Configuration in the Fluorenol Series. 1-Bromofluorenol

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Summary The configuration of 1-bromofluorenol has been related to the sign of its optical rotation by means of an asymmetric reduction using aluminium t-butoxide and octan-2-ol; by analogy, the correlation may be extended to 2-chlorofluorenol.

MEERWEIN–PONNDORF–VERLEY reduction of 1-bromofluorenone[1] with aluminium t-butoxide and *R*-(—)-octan-2-ol yielded (+)-1-bromofluorenol.

The transition state involved in such reductions has been thoroughly investigated[2,3] and if we treat our compound, for the purpose of configurational correlation, as a simple substituted asymmetric carbon atom we find that a model of the preferred transition state shows that the configuration of the predominating enantiomer in the product is the same as that of the reducing alcohol. This is in agreement with the findings for other ketones.[2] Thus *R*-(—)-octan-2-ol will yield preferentially the *R*-bromofluorenol and, as this has been found to have a positive rotation, the configurations of the 1-bromofluorenols are established as *R*-(+)-1-bromofluorenol and *S*-(−)-1-bromofluorenol.

Outline experimental: 1-Bromofluorenone was reduced with aluminium t-butoxide and *R*-(−)-octan-2-ol $[\alpha]_D^{20}$ − 9·8° (*l* 1, *c* 5 in 95% ethanol) in benzene at 10° for 16 h. to give *R*-(+)-1-bromofluorenol $[\alpha]_D^{20}$ + 1·2°, (*l* 1, *c* 5, CHCl$_3$). The fluorenol was isolated from the reaction mixture by first removing the aluminium as hydrated oxide, then the octanol was removed by steam distillation at room temperature under reduced pressure, and finally the residue was chromatographed on silica gel. This yielded unreacted fluorenone (eluted with 40—60° petroleum–benzene) and the pure fluorenol (eluted with benzene) m.p. 145—146° (Kofler). (The racemic fluorenol[4] has m.p. 140—141°.) A similar experiment using *S*-(+)-octan-2-ol $[\alpha]_D^{20}$ + 9·8° (*l* 1, *c* 5, in 95% ethanol) yielded *S*-(−)-1-bromofluorenol $[\alpha]_D^{20}$ − 1·3° (*l* 1, *c* 3, CHCl$_3$).

The Figure shows the experimental curves with the scale adjusted to allow for the concentration *etc*. Unfortunately, for instrumental reasons, there was no overlap with our visual readings.

Since the form of the o.r.d. and the u.v. absorption curves for the 2-chlorofluorenols is similar[5] to that of those for the 1-bromofluorenols it would seem reasonable to assume that the configurations of the chloro-compounds are *R*-(+)-2-chlorofluorenol and *S*-(−)-2-chlorofluorenol.

Measurements of optical rotatory dispersion were made with a Fica Spectropolarimeter.

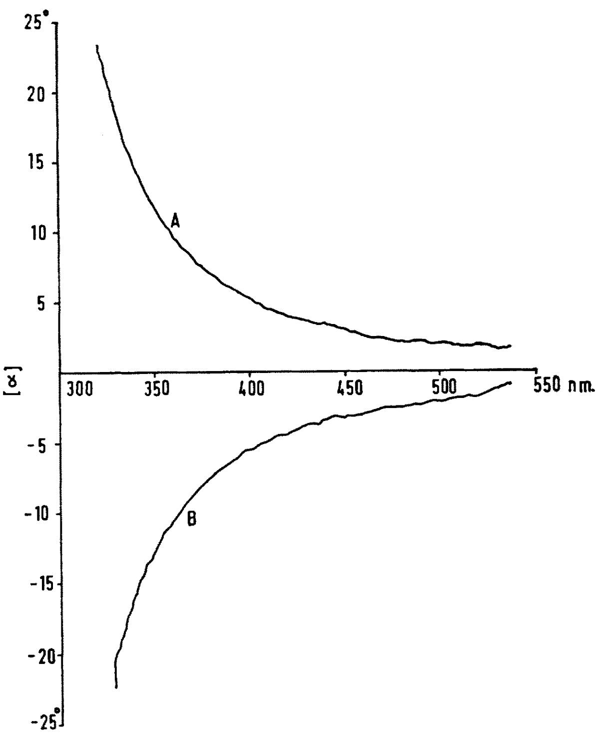

FIGURE. A. *O.r.d. curve of the purified product of M.P.V. reduction of* 1-*bromofluorenone using* R-(−)-*octan*-2-*ol.*

B. *O.r.d. curve of the purified product of a similar reduction using* S-(+)-*octan*-2-*ol.*

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