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Fine Regioselective Tuning in the Oxidation of *sec,sec* 1,2-Diols by Dimethyldioxirane

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Abstract: Non symmetric *sec,sec* 1,2-diols and their O-isopropylidene derivatives undergo a regioselective oxidation by dimethyldioxirane depending on the electronic effects of the substituents. These results support previous views about the concerted O-insertion mechanism via a polar transition state. Copyright © 1996 Elsevier Science Ltd

The selective transformation of hydroxy groups of a diol is always a challenging target for chemists. Many oxidizing agents are known to transform carbinol into carbonyl moieties. The most frequently used oxidants are transition metal compounds,[1] DMSO-based reagents[2] and H_2O_2/metal catalyst systems.[3]

Although they often show good selectivity towards secondary vs primary carbinols, their polluting byproducts remain the most important drawback of their use.

Because of the carbon-carbon cleavage,[4] when the carbinol moiety is a part of a *sec-sec* 1,2-diol unit, the classical oxidants lack mainly the oxidation; silver-carbonate on celite[5] and distannoxane-bromine[6] systems being the only notable procedures reported to mono-oxidize certain symmetric *sec-sec* 1,2-diols.

Hitherto no general procedures for the regioselective mono-oxidation of non-symmetric *sec,sec* 1,2-diol units were known.

Dimethyldioxirane (DMD) represents one of the most versatile oxidizing reagent, having shown a surprising high efficiency and selectivity in the transformation of several functional groups.[7] At the beginning of our studies the general reactivity of dioxiranes towards alcohols was already established[8] and the higher oxidation rate of secondary vs primary alcohols had confirmed the electrophilic character of dioxiranes.

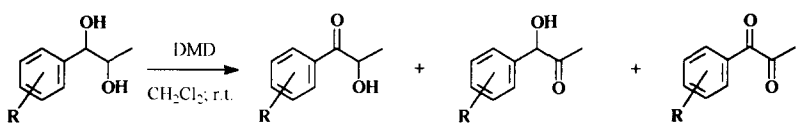
As we recently reported,[9] linear and cyclic 1,2 and 1,3 diols were selectively oxidized to ketols by DMD. We proposed that a strong dipole close to the reactive center, destibilized the transition state and the oxygen insertion did not occur.[10] For this reason the new formed carbonyl moiety, in the course of a diol oxidation, disfavoured the second attack of DMD. Thus the reaction stoped at the first step, leading mainly to ketols.

This characteristic chemical behaviour allowed us to mono-oxidize symmetric *sec-sec* 1,2- and 1,3-diols, affording either α or β-hydroxyketones in high yields.[11]

The aim of this work is to establish possibilities and limits of DMD in the regioselective monooxidation of non symmetric *sec,sec* 1,2-diols, pointing out qualitative rules on the regio-orienting effect of the substituents.

The observed activating and regio-orienting effect of a benzenic ring on the oxidation of carbinols prompted us to study, firstly, the effect of a substituent on the phenyl ring of 1-phenyl-2-methyl-ethyleneglycols **1**, making in competition two centers which showed in other cases to be very reactive with DMD.

Table 1.



1 2 3 4

diol	R	time	conv. %	ratio 2[a] : 3[a] : 4[a]			DMD (eqv.)
1a	H	12h	>96	52	32	16	1.5
1b	p-OCH_3	12h	>96	66	14	20	1.5
1c	o-OH	36h	>96	75	25	-	3
1d	o-NO_2	24h	>96	-	82	18	3
1e	p-NO_2	24h	>96	15	44	41	3

[a] products ratio were calculated by integer values of methyl signal in ^{1}H-NMR spectra of crude

The results are summarized in Table 1. Substrates were transformed in reaction products almost quantitatively, although in different reaction times. The regio-orienting effect of the substituent is also apparent. Compounds **1b** and **1c** which bear ortho and para electron donating groups on the phenyl ring afforded higher amounts of benzyl ketone than **1a**.

Worthy of note the regioselectivity obtained for compound **1c**, which makes this procedure of synthetic value.

A dramatic inversion of regioselectivity is evident for compounds **1d** and **1e**, which produced mainly compound **3**. These results powerfully support a reaction pathway in which a transition state polar in character is involved. It should bear a partially positive charge on the reactive center.

The exceptionally high regioselectivity obtained for compound **1d** comes out from the higher deactivating effect of NO_2 group on benzylic carbinol. The *o*-NO_2 moiety acts both as a electron withdrawing group, through the aromatic ring and as a dipole close to the potential active site (Figure 1). This last effect was also recently estabilished through the reactivity of *sec,sec*-nitrodiols.[12]

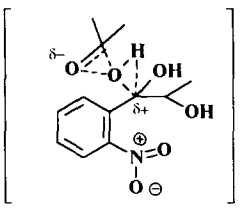
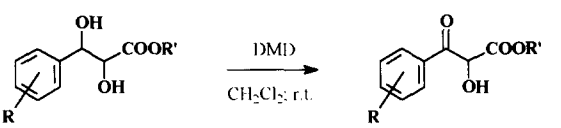


Figure 1

Table 2



5 6

diol	R	R'	time	conv. %	yield of 6	DMD (eq.)
5a	H	CH_3	24h	13	>95[a]	2
5b	*p*-OCH_3	CH_3	24h	>96	>96[a]	2
5c	*o*-OH	CH_3	24-72h	no react.	-	2-4
5d	*o*-OCH_3	CH_3	24-72h	no react.	-	2-4
5e	*o*-NO_2	C_2H_5	24-72h	no react.	-	2-4
5f	*p*-NO_2	C_2H_5	24h	5	80[b]	3

[a]isolated yield [b]GC yield

As showed in Table 2, when the 2-methyl group of compounds **1** was replaced with a carbomethoxyl group, we noted, as expected, a general lowering in reactivity.

Compound **5a**, when treated with DMD (2:1 mol eq.), at room temperature with reaction time of 24h, achieved a conversion of 13%, affording regioselectively **6a**. Excess of DMD and prolonged reaction times could provide a conversion of 30% max, the regioselectivity being unchanged. Thus the deactivating effect of

carbomethoxyl group makes the α-carbinol totally non reactive. **5b**, bearing the electron donating *p*-OCH_3 group, afforded ketol **6b** almost quantitatively, whereas compounds with electron withdrawing substituents on phenyl ring provided conversions of 5% max, yet toward ketols **6**.

Surprisingly the *o*-OH derivative **5c** was inert toward oxidation, although a high conversion toward hydroxyketone **6c**. should be expected. This behaviour is consistent with the result obtained for compound **1c**, which resulted notably less reactive than the corrisponding model **1a**.

Steric hindrance should be put forward for the unreactivity showed by *o*-OCH_3 derivative **5d**. In this case prolonged reaction times provided low conversions toward a mixture of polar products, probably via a radical pathway.[13]

The deactivating effect of a carbomethoxyl moiety toward both α and β carbinols was also confirmed by the reactivity of the alkyl substituted compounds 7 (Table 3).

Table 3

7 8

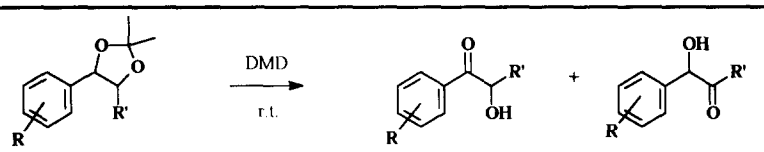
diol	R	R'	time	conv. %	yield of 8	DMD (eq.)
7a	CH_3	CH_3	72h	80	>96[a]	4
7b	cyclohexyl	C_2H_5	72h	57	>96[b]	4
7c	n-C_9H_{19}	CH_3	72h	<10	>96[a]	4

[a]GC yield [b]isolated yield

With longer reaction times and higher amount of DMD ratios than that used for aromatic diols, **7a** and **7b** showed 60% of conversion and reactions proceeded with complete regioselectivity toward β-ketoesters **8**. Long chain diol **7c** was almost inert, probably because of the high conformational freedom of the alkyl chain, which hinders the correct approach of dioxirane on the active site, again yielding **8c** as the only product.

This general chemical behaviour of *sec,sec* 1,2-diols was also confirmed by their *O*-isopropylidene derivatives, as shown in Table 4.

Table 4.



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diol	R	R'	time	conv. %	products (yield%)		DMD (eq.)
9a	H	CH_3	12h	>96	**2a** (85)[a]	**3a** (8)[a]	3
9b	*p*-OCH_3	CH_3	12h	>96	**2b** (>96)		3
9c	*p*-NO_2	CH_3	24h	>96	**2e** (70)[a]	**3e** (15)[a]	5
9d	*p*-OCH_3	$COOCH_3$	48h	>96	**5d** (72)		5

[a]yield calculated via ^{1}H-NMR on crude

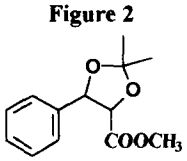
As we previously reported[11] the acetonide of 1-phenyl-1,2-propandiol **9a** was oxidized with higher regioselectivity than the free diol. That result was, to our knowledge, the first regioselective oxidation of non symmetric diols derivatives. Such reactivity was confirmed by Curci et al.[14] using Methyltrifluoromethyldioxirane (MTFMD), although with lower yields in the case of non symmetric *sec,sec* diol derivatives. They noted no loss of optical purity of compounds used, which put forward, again, the concerted Q-insertion mechanism[15] as the main pathway of the reaction.

Compound **9b**, which bears the electron donating *p*-OCH_3 moiety, afforded the benzyl ketone **2b** almost quantitatively. Notable lower reaction rate and regioselectivity were observed in the case of *p*-NO_2 derivative **9c**, again towards compound **2e**.

The carbomethoxyl derivative **9d** was also selectively transformed to the β-hydroxyketone **5d**, although in longer reaction times. The presence of the electron donating *p*-OCH_3 group is crucial for the regioselectivity, since compound **12** (Figure 2) yielded a complex mixture of products, probably through a radical pathway.

Our results establish the possibility to use DMD as regioselective oxidant for aromatic non symmetric *sec,sec*-1,2-diols, being a powerful tool in the prediction of the reactivity of various ring-substituted derivatives.

Figure 2



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They also suggest a transition state polar in character, which is more consistent with a concerted Q-insertion mechanism[15] as opposed to a radical pathway.[16]

EXPERIMENTAL

Starting diols were prepared as reported in literature via Wittig or Wittig-Hörner[17] reactions on the aldehydes, and osmylation of the corresponding olefins.

All reactions were performed, in a typical procedure, by adding a portion (1.5 equivalents) of DMD solution[18] (0.09M in acetone) to a stirred solution of substrate (100 mg) in acetone (1 ml) at room temperature (ca. 25°C) and stirring for 12h. Further amounts of reagent were added until complete conversion of the substrate. Reactions were monitored by TLC and GC, and product ratios calculated by ^{1}H-NMR spectra on crudes. GC-MS was performed on products that were not possible to purify for elementary analysis.

The work-up of all reactions consisted simply in evaporation of the solvent in vacuo. When necessary, the reaction products were purified by flash chromatography[19] eluting with a mixture of petroleum ether and ethyl acetate. Sometimes it was not possible to isolate the regioisomers by this way and we characterized the products in mixture.

^{1}H-NMR spectra were recorded in deuterochloroform solution at 200 or 300 MHz and ^{13}C-NMR-^{1}H broad-band decoupled spectra were recorded in the same solvent at 75 MHz. Chemical shifts δ refer to the signal of tetramethylsilane. Coupling constants *J* were measured in Hz.

2-Hydroxy-1-phenyl-1-propanone (2a), 1-hydroxy-1-phenyl-2-propanone (3a), 1-phenyl-1,2-propandione (4a): (a) 200 mg of 1-phenyl-1,2-propandiol **1a** were reacted with 22 ml of DMD and reacted overnight in the dark. The value of the integrals of methyl signal in ^{1}H-NMR of crude showed a 52:32:16 ratio between **2a**, **3a** and **4a**. By flash chromatography eluting with a mixture of petroleum ether and ethyl acetate 1:1 25 mg of **2a** and 160 mg of an inseparable mixture of **3a** and **4a** were obtained. (b) 250 mg of 1-phenyl-1,2-propandiol isopropylidene derivative **9a** was treated with 1.5 equivalents of DMD and stirred overnight in the dark. The crude showed a mixture 10.6:1 of **2a** and **3a**. By flash chromatography 125 mg (76%) of pure **2a** was obtained, the rest remaining in mixture with **3a**. **2a**: ^{1}H-NMR: δ 1.41 (3H, d, *J* 6), 3.8 (1H, bs), 5.13 (1H, q, *J* 6), 7.4-7.6 (3H, m), 7.9 (2H, dd, *J* 1.4, 8.2). ^{13}C-NMR: δ 22, 69.2, 128.7, 128.9, 134. 202.7. MS m$^+$/z (% rel. int.): 45 (8.1), 51 (9.2), 77 (35), 105 (100). Calc. for $C_9H_{10}O_2$ (150.17) H 6.71, C 71.98; found H 6.57, C 72.11. **3a**: ^{1}H-NMR: δ 2.08 (3H, s), 4.24 (1H, d, *J* 4.3), 5.3 (1H, d, *J* 4.3), 7.3-7.6 (5H, m). MS m$^+$/z (int. rel.): 43 (10), 51 (8.3), 77 (35.4), 79 (60.1), 107 (100). **4a**: ^{1}H-NMR: δ 2.5 (3H, s), 7.45-7.6 (3H, m), 7.98 (2H, dd, *J* 1.2, 7.7). MS m$^+$/z (% rel. int.): 51 (25), 77 (82.5), 78 (10), 105 (94.7), 106 (100). Calc. for $C_9H_8O_2$ (148.16) H 5.44, C 72.96; found H 5.57, C 72.9.

2-Hydroxy-1-[(4-methoxy)-pheny]-1-propanone (2b), 1-hydroxy-1-[(4-methoxy)-phenyl]-2-propanone (3b), 1-[(4-methoxy)-phenyl]-1,2-propandione (4b): (a) reaction performed as for **1a** on 200 mg of 1-[(4-methoxy)-phenyl]-1,2-propandiol gave 190 mg of a mixture of **2b**, **3b**, **4b** in 66:14:20 ratio, as calculated on crude by the integer values of methyl groups of **2b** (δ 1.39), **3b** (δ 2.05) and **4b** (δ 2.47). By flash chromatography 38 mg of **4b** and 145 mg of **2b** were obtained as oil. (b) Reaction between 200 mg of of 1-[(4-methoxy)-phenyl]-1,2-propandiol isopropylidene derivative **9b** and 3 eq. of DMD lead to pure **2b**: ^{1}H-NMR: δ 1.39 (3H, d, *J* 6.8), 3.85 (3H, s), 5.08 (1H, q, *J* 6.8), 6.93 (2H, d, *J* 8.7), 7.89 (2H, d, *J* 8.7). ^{13}C-NMR: δ 22.4, 55.4, 68.8, 114.1, 164.4, 201. Calc. for $C_{10}H_{12}O_3$ (180.20) H 6.71, C 66.65; found H 6.85, C 66.7. **4b**: ^{1}H-NMR: δ 2.47 (3H, s), 6.9 (2H, d, *J* 8.7), 7.95 (2H, d, *J* 8.7). Calc. for $C_{10}H_{10}O_3$ (178.19) H 5.66, C 67.4; found H 5.48, C 67.44.

2-Hydroxy-1-[(2-hydroxy)-phenyl]-1-propanone (2c), 1-hydroxy-1-[(2-hydroxy)-Phenyl]-2-propanone (3c): (a) 250 mg of 1-[(2-hydroxy)-phenyl]-1,2-propandiol **1c** were reacted with DMD (two portion of 25 ml of a 0.09 molar solution in acetone) for 12 hrs. The ^{1}H-NMR revealed that the crude was composed by a 75:25 ratio between **2c** and **3c**. Purification on silica gel gave 210 mg (84%) of an inseparable mixture of **2c** and **3c**. (b) The same reaction on the isopropilidene derivative **9a** gave 235 mg (94%) of the same mixture in 1:10.6 ratio. **2c**: ^{1}H-NMR: δ 1.5 (3H, d, *J* 7.2), 5.19 (1H, q *J* 7.2), 6.8-7.7 (4H, m). MS m$^+$/z (% rel. int.): 45 (5.3), 65 (9.5), 93 (10.1), 121 (100), 122 (25.4). **3c**: ^{1}H-NMR: δ 2.01(3H, s), 5.22(1H, s), 6.8-7.7(4H, m).

1-Hydroxy-1-[(2-nitro)-phenyl]-2-propanone (3d), 1-[(2-nitro)-phenyl]-1,2-propandione (4d): the reaction between 300 mg of of 1-[(2-nitro)-phenyl]-1,2-propandiol **1d** and DMD was performed as above. The crude showed to be a mixture of **3d** and **4d** in 82:18 ratio. Flash chromatography on silica gel eluting with petroleum ether / ethyl acetate 1:1 gave 230 mg of pure **3d**: ^{1}H-NMR: δ 2.18 (3H, s), 5.69 (1H, s), 7.4-7.7 (3H, m), 7.99 (1H, dd, *J* 2, 8.5). ^{13}C-NMR: δ 25.4, 76, 124, 125.2, 129.7, 130.6, 133.9, 205.6. Calc. for $C_9H_9NO_4$ (195.17) H 4.65, C 55.39; found H 4.8, C 55.3. **4d**: (characterized in mixture with 3d) ^{1}H-NMR: δ 2.62 (3H, s), 7.5-7.8 (3H, m), 8.18 (1H, dd, *J* 2, 8.5).

2-Hydroxy-1-[(4-nitro)-phenyl]-1-propanone (2e), 1-hydroxy-1-[(4-nitro)-phenyl]-2-propanone (3e), 1-[(4-nitro)-phenyl]-1,2-propandione (4e): (a) 300 mg of 1-[(4-nitro)-phenyl]-1,2-propandiol and DMD (two portion of 25 ml) gave, after 24h, 290 mg of crude composed by **2e**, **3e**, **4e** in 15:44:41 ratio. Flash chromatography eluting with petroleum ether - ethyl acetate 1:1 gave 105 mg (36%) of **4e** and 160 mg (54%) of a mixture of **2e** and **3e**. (b) 200 mg of 1-[(4-nitro)-phenyl]-1,2-propandiol isopropylidene derivative were in the same conditions converted in a mixture of **2e** and **3e** in ratio 70:15 (GC yield). **2e**: ^{1}H-NMR: δ 1.45 (3H, d, *J* 7), 5.15 (1H, q, *J* 7), 8.08 (2H, d, *J* 8), 8.32 (2H, d, *J* 8). MS m$^+$/z (% rel. int.): 45 (100), 76

(23.4), 104 (43.7), 133 (33.5). **3e** ^{1}H-NMR: δ 2.11 (3H, s), 4.38 (1H, d, *J* 4), 5.2 (1H, d, *J* 4), 7.52 (2H, d, *J* 8), 8.25 (2H, d, *J* 8). MS m^+/z (% rel. int.): 43 (100), 77 (45), 78 (35.4), 105 (39.2), 106 (90.4), 136 (81.4). **4e**: ^{1}H-NMR: δ 2.52 (3H, s), 8.21 (2H, d, *J* 8.3), 8.32 (2H, d, *J* 8.3). MS m^+/z (% rel. int.): 43 (100), 76 (43), 104 (77.5), 134 (20.6), 120 (17.8). Calc. for $C_9H_7NO_4$ (193.16) H 3.65, C 55.95; found H 3.39, C 56.12.

2-Hydroxy-3-keto-3-phenyl-1-(methyl)propionate (6a): 300 mg of 2,3-dihydroxy-3-phenyl-1-(methyl)propionate were treated with two portion of 34 ml of a 0.09 M solution of DMD and stirred at room temp. In the dark for 12h for each portion of reagent. After 24h, 13% (GC yield) of the starting material was converted. Purification via flash chromatography eluting with a mixture of petroleum ether and ethyl acetate 1:1 gave 50 mg (11%) of **6a**: ^{1}H-NMR: δ 3.71 (3H, s), 5.2 (1H, bs), 5.62 (1H, s), 7.5-7.65 (3H, m), 8.08 (2H, d, *J* 7). ^{13}C-NMR: δ 53, 74.3, 128.9, 129.5, 134.8, 169.1, 193.7. Calc. for $C_{10}H_{10}O_4$ (194.19) H 5.19, C 61.85; found H 5.02, C 61.91.

2-Hydroxy-3-keto-3-[(4-methoxy)phenyl]-1-(methyl)propionate (6b): 250 mg of of 2,3-dihydroxy-3-[(4-methoxy)-phenyl]-1-(methyl)propionate **5b** reacted with 25 ml of a 0.09 M solution of DMD to give, after 24h, 240 mg (96%) of **6b**: ^{1}H-NMR: δ 3.68 (3H, s), 3.87 (3H, s,), 5.55 (1H, s), 6.95 (2H, d, *J* 8.7), 8.04 (2H, d, *J* 8.7). ^{13}C-NMR: δ 52.8, 55.5, 73.9, 114.2, 132.1, 133, 165.1, 169.6, 192.1. Calc. for $C_{11}H_{12}O_5$ (224.21) H 5.39, C 58.93; found 5.57, C 58.72.

2-Hydroxy-3-keto-3-[(4-Nitro)phenyl]-1-(methyl)propionate (6f): reaction of of 2,3-dihydroxy-3-[(4-nitro)-phenyl]-1-(methyl)propionate **5f** with DMD, also in excess, lead to low convertion of substrates to **6f**: ^{1}H-NMR: δ 1.21 (3H, t, *J* 7.2), 4.18 (1H, q, *J* 7.2), 5.18 (1H, s), 7.72 (2H, d, *J* 8.9), 8.2 (2H, d, *J* 8.9). ^{13}C-NMR: δ 14.6, 62.1, 74.9, 76.2, 124.1, 129.1, 148.6, 150.8, 173.3, 207.8. MS m^+/z (% rel. int.): 223 (0.7), 150 (100), 104 (25.3), 76 (15.1).

2-Hydroxy-3-keto-1-(methyl)butanoate (8a): 200 mg of 2,3-dihydroxy-1-(methyl)butanoate **7a** were converted in **8a** by reaction with DMD (4 portion of 17 ml of 0.09 M solution) for 72 h. After evaporation of the solvent 165 mg of **8a** was obtained: ^{1}H-NMR: δ 2.3 (3H, s), 3.82 (3H, s), 4.81 (1H, s). ^{13}C-NMR: δ 26.7, 53.2, 78.1, 168.2, 205.1. MS m^+/z (% rel. int.): 43 (100), 73 (10.5), 90 (80.9), 132 (0.5).

2-Hydroxy-3-cyclohexyl-3-keto-1-(ethyl)propionate (8b): 250 mg of 3-cyclohexyl-2,3-dihydroxy-1-(ethyl)propionate **7b** were reacted with DMD (4 portion of 13 ml of 0.09 M solution) for 72 h. The solvent was evaporated on vacuo; after purification via flash chromatography eluting with petroleum ether / ethyl acetate 1:1, 140 mg of **8b** were obtained: ^{1}H-NMR: δ 1.23 (3H, t, *J* 7), 1.1-2.0 (10H, m), 4.22 (2H, q, *J* 7),

4.82 (1H, s). ^{13}C-NMR: δ 13.9, 24.9, 25.4, 25.5, 27.5, 29, 29.1, 46.5, 62.3, 168.7, 207.6. Calc. for $C_{11}H_{18}O_4$ (214.26) H 8.47, C 61.66; found H 8.22, C 61.7.

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