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PREPARATION AND CHARACTERIZATION OF 2,3-DIHYDRO-2,3 BIS (METHYLENE) FURAN

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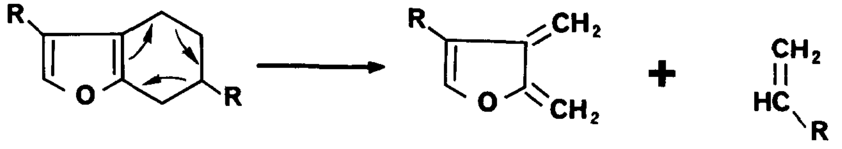
Summary : 2,3-dihydro-2,3 bis (methylene) furan and its 4-methyl derivative have been prepared by flash vacuum thermolysis and characterized by mass spectrometry and chemical trapping.

2,3-dihydro-2,3 bis (methylène) furan (1a), a furanic homolog of the well known o-xylylene [1] is a very unstable species due to the presence of both diene and dienophile moities in the same molecule. (1b) and (1b) have been prepared by a retro Diels Adler reaction of 4,5,6,7-tetrahydro benzofuran (2a) and its dimethylated derivative (2b) :



[I]

2a R=H
2b R=CH_3

1a R=H
1b R=CH_3

This reaction is carried out by flash vacuum thermolysis [2] at temperatures higher than 800°C.

In order to determine optimum conditions for this reaction, the flash thermolyser was coupled to a mass spectrometer [3] in such a way that the mass spectrum (ionization energy 12 eV.) of the pyrolyzate could be recorded at different reactor temperatures. Results for (1a) are summarized in Fig. 1. The optimum temperature for reaction [I] appears to be between 920 and 950°C. At higher temperatures, a secondary reaction [II]

(1a) $\longrightarrow$ cyclopentadiene + CO [II]

becomes increasingly important (cyclopendadiene was identified by the NMR and mass spectra of its adduct with methyl vinyl ketone).

In order to record the (1a) and (1b) NMR spectra, the pyrolysate was trapped in a $CFCl_3$ matrix on a cold finger cooled with liquid nitrogen. However, as the solvent thaws, a white non-soluble solid precipitates (Temperature above -120°C). Use of other trapping solvents such as $CDCl_3$ and CD_3COCD_3 resulted in analogous polymerizations.

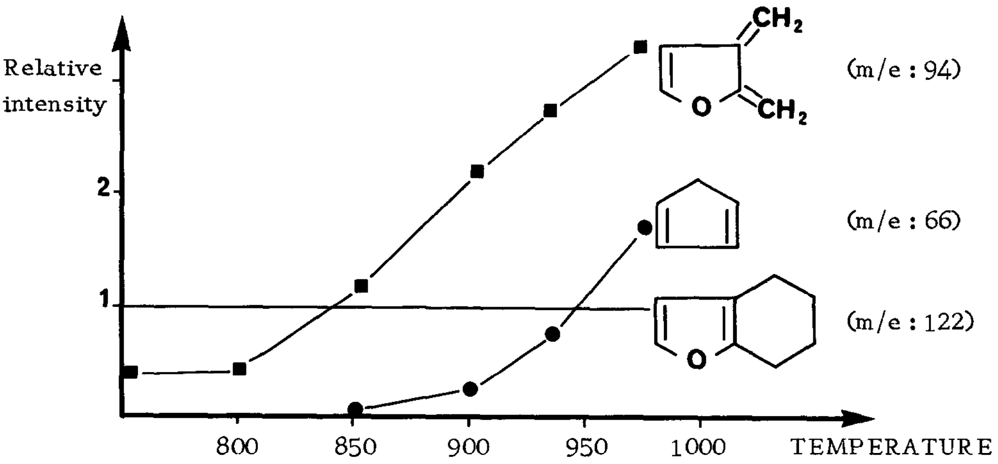
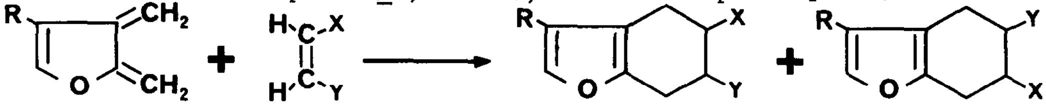


Figure 1 : Intensities of the parent ions of (1a) : m/e 94 and cyclopentadiene : m/e 66 relative to that of the starting materiel (2a) as a function of the reactor temperature.

Characterization of (1a) and (1b) was however achieved by trapping these molecules with various dienophiles (3a, b and c), as shown in equation [III] :



[III]

1a R=H
1b R=CH_3

3a X=H, Y=$COCH_3$
3b X=H, Y=$COOCH_3$
3c X=Y=$COOCH_3$

4a R=X=H, Y=$COCH_3$
4b R=X=H, Y=$COOCH_3$
4c R=CH_3 , X=H, Y=$COCH_3$
4d R=CH_3 , X=H, Y=$COOCH_3$
4e R=CH_3 , X=Y=$COOCH_3$

The adducts (4) were characterized by their NMR and mass spectra.

The yields of formation of (4) from (2) range between 20 and 50%.

When the dienophile is unsymmetrical ($X \neq Y$; 4a, b, c and d) two isomers are obtained as shown in equation [III]. These isomers are not GLC separable. However, when complexed with $Eu(Fod)_3$, the NMR CH_3 signal of the Y group splits into two different signals with an intensity ratio of 1 to 2 if Y=$COOCH_3$ and 1 to 5 if Y=$COCH_3$. In all cases, the predominant isomer is the one with the lowest CH_3 chemical shift. Unfortunately, we have been unable to distinguish between these two isomers.

The (4e) NMR spectrum shows that the cis arrangement of the methyl maleate (3c) is retained in the adduct in accordance with the "cis principle" of the Diels Alder addition[4] .

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