hypothetical biosynthetic intermediates of aromatic natural products.

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Articles

Synthesis of 3-Vinyl-1,2,4-trioxolanes by a [3 + 2] Cycloaddition of Carbonyl Oxides with α,β-Unsaturated Carbonyl Compounds

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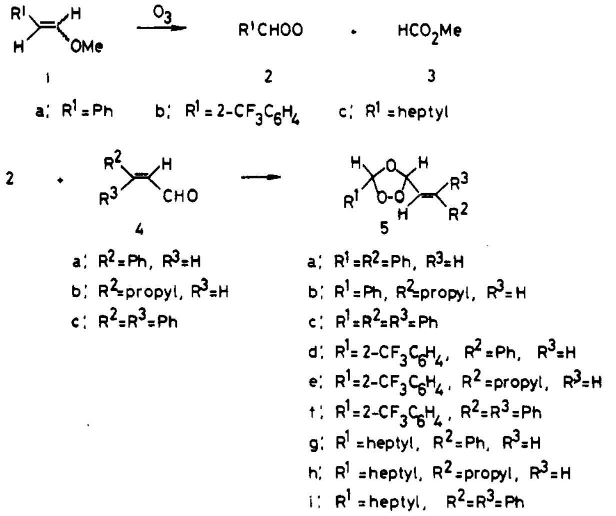
The [3 + 2] cycloaddition of a carbonyl oxide, generated by the ozonolysis of a vinyl ether, to an α,β-unsaturated aldehyde gave the 3-vinyl-1,2,4-trioxolane (α-vinyl ozonide) in moderate yield. In contrast, α,β-unsaturated ketones showed a very poor reactivity with carbonyl oxides. Benzylidenecyclohexanones were exceptions, from which the corresponding 3-vinyl-1,2,4-trioxolanes were obtained in excellent yields. Reaction of the 3-vinyl-1,2,4-trioxolanes with ozone led to the formation of the corresponding diozonides.

Ozonides (1,2,4-trioxolanes) continue to present a synthetic challenge.[1] Griesbaum et al. found that 3-vinyl-1,2,4-trioxolanes, prepared by the monoozonolysis of the corresponding 1,3-butadienes, constitute an interesting class of cyclic peroxides that can serve as precursors to a variety of functionalized 1,2,4-trioxolanes.[2] In developing an alternative method for the synthesis of 3-vinyl-1,2,4-trioxolanes, we conducted ozonolyses of vinyl ethers in the presence of α,β-unsaturated carbonyl compounds. Kuczkowski[3] and we[4] have found that ozonolysis of a vinyl ether in the presence of an added 1,3-dipolarophile reveals a consistent reactivity of the carbonyl oxide toward the added substrate. The reaction of vinyl ethers and ozone proceeds with virtually complete regioselectivity to give the carbonyl oxide–ester pairs,[5] and the esters show relatively low reactivity toward the carbonyl oxides.

Results and Discussion

Ozonolysis of a Vinyl Ether in the Presence of an α,β-Unsaturated Aldehyde. Ozonolysis of 1-phenyl-2-methoxyethene (**1a**) in the presence of *trans*-cinnamaldehyde (**4a**) in methylene chloride or in ether gave 3-phenyl-5-(2-phenylvinyl)-1,2,4-trioxolane (**5a**) in ca. 40% yield (Scheme I and Table I). It is interesting to note, however, that ozonolysis of 1,4-diphenyl-1,3-butadiene in methylene chloride yields a mixture of 3,6-distyryl-1,2,4,5-tetroxane (the dimer of cinnamaldehyde *O*-oxide) and benzaldehyde instead of the expected ozonide **5a**.[6]

Scheme I



From the reactions of **1a–c** with ozone in the presence of α,β-unsaturated aldehydes **4a–c**, the corresponding ozonides (1,2,4-trioxolanes) **5b–i** were obtained in 12–71% yield as mixture of *cis*- and *trans*-isomers (Table I). Tentative assignment of the stereochemistry of the isomeric ozonides was based on the observation that in the

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[1] (a) Bunnelle, W. H. *Chem. Rev.* **1991**, *91*, 335. (b) Kuczkowski, R. L. In *Adv. Oxygenated Processes*; Baumstark, A. L. Ed.; JAI Press: Greenwich, 1991; Vol. 3, p 1–42.

[2] (a) Griesbaum, K.; Bandypadhyay, A. R.; Meister, M. *Can. J. Chem.* **1986**, *64*, 1553. (b) Griesbaum, K.; Zwick, G. *Chem. Ber.* **1985**, *118*, 3041. (c) Griesbaum, K.; Volpp, W.; Greinert, R. *J. Am. Chem. Soc.* **1985**, *107*, 5309. (d) Griesbaum, K.; Volpp, W.; Greinert, R.; Greunig, H.-J.; Schmid, J.; Henke, H. *J. Org. Chem.* **1989**, *54*, 383. (e) Griesbaum, K.; Keul, H.; Agarwal, S.; Zwick, G. *Chem. Ber.* **1983**, *116*, 409.

[3] (a) Keul, H.; Kuczkowski, R. L. *J. Am. Chem. Soc.* **1984**, *106*, 5370. (b) Wojciechowski, B. J.; Chiang, C.-Y.; Kuczkowski, R. L. *J. Org. Chem.* **1990**, *55*, 1120.

[4] (a) Griesbaum, K.; Kim, W.-S.; Nakamura, N.; Mori, M.; Nojima, M.; Kusabayashi, S. *J. Org. Chem.* **1990**, *55*, 6153. (b) McCullough, K. J.; Nakamura, N.; Fujisaka, T.; Nojima, M.; Kusabayashi, S. *J. Am. Chem. Soc.* **1991**, *113*, 1786.

[5] However, see: (a) Bunnelle, W. H.; Meyer, L. A.; Schlemper, E. O. *J. Am. Chem. Soc.* **1989**, *111*, 7612. (b) Bunnelle, W. H. *Ibid.* **1989**, *111*, 7613.

[6] Private information from Prof. K. Griesbaum.

0022-3263/92/1957-1649$03.00/0

Table I. Ozonolysis of Vinyl Ether in the Presence of an α,β-Unsaturated Aldehyde[a]

vinyl ether	α,β-unsaturated aldehyde	products: ozonide (% yield)	products: ozonide cis/trans	products: others (% yield)
1a	**4a**	**5a** (39)	1:2	**6** (12)
1a	**4a**	**5a** (40)[b]	2:3	
1a	**4b**	**5b** (12)		**6** (8)
1a	**4b**	**5b** (13)[b]		
1a	**4c**	**5c** (35)	1:1	**6** (7)
1b	**4a**	**5d** (49)	2:3	
1b	**4b**	**5e** (43)		
1b	**4c**	**5f** (71)		
1c	**4a**	**5g** (31)	1:1	
1c	**4b**	**5h** (39)		
1c	**4c**	**5i** (49)	1:2	

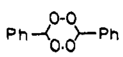
[a] The reactions of vinyl ethers (200 mg) were conducted in CH_2Cl_2 (20 mL) in the presence of an α,β-unsaturated aldehyde (5 mol equiv) at 0 °C unless otherwise noted. [b] The reaction was conducted in ether (20 mL).

Table II. Ozonolysis of Vinyl Ether in the Presence of an α,β-Unsaturated Ketone[a]

ketone	vinyl ether	solvent	products (% yield)	recovered **8** or **9** (%)
8a[b]	**1a**	CH_2Cl_2	**6** (10)	90
8b[c]	**1e**	ether	**12** (15), **14** (65)	
8c[c]	**1b**	ether	**6** (12), **13** (50)	
8c[c]	**1e**	ether	**12** (18), **14** (63)	
9a	**1a**	CH_2Cl_2	**10** (11), **13** (63)	90
9a	**1d**	CH_2Cl_2	**10** (10)	70
9a[d]	**1d**	CH_2Cl_2		100
9b	**1a**	ether	**11a** (10), **13** (50)	85
9c	**1a**	ether	**11b** (17), **13** (65)	65
9d	**1a**	ether	**11b** (17), **13** (60)	65
9e	**1a**	ether	**15a** (73)	22
9e	**1c**	ether	**15b** (38)	44
9e	**1d**	ether	**11c** (17), **15c** (30)	37
9e	**1e**	ether	**11c** (26), **12** (15) **14** (60)	44
9f	**1a**	ether	**11c** (8), **13** (65)	90
9g[d]	**1a**	ether	**17a** (59)	14
9g[d]	**1d**	ether	**17b** (45)	28

[a] Treatment of a 1:1 mixture of ketone and vinyl ether with ozone at −70 °C unless otherwise noted. [b] Ketone:vinyl ether = 5:1. [c] Ketone:vinyl ether = 20:1. [d] Ketone:vinyl ether = 1:2.

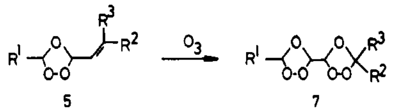
phenyl- and vinyl-substituted ozonide the protons at the 3- and 5-positions in the trans-ozonide appear at lower field than those of the cis-isomer, while the reverse trend holds for the alkyl-substituted ozonides.[7] However, this relationship did not hold for 3-[2-(trifluoromethyl)phenyl]-5-(2-phenylvinyl)-1,2,4-trioxolane (**5d**) (see Experimental Section), and therefore, the stereochemical assignment of ozonide **5d** remains ambiguous.



6

Of the three carbonyl oxide intermediates **2a–c**, the most electron-deficient 2-(trifluoromethyl)benzaldehyde *O*-oxide (**2b**) was the most reactive (as judged by the yields of ozonides **5**) (Table I).[8]

To obtain additional evidence for the structure of the 3-vinyl-1,2,4-trioxolanes, the ozonolysis of *trans*-**5a** was conducted in methylene chloride to give diozonide **7a**, as expected.[9] Under similar conditions, **5f** and **5g** also gave the corresponding diozonides **7f** and **7g**, respectively (eq 1).



(1)

5 7

a: $R^1 = R^2 = Ph$, $R^3 = H$

b: $R^1 = 2\text{-}CF_3C_6H_4$, $R^2 = R^3 = Ph$

c: R^1 = heptyl, $R^2 = Ph$, $R^3 = H$

Ozonolysis of a Vinyl Ether in the Presence of an α,β-Unsaturated Ketone. Ozonolyses of mixtures of vinyl ethers **1a,c–e** and of acyclic (**8a–c**) or cyclic (**9a–c**) ketones were conducted in methylene chloride or in ether. In accordance with the generally recognized lower reactivity of ketones relative to aldehydes,[1] no evidence was obtained for the formation of cycloadducts between the carbonyl oxides and these α,β-unsaturated ketones (Table II); recovery of unreacted ketones was very high. Anhydride **10** obtained from ozonolysis of a 1:1 mixture of **1d** and **9a** (10% yield) was most likely produced by direct reaction of **9a** and ozone, since the reaction of a 2:1 mixture of **1d** and **9a** resulted in quantitative recovery of **9a**. From the reaction with **9b,c** also, the corresponding dicarboxylic acids **11a,b** were obtained in nearly 15% yield.[10]

$R^1R^2C{=}CHOR^3$

1d: $R^1 = R^2 = H$, $R^3 = CH_2CH(CH_3)_2$

1e: $R^1 = R^2 = Ph$, $R^3 = CH_3$

R^1R^2COO

2d: $R^1 = R^2 = H$

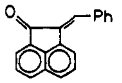
2e: $R^1 = R^2 = Ph$

$R^1CH{=}CHCOR^2$

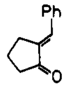
8a: $R^1 = R^2 = Ph$

8b: $R^1 = R^2 = CH_3$

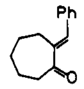
8c: $R^1 = H$, $R^2 = CH_3$



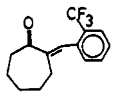
9a



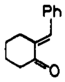
9b



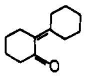
9c



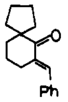
9d



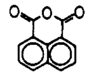
9e



9f



9g



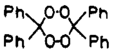
10

$HO_2C(CH_2)_nCO_2H$

11a: n = 3

11b: n = 5

11c: n = 4



12

PhCHO

13

$Ph_2C{=}O$

14

It is well-known that the introduction of an electron-withdrawing substituent enhances the reactivity of a ketone toward carbonyl oxides.[1,11] Thus, 2-[(trifluoro-

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[7] (a) Criegee, R.; Korber, H. *Chem. Ber.* **1971**, *104*, 1807. (b) Murray, R. W.; Youssefyeh, R. D.; Story, P. R. *J. Am. Chem. Soc.* **1966**, *88*, 3655. (c) Keul, H.; Kuczkowski, R. L. *J. Org. Chem.* **1985**, *50*, 3371. (d) Wojciechowski, B. J.; Pearson, W. H.; Kuczkowski, R. L. *Ibid.* **1989**, *54*, 115.

[8] (a) Painter, M. K.; Choi, H. S.; Hillig, K. W., II; Kuczkowski, R. J. *J. Chem. Soc., Perkin Trans. 2*, **1986**, 1025. (b) Murray, R. W.; Morgan, M. M. *J. Org. Chem.* **1991**, *56*, 684.

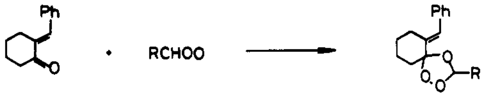
[9] To our knowledge, two examples are known for diozonides having a 3,3′-bi-1,2,4-trioxolane structure: Griesbaum, K.; Volpp, W. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 81 and ref 2d.

[10] Tabuchi, T.; Nojima, M. *J. Org. Chem.*, in press.

[11] (a) Criegee, R.; Bath, S. S.; von Bornhaupt, B. *Chem. Ber.* **1960**, *93*, 2891. (b) Murray, R. W.; Agarwal, S. K. *J. Org. Chem.* **1985**, *50*, 4698. (c) Bunnelle, W. H.; Schlemper, E. O. *J. Am. Chem. Soc.* **1987**, *109*, 612.

methyl)benzylidene]cycloheptanone (**9d**) was prepared, and ozonolysis of a mixture of **1a** and **9d** was undertaken. Even in this case, cycloaddition of benzaldehyde *O*-oxide (**2a**) did not occur.

In marked contrast to the acyclic and cyclic ketones **8a–c** and **9a–d**, benzylidenecyclohexanone (**9e**) reacted with aldehyde *O*-oxides **2a,c,d** very easily, yielding the corresponding [3 + 2] adducts **15a–c** in moderate yields (eq 2 and Table II). However, no evidence was obtained for the formation of a cycloadduct in the case of the bulkier benzophenone *O*-oxide (**2e**). Cyclohexylidenecyclohexanone (**9f**) did not react even with benzaldehyde *O*-oxide, demonstrating that the steric bulk of the α,β-unsaturated ketone also plays an important role in the reactivity.

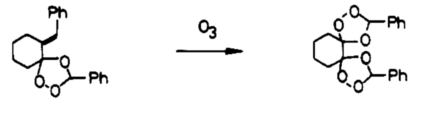


(2)

9e

15a; R=Ph
15b; R=heptyl
15c; R=H

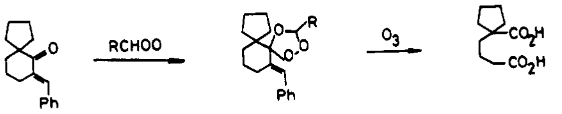
Consistent with the structure of adduct **15a**, treatment with ozone led to the formation of diozonide **16** (eq 3).



(3)

15a 16

To learn whether [3 + 4] cycloaddition between carbonyl oxide and α,β-unsaturated ketone occurs or not, the reaction of carbonyl oxide with 2-benzylidenespiro[5.4]decan-1-one (**9g**) was undertaken. Although the [3 + 2] cycloaddition of carbonyl oxides to the carbonyl group of **9g** was expected to incur significant steric hindrance, the sole isolated products were the corresponding [3 + 2] adducts **17a,b** (Table II and eq 4), suggesting that in the intermolecular case concerted [3 + 2] cycloaddition predominates.[12] Reaction of the 3-vinyl-1,2,4-trioxolane **17** with ozone gave the dicarboxylic acid **18** (eq 4).



(4)

9g

17a; R=Ph
17b; R=H

18

A competition reaction between benzylidenecyclohexanone (**9e**) and cinnamaldehyde (**4a**) was tried. Surprisingly, ketone **9e** reacted much faster than aldehyde **4a** with benzaldehyde *O*-oxide (**2a**); only ozonide **15a** was obtained and in 59% yield. The reason for this abnormally high reactivity of **9e** is unknown.

Experimental Section

Starting Materials. The preparation of vinyl ethers **1a–c** is described elsewhere.[4a] α,β-Unsaturated carbonyl compounds **9a**,[13] **9b–e**,[14] and **9f**[15] were prepared by the reported methods.

Ozonolysis of a Vinyl Ether 1 in the Presence of an α,β-Unsaturated Aldehyde 4. The reaction of a vinyl ether (200 mg) was run in CH_2Cl_2 (20 mL) or in ether (20 mL) in the presence of an α,β-unsaturated aldehyde (5 mol equiv). After evaporation of the solvent in vacuo, the products were separated by column chromatography on silica gel (elution with benzene/hexane (2:3 to 3:2)).

***trans*-3-Phenyl-5-(2-phenylvinyl)-1,2,4-trioxolane (*trans*-5a)**: mp 120–125 °C (from methanol); ^1H NMR δ 5.96 (d, J = 8 Hz, 1 H), 6.15 (dd, J = 16 and 8 Hz, 1 H), 6.19 (s, 1 H), 6.98 (d, J = 16 Hz, 1 H), 7.2–7.7 (m, 10 H); ^{13}C NMR δ 104.45, 105.34, 119.55–139.45; IR 1050, 1025, 980 cm^{-1}. Anal. Calcd for $C_{16}H_{14}O_3$: C, 75.59; H, 5.51. Found: C, 75.62; H, 5.59.

***cis*-3-Phenyl-5-(2-phenylvinyl)-1,2,4-trioxolane (*cis*-5a)**: mp 57.0–58.5 °C (from methanol); ^1H NMR δ 5.91 (d, J = 8 Hz, 1 H), 6.18 (s, 1 H), 6.23 (dd, J = 16 and 8 Hz, 1 H), 6.87 (d, J = 16 Hz, 1 H), 7.2–7.7 (m, 10 H); ^{13}C NMR δ 104.04, 104.69, 121.99–137.66; IR 1060, 1025, 985 cm^{-1}. Anal. Calcd for $C_{16}H_{14}O_3$: C, 75.59; H, 5.51. Found: C, 75.32; H, 5.60.

3-Phenyl-5-(1-pentenyl)-1,2,4-trioxolane (5b): cis–trans mixture; oil; ^1H NMR δ 0.90 (t, J = 8 Hz, 3 H), 1.3–1.7 (m, 2 H), 2.12 (q, J = 7 Hz, 2 H), 4.7–5.3 (m, 2 H), 5.8–6.2 (m, 2 H), 7.2–7.5 (m, 5 H). Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.91; H, 7.27. Found: C, 70.60; H, 7.36.

***trans*-3-Phenyl-5-(2,2-diphenylvinyl)-1,2,4-trioxolane (*trans*-5c)**: mp 77–80 °C (from methanol); ^1H NMR δ 5.75 (d, J = 8 Hz, 1 H), 6.10 (s, 1 H), 6.15 (d, J = 8 Hz, 1 H), 7.2–7.6 (m, 15 H). Anal. Calcd for $C_{22}H_{18}O_3$: C, 80.00; H, 5.45. Found: C, 79.41; H, 5.52.

***cis*-3-Phenyl-5-(2,2-diphenylvinyl)-1,2,4-trioxolane (*cis*-5c)**: mp 83–85 °C (from hexane); ^1H NMR 5.75 (d, J = 8 Hz, 1 H), 6.07 (s, 1 H), 6.12 (d, J = 8 Hz, 1 H), 7.2–7.6 (m, 15 H). Anal. Calcd for $C_{22}H_{18}O_3$: C, 80.00; H, 5.45. Found: C, 79.88; H, 5.54.

***trans*-3-[2-(Trifluoromethyl)phenyl]-5-(2-phenylvinyl)-1,2,4-trioxolane (*trans*-5d)**: oil; ^1H NMR δ 5.76 (d, J = 7 Hz, 1 H), 6.08 (dd, J = 16 and 7 Hz, 1 H), 6.54 (s, 1 H), 6.86 (d, J = 16 Hz, 1 H), 7.1–7.9 (m, 9 H). Anal. Calcd for $C_{17}H_{13}F_3O_3$: C, 63.35; H, 4.04. Found: C, 62.96; H, 4.10.

***cis*-3-[2-(Trifluoromethyl)phenyl]-5-(2-phenylvinyl)-1,2,4-trioxolane (*cis*-5d)**: oil; ^1H NMR δ 5.82 (d, J = 7 Hz, 1 H), 6.08 (dd, J = 16 and 7 Hz, 1 H), 6.47 (s, 1 H), 6.89 (d, J = 16 Hz, 1 H), 7.1–7.9 (m, 9 H). Anal. Calcd for $C_{17}H_{13}F_3O_3$: C, 63.35; H, 4.04. Found: C, 62.96; H, 4.10.

3-[2-(Trifluoromethyl)phenyl]-5-(1-pentenyl)-1,2,4-trioxolane (5e): cis–trans mixture; oil; ^1H NMR δ 0.92 (t, J = 8 Hz, 3 H), 1.3–1.7 (m, 2 H), 2.13 (q, J = 7 Hz, 2 H), 5.3–5.7 (m, 2 H), 5.9–6.2 (m, 1 H), 6.4–6.7 (m, 1 H), 7.5–7.9 (m, 4 H). Anal. Calcd for $C_{14}H_{15}F_3O_3$: C, 58.33; H, 5.21. Found: C, 57.71; H, 5.03.

***trans*-3-[2-(Trifluoromethyl)phenyl]-5-(2,2-diphenylvinyl)-1,2,4-trioxolane (*trans*-5f)**: oil; ^1H NMR δ 5.68 (d, J = 8 Hz, 1 H), 5.99 (d, J = 8 Hz, 1 H), 6.49 (s, 1 H), 7.2–8.0 (m, 14 H). Anal. Calcd for $C_{23}H_{17}F_3O_3$: C, 69.35; H, 4.27. Found: C, 69.20; H, 4.20.

***cis*-3-[2-(Trifluoromethyl)phenyl]-5-(2,2-diphenylvinyl)-1,2,4-trioxolane (*cis*-5f)**: oil; ^1H NMR δ 5.62 (d, J = 8 Hz, 1 H), 5.99 (d, J = 8 Hz, 1 H), 6.47 (s, 1 H), 7.2–8.0 (m, 14 H). Anal. Calcd for $C_{23}H_{17}F_3O_3$: C, 69.35; H, 4.27. Found: C, 68.77; H, 4.17.

***trans*-3-Heptyl-5-(2-phenylvinyl)-1,2,4-trioxolane (*trans*-5g)**: oil; ^1H NMR δ 0.8–0.9 (m, 3 H), 1.2–1.8 (m, 12 H), 5.12 (t, J = 5 Hz, 1 H), 5.56 (d, J = 7 Hz, 1 H), 5.99 (dd, J = 16 and 7 Hz, 1 H), 6.71 (d, J = 16 Hz, 1 H), 7.1–7.4 (m, 5 H). Anal. Calcd for $C_{17}H_{24}O_3$: C, 73.91; H, 8.70. Found: C, 73.76; H, 8.79.

***cis*-3-Heptyl-5-(2-phenylvinyl)-1,2,4-trioxolane (*cis*-5g)**: mp 45–51 °C; ^1H NMR δ 0.8–0.9 (m, 3 H), 1.2–1.8 (m, 12 H), 5.14 (t, J = 5 Hz, 1 H), 5.48 (d, J = 7 Hz, 1 H), 5.95 (dd, J = 16 and 7 Hz, 1 H), 6.79 (d, J = 16 Hz, 1 H), 7.1–7.4 (m, 5 H). Anal. Calcd for $C_{17}H_{24}O_3$: C, 73.91; H, 8.70. Found: C, 73.70; H, 8.78.

3-Heptyl-5-(1-pentenyl)-1,2,4-trioxolane (5h): cis–trans mixture; oil; ^1H NMR δ 0.8–1.0 (m, 6 H), 1.3–1.7 (m, 14 H), 2.08

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(12) However, ozonolysis of 1,2,3,4-tetraphenyl-1,3-cyclopentadiene gave a 1,2,4-trioxepin derivative by intramolecular [3 + 4] cycloaddition of the carbonyl oxide moiety to the α,β-unsaturated carbonyl group: Mori, M.; Nojima, M.; Kusabayashi, S. *J. Am. Chem. Soc.* **1987**, *109*, 4407. For other examples of [3 + 4] cycloaddition between 1,3-dipoles and dipolarophiles having 4 π electrons, see: (a) Huisgen, R.; Mloston, G.; Langhals, E. *J. Am. Chem. Soc.* **1986**, *108*, 6401; *J. Org. Chem.* **1986**, *51*, 4087. (b) Huisgen, R., In *Adv. Cycloaddition*; Curran, D. P., Ed.; JAI Press: Greewich, 1988; Vol. 1, p 1–31. (c) Bahshar, M.; Heydt, H.; Maas, G.; Gumbel, H.; Regitz, M. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 597. (d) Baran, J.; Mayr, H. *J. Am. Chem. Soc.* **1987**, *109*, 6519.

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(q, J = 7 Hz, 2 H), 5.0–5.1 (m, 2 H), 5.2–5.4 (m, 2 H), 5.7–6.0 (m, 1 H). Anal. Calcd for $C_{14}H_{26}O_3$: C, 69.42; H, 10.74. Found: C, 69.28; H, 10.81.

***trans*-3-Heptyl-5-(2,2-diphenylvinyl)-1,2,4-trioxolane (*trans*-5i)**: oil; ^{1}H NMR δ 0.8–0.9 (m, 3 H), 1.2–1.7 (m, 12 H), 5.0–5.2 (m, 1 H), 5.41 (d, J = 8 Hz, 1 H), 5.88 (d, J = 8 Hz, 1 H), 7.1–7.5 (m, 10 H). Anal. Calcd for $C_{23}H_{28}O_3$: C, 78.41; H, 7.95. Found: C, 78.30; H, 8.00.

***cis*-3-Heptyl-5-(2,2-diphenylvinyl)-1,2,4-trioxolane (*cis*-5i)**: oil; ^{1}H NMR δ 0.8–0.9 (m, 3 H), 1.2–1.7 (m, 12 H), 5.0–5.2 (m, 1 H), 5.30 (d, J = 8 Hz, 1 H), 5.84 (d, J = 8 Hz, 1 H), 7.1–7.5 (m, 10 H). Anal. Calcd for $C_{23}H_{28}O_3$: C, 78.41; H, 7.95. Found: C, 78.50; H, 7.70.

Reaction of 3-Vinyl-1,2,4-trioxolanes with Ozone. A solution of 3-[2-(trifluoromethyl)phenyl]-5-(2,2-diphenylvinyl)-1,2,4-trioxolane (**5f**) (292 mg, 0.73 mmol) in CH_2Cl_2 (20 mL) was treated with 2 equiv of ozone at 0 °C. After evaporation of the solvent in vacuo, the crude products were separated by column chromatography on silica gel (elution with benzene/hexane (1:1)) to yield 5-[2-(trifluoromethyl)phenyl]-5′,5′-diphenyl-3,3′-bi-1,2,4-trioxolane (**7f**) in 47% yield (154 mg).

7f: oil; ^{1}H NMR δ 5.41 (s, 2 H), 6.29 (br s, 1 H), 7.1–7.7 (m, 14 H). Anal. Calcd for $C_{23}H_{17}F_3O_6$: C, 61.88; H, 3.81. Found: C, 62.09; H, 3.76.

Ozonolysis of 3-vinyl-1,2,4-trioxolane *trans*-**5a** under similar conditions gave a 30% yield of 5,5′-diphenyl-3,3′-bi-1,2,4-trioxolane (**7a**): mp 114–116 °C (from methanol); ^{1}H NMR δ 5.52 (s, 2 H), 6.03 (s, 2 H), 7.1–7.6 (m, 10 H); IR 1462, 1390, 1320, 1280, 1220, 1085, 1070, 1040, 1030, 995, 760, 698 cm^{-1}. Anal. Calcd for $C_{16}H_{14}O_6$: C, 63.58; H, 4.64. Found: C, 63.21; H, 4.71.

Ozonolysis of *cis*-**5g** under similar conditions resulted in the formation of 34% yield of 5-heptyl-5′-phenyl-3,3′-bi-1,2,4-trioxolane (**7g**) (a 1:1 mixture of two stereoisomers): oil; ^{1}H NMR δ 0.8–0.9 (m, 3 H), 1.2–1.8 (m, 12 H), 5.0–5.3 (m, 3 H), 6.06 (s, 0.5 H), 6.12 (s, 0.5 H), 7.2–7.4 (m, 5 H). Anal. Calcd for $C_{17}H_{24}O_6$: C, 62.96; H, 7.41. Found: C, 63.20; H, 7.30.

Preparation of 2-Benzylidenespiro[5.4]decan-1-one (9g). To a solution of LDA (35 mmol) in DME (40 mL) was added spiro[5.4]decan-1-one[16] (5 g, 33 mol) at 0 °C, and the mixture was stirred for 10 min at this temperature. Benzaldehyde (5.8 g, 55 mmol) dissolved in DME (20 mL) was added, and the reaction was stirred at room temperature for 2 h. Column chromatography of the crude product on silica gel (elution with benzene/hexane (1:1)), followed by crystallization from ethanol gave **9g** in about 50% yield: mp 79–81 °C; ^{1}H NMR δ 1.3–2.3 (m, 12 H), 2.6–3.0 (m, 2 H), 7.3–7.5 (m, 6 H); IR 2950, 2870, 1680, 1600, 1450, 1270, 1140, 750, 695 cm^{-1}. Anal. Calcd for $C_{17}H_{20}O$: C, 85.00; H, 8.33. Found: C, 84.89; H, 8.35.

Ozonolysis of a 1:1 Mixture of Isobutyl Vinyl Ether (1d) and Benzylideneacenaphthenone (9a). Into a mixture of **1d** (1 mmol) and **9a** (1 mmol) in CH_2Cl_2 (20 mL), was passed a stream of ozone at −70 °C. After evaporation of solvent, the crude product was chromatographed on silica gel (elution with benzene/ether (99:1)) to give **9a**. Subsequent elution with benzene/ether (9:1) gave 1,8-naphthalic anhydride (**10**).

Ozonolysis of a Mixture of a Vinyl Ether and Benzylidenecyclohexanone (9e). Ozonolysis of **1a** in the presence of **9e** is representative. A mixture of **1a** (1 mmol) and **9e** (1 mmol) in ether (15 mL) was ozonolyzed at −70 °C. After evaporation of the solvent, the crude product was chromatographed on silica gel (elution with benzene/hexane (3:7)) to give the 3-vinyl-1,2,4-trioxolane **15a**.

1-(Phenylmethylene)-9-phenyl-7,8,10-trioxaspiro[5.4]decane (15a): oil (a mixture of two isomers (44:56)); ^{1}H NMR δ 1.4–3.0 (m, 8 H), 6.05 (s, CH, major), 6.09 (s, CH, minor), 6.81 (s, CH, major), 6.96 (s, CH, minor), 7.1–7.6 (m, 10 H); ^{13}C NMR δ 23.61–37.08, 103.85, 104.15, 110.06, 110.18, 123.29, 124.03, 126.64, 126.86, 127.80–139.05. Anal. Calcd for $C_{20}H_{20}O_3$: C, 77.93; H, 6.49. Found: C, 77.52; H, 6.55.

1-(Phenylmethylene)-9-heptyl-7,8,9,10-trioxaspiro[5.4]decane (15b): oil (a mixture of two isomers (3:7)); ^{1}H NMR δ 0.8–2.9 (m, 23 H), 5.21 (t, J = 4.5 Hz, 1 H), 6.74 (s, CH, minor), 6.83 (s, CH, major), 7.1–7.4 (m, 5 H). Anal. Calcd for $C_{21}H_{30}O_3$: C, 76.36; H, 9.09. Found: C, 76.75; H, 9.13.

1-(Phenylmethylene)-7,8,10-trioxaspiro[5.4]decane (15c): oil; ^{1}H NMR δ 1.3–3.0 (m, 8 H), 5.15 (s, 1 H), 5.19 (s, 1 H), 6.78 (s, 1 H), 7.1–7.5 (m, 5 H). Anal. Calcd for $C_{14}H_{16}O_3$: C, 72.41; H, 6.90. Found: C, 72.70; H, 6.81.

Ozonolysis of a Mixture of a Vinyl Ether and 2-Benzylidenespiro[5.4]decan-1-one (9g). Ozonolysis of **1a** in the presence of **9g** is representative. Through a mixture of **1a** (2 mmol) and **9g** (1 mmol) in ether (15 mL) was passed a stream of ozone at 0 °C. After evaporation of the solvent, the crude product was chromatographed on silica gel (elution with benzene/hexane (3:7)) to give **17a** in 59% yield.

Dispiro[(3-phenyl-1,2,4-trioxolane)-5,1′-cyclohexane-2′,1″-cyclopentane] (17a): oil (a mixture of two isomers (22:78)); ^{1}H NMR δ 1.1–2.8 (m, 14 H), 6.06 (s, CH, minor), 6.09 (s, CH, major), 6.78 (s, CH, minor), 6.86 (s, CH, major), 7.1–7.6 (m, 10 H); ^{13}C NMR δ 23.05–51.41, 102.65 (major), 105.56 (minor), 113.57 (major), 114.13 (minor), 124.19 (major), 124.47 (minor), 126.51 (minor), 126.69 (major), 127.58–139.29. Anal. Calcd for $C_{24}H_{26}O_3$: C, 79.56; H, 7.18. Found: C, 80.08; 7.29.

Dispiro[(1,2,4-trioxolane)-3,1′-(3′-benzylidenecyclohexane)-2′,1″-cyclopentane] (17b): oil; ^{1}H NMR δ 0.9–2.9 (m, 14 H), 5.09 (s, 1 H), 5.31 (s, 1 H), 6.66 (s, 1 H), 7.1–7.6 (m, 5 H). Anal. Calcd for $C_{18}H_{22}O_3$: C, 75.52; H, 7.69. Found: C, 76.00; H, 7.61.

Ozonolysis of 15a or 17a. Through an ether solution (15 mL) of **15a** (1 mmol) was passed 1.5 mmol of ozone at −70 °C. After evaporation of the solvent, the residue was triturated with ether/hexane to give the diozonide **16**, whose physical properties were identical with the product obtained from the ozonolysis of **9e** followed by reaction with benzaldehyde *O*-oxide.[10]

From **17a** was obtained the dicarboxylic acid 18: mp 85–89 °C (from hexane); ^{1}H NMR 1.3–2.5 (m, 14 H), 10.10 (br s, 2 H); IR 3300–2600, 1695, 1405, 1275, 1210, 935 cm^{-1}. Anal. Calcd for $C_{10}H_{16}O_4$: C, 60.00; H, 8.00. Found: C, 60.21; H, 8.04.

Competition Reaction between Benzylidenecyclohexanone (9e) and Cinnamaldehyde (4a). A mixture of **1a** (1.52 mmol), **9e** (282 mg, 1.52 mmol), and **4a** (200 mg, 1.52 mmol) in ether (15 mL) was treated with 1.52 mmol of ozone at −70 °C. After evaporation of solvent, the products were separated by column chromatography on silica gel. The first fraction (elution with benzene/hexane (3:7)) contained **15a** (59% yield). From the second fraction (elution with benzene/hexane (4:1)) was obtained the diozonide **16** (6% yield). The final fraction (elution with benzene/hexane (20:1)) contained a mixture of **9e** (30%) and **4a** (86%).

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