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A PECULIARITY IN THE DEUTERATION OF CERTAIN BICYCLO[2.2.1]HEPTANONES

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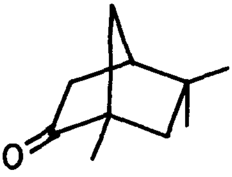
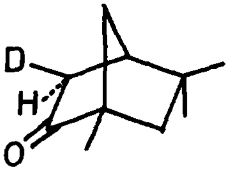
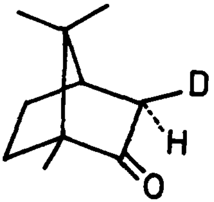
For our studies on the mass spectra of bicyclic monoterpene ketones, we required ketones deuterated in the position adjacent to the carbonyl group. The usual preparative method (NaOD in 50 % dioxane - D_2O at room temperature for three days [*]) applied to isofenchone (I) yielded a monodeuterated compound (isotopic purity 97 % by mass spectral analysis), the deuterium content of which was not appreciably altered by a second exchange carried out by heating the reaction mixture for 20 minutes at 90°.



(I)



(II)



(IV)

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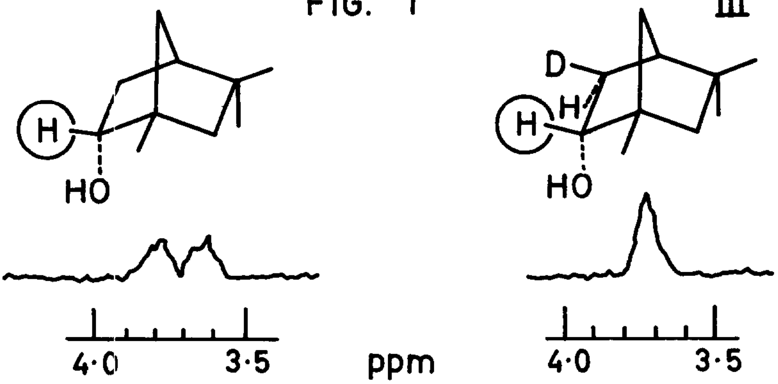
[*] These conditions usually lead to almost complete exchange in one reaction with monoterpene ketones; e.g. menthone gives over 90 % d_3 species.

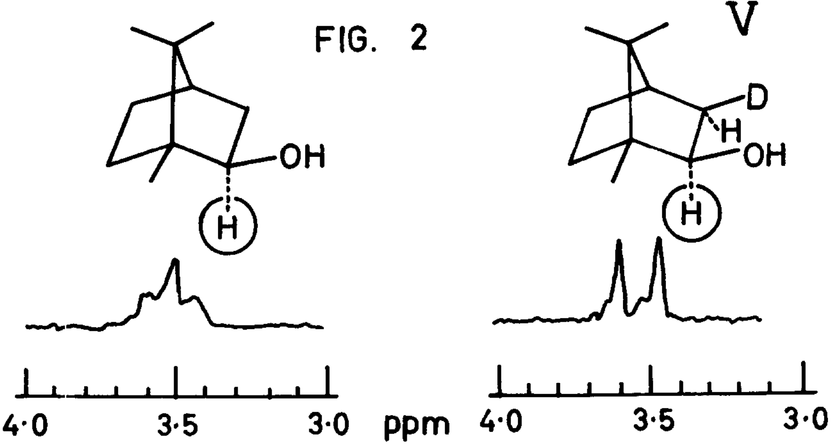
The position of the deuterium was defined as exo-(II) in view of the fact that lithium aluminium hydride reduction (known to give endo-isofenchol (1)) led to a monodeuterated isofenchol (III), the N.M.R. spectrum of which (in CCl_4) had the signal of the carbinol hydrogen as a broad singlet about 3.72 ppm (with respect to TMS) instead of the doublet (with further splitting) at the same position (J approx. 9 cps) that this hydrogen exhibits in endo-isofenchol (see FIG. 1).

FIG. 1



In the case of camphor, the same exo-monodeuteration was observed (IV) (monodeuterated species 85 %, one exchange). Reduction by lithium aluminium hydride (1) gave in this case an isoborneol (V), the N.M.R. spectrum of which exhibited a doublet at 3,53 ppm (J = 8 cps) in place of the multiplet that undeuterated isoborneol shows (2) (see FIG. 2).

FIG. 2



The high stereospecificity of this reaction is surprising since deuterium exchange is not generally very sensitive to stereochemical environment (3), and where selectivity is shown, it is the axial hydrogen that exchanges first (4).

Finally, we have found that norcamphor exchanges under the same conditions to give a product containing 60 % of a d_1 species and only 34 % d_2, the proportions changing to 46 % d_1 and 49 % d_2 after a second exchange, showing that here too, there appears to be some selectivity in the reaction.

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