

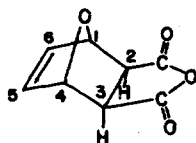
AN NMR STUDY OF THE REACTION OF FURAN WITH
MALEIC ANHYDRIDE AND MALEIC ACID

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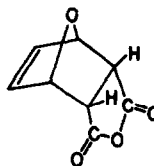
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The Diels-Alder adduct of furan with maleic anhydride has been shown¹ to have the exo configuration (I). The endo isomer (II) has not been reported, but endo-exo pairs of isomers are known from the reactions of furan with maleimide² and maleic acid³. This apparent difference in stereochemistry has led us to investigate the furan-maleic anhydride reaction by proton magnetic resonance.



I



II

- ¹ R.B. Woodward and H. Baer, J. Amer. Chem. Soc. 70, 1161 (1948).
- ² H. Kwart and I. Burchuk, J. Amer. Chem. Soc. 74, 3094 (1952).
- ³ J.A. Berson and R. Swidler, J. Amer. Chem. Soc. 75, 1721 (1953).

The reaction of maleic anhydride (band at 2.91 τ) and furan (bands at 2.51 and 3.58 τ) in acetonitrile solution (solutions in excess furan and in acetone were also studied with similar results) gave rise in the NMR spectrum to new bands at 3.47 (multiplet), 4.57 and 4.66 (overlapping multiplets), 6.12 (1:1:1:1 quartet) and 6.75 τ (singlet). From the spectrum of an authentic sample, the bands at 3.47 (in part)(H5 and H6), 4.66 (H1 and H4) and 6.75 τ (H2 and H3) were identified as those of the exo adduct. The bands at 3.47 (in part), 4.57 and 6.12 τ were assigned to the previously unknown endo adduct. The relative chemical shifts of H2 and H3 in the two isomers are similar to those found in other Diels-Alder adducts⁴. The splittings in the bands of H2 and H3 in the two isomers are as expected from the angular dependence of coupling constants⁵.

Initially, the exo isomer was formed about twice as fast as the endo isomer, but after about a day at room temperature, the endo isomer had almost completely disappeared and only the exo isomer and a little furan and maleic anhydride remained.

Rapid crystallization of the product rich in the endo isomer was achieved by solution at room temperature (or below) in acetone followed by repeated additions of

⁴ R.R. Fraser, Canad. J. Chem. 40, 78 (1962).

⁵ M. Karplus, J. Chem. Phys. 30, 11 (1959); F.A.L. Anet Canad. J. Chem. 39, 2316 (1961).

petroleum ether to give a number of fractions. Recrystallization ultimately gave the almost pure endo adduct as shown by the NMR spectrum. The compound m.p. ca 70° (decomp.) (cf. m.p. of exo adduct, 110° (decomp.)) was characterized by its infrared and NMR spectra.

Although the compound was quite stable in the crystalline state, it was appreciably dissociated in acetone solution into equimolecular amounts of furan and maleic anhydride (no endo adduct formed) after five minutes at room temperature; this decomposition was conveniently followed by NMR. By comparison, the exo adduct, already notorious¹ for its tendency to revert to its components on recrystallization, was only slightly decomposed after a few hours under the same conditions.

Later attempts to isolate the pure endo isomer were thwarted by the tendency of 1:1 complex of the endo and exo isomers to crystallize preferentially.

The reaction of furan and maleic acid in water gave peaks corresponding to the exo adduct (prepared separately by hydration of the pure exo anhydride) and to peaks whose positions and multiplicity showed them to be due to the endo adduct. In this case the reaction was quite slow at room temperature. The endo isomer was formed initially about four times as fast as the exo isomer. After ten days, about equal proportions of the two compounds were present. These results agree with those obtained previously by Berson³.

Thus, the previously observed difference in stereochemical modes of addition of furan with maleic anhydride and maleic acid results mainly from the fact that, under the usual conditions, the former reaction is thermodynamically controlled whilst the later is largely kinetically controlled. As in the reactions of furan with maleimide, the reactions of furan with maleic anhydride and maleic acid are not stereospecific in the kinetically controlled process. Finally, the isomerization of the endo anhydride to the exo anhydride must take place largely by dissociation and recombination, unlike the similar transformation⁶ of the cyclopentadiene-maleic anhydride adduct, but like the isomerization of other Diels-Alder adducts⁷.

⁶ J.A. Berson, R.D. Reynolds and W.M. Jones, J. Amer. Chem. Soc. 78, 6049 (1956).

⁷ J.A. Berson and W.A. Mueller, J. Amer. Chem. Soc. 83, 4940 (1961). J.A. Berson and A. Remanick, J. Amer. Chem. Soc. 83, 4947 (1961).