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Anthracenic and Naphthalenic *vic*-Diepoxides. A New Kind of Isomerization Going Through Fragmentation

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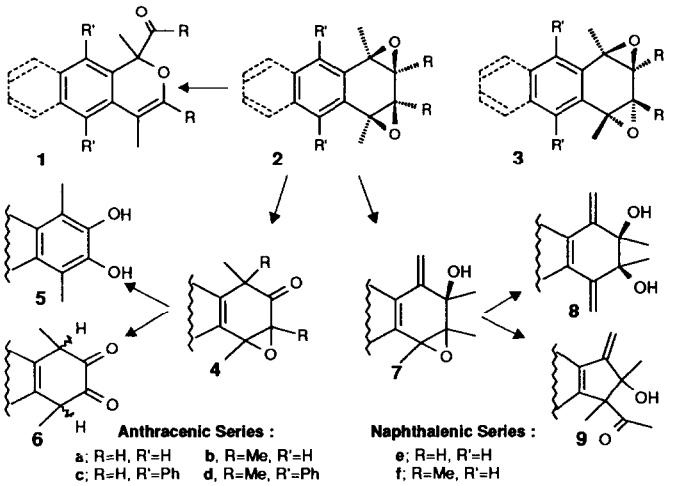
Abstract: When treated with Lewis acids in an anhydrous medium, *syn* and *anti* anthracenic and naphthalenic *vic*-diepoxides **2** and **3** rearrange more or less completely to acyl-benzo or naphthopyrans **1**.This rearrangement, competing with more classical ones, appears to involve a Grob-type fragmentation followed by recyclisation. © 1997 Elsevier Science Ltd.

The behaviour towards protic or Lewis acids in non-aqueous medium of *syn*-diepoxides of type **2**, derived from 1,4-dimethyl-anthracenes or -naphthalenes, should differ according to whether they possess or not methyl substituents at positions 2 and 3. As a matter of fact, as shown on Scheme 1, we have previously observed that simple 1,4-dimethyl derivatives **2a** and **2e** (with R=H) lead ultimately to diphenols **5a** and **5e** when treated with $MgBr_2$-etherate in benzene[1,2] whereas 1,2,3,4-tetramethyl analogues **2b** and **2f** (with R= CH_3) open to di-unsaturated diols **8b** and **8f**, partly when treated alike with $MgBr_2$ or more integrally with *p*-toluenesulphonic acid in THF.[3] In both anthracenic series, the presence of *meso*-phenyl substituents brought about more or less diverging outcomes, **2c** (R=H) leading to a mixture of stereomeric diones **6c**, the less crowed tautomers of **5c**,[2] while **3d**, the *anti* isomer of **2d** (R=CH_3), at present the only one known, rearranged further on to **9d**.[4]



Scheme 1

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Concerning intermediate stages, epoxy-ketones **4a** and **4c** had been already obtained in moderate yields when **2a** and **2c** were treated with $ZnCl_2$ in benzene[2] and we have now found that heating **2b** with LiBr *in THF* affords in good yield the rather unstable epoxy-alcohol **7b**[5], the precursor of **8b**. Moreover, the strong dependence of the isomerization course on the reaction conditions is illustrated by the obtention in high yield of epoxy-ketone **4b**[6] when the heating of **2b** with LiBr, or $MgBr_2$, is carried out in a mixture *THF/H_2O* (50/50).

More unexpected than these findings is now the detection in nearly all series of another isomerization pathway competing more or less notably with the preceding ones and leading to acyl-benzo or -naphthopyrans of type **1**. The same partial rearrangement being also found for *anti*-diepoxides **3**, it can be already assumed that the steric arrangement of moving bonds, if it may eventually come into play, is not a determining factor of the transformation.

From Table 1 which summarizes our results, it appears that many Lewis acids in anhydrous medium are able to promote this isomerization, $LiBF_4$ in acetonitrile (conditions C) appearing the best in comparative experiments (2, 3, 4) with **2b**.

Table I - Reactions of Lewis acids with diepoxides **2** and **3** leading to isomers **1**.

			Products, % yield[b]	
entry	Diepoxide	Conditions[a]	Isom. **1**	Other products
	Syn			
1	**2a**	A	---	**4a**, 86[2]
2	**2b**	B	**1b**, 40	**8b**, 45
3	**2b**	C	**1b**, 57	**8b**, 30
4	**2b**	E	**1b**, 40	**10b**, 15 ; **11b**, 18[6]
5	**2c**	A	**1c**, 40	**4c**, 50 ; **6c**, 8
6	**2f**	C	**1f**, 54	**8f**, 16
	Anti			
7	**3b**	C	**1b**, 35	unidentified
8	**3b**	E	**1b**, 90	---
9	**3c**	D	**1c**, 25	**4c** ; **6c**
10	**3c**	E	**1c**, 25	unidentified
11	**3d**	C	---	**9d**, 50[4]
12	**3d**	E	no reaction	---
13	**3f**	C	**1f**, 17	unidentified
14	**3f**	E	**1f**, 65	unidentified

A - $ZnCl_2$ in benzene, at 0°.

B - $MgBr_2$-etherate freshly prepared according to ref.[7], at r.t.

C - $LiBF_4$, solution 1M in CH_3CN, at r.t.

D - SiO_2 on chromatographic plate, at r.t.

E - $LiClO_4$, extended reflux in CH_2Cl_2[8]*.

a - Experiments generally carried out on 0.1 or 0.2 g. of starting compound .

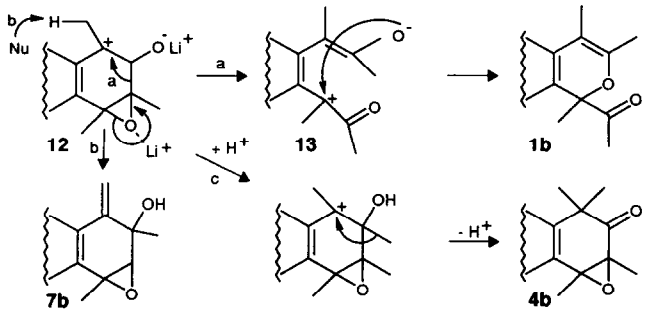
b - Yields of isolated products, after separation by preparative TLC on silica-gel.

* **Caution**: perchlorates, potentially dangerous, should not be used in large amounts or without extreme caution.

A special mention should also be made of $LiClO_4$ in dichloromethane (conditions E) which has been found to give very high yields with several *anti*-diepoxides bearing no *meso*-phenyl substituents.

Structures of the new isomers **1**[9] were essentially deduced from NMR data and especially from the presence in the ^{13}C NMR spectra of all compounds of signals characteristics of an enol-ether moiety with a deshielded C-3 and a strongly shielded C-4.[10] Identification of a carbonyl function, an aldehyde in the case of **1c**, brought also a good evidence in favor of the proposed structures.

To explain this rearrangement, it seems necessary to assume a Grob-type fragmentation followed by recyclisation as shown on Scheme 2. The dipolar ion **12** arising from the opening of one of the epoxide groups is strongly reminiscent of intermediates suggested in the acid-catalysed cleavage of 1,3-diols to alkenes and carbonyl compounds.[11] One then conceives that migration of the 2,3 bond, assisted by the opening of the second epoxide group, can lead to **13** (*path a*) which will recombine immediately to give **1**.



Scheme **2**

Coordination by Li^+ of the second epoxide group concomitant with the opening of the first one is probably required for the rearrangement to occur. This may explain why, in the case of **2b**, rearrangement to **1b** is not observed with LiBr in water or in an oxygenated solvent like THF, which can both solvate strongly the cation. According to conditions, elimination leading to **7b** (*path b*) or isomerization to epoxy-ketone **4b** (*path c*) then takes place. On the other hand, in anhydrous medium, it is expected that reagents like $LiBF_4$ or $LiClO_4$, containing no appreciably nucleophilic anions, give better yields of rearranged products, such as **1b**, than LiBr or $MgBr_2$ with which elimination leading to **7b** may predominate.

Inspection of Table 1 shows that structural features should also play a major role in the competition between the various possible transformations, presence of methyl substituents at positions 2 and 3 being a favourable factor to fragmentation. On the contrary *meso*-phenyl substituents in anthracenic diepoxides appear able to limit or even suppress this way of rearrangement as shown by the unexpected resistance of **3d** towards $LiClO_4$ (experiment 12). In the last case it may be that the bulky phenyl groups prevent more or less the complexation by the Li-catalyst of the epoxide bridges which should precede their opening.

References and notes:

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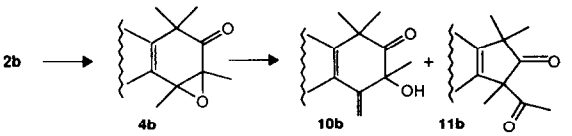
5. **3,4-Epoxy-2-hydroxy-2,3,4-trimethyl-1-methylene-1,2,3,4-tetrahydroanthracene (7b)**: mp 158-160°C; IR(KBr) 3420 cm^{-1} ; ^1H NMR (250 MHz, $CDCl_3$) : δ 1.22 (s, 3H) , 1.70 (s, 3H), 1.92 (s, 3H) **3 *C*H$_3$**, 5.58 (s, 2H) **C*H*$_2$=**, 7.90 (s, 1H) and 7.97 (s, 1H) ***H*-9,10**, 7.44-7.56 (m, 2H) and 7.79-7.89 (m, 2H) ***H*-5 to 8**; ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 12.8, 16.3, 24.6 (**3 *C*H$_3$**), 62.4 and 68.9 (***C*-3,4**), 75.7 (***C*-2**), 108.9 (**C*H*$_2$=**), 125.5 to 127.7 (**6 *C*H arom.**), 133.1 to 133.4 (**4 *C* quat.arom.**), 151.2 (***C*-1**); EIMS (70 eV) m/z, (r.i.): 266 (87), 248 (25), 223 (100).

6. Epoxy-ketone **4b** has been previously obtained by photoisomerization of the corresponding diepoxide **2b**; under acidic treatment, it gives a mixture of **10b** and **11b** (see Ref 3). One can then deduce the transient formation of epoxy-ketone **4b** from **2b** in experiment 4.



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8. $LiClO_4$ (in benzene) has been formerly found to effect a rapid rearrangement to carbonyl derivatives of epoxides involving a tertiary center, see: Rickborn, B. and Gerkin, R *J. Am. Chem. Soc.* **1971**, *93*, 1693-1700.

9. **1-Acetyl-1,3,4- trimethylnaphtho[2,3-*c*]-2*H*-pyran (1b)** : mp 80-82°C; IR($CHCl_3$) 1730, 1660 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.78 (s, 3H) C*H*$_3$**-1**, 2.05 (q, 3H, J= 0.8 Hz) and 2.09 (q, 3H, J= 0.8 Hz) C*H*$_3$**-3,4**, 2.23 (s, 3H) C*H*$_3$**-CO**, 7.34-7.45 (m, 2H) ***H*-7,8**, 7.46 (s, 1H) and 7.52 (s, 1H) ***H*-5,10**, 7.73-7.78 (m, 2H) ***H*-6,9**; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 12.6, 17.4, 22.9, 25.4 (**4 *C*H$_3$**), 85.1 (***C*-1**), 104.8 (***C*-4**), 118.5 to 127.8 (**6 *C*H arom.**), 129.9 to 133.5 (**4 *C* quat.arom.**), 148.5 (***C*-3**), 208.4 (***C*O-CH$_3$**); EIMS (70 eV) m/z (r.i.) 266 (31), 223 (100). Anal. Calc for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81; Found C, 81.13; H, 6.88.

1-Formyl-1,4-dimethyl-5,10-diphenylnaphtho[2,3-*c*]-2*H*-pyran (1c) : mp 204-206°C; IR($CHCl_3$) 1730, 1630 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ 1.21 (d, 3H, J=1.3 Hz) C*H*$_3$**-4**, 1.52 (s, 3H) C*H*$_3$**-1**, 6.42 (q, 1H, J=1,3 Hz) ***H*-3**, 7.20-7.51 (m, 14H) ***H*arom.**, 9.31 (s, 1H) ***H*-CO**; ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 17.3 (*C*H$_3$**-4**), 20.2 (*C*H$_3$**-1**), 84.4 (***C*-1**), 114.6 (***C*-4**), 125.6 to 131.5 (**14 *C*H arom.**), 127.2 to 140.4 (**8 *C* quat.arom.**), 142.2 (***C*H-3**), 191.8 (***C*HO**).EIMS (70 eV) m/z (r.i.) 390 (47), 343 (90), 328 (71).

1-Acetyl-1,3,4-trimethylbenzo[*c*]-2*H*-pyran (1f): oil; IR($CHCl_3$) 1720, 1660 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.70 (s, 3H) C*H*$_3$**-1**, 1.95 (q, 3H, J=1 Hz) and 2.05(q, 3H, J=1 Hz) C*H*$_3$**-3,4**, 2.22 (s, 3H) C*H*$_3$**-CO**, 7.12 (m, 2H) ***H*-5,8**, 7.19 (m, 1H) and 7.30 (m, 1H) ***H*-6,7**; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 12.4, 17.2, 22.4, 25.6 (**4 *C*H$_3$**), 84.8 (***C*-1**), 104.9 (***C*-4**), 120.7 to 128.3 (**4 *C*H arom.**), 130.5 and 132.0 (**2 *C* quat.arom.**), 147.9 (***C*-3**), 209.4 (***C*O-CH$_3$**); EIMS (70 eV) m/z (r.i.) 216 (1), 173 (100).

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