Epoxidation of Enol Silyl Ethers, Phosphates, Esters, and Lactones by Dimethyldioxirane

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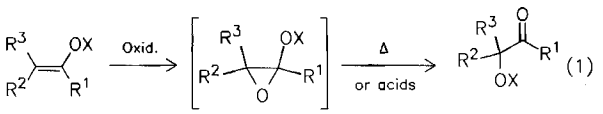
The epoxides **2a–u** (Table 1) of the enol silyl ethers **1a,b**, enol phosphates **1c–k**, and enol esters and lactones **1l–u** were prepared in excellent yields by epoxidation with isolated dimethyldioxirane (**4**) (as acetone solution). These labile epoxides (stable below 0°C) could be isolated in pure form and characterized spectroscopically (IR, ^{1}H and ^{13}C NMR). The derivatives **2p–u** were sufficiently stable so that even C,H analyses were obtained. Warming up to room temperature led to rearrangement to the corresponding α-oxy-functionalized carbonyl products **3**. Since epoxide **2c** was sufficiently resistant towards hydrolysis, it could be prepared by the in situ method.

The epoxidation of enol derivatives **1**, e.g. enol silyl ethers, enol phosphates, and enol acetates, can be problematic in view of the labile nature of the products. This is especially the case when peroxy acids are used as oxidants, because the resulting epoxides **2** readily rearrange to the α-oxy-functionalized carbonyl products **3** (eq. 1). In earlier work on enol acetates it was shown[2] that the more persistent α-acetoxy epoxides can be obtained under carefully controlled conditions and rearrangement thereby avoided. In fact, in this way the naturally occurring epoxy lactone jolkinolide B(2) could be prepared and its structure unambigously established by X-ray analysis[3a] and by total synthesis[3b].



1 2 3

X = $SiMe_3$, $P(OR)_2$, CR oxid. = RCO_3H,

4

In contrast to this, very little is known to date about epoxy phosphates, except that they readily rearrange at moderate temperatures (ca. 60°C) to the α-keto phosphate esters. Nonetheless, the stable *n*-pentyl-substituted representative **2c** (cf. Table 1) could be prepared by epoxidation with *p*-nitroperbenzoic acid, isolated in good yield, spectroscopically characterized, and shown to rearrange at elevated temperatures to the carbonyl product **3c**[4]. In this context, a little suspect appears to be the claim in a Japanese patent[5] that dehydrochlorination of a chlorohydrin by Amberlite IRA 400 in ethanol affords the corresponding epoxy phosphate; under these hydrolysis conditions the epoxy phosphate product should not survive.

The still more labile silyloxy epoxides have been of more interest during the last two decades[6]. Early attempts to epoxidize enol silyl ethers with peroxy acids had led invariably to the corresponding α-silyloxy carbonyl products. Presumably, the silyloxy epoxides were formed as intermediates; however, sterically more hindered or tetrasubstituted representatives could recently[7] be isolated in the epoxidation of enol silyl ethers by *m*-chloroperbenzoic acid (*m*-CPBA) under buffered conditions. Finally, the use of very mild and stable oxygen transfer agent oxaziridine permitted the preparation of resistant silyloxy epoxides from enol silyl ethers even at elevated temperatures[8].

In view of the fact that dimethyldioxirane (**4**) is an efficient but yet mild epoxidant[9], it was of interest to employ this remarkable reagent for the preparation of labile epoxides from enol silyl ethers, enol phosphates, and enol esters and lactones. This synthetic methodology appeared particularly promising because in isolated form (as acetone solution)[10] **4** can be readily prepared and used under nonhydrolytic conditions at low temperature. While our work was in progress[11a–c], in a preliminary report[11d] on the dimethyldioxirane epoxidation of enol silyl ethers it was demonstrated that such labile epoxides can be detected in situ by ^{1}H-NMR spectroscopy. Since reactive oxy-functionalized epoxides constitute potentially useful building blocks in synthetic chemistry, we take this opportunity to disclose the full experimental details for the preparation of the epoxides derived from enol silyl ethers, enol phosphates, and enol esters and lactones. Most of these persistent yet labile epoxides represent novel and interesting combinations of oxy functionalities, the chemistry of which remains to be explored.

Results and Discussion

The various enol derivatives **1a–u** were transformed by isolated dimethyldioxirane (**4**) into the corresponding epoxides **2** in acetone/dichloromethane as solvent in excellent yields (eq. 1). The results are shown in Table 1, in which the equivalents of **4** used, the time of epoxidation, the reaction temperature, and the yields of isolated epoxides are stated.

Most of the above described epoxides are rather labile and rearrange to the corresponding carbonyl compounds

  0009–2940/91/1010–2361 $ 3.50+.25/0

when allowed to stand at room temperature. For this reason the epoxides **2a–o** could not be purified for elemental analysis and were characterized on the basis of their spectral data (cf. Table 2). The disappearance of the C=C stretching vibration in the IR spectra without appearance of a C=O band at about 1700 cm^{-1} confirms the successful conversion of the enol derivatives **1** into their corresponding epoxides **2**. Of course, the shift to higher frequencies of the C=O stretching vibration in **2l–u** is characteristic of epoxy esters and lactones. Moreover, clearly detected are the epoxide proton signals at δ = 2.34–5.23 in the ^{1}H-NMR spectrum and the resonances at δ = 77–94 and 47–72 of the C-1 and C-2 epoxide atoms in the ^{13}C-NMR spectrum (cf. Table 2). In the case of **2n**, according to the chemical shifts of the methyl groups, the *cis* configuration (epoxide-O/4-CH_3 *cis*) is tentatively assigned to the major isomer (δ = 16.7 vs. 13.2 for the minor). Furthermore, epoxides **2l–u** exhibited small molecular ions in the mass spectra, and satisfactory elemental analyses were obtained for the stable derivatives **2p,r–u**.

The dimethyldioxirane epoxidation of enol derivatives **1a–o,q,t,u** readily proceeded at subambient temperatures (–40 to 0°C); this confirms that this dioxirane is an efficient oxygen transfer agent. For the cases **1p,r** elevated temperatures (ca. 20°C) and longer reaction times (up to 7 h) were necessary, while for **1s** a large excess of the dioxirane, ca. 20°C, and a reaction time of 88 h were necessary for its complete conversion. Particularly significant is the quantitative conversion of the enol silyl ethers **1a,b** into their epoxides **2a,b** even at –40°C, because with *N*-sulfonyloxaziridines[8] a temperature of +60°C was necessary, a re-

Table 1. Epoxidation[a] of enol derivatives **1** by dimethyldioxirane (**4**)

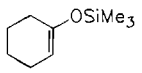
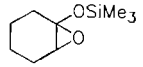
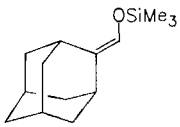
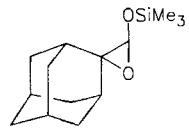
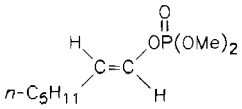
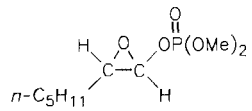
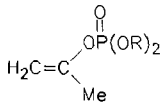
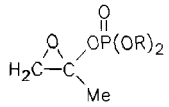
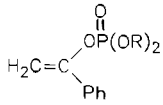
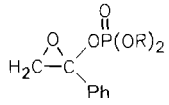
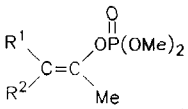
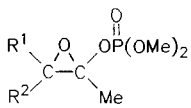
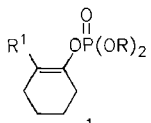
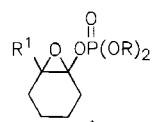
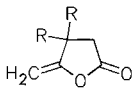
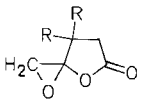
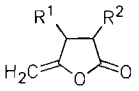
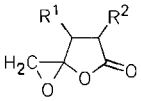
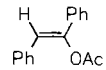
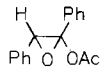
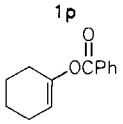
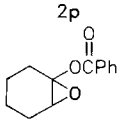
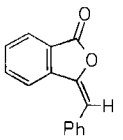
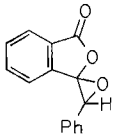
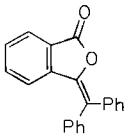
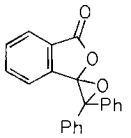
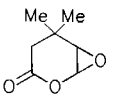
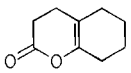
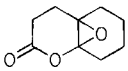
Enol	Equiv. of **4** [b]	Temp. [°C]	Time [h]	Yield (%) [c]	Epoxide
 **1a**	1.15	-40	3	99	 **2a**
 **1b**	1.43	-40	3	98	 **2b**
 **1c**	2.45	0	6	99	 **2c**
					
1d: R = Me	1.52	0	4.5	98	**2d**: R = Me
e: R = Et	1.48	0	3.5	99	**e**: R = Et
					
1f: R = Me	1.34	-10	3.5	96	**2f**: R = Me
g: R = Et	2.02	-10	2	99	**g**: R = Et
					
1h: R^1 = Me; R^2 = H [d]	1.86	-10	2.5	ca. 100	**2h**: R^1 = Me; R^2 = H [d]
i: R^1 = H; R^2 = Me [e]	1.53	-10	2.5	ca. 100	**i**: R^1 = H; R^2 = Me [e]
					
1j: R = Me; R^1 = H	1.48	0	5	ca 100	**2j**: R = Me; R^1 = H
k: R = Et; R^1 = Me	1.56	-10	3	99	**k**: R = Et; R^1 = Me

Table 6 (*Continued*)

Enol	Equiv. of **4** [b]	Temp. [°C]	Time [h]	Yield (%) [c]	Epoxide
					
1l: R = H	1.24	-20	2	91	**2l**: R = H
m: R = Me	1.40	-20	3	96	**m**: R = Me
					
1n: R^1 = Me; R^2 = H	1.28	-20	3.5	95	**2n**: R^1 = Me; R^2 = H [f]
o: R^1 = H; R^2 = Me	1.40	-20	3.5	94	**o**: R^1 = H; R^2 = Me [g]
	1.30	ca. 20	7	84	
1p					**2p**
	1.71	-20	3	96	
1q					**2q**
	1.67	ca. 20	6	ca. 100	
1r					**2r**
	9.04	ca. 20	88	ca. 100	
1s					**2s**
	1.61	-20	3	79	
1t					**2t**
	1.42	-20	3	83	
1u					**2u**

[a] In CH_2Cl_2/CH_3COCH_3 at −40 to ca. 20°C under N_2. — [b] 0.05−0.09 M in acetone. — [c] Yield of isolated pure product after evaporation of the solvent. Epoxides **2a**−**o** were not thermally stable to permit elemental analysis. — [d] *Z*/*E* ratio = 90:10. — [e] *Z*/*E* ratio = 17:83. — [f] d.r. = 60:40. — [g] d.r. = 65:35.

action temperature at which generally these thermally sensitive epoxides cannot be isolated due to rearrangement (eq. 1).

The variations in the temperature for the reactions of enol phosphates **1c**−**k** (cf. Table 1) are due to the fact that optimal temperatures were assessed at which the labile epoxides **2c**−**k** were isolated in pure form without contamination of the corresponding carbonyl compounds **3**. The epoxy phosphate **2c** is the most persistent of all cases studied herein. It is stable at ca. 20°C for 24 h without any significant decomposition or at least for one week at −20°C (monitored by ^{1}H NMR). In fact, **2c** is also quite resistant towards hydrolysis, so that the in situ method[10a] could be employed for the epoxidation of **1c**.

The expected high stereoselectivity[9] of the oxygen transfer by dimethyldioxirane is illustrated by the epoxidation of diastereomeric (*Z*,*E*)-enol phosphates **1h,i**. Although a competition experiment showed that (*Z*)-**1h** was epoxidized by dimethyldioxirane faster than (*E*)-**1i**, after complete conversion the diastereomeric composition of the enol phosphates was preserved in the corresponding epoxides.

The enol lactones **1n,o** present cases where 1,2- and 1,3-asymmetric induction may be effective since the methyl groups attached to the tetrahydrofuranone ring should ste-

Table 2. Selected ^{13}C-NMR spectral data[a] of enol derivatives **1a–u** and epoxides **2a–u** (C-1 and C-2 refer to the C=C or epoxide C atoms, resp.)

Enol derivative	^{13}C NMR C-1	C-2	Epoxide	^{13}C NMR C-1	C-2
1a	150.0	103.9	**2a**	82.0	59.8
1b	126.1	130.9	**2b**	82.5	68.0
1c	135.6	117.6	**2c**	79.3	58.2
1d	152.2	98.3	**2d**	81.8	52.4
1e	151.9	97.7	**2e**	82.0	54.5
1f	152.3	97.2	**2f**	83.2	55.1
1g	152.3	97.3	**2g**	83.1	55.0
1h	145.0	109.0	**2h**	85.7	58.8
1i	144.5	109.5	**2i**	85.7	59.3
1j	147.7	110.5	**2j**	84.2	58.5
1k	141.5	118.7	**2k**	88.7	61.3
1l	155.9	88.6	**2l**	88.3	50.4
1m	166.0	85.7	**2m**	93.6	47.7
1n	161.9	87.5	**2n**	92.3 (90.3[b])	48.8 (48.2[b])
1o	154.6	88.4	**2o**	86.3 (86.9[b])	49.5 (50.9[b])
1p	146.6	116.7	**2p**	85.6	65.6
1q	148.6	114.3	**2q**	83.4	59.3
1r	144.4	107.0	**2r**	90.0	64.3
1s	142.4	124.8	**2s**	92.9	72.1
1t	139.0	116.8	**2t**	77.8	58.3
1u	146.1	109.6	**2u**	87.0	61.5

[a] Cf. Experimental for details. – [b] Values in parentheses for minor diastereomers.

rically hinder the *syn* transfer of oxygen. In fact, 60:40 and 65:35 ratios of diastereomeric epoxide products were registered, which parallel results of nitrile oxide cycloadditions to these substrates[12] (53:47 and 83:17, to **1n** and **1o**). This may reflect the particular situation of conformational equilibria of these enol lactones, but indicates also that the transition state of dimethyldioxirane epoxidations shows little steric demand.

The epoxides of enol esters and lactones are more resistant than those of the enol phosphates and enol silyl ethers, but they require more rigorous conditions in their preparation by dioxirane epoxidation. The long reaction time of 88 h used for the complete conversion of **1s** into **2s** is remarkable since generally tetrasubstituted alkenes are epoxidized fastest by dioxiranes as well as peracids. The reduced reactivity of enol lactone **1s** is presumably caused by the steric hindrance and electronic deactivation of the C=C bond of the *exo*-diphenylmethylene moiety.

The rearrangement of the epoxides of enol silyl ethers and enol esters and lactones is well documented[13]. Indeed, the acid-catalyzed rearrangement of silyloxy-substituted epoxides[6] constitutes an important synthetic route for the preparation of α-hydroxy compounds in the peracid oxidation of enol silyl ethers (eq. 1). Also, we observed that the two silyloxy epoxides **2a,b** rearranged on standing at room temperature to the corresponding α-oxy-functionalized derivatives **3a,b** (detected by NMR), but this aspect was not pursued further.

Analogously, the epoxy phosphates **2d–i** rearranged on standing overnight at room temperature to the corresponding α-dialkoxyphosphinyloxy-substituted carbonyl products **3d–h** (eq. 1). These were isolated in 53–83% yield, and their ^{1}H- and ^{13}C-NMR spectral data were in agreement with those reported (cf. Experimental). As expected, also the labile spiroepoxides **2l–o** decomposed when allowed to stand at room temperature for several days, but the details of this behavior need to be elucidated.

In summary, we have shown that dimethyldioxirane (**4**) is an effective oxidant for the preparation of labile epoxides **2** of enol derivatives **1**, which include enol silyl ethers, enol phosphates, and enol esters and lactones. Stored at sufficiently low temperatures, the rearrangement of these new epoxides into the α-oxy-functionalized carbonyl products **3** (eq. 1) can be sufficiently suppressed, and thereby they can be made available as potentially useful building blocks in synthetic chemistry.

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Experimental

Melting points (uncorrected): Reichert Thermovar hot stage apparatus. – Bulb-to-bulb distillation refers to horizontal short-path distillation in which the crude material was heated in a Büchi Kugelrohr oven. The temperature of the air chamber during distillation is reported as the boiling point. – IR: Perkin-Elmer 1420. – ^{1}H and ^{13}C NMR: Bruker AC 200 (200 MHz) or Bruker AC 250 (250 MHz); chemical shifts refer to $CDCl_3$, [D_6]benzene, or [D_6]acetone. If not stated otherwise, all NMR measurements were performed at room temp. (ca. 20°C). – MS: Varian MAT CH-7.

All solvents were purified according to standard literature methods. Acetone, butanone, and water, used in the preparation of dioxiranes, were distilled twice from EDTA. Potassium monoperoxosulfate, the triple salt 2 $KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$, was used as received from Degussa AG [Caroate®] or Peroxid-Chemie GmbH [Curox®].

3,4-Dihydro-4,4-dimethyl-2*H*-pyran-2-one (**1t**) was commercially available; 1-(trimethylsilyloxy)-1-cyclohexene[14] (**1a**), (trimethylsilyloxymethylene)adamantane[15] (**1b**), (*E*)-1-[(dimethoxyphosphinyl)oxy]-1-heptene[4] (**1c**), 1-[(dimethoxyphosphinyl)oxy]-1-methylethylene[16] (**1d**), 1-[(diethoxyphosphinyl)oxy]-1-methylethylene[17] (**1e**), 1-[(dimethoxyphosphinyl)oxy]-1-phenylethylene[18] (**1f**), 1-[(diethoxyphosphinyl)oxy]-1-phenylethylene[16] (**1g**), (*Z*)-1-[(dimethoxyphosphinyl)oxy]-1,2-dimethylethylene[19] (**1h**), (*E*)-1-[(dimethoxyphosphinyl)oxy]-1,2-dimethylethylene[19] (**1i**), 1-[(dimethoxyphosphinyl)oxy]-1-cyclohexene[20] (**1j**), 1-[(diethoxyphosphinyl)oxy]-2-methyl-1-cyclohexene[18] (**1k**), γ-methylene-γ-butyrolactones[21] (**1l–o**), (*Z*)-α-acetoxystilbene[2c] (**1p**), 1-cyclohexen-1-yl benzoate[22] (**1q**), (*E*)-3-benzylidenephthalide[23] (**1r**), 3-benzhydrylideneisobenzofuran-1(3*H*)-one[24] (**1s**) and 2-oxabicyclo[4.4.0]dec-1(6)-en-3-one[25] (**1u**) were prepared by standard literature procedures. Dimethyldioxirane (**4**) (as acetone solution) was prepared according to the published procedure[10a]; the peroxide content was determined by oxidation of methyl phenyl sulfide, the latter quantitatively by ^{1}H-NMR spectrometry. The dimethyldioxirane solutions were stored over molecular sieves (4 Å) at –20°C.

General Procedure for the Epoxidation of Enol-Type Substrates: A solution of dimethyldioxirane (**4**) (1.1–3.5 equiv.) in acetone

(0.050–0.087 M), dried with molecular sieves (4 Å) at −20°C, was rapidly added to a cooled and stirred solution of **1a–u** (0.50–1.13 mmol) in absolute CH_2Cl_2 (10 ml) under N_2 (for specific conditions cf. Table 1). Stirring was continued until complete consumption of the enol-type substrate except for derivative **1s**, for which additional batches of dioxirane **4** and further stirring were necessary to achieve complete conversion. The solvent was removed in vacuo (0 to ca. 20°C/15 Torr) to yield the labile epoxides **2a–u** in excellent yields and with high purity (IR, ^1H NMR). At room temp. (ca. 20°C) most of these labile epoxides decomposed rapidly.

1-(Trimethylsilyloxy)-7-oxabicyclo[4.1.0]heptane (**2a**), 134 mg (99%) was isolated as a colorless liquid according to the above procedure at −40°C for 3 h, in which a total of 10 ml of 0.084 M (0.084 mmol) dioxirane **4** and 124 mg (0.73 mmol) of 1-(trimethylsilyloxy)-1-cyclohexene (**1a**) were employed. – IR (CCl_4): $\tilde{\nu}$ = 2960 (w) cm^{-1}, 2860 (w), 1450 (w), 1435 (w), 1365 (m), 1250 (m), 1220 (s), 1180 (m), 1120 (m), 1070 (w), 985 (w), 975 (m), 965 (m), 920 (w), 890 (m), 870 (m), 850 (m), 660 (w). – ^1H NMR (200 MHz, C_6D_6): δ = 0.26–0.30 (m, 9H), 1.01–1.05 (m, 1H), 1.22–1.39 (m, 3H), 1.56–1.64 (m, 2H), 3.11–3.14 (m, 1H). – ^{13}C NMR (50 MHz, C_6D_6): δ = 1.2, 20.1, 21.0, 25.3, 31.5, 59.8, 82.0.

3'-(Trimethylsilyloxy)spiro[adamantan-2,2'-oxirane] (**2b**): Obtained as described above, 166 mg (98%), colorless liquid, from 13 ml of 0.074 M (0.96 mmol) dioxirane **4** and 159 mg (0.67 mmol) of **1b** at −40°C for 3 h. – IR (CCl_4): $\tilde{\nu}$ = 2920 (w) cm^{-1}, 2850 (m), 1450 (m), 1375 (m), 1280 (m), 1260 (m), 1250 (s), 1210 (m), 1160 (m), 1130 (s), 1115 (m), 1100 (m), 1080 (m), 1030 (w), 975 (m), 920 (m), 890 (m), 870 (s), 845 (s), 665 (w). – ^1H NMR (200 MHz, C_6D_6): δ = 0.26 (s, 9H), 1.32–2.23 (m, 14H), 4.67 (s, 1H). – ^{13}C NMR (50 MHz, C_6D_6): δ = 0.2, 27.5, 28.2, 30.7, 34.3, 35.1, 35.5, 36.4, 37.0, 68.0, 82.5.

(E)-2-[(Dimethoxyphosphinyl)oxy]-3-pentyloxirane (**2c**): 234 mg (99%), colorless liquid, obtained from 30 ml of 0.081 M (2.43 mmol) dioxirane **4** and 220 mg (0.99 mmol) of **1c** at 0°C for 6 h. – IR (CCl_4): $\tilde{\nu}$ = 2970 (w) cm^{-1}, 2940 (m), 2860 (m), 1460 (w), 1305 (m), 1290 (m), 1195 (w), 1120 (m), 1060 (s), 930 (w), 890 (m), 865 (m). – ^1H NMR (200 MHz, C_6D_6): δ = 0.73–0.79 (m, 3H), 1.06–1.16 (m, 8H), 2.98–3.03 (m, 1H), 3.40–3.53 (m, 6H), 5.02 (dd, J_1 = 3.26, J_2 = 0.69 Hz, 1H). – ^{13}C NMR (50 MHz, C_6D_6): δ = 14.1 (CH_3CH_2), 22.7 (CH_2), 25.0 (CH_2), 29.4 (CH_2), 31.5 (CH_2CHO), 54.0 (d, $J_{C,P}$ = 2.96 Hz, OCH_3), 54.1 (d, $J_{C,P}$ = 2.70 Hz, OCH_3), 58.2 (d, $J_{C,P}$ = 6.85 Hz, CH_2CHO), 79.3 (d, $J_{C,P}$ = 4.53 Hz, OCHO).

2-[(Dimethoxyphosphinyl)oxy]-2-methyloxirane (**2d**): 170 mg (98%), colorless liquid, obtained from 20 ml of 0.072 M (1.44 mmol) dioxirane and 158 mg (0.95 mmol) of **1d** at 0°C for 4.5 h. – IR (CCl_4): $\tilde{\nu}$ = 3010 (w) cm^{-1}, 2960 (m), 2860 (w), 1400 (w), 1360 (w), 1300 (m), 1280 (m), 1220 (m), 1190 (m), 1110 (m), 1095 (m), 1055 (s), 1030 (s), 990 (m), 910 (w), 890 (w), 875 (m), 860 (m). – ^1H NMR (200 MHz, C_6D_6): δ = 1.62 (d, J = 0.47 Hz, 3H), 2.57 (dd, J_1 = 4.24, J_2 = 0.70 Hz, 1H), 3.12 (d, J = 4.24 Hz, 1H), 3.62 (d, J = 4.51 Hz, 3H), 3.63 (d, J = 4.51 Hz, 3H). – ^{13}C NMR (50 MHz, C_6D_6): δ = 20.4 (d, $J_{C,P}$ = 2.13 Hz, $OCCH_3$), 52.4 (d, $J_{C,P}$ = 4.51 Hz, CH_2O), 54.1 (d, $J_{C,P}$ = 3.00 Hz, OCH_3), 54.2 (d, $J_{C,P}$ = 3.21 Hz, OCH_3), 81.8 (d, $J_{C,P}$ = 5.97 Hz, $OCCH_3$).

2-[(Diethoxyphosphinyl)oxy]-2-methyloxirane (**2e**): 140 mg (99%), colorless liquid, obtained from 15 ml of 0.066 M (0.99 mmol) dioxirane **4** and 130 mg (0.67 mmol) of **1e** at 0°C for 3.5 h. – IR (CCl_4): $\tilde{\nu}$ = 2980 (w) cm^{-1}, 2930 (w), 2910 (w), 1400 (w), 1390 (w), 1370 (w), 1360 (w), 1270 (m), 1215 (m), 1165 (m), 1105 (m), 1090 (m), 1035 (s), 980 (m), 890 (w), 870 (w). – ^1H NMR (200 MHz, C_6D_6): δ = 0.99–1.10 (m, 6H), 1.57 (d, J = 0.57 Hz, 3H), 2.34 (d, J = 4.39 Hz, 1H), 3.17 (dd, J_1 = 4.39, J_2 = 0.69 Hz, 1H), 3.83–4.00 (m, 4H). – ^{13}C NMR (50 MHz, C_6D_6): δ = 16.1 (t, J = 7.10 Hz, OCH_2CH_3), 20.9 ($OCCH_3$), 54.5 (d, $J_{C,P}$ = 3.02 Hz, CH_2O), 63.3 (d, $J_{C,P}$ = 5.75 Hz, OCH_2CH_3), 63.8 (dd, J_1 = 3.49, J_2 = 1.90 Hz, OCH_2CH_3), 82.0 (d, $J_{C,P}$ = 4.93 Hz, $OCCH_3$).

2-[(Dimethoxyphosphinyl)oxy]-2-phenyloxirane (**2f**): 213 mg (97%), colorless liquid, obtained from 15 ml of 0.080 M (1.20 mmol) dioxirane **4** and 206 mg (0.90 mmol) of **1f** at −10°C for 3.5 h. – IR (CCl_4): $\tilde{\nu}$ = 3080 (w) cm^{-1}, 3010 (w), 2970 (w), 2880 (w), 1450 (m), 1370 (w), 1305 (m), 1285 (m), 1250 (m), 1190 (m), 1065 (s), 1035 (m), 1015 (m), 1005 (m), 970 (m), 920 (m), 865 (m), 705 (m). – ^1H NMR (200 MHz, C_6D_6): δ = 2.52 (dd, J_1 = 4.59, J_2 = 0.58 Hz, 1H), 3.41 (dd, J_1 = 11.50, J_2 = 6.42 Hz, 6H), 3.69 (dd, J_1 = 4.59, J_2 = 0.73 Hz, 1H), 7.09–7.17 (m, 3H), 7.49–7.53 (m, 2H). – ^{13}C NMR (50 MHz, C_6D_6): δ = 54.1 (t, $J_{C,P}$ = 6.89 Hz, OCH_3), 55.1 (d, $J_{C,P}$ = 3.02 Hz, CH_2O), 83.2 (d, $J_{C,P}$ = 7.90 Hz, $OCCH_3$), 126.3 (arom.), 128.7 (arom.), 129.4 (arom.), 136.0 (d, $J_{C,P}$ = 4.73 Hz, arom.).

2-[(Diethoxyphosphinyl)oxy]-2-phenyloxirane (**2g**): 176 mg (99%) colorless liquid, obtained from 15 ml of 0.087 M (1.31 mmol) dioxirane **4** and 167 mg (0.65 mmol) of **1g** at −10°C for 2 h. – IR (CCl_4): $\tilde{\nu}$ = 3090 (w) cm^{-1}, 3060 (w), 3020 (m), 2950 (w), 2930 (w), 1500 (m), 1470 (m), 1415 (m), 1395 (m), 1310 (s), 1280 (m), 1190 (m), 1160 (m), 1120 (m), 1100 (s), 1080 (s), 1040 (s), 940 (m), 860 (m), 720 (m). – ^1H NMR (200 MHz, C_6D_6): δ = 1.05 (tq, J_1 = 7.04, J_2 = 1.06 Hz, 6H), 2.61 (dd, J_1 = 4.67, J_2 = 0.26 Hz, 1H), 4.67 (dd, J_1 = 4.67, J_2 = 0.64 Hz, 1H), 3.92–4.04 (m, 4H), 7.16–7.25 (m, 3H), 7.60–7.65 (m, 2H). – ^{13}C NMR (50 MHz, C_6D_6): δ = 15.9 (d, $J_{C,P}$ = 7.35 Hz, OCH_2CH_3), 55.0 (d, $J_{C,P}$ = 3.47 Hz, CH_2O), 64.0 (t, $J_{C,P}$ = 6.94 Hz, OCH_2CH_3), 83.1 (d, $J_{C,P}$ = 5.74 Hz, OCPh), 126.4 (arom.), 128.6 (arom.), 129.3 (arom.), 136.3 (arom.).

(Z)-2-[(Dimethoxyphosphinyl)oxy]-2,3-dimethyloxirane (**2h**): 219 mg (ca. 100%), *Z*/*E* 90:10, colorless liquid, obtained from 20 ml of 0.084 M (1.67 mmol) dioxirane **4** and 201 mg (0.90 mmol) of **1h** at −10°C for 2.5 h. – IR (CCl_4): $\tilde{\nu}$ = 3010 (w) cm^{-1}, 2970 (w), 2950 (w), 2850 (w), 1450 (w), 1385 (w), 1375 (w), 1320 (w), 1290 (m), 1270 (m), 1230 (m), 1185 (m), 1120 (m), 1095 (m), 1040 (s), 1000 (s), 975 (m), 905 (m), 880 (w), 850 (w). – ^1H NMR (200 MHz, C_6D_6): δ = 0.88 (d, J = 5.52 Hz, 3H), 1.52 (d, J = 0.32 Hz, 3H), 3.36–3.49 (m, 7H). – ^{13}C NMR (50 MHz, C_6D_6): δ = 13.4 (CH_3CHO), 17.2 (d, $J_{C,P}$ = 1.96 Hz, CH_3CO), 53.8 (d, $J_{C,P}$ = 2.72 Hz, OCH_3), 53.9 (d, $J_{C,P}$ = 2.97 Hz, OCH_3), 58.8 (d, $J_{C,P}$ = 4.08 Hz, CH_3CHO), 85.7 (d, $J_{C,P}$ = 5.74 Hz, CH_3CO).

(E)-2-[(Dimethoxyphosphinyl)oxy]-2,3-dimethyloxirane (**2i**): 149 mg (ca. 100%), *Z*/*E* 17:83, colorless liquid, obtained from 15 ml of 0.077 M (1.16 mmol) dioxirane **4** and 137 mg (0.76 mmol) of **1i** at −10°C for 2.5 h. – IR (CCl_4): $\tilde{\nu}$ = 3040 (w) cm^{-1}, 2995 (m), 2880 (w), 1505 (w), 1465 (m), 1400 (m), 1300 (s), 1220 (m), 1205 (m), 1160 (m), 1130 (m), 1115 (m), 1060 (s), 1010 (s), 990 (s), 930 (m), 890 (m), 870 (s), 640 (w). – ^1H NMR (200 MHz, C_6D_6): δ = 1.21 (d, J = 5.34 Hz, 3H), 1.65 (s, 3H), 2.47 (dq, J_1 = 5.34, J_2 = 1.48 Hz, 1H), 3.34–3.49 (m, 6H). – ^{13}C NMR (50 MHz, C_6D_6): δ = 13.0 (CH_3CHO), 21.2 (CH_3CO), 53.8 (d, $J_{C,P}$ = 4.03 Hz, OCH_3), 53.9 (d, $J_{C,P}$ = 6.19 Hz, OCH_3), 59.3 (d, $J_{C,P}$ = 6.09 Hz, CH_3CHO), 85.7 (d, $J_{C,P}$ = 6.09 Hz, CH_3CO).

1-[(Dimethoxyphosphinyl)oxy]-7-oxabicyclo[4.1.0]heptane (**2j**): 162 mg (ca. 100%), colorless liquid, obtained from 15 ml of 0.072 M (1.08 mmol) dioxirane **4** and 151 mg (0.73 mmol) of **1j** at 0°C for 5 h. – IR (CCl_4): $\tilde{\nu}$ = 2970 (w) cm^{-1}, 2860 (m), 1460 (m), 1450 (m), 1435 (m), 1370 (m), 1345 (w), 1300 (m), 1285 (m), 1200 (m), 1185 (m), 1170 (m), 1100 (m), 1080 (m), 1055 (s), 1020 (m), 980 (m), 930 (m),

920 (m), 900 (m), 890 (m), 860 (m), 670 (w). – ^{1}H NMR (200 MHz, C_6D_6): δ = 1.17–2.26 (m, 8H), 3.48 (d, J = 3.59 Hz, 1H), 3.63 (dd, J_1 = 11.40, J_2 = 2.34 Hz, 6H). – ^{13}C NMR (50 MHz, C_6D_6): δ = 18.8, 19.9, 24.0, 28.4, 54.0 (d, $J_{C,P}$ = 2.95 Hz), 54.1 (d, $J_{C,P}$ = 2.95 Hz), 58.5 (d, $J_{C,P}$ = 4.15 Hz), 84.2 (d, $J_{C,P}$ = 6.60 Hz).

1-[(Diethoxyphosphinyl)oxy]-6-methyl-7-oxabicyclo[4.1.0]heptane (**2k**): 165 mg (99%), colorless liquid, obtained from 12 ml of 0.082 M (0.98 mmol) dioxirane **4** and 157 mg (0.63 mmol) of **1k** at −10°C for 3 h. – IR (CCl_4): $\tilde{\nu}$ = 2990 (w) cm^{-1}, 2950 (m), 2870 (w), 1450 (w), 1440 (w), 1390 (w), 1380 (w), 1370 (w), 1360 (w), 1260 (m), 1250 (m), 1215 (w), 1190 (m), 1170 (m), 1150 (m), 1100 (w), 1040 (s), 980 (s), 920 (m), 890 (w), 660 (w). – ^{1}H NMR (250 MHz, C_6D_6): δ = 0.90 (dt, J_1 = 7.07, J_2 = 0.93 Hz, 6H), 0.96–1.15 (m, 2H), 1.20 (s, 3H), 1.25–1.49 (m, 2H), 1.98–2.13 (m, 2H), 2.32–2.43 (m, 2H), 3.72–3.93 (m, 4H). – ^{13}C NMR (63 MHz, C_6D_6): δ = 16.1 (d, $J_{C,P}$ = 6.54 Hz, OCH_2CH_3), 19.0 (CH_3CO), 20.3 (CH_2), 21.1 (CH_2), 29.8 (CH_2), 30.8 (CH_2), 61.3 (d, $J_{C,P}$ = 5.09 Hz, CH_3CO), 63.5 (d, $J_{C,P}$ = 3.46 Hz, OCH_2CH_3), 63.6 (d, $J_{C,P}$ = 3.77 Hz, OCH_2CH_3), 88.7 (d, $J_{C,P}$ = 6.14 Hz, OCO).

1,4-Dioxaspiro[2.4]heptan-5-one (**2l**): 110 mg (91%), colorless liquid, obtained from 25 ml of 0.052 M (1.31 mmol) dioxirane **4** and 104 mg (1.06 mmol) of **11** at −20°C for 2 h. – IR (CCl_4): $\tilde{\nu}$ = 3070 (w) cm^{-1}, 3010 (w), 2950 (w), 1815 (s), 1500 (m), 1450 (m), 1420 (m), 1405 (m), 1290 (s), 1260 (m), 1185 (m), 1165 (m), 1135 (s), 1115 (s), 1050 (w), 960 (s), 910 (s), 880 (m), 840 (m). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.32–2.43 (m, 1H), 2.67–3.01 (m, 3H), 2.97 and 3.31 (AB system, J = 3.72 Hz, 2H). – ^{13}C NMR (63 MHz, $CDCl_3$): δ = 26.0 (t), 28.1 (t), 50.4 (t), 88.3 (s), 174.1 (s). – MS (70 eV): m/z (%) = 114 (8) [M^+], 96 (8) [$M^+ - H_2O$], 86 (5) [$M^+ - CO$], 85 (32) [$M^+ - CHO$], 84 (19) [$M^+ - CH_2O$], 68 (4) [$M^+ - CH_2O_2$], 56 (100) [$M^+ - C_2O_2$], 42 (60) [$M^+ - C_3H_4O_2$], 29 (25) [$M^+ - C_4H_5O_2$], 28 (95) [$M^+ - C_4H_6O_2$].

7,7-Dimethyl-1,4-dioxaspiro[2.4]heptan-5-one (**2m**): 145 mg (96%), colorless liquid, obtained from 20 ml of 0.074 M (1.48 mmol) dioxirane **4** and 134 mg (1.06 mmol) of **1m** at −20°C for 3 h. – IR (CCl_4): $\tilde{\nu}$ = 3070 (w) cm^{-1}, 2980 (w), 2940 (w), 1820 (s), 1490 (m), 1420 (w), 1400 (w), 1380 (w), 1250 (w), 1230 (m), 1210 (m), 1200 (m), 1120 (w), 1090 (s), 1020 (w), 980 (m), 925 (s), 880 (w). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.11 (s, 3H), 1.25 (s, 3H), 2.54 and 2.71 (AB system, J = 17.43 Hz, 2H), 2.95 and 3.23 (AB system, J = 3.53 Hz, 2H). – ^{13}C NMR (63 MHz, $CDCl_3$): δ = 21.7 (q), 25.4 (q), 37.3 (s), 42.8 (t), 47.7 (t), 93.6 (s), 173.1 (s). – MS (70 eV): m/z (%) = 142 (0.3) [M^+], 113 (3) [$M^+ - CHO$], 99 (0.5) [$M^+ - C_2H_2O$], 83 (5) [$M^+ - C_2H_3O_2$], 70 (7) [$M^+ - C_3H_4O_2$], 56 (100) [$M^+ - C_3H_2O_3$], 42 (15) [$M^+ - C_3H_4O_3$], 41 (40) [$M^+ - C_3H_5O_3$], 39 (16) [$M^+ - C_3H_7O_3$], 28 (13) [$M^+ - C_6H_{10}O_2$].

7-Methyl-1,4-dioxaspiro[2.4]heptan-5-one (**2n**): 138 mg (95%), d.r. 60:40, colorless liquid, obtained from 20 ml of 0.073 M (1.46 mmol) dioxirane **4** and 127 mg (1.13 mmol) of **1n** at −20°C for 3.5 h. – IR (CCl_4): $\tilde{\nu}$ = 3060 (w) cm^{-1}, 2960 (w), 2920 (w), 1810 (s), 1480 (w), 1440 (w), 1410 (w), 1390 (w), 1370 (w), 1280 (w), 1250 (w), 1220 (m), 1165 (w), 1150 (w), 1130 (m), 1115 (s), 1070 (w), 1010 (m), 960 (m), 910 (m). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.05 and 1.21 (2 d, J = 6.87 and 7.16 Hz, 3H, CH_3 of minor and major isomers), 2.35–3.12 (m, 3H), 2.93, 3.30 and 3.02, 3.20 (AB of minor and major isomers, J = 3.59 and 3.64 Hz, 2H). – ^{13}C NMR (63 MHz, $CDCl_3$): major isomer, δ = 16.7 (q), 33.2 (d), 36.3 (t), 48.8 (t), 92.3 (s), 173.6 (s); minor isomer, δ = 13.2 (q), 31.7 (t), 35.7 (d), 48.2 (t), 90.3 (s), 173.4 (s). – MS (70 eV): m/z (%) = 128 (0.6) [M^+], 110 (0.4) [$M^+ - O$], 99 (6) [$M^+ - CHO$], 70 (24) [$M^+ - C_2H_2O_2$], 69 (5) [$M^+ - C_2H_3O_2$], 56 (16) [$M^+ - C_3H_4O_2$], 43 (15) [$M^+ - C_3H_2O_3$], 42 (100) [$M^+ - C_3H_2O_3$], 41 (25) [$M^+ - C_3H_3O_3$], 39 (14) [$M^+ - C_3H_5O_3$].

6-Methyl-1,4-dioxaspiro[2.4]heptan-5-one (**2o**): 125 mg (94%), d.r. 65:35, colorless liquid, obtained from 15.5 ml of 0.074 M (1.15 mmol) dioxirane **4** and 117 mg (1.04 mmol) of **1o** at −20°C for 3.5 h. – IR (CCl_4): $\tilde{\nu}$ = 3070 (w) cm^{-1}, 2980 (w), 2940 (w), 1815 (s), 1490 (w), 1455 (w), 1445 (w), 1405 (w), 1380 (w), 1330 (w), 1285 (w), 1240 (w), 1140 (m), 1130 (m), 1095 (m), 1085 (m), 1035 (m), 970 (m), 940 (m), 870 (m). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.37 and 1.42 (2 d, J = 7.21 and 7.22 Hz, 3H, CH_3 of major and minor isomers), 2.10–3.17 (m, 3H), 2.94, 3.25 and 2.96, 3.31 (AB of minor and major isomers, J = 3.90 and 3.63 Hz, 2H). – ^{13}C NMR (63 MHz, $CDCl_3$): major isomer, δ = 15.5 (q), 34.4 (d), 34.6 (t), 49.5 (t), 86.3 (s), 177.4 (s); minor isomer, δ = 16.4 (q), 33.9 (t), 35.6 (d), 50.9 (t), 86.9 (s), 176.8 (s). – MS (70 eV): m/z (%) = 128 (1) [M^+], 110 (0.5) [$M^+ - O$], 99 (6) [$M^+ - CHO$], 70 (19) [$M^+ - C_2H_2O_2$], 69 (7) [$M^+ - C_2H_3O_2$], 56 (15) [$M^+ - C_3H_4O_2$], 43 (17) [$M^+ - C_3HO_3$], 42 (100) [$M^+ - C_3H_2O_3$], 41 (28) [$M^+ - C_3H_3O_3$], 39 (15) [$M^+ - C_3H_5O_3$].

(Z)-2-Acetoxy-2,3-diphenyloxirane (**2p**): 106 mg (84%), colorless needles, m.p. 61–62°C (from $CHCl_3$/petroleum ether), obtained from 10 ml of 0.073 M (0.73 mmol) dioxirane **4** and 118 mg (0.50 mmol) of **1p** at ca. 20°C for 7 h. – IR (CCl_4): $\tilde{\nu}$ = 3080 (w) cm^{-1}, 3040 (w), 1770 (s), 1500 (w), 1455 (w), 1450 (w), 1370 (m), 1280 (w), 1220 (s), 1200 (m), 1190 (s), 1115 (m), 1040 (m), 1025 (m), 975 (m), 915 (m), 895 (w), 705 (s), 675 (m). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.90 (s, 3H), 4.16 (s, 1H), 7.31–7.43 (m, 8H), 7.44–7.52 (m, 2H). – ^{13}C NMR (63 MHz, $CDCl_3$): δ = 20.6 (q), 65.6 (d), 85.6 (s), 125.7 (d), 127.0 (d), 128.1 (d), 128.6 (d), 128.7 (d), 129.1 (d), 133.1 (s), 135.5 (s), 168.8 (s). – MS (70 eV): m/z (%) = 238 (0.1) [$M^+ - O$], 212 (1) [$M^+ - C_2H_2O$], 211 (6) [$M^+ - C_2H_3O$], 196 (2) [$M^+ - C_2H_2O_2$], 167 (2) [$M^+ - C_7H_3$], 165 (2) [$M^+ - C_7H_5$], 105 (100) [$M^+ - C_9H_9O_2$], 90 (3) [$M^+ - C_9H_6O_3$], 77 (27) [$M^+ - C_{10}H_9O_3$], 51 (7) [$M^+ - C_{12}H_{11}O_3$].

$C_{16}H_{14}O_3$ (254.3) Calcd. C 75.58 H 5.55
Found C 75.82 H 5.36

7-Oxabicyclo[4.1.0]hept-1-yl Benzoate[2d] (**2q**): 131 mg (96%), colorless liquid, obtained from 15 ml of 0.071 M (1.06 mmol) dioxirane **4** and 128 mg (0.062 mmol) of **1q** at −20°C for 3.0 h.

(E)-3'-Phenylspiro[isobenzofuran-1(3H),2'-oxiran]-3-one (**2r**): 225 mg yield ca. 100% at 97% conversion, colorless needles, m.p. 134–135°C (from $CHCl_3$/petroleum ether), obtained from 20 ml of 0.081 M (1.62 mmol) dioxirane **4** and 216 mg (0.97 mmol) of **1r** at ca. 20°C for 7.0 h. – IR (CCl_4): $\tilde{\nu}$ = 3090 (w) cm^{-1}, 3070 (w), 3040 (w), 2980 (w), 1800 (s), 1610 (w), 1500 (w), 1465 (w), 1455 (w), 1430 (w), 1340 (w), 1280 (w), 1250 (m), 1160 (m), 1125 (m), 1065 (m), 990 (m), 925 (m), 885 (w), 695 (m), 685 (m). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 4.64 (s, 1H), 7.39–7.43 (m, 3H), 7.50–7.55 (m, 3H), 7.65 (dt, J_1 = 7.48, J_2 = 0.84 Hz, 1H), 7.77 (dt, J_1 = 7.50, J_2 = 1.01 Hz, 1H), 7.56 (d, J = 7.56 Hz, 1H). – ^{13}C NMR (63 MHz, $CDCl_3$): δ = 64.3 (d), 90.0 (s), 121.5 (d), 125.7 (d), 127.5 (d), 127.8 (s), 129.1 (d), 131.5 (d), 131.8 (s), 134.9 (s), 142.7 (s), 166.7 (s). – MS (70 eV): m/z (%) = 238 (5) [M^+], 222 (5) [$M^+ - O$], 209 (2) [$M^+ - CHO$], 194 (1) [$M^+ - C_2H_4O$], 165 (5) [$M^+ - C_2HO_3$], 132 (57) [$M^+ - C_7H_6O_2$], 105 (15) [$M^+ - C_8H_5O_2$], 104 (100) [$M^+ - C_8H_6O_2$], 89 (6) [$M^+ - C_8H_5O_3$], 76 (35) [$M^+ - C_9H_6O_3$].

$C_{15}H_{10}O_3$ (238.25) Calcd. C 75.62 H 4.23
Found C 76.04 H 4.25

3,3'-Diphenylspiro[isobenzofuran-1(3H),2'-oxiran]-3-one (**2s**): 106 mg (ca. 100%), colorless needles, m.p. 161–162°C (from $CHCl_3$/petroleum ether), obtained from 81.5 ml of 0.081 M (6.60

mmol) dioxirane **4** and 218 mg (0.73 mmol) of **1s** at ca. 20°C for 88.0 h. – IR (CCl_4): $\tilde{\nu}$ = 3090 (w) cm^{-1}, 1820 (s), 1510 (w), 1480 (w), 1460 (w), 1260 (w), 1160 (w), 1110 (w), 1005 (m), 970 (m), 965 (m), 905 (w), 710 (m), 705 (m), 695 (m), 680 (w), 630 (w). – ^1H NMR (250 MHz, $CDCl_3$): δ = 6.24 (d, J = 7.71 Hz, 1H), 7.30–7.46 (m, 8H), 7.50–7.57 (m, 4H), 7.88 (d, J = 7.60 Hz, 1H). – ^{13}C NMR (63 MHz, $CDCl_3$): δ = 72.1 (s), 92.9 (s), 124.4 (d), 125.3 (d), 127.6 (d), 127.7 (d), 128.2 (d), 128.4 (d), 128.7 (d), 128.8 (d), 131.2 (d), 134.1 (d), 135.7 (s), 135.9 (s), 141.6 (s), 166.7 (s). – MS (70 eV): *m/z* (%) = 314 (5) [M^+], 298 (3) [$M^+ - O$], 239 (2) [$M^+ - C_6H_3$], 209 (2) [$M^+ - C_7H_5O$], 181 (1) [$M^+ C_8H_5O_2$], 167 (14) [$M^+ - C_9H_7O_2$], 166 (96) [$M^+ - C_9H_8O_2$], 165 (30) [$M^+ - C_9H_9O_2$], 132 (15) [$M^+ - C_{13}H_{10}O$], 105 (16) [$M^+ - C_{14}H_9O_2$], 104 (100) [$M^+ - C_{14}H_{10}O_2$], 77 (15) [$M^+ - C_{15}H_9O_3$], 76 (35) [$M^+ - C_{15}H_{10}O_3$].

$C_{21}H_{14}O_3$ (314.3) Calcd. C 80.24 H 4.49
Found C 80.21 H 4.57

5,5-Dimethyl-2,7-dioxabicyclo[4.1.0]heptan-3-one (**2t**): 88 mg (79%), colorless liquid, b.p. 100°C/0.15 Torr, obtained from 28 ml of 0.045 M (1.26 mmol) dioxirane **4** and 99 mg (0.79 mmol) of **1t** at –20°C for 3.0 h. – IR (CCl_4): $\tilde{\nu}$ = 3060 (m) cm^{-1}, 2970 (s), 2930 (m), 2870 (m), 1770 (s), 1470 (m), 1440 (m), 1410 (m), 1390 (m), 1370 (m), 1310 (m), 1275 (s), 1260 (m), 1235 (s), 1200 (s), 1175 (m), 1130 (s), 1105 (m), 1045 (m), 1010 (m), 970 (m), 955 (m), 940 (w), 860 (s), 705 (m). – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.12 (s, 3H), 1.26 (s, 3H), 2.23 (dd, J_1 = 15.88, J_2 = 1.48 Hz, 1H), 2.49 (dd, J_1 = 15.88, J_2 = 0.50 Hz, 1H), 3.01 (dd, J_1 = 2.55, J_2 = 1.58 Hz, 1H), 5.23 (d, J = 2.70 Hz, 1H). – ^{13}C NMR (63 MHz, $CDCl_3$): δ = 23.7 (q), 24.6 (q), 31.3 (s), 41.2 (t), 58.3 (d), 77.8 (d), 167.3 (s). – MS (70 eV): *m/z* (%) = 142 (1) [M^+], 113 (15) [M^+ – CHO], 100 (34) [$M^+ - C_3H_6$], 85 (7) [$M^+ - C_3H_5O$], 72 (65) [$M^+ - C_4H_6O$], 71 (11) [$M^+ - C_4H_7O$], 57 (100) [$M^+ - C_4H_5O_2$], 56 (23) [$M^+ - C_4H_6O_2$], 43 (48) [$M^+ - C_5H_7O_2$], 39 (25) [$M^+ - C_4H_7O_3$].

$C_7H_{10}O_3$ (142.2) Calcd. C 59.14 H 7.09
Found C 59.18 H 7.15

2,11-Dioxatricyclo[4.4.1.0^{1,6}]undecan-3-one (**2u**): 109 mg (83%), colorless liquid, b.p. 110°C/0.01 Torr, obtained from 25 ml of 0.045 M (1.13 mmol) dioxirane **4** and 120 mg (0.78 mmol) of **1u** at –20°C for 3.0 h. – IR (CCl_4): $\tilde{\nu}$ = 2970 (m) cm^{-1}, 2860 (w), 1770 (s), 1440 (w), 1420 (m), 1365 (m), 1345 (m), 1320 (w), 1280 (w), 1250 (m), 1220 (m), 1205 (m), 1200 (m), 1170 (m), 1150 (s), 1120 (w), 1095 (s), 1085 (s), 1025 (m), 1000 (w), 970 (w), 965 (m), 925 (w), 885 (w), 870 (w), 660 (w). – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.20–2.54 (m, 12H). – ^{13}C NMR (63 MHz, $CDCl_3$): δ = 19.8 (t), 19.9 (t), 24.7 (t), 27.4 (t), 27.5 (t), 27.8 (t), 61.5 (s), 87.0 (s), 168.1 (s). – MS (70 eV): *m/z* (%) = 168 (2) [M^+], 152 (7) [$M^+ - O$], 140 (6) [$M^+ - CO$], 124 (30) [$M^+ - CO_2$], 112 (15) [$M^+ - C_2O_2$], 111 (100) [$M^+ - C_2HO_2$], 83 (24) [$M^+ - C_2H_2O_3$], 67 (33) [$M^+ - C_3H_6O_3$], 56 (44) [$M^+ - C_4H_5O_3$], 41 (48) [$M^+ - C_5H_7O_3$], 39 (47) [$M^+ - C_5H_9O_3$], 28 (79) [$M^+ - C_8H_{12}O_2$].

$C_9H_{12}O_4$ (168.2) Calcd. C 64.27 H 7.19
Found C 64.33 H 7.23

Epoxidation of (E)-1-[(Dimethoxyphosphinyl)oxy]hept-1-ene (**1c**) *by Ethylmethyldioxirane Generated in situ from Caroate and 2-Butanone:* To a cooled (0–5°C), mechanically vigorously stirred mixture of 3.33 g (15.0 mmol) of **1c**, 2-butanone (50 ml) and phosphate buffer (0.177 g of KH_2PO_4 and 0.648 g of Na_2HPO_4 in 150 ml of water) was added slowly within ca. 2.5 h a saturated aqueous solution of Caroate [58 g (0.094 mol) of 2 $KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$ in 200 ml of water]. The pH of the mixture was kept constant throughout the reaction at 7.3–7.5 by the help of 15% aqueous KOH. After 1.0 h of additional stirring, solid NaCl was added to the cloudy reaction mixture until saturation; the organic phase was separated by decantation, and the aqueous phase was extracted with CH_2Cl_2 (4 × 50 ml). The combined organic layers were dried with $MgSO_4$, and the solvent was evaporated (ca. 20°C/15 Torr) to afford epoxide **2c** (2.95 g, 83%) as a colorless liquid; for spectral data see above.

Rearrangement of Epoxides **2** *to Carbonyl Products* **3**: A C_6D_6 solution of the enol phosphate epoxides **2d–i** was allowed to stand overnight at room temp. After 12 h the ^1H- and ^{13}C-NMR spectra of the crude reaction mixture indicated the complete conversion of **2d–i** into the α-[(dialkoxyphosphinyl)oxy]-substituted ketones **3**. Distillation (Büchi Kugelrohr oven) afforded carbonyl compounds **3** in good to moderate yields.

Ketone **3d**[26]: 129 mg (76%), colorless liquid, obtained from 170 mg (0.93 mmol) of **2d**. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.72 (s, 3H), 3.56 (d, J = 11.20 Hz, 6H), 4.38 (d, J = 10.62 Hz, 2H). – ^{13}C NMR (63 MHz, $CDCl_3$): δ = 20.8 (C-1), 53.8 (d, $J_{C,P}$ = 5.89 Hz, OCH_3), 70.4 (d, $J_{C,P}$ = 5.64 Hz, C-3), 201.2 (d, $J_{C,P}$ = 4.78 Hz, C-2).

Ketone **3e**[26]: 74 mg (53%), colorless liquid, obtained from 140 mg (0.67 mmol) of **2e**. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.32–1.39 (m, 6H), 2.22 (s, 3H), 4.04–4.26 (m, 4H), 4.59 (d, J = 9.54 Hz, 2H). – ^{13}C NMR (63 MHz, $CDCl_3$): δ = 16.1 (d, $J_{C,P}$ = 2.77 Hz, OCH_2CH_3), 16.2 (d, $J_{C,P}$ = 2.64 Hz, OCH_2CH_3), 26.0 (C-1), 63.7 (d, $J_{C,P}$ = 5.79 Hz, OCH_2CH_3), 64.4 (d, $J_{C,P}$ = 5.85 Hz, OCH_2CH_3), 70.8 (d, $J_{C,P}$ = 5.79 Hz, C-3), 202.5 (d, $J_{C,P}$ = 5.85 Hz, C-2).

Ketone **3f**[26]: 183 mg (86%), colorless liquid, obtained from 213 mg (0.87 mmol) of **2f**. – ^1H NMR (250 MHz, $CDCl_3$): δ = 3.56 (d, J = 11.22 Hz, 6H), 5.09 (d, J = 10.94 Hz, 2H), 6.98–7.18 (m, 3H), 7.56–7.67 (m, 2H). – ^{13}C NMR (63 MHz, $CDCl_3$): δ = 54.3 (d, $J_{C,P}$ = 5.97 Hz, OCH_3), 69.3 (d, $J_{C,P}$ = 5.16 Hz, C-2), 127.9 (arom.), 128.8 (arom.), 133.6 (arom.), 134.4 (arom.), 192.3 (d, $J_{C,P}$ = 4.34 Hz, C-1).

Ketone **3g**[27]: 146 mg (83%), colorless liquid, obtained from 176 mg (0.65 mmol) of **2g**. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.98–1.16 (m, 6H), 4.00–4.12 (m, 4H), 5.12 (d, J = 10.55 Hz, 2H), 7.00–7.19 (m, 3H), 7.63–7.68 (m, 2H). – ^{13}C NMR (63 MHz, $CDCl_3$): δ = 16.1 (d, $J_{C,P}$ = 3.71 Hz, OCH_2CH_3), 64.1 (d, $J_{C,P}$ = 5.79 Hz, OCH_2CH_3), 69.1 (d, $J_{C,P}$ = 5.09 Hz, C-2), 128.0 (arom.), 128.8 (arom.), 133.6 (arom.), 134.5 (arom.), 192.4 (d, $J_{C,P}$ = 4.78 Hz, C-1).

Ketone **3h**[28]: 173 mg (79%), colorless liquid, obtained from 219 mg (0.90 mmol) of **2h**. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.41 (d, J = 6.89 Hz, 3H), 2.18 (s, 3H), 3.64–3.80 (m, 6H), 4.64–4.76 (m, 1H). – ^{13}C NMR (63 MHz, $CDCl_3$): δ = 18.2 (d, $J_{C,P}$ = 4.53 Hz, C-4), 25.5 (C-1), 54.5 (d, $J_{C,P}$ = 6.15 Hz, OCH_3), 54.7 (d, $J_{C,P}$ = 6.02 Hz, OCH_3), 78.6 (d, $J_{C,P}$ = 5.87 Hz, C-3), 205.9 (d, $J_{C,P}$ = 5.69 Hz, C-2).

Ketone **3h**[28]: 118 mg (79%), colorless liquid, obtained from 149 mg (0.76 mmol) of **2i** (cf. above for spectral data).

CAS Registry Numbers

1a: 6651-36-1 / **1b**: 127632-97-7 / **1c**: 132170-11-7 / **1d**: 4185-82-4 / **1e**: 5954-28-9 / **1f**: 4202-12-4 / **1g**: 1021-45-0 / **1h**: 50432-20-7 / **1i**: 50523-01-8 / **1j**: 3719-53-7 / **1k**: 30908-58-8 / **1l**: 10008-73-8 / **1m**: 65371-43-9 / **1n**: 65371-42-8 / **1o**: 89609-42-7 / **1p**: 13892-81-4 / **1q**: 13163-64-9 / **1r**: 4767-55-9 / **1s**: 1801-25-8 / **1t**: 76897-39-7 / **1u**: 700-82-3 / **2a**: 127632-98-8 / **2b**: 127632-99-9 / **2c**: 132170-12-8 / **2d**: 132170-13-9 / **2e**: 132170-14-0 / **2f**: 132170-15-1 / **2g**: 132170-16-2 / **2h**: 132170-17-3 / **2i**: 132170-18-4 / **2j**: 132170-19-5 / **2k**: 132170-20-8 / **2l**: 126091-78-9 / **2m**: 126091-79-0 / *cis*-**2n**:

126091-80-3 / *trans*-**2n**: 126091-81-4 / *cis*-**2o**: 126091-82-5 / *trans*-**2o**: 126091-83-6 / **2p**: 135455-96-8 / **2q**: 62183-31-7 / **2r**: 135455-97-9 / **2s**: 135455-98-0 / **2t**: 126186-97-8 / **2u**: 126091-84-7 / **3d**: 30094-70-3 / **3e**: 30935-85-4 / **3f**: 13392-51-3 / **3g**: 33348-51-5 / **3h**: 19063-36-6 / **4**: 74087-85-7

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