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SPIRANS I. A NEW REACTION LEADING TO THE FORMATION OF 3,3'-SPIROBICHROMAN SYSTEM. HYPOCHROMISM IN SPIRANS

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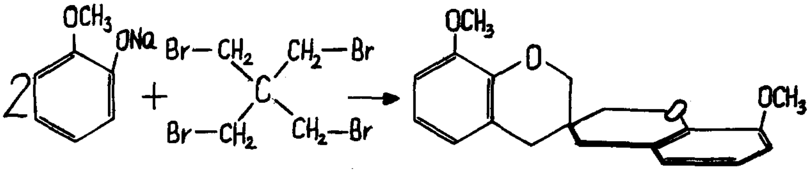
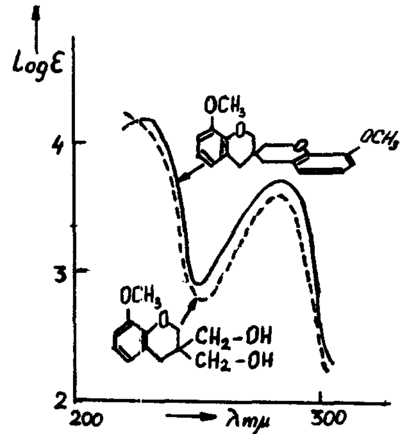
The formerly described reaction[1] yielding 8-methoxy-3,3-bis-hydroxymethylchroman from dibromohydrin of pentaerythritol and sodium guaiacolate has been modified by using pentaerythrityl tetrabromide in the reaction. In similar conditions /refluxing for 80 h in xylene/ 8,8'-dimethoxy-3,3'-spirobichroman was obtained in 10% yield, colourless plates /from boiling xylene/, m.p. 190-91°. Anal. Calcd. for $C_{19}H_{20}O_4$: C, 73.06; H, 6.45%. Found: C, 72.68; H, 6.26%



The molecular weight determination by the Rast method: 326,9; Calcd: 312,25

The compound shows absorption at 739, 774 /trisubstituted benzene-ring/ 833, 907, 1032 /charact. for chroman/, 1053, 1126, 1185, 1223, 1252 /charact. for chroman/ 1335, 1455, 1470, 1513, 1592 /aromat./, 2831 cm^{-1}/OCH_3/. The shape of the UV absorption curve for this spiro-compound is the same as for the cited chroman, the positions of the maximum and minimum /characteristic for the chroman system/ being identical: spiran λ_{min} 249 /log ε 2,85/, λ_{max} 280 /log ε 3,73/; chroman λ_{min} 249 /log ε 2,78/, λ_{max} 280 mμ /log ε 3,60/ /all in n-propanol/.



The ratio of the extinction coefficients at λ_{max} for the pair of the compounds is 1:1,35. The ratio is surprisingly low taking into account the fact that the same ratio for the "monomer-dimer" pair, where the "dimer" is an atropisomeric compound, amounts to 1:2,5 whereas the ratio for pairs with free rotation of the "dimer" amounts to 1:10 or even to 1:100[2].

In my case, the discussed chroman compound may be regarded as the "monomer" of the presented spiran because its substituents in position 3 are "empty" for UV light. On the other hand, the mentioned spiran may be treated as the "dimer" of chroman, with extreme, fixed atropisomerism.

The cited ratio of the extinction coefficients at λ_{max} would indicate hypochromism of the spiran compound corresponding to the UV light absorption by biological polymers /polynucleotides/. They exhibit little apparent change in frequency and band shape when transforming a random-coil to a double-stranded helix-form, however, there is a pronounced decrease in absorption intensity /hypochromism/ and the ultraviolet light absorption of a polynucleotide is considerably less than the sum of the absorptions of its constituent nucleotides[3].

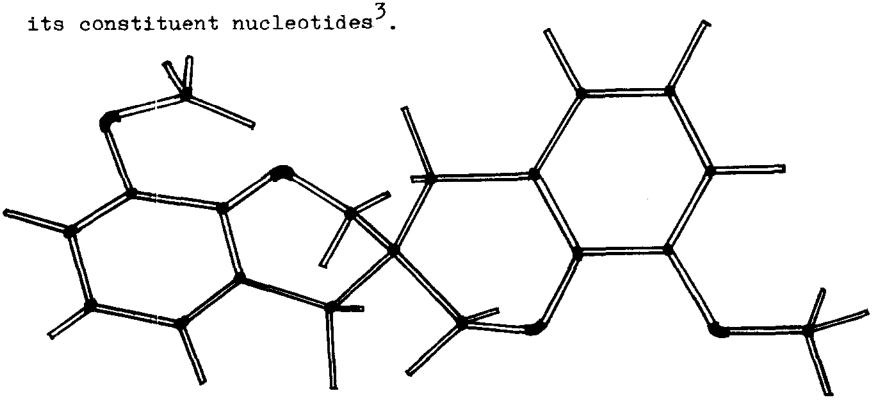


FIG.1

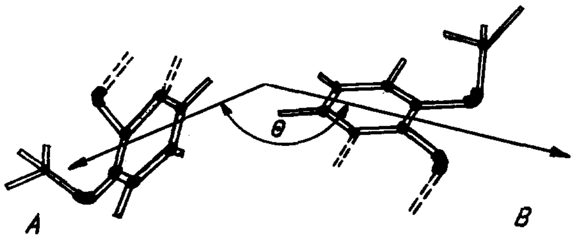


FIG.2

It should be noted that the most probable conformation of the spiran is the form /FIG.1/ in which both oxygen atoms of the pyran rings are at the greatest distance from one another, the angle θ between the plane of benzene ring A and that of benzene ring B being ca 135° /measured from the stereo-models of Dreiding/ /FIG.2/.

The spiran was subjected to cleavage by the action of pyridine hydrochloride /5h,190°/ yielding chlorinefree 8,8'-dihydroxy-3,3'-spirobichroman /waxy product/ which was characterised as bis-3,5-dinitro-benzoate, yellow-red irregular plates /from a mixture of ethyl acetate and cyclohexane/, m.p.142°/decomp./.Anal. Calcd. for $C_{31}H_{20}O_{14}N_4$: C, 55.36; H, 3.00; N, 8.33%. Found: C, 54.98; H, 3.19; N, 8.74%. The IR-spectra are consistent with the above given formulation; UV spectrum /in n-propanol/: λ_{max}2,14 /log ε 4,93/; 302-306 mμ/log ε 3,42-3,40/.

The above described cleavage is not typical[4] because the pyran rings are preserved. This is clear when we assume that the hydrogen atoms of hydroxyl groups formed in positions 8 and 8' protect the oxygen atoms of the pyran rings from the action of the cleaving agent.

To determinate the scope of the reaction the condensation of sodium o-nitrophenolate with pentaerythrityl tetrabromide was investigated. Two ethers were isolated: mono-o-nitrophenyl ether of tribromohydrin of pentaerythritol, pale yellow plates /alcohol/, m.p. 91-92°. Anal. Calcd. for $C_{11}H_{12}O_3NBr_3$: C, 29.62; H, 2.71; N, 3.14; Br, 53.76%. Found: C, 29.94; H, 2.82; N, 3.54; Br,54.07% and bis-o-nitrophenyl ether of dibromohydrin of pentaerythritol, pale yellow plates, m.p. 136-38°. Anal. Calcd. for $C_{17}H_{16}O_6N_2Br_2$: C,40.50; H, 3.20; N, 5.56; Br, 31.70%. Found: C, 40.15; H, 3.33; N, 5.20; Br, 31.49%. It should be noted that the crystals of the last compound exhibit extreme hydrophobic properties.

The formation of these nitroethers proves the proposed mechanism of the reaction according to which ethers are formed in the first step /Williamson reaction/ which then undergo cyclisation with the formation of a chroman ring.

The cyclisation may however occur only in the presence of an electro-negative substituent in the o-position to the formerly introduced substituent. In the case of a nitro-group in the o-position the cyclisation does not occur because the vicinal position is not activated.

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