Demonstration of Geometrical Isomerism in Arylazoalkanes

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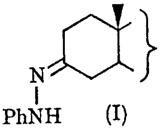
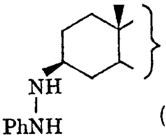
THE *cis*-form of azobenzene was prepared by Hartley in 1938[1] by irradiation of a solution of the *trans*-form. An equilibrium mixture was obtained from which he isolated about 20% of the *cis*-compound, which was stable in the solid state in the dark. More recently, Hutton and Steele[2] have prepared the *cis*-form of azomethane by gas-phase photolysis of the *trans*-form.

We now describe the isolation of the *cis*-form in the remaining class of azo-compounds, namely mixed azo-compounds or arylazoalkanes.

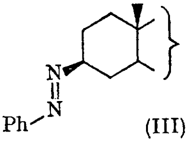
Reduction of cholestan-3-one phenylhydrazone (I) with lithium aluminium hydride gave 1-phenyl-2-(3β-cholestanyl)hydrazine (II), m.p. 170—172°, $[\alpha]_D^{23}$ −18·3° ($CHCl_3$) which was readily oxidised by air or mercuric oxide to 3β-phenylazocholestane, m.p. 139—140° $[\alpha]_D^{23}$ +22° ($CHCl_3$) λ_{max} ($CHCl_3$) 269, and 404 mμ (ε 10,300 and 180) to which we ascribe the *trans*-configuration (III). The 3β-stereochemistry was shown by Raney nickel-catalysed hydrogenation to 3β-aminocholestane, characterised as the known[3] *N*-acetyl derivative. Irradiation of the *trans*-compound in ether for 48 hr., in a mixture of daylight and artificial light, gave two compounds which were separated by preparative thin-layer chromatography into starting material (R_F 0·85) and a new yellow substance (R_F 0·3) (22%), m.p. 111—113° $[\alpha]_D^{23}$ −4·4° ($CHCl_3$) λ_{max}($CHCl_3$) 244·5 and 394 mμ (ε 5650 and 310) to which we assign the *cis*-3β-phenylazocholestane structure, (IV), since lithium aluminium hydride reduction gave 1-phenyl-2-(3β-cholestanyl)-hydrazine (II), identical to the previous sample and which could be further oxidised back to the 3β-*trans*-azo-compound (III). The ultraviolet spectrum of the *cis*-compound showed, by analogy with *cis*- and *trans*-azobenzene,[4] the expected changes in the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ bands. The optical rotatory dispersion spectrum of the *cis*-form is greatly different from the *trans*, the sign of the Cotton effect being opposite and the amplitude being about seven times larger; this amplitude difference is in keeping with the difference in ease of rotation about the C(3)–N bond of the chromophore in the two isomers; if the geometries of the *cis*- and *trans*-forms resemble those of the azobenzene analogues, then it is possible that the greater chirality of the *cis*-form (IV) also contributes to the difference in amplitude.



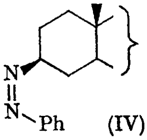
(I)



(II)



(III)



(IV)

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