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SYNTHESIS OF 2,2-BIS-/4-HYDROXY-3,5-DI-(2-BENZOTRIAZOLYL) PHENYL/PROPANE

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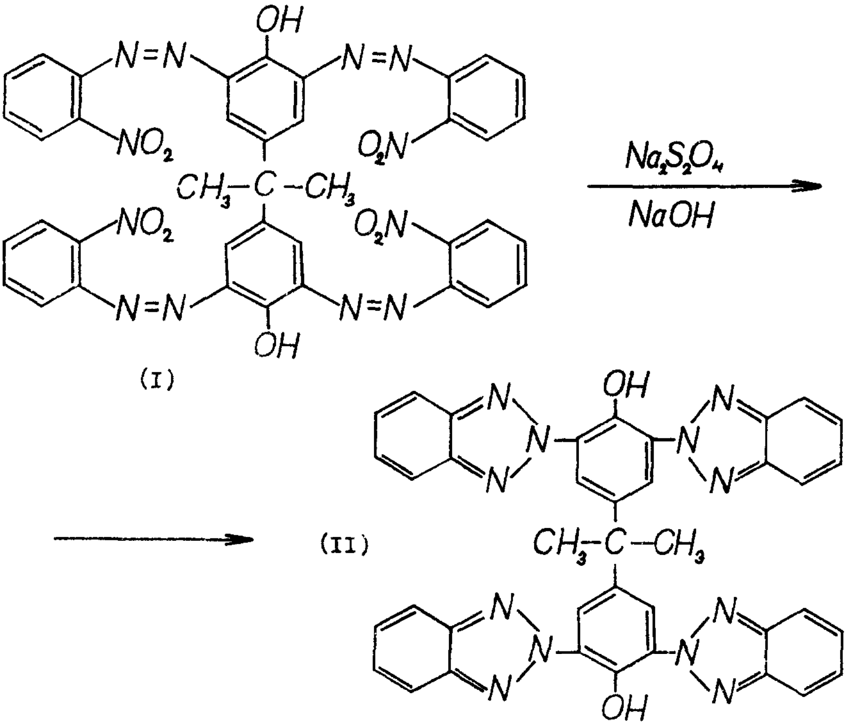
2-(2'-Hydroxyphenyl)benzotriazole derivatives are important ultraviolet screening agents (1).It was therefore interesting to prepare some derivatives of the series mentioned starting from 2,2-bis-(4-hydroxyphenyl)propane (DIAN),which easily undergoes electrophilic substitutions (2),and to compare their infrared and ultraviolet absorption spectra with those of known compounds of benzotriazole series.

Dian gives on treatment with o-nitrobenzenediazonium chloride in presence of at least equivalent amount of alkaline hydroxide at about 10° 2,2-bis -(4-hydroxy-3,5-di-/2-nitrophenylazo/phenyl)propane (I),m.p.106-8°,in 75% yield.Satisfactory carbon,hydrogen,and nitrogen analyses were obtained for this and all other new compouns reported.When an alkaline carbonate or acetate is used instead of hydroxide or when the reaction is carried out in ethanol,dian decomposes,yielding 2-nitro-4'-hydroxyazobenzene.

The compound I refluxed with acetic acid for 15 min.,gives 2,2-bis-/4-acetoxy-3,5-di-(2-nitrophenylazo)phenyl/propane (Ia) m.p.202-3°,in 84% yield.

Reduction of the azocompound I was carried out by sodium hydrosulfite in 5% alkaline hydroxide.After passing CO_2 through the cooled reaction mixture,the 2,2-bis-/4-hydroxy-3,5-di-(2-benzotriazolyl)phenyl/propane (II)was obtained,having m.p. 278° (xylene).



(I)

(II)

Methylation of II with dimethyl sulfate in 2% alkaline hydroxide gives 2,2-bis-/4-methoxy-3,5-di-(2-benzotriazolyl) phenyl/propane /IIa/,m.p.220°/80% acetic acid /,in 80% yield.

Similarly gives II with acetic anhydride 2,2-bis-(4-acetoxy-3,5-di-(2-benzotriazolyl)phenyl/propane (IIb),m.p.230° (n-butanol).

The compound II shows a broad absorption band in the infrared at 3170 cm^{-1}.which is not present with compounds IIa and IIb and is therefore assigned to hydrogen-bonded OH-group. For compounds II,IIa,and IIb show no absorption bands owing to a free OH-group in carbon tetrachloride solutions /6.10^{-3}M/ a conclusion can be made that the compound II forms only intramolekular hydrogen bonding between the OH-group and the ring nitrogen atom.

Ultraviolet spektra of compounds II,IIa,and IIb contain two absorption bands at 310,and 230 nm,the former beeing predominant.

It is interesting that substitution of hydrogen atom of the OH-group in II with CH_3- or CH_3CO- group nearly does not change the character of the ultraviolet spectrum,whereas the intramolecular hydrogen bonding between OH-group and ring nitrogen atom at 2-/2-hydroxyphenyl/benzotriazole derivatives gives rise to a new,very intensive absorption band ,shifted towards the visible region (3).The ultraviolet absorption spectra of prepared II,IIa, and IIb are therefore very similar to that of 2-phenylbenzotriazole (4),the compound having in orthoposition to the ring nitrogen atom neither OH- nor any other group.

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