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THE SPIROBICHROMAN-DIHYDROXYSPIROBIINDANE REARRANGEMENT

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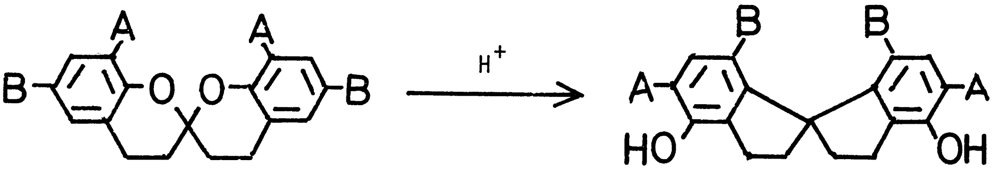
Rearrangement of 2,2'-spirobichroman derivatives having electron donating substituents into 4,4'-dihydroxy-1,1'-spirobiindane analogues was effected by boiling solution of the former in HBr- or HI-HBr-acetic acid.

The author reports here the rearrangement of 2,2'-spirobichroman derivatives[1)] into 4,4'-dihydroxy-1,1'-spirobiindane analogues substantiating a novel[2)] intramolecular alkylation of the aromatic ring.

By heating 6,6'-dimethoxy- (Ia), 6,6',8,8'-tetramethyl- (Ib) and 6,6'-dimethyl- (Ic) 2,2'-spirobichroman with HBr-acetic acid and HI-HBr-acetic acid[3)], 4,4',7,7'-tetrahydroxy- (IIa), 4,4'-dihydroxy-5,5',7,7'-tetramethyl- (IIb) and 4,4'-dihydroxy-7,7'-dimethyl- (IIc) 1,1'-spirobiindane having m.p. 234°, 186° and 219°, respectively, were obtained in the yields decreasing in this order while 6,6'-dichloro-2,2'-spirobichroman (Id) did not yield any products with these reagents. The results are summarized in table 1 and figure 1.

Fig. 1



$I_{a,b,c,d,e,f}$

a: A= H, B= OCH_3; b: A=B= CH_3
c: A= H, B= CH_3; d: A= H, B= Cl
e: A= H, B= OH,OCH_3; f: A= H, B= OH

$II_{a,b,c}$

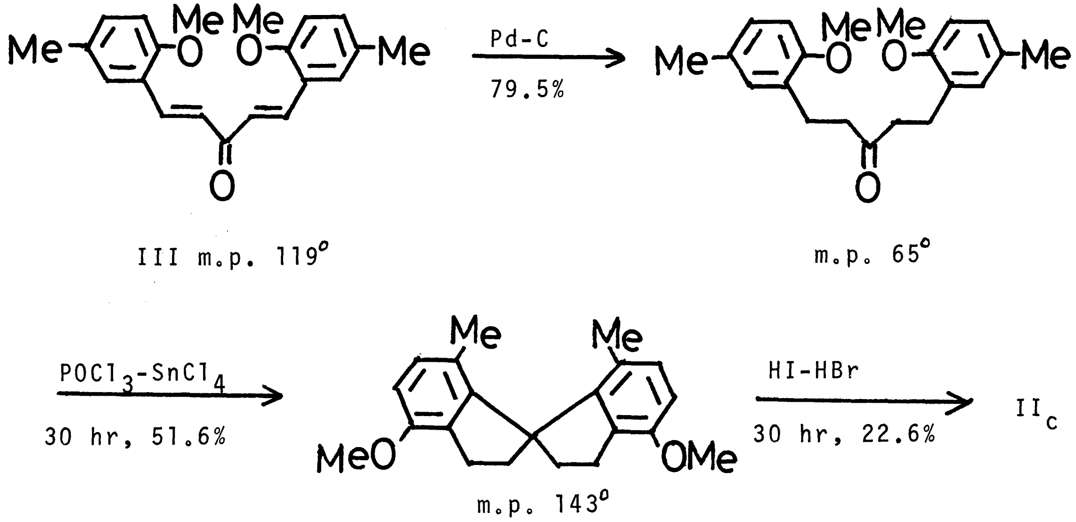
a: A= H, B= OH
b: A=B= CH_3
c: A= H, B= CH_3

Table 1. Conditions and yields of products of the rearrangement reaction.

Reactant	Acid	Reaction temp./°C	Reaction time/hr	Products (%)
Ia	HBr-AcOH	80	4	Ia(28.8),Ie(25.6),If(11.3),IIa(3.5)
Ia	HBr-AcOH	80	40	If(9.9),IIa(40.8)
Ia	HBr-AcOH	95	14	If(2.8),IIa(64.7)
Ib	HBr-AcOH	95	52	IIb(62.2)
Ic	HI-HBr-AcOH	reflux	16	IIc(15.3)
Id	HBr-AcOH	95	60	no appreciable products
Id	HI-HBr-AcOH	reflux	16	

The structure of IIc was established both by NMR δ($CDCl_3$), 6.94 2H d J=8, 6.74 2H d J=8, 4.50 2H s, 2.88 4H t J=8, 2.18 4H t J=8, 1.82 6H s and the following synthesis[4]. III was obtained from 5-methylsalicylaldehyde via condensation with acetone followed by methylation in 65.5% yield. In order to effect optical resolution, toluene solution of IIc was treated with (+)-α-phenylethylisocyanate and a drop of pyridine and refluxed for 46 hours to yield urethan A m.p. 148°, $[\alpha]_D^{18}$ -103°(c=0.31 MeOH) and urethan B m.p. 98°, $[\alpha]_D^{18}$-108°(c=0.28 MeOH). Enantiomers, (+)-IIc m.p. 194°, $[\alpha]_D^{20}$+76.6° and (-)-IIc m.p. 194°, $[\alpha]_D^{20}$-69.9°, were obtained by the hydrolysis of urethanes A and B with alcoholic KOH, respectively. In the ESR spectra of (+)- and (-)-IIc in the ambient atmosphere, a triplet (g=2.0023, A=60G) and a singlet (g=2.0023) absorption, respectively, were observed together with the O_2 singlet[5].

Fig. 2



Structures of IIa and IIb were assigned on the basis of their NMR spectra[6].

Main reaction products of Ia at 80° in 4 hours, were 6-hydroxy-6'-methoxy-2,2'-spirobichroman (Ie) m.p. 152° and 6,6'-dihydroxy-2,2'-spirobichroman (If) m.p. 222° which gradually rearranged to IIa on prolonged reactions and IIa was the main product at 95° in 14 hours.

The attack at methoxyl groups in preference to chroman oxygen atoms should be due to the steric hindrance of tertiary carbon atoms pertained to the latter.

The stability of Id in the acid solutions and the milder conditions for effecting the rearrangement of Ia and Ib, indicates that the reaction is an electrophilic substitution of the aromatic rings by the carbonium ions[7] formed by the protonation of oxygen atoms followed by cleavage of the chroman rings.

The deep blue color λ(reflectance) 530nm[8] of IIa-dihydrate is remarkable. The complex is stable in water, chloroform and heptane but decomposed by ethanol, dioxane and pyridine. And as there are no absorption peaks due to radical formation in the ESR spectrum, the complex is supposed not to be a charge transfer but a clathrate compound.

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References.

1) Two methods are available for the synthesis. a) P. T. Mora and T. Szeki, J. Am. Chem. Soc., 72, 3009 (1950); b) T. Tanaka and T. Tomimatsu, Abstracts of papers of the 8th congress of heterocyclic chemistry, Kyoto, Japan. 1975, p. 194-7. Ia m.p. 142° was synthesized by a. Ib m.p. 168° , Ic m.p. 130° and Id m.p. 207° were prepared both by a and b. Typical pattern among the NMR spectra of I is represented by that of Id $\delta(CDCl_3)$ 7.14 2H d J=2; 7.06 2H q J=9.1,2; 6.68 2H d J=9.1; 3.28 2H oct J=4.5,6.1,16.6; 2.72 2H oct J=6.1,3.0,16.6; 2.24 2H oct J=13.6,6.1,3.0; 1.94 2H sext J=13.6,13.6,4.5.

2) Spiro-compounds via rearrangement: A. P. Krapcho, Synthesis, 1974, 383; ibid., 1976, 425.

3) 12 Ml CH_3COOH and 2 ml HBr, or 4 ml CH_3COOH, 3 ml HBr and 0.3 ml HI per 100 mg spirobichroman.

4) Spirobiindane synthesis: S. Hagishita, K. Kuriyama, M. Hayashi, Y. Nakano, K. Shingu and M. Nakagawa, Bull. Chem. Soc. Jpn., 44, 196 (1971); R. K. Hill and D. A. Cullison, J. Am. Chem. Soc., 95, 1229 (1973); J. H. Brewster and R. T. Prudence, ibid., 95, 1217 (1973).

5) Since these absorptions are not observed in the spectra of the benzene solutions of (+)- and (-)-IIc, they may be ascribed to the interactions of these molecules with the O_2 electron spin. No such absorptions were not observed in the spectrum of racemic IIc.

6) IIa-$2H_2O$ $\delta(CDCl_3)$ 7.50 2H s, 6.60 2H d J=8, 6.53 2H d j=8, 6.42 2H s, 3.20 4H s, 3.01 4H t J=8, 2.83 4H t J=8; IIb $\delta(CDCl_3)$ 6.90 2H s, 4.56 2H s, 3.02 4H sext, 2.20 10H s (overlap), 2.76 6H s.

7) J-P. Gesson, L. D. Giusto and J-C. Jaquesy, Tetrahedron, 34, 1715 (1978). We have at present no evidence of such concerted mechanism as is observed of dienone-phenol rearrangement.

8) λ(EtOH) nm(log ε); IIa 201.5(5.32), 227(sh 4.60), 290(4.32); IIb 206.5(4.93), 231(sh 4.34), 277(sh 3.53), 284.5(3.59); IIc 206(4.94), 228(sh 4.45), 277(3.53), 283.5(3.54).

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