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STUDIES IN CLAISEN REARRANGEMENT - I
2-BUTYN-1,4-DIYL BIS-(ARYL ETHERS)

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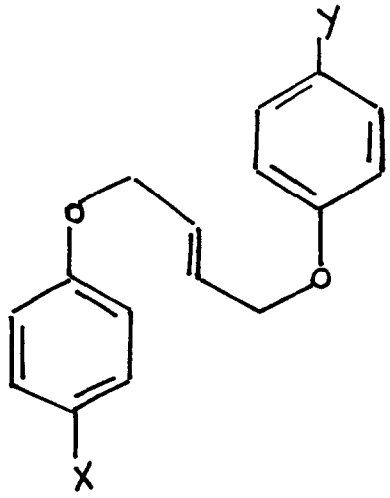
The subtler aspects of the mechanism of the Claisen rearrangement of aryl allyl ethers have been the target of concerted attack in recent times by several groups of investigators (1). We have recently embarked on a programme of work that may shed some light on the nature of the transition state of this well-known rearrangement - through a study of the products from the pyrolysis of dissymmetric 2-buten-1,4-diyl bis-(aryl ethers) of the following type:

X = electron withdrawing
Y = electron releasing



The preliminary step to this objective was the synthesis of the corresponding 2-butyn-1,4-diyl bis-(aryl ethers). The easy availability of the latter compounds from sodium aryloxides and 1,4-dichloro-2-butyne (2) was a tempting invitation to investigate the possibility of " Claisen rearrangement " of these propargyl ethers as well.

A survey of the literature since 1920 reveals several unsuccessful attempts at

the rearrangement of phenyl propargyl ethers (2,3,4,5.) Such failures led uniformly to the apparently reasonable conclusion that the linear triple bonded system was not amenable to a six-centred geometry obtaining in the rearrangement of allyl ethers. However, Prof.Hurd had clearly envisaged the possibility of the formation of ortho allenylphenol or the 2-methylbenzofuran in the rearrangement of phenyl propargyl ethers (4). The failure to isolate any characterisable compound was attributed to the ease of polymerisation of the coumaran or the allenylphenol. Nearly twenty years later, Russel Gaertner (6) showed the reversible equilibrium obtaining between the ortho allenylphenoxide anion and the corresponding anion of the 2-methylbenzofuran. Against this background was begun our investigation.

Refluxing a solution of 1,4-bis-(p-chlorophenoxy)-2-butyne, m.p.87°, in diethylaniline for 10 hours afforded in 40% yield a product melting at 164°. Elementary analysis indicated it to be isomeric with the starting substance. The UV absorption in EtOH was closely similar to that of the starting material suggesting no extra conjugation had been created. The compound was insoluble even in Claisen alkali. It was saturated to bromine, and permanganate. It survived an ozonolysis and resisted hydrogenation as well as dehydrogenation. It was unaffected by selenium dioxide in acetic acid. The infrared spectrum showed bands in the 11 micron region, not present in the starting material, indicating the presence of 1,2,4-trisubstituted benzene rings in the rearranged compound. The N.M.R. spectrum* of the compound revealed twelve protons characterisable as follows: six aromatic protons at 7.11 p.p.m. ; three aliphatic protons as a singlet at 1.74 p.p.m. ; one coupled benzylic proton at 4.22 p.p.m. ; two coupled methylene protons at 3.68 p.p.m.

Among the different structures possible for the rearranged product, the more rational and mechanistically feasible ones are outlined in the accompanying chart (Chart I.). The mode of formation of these structures from the substituted ortho allenylphenol can be easily visulaised. All the four formulations satisfy the chemical reactions of a saturated ring system incorporating unconjugated benzene rings. However, formulae II and III can be

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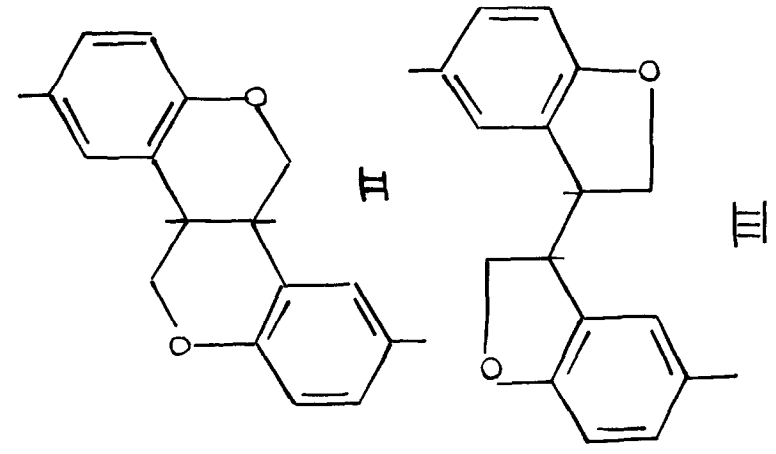
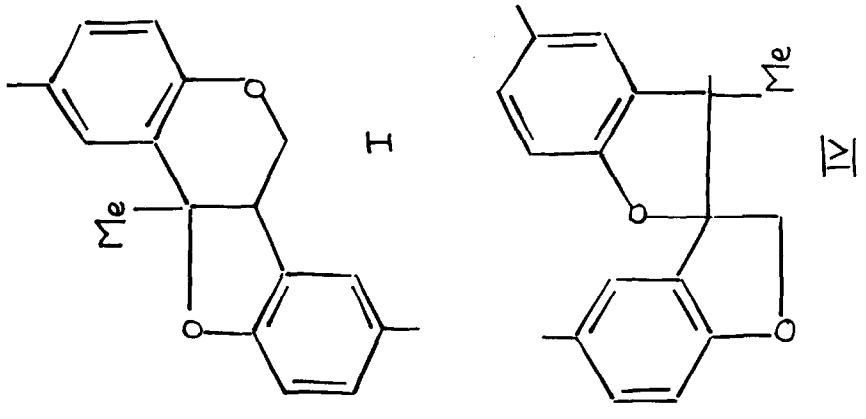
*N.M.R. measurements were made in a Varian A-60 instrument using $CDCl_3$ solutions and tetramethylsilane as internal reference. All compounds gave satisfactory elemental analyses.



II III



I IV

readily ruled out from the N.M.R. spectrum because they carry no methyl group. Structure IV has a methyl group on a benzylic carbon carrying a hydrogen whereas the N.M.R. spectrum clearly shows an unsplit singlet for the aliphatic methyl group. Therefore structure I alone is consistent with all the chemical reactions, the ultraviolet, infrared and N.M.R. spectral data.

The mechanistic pathway presented in Chart II is unexceptional in the light of the work of Gaertner (6). Besides such internal addition of a phenol to an ortho allylic double bond yielding a coumaran derivative is a commonly encountered side-reaction in the Claisen rearrangement of aryl allyl ethers (7). In the present study, the intermediate compound viz., 2-methyl-3-p-chlorophenoxymethyl benzofuran, itself being another allyl ether undergoes a Claisen rearrangement followed by internal addition to yield the pyran derivative (8).

To our knowledge, this is the first successful report* of the rearrangement of an ARYL PROPARGYL ETHER to a well-characterised coumaran derivative.

We are currently investigating the rearrangement of related but dissymmetric 2-butyn-1,4-diyl bis-(aryl ethers). Work is also in progress on the corresponding butenyl ethers.

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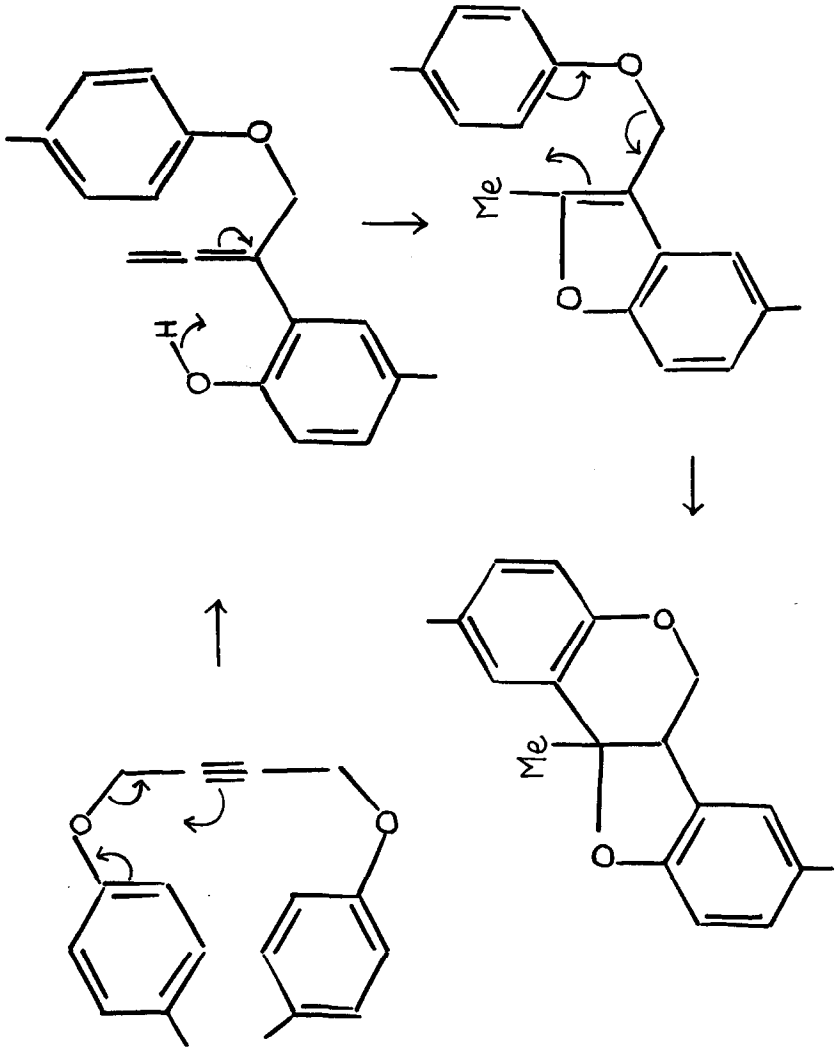
* While the present study had nearly been completed, a publication from Japan (9) detailed the rearrangement of 2-naphthyl propargyl ether under similar conditions to the corresponding PYRAN derivative. Our study is unique in affording a benzofurano-benzopyran system from an acetylenic diether.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