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Preparation of some Dihalogenodihydronaphthopyrans and Derivatives

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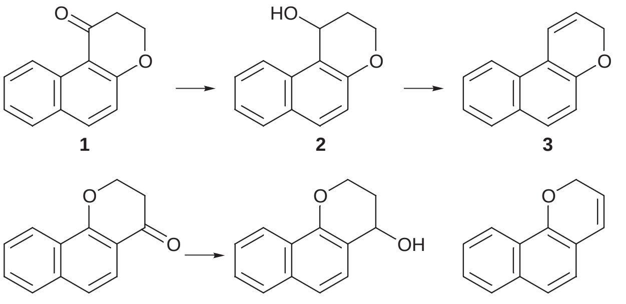
The preparations of 3,4-dihalogeno-3,4-dihydro-2*H*-naphtho[1,2-*b*]pyrans and 1,2-dihalogeno-2,3-dihydro-1*H*-naphtho[2,1-*b*]pyrans and their conversion into some related naphthopyran derivatives are described.

3*H*-Naphtho[2,1-*b*]pyran **3** was obtained by the dehydration of 2,3-dihydro-1*H*-naphtho[2,1-*b*]pyran-1-ol **2** on boiling with acetic acid, heating with potassium hydrogen sulfate or by pyrolysis of the related acetate. Alcohol **2** was prepared by the reduction of 2,3-dihydronaphtho[2,1-*b*]pyran-1-one **1**[1] with sodium borohydride in methanol. Similar treatment of 3,4-dihydro-2*H*-naphtho[1,2-*b*]pyran-4-ol **5** obtained from 2,3-dihydro 1,2-*b*]pyran-4-one **4**[2] afforded a trimer and no 2*H*-naphtho[1,2-*b*]pyran **6**.



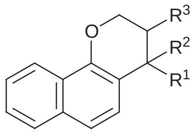
1 **2** **3**

4 **5** **6**

The reaction between ketones **4** and **1** and bromine in either chloroform or diethyl ether gave the bromoketones **7a** and **8a**, which on reduction with sodium borohydride in methanol yielded *cis*-3-bromo-3,4-dihydro-2*H*-naphtho-[1,2-*b*]pyran-4-ol **7b** and *cis*-2-bromo-2,3-dihydro-1*H*-naphtho[2,1-*b*]pyran-1-ol **8b**[1,3] respectively. The *cis*-chlorohydrins **7c** and **8c** were obtained in the same way by reduction of the chloroketones **7d** and **8d**, prepared by reacting the ketones **4** and **1** with sulfuryl chloride in chloroform. The halogenoketones **7a**, **7d**, **8a** and **8d** were also obtained by oxidation of the related *cis*- and *trans*-halogenohydrin with a solution of chromium trioxide in acetic acid and water.

trans-3,4-Dihalogeno-3,4-dihydro-2*H*-naphtho[1,2-*b*]pyrans **7e** and *trans*-1,2-dihalogeno-2,3-dihydro-1*H*-naphtho-[2,1-*b*]pyrans **8e**, were prepared from the appropriate *cis*- or *trans*-halogenohydrin and an equimolar proportion of phosphorus trihalide. *trans*-1,2-Dibromo- and 1,2-dichloro-2,3-dihydro-1*H*-naphtho[2,1-*b*]pyrans **8e** ($R^1 = R^2 =$ Br or Cl) were also obtained by addition of the required halogen to 3*H*-naphtho[2,1-*b*]pyran **3**. Boiling the appropriate dihalogenodihydronaphthopyran in either methanol or ethanol furnished the 4-alkoxy-3-halogeno and 1-alkoxy-2-halogeno derivatives **7f** and **8f**.

The hydrolysis of 3,4-dihalogeno-3,4-dihydro-2*H*-naphtho[1,2-*b*]pyrans **7e** and 1,2-dihalogeno-2,3-dihydro-1*H*-naphtho[2,1-*b*]pyrans **8e** in boiling acetone containing water and potassium hydroxide afforded *trans*-3-halogeno-3,4-dihydro-2*H*-naphtho[1,2-*b*]pyran-4-ols **7b** and **7c** and *trans*-2-halogeno-2,3-dihydro-1*H*-naphtho[2,1-*b*]-pyran-1-ols **8b** and **8c**, respectively.



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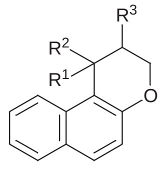

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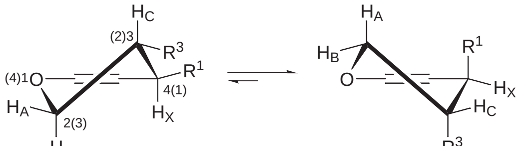
a R^1R^2 = O, R^3 = Br
b R^1 = OH, R^2 = H, R^3 = Br
c R^1 = OH, R^2 = H, R^3 = Cl
d R^1R^2 = O, R^3 = Cl
e $R^1 = R^3$ = halogen, R^2 = H
f R^1 = alkoxy, R^2 = H, R^3 = halogen
g $R^1 = R^2$ = H, R^3 = OH
h R^1 = alkoxy, R^2 = H, R^3 = OH
i R^1 = Cl, R^2 = H, R^3 = OH
j $R^1 = R^3$ = OH, R^2 = H

Comparison of the observed vicinal coupling constants (Table 1) with those predicted by the Karplus $\cos^2\phi$ equation, for the measured dihedral angles between H_c and H_x obtained from Dreiding models, showed that, in all the 3,4-dihalogeno-3,4-dihydro-2*H*-naphtho[1,2-*b*]pyrans **7e** and 1,2-dihalogeno-2,3-dihydro-1*H*-naphtho[2,1-*b*]pyrans **8e**, studied, the most probable configuration is that with the 3- and 4- and (1-) and (2-) substituents *trans*- and axial **9b**.



9a **9b**

Pyran ring numbering: (1,2-*b*) series 1–4; (2,1-*b*) series (1)–(4)

The halogenohydrins **7b**, **7c**, **8b** and **8c** when treated with powdered potassium hydroxide in diethyl ether yielded 3,4-epoxy-3,4-dihydro-2*H*-naphtho[1,2-*b*]pyran **11** and 1,2-epoxy-2,3-dihydro-1*H*-naphtho-[2,1-*b*]pyran **12** respectively.

The epoxides **11** and **12** have been converted into 3,4-dihydro-2*H*-naphtho[1,2-*b*]pyran-3-ol **7g** and 2,3-dihydro-1*H*-naphtho[2,1-*b*]pyran-2-ol **8g**, by reduction with lithium aluminium hydride and with an alcohol or on treatment with hydrogen chloride in diethyl ether,4-alkoxy-3,4-dihydro-2*H*-naphtho-[1,2-*b*]pyran-3-ol **7h** 1-alkoxy-2,3-dihydro-1*H*-naphtho[2,1-*b*]pyran-2-ol **8h**, 4-chloro-3,4-dihydro-2*H*-naphtho[1,2-*b*]pyran-3-ol **7i** and 1-chloro-2,3-dihydro-1*H*-naphtho[2,1-*b*]pyran-2-ol **8i**, respectively. Hydrolysis of chlorohydrins **7i** and **8i** afforded 3,4-

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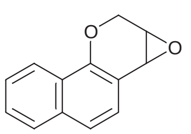
Table 1 Chemical shifts and coupling constants for the 3- and 4-hydrogen atoms (H_c and H_x) in 3,4-dihalogeno-3,4-dihydro-2*H*-naphtho[1,2-*b*]pyrans and the (2-) and (1-)-hydrogen atoms (H_c and H_x) in 1,2-dihalogeno-2,3-dihydro-1*H*-naphtho[2,1-*b*]pyrans[a]

	Substituent		Chemical shift (δ) (CD_3Cl)				Coupling constant (J/Hz)				
Compound	R^1	R^3	H_x	H	H_A	H_B	J_{CX}	J_{AC}	J_{BC}	J_{BX}	J_{AB}
7e	Br	Br	5.62	4.83	5.08	4.5	2.1	1.5	2.1	2.2	12.2
7e	Cl	Br	5.35	4.68	4.84	4.43	1.8	1.2	1.7	2.4	12.1
7e	Cl	Cl	5.21	4.38	4.81	4.53	2.5	1.7	1.9	2.0	12.7
7e	Br	Cl	5.40	4.60	4.97	4.41	2.2	1.4	1.7	2.2	12.1
8e	Br	Br	5.94	4.87	5.08	4.40	2.2	1.5	2.2	2.3	12.8
8e	Cl	Br	5.80	4.75	4.93	4.45	2.2	1.5	2.2	2.1	12.5
8e	Br	Cl	5.75	4.73	5.02	4.33	2.1	1.4	2.1	2.1	12.4

[a]The theoretical coupling constants (J_{CX}) obtained by the Karplus $\cos^2 \phi$ equation,[6] for possible configurations are 10.5 (**9a**), 1.8 (**9b**), 3.3 and 3.3 Hz.

dihydro-2*H*-naphtho[1,2-*b*]pyran-3,4-diol **7j** and 2,3-dihydro-1*H*-naphtho[2,1-*b*]pyran-1,2-diol **8i**, respectively.



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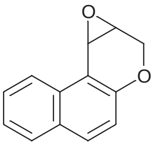

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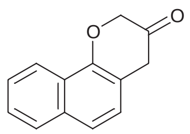

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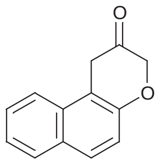

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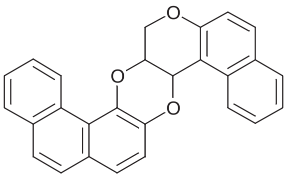

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Pyrolysis of either the chlorohydrins **7i** and **8i** or the alkoxy derivatives **7h** and **8h** or dehydration of the diols **7j** and **8j** furnished 2,4-dihydronaphtho[1,2-*b*]pyran-3-one **13** and 1,3-dihydronaphtho[2,1-*b*]pyran-2-one **14** respectively. 1,2-Epoxy-2,3-dihydro-1*H*-naphtho[2,1-*b*]pyran **12** when kept in diethyl ether for two weeks gave a dimer, probably possessing structure **15**.[8]

Techniques used: ^{1}H NMR and mass spectrometry

References: 9

Tables 1–3: ^{1}H NMR and analytical data

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References cited in this synopsis

1 B. Bachmann and H. A. Lavine, *J. Am. Chem. Soc.*, 1947, **69**, 2341.
2 J. Colonge and A. Guyot, *Bull. Soc. Chim. Fr.*, 1958, 325.
3 W. D. Cotterill, J. Cottam and R. Livingstone, *J. Chem. Soc. C*, 1970, 1006.
6 M. Karplus, *J. Chem. Phys.*, 1959, **30**, 11.
8 J. B. Abbott, C. J. France, R. Livingstone and D. P. Morey, *J. Chem. Soc. C*, 1967, 1472.