Synthesis and Decomposition of *E*- and *Z*-3,3,5-Trisubstituted 1,2-Dioxolanes

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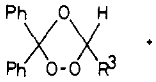
Abstract: The reactions of a number of ozonides and olefins in the presence of boron trifluoride–diethyl ether gave the corresponding mixtures of (*E*)- and (*Z*)-1,2-dioxolanes in 12–70% yield. The decomposition of the *E*–*Z* isomeric 1,2-dioxolanes **3a–c** was undertaken under a variety of conditions, i.e., thermal, $TiCl_4$-mediated, $FeSO_4$-catalyzed, and $LiAlH_4$-mediated decompositions.

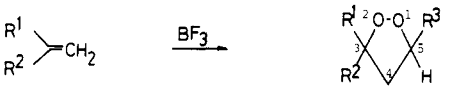
Of relevance to prostanoid endo peroxide chemistry, synthesis[1,2] and decomposition[1,3] of 1,2-dioxolanes has attracted great attention. While developing a general synthetic method for cyclic peroxides from ozonides,[4] we discovered that the reactions of ozonides and olefins in the presence of boron trifluoride–diethyl ether give the corresponding mixtures of (*E*)- and (*Z*)-1,2-dioxolanes.[5] In this paper we report details of the synthesis and the mode of decomposition of some *E*–*Z* isomeric pairs of 1,2-dioxolanes under a variety of conditions.

Results and Discussion

Synthesis of (*E*)- and (*Z*)-1,2-Dioxolanes. The reaction of triphenylethylene ozonide (**1a**) or 1,1-diphenylhept-1-ene ozonide (**1b**) with the 1,1-disubstituted ethylenes **2a**–i in the presence of boron trifluoride–diethyl ether gave the corresponding 1,2-dioxolanes **3a–l** (eq 1 and Table I). In the case of the alkenes **2a–g**, the dioxolanes **3a–g,j** were obtained as aporoximately 1:1 mixtures of *E* and *Z* isomers. These stereoisomeric 1,2-dioxolanes were separated from each other by column chromatography on silica gel (the exception was **3j**). Bis(α-hydroxybenzyl) peroxide (**1c**) could also be used successfully in place of **1a** (eq 2 and Table I).



1a, R^1 = Ph
1b, R^1 = pentyl



(1)

2a, R^1 = Ph; R^2 = Me
2b, R^1 = Ph; R^2 = Et
2c, R^1 = heptyl; R^2 = Me
2d, R^1 = Pr; R^2 = Me
2e, R^1 = Et; R^2 = Me
2f, R^1 = *i*-Pr; R^2 = Me
2g, R^1 = Ph; R^2 = *i*-Pr
2h, R^1 = R^2 = Ph
2i, R^1, R^2 = $-(CH_2)_5-$

3a, R^1 = R^3 = Ph; R^2 = Me
3b, R^1 = R^3 = Ph; R^2 = Et
3c, R^1 = heptyl; R^2 = Me, R^3 = Ph
3d, R^1 = Pr; R^2 = Me; R^3 = Ph
3e, R^1 = Et; R^2 = Me; R^3 = Ph
3f, R^1 = *i*-Pr; R^2 = Me; R^3 = Ph
3g, R^1 = R^3 = Ph; R^2 = *i*-Pr
3h, R^1 = R^2 = R^3 = Ph
3i, R^1, R^2 = $-(CH_2)_5-$; R^3 = Ph
3j, R^1 = Ph; R^2 = Me; R^3 = pentyl
3k, R^1 = R_2 = Ph; R^3 = pentyl
3l, R^1, R^2 = $-(CH_2)_5-$; R^3 = pentyl

Table I. Synthesis of 1,2-Dioxolanes

ozonide or peroxide	alkene	1,2-dioxolane	yield, %[a]	*Z*/*E* ratio
1a	2a	3a	70	51:49
1a	2b	3b	55	43:57
1a	2c	3c	28	50:50
1a	2d	3d	34	46:54
1a	2e	3e	32	56:44
1a	2f	3f	22	50:50
1a	2g	3g	24	68:32
1a	2h	3h	32	
1a	2i	3i	21	
1b	2a	3j	39[b]	
1b	2h	3k	12	
1b	2i	3l	39	
1c	2a	3a	50	39:61
1c	2b	3b	40	34:66
1c	2c	3c	21	50:50
1c	2d	3d	32	47:53
1c	2e	3e	41	50:50
1c	2f	3f	10	60:40
1c	2g	3g	13	64:36
1c	2h	3h	30	
1c	2i	3i	22	

[a] The isolated yield. [b] The *Z*/*E* ratio was not determined.

Table II. Reaction of 1a or 1c with Monodeuterated Alkene in the Presence of $BF_3{\cdot}OEt_2$[a]

oxonide or peroxide	alkene	1,2-dioxolane yield, %	1,2-dioxolane 4:5:6:7	syn/anti approach[b]	product *Z*/*E* ratio[c]
1a[d]	2a-*2-d*	45	16:14:42:28	30:70	44:56
1a	2a-*2-d*	70	19:12:40:29	31:69	48:52
1a	2j-*1-d*	28	13:9:39:39	22:78	52:48
1c	2a-*2-d*	48	17:19:44:20	36:64	37:63
1c	2j-*1-d*	20	18:15:39:28	33:67	46:54

[a] The reaction was performed in the presence of an equimolar amount of boron trifluoride–diethyl ether for 20 min. [b] The (4 + 5)/(6 + 7) ratio. [c] The (4 + 7)/(5 + 6) ratio. [d] The reaction was performed in the presence of 0.05 mol equiv of boron trifluoride–diethyl ether for 3 min.

$$\underset{\mathbf{1c}}{\mathrm{PhCH(OH)OOCH(OH)Ph}} + \mathbf{2a}\text{–i} \xrightarrow{BF_3{\cdot}OEt_2} \mathbf{3a}\text{–i} \quad (2)$$

The reactions of 1,1-diphenyl-2,2-dimethylethylene ozonide or bis(α-hydroxycyclohexyl) peroxide with α-methylstyrene (**2a**) did not give the corresponding 1,2-dioxolanes. The reactions of the ozonide **1a** with styrene, 1,1-diphenyl-2-methylethylene, and *trans*-stilbene also did not produce the corresponding 1,2-dioxolanes. These results would suggest that this method is effective

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(1) Leading reviews for 1,2-dioxolanes and the related peroxides: (a) Balci, M. *Chem. Rev.* **1981**, *81*, 91. (b) Porter, N. A. In "Free Radicals in Biology"; Pryor, W. A., Ed., Academic Press: New York, 1980; Vol. 4. (c) Nicolaou, K. C.; Gasic, G. P.; Barnette, W. E. *Angew, Chem., Int. Ed. Engl.* **1978**, *17*, 293.

(2) (a) Salomon, M. F.; Salomon, R. G. *J. Am. Chem. Soc.* **1977**, *99*, 3500. (b) Porter, N. A.; Gilmore, D. W. *Ibid.* **1977**, *99*, 3503. (c) Wilson, R. M.; Rekers, J. W. *Ibid.* **1981**, *103*, 206. (d) Adam, W.; Sanabia, J. *Ibid.* **1977**, *99*, 2735. (e) Adam, W.; Birke, A.; Cadiz, C.; Diaz, S.; Simon, D.; Rodriguez, A. *J. Org. Chem.* **1978**, *43*, 1154. (f) Bloodworth, A. J.; Eggelte, H. J. *J. Chem. Soc., Perkin Trans. 1* **1981**, 1375. (g) Kropf, H.; von Wallis, H. *Synthesis*, **1981**, 237.

(3) (a) Thermolysis: Adam, W.; Duran, N. *J. Am. Chem. Soc.* **1977**, *99*, 2729. (b) Acidolysis: ref 2c. (c) Decomposition with low-valent metal: Suzuki, M.; Noyori, R. *Ibid.* **1981**, *103*, 5606. (d) LAH reduction: ref 3a.

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(5) Miura, M.; Yoshida, M.; Nojima, M.; Kusabayashi, S. *J. Chem. Soc., Chem. Commun.* **1982**, 397.

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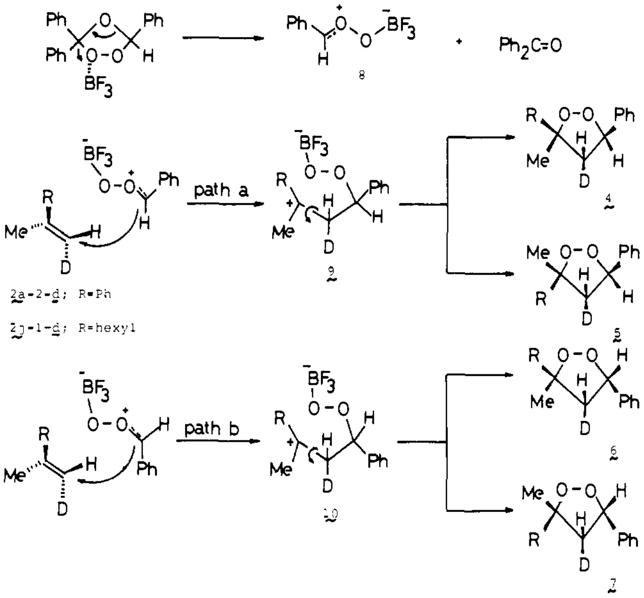
Scheme I



only for the synthesis of 3,3,5-trisubstituted 1,2-dioxolanes.

To obtain an insight into the mechanism of this reaction, the reaction of the ozonide **1a** with (*E*)-1-methyl-2-deuteriostyrene (**2a**-*2-d*) was undertaken in the presence of boron trifluoride-diethyl ether for 3 min. The products were a mixture of four mondeuterated 1,2-dioxolanes **4–7**, the composition being 16:14:42:28 (Table II). A similar product composition was also obtained from the reaction of **1a** with (*E*)-2-methyl-1-octene-*1-d* (**2j**-*1-d*). The mechanism in Scheme I seems to rationalize these results most satisfactory. If it is presumed that the acid-mediated decomposition of ozonides proceeds via the acid-coordinated carbonyl oxides,[6,7] then the first step of the reaction would involve attack of the BF_3-coordinated carbonyl oxide **8** on the alkene to yield two intermediates **9** and **10**, which in turn leads to ring closure to provide 1,2-dioxolanes. However, the rate of the ring closure is significantly slower than C–C bond rotation, and consequently, four isomeric products are produced. This mechanism in Scheme I illustrates that the ratio of (**4a** + **5a**) to (**6a** + **7a**) corresponds to the ratio of two approaches of the BF_3-coordinated carbonyl oxide **8** to the alkene **2a**-*2-d*. The observed ratio of 3:7 suggests that the approach in which the two phenyl groups are placed anti is significantly favored (path b). Probably, a relatively large steric hindrance in the alternative approach (path a) is responsible. However, the C–C bond rotation would be significantly faster than the ring closure, and as a result, the (*E*)- and (*Z*)-1,2-dioxolanes would be obtained in roughly equal amounts.

Table III. Thermolysis of 1,2-Dioxolanes

1,2-dioxolane	reaction time, h	yield of product, mol %[a] 11	12	13
E-3a	2	162		9
Z-3a	2	162		9
E-3b	2	71	69	14
Z-3b	2	73	65	14
E-3c	4	57	64	
Z-3c	4	51	62	

[a] The yield was determined by GLC.

Table IV. Thermal Decomposition of a Mixture of (*E*)- and (*Z*)-1,2-Dioxolanes

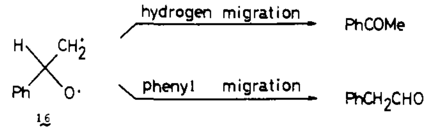
1,2-dioxolane	time, min	conversion, %	*E*/*Z* ratio[a]
3a	0	0	54:46
3a	10	10	53:47
3a	60	81	50:50
3b	0	0	42:58
3b	10	12	43:57
3b	30	36	48:52
3b	60	74	48:52

[a] The ratio was determined by NMR spectroscopy.

This fact leads us to deduce that (*E*)- and (*Z*)-1,2-dioxolanes have a similar stability. This trend is also observed between *E*- and *Z*-3-substituted 1-cyclopentanols.[8]

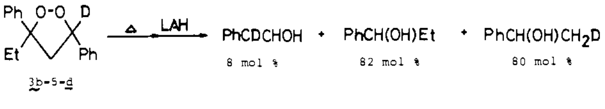
Thermolysis of (*E*)- and (*Z*)-1,2-Dioxolanes. Thermolysis of the isomeric 1,2-dioxolanes **3a–c** was performed at 160 °C. The products were a mixture of fragmentation and rearrangement carbonyl compounds **11–13** (Table III and Scheme II). The reaction followed first-order kinetics; the rate constants were $(1.4 \pm 0.2) \times 10^{-4}\ s^{-1}$ for *Z*-**3b** and $(1.2 \pm 0.2) \times 10^{-4}\ s^{-1}$ for *E*-**3b**, suggesting that there exists no significant difference in the rate of the decomposition between these two stereoisomers (see also the data in Table IV).

On the basis of the product, kinetic, and stereolabeling results for the thermal fragmentation of a series of 3,3,5,5-tetrasubstituted 1,2-dioxolanes, Adam and Duran[3a] have proposed a mechanism involving two-bond cleavage leading to the 1-oxatrimethylene radical and ketone (Scheme II). In this framework, we now attempt to rationalize the results obtained from the thermolysis of the 1,2-dioxolanes **3a–c**. As the data in Table III indicate, the ketones **11** and **12** were the major products in all cases, suggesting that path a in Scheme II is preferred, i.e., the order of ejection of carbonyl compounds follows the sequence: $CH_3(CH_2)COMe \geq PhCOMe > PhCHO$. The absence of phenylacetaldehyde in the products would suggest that in the 1,3-diradical **16**, hydrogen migration is significantly preferred than phenyl migration (eq 3).



(3)

Consistent with this, the thermolysis of the monodeuterated 1,2-dioxolane **3b**-*5-d* followed by lithium aluminum hydride (LAH) reduction, provided 1-phenylethanol-*2-d* along with benzyl-*α-d* alcohol and 1-phenylpropanol (eq 4). This trend of



(4)

migrating aptitutdes, H > Ph, is the same as that observed in the thermolysis of α-epoxy lactones[9] and the photolysis of saturated epoxides,[10] α-epoxy ketones,[11] α-epoxy olefins,[12] aryloxylanes,[13]

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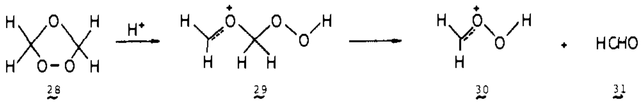
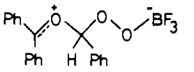
(6) MO calculations suggest that acid-catalyzed decomposition of ethylene ozonide (**28**) provides first the carboxonium ion **29**, which in turn decomposes into a mixture of protonated formaldehyde *O*-oxide (**30**) and formaldehyde



(**31**). The carboxonium ion **29** is, however, 36 kcal/mol more stable than **30** + **31**, suggesting that the corresponding carboxnium ion **32**, formed from



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the ozonide **1a**, rather than the BF_3-coordinated carbonyl oxide **8** would be a real intermediate leading to 1,2-dioxolanes. Both of these species **32** and **8**, however, lead to a same mechanistic interpretation for the formation of the 1,2-dioxolane, and therefore, for convenience, the argument in this paper is advanced by postulating the key intermediate in this reaction is the BF_3-coordinated carbonyl oxide **8**.

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Scheme II

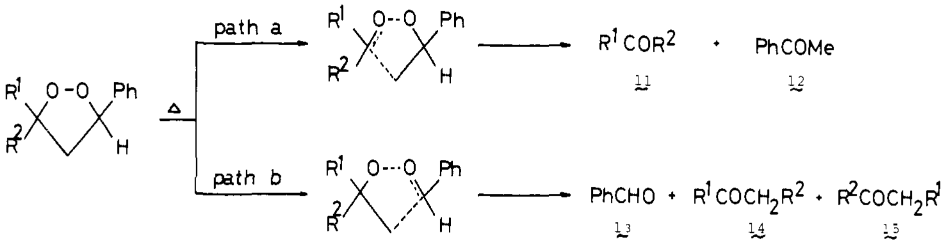


Table V. $TiCl_4$-Mediated Decomposition of 1,2-Dioxolanes[a]

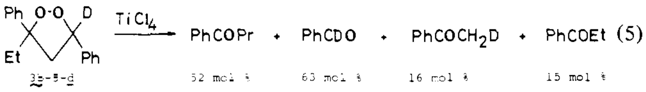
1,2-dioxolane	yield of product, mol %[b]					path a/ path b[c]
	11	12	13	14	15	
E-3a	89		42	31		55:45
E-3a[d]	45		23	15		54:46
Z-3a	87		49	28		53:47
E-3b	20	22	46	67		27:73
E-3b	36	27	79	36		36:64
E-3c	42	35	32	40	11	48:52
E-3c[e]	20	16	15	19	5	48:52
Z-3c	23	26	41	20	54	31:69

[a] The reaction was performed in the presence of an equimolar amount of $TiCl_4$ at −30 °C for 15 min unless otherwise noted. [b] The yield was determined by GLC. [c] The (11 + 12)/(13 + 14 + 15) ratio. [d] The reaction for 2 min. Only *E*-3a was recovered (40%). [e] The reaction for 2 min. Only *E*-3c was recovered (50%).

and α-nitro epoxides,[14] in which the sequence H > Me > Ph is observed. Adam and Duran[3a] have found the order Me > Ph for the thermolysis of 3,3,5,5-tetrasubstituted 1,2-dioxolanes. From **3a** and **3b**, a small amount of benzaldehyde (**13**) was also obtained. We failed, however, to isolate the carbonyl compounds **14** and **15**, which would be formed together with **13** (path b in Scheme II).

$TiCl_4$-Mediated Decomposition of (*E*)- and (*Z*)-1,2-Dioxolanes. The reaction of the 1,2-dioxolanes **3a–c** in the presence of an equimolar amount of $TiCl_4$ at −30 °C provided a mixture of the carbonyl compounds **11–15** (Table V). When the data in Table V were compared with those from the thermolysis (Table III), the following characteristics were noted: (a) Although the ketones **11** and **12** were the exclusive or predominant products in the thermolysis, the acidolysis yielded, together with **11** and **12**, the carbonyl compounds **13–15** in considerable amounts. (b) The product distribution was influenced by the stereochemistry of the 1,2-dioxolanes to a small but significant extent, this trend being in marked contrast to that observed in the thermolysis.

A most probable mode of decomposition of the 1,2-dioxolanes is shown in Scheme III. The first step would involve coordination of $TiCl_4$ to one of the peroxidic oxygens of the 1,2-dioxolanes. The coordination to the oxygen at the 1-position would be followed by the cleavage of the O–O and C(3)–C(4) bonds. Subsequently, the C-5 hydrogen would migrate to C-4, and as a result, an equimolar mixture of **11** and **12** would be obtained (path a in Scheme III). In contrast, the 1,2-dioxolanes, coordinated by $TiCl_4$ at O(2), would yield a mixture of the carbonyl compounds **13–15**, as illustrated in path b in Scheme III. It is worth noting that we failed to detect the formation of phenyl-migrated products, $PhCH_2CHO$ (path a) or $PhCH_2COR^2$ **15** (path b). Consistent with this, the reaction of monodeuterated 1,2-dioxolane **3b**-*5*-*d* with $TiCl_4$ yielded acetophenone-α-*d* and butyrophenone together with propiophenone and benzaldehyde-*d* (eq 5). These results would suggest that the migrating ability of the phenyl group is significantly lower than that of hydrogen and alkyl substituents. This trend is clearly inconsistent with that found in the acid-catalyzed decomposition of epoxides; aryl > H > Et > Me.[15] Rather this trend is consistent with that observed for the 1-oxatrimethylene diradical.[9-14]



Scheme III

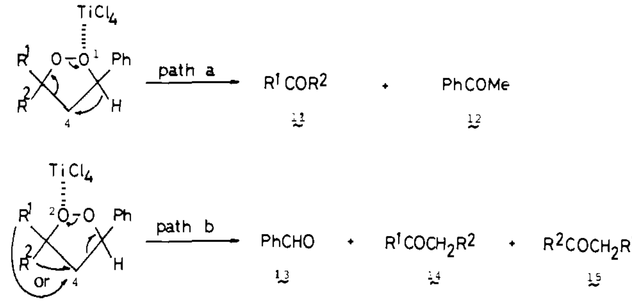


Table VI. Reaction of a *Z*-*E* Mixture of 1,2-Dioxolanes in the Presence of $TiCl_4$[a]

1,2-dioxolane (*Z*/*E*)	recovered 1,2-dioxolane	
	%	*Z*/*E*
3a (50:50)	43	80:20
3b (40:60)	31	70:30
3c (50:50)	30	10:90
3d (50:50)	43	10:90

[a] The reaction was performed in the presence of 0.5 mol equiv of $TiCl_4$ at −30 °C for 15 min.

To see if the rate of $TiCl_4$-mediated decomposition is a function of the stereochemistry of the 1,2-dioxolanes, roughly 1:1 mixtures of the *E*–*Z* pairs of the 1,2-dioxolanes **3a–d** were treated with 0.5 mol equiv of $TiCl_4$, and the compositions of the recovered 1.2-dioxolanes were determined by NMR spectroscopy (Table VI). The data revealed the following: (a) The two stereoisomeric 1,2-dioxolanes decomposed at significantly different rates, this trend being in marked contrast to that observed in the thermolysis (Table IV). (b) In the case of 3,5-diphenyl-3-methyl-1,2-dioxolane (**3a**) and 3,5-diphenyl-3-ethyl-1,2-dioxolane (**3b**), the *E* isomers decomposed faster than the *Z* isomers. In direct contrast, the rate of decomposition of (*Z*)-3-heptyl-3-methyl-5-phenyl-1,2-dioxolane (*Z*-**3c**) and (*Z*)-3-methyl-3-propyl-5-phenyl-1,2-dioxolane (*Z*-**3d**) was significantly larger than that of the corresponding *E* isomers. In connection with this, it was noted that interconversion of two stereoisomeric 1,2-dioxolanes does not occur under the reaction conditions, as exemplified by the examination of stereochemistry of the unreacted peroxide after partial decomposition (Table V). The same trend was also observed in the thermal decomposition.

A brief comment is made regarding the notable effects of the stereochemistry of the 1,2-dioxolanes on the rate of decomposition and on the product composition. We expect that the 1,2-dioxolanes adopt conformations in which the steric interactions between the phenyl substituent at C-5 and the bulky R¹ at C-3 are minimized. Since cyclopentane derivatives are prone to adopt either envelope or half-chair conformations,[16] it is likely that the *Z* isomer has

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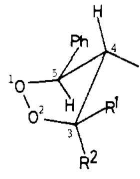
Table VII. Decomposition of 1,2-Dioxolanes with $FeSO_4$[a]

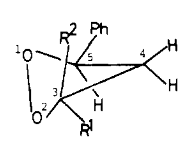
1,2-dioxolane	$FeSO_4$, mol equiv	product yield, mol %[b]					
		11	**17**	18	19	**20**	**21**
E-3a	0.5	70	29	14	4	4	
Z-3a	0.5	72	36	11	8	7	
E-3b	1.0	21					49
Z-3b	1.0	14					36

[a] The reaction was performed in aqueous THF for 2 h under a nitrogen atmosphere. [b] The yield was determined by GLC.

an envelope conformation, whereas a half-chair conformation is important in the case of the *E* isomer. If the migrating ability of a particular substituent is controlled only by steric factors, then molecular models suggest that the order of migration of substituents at C-3 and C-5 follows the sequence: pseudoequatorial substituent in the envelope form > pseudoequatorial substituent in the half-chair form > pseudoaxial substituent in the half-chair form > pseudoaxial substituent in the envelope form.[17] The product compositions obtained from the decomposition of (*E*)- and (*Z*)-3-heptyl-3-methyl-5-phenyl-1,2-dioxolanes (**3c**), in which both the methyl and heptyl groups can migrate, allow an assessment of the validity of this hypothesis. When the yields of the methyl-migrated product $Me(CH_2)_6COEt$ **14** are compared, the *E* isomer provided this compound in a greater percentage than the *Z* isomer, suggesting that the pseudoaxial methyl substituent in the half-chair form would migrate more readily than the pseudoaxial methyl substituent in the envelope form. *E*- and *Z*-**3c** yielded the heptyl-migrated product $Me(CH_2)_7COMe$ **15** in 11% and 54% yields, respectively, suggesting that the pseudoequatorial heptyl substituent in the envelope form has a greater migrating ability than the pseudoequatorial heptyl substituent in the half-chair form. These results lead us to deduce that the conformations of the 1,2-dioxolanes as well as the migrating aptitude of the substituents are important in determining the stereochemical dependence of the relative rate of the decomposition and the product composition.

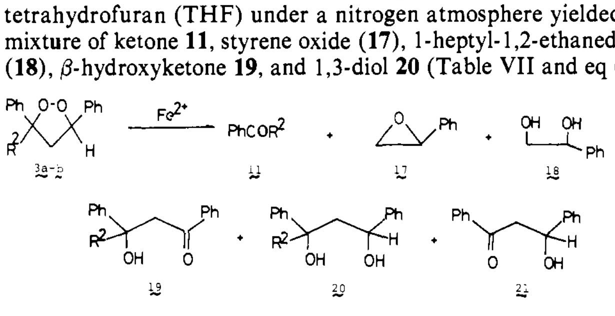


envelope form



half-chair form

Decomposition of (*E*)- and (*Z*)-1,2-Dioxolanes with $FeSO_4$. Treatment of *E*- or *Z*-**3a** with 0.5 mol equiv of $FeSO_4$ in aqueous tetrahydrofuran (THF) under a nitrogen atmosphere yielded a mixture of ketone **11**, styrene oxide (**17**), 1-heptyl-1,2-ethanediol (**18**), β-hydroxyketone **19**, and 1,3-diol **20** (Table VII and eq 6).



(6)

In contrast, the reaction of *E*- or *Z*-**3b** gave, along with **11**, the ketol **21** as the major product. The stereochemistry of the 1,2-dioxolanes **3a**–**b** did not exert a significant influence on the product composition or on the rate of the decomposition; when an equimolar mixture of *E*- and *Z*-**3a** was treated with 0.3 mol equiv of $FeSO_4$, 48% of the 1,2-dioxolane **3a** was recovered, the *E*/*Z* ratio being 44:56. A similar trend was also observed in the case of E–Z-**3b**.

Since low-valent metals are the selective reagents to cleave the O–O bond of peroxides by a process involving single electron transfer (SET),[3c,18] it is reasonable to expect that the first step of the reaction of **3** with $FeSO_4$ also involves SET to yield two radical anions **22** and **23** (Scheme IV). Ejection of $PhCOR^2$ from the intermediate **22** produces the new radical anion **24**, which in turn yields the epoxide **17**. The epoxide **17** is a reasonable precursor of the diol **18**. Thus, treatment of **17** with $FeSO_4$ in aqueous THF gave the diol **18** in 50% yield. Furthermore, elimination of ethyl radical from the intermediate **22** provides the ketol **21**. These experimental results interpreted as the ease of β-bond fission in the intermediate **22** determining the course of the reaction give the following order for ease of β-bond fission: C(3)–Et > C(3)–C(4) > C(3)–Me, C(3)–Ph. It is worth noting that the order of ejection of the alkyl radical R· from the alkoxy radical $R_3O·$ follows the sequence *i*-Pr > Et > Me > Ph, i.e., the order of the stability of the radicals.[19] The predominant formation of the ketol **21** from **3b** and the isolation of $PhCOR^2$ (**11**, R = Me), epoxide **17**, and diol **18** in considerable amounts from the reaction of **3a** suggest that of the two possible anion radicals **22** and **23**, the contribution of **22** is significantly larger than that of **23**.

Scheme IV

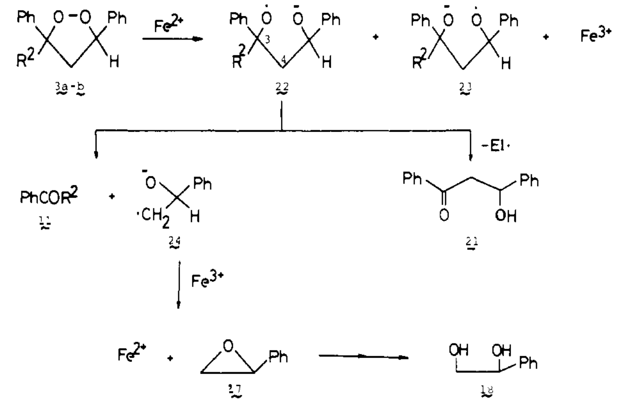


Table VIII. Reduction of 1,2-Dioxolanes with Lithium Aluminum Hydride[a]

1,2-dioxolane	product yield, mol %[b]		
	20	25	**26**
E-3a	59	59	
Z-3**a**	75	28	
E-3b	77	60	45
Z-3b	81	13	9
E-3c	85		
Z-3c	73	16	15

[a] A solution of a 1,2-dioxolane and LAH (2 mol equiv) in ether was refluxed for 2 h. [b] The yield was determined by GLC.

Lithium Aluminum Hydride Reduction of (*E*)- and (*Z*)-1,2-Dioxolanes. Treatment of the 1,2-dioxolanes **3a**–**c** with lithium aluminum hydride (LAH) yielded mainly the expected diol **20**, the reduction proceeding stereospecifically, i.e., the reduction of the *Z* isomer provided exclusively the erythrodiol, whereas only the threo isomer was obtained from the (*E*)-1,2-dioxolane.[3a] However, this reduction was accompanied by the formation of C–C bond-cleavage products, $R^1CH(OH)R^2$ **25** and 1-phenylethanol (**26**) (eq 7 and Table VIII). Moreover, the product

$$\mathbf{3a\text{–}c} \xrightarrow{\text{LiAlH}_4} \underset{\mathbf{20}}{R^1R^2C(OH)CH_2CH(OH)Ph} + \underset{\mathbf{25}}{R^1CH(OH)R^2} + \underset{\mathbf{26}}{PhCH(OH)Me} \qquad (7)$$

a, R^1 = Ph, R^2 = Me. **b**, R^1 = Ph; R^2 = Et. **c**, R^1 = heptyl, R^2 = Me

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[17] The order for ease of the back-side attack: Eliel, E. L. "Stereochemistry of Carbon Compounds"; McGraw-Hill: New York, 1962.

(18) (a) Hyde, M. R.; Espenson, J. H. *J. Am. Chem. Soc.* **1976**, *98*, 4463. (b) Kochi, J. K. "Organometallic Mechanism and Catalysis"; Academic Press: New York, 1978.

(19) (a) Wijnen, M. H. *J. Am. Chem. Soc.* **1960**, *82*, 3034. (b) Walling, C.; Wagner, P. J. *Ibid.* **1964**, *86*, 3368. (c) Zavistas, H. A.; Seltzer, S. *Ibid.* **1964**, *86*, 3836.

Table IX. Reaction of 1,2-Dioxolanes with Triethylamine[a]

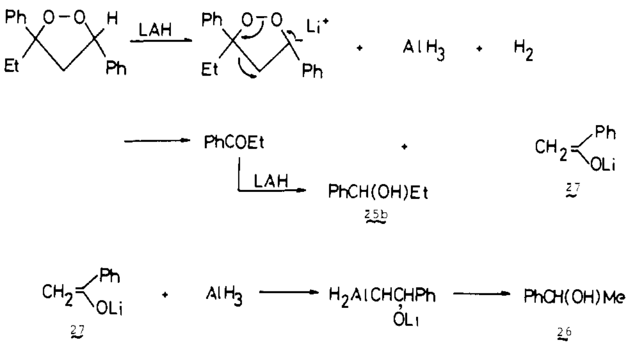
1,2-dioxolane	product yield, mol % 11	product yield, mol % 12
E-3a	150	
Z-3a	150	
E-3b	77	83
Z-3b	72	72
3h	94	83

[a] The reaction was performed in the presence of 0.1 mol equiv of triethylamine in methylene chloride at 20 °C for 2 h. [b] The yield was determined by GLC.

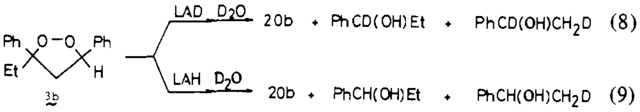
composition was a marked function of the stereochemistry of the 1,2-dioxolanes. For **3a–b** the *E* isomers afforded the corresponding cleavaged products **25** and **26** in relatively larger amounts, whereas for **3c** the *Z* isomer produced these products, **25** and **26**, in a greater amount. The reaction of a mixture of *E*- and *Z*-**3a** (the ratio = 63:38) with 0.5 mol equiv of LAH for 2 h resulted in recovery of the *E–Z* mixture of **3a** (36%), the composition being 58:42. This result suggests that these two isomers decompose at a similar rate.

A possible mechanism rationalizing the formation of the C–C bond-cleavage products **25** and **26** is illustrated in Scheme V. The first step of the reaction involves abstraction of hydrogen from C-5. Subsequent electron migration provides a mixture of propiophenone and the intermediate **27**, the former being reduced by LAH to yield the alcohol **25b**, whereas hydroalumination of the latter intermediate **27** and subsequent workup with water would produce the alcohol **26**.

Scheme V



The following results seem to support this proposed mechanism: (a) Lithium aluminum deuteride (LAD) reduction of *E*-**3b** followed by workup with D_2O gave a mixture of 1-phenyl-1-ethanol-*1,2-d*$_2$, 1-phenylpropanol-*1-d*, and the diol **20b** (eq 8). (b)



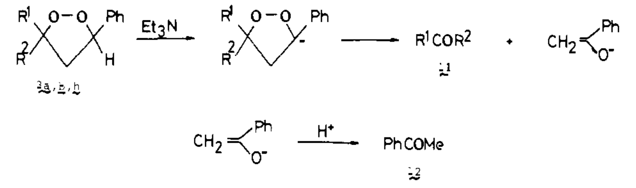
Treatment of **3b** with LAH followed by workup with D_2O yielded 1-phenyl-1-ethanol-*2-d* (eq 9). In connection with this, treatment of **3a,b,h** with triethylamine in methylene chloride gave an equimolar mixture of R^1COR^2 (**11**) and acetophenone (**12**) (Table IX). The first step of this reaction also must involve the abstraction of the hydrogen from C-5,[20] followed by electron mi-

Table X. The Physical Properties of 1,2-Dioxolanes[a]

1,2-dioxolane	m/e (M⁺)	^{1}H NMR, δ
E-3a		1.66 (s, 3 H), 2.87 (d × d, *J* = 12.0 and 7.8 Hz, 1 H), 3.14 (d × d, *J* = 12.0 and 7.5 Hz, 1 H), 5.42 (t, *J* = 7.8 Hz, 1 H), 7.2–7.5 (m, 10 H)
Z-3a[b]		1.63 (s, 3 H), 2.68 (d × d, *J* = 12.0 and 8.1 Hz, 1 H), 3.29 (d × d, *J* = 12.0 and 7.2 Hz, 1 H), 5.15 (t, *J* = 7.8 Hz, 1 H), 7.2–7.5 (m, 10 H)
E-3b		0.85 (t, *J* = 7.2, 3 H), 2.01 (q, *J* = 7.2, 2 H), 2.86 (d × d, *J* = 12.0 and 8.1 Hz, 1 H), 3.18 (d × d, *J* = 12.0 and 8.1 Hz, 1 H), 5.37 (t, *J* = 8.1 Hz, 1 H), 7.2–7.5 (m, 10 H)
Z-3b		0.79 (t, *J* = 7.2 Hz, 3 H), 1.99 (q, *J* = 7.2 Hz, 2 H), 2.70 (d × d, *J* = 12.0 and 8.7 Hz, 1 H), 3.27 (d × d, *J* = 12.0 and 7.5 Hz, 1 H), 5.12 (t, *J* = 8.1 Hz, 1 H), 7.2–7.5 (m, 10 H)
E-3c		0.7–1.8 (m, 15 H), 2.68 (d × d, *J* = 12.0 and 7.8 Hz, 1 H), 2.72 (d × d, *J* = 12.0 and 7.8 Hz, 1 H), 5.29 (t, *J* = 7.8 Hz, 1 H), 7.2–7.6 (m, 5 H)
Z-3c		0.7–1.8 (m, 15 H), 2.30 (d × d, *J* = 12.0 and 7.8 Hz, 1 H), 2.81 (d × d, *J* = 12.0 and 7.8 Hz, 1 H), 5.24 (t, *J* = 7.8 Hz, 1 H), 7.2–7.6 (m, 5 H)
E-3d[c]	206	0.91 (t, *J* = 7.2 Hz, 3 H), 1.35 (s, 3 H), 1.18–1.90 (m, 4 H), 2.36 (d × d, *J* = 12.0 and 7.8 Hz, 1 H), 2.69 (d × d, *J* = 12.0 and 7.8 Hz, 1 H), 5.26 (t, *J* = 7.8 Hz, 1 H), 7.1–7.8 (m, 5 H)
Z-3d[d]	206	0.95 (t, *J* = 6.3, 3 H), 1.39 (s, 3 H), 1.34–1.85 (m, 4 H), 2.36 (d × d, *J* = 12.0 and 7.8 Hz, 1 H), 2.83 (d × d, *J* = 12.0 and 7.8 Hz, 1 H), 5.22 (t, *J* = 7.8 Hz, 1 H), 7.2–7.7 (m, 5 H)
E-3e		0.84–1.10 (m, 3 H), 1.39 (s, 3 H), 1.52–1.94 (m, 2 H), 2.40 (d × d, *J* = 12.0 and 7.8 Hz, 1 H), 2.71 (d × d, *J* = 12.0 and 7.8 Hz, 1 H), 5.30 (t, *J* = 7.8 Hz, 1 H), 7.2–7.8 (m, 5 H)
Z-3e		0.84–1.10 (m, 3 H), 1.39 (s, 3 H), 1.52–1.94 (m, 2 H), 2.25 (d × d, *J* = 12.0 and 7.8 Hz, 1 H), 2.81 (d × d, *J* = 12.0 and 7.8 Hz, 1 H), 5.22 (t, *J* = 7.8 Hz, 1 H), 7.2–7.8 (m, 5 H)
E-3f		0.84–1.16 (m, 6 H), 1.26 (s, 1 H), 1.60–2.20 (m, 1 H), 2.40 (d × d, *J* = 12.0 and 8.7 Hz, 1 H), 2.64 (d × d, *J* = 12.0 and 7.5 Hz, 1 H), 5.31 (t, *J* = 8.1 Hz, 1 H), 7.2–7.8 (m, 5 H)
Z-3f		0.84–1.16 (m, 6 H), 1.32 (s, 1 H), 1.60–2.20 (m, 1 H), 2.19 (d × d, *J* = 12.0 and 8.1 Hz, 1 H), 2.83 (d × d, *J* = 12.0 and 8.1 Hz, 1 H), 5.16 (t, *J* = 8.1 Hz, 1 H), 7.2–7.8 (m, 5 H)
E-3g		0.76–1.04 (m, 6 H), 2.0–2.4 (m, 1 H), 2.88 (d × d, *J* = 12.0 and 8.4 Hz, 1 H), 3.24 (d × d, *J* = 12.0 and 8.4 Hz, 1 H), 5.32 (t, *J* = 8.4 Hz, 1 H), 7.0–7.7 (m, 10 H)
Z-3g		0.76–1.04 (m, 6 H), 2.0–2.4 (m, 1 H), 2.75 (d × d, *J* = 12.0 and 8.7 Hz, 1 H), 3.37 (d × d, *J* = 12.0 and 6.6 Hz, 1 H), 5.04 (t, *J* = 7.8 Hz, 1 H), 7.0–7.7 (m, 10 H)
3h[b,e]	302	3.26 (d × d, *J* = 12.0 and 8.4 Hz, 1 H), 3.72 (d × d, *J* = 12.0 and 7.5 Hz, 1 H), 5.36 (t, *J* = 7.8 Hz, 1 H), 7.1–7.6 (m, 15 H)
3i[f]	218	1.2–2.0 (m, 10 H), 2.10 (d × d, *J* = 12.0 and 7.8 Hz, 1 H), 2.73 (d × d, *J* = 12.0 and 7.8 Hz, 1 H), 5.26 (t, *J* = 7.8 Hz, 1 H), 7.2–7.5 (m, 5 H)
3j[g]		0.87 (t, *J* = 7.2, Me), 1.05–1.56 (m, CH_2), 1.56 (s, Me), 1.59 (s, Me), 2.16–3.12 (m, CH_2), 4.06–4.56 (m, CH), 7.1–7.6 (m, Ar)
3k		1.1–2.1 (m, 11 H), 2.88 (d × d, *J* = 12.0 and 7.8 Hz, 1 H), 3.42 (d × d, *J* = 12.0 and 7.5 Hz, 1 H), 4.41 (m, 1 H), 7.2–7.6 (m, 10 H)
3l		0.8–1.8 (m, 21 H), 1.86 (d × d, *J* = 12.0 and 7.5 Hz, 1 H), 2.38 (d × d, *J* = 12.0 and 7.5 Hz, 1 H), 4.08–4.40 (m, 1 H)

[a] The 1,2-dioxolane was an oil unless otherwise noted. [b] Taken from the data in ref 2g. [c] Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.70; H, 8.79. Found: C, 75.39; H, 8.57. IR 2900, 1450, 1370, 750, 690 cm^{-1}. [d] IR 2900, 1450, 1370, 750, 690 cm^{-1}. [e] Mp 63–65 °C (from benzene-hexane). [f] Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 77.03; H, 8.36. IR 2900, 1450, 750, 700 cm^{-1}. [g] A mixture of E–Z isomers.

Scheme VI



gration and subsequent proton transfer to yield **11** and **12** (Scheme VI). The reaction of a mixture of 31% *Z*-**3a** and 69% *E*-**3a** revealed that these isomers decompose in exactly an equal rate.

Experimental Section

(*E*)-2-Methyl-1-octene-*1-d* was prepared by the reaction of methylmagnesium bromide with 1-octyne in the presence of copper iodide, followed by workup with a mixture of deuterium chloride, acetic acid-*d*, and deuterium oxide:[21] ^{1}H NMR δ 0.7–2.3 (16 H), 4.64 (s, 1 H). (*E*)-1-Methyl-2-deuteriostyrene was obtained from phenylacetylene by the same procedure: ^{1}H NMR δ 2.12 (s, 3 H), 5.32 (s, 1 H), 7.1–7.5 (m, 5 H).

Synthesis and Assignment of (*E*)- and (*Z*)-1,2-Dioxolanes. To a solution of an olefin (2 mmol) and an ozonide (2 mmol) in methylene chloride (10 mL) kept at 0 °C was added a solution of boron trifluoride–diethyl ether (2 mmol) in methylene chloride (5 mL) in one portion, and the reaction was continued at this temperature for 20 min. Then the reaction mixture was poured into hydrochloric acid and extracted with ether. The ether solution was washed with aqueous KOH and saturated brine, dried (Na_2SO_4), and evaporated. Column chromatography on silica gel (elution with 1:1 benzene–hexane) afforded first the 1,2-dioxolane and then benzophenone. When the 1,2-dioxolane was a mixture of *E* and *Z* isomers, these isomers were separated from each other by elaborate column chromatography on silica gel. The *Z* isomer was eluted first followed by the *E* isomer. The stereochemistry was determined by analysis of ^{1}H NMR spectra. On the basis of the expected field effects on chemical shifts,[22] the extent of the downfield shift of the hydrogens at C-4 was presumed to decrease in the following order: the pseudoequatorial hydrogen in the *Z* form > the pseudoequatorial hydrogen in the *E* form > the pseudoaxial hydrogen in the *E* form > the pseudoaxial hydrogen in the *Z* form, i.e., as the different conformations of two stereoisomers suggest; for the *E* isomer the two hydrogens at C-4 would have a similar chemical shift, whereas a significant difference in the chemical shifts is expected for the *Z* isomer. Consistent with this, for *Z*-**3a** irradiation of the band of the hydrogen at C-5 [δ 5.37 (t, *J* = 7.8 Hz)] resulted in the increase of the integrated intensity of the pseudoequatorial hydrogen at C-4 syn to the C-5 hydrogen [δ 3.29 (d, *J* v 12.0 Hz); 10 ± 2%], whereas the anti hydrogen [δ 2.87 (d, *J* = 12.0 Hz)] did not give rise to any significant change in the intensity.[23]

Reaction of 1a with (*E*)-1-Methyl-2-deuteriostyrene in the Presence of Boron Trifluoride–Diethyl Ether. The reaction of **1a** with **2a**-*2-d* afforded the monodeuterated 1,2-dioxolanes. Column chromatography on silica gel gave two fractions. The NMR spectrum of the first fraction showed that the signals attributable to the hydrogens at C-4 appear at δ 2.68 (d, *J* = 8.1 Hz) and 3.29 (d, *J* = 8.1 Hz), the ratio of the peak areas being 2:3. On the basis described above, the minor isomer and the major one of this fraction were assigned as **4a** and **7a**, respectively. In the case of the second fraction, the hydrogens at the same position appeared at δ 2.87 (d, *J* = 7.8 Hz) and 3.14 (d, *J* = 7.5 Hz), the ratio of the peak areas being 23:77. From the chemical shifts, the minor isomer and the major one of this fraction were assigned as **5a** and **6a**, respectively.

Reaction of 1a with (*E*)-2-Methyl-1-octene-*1-d* in the Presence of Boron Trifluoride–Diethyl Ether. The reaction of **1a** with **2j**-*1-d* afforded the monodeuterated 1,2-dioxolanes. Column chromatography on silica gel gave two fractions. The first fraction was a mixture of **4j** and **7j** (15% yield, **4j**/**7j** = 1:3) and the second fraction was a mixture of **5j** and **6j** (13% yield, **5j**/**6j** = 19:91). To determine the product composition, the mixture of **4j** and **7j** was irradiated at δ 5.16 to give the four signals: δ 2.28 (**4j**), 2.38 (**5j**), 2.68 (**6j**), 2.79 (**7j**), the peak areas being compared.

Thermolysis of 3,5-Diphenyl-3-ethyl-1,2-dioxolane-*5-d*. A glass tube containing **3b**-*5-d* (1 mmol) and anhydrous benzene (2 mL) was evacuated and sealed. The reaction was performed at 160 °C for 2 h. Treatment of the crude products with LAH afforded a mixture of benzyl alcohol, 1-phenylethanol, and 1-phenylpropanol in yields of 8%, 82%, and 80%, respectively. Analysis by GC-MS confirmed the formation of benzyl alcohol-*α-d* [*m*/*e* 109 (M^+)], 1-phenylethanol-*2-d* [*m*/*e* 123 (M^+)], and 1-phenylpropanol [*m*/*e* 136 (M^+)].

Rate of Decomposition of *E*- or *Z*-3b. A solution of a peroxide (7 mmol) and diphenylmethane (4 mmol; an internal standard) in decane (5 mL) in a capped tube was kept at 160 °C. An aliquot was withdrawn periodically, and the yield of the unreacted 1,2-dioxolane was determined by ^{1}H NMR spectroscopy.

Thermolysis of an *E*–*Z* Mixture of 1,2-Dioxolanes. A solution of the *E*–*Z* mixture of the dioxolane (7 mmol) and diphenylmethane (4 mmol; an internal standard) in decane was refluxed (176 °C). The yield and composition of the unreacted 1,2-dioxolanes were determined as above.

$TiCl_4$-Mediated Decomposition of 3,5-Diphenyl-3-ethyl-1,2-dioxolane-*5-d*. To a solution of **3b**-*5-d* (1 mmol) in methylene chloride (15 mL) a mixture of $TiCl_4$ (1 mmol) and methylene chloride (5 mL) was added in one portion at −30 °C. The reaction was continued at −30 to −20 °C for a further 15 min. After conventional workup, the products were analyzed by GLC to contain benzaldehyde (63%), acetophenone (16%), propiophenone (15%), and butyrophenone (52%). Analysis gy GC-MS revealed that the products were a mixture of benzaldehyde-*α-d* [*m*/*e* 107 (M^+)], acetophenone-*α-d* [*m*/*e* 121 (M^+)], propiophenone [*m*/*e* 134 (M^+)], and butyrophenone [*m*/*e* 148 (M^+)].

LAH Reduction of 1,2-Dioxolane. To a solution of *E*-**3a** (1 mmol) in anhydrous ether (30 mL) was added LAH (2 mmol), and the reaction was continued for 2 h under reflux. Column chromatography on silica gel afforded 1-phenylethanol and *threo*-**20a**. *threo*-**20a** was a solid: mp 89–92 °C (from benzene–hexane); *m*/*e* 242 (M^+); ^{1}H NMR δ 1.68 (s, 3 H), 1.87 (d × d, *J* = 14.7 and 3.0 Hz, 1 H), 2.10 (d × d, *J* = 14.7 and 9.3 Hz, 1 H), 3.97 (s, 2 H), 5.06 (d × d, *J* = 9.3 and 3.0 Hz, 1 H), 7.0–7.5 (m, 10 H). Anal. ($C_{16}H_{18}O_2$) C, H. *erythro*-**20a** was an oil: *m*/*e* 242 (M^+); ^{1}H NMR δ 1.42 (s, 3 H), 1.94–2.32 (m, 2 H), 3.48 (s, 1 H), 4.35 (d × d, *J* = 8.4 and 5.4 Hz, 1 H), 4.68 (s, 1 H), 7.0–7.7 (m, 10 H). Anal. ($C_{16}H_{18}O_2$) C, H. *erythro*-**20b** was an oil: ^{1}H NMR δ 0.72 (t, *J* = 6.6 Hz, 3 H), 1.72 (q, *J* = 6.6 Hz, 2 H), 1.90–2.34 (m, 2 H), 4.40 (d × d, *J* = 8.7 and 4.8 Hz, 1 H), 7.0–7.8 (m, 10 H). *threo*-**20b** was an oil: *m*/*e* 256 (M^+); ^{1}H NMR δ 0.74 (*J* = 7.5 Hz, 3 H), 1.80–2.60 (m, 4 H), 3.56 (s, 2 H), 5.10 (d × d, *J* = 8.4 and 5.7 Hz, 1 H), 7.0–7.5 Hz (m, 10 H). Anal. ($C_{17}H_{20}O_2$) C, H. *threo*-**20c** was an oil: ^{1}H NMR δ 0.88 (t, *J* = 6.0 Hz, 3 H), 1.36 (s, 3 H), 1.0–2.0 (m, 17 H), 3.30 (s, 2 H), 5.05 (d × d, *J* = 10.5 and 2.7 Hz, 1 H), 7.2–7.4 (m, 5 H). *erythro*-**20c** was an oil: ^{1}H NMR δ 0.90 (t, *J* = 6.0 Hz, 3 H), 1.15 (s, 3 H), 1.0–2.0 (m, 17 H), 3.42 (s, 2 H), 4.98 (d × d, *J* = 9.6 and 4.2 Hz, 1 H), 7.2–7.5 Hz (m, 5 H).

A mixture of *E*-**3b** (1 mmol), LAD (2 mmol), and ether (30 mL) was refluxed for 2 h and then decomposed with D_2O. Analysis by ^{1}H NMR spectroscopy and GC-MS revealed that the products were a mixture of *threo*-**20b** [*m*/*e* 256 (M^+); ^{1}H NMR δ 5.10 (d × d, *J* = 8.4 and 5.7 Hz)], 1-phenylpropanol-*1-d* [*m*/*e* 137 (M^+)], and 1-phenylethanol-*1,2-d*$_2$ [*m*/*e* 124 (M^+)].

Treatment of *E*-**3b** (1 mmol) with LAH (2 mmol) followed by workup with D_2O gave a mixture of *threo*-**20b** [*m*/*e* 256 (M^+)], 1-phenylpropanol [*m*/*e* 136 (M^+); ^{1}H NMR δ 4.50 (t, *J* = 6.6 Hz)], and 1-phenylethanol-*2-d* [*m*/*e* 123 (M^+); ^{1}H NMR δ 4.80 (t, *J* = 6.0 Hz).

Decomposition of 1,2-Dioxolanes with $FeSO_4$. In a 50-mL flask, equipped with a magnetic stirrer and maintained under N_2, were added $FeSO_4 \cdot 7H_2O$ (0.5 mmol) and then deionized water (7 mL). Subsequently a solution of *E*-**3a** in THF (10 mL) was added by a syringe, and the reaction was continued at room temperature for 2 h. Column chromatography on silica gel afforded first a mixture of acetophenone and styrene oxide. From the second fraction was obtained a mixture of 1-phenylethanediol, the ketol **19a**, and the threo diol **20a**. Ketol **19a** was a solid: mp 52–55 °C; ^{1}H NMR δ 1.57 (s, 3 H), 3.30 (d, *J* 17.4 Hz, 1 H), 3.78 (d, *J* = 17.4 Hz, 1 H), 4.85 (s, 1 He, 7.1–8.0 (m, 10 H); IR 3300–3600, 1670, 1220 cm^{-1}.

Reaction of *E*-**3b** under the same conditions gave propiophenone and ketol **21**. Ketol **21** was a solid: mp 50–51 °C: ^{1}H NMR δ 3.30 (d, *J* = 6.0 Hz, 2 H), 3.53 (d, *J* = 3.2 Hz, 1 H), 5.26 (t × d, *J* = 6.0 and 3.2 Hz, 1 H), 7.1–7.5 (m, 6 H), 7.7–8.0 (m, 4 H); IR 3200–3600, 1680, 1450, 1210 cm^{-1}.

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Registry No. **1a**, 23246-12-0; **1b**, 73258-07-8; **1c**, 21143-47-5; **2a**, 98-83-9; **2a**-*2-d*, 69912-51-2; **2b**, 2039-93-2; **2c**, 2980-71-4; **2d**, 763-29-1; **2e**, 563-46-2; **2f**, 563-78-0; **2g**, 17498-71-4; **2h**, 530-48-3; **2i**, 1192-37-6; **2j**-*1-d*, 86766-08-7; (*Z*)-**3a**, 78485-07-1; (*E*)-**3a**, 78485-08-2; (*Z*)-**3b**, 86766-09-8; (*E*)-**3b**, 86766-10-1; **3b**-*5-d*, 86766-11-2; (*Z*)-**3c**, 86766-12-3;

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Organoboranes. 32. Homologation of Alkylboronic Esters with Methoxy(phenylthio)methyllithium: Regio- and Stereocontrolled Aldehyde Synthesis from Olefins via Hydroboration

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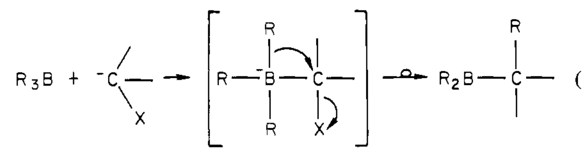
Abstract: Homologation of 2-alkyl-1,3,2-dioxaborinanes, RBO$_2$C$_3$H$_6$ (**1**), to α-methoxyalkyl derivatives, RCH(OMe)BO$_2$C$_3$H$_6$ (**2**), was achieved by reaction with LiCH(OMe)SPh, followed by treatment with HgCl$_2$. The intermediates **2** were smoothly oxidized with hydrogen peroxide in a pH 8 phosphate buffer to give the corresponding aldehydes, RCHO (**3**). The alkyl groups of **1** were introduced by the hydroboration method. Thus, heptanal, 3-phenylbutanal, 2-ethylpentanal, cyclohexanecarbaldehyde, *trans*-2-methylcyclopentanecarbaldehyde, and *exo*-norbornanecarbaldehyde were prepared in fair to good yields from 1-hexene, 2-phenylpropene, 3-hexene, cyclohexene, 1-methylcyclopentene, and norbornene, respectively. Furthermore, both *threo*- and *erythro*-2,3-dimethylpentanal were obtained in 96% diastereomeric purity from (*E*)- and (*Z*)-3-methyl-2-pentene, respectively. The migration of the alkyl group from boron to carbon proceeds with retention of configuration. Thus, by taking every advantage of the hydroboration reaction, this sequence provides a new method for introducing the formyl group into olefins in a regio- and stereocontrolled manner.

The carbenoid-induced 1,2-migration of organic groups from boron to carbon (eq 1) is one of the most convenient and promising C–C bond-forming reactions via organoboranes, R$_3$B.[1] A large number of carbenoid reagents have been successfully applied for such transformations. In many of these reactions, only one of the three R groups are utilized.

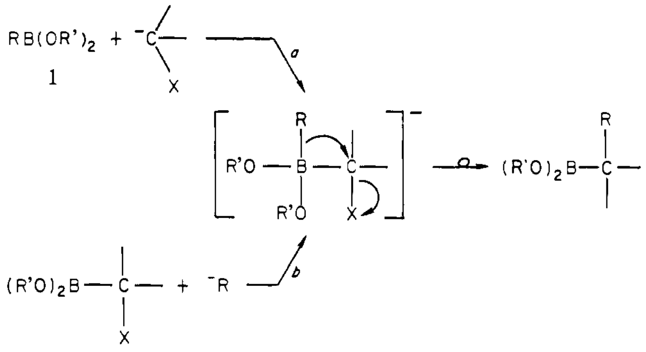


(1)

In some cases the use of 9-organyl-9-borabicyclo[3.3.1]nonanes circumvents this difficulty.[2] However, in other cases, these derivatives are not effective.[3] Accordingly, there would be major advantages in developing synthetic reactions that could utilize boronic esters **1** with their single organic group as the boron component (approach *a* in Scheme I).

In fact, in the boron-assisted substitution reaction (approach *b*)[4] and some other related reactions,[5] alkoxy has been effectively used as a nonmigrating "blocking" group. We are particularly interested in approach *a* since in this way those organic groups that are readily formed by the hydroboration reaction can be further incorporated into organic molecules.

Scheme I



Intermediates **1** are now readily available by hydroboration of alkenes with dihaloboranes, followed by alcoholysis.[6] However,

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