

## Identification of the Addition Products Formed in the Chlorination of Benzofuran

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The *cis* and *trans* isomers of 2,3-dichloro-2,3-dihydrobenzofuran have been prepared and their reactions studied in the presence and in the absence of bases. Some data on the influence of the experimental conditions on the stereochemical course of the reaction are also reported.

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Sir:

In the course of our study, aimed to define the role of addition compounds in the mechanism of both conventional and non-conventional electrophilic substitution of heteroaromatic substrates (1), a detailed investigation of the chlorination of benzofuran has been carried out. Despite the fact that the formation of an addition product during this reaction is well known (2,3), no information is available on the structure of the adduct and on the stereochemistry of the reaction.

For the first time both the *cis* and *trans* isomers of 2,3-dichloro-2,3-dihydrobenzofuran have been prepared and their reactions studied in the presence and in the absence of bases. Moreover, some data on the influence of the experimental conditions on the stereochemical course of the reaction have been obtained.

Benzofuran was chlorinated by molecular chlorine in ether at  $-5.0^{\circ}$  and the crude reaction product chromatographed twice on deactivated silica gel using petroleum ether as eluent. Two products were isolated: the nmr spectrum in carbon tetrachloride of compound I (m.p.  $43-44^{\circ}$ ) exhibited peaks at  $\delta$  6.88-7.55 (4H, m), 6.40 (1H, s), and 5.38 (1H, s) whereas the nmr spectrum in carbon tetrachloride of compound II (a liquid, at room temperature) showed peaks at  $\delta$  6.76-7.42 (4H, m), 6.48 (1H, d,  $J = 6$  cps), and 5.50 (1H, d,  $J = 6$  cps). The spectrum of compound I is in agreement with the structure of *trans*-2,3-dichloro-2,3-dihydrobenzofuran, whereas that of compound II is in agreement with the structure of the *cis* isomer.

Accordingly, the spectrum of compound I is similar to that observed for *trans*-2,3-dibromo-2,3-dihydrobenzofuran; the two singlets at  $\delta$  6.40 and 5.38 are due to the 2-H and 3-H atoms, respectively, and resonate at higher fields than in the starting benzofuran. The absence of any coupling between the two protons indicates a

dihedral angle of *ca.*  $90^{\circ}$  consistent with the *trans* structure. On the contrary, in the spectrum of compound II the peaks of 2-H and 3-H,  $\delta$  6.48 and 5.50, respectively, exhibit substantial coupling, indicating a dihedral angle of *ca.*  $30^{\circ}$ , consistent with the structure of the *cis*-adduct.

Further evidence of the structure of the two adducts is given by the solvent effect on the chemical shifts. A diamagnetic shift is always observed for the 2-H and 3-H peaks when the spectrum is run in perdeuteriobenzene, because of the ring current of the benzene ring. The  $\Delta\delta$  values are larger for the *cis*-isomer (0.54 and 0.64 for 2-H and 3-H, respectively) than for the *trans*-isomer (0.16 and 0.29), since in the former case the solvent molecules can get closer to the hydrogen atoms without being hindered by the chlorine atoms (4).

The structure of the two isomers is also confirmed by their chemical properties. Both I and II, when treated with sodium ethoxide/ethanol, give the expected elimination product, 3-chlorobenzofuran, but the reaction of II is much more rapid than that of I, as an *anti* elimination is possible only for the *cis*-adduct. The rate constant for compound I at  $30^{\circ}$  is  $0.001 M^{-1} s^{-1}$  whereas that for compound II is too large to be determined by conventional techniques.

In acetic acid, at  $100^{\circ}$ , I reacts by a solvolytic process to yield mainly 2-chlorobenzofuran, whilst II, in the same solvent at  $80^{\circ}$ , is isomerized into I, in agreement with the greater stability of the *trans*-adducts. The detailed mechanism of the decomposition of the adducts will be reported in a subsequent paper.

When the chlorination of benzofuran is carried out with molecular chlorine the isomeric distribution between I and II appears to be little influenced by the experimental conditions. The *trans/cis* ratio, determined by nmr analysis of the reaction mixture, is *ca.* 1 in ether, in acetic acid, and in carbon tetrachloride either at  $0^{\circ}$  or

25°. In no case the ratio is affected by the light, thus indicating that a heterolytic process is involved. A prevalence of *trans*-addition (*trans/cis* ratio *ca.* 2) is observed when iodobenzene dichloride in carbon tetrachloride is the chlorinating agent, in agreement with literature data (5).

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#### REFERENCES AND NOTES

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