene moiety by the *tert*-butyl and the two phenyl substituents.

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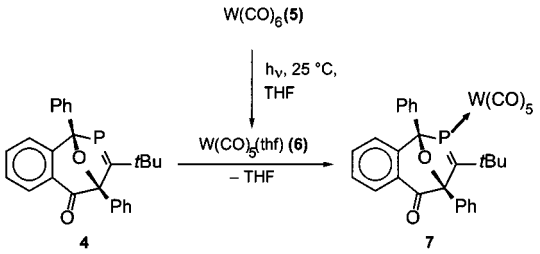
When the charge distribution in the carbonyl ylide **2** is considered together with the polarity of the P−C triple bond, which is characterized by a positively polarized phosphorus atom, the experimentally observed regiochemistry of this 1,3-dipolar cycloaddition reaction is somewhat surprising. However, the direction of addition of the phosphaalkyne to the carbonyl ylide dipole **2** is in complete harmony with that observed in the reactions of isomünchnones with phosphaalkynes.[8] The addition of the phosphaalkyne **3** to carbonyl ylides is not charge controlled and can apparently be interpreted as a characteristic property of this class of dipoles. In order to achieve a better understanding of the regioselectivity of this cycloaddition ab initio studies are currently being performed.

The constitution of compound **4** can be derived unequivocally from its NMR and mass spectroscopic data. Thus, the ^{31}P NMR chemical shift value of $\delta = 261.4$ is characteristic of an isolated P−C double bond.[13] The ^{13}C NMR spectrum provides further diagnostic information. Accordingly, the signal for the carbon atom of the P−C double bond appears at $\delta = 212.5$ as a doublet split by a $^1J_{C\text{-}P}$ coupling of 45.0 Hz. The signals for the two bridgehead carbon atoms C-1 and C-3 observed at $\delta = 94.4$ and $\delta = 98.0$, respectively, are also relevant for the structure elucidation. As a consequence of the neighboring carbonyl group the signal shifted more to low field is assigned to the carbon atom C-3. This interpretation is supported by the observed C-P coupling constants: C-1 experiences a $^1J_{C\text{-}P}$ coupling of 37.8 Hz, while the $^2J_{C\text{-}P}$ coupling of C-3 is appreciably smaller (8.9 Hz). The proposed structure of **4** was also confirmed by an X-ray crystallographic analysis.[8,14] It should also be mentioned that the two bridgehead atoms C-1 and C-3 of the phosphaalkene **4** are chiral centers. However, since the two chiral carbon atoms cannot change their configurations independently on account of the oxygen bridge, compound **4** occurs only as a racemic mixture.

Complexation of the Phosphaalkene 4

The free electron-pair of a low-coordinated phosphorus atom can often be complexed by a group 6 metal pentacarbonyl fragment.[15] As expected, treatment of the phosphaalkene **4** with the pentacarbonyltungsten fragment **6** generated from **5** leads to formation of the tungsten complex **7** (Scheme 2).

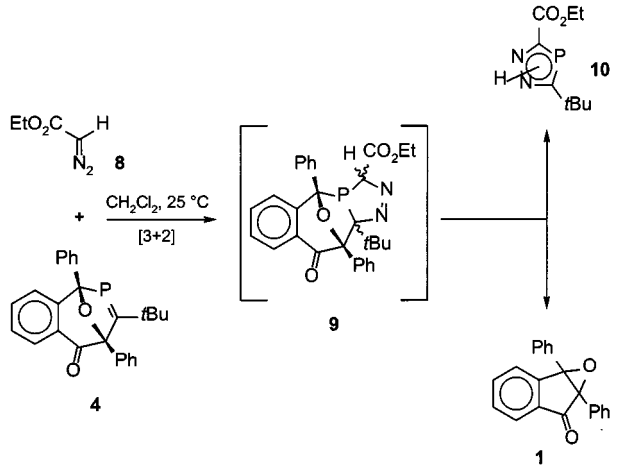


Scheme 2. Complexation of phosphaalkene **4**

The η^1-coordination of the phosphorus atom is demonstrated by the shift to higher field of the ^{31}P NMR signal from $\delta = 261.4$ in compound **4** to $\delta = 235.7$ in the metal complex **7**.[16] The phosphorus atom in **7** experiences a typical $^1J_{P\text{-}W}$ coupling of 262.7 Hz. An η^2-coordination can be discounted since, according to the available literature data, this would have led to an appreciably larger shift to higher field.[17] The constitution of complex **7** is also supported by its mass spectrum and the IR absorptions for the CO ligands at $\tilde{\nu} = 1950$ and 2078 cm^{-1}.

Reactivity Towards Diazo Compounds

When the phosphaalkene derivative **4** is allowed to react with ethyl diazoacetate at 0 °C a rapid change in the color of the reaction solution from light yellow to violet is observed. However, instead of the expected cycloaddition product **9**, workup of the reaction finally affords the 1,2,4-diazaphosphole **10** as well as **1** (Scheme 3).

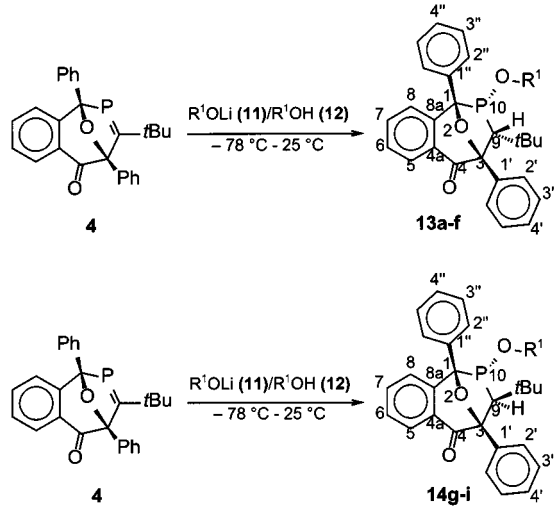


Scheme 3. Reactivity of **4** towards diazo compounds

Formation of the compound **10** can only be explained in terms of a rapid decomposition of the spectroscopically undetectable intermediate **9** with concomitant formation of the oxirane **1**. A geometry optimization of the intermediate **9** at the PM3 level of theory reveals a highly stretched bond between the phosphorus atom and the neighboring bridgehead carbon atom.[8] The resultant weakness of this highly relevant bond for the structure **9** may explain the decomposition of the latter into the diazaphosphole **10** and the oxirane **1**. The constitution of product **10** has been unambiguously confirmed by a comparison of its NMR spectroscopic data with those of the methyl ester derivative synthesized by Regitz.[18]

Reactivity Towards Lithium Alkoxides

H-acidic compounds like alcohols undergo addition to phosphaalkene moieties due to the difference in electronegativity between the phosphorus and carbon atoms.[19] When the reactivity of a phosphaalkene unit is not sufficient for the addition of an alcohol molecule, the use of the respective alkoxide often renders the desired reaction possible.[20] Since the newly synthesized phosphaalkene derivative **4** did not react with equimolar amounts of any alcohol tested, it was treated with solutions of the lithium



11-13	a	b	c	d	e	f
R^1	Me	Et	Prop	*t*Bu	*i*Pr	c-C_6H_{11}

11, 12, 14	g	h	i
R^1	CH_2COMe	CH_2COEt	CH_2COPh

Scheme 4. Reactivity of **4** towards lithium alkoxides

alkoxides **11a–i** in THF instead. The solutions of the alkoxides **11a–i** were always freshly prepared and also contained equimolar amounts of the respective alcohols **12a–i.**

The novel phosphinites **13** and **14** were isolated as the products of these reactions (Scheme 4).

Addition of an alcohol molecule to the phosphaalkene unit of compound **4** generates two new stereocenters so that the newly prepared phosphinites possess a total of four centers of chirality. Since the chiral bridgehead carbon atoms C1 and C3 cannot change their configurations independently, four different stereoisomeric phosphinites **13–16** are feasible as reaction products. Figure 1 shows these four different diastereomers together with their enthalpies of formation ΔH_f as calculated at the PM3 level of theory. As is readily apparent from purely steric considerations, the diastereomer **15**, in which the newly introduced substituents exist in the same spatial directions as the two phenyl substituents, is the energetically most unfavorable form. And structure **16**, the most favorable one according to PM3 calculations, is not generated in this experiment because the formation of **16** would involve an attack of the alkoxide from the sterically most hindered site of **4**.

When the formation of the phosphinites **13** and **14** is monitored by ^{31}P NMR spectroscopy diastereoselective reaction pathways are observed in all cases. After workup of the reaction mixture by flash chromatography on silica gel 60, the compounds **13** and **14** are obtained as pure diastereomers. The clear differences in the ^{31}P NMR spectroscopic data of the phosphinites **13a–f** and **14g–i**, however, indicate that two different diastereomers have been formed. The change from the simple primary or secondary alcohols **12a–f** to the α-hydroxy ketones **12g–i** apparently has a decisive effect on the preferred diastereomeric form of the phosphinites. Assuming that the alkoxides **11g–i** form a chelated structure with the lithium cation, which strongly

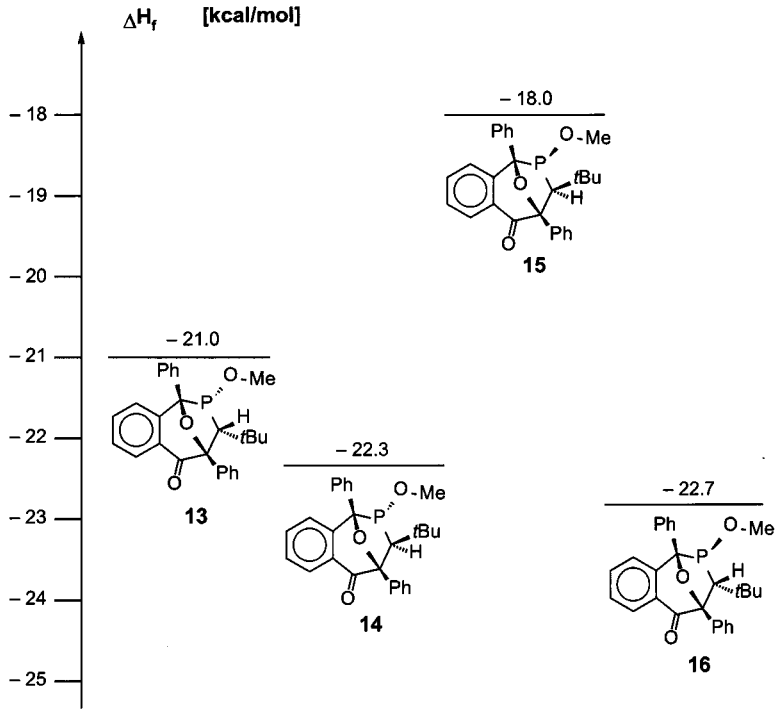
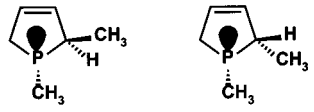


Figure 1. The four possible diastereomeric forms **13–16** of the phosphinites and the corresponding enthalpies of formation (ΔH_f)

favors the observed *syn* addition, gives a possible explanation of this experimental observation.

The exact structure elucidation of the isolated phosphinites **13** and **14** is only possible by consideration of the $^2J_{C-P}$ coupling constants in their ^{13}C NMR spectra. It is known that the magnitudes of the $^2J_{C-P}$ coupling constants are strongly dependent on the position of the corresponding carbon atom with respect to the free electron pair on the phosphorus atom,[21] as has been demonstrated by appropriate measurements on the cyclic phosphane derivatives **17** and **18** (Figure 2).[22]



$^2J_{C,P}$ = 32 Hz $^2J_{C,P}$ = 0 Hz

17 **18**

Figure 2. Influence of the *syn*- and *anti*-positions on the magnitude of the $^2J_{C-P}$ coupling constant

In the case of a *syn*-arrangement, large coupling constants are observed whereas in the case of an *anti*-arrangement the $^2J_{C-P}$ couplings can disappear completely. When the ^{13}C NMR signals of the quaternary carbon atoms of the *tert*-butyl substituents of the phosphinites **13a−f** are viewed no doublet splittings are observed. This indicates that the *tert*-butyl substituent and the alkoxy group on the phosphorus atom must have the same spatial direction. This immediately precludes the diastereomeric forms **14** and **16**. The differentiation between the diastereomers **13** and **15** is now possible by consideration of the signal of the *ipso*-carbon atom C-1′′ in the aromatic substituent at C-1. In the phosphinites **13a−f** this exhibits an average $^2J_{C-P}$ coupling of 16.4 Hz. Thus, the structure shown for the phosphinites **13a−f** may be considered to be confirmed.

The ^{13}C NMR spectra of the phosphinites **14g−i** are indicative of a completely different situation. In these cases the signals for the quaternary carbon atoms of the *tert*-butyl substituents exhibit an average $^2J_{C-P}$ coupling constant of 12.3 Hz; these experimental observations exclude the diastereomeric forms **13** and **15**. Since a $^2J_{C-P}$ coupling to the *ipso*-carbon atom C-1′′ is observed at the same time, the products must be the phosphinites **14g−i**.

Experimental Section

General Remarks: All experiments were carried out under argon (purity > 99.998%) in previously evacuated and heated Schlenk vessels. When the reaction mixture had to be heated to temperatures above the boiling point of the solvent, special pressure Schlenk tubes (glass tubes, 3 × 5 cm, wall thickness 2 mm) with screw-threaded, Teflon stoppers and Teflon stopcocks were used. The solvents were dried by standard procedures, distilled, and stored under argon until used. Melting points were determined with a Mettler FP61 apparatus (heating rate 2 °C min^{-1}) and are uncorrected. NMR spectra were recorded with Bruker WP200 and Bruker AMX 400 instruments. Chemical shifts for ^1H and ^{13}C NMR spectra are reported in ppm relative to tetramethylsilane as the internal standard; the chemical shifts for ^{31}P are expressed relative to external 85% orthophosphoric acid. Elemental analyses were performed with a Perkin−Elmer-Analyser 2400. IR spectra were measured with a Perkin−Elmer 16 PC FT-IR spectrophotometer and mass spectra were recorded with a Finnigan MAT90 spectrometer. Compounds **1**[23] and **3**[24] were prepared according to published methods.

9-*tert*-Butyl-1,3-diphenyl-10-phospha-1,3-etheno-1*H*-benzopyran-4(3*H*)-one (4): A solution of oxirane **1** (2.0 g, 6.7 mmol) and phosphaalkyne **2** (670 mg, 6.7 mmol) in 15 mL of CH_2Cl_2 was heated for 18 h at 150 °C under 5 bar Ar overpressure. After evaporation of the solvent the residue was dissolved in 5 mL of CH_2Cl_2 and subjected to flash chromatography[12] on silica gel 60 with an *n*-pentane/diethyl ether mixture (80:1) to furnish the product as a pale yellow solid. Yield: 2.0 g (75%); m.p. 96 °C. − ^1H NMR ($CDCl_3$): δ = 1.04 [d, $^4J_{H-P}$ = 1.2 Hz, 9 H, C(C*H*$_3$)$_3$], 6.81−8.09 (m, 9 H, aryl-H). − ^{13}C NMR ($CDCl_3$): δ = 32.9 [d, $^3J_{C-P}$ = 12.8 Hz, C(*C*H$_3$)$_3$], 39.4 [d, $^2J_{C-P}$ = 12.1 Hz, *C*(CH$_3$)$_3$], 94.4 (d, $^1J_{C-P}$ = 37.8 Hz, C-1), 98.0 (d, $^2J_{C-P}$ = 8.9 Hz, C-3), 122.8 (s), 127.7 (s), 127.9 (s), 128.00 (s), 128.03 (s), 128.1 (s), 128.3 (s), 128.6 (s), 129.0 (s), 132.4 (s), aryl-C, 126.7 (s), 148.3 (s), C-4a, C-8a, 138.5 (d, $^3J_{C-P}$ = 4 Hz, C-1′), 139.9 (d, $^2J_{C-P}$ = 10.4 Hz, C-1′′), 189.6 (d, $^3J_{C-P}$ = 10.4 Hz, C-4), 212.5 (d, $^1J_{C-P}$ = 45.0 Hz, C-9). − ^{31}P NMR ($CDCl_3$): δ = 261.4 (s). − IR (CCl_4): $\tilde{\nu}$ = 2962 (s, CH), 1698 (vs, C=O), 1594 (s), 1492 (m), 1448 (w), 1446 (s), 1364 (m), 1280 (s), 1200 (s), 1184 (m), 1060 (m), 1027 (s), 836 (s) cm^{-1}. − MS (70 eV, EI): *m*/*z* (%) = 398 (5.6) [M]$^+$, 342 (2.8) [M − C_4H_8]$^+$, 326 (31.8) [M − *t*BuCP − O]$^+$, 105 (37.6) [Ph − CO]$^+$, 77 (16.6) [C_6H_5]$^+$, 57 (47.0) [C_4H_9]$^+$. − $C_{26}H_{23}O_2P$ (398.43): calcd. C 78.39, H 5.78; found C 77.50, H 5.75.

10-η^1-[9-*tert*-Butyl-1,3-diphenyl-10-phospha-1,3-etheno-1*H*-benzopyran-4(3*H*)-9-one]pentacarbonyltungsten (7): Phosphaalkene **4** (102 mg, 0.3 mmol) in THF (5 mL) was added to a solution of $W(CO)_5$thf **(6)**, freshly prepared by irradiation of $W(CO)_6$ **(5)** (108 mg, 0.3 mmol) in THF (50 mL). After 14 h the solvent was removed at 25 °C/0.001 mbar and the residue was subjected to flash chromatography on silica gel 60 (*n*-pentane/diethyl ether = 25:1) to furnish the product **7** as an orange-red solid. Yield: 68 mg (30%); m.p. 165 °C. − ^1H NMR ($CDCl_3$): δ = 1.22 [s, 9 H, C(C*H*$_3$)$_3$], 7.30−8.31 (m, 14 H, aryl-H). − ^{13}C NMR ($CDCl_3$): δ = 34.3 [d, $^3J_{C-P}$ = 10.9 Hz, C(*C*H$_3$)$_3$], 38.7 [d, $^2J_{C-P}$ = 3.6 Hz, *C*(CH$_3$)$_3$], 95.4 (d, $^1J_{C-P}$ = 17.4 Hz, C-1), 100.0 (d, $^2J_{C-P}$ = 3.6 Hz, C-3), 122.5 (s), 125.3 (s), 128.2 (s), 128.4 (s), 128.9 (s), 129.1 (s), 129.7 (s), 130.1 (s), 131.0 (s), 132.5 (s), aryl-C, 127.5 (s), 142.9 (s), C8a, C4a, 135.4 (d, $^3J_{C-P}$ = 7.3 Hz, C-1′), 138.4 (d, $^2J_{C-P}$ = 8.0 Hz, C-1′′), 187.3 (d, $^3J_{C-P}$ = 13.8 Hz, C-4), 194.3 (d, $^2J_{C-P}$ = 8.7 Hz, CO-*cis*), 195.9 (d, $^2J_{C-P}$ = 40.7 Hz, CO-*trans*), 197.7 (d, $^1J_{C-P}$ = 32.7 Hz, C-9). − ^{31}P NMR ($CDCl_3$): δ = 235.7 (s, $^1J_{P-W}$ = 262.7 Hz). − IR (CCl_4): $\tilde{\nu}$ = 2078 [vs, W(CO)], 1950 [vs, W(CO)], 1698 (s, C=O) cm^{-1}. − MS (70 eV, EI): *m*/*z* (%) = 722 (6.9) [M]$^+$, 694 (6.3) [M − CO]$^+$, 638 (57.6) [M − 3CO]$^+$, 582 (24.5) [M − 5CO]$^+$, 398 (53.5) [M − $W(CO)_5$]$^+$, 342 (38.1) [M − $W(CO)_5$ − C_4H_8]$^+$, 265 (26.0) [M − $W(CO)_5$ − C_4H_8 − C_6H_5]$^+$, 105 (100.0) [Ph − CO]$^+$, 77 (43.7) [C_6H_5]$^+$, 57 (43.7) [C_4H_9]$^+$.

Ethyl 5-*tert*-Butyl-[1,2,4]-diazaphosphole-3-carboxylate (10): The phosphaalkene **4** (300 mg, 0.75 mmol) was dissolved in 15 mL of CH_2Cl_2 and cooled to 0 °C. To this solution was added an equimolar amount of the diazo compound **8** (86 mg, 0.75 mmol). The mixture was allowed to warm to room temp. during 24 h. After the evaporation of the solvent the residue was extracted three times with *n*-pentane (20 mL each). The combined pentane extracts were filtered through a pad of Celite and, after removal of the solvent,

the product **10** was isolated as a pale yellow solid. The insoluble residue consisted mainly of the oxirane **1** (IR comparison with an authentic sample[23]). Yield: 72 mg (45%); m.p. 142 °C. − ^{1}H NMR ($CDCl_3$): δ = 0.95 (t, $^3J_{H-H}$ = 7.1 Hz, 3 H, $CO_2CH_2CH_3$), 1.43 [s, 9 H, $C(CH_3)$], 4.03 (q, $^3J_{H-H}$ = 7.1 Hz, 2 H, $CO_2CH_2CH_3$), 12.52 (s, 1 H, N*H*). − ^{13}C NMR ($CDCl_3$): δ = 14.1 (s, $CO_2CH_2CH_3$), 31.7 [d, $^3J_{C-P}$ = 7.2 Hz, $C(CH_3)_3$], 31.7 [d, $^2J_{C-P}$ = 14 Hz, $C(CH_3)_3$], 61.4 (s, $CO_2CH_2CH_3$), 163.2 (d, $^2J_{C-P}$ = 21.7 Hz, $CO_2CH_2CH_3$), 164.0 (d, $^1J_{C-P}$ = 57.0 Hz, C-3), 192.9 (d, $^1J_{C-P}$ = 62.2 Hz, C-5). − ^{31}P NMR ($CDCl_3$): δ = 96.3 (s). − IR (pentane): $\tilde{\nu}$ = 3261 (w, NH), 1759 (vs, C=O) cm^{-1}. − MS (70 eV, EI): *m/z* (%) = 214 (35.0) $[M]^+$, 199 (65.7) $[M - CH_3]^+$, 185 (14.2) $[M - C_2H_5]^+$, 169.1 (11.8) $[M - C_2H_5O]^+$, 158 (19.5) $[M - C_4H_9]^+$, 153 (100.0) $[M - CH_3 - C_2H_5]^+$, 130 (32.5) $[M - C_4H_9 - C_2H_5]^+$; $C_9H_{15}N_2O_2P$ (214.20).

10-Alkoxy-9-*tert*-butyl-1,3-diphenyl-10-phospha-1,3-ethano-1*H*-benzopyran-4(3*H*)-one (13, 14). − General Procedure: The phosphaalkene **4** was dissolved in 15 mL of THF and cooled to −78 °C. Then, an equimolar amount of a freshly prepared solution of the appropriate lithium alkoxide in THF was added and the reaction mixture allowed to warm to room temp. during 16 h. After removal of the solvent the residue was subjected to flash chromatography on silica gel 60 (*n*-pentane/diethyl ether = 50:1 for **13a-f** and *n*-pentane/diethyl ether = 20:1 for **14g−i**) to furnish the phosphinites **13** and **14** as white solids.

Preparation of the Lithium Alkoxides − General Procedure: The appropriate alcohol (16 mmol) was dissolved in 10 mL of THF and the resulting mixture was cooled to 0 °C in an ice bath. To this mixture was added dropwise 5 mL of a 1.6 M *n*BuLi solution in *n*-hexane. The resulting mixture was stirred for 15 min at 0 °C and then used in the preparation of the phosphinites **13** and **14**.

9-*tert*-Butyl-10-methoxy-1,3-diphenyl-10-phospha-1,3-ethano-1*H*-benzopyran-4(3*H*)-one (13a): Yield: 101 mg (36%); m.p. 87 °C. − ^{1}H NMR ($CDCl_3$): δ = 0.89 [d, $^4J_{H-P}$ = 1.4 Hz, 9 H, $C(CH_3)_3$], 2.49 (d, $^2J_{H-P}$ = 12.9 Hz, 1 H, H at C-9), 3.43 (d, $^3J_{H-P}$ = 12.7 Hz, 3 H, OCH_3), 7.25−7.42 (m, 7 H), 7.47−7.53 (m, 2 H), 7.81−7.83 (m, 2 H), 8.18−8.19 (m, 1 H), 8.50 (d, 2 H) aryl-H. − ^{13}C NMR ($CDCl_3$): δ = 32.1 [d, $^3J_{C-P}$ = 7.6 Hz, $C(CH_3)_3$], 35.4 [s, $C(CH_3)_3$], 58.2 (d, $^1J_{C-P}$ = 21.4 Hz, C-9), 63.9 (d, $^2J_{C-P}$ = 30.6 Hz, C-a), 87.4 (d, $^2J_{C-P}$ = 1.5 Hz, C-3), 93.6 (d, $^1J_{C-P}$ = 23.6 Hz, C-1), 126.0 (d, J_{C-P} = 3.8 Hz), 127.2 (s), 127.8 (s), 128.0 (s), 128.2 (s), 128.7 (d, J_{C-P} = 9.1 Hz), 128.8 (s), 128.9 (s), 129.5 (s), 130.6 (s), aryl-C, 133.0 (s), 137.3 (s), C-4a, C-8a, 139.9 (d, $^3J_{C-P}$ = 6.1 Hz, C-1′), 143.8 (d, $^2J_{C-P}$ = 16.7 Hz, C-1′′), 193.0 (s, C-4). − ^{31}P NMR ($CDCl_3$): δ = 131.4 (s). − IR (CCl_4): $\tilde{\nu}$ = 2956 (m, −CH), 1702 (vs, C=O), 1596 (m), 1493 (w), 1447 (m), 1285 (w), 1223 (m), 1037 (s), 838 (w) cm^{-1}. − MS (70 eV, EI): *m/z* (%) = 430 (2.2) $[M]^+$, 398 (52.8) $[M - MeOH]^+$, 373 (31.8) $[M - tBu]^+$, 352 (100) $[M - CH_3OP - H - CH_3]^+$, 337 (38.4) $[M - CH_3OPH - 2CH_3]^+$, 298 (68.5) $[C_{21}H_{14}O_2]^+$, 270 (10.5) $[C_{21}H_{14}O_2 - CO]^+$, 221 (12.9) $[C_{21}H_{14}O_2 - Ph]^+$, 193 (44.8) $[C_{21}H_{14}O_2 - PhCO]^+$, 165 (55.1) $[C_{21}H_{14}O_2 - PhCO - CO]^+$, 105 (80.1) $[Ph - CO]^+$, 77 (37.7) $[C_6H_5]^+$, 57 (33.9) $[C_4H_9]^+$.

9-*tert*-Butyl-10-ethoxy-1,3-diphenyl-10-phospha-1,3-ethano-1*H*-benzopyran-4(3*H*)-one (13b): Yield: 120 mg (42%); m.p. 92 °C. − ^{1}H NMR ($CDCl_3$): δ = 0.87 [d, $^4J_{H-P}$ = 1.0 Hz, 9 H, $C(CH_3)_3$], 0.91 (pt, $^3J_{H-H}$ = 7.1 Hz, 6.9 Hz, 3 H, OCH_2CH_3), 2.46 (d, $^2J_{H-P}$ = 12.9 Hz, 1 H, H at C-9), 3.44 (m, $^3J_{H-H}$ = 6.9 Hz, $^2J_{H-H}$ = 9.9 Hz, 1 H) and 3.73 (m, $^3J_{H-H}$ = 7.1 Hz, $^2J_{H-H}$ = 9.9 Hz, 1 H, OCH_2CH_3), 7.30−7.37 (m, 7 H), 7.42−7.49 (m, 2 H), 7.80−7.82 (m, 2 H), 8.15−8.17 (m, 1 H), 8.50 (d, 2 H) aryl-H. − ^{13}C NMR ($CDCl_3$): δ = 16.7 (d, $^3J_{C-P}$ = 6.7 Hz, C-b), 31.7 [d, $^3J_{C-P}$ = 7.3 Hz, $C(CH_3)_3$], 34.9 [s, $C(CH_3)_3$], 63.7 (d, $^1J_{C-P}$ = 30.5 Hz, C-9), 66.9 (d, $^2J_{C-P}$ = 19.3 Hz, C-a), 86.9 (s, C-3), 93.3 (d, $^1J_{C-P}$ = 25.3 Hz, C-1), 125.5 (d, J_{C-P} = 2.5 Hz), 126.8 (s), 127.3 (s), 127.6 (s), 127.7 (s), 128.2 (s), 128.3 (s), 128.6 130.3 (s), 132.6 (s), aryl-C, 129.2 (d, J_{C-P} = 2.6 Hz), 137.2 (s), C-4a, C-8a, 139.6 (d, $^3J_{C-P}$ = 6.0 Hz, C-1′), 143.5 (d, $^2J_{C-P}$ = 15.9 Hz, C-1′′), 192.7 (s, C-4). − ^{31}P NMR ($CDCl_3$): δ = 133.2 (s). − IR (CCl_4): $\tilde{\nu}$ = 2955 (m, C−H), 1706 (vs, C=O), 1595 (m), 1493 (m), 1447 (w), 1223 (m), 1219 (m), 1046 (s), 926 (m), 837 (w) cm^{-1}. − MS (70 eV, EI): *m/z* (%) = 444 (2.4) $[M]^+$, 387 (42.5) $[M - tBu]^+$, 352 (100) $[M - CH_3CH_2OP - H - CH_3]^+$, 337 (44.2) $[M - CH_3CH_2OPH - 2CH_3]^+$, 298 (93.8) $[C_{21}H_{14}O_2]^+$, 270 (15.4) $[C_{21}H_{14}O_2 - CO]^+$, 221 (17.2) $[C_{21}H_{14}O_2 - Ph]^+$, 193 (12.0) $[C_{21}H_{14}O_2 - PhCO]^+$, 165 (29.9) $[C_{21}H_{14}O_2 - PhCO - CO]^+$, 105 (54.9) $[Ph - CO]^+$, 77 (27.7) $[C_6H_5]^+$, 57 (22.1) $[C_4H_9]^+$. − $C_{28}H_{29}O_3P$ (444.50): calcd. C 75.59, H 6.58; found C 74.89, H 6.51.

9-*tert*-Butyl-1,3-diphenyl-10-propoxy-10-phospha-1,3-ethano-1*H*-benzopyran-4(3*H*)-one (13c): Yield: 130 mg (46%); m.p. 107 °C. − ^{1}H NMR ($CDCl_3$): δ = 0.66 (dd, $^3J_{H-H}$ = 7.4 Hz, 7.3 Hz, 3 H, $OCH_2CH_2CH_3$), 0.87 [d, $^4J_{H-P}$ = 1.5 Hz, 9 H, $C(CH_3)_3$], 1.26 (m, 2 H, $OCH_2CH_2CH_3$), 2.47 (d, $^2J_{H-P}$ = 12.6 Hz, 1 H, H at C-9), 3.35 (dq, $^3J_{H-H}$ = $^3J_{H-P}$ = 6.9 Hz, $^2J_{H-H}$ = 9.6 Hz, 1 H) and 3.64 (dq, $^3J_{HH}$ = $^3J_{H-P}$ = 6.4 Hz, $^2J_{H-H}$ = 9.6 Hz, 1 H, $OCH_2CH_2CH_3$), 7.31−7.40 (m, 7 H), 7.45−7.49 (m, 2 H), 7.82−7.84 (m, 2 H), 8.17−8.19 (m, 1 H), 8.51 (bd, 2 H) aryl-H. − ^{13}C NMR ($CDCl_3$): δ = 10.4 (s, C-c), 24.6 (d, $^3J_{C-P}$ = 7.3 Hz, C-b), 32.0 [d, $^3J_{C-P}$ = 7.3 Hz, $C(CH_3)_3$], 35.2 [s, $C(CH_3)_3$], 64.2 [d, $^1J_{C-P}$ = 30.5 Hz, C-9], 73.0 (d, $^2J_{C-P}$ = 18.1 Hz, C-a), 87.2 (s, C-3), 93.6 (d, $^1J_{C-P}$ = 24.7 Hz, C-1), 125.8 (d, J_{C-P} = 2.9 Hz), 127.2 (s), 127.6 (s), 127.9 (s), 128.1 (s), 128.2 (s), 128.5 (s), 128.6, 129 (s), 132.9 (s) aryl-C, 129.6 (d, J_{C-P} = 2.2 Hz), 137.5 (s), C-4a, C-8a, 140.0 (d, $^3J_{C-P}$ = 7.4 Hz, C-1′), 143.9 (d, $^2J_{C-P}$ = 16.0 Hz, C-1′′), 193.0 (s, C-4). − ^{31}P NMR ($CDCl_3$): δ =133.0 (s). − IR (CCl_4): $\tilde{\nu}$ = 2957 (m, C−H), 1704 (vs, C=O), 1595 (m), 1447 (s), 1283 (m), 1223 (m), 1206 (m), 1064 (m), 1038 (m) 837 (w) cm^{-1}. − MS (70 eV, EI): *m/z* (%) = 458 (0.7) $[M]^+$, 401 (23.5) $[M - tBu]^+$, 352 (100) $[M - CH_3CH_2CH_2OP - H - CH_3]^+$, 337 (25.3) $[M - CH_3CH_2CH_2OPH - 2CH_3]^+$, 298 (70.3) $[C_{21}H_{14}O_2]^+$, 270 (5.6) $[C_{21}H_{14}O_2 - CO]^+$, 221 (4.4) $[C_{21}H_{14}O_2 - Ph]^+$, 193 (1.8) $[C_{21}H_{14}O_2 - PhCO]^+$, 165 (1.0) $[C_{21}H_{14}O_2 - PhCO - CO]^+$, 105 (11.8) $[Ph - CO]^+$, 57 (2.0) $[C_4H_9]^+$. − $C_{29}H_{31}O_3P$ (458.50): calcd. C 75.29, H 6.77; found C 74.25, H 6.69.

9-*tert*-Butyl-10-neopentyloxy-1,3-diphenyl-10-phospha-1,3-ethano-1*H*-benzopyran-4(3*H*)-one (13d): Yield: 105 mg (34%); m.p. 107 °C. − ^{1}H NMR ($CDCl_3$): δ = 0.46 [s, 9 H, $OCH_2C(CH_3)_3$], 0.73 [d, $^4J_{H-P}$ = 1.0 Hz, 9 H, $C(CH_3)_3$], 2.36 (d, $^2J_{H-P}$ = 12.1 Hz, 1 H, H at C-9), 2.94 (dd, $^1J_{H-H}$ = 8.6 Hz $^3J_{H-P}$ = 6.8 Hz, 1 H) and 3.20 [dd, $^1J_{H-H}$ = 8.6, $^3J_{H-P}$ = 2.6 Hz, 1 H, $OCH_2C(CH_3)_3$], 7.16−7.32 (m, 9 H), 7.68−7.70 (m, 2 H), 8.03−8.05 (m, 1 H), 8.42 (bd, 2 H) aryl-H. − ^{13}C NMR ($CDCl_3$): δ = 26.0 [s, $OCH_{A-B}C(CH_3)_3$], 31.9 [d, $^3J_{C-P}$ = 8.0 Hz, $C(CH_3)_3$], 32.5 [d, $^3J_{C-P}$ = 9.6 Hz, $OCH_{A-B}C(CH_3)_3$], 34.9 [s, $C(CH_3)_3$], 64.5 (d, $^1J_{C-P}$ = 32.1 Hz, C-9), 80.9 (d, $^2J_{C-P}$ = 16.0 Hz, C-a), 86.7 (s, C-3), 93.6 (d, $^1J_{C-P}$ = 24.9 Hz, C-1), 125.6 (d, J_{C-P} = 2.4 Hz), 126.9 (s), 127.4 (s), 127.7 (s), 127.8 (s), 128.3 (s), 128.4 (s), 128.7, 130.4 (s), 132.7 (s) aryl-C, 129.4 (s), 137.3 (s), C-4a, C-8a, 139.7 (d, $^3J_{C-P}$ = 6.4 Hz, C-1′), 143.7 (d, $^2J_{C-P}$ = 16.0 Hz, C-1′′), 192.7 (s, C-4). − ^{31}P NMR ($CDCl_3$): δ = 130.2 (s). − IR (CCl_4): $\tilde{\nu}$ = 2956 (s, CH), 1706 (vs, C=O), 1595 (w), 1493 (w), 1447 (m), 1207 (m), 1036 (m), 1012 (s), 837 (m), 817 (w) cm^{-1}. − MS (70 eV, EI): *m/z* (%) = 486 (0.3) $[M]^+$, 429 (13.7) $[M - tBu]^+$, 352 (100) $[M - (CH_3)_3CCH_2OP -$

H − CH_3]$^+$, 337 (22.5) [M − $(CH_3)_3CCH_2OPH$ − 2CH_3]$^+$, 298 (63.1) [$C_{21}H_{14}O_2$]$^+$, 270 (4.5) [$C_{21}H_{14}O_2$ − CO]$^+$, 221 (3.1) [$C_{21}H_{14}O_2$ − Ph]$^+$, 193 (1.2) [$C_{21}H_{14}O_2$ − PhCO]$^+$, 165 (0.7) [$C_{21}H_{14}O_2$ − PhCO − CO]$^+$, 105 (7.7) [Ph − CO]$^+$, 77 (1.2) [Ph]$^+$, 57 (0.9) [C_4H_9]$^+$. − $C_{31}H_{35}O_3P$ (486.58): calcd. C 76.54, H 7.20; found C 76.16, H 7.28.

9-*tert*-Butyl-10-isopropoxy-1,3-diphenyl-10-phospha-1,3-ethano-1*H*-benzopyran-4(3*H*)-one (13e): Yield: 110 mg (36%); m.p. 109 °C. − ^{1}H NMR ($CDCl_3$): δ = 0.59 [d, $^3J_{H-H}$ = 6.2 Hz, 3 H, CH(CH_3)$_2$], 0.88 [d, $^4J_{H-P}$ = 1.2 Hz, 9 H, C(CH_3)$_3$], 1.17 [d, $^3J_{H-H}$ = 6.2 Hz, 3 H, CH(CH_3)$_2$], 2.47 (d, $^2J_{H-P}$ = 12.1 Hz, 1 H, H at C-9), 3.79 [ds, $^3J_{H-H}$ = 6.2 Hz, $^3J_{H-P}$ = 3.3 Hz, 1 H, CH(CH$_3$)$_2$], 7.34−7.49 (m, 9 H), 7.87−7.89 (m, 2 H), 8.18−8.20 (m, 1 H), 8.55 (bd, 2 H) aryl-H. − ^{13}C NMR ($CDCl_3$): δ = 23.3 (d, $^3J_{C-P}$ = 4.6 Hz), 24.1 (d, $^3J_{C-P}$ = 3.0 Hz), C-b, C-c, 31.5 [d, $^3J_{C-P}$ = 7.7 Hz, C(CH_3)$_3$], 34.7 [s, C(CH$_3$)$_3$], 64.0 (d, $^1J_{C-P}$ = 29.7 Hz, C-9), 74.0 (d, $^2J_{C-P}$ = 16.7 Hz, C-a), 86.7 (s, C-3), 93.5 (d, $^1J_{C-P}$ = 27.6 Hz, C-1), 125.3 (d, J_{C-P} = 2.5 Hz), 126.9 (s), 127.3 (s), 127.6 (s), 127.7 (s), 128.2 (s), 128.3 (s), 128.7, 130.5 (s), 132.5 (s) aryl−C, 129.5 (s), 137.4 (s), C-4a, C-8a, 139.8 (d, $^3J_{C-P}$ = 6.9 Hz, C-1′), 143.6 (d, $^2J_{C-P}$ = 16.0 Hz, C-1′′), 192.8 (s, C-4). − ^{31}P NMR ($CDCl_3$): δ = 133.0 (s). − IR (CCl_4): ṽ = 1958 (s, CH), 1706 (vs, C=O), 1595 (m), 1493 (w), 1447 (s), 1369 (m), 1283 (w), 1223 (m), 1206 (m), 1187 (w), 1106 (w), 1035 (s), 964 (s), 864 (w), 837 (m) cm^{-1}. − MS (70 eV, EI): *m*/*z* (%) 458 (1.4) [M]$^+$, 401 (32.1) [M − *t*Bu]$^+$, 398 (26.3) [M − *i*C_3H_8OH]$^+$, 352 (94.3) [M − *i*C_3H_8OPH − CH_3]$^+$, 337 (29.4) [M − *i*C_3H_8OP − H − 2CH_3]$^+$, 298 (100) [$C_{21}H_{14}O_2$]$^+$, 270 (43.6) [$C_{21}H_{14}O_2$ − CO]$^+$, 221 (10.6) [$C_{21}H_{14}O_2$ − Ph]$^+$, 193 (8.9) [$C_{21}H_{14}O_2$ − PhCO]$^+$, 165 (11.2) [$C_{21}H_{14}O_2$ − PhCO − CO]$^+$, 105 (28.9) [Ph − CO]$^+$, 77 (33.4) [Ph]$^+$, 57 (8.9) [C_4H_9]$^+$.

9-*tert*-Butyl-10-cyclohexoxy-1,3-diphenyl-10-phospha-1,3-ethano-1*H*-benzopyran-4(3*H*)-one (13f): Yield: 85 mg (29%); m.p. 117 °C. − ^{1}H NMR ($CDCl_3$): δ = 0.88 [s, C(CH_3)$_3$], 0.90−1.68 (m, 10 H), 2.48 (d, $^2J_{H-P}$ = 12.0 Hz, 1 H, H at C-9), 3.44 (m, 1 H), 7.34−7.49 (m, 9 H), 7.87−7.89 (m, 2 H), 8.18−8.20 (m, 1 H), 8.57 (bd, 2 H) aryl-H. − ^{13}C NMR ($CDCl_3$): δ = 24.4 (d, $^5J_{C-P}$ = 5.1 Hz, C-d), 25.5 (s, C-c, C-e), 31.9 [d, $^3J_{C-P}$ = 8.0 Hz, C(CH_3)$_3$], 33.8 (d, $^3J_{C-P}$ = 3.7 Hz), 34.5 (d, $^3J_{C-P}$ = 2.9 Hz) C-b, C-f, 35.0 [s, C(CH$_3$)$_3$], 64.4 (d, $^1J_{C-P}$ = 30.5 Hz, C-9), 80.1 (d, $^2J_{C-P}$ = 15.3 Hz, C-a), 86.9 (s, C-3), 93.9 (d, $^1J_{C-P}$ = 28.4 Hz, C-1), 125.6 (d, J_{C-P} = 2.9 Hz), 127.2 (s), 127.5 (s), 127.9 (s), 128.0(s), 128.5 (s), 129.0 (s), 128.7, 130.7 (s), 132.9 (s) aryl-C, 129.7 (s), 137.8 (s), C-4a, C-8a, 140.1 (d, $^3J_{C-P}$ = 6.6 Hz, C-1′), 143.9 (d, $^2J_{C-P}$ = 16.0 Hz, C-1′′), 193.2 (s, C-4). − ^{31}P NMR ($CDCl_3$): δ = 126.1 (s). − IR (CCl_4): ṽ = 2934 (s, CH), 1706 (s, C=O), 1595 (m), 1493 (w), 1446 (s), 1369 (w), 1282 (w), 1223 (m), 1206 (m), 1187 (w), 1039 (s), 1016 (m), 977 (m), 853 (w), 837 (w), 816 (w) cm^{-1}. − MS (70 eV, EI): *m*/*z* (%) = 498 (0.2) [M]$^+$, 441 (12.3) [M − *t*Bu]$^+$, 352 (100) [M − $C_6H_{11}OP$ − H − CH_3]$^+$, 337 (27.0) [M − $C_6H_{11}OPH$ − 2CH_3]$^+$, 298 (68.3) [$C_{21}H_{14}O_2$]$^+$, 270 (7.3) [$C_{21}H_{14}O_2$ − CO]$^+$, 221 (7.2) [$C_{21}H_{14}O_2$ − Ph]$^+$, 193 (7.5) [$C_{21}H_{14}O_2$ − PhCO]$^+$, 165 (15.8) [$C_{21}H_{14}O_2$ − PhCO − CO]$^+$, 105 (36.0) [Ph − CO]$^+$, 77 (11.1) [Ph]$^+$, 57 (6.9) [C_4H_9]$^+$. − $C_{32}H_{35}O_3P$ (498.60): calcd. C 77.11, H 7.03; found C 76.72, H 6.95.

9-*tert*-Butyl-10-(2-oxopropoxy)-1,3-diphenyl-10-phospha-1,3-ethano-1*H*-benzopyran-4(3*H*)-one (14g): Yield: 160 mg (54%); m.p. 131 °C. − ^{1}H NMR ($CDCl_3$): δ = 1.0 [s, 9 H, C(CH_3)$_3$], 1.83 (s, 3 H, CH_2COCH_3), 3.43 (d, $^2J_{H-P}$ = 8.4 Hz, 1 H, H at C-9), 4.05 (dd, $^1J_{H-H}$ = 17.2 Hz, $^3J_{H-P}$ = 8.0 Hz, 1 H) and 4.15 (dd, $^2J_{H-H}$ = 17.2 Hz, $^3J_{H-P}$ = 7.1 Hz, 1 H, CH_2COCH$_3$), 7.34−7.49 (m, 9 H), 7.68−7.70 (m, 2 H), 8.06−8.08 (m, 2 H), 8.18−8.20 (bd, 1 H) aryl-H. − ^{13}C NMR ($CDCl_3$): δ = 25.5 (s, C-c), 31.3 [s, C(CH_3)$_3$], 32.5 [d, $^2J_{C-P}$ = 18.1 Hz, C(CH$_3$)$_3$], 70.2 (d, $^1J_{C-P}$ = 35.8 Hz, C-9), 74.7 (d, $^2J_{C-P}$ = 12.4 Hz, C-a), 90.9 (d, $^2J_{C-P}$ = 2.8 Hz, C-3), 92.9 (d, $^1J_{C-P}$ = 27.3 Hz, C-1), 125.6 (d, J_{C-P} = 6.6 Hz), 127.4 (s), 127.5 (s), 127.8 (s), 127.9 (s), 128.0 (d, J_{C-P} = 2.8 Hz), 128.3 (d, J_{C-P} = 2.4 Hz), 128.4 (s), 128.5 (s), 133.7 (s) aryl-C, 130.9 (d, J_{C-P} = 3.2 Hz), 139.1 (s), 140.5 (s), C-4a, C-8a, C-1′, 142.4 (d, $^2J_{C-P}$ = 22.9 Hz, C-1′′), 193.2 (s, C-5), 205.9 (s, CH_3CO). − ^{31}P NMR ($CDCl_3$): δ = 154.5 (s). − IR (CCl_4): ṽ = 2960 (m, CH), 1709 and 1693 (vs, C=O), 1596 (m), 1494 (w), 1474 (w), 1446 (m), 1357 (m), 1208 (m), 1060 (s), 850 (w), 790 (w) cm^{-1}. − MS (70 eV, EI): *m*/*z* (%) = 472 (4.3) [M]$^+$, 415 (18.9) [M − *t*Bu]$^+$, 352 (100) [M − CH_3COCH_2OP − H − CH_3]$^+$, 337 (28.6) [M − CH_3COCH_2OPH − 2CH_3]$^+$, 298 (49.8) [$C_{21}H_{14}O_2$]$^+$, 270 (2.9) [$C_{21}H_{14}O_2$ − CO]$^+$, 221 (2.0) [$C_{21}H_{14}O_2$ − Ph]$^+$, 105 (6.0) [Ph − CO]$^+$, 57 (6.9) [C_4H_9]$^+$.

9-*tert*-Butyl-10-(2-oxobutoxy)-1,3-diphenyl-10-phospha-1,3-ethano-1*H*-benzo-pyran-4(3*H*)-one (14h): Yield: 155 mg (52%); m.p. 132 °C. − ^{1}H NMR ($CDCl_3$): δ = 1.43 (dd, $^3J_{H-H}$ = 7.1, 7.3 Hz, 3 H, $OCH_2COCH_2CH_3$), 1.0 [s, 9 H, C(CH_3)$_3$], 2.02 (dq, $^2J_{H-H}$ = 18.4 Hz, $^3J_{H-H}$ = 7.3 Hz, 1 H) and 2.18 (dq, $^1J_{H-H}$ = 18.4 Hz, $^3J_{H-H}$ = 7.1 Hz, 1 H, $OCH_2COCH_2CH_3$), 3.41 (d, $^2J_{H-P}$ = 8.3 Hz, 1 H, H at C-9), 4.07 (dd, $^1J_{H-H}$ = 17.1 Hz, $^3J_{H-P}$ = 8.0 Hz, 1 H) and 4.13 (dd, $^1J_{H-H}$ = 17.1 Hz, $^3J_{H-P}$ = 7.3 Hz, 1 H, $OCH_2COCH_2CH_3$), 7.30−7.48 (m, 9 H), 7.68−7.70 (m, 2 H), 8.06−8.08 (m, 2 H), 8.18−8.20 (bd, 1 H) aryl-H. − ^{13}C NMR ($CDCl_3$): δ = 6.9 (s, C-d), 31.3 [d, $^3J_{C-P}$ = 9.4 Hz, C(CH_3)$_3$], 31.7 (s, C-c), 32.5 [d, $^2J_{C-P}$ = 18.4 Hz, C(CH$_3$)$_3$], 70.2 (d, $^1J_{C-P}$ = 35.7 Hz, C-9), 74.4 (d, $^2J_{C-P}$ = 12.5 Hz, −C-a), 90.9 (d, $^2J_{C-P}$ = 2.7 Hz, C-3), 92.8 (d, $^1J_{C-P}$ = 27.0 Hz, C-1), 125.7 (d, J_{C-P} = 4.2 Hz), 127.4 (d, J_{C-P} = 1.1 Hz), 127.5 (d, J_{C-P} = 1.4 Hz), 127.8 (s), 127.9 (s), 128.0 (s), 128.1 (s), 128.4 (s), 128.5 (s), 133.8 (s) aryl-C, 130.9 (d, J_{C-P} = 3.1 Hz), 139.1 (d, J_{C-P} = 3.8 Hz), 140.6 (s), C-4a, C-8a, C-1′, 142.6 (d, $^2J_{C-P}$ = 22.5 Hz, C-1′′), 194.0 (s, C-5), 206.6 (s, EtCO). − ^{31}P NMR ($CDCl_3$): δ = 154.3 (s). − IR (CCl_4): ṽ = 2960 (m), 1711 and 1692 (vs, C=O), 1595 (m), 1493 (w), 1446 (m), 1283 (m), 1208 (s), 1060 (s), 1020 (s), 792 (w) cm^{-1}. − MS (70 eV, EI): *m*/*z* (%) = 486 (2.1) [M]$^+$, 429 (23.3) [M − *t*Bu]$^+$, 352 (48.3) [M − $EtCOCH_2OP$ − H − CH_3]$^+$, 337 (37.8) [M − $EtCOCH_2OPH$ − 2CH_3]$^+$, 298 (100) [$C_{21}H_{14}O_2$]$^+$, 270 (5.5) [$C_{21}H_{14}O_2$ − CO]$^+$, 221 (6.2) [$C_{21}H_{14}O_2$ − Ph]$^+$, 105 (66.0) [Ph − CO]$^+$, 77 (23.2) [Ph]$^+$, 57 (15.4) [C_4H_9]$^+$.

9-*tert*-Butyl-1,3-diphenyl-10-(2-phenyl-2-oxoethoxy)-10-phospha-1,3-ethano-1*H*-benzopyran-4(3*H*)-one (14i): Yield: 155 mg (44%); m.p. 138 °C. − ^{1}H NMR ($CDCl_3$): δ = 0.96 [s, 9 H, C(CH_3)$_3$], 3.52 (d, $^2J_{H-P}$ = 8.3 Hz, 1 H, H at C-9), 4.65 (dd, $^2J_{H-H}$ = 16.7 Hz, $^3J_{H-P}$ = 8.3 Hz, 1 H) and 4.95 (dd, $^1J_{H-H}$ = 16.7 Hz, $^3J_{H-P}$ = 8.3 Hz, 1 H, OCH_2COPh), 7.30−7.55 (m, 12 H), 7.65−7.74 (m, 4 H), 7.98−8.00 (m, 2 H), 8.16−8.17 (bd, 1 H) aryl-H. − ^{13}C NMR ($CDCl_3$): δ = 31.3 [d, $^3J_{C-P}$ = 9.2 Hz, C(CH_3)$_3$], 32.6 [d, $^2J_{C-P}$ = 18.5 Hz, C(CH$_3$)$_3$], 69.4 (d, $^1J_{C-P}$ = 36.6 Hz, C-9), 74.4 (d, $^2J_{C-P}$ = 11.2 Hz, C-a), 91.3 (d, $^2J_{C-P}$ = 2.3 Hz, C-3), 93.0 (d, $^1J_{C-P}$ = 27.0 Hz, C-1), 125.7 (d, J_{C-P} = 4.5 Hz), 127.4 (s), 127.5 (d, J_{C-P} = 1.6 Hz), 127.7 (s), 127.8 (s), 127.9 (s), 128.0 (s), 128.1 (s), 128.2 (s), 128.4 (s), 128.5 (s), 128.6 (s), 133.6 (s), 134.4 (s), aryl-C, 131.0 (s), 133.6 (s), 139.3 (d, J_{C-P} = 4.1 Hz), 140.3 (s), C-4a, C-8a, C-1′, 142.7 (d, $^2J_{C-P}$ = 22.5 Hz, C-1′′), 194.0 (s, C-4), 195.1 (s, PhCO). − ^{31}P NMR ($CDCl_3$): δ = 154.0 (s). − IR (CCl_4): ṽ = 2959 (m, CH), 1701 and 1693 (vs, C=O), 1597 (m), 1446 (m), 1283 (m), 1225 (m), 1209 (m), 1110 (w), 1071 (w), 850 (w) cm^{-1}. − MS (70 eV, EI): *m*/*z* (%) = 534 (2.2) [M]$^+$, 477 (17.2) [M − *t*Bu]$^+$, 352 (46.2) [M − $PhCOCH_2OP$ − H − CH_3]$^+$, 337 (46.6) [M − $PhCOCH_2$-OPH − 2CH_3]$^+$, 298 (64.1) [$C_{21}H_{14}O_2$]$^+$, 270 (8.8) [$C_{21}H_{14}O_2$ −

$CO]^+$, 221 (8.8) $[C_{21}H_{14}O_2 - Ph]^+$, 105 (100) $[Ph - CO]^+$, 77 (30.9) $[Ph]^+$, 57 (14.2) $[C_4H_9]^+$.

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