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The geometrical isomers of 2,3-difluoro-2,3-dihydrobenzofuran have been prepared and their structure assigned on the basis of the nmr spectra. Some suggestions on the conformational situation of two adducts are also reported.

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Sir:

In the course of our study, aimed to determine the mechanism of the dehydrohalogenation reactions of 2,3-dihalogeno-2,3-dihydrobenzofurans (1-3), a simple route to obtain *trans*- (I) and *cis*-2,3-difluoro-2,3-dihydrobenzofuran (II) from the corresponding *trans*-dibromo derivative has been developed. In this paper we describe the procedure for the preparation of these compounds and discuss their structure and conformation on



I

II

the basis of the nmr spectra. Formation of a 2,3-difluoro-2,3-dihydrobenzofuran as a minor product of the reaction between benzofuran and fluoroxytrifluoromethane has been reported, however, no information on the structure and stereochemistry of this adduct was given (4).

In our work, dry silver fluoride was added to a solution of *trans*-2,3-dibromo-2,3-dihydrobenzofuran in benzene:acetonitrile (9:1) at *ca.* 0°, in the dark, and the mixture stirred for about five hours. The crude reaction product was chromatographed on silica gel using petroleum ether as the eluent. Besides a certain amount of the expected elimination products, two liquid compounds A and B (A:B *ca.* 0.7:1) could be isolated (overall yield *ca.* 60%). The mass spectrum (parent peak at *m/e* 156 for both compounds) and the nmr spectrum in perdeuteriobenzene at 90 MHz [compound A:  $\delta$  7.16-6.51 (4H, m), 5.91 (1H, dd), 5.39 (1H, dd) and compound B:  $\delta$  7.19-6.53 (4H, m), 5.52 (1H, ddd), 5.25 (1H, ddd)] are in agreement with the structure of a 2,3-difluoro-2,3-dihydrobenzofuran. Accordingly, the nmr spectra of both adducts are similar to those of 2,3-dihalogeno-2,3-dihydrobenzofurans with 2-H and 3-H atoms resonating at higher fields than in benzofuran (5-7). Moreover, both compounds when treated with potassium *t*-butoxide in *t*-butyl alcohol at 30° underwent a dehydrohalogenation reaction giving the expected amount of

hydrofluoric acid (titration by 0.05 *M* thorium nitrate).

On the basis of the vicinal coupling constants between 2-H and 3-H atoms, it is possible to ascribe the *trans* structure (I) to compound A and the *cis* structure (II) to compound B. Accordingly, in the nmr spectrum of A we note two double doublets at  $\delta$  5.91 and 5.39 due to the coupling of 2-H and 3-H atoms with the fluorine atoms ( $^2J_{H_2F} = 58.2$  Hz,  $^3J_{H_2F} = 11.4$  Hz,  $^2J_{H_3F} = 54.6$  Hz,  $^3J_{H_3F} = 11.4$  Hz). This clearly means that the two protons are not coupled with each other ( $J_{H_2H_3} \sim 0$  Hz), thus indicating a dihedral angle ( $\sim 90^\circ$ ) between the C<sub>2</sub>-H and C<sub>3</sub>-H bonds consistent with a *trans* structure (5-7). On the contrary, in the nmr spectrum of B the signal of 2-H and 3-H atoms at  $\delta$  5.52 and 5.25 are double double doublets which indicates that, besides coupling with fluorine ( $^2J_{H_2F} = 61.2$  Hz,  $^3J_{H_2F} = 2.9$  Hz,  $^2J_{H_3F} = 54.9$  Hz,  $^3J_{H_3F} = 14.1$  Hz), these protons are also coupled with each other. The  $J_{H_2H_3}$  value (4.5 Hz) is similar to the corresponding value (6 Hz) exhibited by *cis*-2,3-dichloro-2,3-dihydrobenzofuran (7).

The heterocyclic ring of benzofuran is probably not planar and two envelope conformer are possible with very small barrier to inversion (8). Therefore, the very low value of  $J_{H_2H_3}$  ( $\sim 0$  Hz) in the *trans* isomer would suggest that this compound exists predominantly in the conformation where both the C-F bonds occupy a pseudo-axial position probably due to the large "anomeric" effect of a C-2 fluorine substituent (9,10). This effect should also play an important role on the conformational situation of the *cis* isomer, since the observed values of proton-fluorine vicinal coupling suggest that II preferentially exists in a conformation where the C<sub>2</sub>-F bond is again pseudo-axial and C<sub>3</sub>-F bond is pseudo-equatorial. Accordingly, the low value (11) of  $^3J_{H_2F}$  suggests that C<sub>2</sub>-H and C<sub>3</sub>-F bonds form a dihedral angle of 90-100° (12), whereas the dihedral angle between C<sub>2</sub>-F and C<sub>3</sub>-H is expected to be larger (120-130°) (12) than the former on the basis of the relatively high value of  $^3J_{H_3F}$ . A support of this hypothesis

is given by the temperature dependence of  $^3J_{HF}$  coupling constants of compound II. The nmr spectra in tetrachloroethylene at 100 MHz showed that, on increasing the

temperature from 25° to 100°,  $^3J_{H_2F}$  decreases of 0.7 Hz, whereas  $^3J_{H_3F}$  increases of the same amount, thus indicating a slight shift of the conformational equilibrium. Interestingly enough the  $J_{H_2H_3}$  value remains constant as expected since the dihedral angle between C<sub>2</sub>-H and C<sub>3</sub>-H bonds is almost identical in the two conformers (8).

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