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Dimers of Some 6-Substituted 2,2-Dimethyl-2*H*-naphtho[1,2-*b*]pyrans

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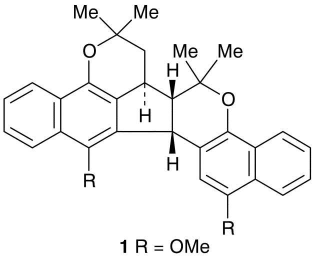
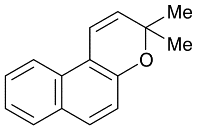
The reactions of 4-(4-chloro-, 4-bromo- and 4-methyl-1-hydroxy-2-naphthyl)-2-methylbut-3-en-2-ols in acetic acid containing a few drops of sulfuric acid or in methanol saturated with hydrogen chloride furnished dimers of the related 6-substituted 2,2-dimethyl-2*H*-naphtho[1,2-*b*]pyrans.

It has been reported that under acid conditions the natural product lapachenole, 6-methoxy-2,2-dimethyl-2*H*-naphtho-[1,2-*b*]pyran, gave dimer **1**[1] and that 3,3-dimethyl-3*H*-naphtho[2,1-*b*]pyran (**2**) on boiling with formic acid or acetic acid containing a very small amount of sulfuric acid or with methanolic hydrogen chloride afforded dimer **3**. Treatment of 4-(2-hydroxy-1-naphthyl)-2-methylbut-3-en-2-ol (**4**) under similar conditions with either formic acid or acetic acid containing a small amount of sulfuric acid yielded dimer **3**, but with methanolic hydrogen chloride a second dimer **5** was also obtained.[2]



1 R = OMe
12 R = Me



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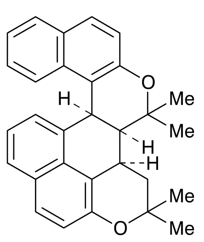

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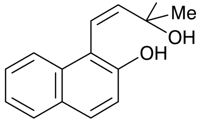

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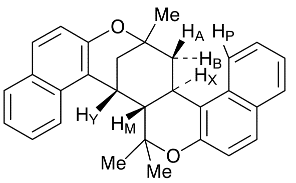

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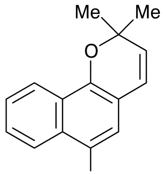
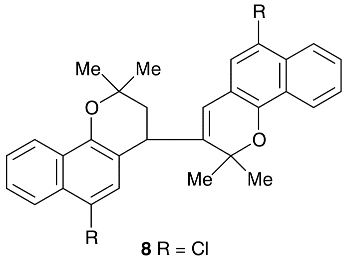


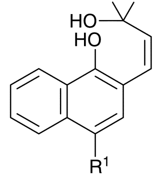
6 R = Cl
7 R = Br
10 R = Me



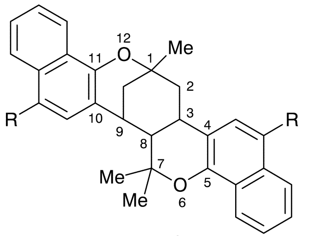
8 R = Cl
9 R = Br
11 R = Me

Treatment of 6-chloro- and 6-bromo-2,2-dimethyl-2*H*-naphtho[1,2-*b*]pyrans (**6** and **7**) in acetic acid with a few drops of sulfuric acid, furnished during two days standing dimers, 6-chloro/bromo-3,4-dihydro-2,2-dimethyl-4-(6-chloro/bromo-2,2-dimethyl-2*H*-naphtho[1,2-*b*]pyran-3-yl)-2*H*-naphtho[1,2-*b*]pyrans (**8** and **9**), respectively. Under similar conditions 2,2,6-trimethyl-2*H*-naphtho[1,2-*b*]pyran (**10**) yielded a mixture (*ca.* 1:1) of two dimers, 3,4-dihydro-2,2,6-trimethyl-4-(2,2,6-trimethyl-2*H*-naphtho[1,2-*b*]pyran-3-yl)-2*H*-naphtho[1,2-*b*]pyran (**11**) and 6,6a,6b,7,8,14b-hexahydro-6,6,8.8,14,16-hexamethyldibenzo[*h*,*h*′]cyclopenta[1,2-*c*:5,4,3-*d*′*e*]bis[1]benzopyran (**12**).[3]

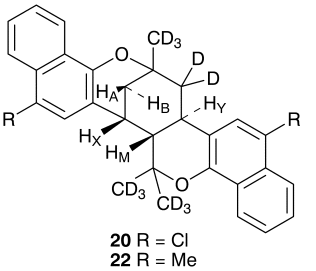
It has been found that treatment of 4-(4-chloro-, 4-bromo- and 4-methyl-1-hydroxy-2-naphthyl)-2-methylbut-3-en-2-ols (**13**, **14** and **15**) in acetic acid with a few drops of sulfuric acid or with methanol saturated with hydrogen chloride afforded dimers **16**, **17** and **18**, 1,7,7-trimethyl-6,12-dioxa-bis(4-substituted-naphtho)[1,2:5,4-12:10]tricyclo-[7.3.1.0^{3,8}]dodecanes, of the corresponding naphthopyrans **6**, **7** and **10** and not any of the dimers, **8**, **9**, **11** and **12** obtained on similar treatment of the original naphtho-[1,2-*b*]pyrans. This differed from the related reaction of 4-(2-hydroxy-1-naphthyl)-2-methylbut-3-en-2-ol (**4**), when two dimers **3** and **5** were obtained, the former also being obtained direct from the parent naphtho[2,1-*b*]pyran (**2**).



13 R^1 = Cl; R^2 = Me
14 R^1 = Br; R^2 = Me
15 R^1 = R^2 = Me
19 R^1 = Cl; R^2 = CD$_3$
21 R^1 = Me; R^2 = CD$_3$



16 R = Cl
17 R = Br
18 R = Me



20 R = Cl
22 R = Me

The ^{1}H NMR spectrum of dimer **16** showed the presence of three methyl groups, seven unresolvable protons and ten aromatic protons, suggesting a structure analogous to that of dimer **5**. A similar spectrum with two extract methyl groups was obtained for dimer **18**.

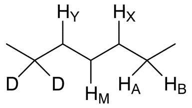


Fig. 1

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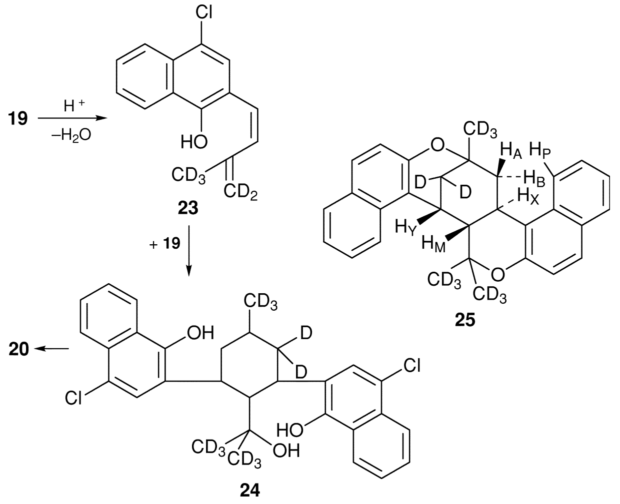

Scheme 1

The ^1H NMR spectrum of dimer **16** was simplified by comparing it with the spectrum of dimer **20** obtained from 4-(4-chloro-1-hydroxy-2-naphthyl)-2-([$^2H_3$]methyl)-[1,1,1-$^2H_3$]but-3-en-2-ol (**19**), which was typical of that obtained from a terminal methylene attached to three successive methine groups. The broadening of the doublet associated with H_Y suggested that it was coupled to deuterium (Fig. 1) and thus indicated the arrangement of the non-aromatic protons in dimer **20** and hence of the seven non-aromatic protons in dimer **16**. The same pattern of chemical shifts and coupling constants were shown by dimer **22** obtained from 4-(4-methyl-1-hydroxy-2-naphthyl)-2-([$^2H_3$]methyl)[1,1,1-$^2H_3$]but-3-en-2-ol (**21**).

A mechanism (Scheme 1) for the formation of dimer **20** is probably similar to that for the formation of dimer **25** and involves the initial formation of a butadiene intermediate **23** by dehydration of the allylic alcohol **19**, followed by a Diels–Alder addition to a second molecule **19**, as the dienophile, to give the dipentene intermediate **24**, which on cyclization affords dimer **20**. Dimer **20** differs from dimer **25** in the position of the two deuterium atoms.

Techniques used: ^1H NMR, mass spectrometry

References: 4

Figures: 1

Tables: 1

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