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Oxidation of organometallic compounds (RM, M = Li, MgBr, ZnBr, CuCNLi, Cu(R)CNLi$_2$) with ^{t}BuOOLi, Ti(O^{i}Pr)$_4$-mediated with ^{t}BuOOH, and with O$_2$, to give alcohols (ROH). Are radicals R$^\bullet$ involved?

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This work is dedicated to Professor Dr. Jean Normant on the occasion of his 65th birthday

Abstract

Organometallic compounds (RM, M = Li, MgBr, ZnBr, Cu(CN)Li, CuR(CN)Li$_2$) are oxidized with ^{t}BuOOLi (or PhCMe$_2$OOLi) (method A) to the corresponding alcohols (ROH), in good to very good yields. This oxidation works also well with the *protic* system Ti(O^{i}Pr)$_4$ + ^{t}BuOOH (method B) in the case of RM, M = Li, MgBr and ZnBr. Stereochemical studies with the configurationally stable *cis*- and *trans*-cyclopropyl metal compounds, *cis*- and *trans*-**1**-M, respectively, show that the reactions of RM, M = Li, MgBr, with ^{t}BuOOLi (method A) and Ti(O^{i}Pr)$_4$ + ^{t}BuOOH (method B) follow a S$_N$2-type pathway of the nucleophile RM at the electrophilic (although anionic!) oxygen atom of ^{t}BuOOLi(TiX$_3$) to give ROM (isolated as the esters **2**) with retention of configuration at R. In contrast, the oxidations with dioxygen O$_2$ (method C) occur with loss of stereochemistry in the cyclopropyl alcohols ROH (RM, M = Li, MgBr), and additional formation of cyclopropyl dimers R–R **3** in the case of RM, M = Cu(CN)Li, CuR(CN)Li$_2$. This is due to facile electron transfer from RM to O$_2$ and fast isomerization (dimerization) of the intermediate radicals R$^\bullet$. The high tendency of RM cuprates, M = Cu(CN)Li, CuR(CN)Li$_2$, for electron transfer reactions is also indicated by some loss of stereospecificity in the formation of ROH, and some dimer **3** formation, even with the oxidant ^{t}BuOOLi (method A) . © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Organometallic compounds; Oxidations; Alcohols

1. Introduction

TiX$_4$-catalyzed(mediated) oxidation reactions deserve special interest since a heterogeneous Ti^{IV}/SiO$_2$ catalyst had been developed by Shell [1], and since Sharpless had published the catalytic enantioselective epoxidation of allylic alcohols with titanium tetra-isopropoxide Ti(O^{i}Pr)$_4$, ^{t}butylhydroperoxide ^{t}BuOOH and (+)- or (−)-diethyl tartrate [2]. Related systems were used by Kagan [3] for the enantioselective oxidation of sulfides to sulfoxides, the α-hydroxylation of (RO)$_3$Ti-enolates by Schulz [4], and the epoxidation of hydroperoxy-olefins by Adam [5]. In the following we show that the *protic* system Ti(O^{i}Pr)$_4$ + ^{t}BuOOH can also be used, besides the oxenoids [6a,b] lithium *t*-butylhydroperoxide (^{t}BuOOLi) or lithium cumylhydroperoxide (PhCMe$_2$OOLi) [6], for the oxidation of organometallic compounds (RM, M = Li) [6], MgBr and ZnBr; in the case of M = CuCNLi and Cu(R)CNLi$_2$ the oxidation works only with ^{t}BuOOLi in good yields. Furthermore, the stereochemistry of some of these oxidation reactions is compared with the stereochemistry of the oxidations of the corresponding organometallic compounds (RM) with dioxygen O$_2$.

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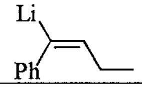
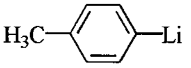
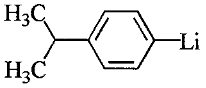
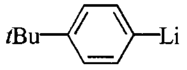
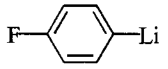
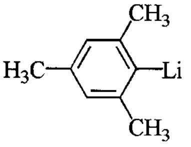
Table 1
Oxidation reactions of RLi with ^{t}BuOOLi (PhCMe$_2$OOLi) (method A), and Ti(O^{i}Pr)$_4$ + ^{t}BuOOLi (method B), respectively, to give, after acid work-up, ROH; yields of ROH (%)

No	RLi	ROH [%] Method A *t*BuOOLi	 Method B Ti(O*i*Pr)$_4$ + *t*BuOOH
1	*n*BuLi	85	69
2	*s*BuLi	70	83
3	*t*BuLi	81	38
4	PhLi	85	87
5		45[a)]	72[a)]

[a)] 1-Phenylbutan-1-one was isolated

Table 2
Oxidation of RM with ^{t}BuOOLi (method A) and /or Ti(O*i*prop)$_4$+ ^{t}BuOOH (method B) to give alcohols ROH; yields of ROH (%)

No	RM	ROH [%] Method A	B
1		-	89
2		-	80
3		-	70
4		-	84
5		-	78
6	PhCH$_2$Li	85	
7	*n*OctylMgBr	-	96
8	*s*OctylMgBr	-	85
9	*t*BuMgBr	-	14
10	PhMgBr	-	90
11	PhCH$_2$MgBr	67	71
12	*n*OctylZnBr	91	95
13	(*n*Octyl)$_2$Zn	-	70
14	*n*BuCuCNLi	84	-
15	(*n*Bu)$_2$CuCNLi$_2$	82	-
16	*t*BuCuCNLi	89	-
17	(*t*Bu)$_2$CuCNLi$_2$	90	-
18	PhCuCNLi	83	-
19	Ph$_2$CuCNLi$_2$	78	-
20	PhCH$_2$CuCNLi	56[a)]	-
21	(PhCH$_2$)$_2$CuCNLi$_2$	67[b)]	-

[a)] together with 19% bibenzyl;
[b)] together with 14% bibenzyl

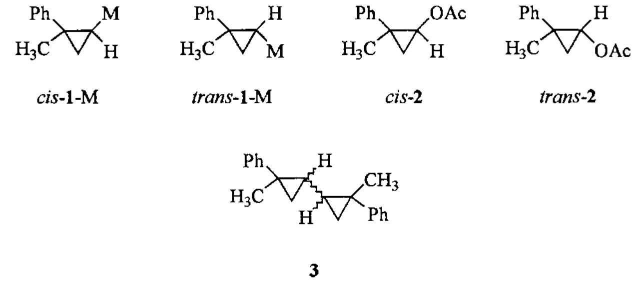
2. Results and discussion

In Table 1, oxidations of RLi compounds with ^{t}BuOOLi (PhCMe$_2$OOLi) [6] (method A) and Ti(O^{i}Pr)$_4$ + ^{t}BuOOH (method B), respectively, are compared with each other. In general, both methods lead to similar results. Exceptions: ^{t}BuLi (entry 3) is only poorly oxidized by Ti(O^{i}Pr)$_4$ + ^{t}BuOOH (method B), while the vinyllithium species (entry 5) gives higher yields with this method.

Table 2 summarizes different organometallic compounds (RM) and their oxidation reactions with ^{t}BuOOLi (method A) and/or Ti(O^{i}Pr)$_4$ + ^{t}BuOOH (method B).

Entries 1–5 show the facile transformation of aryllithium compounds via method B into phenols although the solution contains a proton [7–10]. Similarly, the oxidation of Grignard compounds [11] succeeds in high yields except for the ^{t}Butyl case (entries 7–10). Benzyl-Li (entry 6) and benzyl-MgBr (entry 11) are oxidized to benzyl alcohol without the formation of bibenzyl [12]. Entries 12 and 13 are representative for the preparation of ROH from Zn compounds [13]. The preferential oxidation reactions of the cuprates to the alcohols (ROH) (entries 14–19) are of special interest, since cuprates are known for their facile formation of coupling products R–R in oxidation reactions, at least with O$_2$ [14]. The coupling product bibenzyl indeed is observed in the case of the benzyl cuprates (entries 20 and 21): apart from benzyl alcohol, these easily oxidized species lead to 19% and 14%, respectively, of bibenzyl. In the case of the cuprates the oxidations to the alcohols ROH with Ti(O^{i}Pr)$_4$ + ^{t}BuOOH (method B) give much poorer yields than with ^{t}BuOOLi (method A). Therefore only the latter ones are listed in Table 2.

Earlier studies of the oxidation of diastereomeric, configurationally stable cyclopropyl- [6d] and vinyllithium species [6e] showed the intermediate formation of radicals R$^\bullet$ (or radical pairs R$^\bullet$ $^\bullet$OOLi) in which stereoisomerization at the former carbanionic carbon atom takes place, if the oxidation is performed with O$_2$. In contrast, a S$_N$2-type reaction of the nucleophile RLi at the anionic, electrophilic oxenoid oxygen atom of ^{t}BuOOLi should be responsible for the retention of configuration at the carbanionic carbon atom in this oxidation reaction [6d,e], which is in agreement with calculations [15]. In order to find out whether the oxidations described in Tables 1 and 2 follow an electron transfer pathway via intermediate radicals R$^\bullet$, or via a S$_N$2-type oxygen transfer of the oxenoid oxygen atom of ^{t}BuOOM (M = Li, TiX$_3$) onto RM, stereochemical studies were performed with the cyclopropyl metal compounds *cis*-**1**-M and *trans*-**1**-M, respectively [20], see Scheme 1. Depending on the mechanism, the oxidation leads to one of the esters **2** (after acylation of the first formed alcoholate) with retention of configura-



Scheme 1. *cis*- and *trans*-**1**-M, the ester oxidation (and acylation) products *cis*- and *trans*-**2**, and the radical dimers **3** (mixture of isomers).

tion at carbon (S_N2-type), or, in the case of electron transfer and radical intermediates, to both stereoisomeric esters **2**, and possibly to the dimers **3** (mixture of isomers), see Scheme 1. The results of the oxidations of **1**-M with ^{t}BuOOLi (method A) and Ti(O^{i}Pr)$_4$ + ^{t}BuOOH (method B) are listed in Table 3 together with those of the oxidations of **1**-M with O_2 (method C).

The oxidations of the Li-compounds *cis*-**1**-Li and *trans*-**1**-Li with O_2 (method C) and ^{t}BuOOLi (method A) in entries 1 and 2 agree with earlier results [6d,e]: O_2 (method C) leads to stereoisomeric esters **2**, and ^{t}BuOOLi (method A) oxidizes only to *one* stereoisomer with retention of configuration. The latter is also true for Ti(O^{i}Pr)$_4$ + ^{t}BuOOH (method B) as the oxidant. Dimers **3** are not formed in all these cases, not even with O_2 (method C). The Grignard compounds *cis*-**1**-MgBr and *trans*-**1**-MgBr (entries 3 and 4) are also oxidized by Ti(O^{i}Pr)$_4$ + ^{t}BuOOH (method B) with retention of configuration to give the esters **2**. Again dimers **3** are not formed. This is similarly the case for oxidations with ^{t}BuOOLi (method A) although the yields are much smaller. Grignard species RMgX, like organolithium compounds RLi, can thus be transformed stereospecifically in the respective alcohols ROH by oxidation reactions with oxenoids ROOM. The oxidation of the cuprates with O_2 (method C) (entries 5, 7, 9 and 11) is rather different from the above discussed results: both isomeric esters **2** together with significant amounts of the dimers **3** indicate a mechanism of the O_2-oxidation which is not the same as in the case of the O_2-oxidations of RLi and RMgX, and in which an electron transfer $Cu^I \rightarrow Cu^{II}$ might be involved [14]. In the oxidation reactions of the same cuprates with ^{t}BuOOLi (method A, see entries 6, 8, 10 and 12) the esters **2**, with retention of configuration, are generally the preferred products. However, in entry 8 5% of *cis*-**2** are also found together with 3% of the dimers **3**. Three percent of the dimers **3** are likewise formed in entry 12. Thus, ^{t}BuOOLi (method A) has, as in the case of cuprates, a strong tendency for S_N2-like transfer of oxygen. However, an electron transfer pathway seems also accessible. The formation of bibenzyl (entries 21 and 22, Table 2) support these observations.

3. Conclusion

RLi, RMgBr, RCuCNLi and $R_2CuCNLi_2$ are oxidized by O_2 (method C) to the corresponding alcohols ROH via radical intermediates as shown by loss of stereochemistry at the nucleophilic carbon atom of configurationally stable cyclopropyl metal compounds. Dimers R–R are only formed in the oxidation of cuprates. In contrast, by the oxenoid systems ^{t}BuOOLi (method A) and Ti(O^{i}Pr)$_4$ + ^{t}BuOOH (method B), RLi and RMgBr [16] are oxidized to ROH with retention of configuration at R, probably via a S_N2-type mechanism. Some stereoisomerization as well as dimer formation is observed in some cases of the oxenoid oxidation reactions (method A) of cuprates of the type RCuCNLi

Table 3
Stereochemistry of the oxidations of *cis*- and *trans*-**1**-M, respectively, to give *cis*- and *trans*-**2** and the dimers **3**, respectively, with different oxidants; yields of **2** and **3** (%)

Entry	**1**-M	Method A ^{t}BuOOLi		Method B Ti(O*i*prop)$_4$+^{t}BuOOH		Method C O_2		**3**
		cis-**2**	*trans*-**2**	*cis*-**2**	*trans*-**2**	*cis*-**2**	*trans*-**2**	
1	*cis*-**1**-Li	47	0	68	0	39	38	0
2	*trans*-**1**-Li	0	37	0	43	8	72	0
3	*cis*-**1**-MgBr	25	0	79	0	–	–	0
4	*trans*-**1**-MgBr	0	12	0	60	–	–	0
5	(*cis*-**1**)$_2$-CuCNLi$_2$	–	–	–	–	19	8	60
6	(*cis*-**1**)$_2$-CuCNLi$_2$	77	0	–	–	–	–	0
7	(*trans*-**1**)$_2$-CuCNLi$_2$	–	–	–	–	9	33	26
8	(*trans*-**1**)$_2$-CuCNLi$_2$	5	58	–	–	–	–	3
9	*cis*-**1**-CuCNLi	–	–	–	–	16	38	35
10	*cis*-**1**-CuCNLi	86	0	–	–	–	–	0
11	*trans*-**1**-CuCNLi	–	–	–	–	15	18	25
12	*trans*-**1**-CuCNLi	0	76	–	–	–	–	3

and $R_2CuCNLi_2$. Although such cuprates have a strong tendency for oxidation with electron transfer they are oxidized by ^{t}BuOOLi (method A) preferentially to the alcohols ROH with a high degree of retention of configuration, and in high yields.

4. Experimental

4.1. General remarks

4.1.1. Analytical GC

Sichromat (Siemens) with an Integrator Chromatopac C-R3A (Shimadzu). Column: glass capillary column SE 52 (0.3 mm × 30 m), helium (0.85 bar).

4.1.2. Preparative GC

Aerograph A-90-P3 (Wilkens Instruments & Research Inc.). Steel column, 5% carbowax 20 M on chromosorb G AW-DMCS 80–100 mesh, helium.

4.1.3. Column chromatography

Silicagel 60 (Merck), 0.063–0.200 mm.

4.1.4. Chromatotron

Modell 7924T (Harrison Research), silicagel 60 PF_{256} (Merck).

4.1.5. Preparation of RM (Tables 1 and 2)

The organometallic compounds (RM) outlined in Tables 1 and 2 were prepared according to standard procedures in Et_2O or THF.

4.2. *cis- and trans-1-Bromo-2-methyl-2-phenyl-cyclopropanes (prepared according to Schneider [17a])*

To 145 g (0.50 mol) of 1,1-dibromo-2-methyl-2-phenyl-cyclopropane (prepared according to Dehmlow [18]) in 600 ml acetic acid were added at 60°C, 200 g (3.00 mol) of Zn powder. The solution was stirred at 60°C for 10 h and then poured into 500 ml of cold water. The mixture was extracted four times with 200 ml of hexane, the hexane solution dried with $MgSO_4$, hexane removed, and the mono-bromides distilled in vacuo (b.p. 55°C, 0.05 Torr). Yield: 70.7 g (0.34 mol), 67% *cis*:*trans* mixture with a 1.3:1 ratio (by NMR).

Cis- and *trans*-1-bromo-2-methyl-2-phenyl-cyclopropane were separated on a silicagel column with a petrol ether/$CHCl_3$ mixture (25:1); R_f (*cis*) 0.31; R_f (*trans*) 0.22.

4.3. *cis-1-Bromo-2-methyl-2-phenyl-cyclopropane [19]*

^{1}H-NMR($CDCl_3$): $\delta = 1.27–1.34$ (m, 2 H, CH_2), 1.46 (s, 3 H, CH_3), 3.03 (dd, $J_{cis} = 7.08$ Hz, $J_{trans} = 4.69$ Hz, 1 H, C*H*Br), 7.17–7.42 (m, 5 H, Ph-*H*); ^{13}C-NMR ($CDCl_3$): $\delta = 22.1$ (C8), 27.0 (C2), 27.3 (C1), 27.6 (C3), 126.8, 127.1, 129.4, 142.2 (Ph-*C*).

4.4. *trans-1-Bromo-2-methyl-2-phenyl-cyclopropane [19]*

^{1}H-NMR ($CDCl_3$): $\delta = 1.00$ (dd, $J_{trans} = 4.74$ Hz, $J_{gem} = 6.44$ Hz, 1 H, CH_2 (*cis*)), 1.54 (s, 3 H, CH_3), 1.58 (pseudo t, $J = 7.2$ Hz, 1 H, CH_2 (*trans*)), 3.15 (dd, $J_{trans} = 4.67$ Hz, $J_{cis} = 7.97$ Hz, 1 H, C*H*Br), 7.11–7.23 (m, 5 H, Ph-*H*); ^{13}C-NMR ($CDCl_3$): $\delta = 23.3$ (C8), 23.9 (C3), 25.8 (C2), 30.5 (C1), 126.5, 127.0, 127.5, 144.5 (Ph-*C*).

4.5. *cis-1-Lithio-2-methyl-2-phenyl-cyclopropane (cis-**1**-Li)*

To a solution of 0.42 g (2.00 mmol) *cis*-1-bromo-2-methyl-2-phenyl-cyclopropane in 15 ml Et_2O was added at −78°C, 2.75 mL (4.40 mmol) of ^{t}BuLi (1.6 M) in hexane, and then stirred for 60 min at that temperature. *Cis*-**1**-Li is formed with complete retention of configuration [20]. This solution was used for oxidation reactions with methods A, B and C, respectively.

4.6. *trans-1-Lithio-2-methyl-2-phenyl-cyclopropane (trans-**1**-Li)*

trans-**1**-Li [20] was prepared exactly as *cis*-**1**-Li.

4.7. *cis- and trans-1-MgBr-2-methyl-2-phenyl-cyclopropane (cis-**1**-MgBr and trans-**1**-MgBr, respectively)*

cis- and *trans*-**1**-MgBr, respectively, were prepared from *cis*-**1**-Li and *trans*-**1**-Li, respectively. The solutions of *cis*(*trans*)-**1**-Li were added at −78°C to 0.37 g (2.00 mmol) of $MgBr_2$ in 15 ml of THF and stirred for 60 min at that temperature [20].

4.8. *Lithium [cis-(1-(2-methyl-2-phenyl-2-cyclopropyl))-(cyano)-cuprate] (cis-**1**-CuCNLi) [21]*

A total of 0.18 g (2.00 mmol) of CuCN and 15 ml of THF were cooled to −78°C, and then 2.00 mmol of a solution of *cis*-**1**-Li added to the suspension of CuCN. After solution of CuCN (30 min at −78°C and 30 min at −45°C) the cuprate solutions are ready for the oxidation reactions [21].

4.9. *trans-**1**-CuCNLi [21]*

The preparation of *trans*-**1**-CuCNLi followed exactly the preparation of *cis*-**1**-CuCNLi.

4.10. Lithium [bis(cis-1-(2-methyl-2-phenyl-cyclopropyl)-cuprate]·LiCN ((cis-**1**)$_2$-CuCNLi$_2$) [21]

The preparation of (*cis*-**1**)$_2$-CuCNLi$_2$ followed the preparation of *cis*-**1**-CuCNLi except that 0.09 g (1.00 mmol) CuCN were used.

4.11. (trans-**1**)$_2$-CuCNLi$_2$ [21]

The preparation is analogous to that of (*cis*-**1**)$_2$-CuCNLi$_2$.

4.12. cis-2-Methyl-2-phenyl-cyclopropyl acetate (cis-**2**)

To a solution of *cis*-**1**-Li in Et$_2$O was added at −78°C, 1.5 molecular equivalents of ^{t}BuOOLi (or PhCMe$_2$OOLi), and then stirred at −78°C for 1 h. After addition of 1.2 molecular equivalents of acetic acid anhydride, the solution was warmed to 20°C. Addition of an aqueous solution of NH$_4$Cl and extraction with Et$_2$O, drying of the etheral solution with MgSO$_4$ and removal of Et$_2$O, allowed the isolation of *cis*-**2** after chromatography with a PE 40/60 ethyl acetate gradient in 47% yield. If the oxidation is performed at −78°C for 3 h, the yield of *cis*-**2** is 90%. At 0°C, 91% *cis*-**2** is isolated after 1 h. *trans*-**2** is not found in any of these reactions (analysis by analytical GC) [22].

^{1}H-NMR(CDCl$_3$): $\delta = 0.99$ (t, $J = 6.6$ Hz, 1 H, CH$_2$ (*trans*)), 1.26 (dd, $J_{\text{gem}} = 6.04$ Hz, $J_{\text{trans}} = 3.04$ Hz, 1 H, CH_2 (*cis*)), 1.33 (s, 3 H, CCH_3), 1.70 (s, 3 H, C(O)CH_3), 4.09 (dd, $J_{cis} = 6.8$ Hz, $J_{trans} = 3.4$ Hz, 1 H, CH(O)), 7.15–7.24 (m, 5 H, Ph–H); ^{13}C-NMR (CDCl$_3$): $\delta = 17.6$ (C10), 20.6 (C9), 25.4 (C2), 26.5 (C3), 57.4 (C1), 126.4, 127.1, 129.0, 141.0 (Ph–C), 171.8 (C8).

4.13. trans-2-Methyl-2-phenyl-cyclopropyl acetate (trans-**2**)

The preparation followed the preparation of *cis*-**2** except that *trans*-**1**-Li was used. Isolated yields after column chromatography with a PE 40/60 ethyl acetate gradient: at −78°C, 1 h: 37%; at −78°C, 3 h: 84%; at 0°C, 1 h: 82%. *Cis*-**2** is not formed in any of these reactions (analytical GC) [22].

^{1}H-NMR(CDCl$_3$): $\delta = 0.89$ (dd, $J_{\text{trans}} = 3.07$ Hz, $J_{\text{gem}} = 6.03$ Hz, 1 H, CH_2 (*cis*)), 1.23 (bt, $J = 6.8$ Hz, 1 H, CH$_2$ (*trans*)), 1.32 (s, 3 H, CCH_3), 2.07 (s, 3 H, C(O)CH_3); 4.11 (dd, $J_{trans} = 3.7$ Hz, $J_{cis} = 7.3$ Hz, 1 H, CH(O)), 7.11–7.34 (m, 5 H, Ph–H); ^{13}C-NMR (CDCl$_3$): $\delta = 17.7$ (C10), 20.0 (C9), 20.7 (C3), 26.0 (C2), 59.0 (C1), 126.4, 127.5, 127.8, 144.8 (Ph–C), 171.8 (C8).

4.14. Stereoisomeric coupling products **3**

Into a solution of *cis*-**1**-CuCNLi in Et$_2$O–THF was bubbled O$_2$ first at −78°C for 1 h and then for 30 min on warming to 0°C. Addition of acetic anhydride (one molecular equivalent) was added to trap the alcoholates. Addition of an aqueous NH$_4$Cl-solution and extraction with Et$_2$O (see the preparation of *cis*-**3**) led to a mixture of *cis*-**2**, *trans*-**2** and **3**, which was separated on a Chromatotron (PE 40/60 ethyl acetate gradient). **3** was isolated in 35% yield.

^{1}H-NMR(CDCl$_3$): $\delta = 0.56$–0.61 (m, 2 H), 0.74–0.92 (m, 1 H), 1.13–1.15 (m, 1 H), 1.17–1.26 (m, 2 H), 1.54 (s, 6 H, CH_3), 7.13–7.28 (m, 10 H, Ph–H); ^{13}C-NMR (CDCl$_3$): $\delta = 20.9$ (C3), 21.2 (C1), 24.1 (C2), 25.8 (C8), 125.3, 126.5, 128.1, 148.4 (Ph-C).

4.15. Oxidation with ^{t}BuOOLi (method A)

The oxidations with ^{t}BuOOLi (PhCMe$_2$OOLi) were performed as detailed in the preparation of *cis*-**2** (trapping with acetic acid anhydride to give the esters). For the stereochemical studies summarized in Table 3 the reactions were stopped after 1 h at −78°C. The synthetically oriented data of Tables 1 and 2 were received after 12 h at −78°C and warming up to room temperature (r.t.). Hydrolysis, to give the alcohols (phenols) ROH, was performed with 2 N HCl. The alcohols (phenols) were extracted with Et$_2$O, dried, Et$_2$O removed, and the alcohol (phenol) analysed by NMR and GC [22] (comparison with authentic sample if possible).

4.16. Oxidation with Ti(O^{i}Pr)$_4$ + ^{t}BuOOH (method B)

The RM (Tables 1–3) were reacted with two molecular equivalents of Ti(O^{i}Pr)$_4$ at −78°C and then warmed to 0°C for 15 min. After cooling to −78°C, one molecular equivalent of ^{t}BuOOH was added. The results of Table 3 were received after 1 h reaction time at −78°C and trapping of the alcoholate with acetic anhydride. The synthetically oriented reactions of Tables 1 and 2 were run for 12 h at −78°C and then warmed to r.t. For the isolation of the alcohols (phenols) the reaction mixture was hydrolysed with 2 N HCl, the alcohols (phenols) extracted with Et$_2$O, the solution dried with MgSO$_4$, Et$_2$O removed, and the alcohol (phenol) analysed by NMR and GC [22] (comparison with authentic sample, if possible).

4.17. Oxidation with dioxygen O$_2$ (method C)

Dioxygen O$_2$ was bubbled through the solutions of the RM listed in Table 3 for 1 h at −78°C. Then the reactions were stopped with acetic acid anhydride and worked up as outlined in the preparation of *cis*-**2** and analysed by NMR and GC [22].

4.18. Preparation of ^{t}BuOOH

The commercial product (Peroxo-Chemie GmbH) is a 80% solution in water. It is extracted with CH_2Cl_2 and dried over $MgSO_4$ for 3 days. Removal of the solvent occurs at 400 mm. At 10 mm, ^{t}BuOOH distills at 30°C.

4.19. Preparation of ^{t}BuOOLi

To a solution of ^{t}BuOOH in THF at -78°C, was added slowly one molecular equivalent of a 1.6 N solution of ^{n}BuLi in hexane. After 20 min at -78°C the solution is ready for use.

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