Some Halogeno and Related Derivatives of 6-Chloro-2,2-dimethyl-2*H*-naphtho[1,2-*b*]pyran

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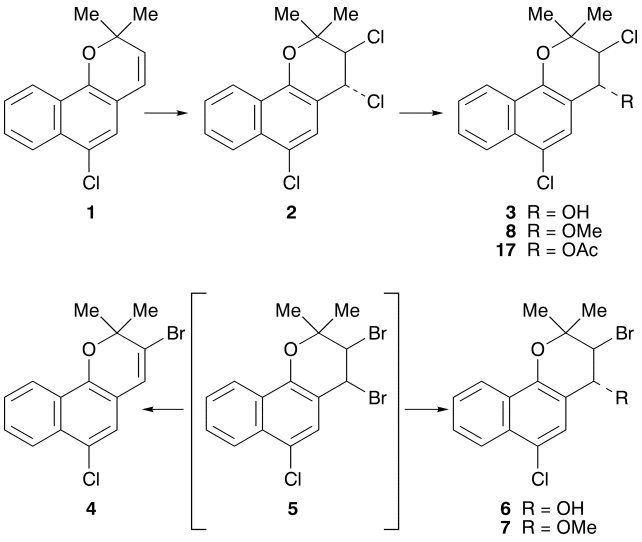
The conversions of 6-chloro-2,2-dimethyl-2*H*-naphtho[1,2-*b*]pyran into 3,4,6-trichloro-3,4-dihydro-2,2-dimethyl-2*H*-naphtho[1,2-*b*]pyran and 3-bromo-6-chloro-2,2-dimethyl-2*H*-naphtho[1,2-*b*]pyran are described, together with the preparations of some related halogenohydrins and halogenoketones and derivatives derived from them.

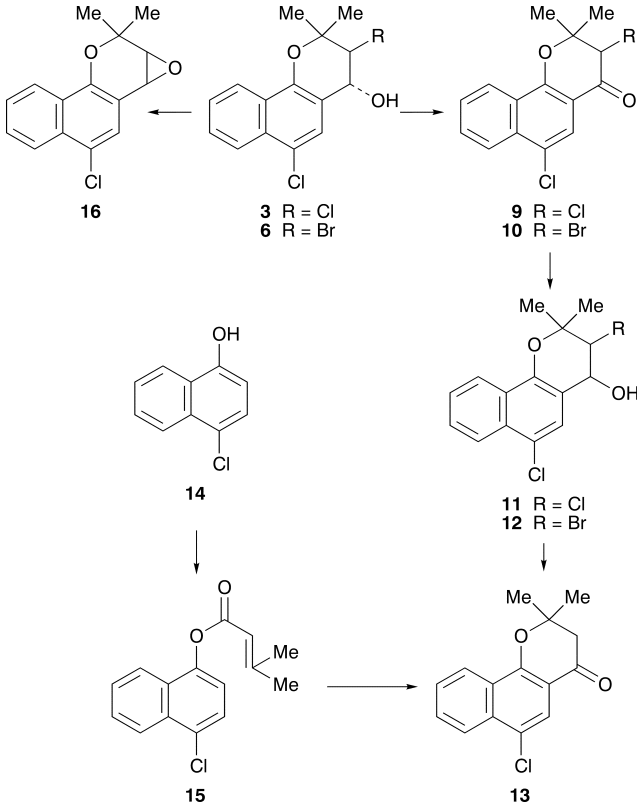
3,4,6-Trichloro-3,4-dihydro-2,2-dimethyl-2*H*-naphtho[1,2-*b*]-pyran (**2**) was prepared by passing chlorine into a solution of 6-chloro-2,2-dimethyl-2*H*-naphtho[1,2-*b*]pyran (**1**) in carbon tetrachloride at 0 °C. Similar treatment of the chloronaphthopyran **1** with bromine resulted in the evolution of hydrogen bromide and the isolation of 3-bromo-6-chloro-2,2-dimethyl-2*H*-naphtho[1,2-*b*]pyran (**4**). The trichloronaphthopyran **2** was also obtained from **1** and sulfuryl chloride in benzene and by the treatment of *cis*- or *trans*-3,6-dichloro-3,4-dihydro-2,2-dimethyl-2*H*-naphtho-[1,2-*b*]pyran-4-ol (**3**) with phosophorus pentachloride in benzene.

Evidence for the initial formation of 3,4-dibromo-6-chloro-3,4-dihydro-2,2-dimethyl-2*H*-naphtho[1,2-*b*]pyran (**5**) was obtained when the gum from the original addition of bromine to the chloronaphthopyran **1**, and which continued to evolved hydrogen bromide, was boiled with either aqueous acetone or dry methanol to yield *trans*-3-bromo-6-chloro-3,4-dihydro-2,2-dimethyl-2*H*-naphtho[1,2-*b*]pyran-4-ol (**6**) and 3-bromo-6-chloro-3,4-dihydro-4-methoxy-2,2-dimethyl-2*H*-naphtho[1,2-*b*]pyran (**7**), respectively. Similarly the trichloronaphthopyran **2** and chlorohydrin **3** were converted into 3,6-dichloro-3,4-dihydro-4-methoxy-2,2-dimethyl-2*H*-naphtho[1,2-*b*]pyran (**8**).



The structure assigned to the chlorohydrin **3** and the bromohydrin **6** was determined by the following conversions. The halogenohydrins **3** and **6** were oxidised by chromic oxide in acetic acid to give the corresponding halogenoketones **9** and **10**, which on reduction with either lithium aluminium hydride or sodium tetrahydroborate gave, respectively, 3,6-dichloro- and 3-bromo-6-chloro-3,4-dihydro-2,2-dimethyl-2*H*-naphtho[1,2-*b*]pyran-4-ol (**11** and **12**). Treatment of these halogenohydrins **11** and **12** with potassium hydroxide in diethyl ether resulted in the *β*-elimination of halogen and the resultant enol afforded 6-chloro-3,4-dihydro-2,2-dimethyl-2*H*-naphtho[1,2-*b*]pyran-4-one (**13**), which was identical to an authentic sample obtained by the Fries rearrangement of 4-chloro-1-naphthyl *β*,*β*-dimethylacrylate (**15**), prepared from 4-chloro-1-naphthol (**14**) and *β*,*β*-dimethylacryloyl chloride.

The formation of the ketone **13** from the halogenohydrins **11** and **12** indicated that they possessed a *cis* configuration, whereas similar treatment of the halogenohydrins **3** and **6** with potassium hydroxide in diethyl ether furnished 6-chloro-3,4-epoxy-3,4-dihydro-2,2-dimethyl-2*H*-naphtho-[1,2-*b*]pyran (**16**) showing that they possessed a *trans* configuration.[3] Their configurations are also supported by ^{1}H NMR spectral data, which on comparison with that of related benzo[*b*]pyran derivatives[2] indicated that the configuration of compounds **2**, **3** and **6** is *trans* and equatorial and that the methoxy derivatives **7** and **8** is *trans* and mainly axial.[4]



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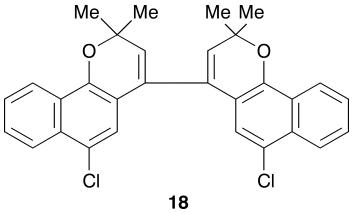
Treatment of the halogenoketones **9** and **10** with zinc in boiling acetic acid did not afford the expected ketone **13**, but 6,6′-dichloro-2,2,2′,2′-tetramethyl-4,4′-bi(2*H*-naphtho-[1,2-*b*]pyran) (**18**) whose structure was supported by its mass spectrum and by comparison with the formation of 6,6′-dibromo-2,2,2′,2′-tetramethyl-4,4′-bi(2*H*-benzo[*b*]pyran) from 3,6-dibromo-2,3-dihydro-2,2-dimethylbenzo[*b*]pyran-4-one.[6]



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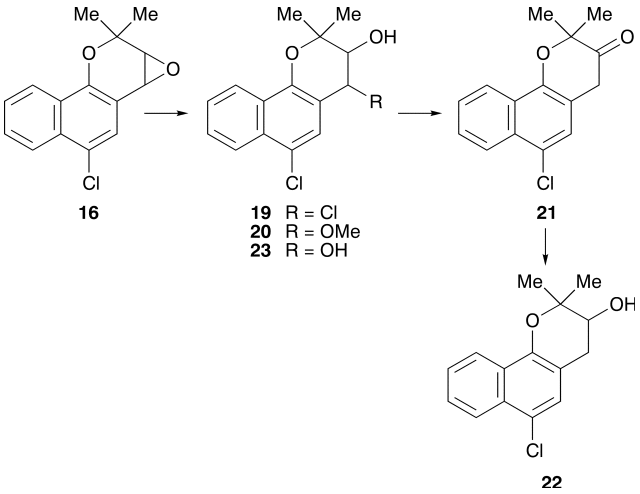
Ring opening of the epoxide ring of 6-chloro-3,4-epoxy-3,4-dihydro-2,2-dimethyl-2*H*-naphtho[1,2-*b*]pyran (**16**) with dry hydrogen chloride in diethyl ether gave 4,6-dichloro-3,4-dihydro-2,2-dimethyl-2*H*-naphtho[1,2-*b*]pyran-3-ol (**19**), which on boiling with methanol afforded 6-chloro-3,4-dihydro-4-methoxy-2,2-dimethyl-2*H*-naphtho[1,2-*b*]pyran-3-ol (**20**). Pyrolysis of the chlorohydrin **19** resulted in the loss of hydrogen chloride and the formation of 6-chloro-3,4-dihydro-2,2-dimethyl-2*H*-naphtho[1,2-*b*]pyran-3-one (**21**), which on reduction with sodium tetrahydroborate in methanol yielded 6-chloro-3,4-dihydro-2,2-dimethyl-2*H*-naphtho[1,2-*b*]pyran-3-ol (**22**).

The epoxide **16** on boiling with aqueous acetone furnished 6-chloro-3,4-dihydro-2,2-dimethyl-2*H*-naphtho[1,2-*b*]pyran-3,4-diol (**23**). A number of interconversions of some of the derivatives reported above are described.



16 **19** R = Cl **20** R = OMe **23** R = OH **21**

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Techniques used: IR, ^{1}H NMR, mass spec.

References: 6

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