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The Pyrolysis of Pentafluorophenyl Allyl Ether : The Formation of a Stable Cyclohexa-2,5-dienone

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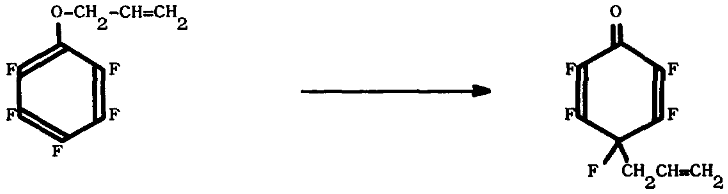
The thermal rearrangement of phenyl allyl ethers to isomeric 2-allyl phenols (the Claisen Rearrangement) is known to proceed via the intermediacy of cyclohexadienones.[1] When the 2,6-positions are substituted, 4-allyl phenols are formed.[2] Normally, the dienone intermediates rapidly tautomerise to phenolic products, though in one case,[3] 1,1-diallyl-2-naphthalenone has been isolated in 55% yield from the attempted Claisen Rearrangement of 1-allyl-2-allyloxynaphthalene.

The pyrolysis of pentafluorophenyl allyl ether (I) in the vapour phase at 365° has now been shown to give as the major product the stable 4-allyl 2,3,4,5,6-pentafluoro-2,5-cyclohexadienone (II) in 32% yield:



(I) (II)

Treatment of pentafluorophenol[4] with excess allyl bromide in dry acetone in the presence of anhydrous potassium carbonate at reflux temperature for 22 hr. gave pentafluorophenyl allyl ether (I) b.p. 49°/8 mm. (88% yield). The ether was distilled at 0·05 mm. through a 6" silica tube packed with silica wool at 365°, over a period of 15 minutes, and the product re-cycled through the pyrolysis tube a further five times under identical conditions. Vapour phase chromatographic analysis of the product on a di-n-decylphthalate column at 125° showed the presence of one major component accompanied by unchanged starting material, pentafluorophenol and three unidentified minor components. The major component, the cyclohexa-2,5-dienone (II), m.p. 27·5-29·0°, was separated from the mixture by chromatography on Silica CC-7 (100-200 mesh) using carbon tetrachloride as solvent. The structure of (II) was deduced principally from its ^{19}F n.m.r. spectrum in CCl_4, which showed three multiplets with intensities in the ratio 2:2:1 due to fluorine atoms centred at 154•6 p.p.m. (a singlet, due to magnetically equivalent fluorine atoms at C-2 and C-6), 136•8 p.p.m. [a doublet (J_{F-F} = 31 cps) due to magnetically equivalent fluorine atoms at C-3 and C-5], and at 160•1 p.p.m. [a triplet of triplets (J_{F-F} = 31 cps, J_{H-F} = 8 cps) due to one fluorine atom at C-4], upfield from $CFCl_3$ as external reference. The dienone structure of II was shown from its ultra-violet spectrum [$\lambda_{max.}$ 225 mµ (ε = 12,900); $\lambda_{max.}$ 271•5 mµ (ε = 860) in cyclohexane].

Russian workers[5] have reported the preparation of 4-nitro-2,3,4,5,6-pentafluorocyclohexa-2,5-dienone by the reaction of nitric acid on pentafluorophenol, and have studied some of its reactions.[6] The present work adds a new synthetic route to these highly fluorinated cyclohexa-2,5-dienones.

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