N.m.r. Evidence for Covalent Adducts as Intermediates in the Bromination of Furan†

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Summary Evidence for the formation of *cis*- and *trans*-2,5-dibromo-2,5-dihydrofuran and of *trans*-2,3-dibromo-2,3-dihydrofuran in the bromination of furan in CS_2 was obtained by an n.m.r. study.

In a recent n.m.r. study we showed that bromination of benzofuran involves the immediate formation of a covalent adduct to the 2,3 double bond.[1] This adduct was shown to be formed in a side-equilibrium and therefore was not an intermediate on the direct route to the ring or side-chain substituted products.[1] We now report the results of a similar study on the bromination of furan.

Bromination of furan in CCl_4 is known to give a mixture of 2-bromo- and 2,5-dibromo-furan.[2] This reaction was thought to be initiated by a 2,5-addition of bromine to the furan nucleus, on the basis of the formation of 2,5-diacetoxy-2,5-dihydrofuran in a solution of acetic acid containing two moles of potassium acetate.[3] Nevertheless, no direct evidence for the formation of adducts in the bromination of furan has been given so far.

As in our previous study[1] we carried out the reaction in CS_2 in an n.m.r. tube placed in the probe of a JEOL C-60HL instrument, at −50 °C, using a deficiency of molecular halogen. The spectrum taken immediately is shown in the Figure. The observed pattern changes in a few hours to a simpler one typical of a mixture of the starting material and 2-bromofuran; δ 7·35 (1H, dd, $J_{4,5}$ 2·2 Hz, $J_{3,5}$ 1·2 Hz, H-5), 6·31 (1H, m, H-4), 6·25 (1H, m, H-3);[4] on warming the probe to room temperature.

The spectrum given in the Figure shows signals at δ 7·33 (2H, t, α-H) and 6·27 (2H, t, β-H), attributable to excess furan, whereas the signals at δ 7·10, 6·96, and 6·33 are attributed to *trans*- and *cis*-2,5-dibromo-2,5-dihydrofuran.

In particular the *trans*-adduct gives rise to the peak at δ 7·10 (2H, s, α-H), and the *cis*-adduct to the peak at 6·96 (2H, s, α-H), whereas the peak at 6·33 (4H, s, β-H) is generated by the superimposition of the vinylic protons of both geometrical isomers. This hypothesis is supported by the following n.m.r. literature data on analogous 2,5-dihydrofurans substituted by acetoxy[5,6] and methoxy[6–10] groups: (a) in all cases the ring protons of the two isomers give rise to only two peaks since the $J_{2,3}$ coupling constant is negligibly small; (b) the vinylic protons of the two isomers have practically the same chemical shift; (c) the α-protons of the *cis*-adduct are shifted upfield with respect to the α-protons of the *trans*-isomer.[8,10]

The *cis* : *trans* adduct ratio (*ca.* 3) obtained, in our case, by the integration of peaks at δ 6·96 and 7·10 is also similar to

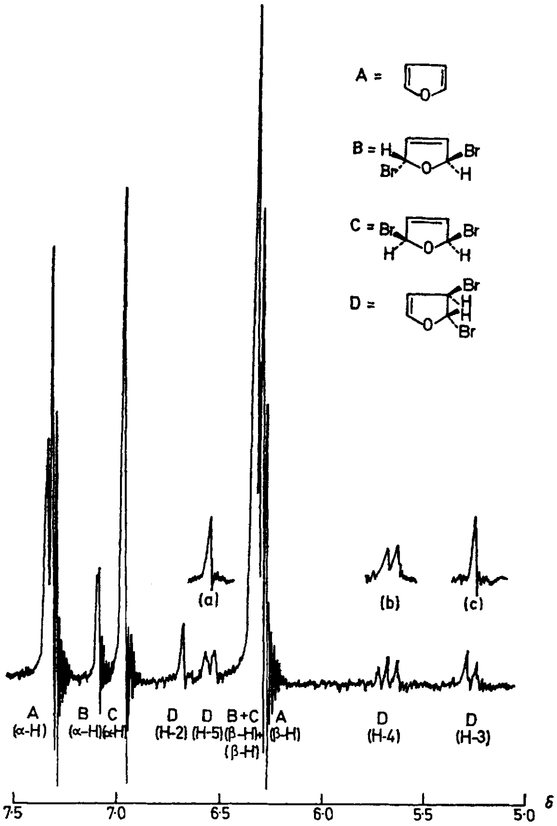

Figure. N.m.r. spectrum of the reaction mixture in the bromination of furan in CS_2 at −50 °C. Peaks (a) and (c) represent protons D(H-5) and D(H-3) respectively, on irradiation of D(H-4); peak (b) represents proton D(H-4) on independent irradiation of D(H-5) or D(H-3).

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that (7 : 3) detected in the methoxy derivatives obtained by methanolic bromination.[8]

In addition to the expected 2,5-adducts we found that 20% of the intermediate material is a third compound, responsible for the pattern at δ 6·69, 6·55, 5·65, and 5·25. Since each peak is given by one proton, this compound is thought to be the *trans*-2,3-dibromo-2,3-dihydrofuran[11] on the basis of the multiplicity of signals, the magnitude of the coupling constants, and decoupling experiments. The peak at δ 6·69 is a singlet given by the 2-proton, which cannot be coupled with the 3-proton because the dihedral angle in the *trans*-configuration is close to 90°. The peak at δ 6·55 is a doublet, due to the 5-proton, with a coupling constant $J_{4,5}$ 2·8 ± 0·2 Hz. The peak at δ 5·25 is also a doublet ($J_{3,4}$ 2·8 ± 0·2 Hz), and is due to the 3-proton. Both these two signals become singlets by irradiating‡ the triplet at δ 5·65, which is therefore given by the 4-proton. On the other hand, irradiating either of the two doublets changes the triplet at δ 5·65 to a doublet. The values of the two coupling constants are responsible for the signal of the 4-proton being a triplet rather than a quartet. $J_{4,5}$ and $J_{3,4}$ values about 2·6—2·8 Hz are typical for 2,3- dihydrofurans.[12]

It is interesting to note that the magnitudes of the upfield shifts of the proton signals with respect to the starting material are very close to those observed for benzofuran, which undergoes a 2,3 addition. The Δδ value for the α-proton is 0·64 p.p.m. for furan and 0·65 p.p.m. for benzofuran, whereas Δδ for the β-proton is 1·06 p.p.m. for the former and 0·96 p.p.m. for the latter.[1]

A further proof of the structure of the adducts, especially the latter, is given by the spectrum of the reaction mixture when 2,5-dideuteriofuran is used as starting material; no peak attributed to α-protons is present, and the triplet at δ 5·65 becomes a doublet.

This work represents the first experimental evidence of the existence of dibromodihydrofurans, but we cannot yet say whether the reaction proceeds *via* an addition-elimination mechanism or the adducts are just formed in a side-equilibrium, since in both cases the same product, 2-bromofuran, is expected.

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‡ The decoupling experiments were carried out on a Varian HA-100.

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