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Stereoselective Synthesis of Phosphoranyl Aryloxiranes through the Addition of a Nucleophilic Stable Carbene to Aromatic Aldehydes

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The [2+1] addition of the stable (phosphanyl)(silyl)carbene **1** to aromatic aldehydes affords phosphoranyl aryloxiranes, a new class of polyfunctional epoxides, in high yields and excellent diastereoselectivity. No reaction is observed for aldehydes bearing strongly electron-donating groups. Theoretical calculations show a good correlation between Gibbs activation energy and the electronic nature of the substituent on the phenyl ring.

Introduction

Differently substituted aryloxiranes are interesting molecules that have proven their usefulness for a number of diverse uses. For instance, they have been used in the preparation of β-adrenergic compounds,[1] in the development of new protein tyrosine phosphatase inactivators,[2] and as components of synthetic polyol ester-based lubricating oils.[3] Aryloxiranes are also useful synthetic intermediates for the preparation of products such as sympathomimetics of the aminoethanol type,[4] some Indane derivatives,[5] and aryl 2-oxazolidinones[6] and butyrolactones.[7]

The most common methods used to synthesize aryloxiranes are the Corey−Chaykovsky reaction between an aromatic aldehyde and dimethylsulfonium methylide under traditional[8] and phase-transfer conditions,[9] along with the reductive cyclization of an α-bromomethyl aromatic ketone,[10] and the Darzens reaction, as well as other methods. A new methodology has been published that is based on the epoxidation of phenyl-substituted *trans*-alkenes with hydrogen peroxide, catalyzed by methyltrioxorhenium in the presence of 3-cyanopyridine and pyridine.[11] The effective reaction of aromatic aldehydes with aryl diazoacetate catalyzed by rhodium(II) acetate to afford aryloxiranes has been recently described by Doyle,[12] the experimental results being consistent with the intermediacy of ylide species. Previous to Doyle's work, Aggarwal satisfactorily accomplished the epoxidation of aldehydes by reaction with metal carbenes, which were intercepted by an organic sulfide in such a way that the epoxidation occurred via a sulfur ylide.[13] Otherwise, early attempts to synthesize aryloxiranes from aldehydes through metal-catalyzed reactions with diazocarbonyl compounds failed due to the competition with other side processes.[14]

Very recently, we have reported on the reactions of aliphatic aldehydes with [bis(diisopropylamino)phosphino](trimethylsilyl)carbene, **1**, which afford mixtures of alkyloxiranes and 2-alkyl-1-phosphinyl-1-silylolefins (Scheme 1).[15] The latter result from the rearrangement of an intermediate oxaphosphetene produced through a [2+2]-like cycloaddition to the carbonyl group. The ambivalent reactivity of the stable (phosphino)(silyl)carbene **1** with carbonyl derivatives is certainly due to its vinyl ylide form (Scheme 1). In contrast, although most nucleophilic carbenes, including stable *N*-hetero-

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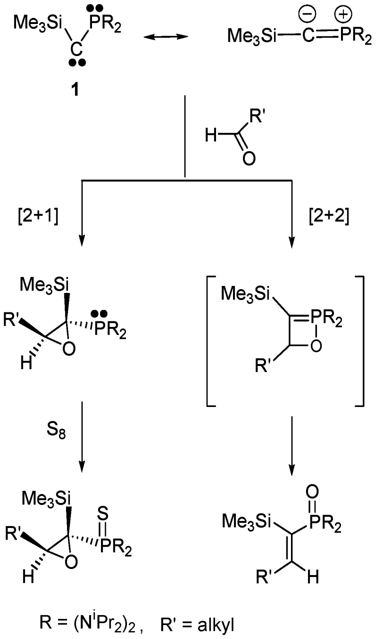
SCHEME 1



cyclic carbenes,[16] catalyze the benzoin condensation,[17] early studies showed that **1**[18] readily reacted with benzaldehyde affording the corresponding oxirane.[19]

The occurrence of the [2+2] competitive process reduces the interest of the reactions between **1** and aliphatic aldehydes for synthetic purposes. In contrast, now we report the reactions of carbene **1** with several aromatic aldehydes as a useful and efficient method for the synthesis of phosphoranyl aryloxiranes, a new class of polyfunctional epoxides. The influence of the substituents at the para position of the phenyl ring was investigated to account for electronic effects that favor or hinder the addition of the carbene and, consequently, to establish the scope of this synthetic methodology. Theoretical calculations were done to support and rationalize the experimental results.

Results and Discussion

Benzaldehyde **2** and *p*-substituted-arylaldehydes **3**−**10** (Scheme 2, X = F, Cl, Br, $C(O)CH_3$, NO_2, CF_3, CH_3, and OCH_3) reacted almost instantaneously with carbene **1** in THF solutions at room temperature to afford exclusively the corresponding phosphanyl aryloxiranes (no traces of the [2+2]-process were detected). The reactions were monitored by ^{31}P NMR reaching completion in 5−10 min. The phosphine fragment was stabilized by subsequent thiolation with elemental sulfur to afford the corresponding thioxophosphoranyl oxiranes **13**−**21**, in 65−87% yield (Scheme 2, Table 1). These compounds were purified and fully charaterized. All the resulting compounds, with the exception of **16** that is oily in nature, are solids that crystallized readily. The high stereoselectivity of the addition affording oxiranes with trans stereochemistry (with respect to the phosphino group) as single diastereoisomers is particularly noteworthy. This configuration was unambiguously assigned by X-ray diffraction analysis of suitable crystals of **13** produced from benzaldehyde[20] and was the same configuration observed for epoxides from aliphatic aldehydes.[15]

SCHEME 2

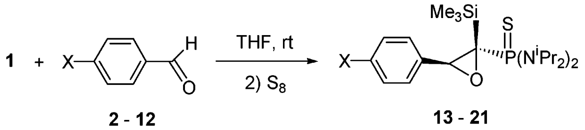


TABLE 1. Melting Points and Isolated Yields of Oxiranes from Reaction of Carbene 1 with Aromatic Aldehydes

aldehyde	oxirane	X	mp[a] (°C)	% yield[b]
2	**13**	H	142−144	80
3	**14**	F	189−190	87
4	**15**	Cl	115−116	77
5	**16**	Br	oil	70
6	**17**	$C(O)CH_3$	146−147	69
7	**18**	NO_2	146−148	72
8	**19**	CF_3	95−96	70
9	**20**	CH_3	118−120	71
10	**21**	OCH_3	124−126	65
11		$NHC(O)CH_3$		
12		$N(CH_3)_2$		

[a] From methanol solutions, except for **13** from ether−methanol. [b] Yield after crystallization.

Experimentally, the reactivity observed was similar both for aldehydes bearing strongly electron-withdrawing groups, such as nitro, acetyl, or trifluoromethyl, and for electron-donating groups such as *p*-tolualdehyde, **9**, or *p*-anisaldehyde, **10**. Nevertheless, *p*-acetamido- and *p*-dimethylaminobenzaldehyde, **11** and **12**, remained unaltered after 20 h under the reaction conditions. Calculations were done to rationalize the electronic effect of the substituents on the reactivity of the aldehydes investigated. These calculations have been done for the reactions of [bis(dimethylamino)phosphino](silyl)carbene **1′** ($Me_2N_2P\text{-}C\text{-}SiH_3$) with benzaldehyde and several para-substituted derivatives. A schematic transition state structure is shown in Figure 1 and the results are summarized in Table 2. We have only considered transition states leading to trans isomers, since they are the only experimentally observed products. For benzaldehyde, **2**, we have also located the transition state for the formation of the cis isomer with an activation Gibbs energy of 24.1 kcal mol^{-1} in the gas phase and 26.7 kcal mol^{-1} in THF solution. These values are higher than those reported in Table 2 for the trans isomer. The difference between cis and trans transition states is expected to be greater for reactions involving **1** due to its larger steric requirements. Since the X substituent

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[20] In an earlier work,[21] cis stereochemistry was attributed to compound **2** on the basis of the NMR data.

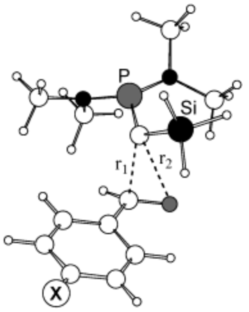

FIGURE 1. Transition state for the reaction between **1′** and an aromatic aldehyde.

TABLE 2. LUMO Energy of Aldehydes, Lengths of the Newly Created Bonds, Net Charge on the Carbene Fragment at the Transition States, and Gibbs Activation Energies Computed for the Reactions between 1′ and Aromatic Aldehydes

aldehyde	ϵ_{LUMO}[a]	r_1[b]	r_2[b]	Q[a]	$\Delta G^{\ddagger}$[c]
2	−0.0629	2.029	2.416	0.151	23.9 (24.1)
5	−0.0733	2.023	2.433	0.172	23.1 (23.2)
7	−0.1146	2.020	2.471	0.212	20.8 (21.0)
10	−0.0511	2.027	2.387	0.130	25.0 (26.2)
12	−0.0391	2.031	2.346	0.097	26.7 (28.8)

[a] In atomic units. [b] In Å. See Figure 1. [c] At 1 atm and 298.15 K in kcal mol^{-1}. Values in THF solution are given in parentheses.

in the aromatic aldehydes is remote from the carbonyl group, steric effects are not expected to vary from one aldehyde to another. The transition state geometries for all the reactions are similar. The C−C distance (r_1) ranges between 2.02 and 2.03 Å, while the C−O distance (r_2) varies within a broader range (2.37−2.47 Å). In all cases electronic charge transfer in the transition state occurs from the carbene to the aldehyde, regardless of the character of the X group, so that the most dominant frontier orbital interaction involves donation from the HOMO of the carbene to the LUMO (π^*_{CO}) of the aldehyde. The magnitude of this charge transfer correlates well with the LUMO energy. For the most electron-withdrawing aldehyde **7** (X = NO_2) the transition state has the shortest C−C and the longest C−O bond distances. In contrast, for the most weakly electron-accepting aldehyde **12** (X = $N(CH_3)_2$), the shortest C−O distance is observed, so that the reverse interaction (π_{CO} with LUMO of carbene) also plays a role. The Gibbs activation energies exhibit a good correlation with the electron-withdrawing ability of the aldehydes. The presence of electron-withdrawing groups (NO_2 and Br) lowers the value of the Gibbs activation energies with respect to benzaldehyde, whereas electron-donating groups (OCH_3 and $N(CH_3)_2$) lead to an increase. The differences in Gibbs activation energies are larger in THF solution than in the gas phase due to the polarity of the transition states. From an experimental point of view the reaction has been observed for all aldehydes except **12**, which is predicted to be the least reactive. Taking the reaction of benzaldehyde as a reference, the reaction of *p*-dimethylaminobenzaldehyde, **12**, with **1′** would be 2790 times slower at 25 °C. The ratio of the rate constants for the reaction of *p*-methoxybenzaldehyde, **10**, is only 35. These results are in qualitative agreement with the experimental observations.

Concluding Remark

The useful and efficient synthesis of a variety of phosphoranyl aryloxiranes has been accomplished in a highly stereoselective manner. The scope of this reaction is limited by the presence of strongly electron-donating groups on the aromatic ring.

Experimental Section

Computational Details. Calculations were done with the Gaussian-98 program[22] at the B3LYP/6-31G(d)[23,24] level of calculation. Geometries of reactants and transition states have been fully optimized and harmonic vibrational frequencies have been computed to define them as energy minima or transition states.[24] The effect of solvation by THF has been included by using the conductor-like screening model.[25]

General Procedure for the Synthesis of Epoxides 13−21. Aldehyde (1 equiv) was added to a THF solution (3 mL) of carbene **1**[19] (3 mmol, 1 equiv) at room temperature. The resulting mixture was stirred, and the progress of the reaction was monitored by ^{31}P NMR spectroscopy. After completion (5−10 min), an excess of elemental sulfur was added and the mixture was stirred for 2 h. The solvent was then evaporated under vacuum. The resultant oxiranes were purified by column chromatography on silica gel (hexane/ether, 9/1) and then crystallized from methanol, except **13**, **14**, and **18**, which crystallized without prior chromatography, and **16**, which was an oil. Spectroscopic data for **13** are in agreement with those previously described.[21] Data for the new compounds **14−21** follow.

(2*R*,*S*/3*R*,*S*)-2-[Bis(diisopropylamino)thioxophosphoranyl]-2-trimethylsilyl-3-[4′-fluorophenyl]oxirane, 14. Yield 220 mg, 87.4%. Mp 189−190 °C (from ether/MeOH). ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.06 (s, 9 H), 1.41−1.52 (complex absorption, 24 H), 3.95−4.25 (complex absorption, 4 H), 4.46 (d, $^3J_{P-H}$ = 8.8 Hz, 1 H), 7.06 (dd, $^3J_{F-H}$ = $^3J_{H-H}$ = 8.7 Hz, 2 H), 7.33 (dd, $^3J_{H-H}$ = 8.7 Hz, $^4J_{F-H}$ = 5.4 Hz, 2 H). ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 1.60, 23.94, 25.19, 47.80 (d, $^2J_{C-P}$ = 5.2 Hz), 49.12 (d, $^2J_{C-P}$ = 5.2 Hz), 60.95 (d, $^1J_{C-P}$ = 69.6 Hz), 61.65, 114.92 (d, $^2J_{F-C}$ = 21.5 Hz), 128.80 (d, $^3J_{F-C}$ = 7.6 Hz), 131.64, 162.47 (d, $^1J_{F-C}$ = 245.1 Hz). ^{31}P NMR (101.2 MHz, $CDCl_3$) δ 84.07. ^{19}F NMR (235.2 MHz, $CDCl_3$) δ −114.31. Anal. Calcd for $C_{23}H_{42}N_2OSiPSF$: C, 58.44; H, 8.96; N, 5.93; S, 6.78. Found: C, 58.44; H, 9.21; N, 5.90; S, 7.12.

(2*R*,*S*/3*R*,*S*)-2-[Bis(diisopropylamino)thioxophosphoranyl]-2-trimethylsilyl-3-[4′-chlorophenyl]oxirane, 15. Yield 250 mg, 77.5%. Mp 115−116 °C (from MeOH). ^{1}H NMR (250 MHz, $CDCl_3$) δ 0.02 (s, 9 H), 1.35−1.47 (complex absorption, 24 H), 3.90−4.20 (complex absorption, 4 H), 4.40 (d, $^3J_{P-H}$ = 8.8 Hz, 1 H), 7.30 (complex absorption, 4H). ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 1.67, 23.98, 25.17, 47.83 (d, $^2J_{C-P}$ = 4.8 Hz),

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49.16 (d, $^{2}J_{C-P}$ = 4.8 Hz), 61.20 (d, $^{1}J_{C-P}$ = 68.7 Hz), 61.70, 128.16, 128.56, 133.81, 134.55. ^{31}P NMR (101.2 MHz, CDCl$_3$) δ 84.31. MS, [M + Na]$^+$ 511.1

(2*R*,*S*/3*R*,*S*)-2-[Bis(diisopropylamino)thioxophosphoranyl]-2-trimethylsilyl-3-[4′-bromophenyl]oxirane, 16. Yield 200 mg, 70.0%. Yellow oil (unstable under the purification conditions). ^{1}H NMR (250 MHz, CDCl$_3$) δ 0.04 (s, 9 H), 1.51−1.64 (complex absorption, 24 H), 4.10−4.35 (complex absorption, 4 H), 4.54 (d, $^{3}J_{P-H}$ = 8.6 Hz, 1 H), 7.47−7.63 (complex absorption, 4 H). ^{13}C NMR (62.5 MHz, CDCl$_3$) δ 0.44, 23.54, 25.15, 48.04 (d, $^{2}J_{C-P}$ = 5.7 Hz), 48.60 (d, $^{2}J_{C-P}$ = 5.7 Hz), 61.02 (d, $^{1}J_{C-P}$ = 69.1 Hz), 61.64, 127.94, 131.26, 133.38, 135.42. ^{31}P NMR (101.2 MHz, CDCl$_3$) δ 83.88. MS, [M + Na]$^+$ 555.2.

(2*R*,*S*/3*R*,*S*)-2-[Bis(diisopropylamino)thioxophosphoranyl]-2-trimethylsilyl-3-[4′-acetylphenyl]oxirane, 17. Yield 190 mg, 69.1%. Mp 146−147 °C (from MeOH). ^{1}H NMR (250 MHz, CDCl$_3$) δ 0.01 (s, 9 H), 1.37−1.48 (complex absorption, 24 H), 2.60 (s, 3 H), 3.91−4.19 (complex absorption, 4 H), 4.47 (d, $^{3}J_{P-H}$ = 8.8 Hz, 1 H), 7.47 (d, $^{3}J_{H-H}$ = 8.2 Hz, 2 H), 7.92 (d, $^{3}J_{H-H}$ = 8.2 Hz, 2 H). ^{13}C NMR (62.5 MHz, CDCl$_3$) δ 1.65, 23.98, 25.17, 26.63, 47.88 (d, $^{2}J_{C-P}$ = 4.8 Hz), 49.21 (d, $^{2}J_{C-P}$ = 4.8 Hz), 61.53 (d, $^{1}J_{C-P}$ = 68.7 Hz), 61.97, 127.46, 127.96, 136.69, 197.59. ^{31}P NMR (101.2 MHz, CDCl$_3$) δ 84.00. MS, [M + Na]$^+$ 519.2.

(2*R*,*S*/3*R*,*S*)-2-[Bis(diisopropylamino)thioxophosphoranyl]-2-trimethylsilyl-3-[4′-nitrophenyl]oxirane, 18. Yield 240 mg, 72.2%. Mp 146−148 °C (from MeOH). ^{1}H NMR (250 MHz, CDCl$_3$) δ 0.02 (s, 9 H), 1.37−1.48 (complex absorption, 24 H), 3.90−4.20 (complex absorption, 4 H), 4.49 (d, $^{3}J_{P-H}$ = 8.9 Hz, 1 H), 7.55 (d, $^{3}J_{H-H}$ = 8.7 Hz, 2 H), 8.19 (d, $^{3}J_{H-H}$ = 8.7 Hz, 2 H). ^{13}C NMR (62.5 MHz, CDCl$_3$) δ 1.70, 23.96, 25.14, 47.89 (d, $^{2}J_{C-P}$ = 4.3 Hz), 49.25 (d, $^{2}J_{C-P}$ = 4.3 Hz), 61.63, 61.97 (d, $^{1}J_{C-P}$ = 68.7 Hz), 123.20, 128.13, 143.69, 147.63. ^{31}P NMR (101.2 MHz, CDCl$_3$) δ 83.20. MS, [M + Na]$^+$ 522.1.

(2*R*,*S*/3*R*,*S*)-2-[Bis(diisopropylamino)thioxophosphoranyl]-2-trimethylsilyl-3-[4′-trifluoromethylphenyl]oxirane, 19. Yield 250 mg, 70.4%. Mp 95−96 °C (from MeOH). ^{1}H NMR (250 MHz, CDCl$_3$) δ 0.01 (s, 9 H), 1.36−1.48 (complex absorption, 24 H), 3.91−4.18 (complex absorption, 4 H), 4.47 (d, $^{3}J_{P-H}$ = 8.6 Hz, 1 H), 7.49 (d, $^{3}J_{H-H}$ = 8.2 Hz, 2 H), 7.59 (d, $^{3}J_{H-H}$ = 8.2 Hz, 2 H). ^{13}C NMR (62.5 MHz, CDCl$_3$) δ 1.37, 23.71, 24.91, 47.61 (d, $^{2}J_{C-P}$ = 4.8 Hz), 49.02 (d, $^{2}J_{C-P}$ = 4.8 Hz), 61.15 (d, $^{1}J_{C-P}$ = 69.6 Hz), 61.49, 124.63 (d, $^{3}J_{C-F}$ = 3.8 Hz), 127.33, 128.7 (d, $^{1}J_{C-F}$ = 268.2 Hz), 129.97 (d, $^{2}J_{C-F}$ = 32.4 Hz), 139.92. ^{31}P NMR (101.2 MHz, CDCl$_3$) δ 83.87. ^{19}F NMR (235.2 MHz, CDCl$_3$) δ −62.93. MS, [M + Na]$^+$ 545.1.

(2*R*,*S*/3*R*,*S*)-2-[Bis(diisopropylamino)thioxophosphoranyl]-2-trimethylsilyl-3-[4′-toluyl]oxirane, 20. Yield 195 mg, 71.1%. Mp 118−120 °C (from MeOH). ^{1}H NMR (250 MHz, CDCl$_3$) δ 0.02 (s, 9 H), 1.36−1.48 (complex absorption, 24 H), 2.33 (s, 3 H), 3.92−4.21 (complex absorption, 4 H), 4.42 (d, $^{3}J_{P-H}$ = 8.6 Hz, 1 H), 7.12 (d, $^{3}J_{H-H}$ = 8.0 Hz, 2 H), 8.19 (d, $^{3}J_{H-H}$ = 8.0 Hz, 2 H). ^{13}C NMR (62.5 MHz, CDCl$_3$) δ 1.61, 21.23, 23.99, 25.20, 47.81 (d, $^{2}J_{C-P}$ = 4.7 Hz), 49.11 (d, $^{2}J_{C-P}$ = 4.7 Hz), 60.89 (d, $^{1}J_{C-P}$ = 69.6 Hz), 62.15, 127.08, 128.57, 132.83, 137.65. ^{31}P NMR (101.2 MHz, CDCl$_3$) δ 84.76. MS, [M + Na]$^+$ 491.2.

(2*R*,*S*/3*R*,*S*)-2-[Bis(diisopropylamino)thioxophosphoranyl]-2-trimethylsilyl-3-[4′-methoxyphenyl]oxirane, 21. Yield 184 mg, 65.3%. Mp 124−126 °C (from MeOH). ^{1}H NMR (250 MHz, CDCl$_3$) δ 0.05 (s, 9 H), 1.38−1.51 (complex absorption, 24 H), 3.80 (s, 3H), 3.98−4.22 (complex absorption, 4 H), 4.43 (d, $^{3}J_{P-H}$ = 8.4 Hz, 1 H), 6.87 (d, $^{3}J_{H-H}$ = 8.7 Hz, 2 H), 7.29 (d, $^{3}J_{H-H}$ = 8.7 Hz, 2 H). ^{13}C NMR (62.5 MHz, CDCl$_3$) δ 1.5, 23.87, 25.09, 47.64 (d, $^{2}J_{C-P}$ = 5.3 Hz), 48.92 (d, $^{2}J_{C-P}$ = 5.3 Hz), 55.14, 60.77 (d, $^{1}J_{C-P}$ = 69.6 Hz), 61.82, 113.24, 127.65, 128.14, 159.29. ^{31}P NMR (101.2 MHz, CDCl$_3$) δ 84.71. MS, [M + Na]$^+$ 507.2.

Crystallographic data for 13: $C_{23}H_{43}N_2OPSSi$, M_w 454.71, orthorhombic, space group *Pbca* with a = 12.598(1) Å, b = 14.212(1) Å, c = 29.344(2) Å, V = 5253.7(7) Å^3, Z = 8. 29363 reflections (5368 independent, R_{int} = 0.0523), largest electron density residue 0.310 e·Å^{-3}, R_1 (for $I > 2\sigma(I)$) = 0.0395 and wR_2 = 0.1007 (all data). Data were collected at low temperature (T = 193(2) K), using an oil-coated shock-cooled crystal on a Bruker-AXS CCD 1000 diffractometer with Mo Kα radiation (λ = 0.71073 Å). The structure was solved by direct methods (SHELXS-97)[26] and all non-hydrogen atoms were refined anisotropically, using the least-squares method on F^2.[27]

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Supporting Information Available: General experimental details; Cartesian coordinates and total energies for carbene **1′**, aldehydes **2**, **5**, **7**, **10**, and **12**, and transition states; crystal data, structure refinement, bond lengths, and angles for compound **13**; ^{1}H and ^{13}C NMR spectra of compounds **13**−**21**. This material is available free of charge via the Internet at http://pubs.acs.org.

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