Co-ordination at a Silicon Atom: Effects on Optical Rotatory Dispersion of α-Silyl-ketones

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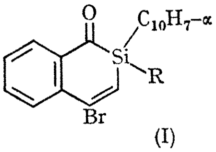
WE have reported previously[1,2] the synthesis of bicyclic α-silyl ketones (I).



(I)

(a) R=Me
(b) R=Et
(c) $R=Pr^n$
(d) $R=Bu^i$
(e) R=Ph

We have now measured the o.r.d. of the optically active ketones which absorb in the visible region between 400 and 500 nm., and have found that the curves are solvent-dependent.

The curves shown in Figures 1 and 2 were measured with the ketone (Ib); the solvents employed are listed in the respective captions.

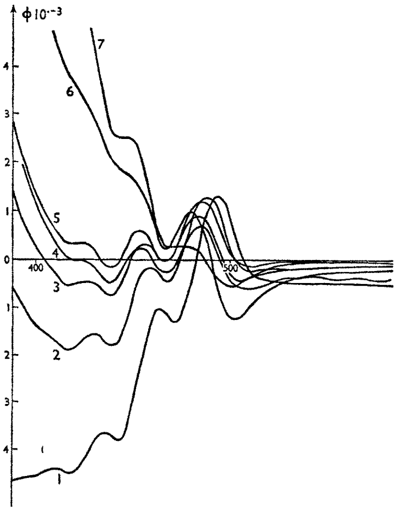


FIGURE 1. *O.r.d. of* (Ib) *in*: (1) cyclohexane; (2) ethyl ether; (3) tetrahydrofuran; (4) anisole; (5) glycol dimethylether; (6) methanol; (7) acetic acid.

In the solvents studied, the curves show a complex Cotton effect corresponding to the $n \rightarrow \pi^*$ transition of the carbonyl group in the 400—550 nm. region. In cyclohexane, the o.r.d. shows a maximum near 500 nm., then the curves become negative. When the basicity of the solvent increases, the positive maximum becomes negative, and in very basic solvents, Me_2SO and $HCONMe_2$, there is practically an inversion of the o.r.d. curve. Solvents of intermediate basicity give intermediate effects.

Although solvent effects on o.r.d. or c.d. have been described for carbonyl compounds[3] our results seem to indicate new interactions between α-silyl-ketone and solvent. The important feature is the effect of the basicity of the solvent on the o.r.d. curves, and we believe that this phenomenon can be related to the racemisation of chlorosilane by the same electron-donor solvents.[4]

For instance, the order of efficiency of ethers during racemisation of chlorosilane is glycol dimethyl ether > tetrahydrofuran > ethyl ether; the same order is observed in the modification of o.r.d. curves. The aprotic solvents Me_2SO, $HCONMe_2$, and hexamethylphosphoramide, which cause instantaneous racemisation, also have profound effects on o.r.d.

The mechanism suggested for chlorosilane racemisation was an extension of the silicon atom co-ordination.[4] It is also known that the anomalous spectral properties of α-silyl-ketones are caused by the presence of the silicon atom adjacent to the carbonyl.[5]

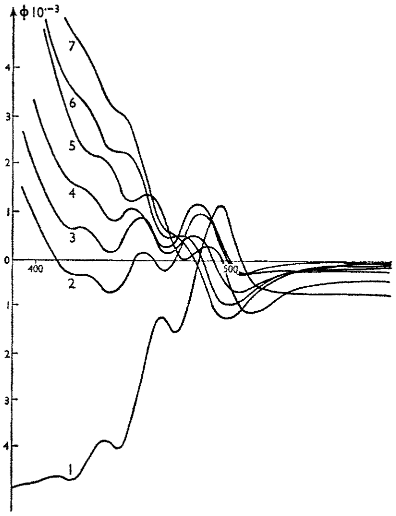


FIGURE 2. *O.r.d. of* (Ib) *in*: (1) cyclohexane; (2) hexamethylphosphoramide; (3) ethyl acetate; (4) pyridine; (5) acetone; (6) dimethylformamide; (7) dimethyl sulphoxide.

We therefore suppose that interactions of basic solvents with α-silyl-ketones can be rationalized in term of co-ordination of the basic part of the solvent molecule with the available 3*d*-orbitals of silicon. This situation is responsible for the solvent-dependent o.r.d. curves of α-silyl-ketones.

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