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FURANODECALIN SYNTHESIS USING INTRAMOLECULAR DIELS-ALDER REACTIONS OF VINYLFURANS

By John A Cooper, Philip Cornwall, Colin P. Dell,
and David W. Knight,*

Chemistry Department, University Park,
Nottingham, NG7 2RD.

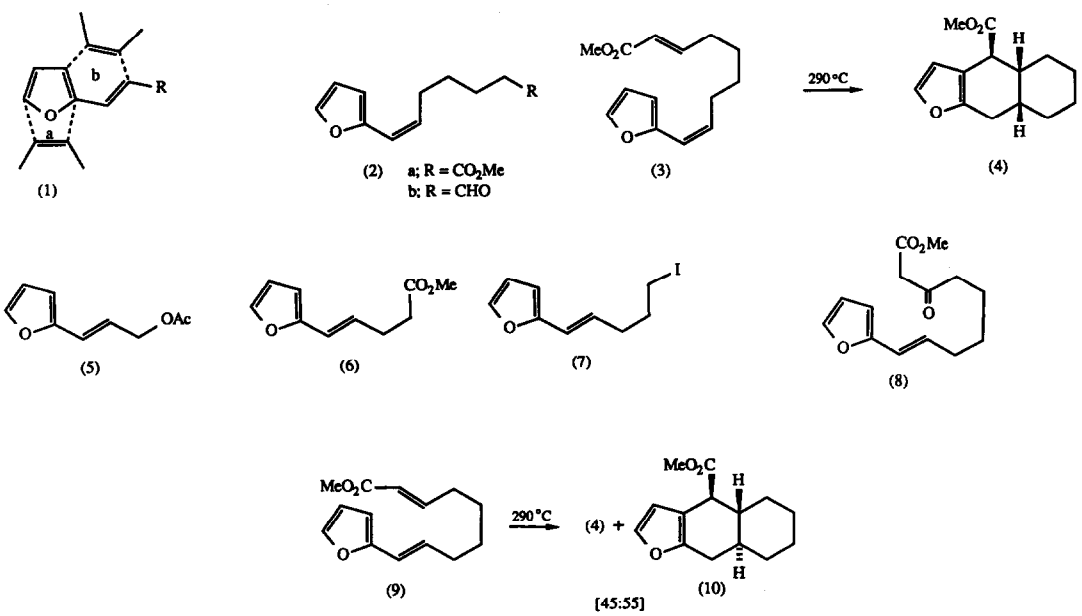
Summary:- Intramolecular Diels-Alder cyclisations of the 2-vinylfurans (3), (9), (11) and (16) occur smoothly at 280-290°C to give the corresponding furanodecalins in 63-97% yields; the 3-substituted furans (18) and (20) behave similarly and in both series, cyclisations of the cis-isomers [i.e. (3) and (18)] are stereospecific, giving only cis-fused furanodecalins [(4) and (19)].

A vinylfuran function (1) can behave as a Diels-Alder diene in two ways, either by dienophile addition across the furan ring (path a) or by addition across the diene unit which includes the vinyl substituent (path b). Numerous examples of path a have been documented; indeed one of the first examples of the Diels-Alder reaction to be recognised was that between maleic anhydride and furan via this pathway.[1] More recently, intramolecular versions[2] of cycloadditions to furans by path a have been extensively studied.[2,3] By contrast, cycloadditions via path b are much less well known; intermolecular additions of dimethyl acetylenedicarboxylate and maleate to simple vinylfurans (1) have been effected in poor to moderate yields using high pressure.[4] Intramolecular versions are even rarer having only been used to prepare a few [5.6.5] ring systems with fumaryl[5] or acetylene-based[6] dienophiles, while two examples using allenecarboxylates provide [5.6.6] benzofuranolactones in rather poor yields.[7] Herein we report that furanodecalins can be readily obtained in good to excellent yields via path b (1) using simple unsaturated esters as dienophiles.

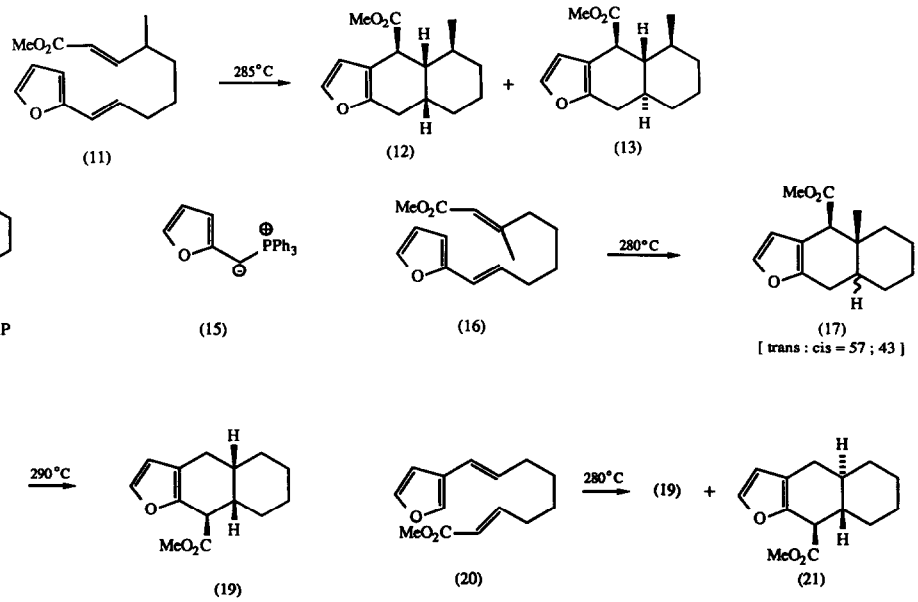
The (2E,8Z)-nonadienoate (3) was prepared from 2-furaldehyde by sequential Wittig condensation with 5-carboxypentyltriphenylphosphonium bromide (NaH; DMSO) and esterification (CH_2N_2), to give the (Z)-heptenoate (2a) in 65% yield, followed by conversion to the corresponding aldehyde (2b) [$LiAlH_4$-Et_2O; PCC] and a second Wittig condensation using Ph_3PCHCO_2Me. [ca. 70% from (2a)]. Compound (3) was unaffected by thermolysis [C_6H_6-sealed tube] either at up to 220°C, or under aqueous conditions.[8] Remarkably however, on heating to 290°C [toluene or n-heptane] ester (3) was converted into the furanodecalin (4) in essentially quantitative yield. The expected cis disposition of the ester and

adjacent ring junction proton in product (4) was consistent with the presence of a resonance at δ 3.41 (br. d, J 3.8 Hz) assigned to the proton α- to the ester. The cis-ring fusion was indicated by the relative narrowness of the methylene envelope and confirmed by the ^{13}C spectrum.[9] The exclusive formation of the cis-decalin (4) is to be expected as all known examples[2] of intramolecular Diels-Alder reactions involving cis-dienes proceed via an anti transition state, in this case following the Alder endo rule. Cyclisations of cis-dienes are often low-yielding due to competing [1.5]-hydride shifts[2,10] which presumably do not interfere, because the furan aromaticity would be lost during such a process and only regained by reversal of the shift.

A different route was used to obtain the (2E,8E)-nonadienoate (9). Allylic acetate (5)[11] was homologated to the ester (6) using methyl phenylsulphonylacetate [NaH; $Pd(PPh_3)_4$][12] followed by desulphurisation; standard transformations [(i) $LiAlH_4$, Et_2O; (ii) TsCl, py; (iii) NaI, $(CH_3)_2CO$] then lead to the iodide (7). [48% from acetate (5)]. Alkylation of the dianion of methyl acetoacetate[13] by iodide (7) provided keto-ester (8) (65%) which was converted into the dienoate (9) by reduction [$NaBH_4$], mesylation and elimination using DBU, (80%). Thermolysis of ester (9) at 290°C as described above gave a 90% isolated yield of the cis- furanodecalin (4) and the trans-isomer (10) in a ratio of 45:55. The trans-decalin was characterised by a resonance at δ 3.22 (ddd, J 9.9, 3.0, and 1.6 Hz, C<u>H</u>CO_2Me),[14] a much broader and more detailed methylene envelope and particularly by the ^{13}C data.[9] Such a lack of stereoselectivity is common in cyclisations of related trans-dienes, as is a preference for the formation of the trans-decalin via an anti (endo)-transition state.[2]



The methyl homologue (11) was also prepared from iodide (7) but using the dianion of methyl 3-oxopentanoate, and underwent cyclisation [C_6H_6, 285°C, 14 h] to give, in 68% yield, a mixture of four isomers in a ratio of ca. 20:14:4:3 according to proton n.m.r. Separation using hplc (5μ porasil; ether-petrol 1:10) gave pure trans-decalin (13) and a mixture of the remaining three products, the major of which was the cis-decalin (12), both compounds being identified by comparative ^1H and ^{13}C n.m.r. data, as described above. The two minor products are thus the corresponding decalins having an anti-methyl group formed via a less favoured transition state in which the methyl group adopts a pseudo-axial orientation.[2] Again, a slight preference for the trans-isomer is evident. The isomeric methyl homologue (16) was obtained (60%) from ester (14a)[15] by conversion to the aldehyde (14b) [p-TSA-MeOH then PCC] and condensation with phosphorane (15).[16] Thermolysis in toluene at 280°C for 16h gave, in 63% yield, a trans-cis mixture (17) (57:43) of furanodecalins, separable by chromatography using silica gel (10% ether-petrol), and identified by ^1H and ^{13}C n.m.r. data.[9] Attempts to obtain a different stereoselectivity by using the (2Z,8E)-isomer of (3) failed as upon thermolysis (290°C) the substrate underwent partial decomposition and extensive isomerization to the (2E,8E)-isomer (9), prior to cyclisation.



This methodology is equally suited to 3-vinylfurans. Thus, thermoloysis [toluene, 290°C, 16h] of the (2E,8Z) ester (18), obtained from 3-furaldehyde [cf.(3)] gave, in 97% yield, only the cis-furanodecalin (19) whereas the corresponding all-trans isomer (20) afforded a mixture of decalins (19) and (21) [40:60] in 83% yield, after heating to 280°C in heptane for 16h. These observations closely parallel those made with the 2-furyl series.

In conclusion, the good to excellent yields obtained from these cyclisations together with the wide variety of possible synthetic approaches to the precursors should make this a versatile method for preparing furanodecalins, the major limitation being the requirement for good thermal stability in any additional functional groups which may be present.

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References and Footnotes

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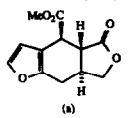
14. The corresponding resonance in compound (a) is closely similar: δ 3.65 (ddd, J 10.8, 3.0, and 1.6 Hz).[5]



(a)

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