

The Reactions of Furfuryl Alcohols with Maleic Anhydride

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The reactions of furfuryl alcohols (1a) and (1b) with maleic anhydride were investigated and, for the first time, conditions defined for the production of intramolecular Diels–Alder adducts. Under basic conditions the adducts (3a, b) yield phthalides in high yield. Furfuryl alcohols (1c) and (8a) afford normal intermolecular Diels–Alder adducts with maleic anhydride.

Intramolecular Diels–Alder (IMDA) reactions of furans, thiophenes, and pyrroles offer considerable scope for the synthesis of heterocycles and unusually substituted benzenoids.^{1–3} A special case of an IMDA reaction involving a furan nucleus was reported for furanophane⁴ and was utilised for the synthesis of the *cis*-indanyl dianion.⁵ A striking and more general type of IMDA reaction involving furans is that of *N*-aryl-*N*-furfurylallylamines,⁶ their salts, and the corresponding amides.⁷ Despite having a non-activated alkene group, the amines undergo spontaneous cyclisation by an IMDA reaction and this has recently been used for a chiral synthesis.⁸ Attempts to generalise the reaction have met with limited success¹ and, in particular, linking the diene and electrophile by an ester grouping led to substrates which did not undergo IMDA reactions, a result attributed to conformational effects.¹ In our hands linkage by an ether group was also ineffective.⁹

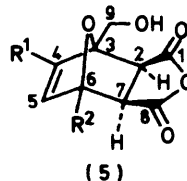
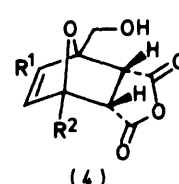
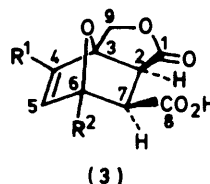
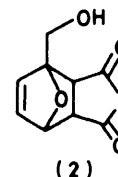
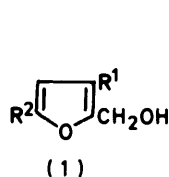
We decided to study the reactions of the furfuryl alcohols (1a–c) and (8a) with maleic anhydride in the hope that the intermediate esters would be formed competitively with the normal Diels–Alder adducts and that the dienophilic double bonds of the esters would be sufficiently activated to initiate IMDA reactions. While our work was in progress the reactions of maleic anhydride in diethyl ether or benzene with (1a) and (1c) were reported to yield the IMDA adducts (3a) and (3c).¹⁰ No spectroscopic data for the adducts were given, but after hydrogenation they were converted electrochemically into 2-oxabicyclo[2.2.1]heptane-7-*syn*-carboxylic acids,¹¹ a result taken as proof of the assigned structures. However, the physical characteristics reported for these adducts led us to suspect that they were simply the normal intermolecular adducts (5a) and (5c). In this paper we report our own work in this area, which is part of a broader investigation, and describe for the first time (see ref. 12 for preliminary report) the preparation of true IMDA adducts from this reaction.

Results and Discussion

It is known that the Diels–Alder adducts obtained from furan derivatives are thermally labile and readily revert to the starting materials.¹³ We therefore carried out all our reactions at room temperature (*ca.* 25 °C).

Furfuryl alcohol (1a) is reported¹⁴ to react with maleic anhydride to yield an unstable adduct, m.p. 82–83 °C, reported as having structure (2) on the basis of the formation of a monoacetate. We reacted equimolar proportions of the furan (1a) and maleic anhydride in diethyl ether, acetone, and ethyl acetate and obtained only the adduct (5a), fully characterised spectroscopically (see Experimental section). In particular it showed the expected anhydride i.r. absorptions at 1 870 and 1 790 cm⁻¹. Kawanisi and his co-workers¹⁰ obtained a product, m.p. 82–83 °C, which they claimed was the IMDA adduct (3a).

In the solid state, compound (5a) is stable for *ca.* 48 h at



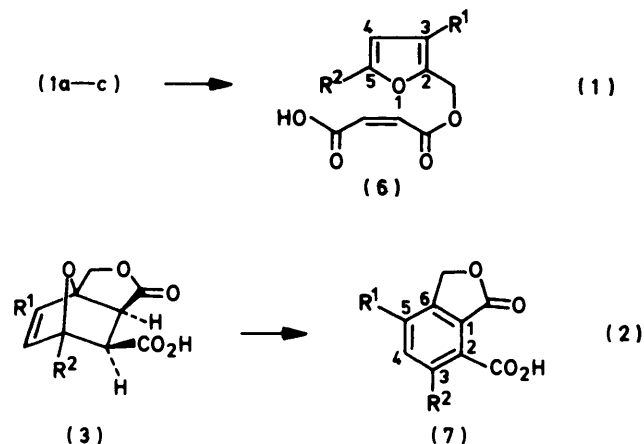
- a ; R¹ = R² = H
 b ; R¹ = Me, R² = H
 c ; R¹ = H, R² = Me

25 °C, but in solution it rapidly reverts to its components which then undergo the extensive polymerisation always observed if the reaction mixture is warmed.

A mixture of maleic anhydride and compound (1a) in chloroform at 25 °C for seven days gave a 60 : 40 mixture † of compound (5a) and the long sought IMDA adduct (3a); the latter compound had m.p. 123–124 °C (decomp.). The two adducts are readily distinguishable as (5a) has the typical anhydride bands in the i.r. previously mentioned, whilst (3a) shows lactone and acid absorptions at 1 785 and 1 710 cm⁻¹. Compound (5a) is acetone-soluble and readily removed from the mixture to leave pure adduct (3a). Alternatively, moisture catalyses the conversion of (5a) into (3a) so allowing us to formulate the intermolecular adduct as the *exo*-adduct (5a) as well as to obtain pure (3a) in 75% yield (see Experimental section). The ester (6a) presumed to be an intermediate in the formation of adduct (3a), was prepared as in equation (1) and cyclised to give (3a) in *ca.* 40% yield in any solvent used. Thus the role of the chloroform in the reaction between furfuryl alcohol and maleic anhydride is to favour esterification rather than intermolecular Diels–Alder reaction.

We next turned our attention to the aromatisation of the adduct (3a) [equation (2)] but were unable to produce the phthalide (7a) under acidic conditions^{6,15} (H₃PO₄, HBr, H₂SO₄, CH₃CO₂H, AlCl₃, AlCl₃, F₃B–OEt₂) despite extensive

† Calculated by integration of the bridgehead hydrogen signals in the ¹H n.m.r. spectrum.

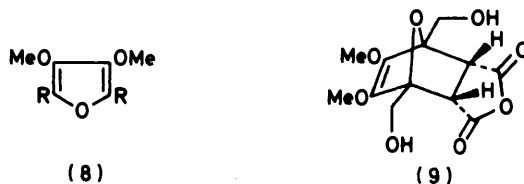


experimentation. However, with Bu^iLi or 3M NaOMe in methanol, compound (3a) was converted into phthalide 7-carboxylic acid (7a) in 90% yield. Compound (7a) had previously¹⁶ been prepared in 15–30% yield from hemimellitic acid derivatives. The normal Diels–Alder adduct (5a) also gives the phthalide (7a) on treatment with 3M NaOMe , but in 45% yield only.

Encouraged by these results we studied the reaction of the alcohol (1b) with maleic anhydride, and found that in chloroform we could obtain a 70% yield of the IMDA adduct (3b), m.p. 123–125 °C (decomp.). By monitoring the reaction by ^1H n.m.r. spectroscopy it could be seen that the initial product was the *endo*-adduct (4b), δ 1.8 (d, CH_3).^{*} After 30 min the concentrations of (4b) and the *exo*-adduct (5b), δ 1.9 (d, CH_3) and 5.3 (d, 6-H), were the same and after 8 h the signals due to (4b) could no longer be discerned. Instead the IMDA adduct (3b), δ 4.98 (br s, 6-H), was formed and steadily increased in concentration until after 36 h it precipitated from solution.

Removal of solvent from an ethereal reaction mixture of the furan (1b) with maleic anhydride gave a gum that was essentially the adduct (5b). The ester (6b) was prepared as in equation (1) and readily cyclised to give the adduct (3b) in 30% yield. As before, treatment of (3b) with 3M NaOMe afforded the corresponding phthalide, (7b), in 90% yield.

Ester (6c) proved to be very labile, though isolable. In line with this, when the alcohol (1c) reacted with maleic anhydride in chloroform only polymeric products resulted. The reaction showed initial formation of the *endo*-adduct (4c), δ 1.7 (s, 6-Me), but after 15 min the *exo*-adduct (5c), δ 1.65 (s, 6-Me), was also present in equal concentration to (4c); the latter adduct had virtually disappeared after 6 h. Pure *exo*-adduct (5c) decomposed to give the addends which then polymerised. In diethyl ether, however, the unstable *endo*-adduct (4c), m.p. 83–84 °C, was isolable by filtration, and from the mother liquors the *exo*-adduct (5c), m.p. 88–89 °C, could be isolated, but no IMDA product (3c) was obtained. In the i.r. region both adduct (4c) and (5c) exhibit anhydride absorption as well as that due to a free hydroxy group, whilst in the ^1H n.m.r. spectra the carbonyl methylene hydrogen signal is at δ 4.05 and 4.1, respectively, in line with the spectra of other intermolecular adducts and quite different in shape and position from the methylene protons of the lactone rings of compounds (3a) and (3b) which appear as well defined pairs of doublets at δ 4.35–4.9. The structures assigned to compounds (4c) and (5c) are therefore firm and it would appear that the compound previously claimed as (3c)¹⁰ is in fact most



a ; R = CH_2OH
b ; R = CO_2Me

likely the *exo*-adduct (5c). Thus the reaction of compound (1c) with maleic anhydride follows the typical kinetic and thermodynamic pattern encountered in Diels–Alder reactions.¹⁷ Neither (4c) nor (5c) were aromatised with 3M NaOMe .

We finally studied the reaction of maleic anhydride with the alcohol (8a), which was prepared by reduction of the diester (8b)¹⁸ with lithium aluminium hydride.¹⁹ In both diethyl ether and chloroform there was a very ready reaction to give an anhydride adduct which did not undergo lactonisation and to which therefore we tentatively ascribe the *endo*-structure (9).

Experimental

M.p.s were determined on a Gallenkamp m.p. apparatus using capillary tubes. I.r. spectra were recorded on a Unicam SP1050 i.r. spectrometer. ^1H N.m.r. spectra were recorded on a Varian HA-100 spectrometer. Furfuryl alcohol (1a) (Hopkin and Williams) was purified by distillation. 3-Methylfurfuryl alcohol (1b), b.p. 90–92 °C at 12 mmHg, was prepared by the LiAlH_4 reduction of methyl 3-methyl-2-furoate.²⁰ 5-Methylfurfuryl alcohol (1c), b.p. 81–82 °C at 15 mmHg, was prepared by the LiAlH_4 reduction of 5-methyl-2-furaldehyde (Aldrich). The alcohol (8a) was prepared by the LiAlH_4 reduction of the diester (8b).¹⁸ Maleic anhydride (Fluka) was used as received. ^1H N.m.r. data for the adducts are given in the Table.

Reaction of the Alcohol (1a) with Maleic Anhydride in Diethyl Ether.—Maleic anhydride (2.0 g, 20 mmol) was dissolved in dry diethyl ether (10 ml) and to the stirred solution was added furfuryl alcohol (1a) (2.0 g, 20 mmol). The clear yellow solution was stirred for 24 h at 25 °C, then was cooled to 0 °C and the deposited solid (5a) was collected by filtration (3.2 g), m.p. 82–83 °C (lit.,¹⁴ 82 °C); ν_{max} . (Nujol) 3 400, 3 100, 1 870, and 1 790 cm^{-1} ; n.m.r. see Table.

Reaction of the Alcohol (1a) with Maleic Anhydride in CHCl_3 .—Maleic anhydride (2.0 g, 20 mmol) was dissolved in CHCl_3 (10 ml) and furfuryl alcohol (1a) (2.0 g, 20 mmol) was then added at 25 °C. The pale yellow solution was left for 7 d at 25 °C during which time it turned dark. The reaction mixture was filtered, washed with cold acetone (5 ml), and dried to give a 60 : 40 mixture of adducts (5a) and (3a) (3.5 g). The entire mixture was well powdered and moistened with water (1.5 ml). After 24 h at 25 °C the solid was filtered off and washed with cold acetone to give the adduct (3a) (3.0 g). Recrystallisation from acetone gave an analytical sample, m.p. 123–124 °C (decomp.) (Found: C, 54.95; H, 4.15. $\text{C}_9\text{H}_8\text{O}_5$ requires C, 55.1; H, 4.1%); ν_{max} . (KBr) 1 785 and 1 710 cm^{-1} ; n.m.r. see Table.

The *methyl ester*, m.p. 109–110 °C, was prepared by reaction of the adduct (3a) with dimethyl sulphate and potassium carbonate in acetone (Found: C, 57.1; H, 4.7. $\text{C}_{10}\text{H}_{10}\text{O}_5$ requires C, 57.1; H, 4.8%); ν_{max} . (Nujol) 1 790 and 1 730 cm^{-1} ; n.m.r. see Table.

* The ^1H n.m.r. positional assignments refer to the arbitrary numbering schemes shown on formulae (3), (5), (6), and (7).

Table. ¹H N.m.r. spectra ^a of Diels-Alder adducts of furfuryl alcohols

Proton	(3a) ^c	(3a-Methyl ester) ^b	(5a) ^b	(3b) ^b	(5b) ^c	(4c) ^b	(5c) ^b	(9) ^d
2	3.12 (d, J 9)	2.99 (d, J 10)	3.45 (d, J 13)	3.09 (d, J 13)	3.35 (d, J 11)	3.55 (d, J 11)*	3.40 (d, J 9)†	} 3.76 (s)
7	2.80 (d, J 9)	2.83 (d, J 10)	2.74 (d, J 13)	2.74 (d, J 13)	3.1 (d, J 11)	3.9*	3.58 (d, J 9)†	
4	6.68 (d, J 6)	6.6 (d, J 6)	} 6.5 (s)	} 6.05 (m)	} 6.1 (m)	} 6.4 (m)	6.45 (d, J 10)‡	} —
5	6.56 (dd, J, 6, J ₂ , 3)	6.5 (dd, J, 6, J ₂ , 3)					6.1 (m)	
6	5.16 (d, J 3)	5.22 (d, J 3)	5.23 (brs)	4.98 (brs)	5.3 (brs)	—	—	} 3.82 (d, J 3)
9	{ 4.56 (d, J 11) 4.90 (d, J 11)	{ 4.66 (d, J 12) 4.84 (d, J 12)	{ 3.84 (d, J 17) 4.17 (d, J 17)	{ 4.35 (d, J 17) 4.81 (d, J 17) 1.9 (d, J 3)	4.1 (brs)	{ 4.05 (brs) 1.7 (brs)	4.1	
CMe	—	—	—	—	—	—	1.65 (s)	3.64 (s)
OMe	—	3.76 (s)	—	—	—	—	—	4.8—5.3
OH	—	—	—	—	—	—	—	—

^a Signal values in δ . *J*-values in Hz. Arbitrary numbering schemes used [see structures (3), (5), (6), and (7)]. ^b Run in CDCl₃. ^c Run in (CD₃)₂CO. ^d Run in (CD₃)₂SO. ^e *ca.* 6.3

* , † , ‡ Assignments within each pair of signals may be interchanged.

Reaction of the Alcohol (1b) with Maleic Anhydride.—(a) *In diethyl ether.* Maleic anhydride (0.98 g, 10 mmol) was dissolved in dry diethyl ether (5 ml) and the furfuryl alcohol (1b) (1.1 g, 10 mmol) was added to the stirred solution at 25 °C. After 24 h a viscous oil had separated from the solution. The solvent was evaporated under reduced pressure and the ¹H n.m.r. spectrum of the residue indicated that it was essentially *exo*-adduct (5b); n.m.r. see Table.

(b) *In CHCl₃.* Maleic anhydride (0.98 g, 10 mmol) was dissolved in CHCl₃ (5 ml) and the furfuryl alcohol (1b) (1.1 g, 10 mmol) was added to the stirred solution. The pale yellow solution was left at 25 °C for 36 h. The deposited *adduct* (3b) was filtered off, washed with cold CHCl₃, and dried (1.5 g). Recrystallisation from acetone afforded an analytical sample, m.p. 123–125 °C (decomp.) (Found: C, 57.0; H, 5.05. C₁₀H₁₀O₅ requires C, 57.1; H, 4.8%); ν_{\max} (KBr) 1 790 and 1 750 cm⁻¹; n.m.r. see Table.

Reaction of the Alcohol (1c) with Maleic Anhydride in Diethyl Ether.—Maleic anhydride (2.0 g, 20 mmol) was dissolved in diethyl ether (10 ml) and the furfuryl alcohol (1c) (2.2 g, 20 mmol) was added to the stirred solution at 25 °C. After 3 h the *adduct* (4c) had precipitated from solution. The solid was filtered off, washed with cold diethyl ether, and dried (2.2 g), m.p. 83–84 °C; ν_{\max} (Nujol) 3 440, 1 860, and 1 780 cm⁻¹; n.m.r. see Table.

On cooling the filtrate a mixture of *adducts* (4c) and (5c) was obtained (1.7 g). The mixture was dissolved in acetone (8 ml) and left at 25 °C for 12 h to decompose the *endo*-*adduct* (4c). The acetone was evaporated at 12 mmHg and the residue was dissolved in a minimum amount of diethyl ether (5 ml) and the solution was cooled to -15 °C. The *exo*-*adduct* (5c) crystallised out and was collected by filtration (1.0 g), m.p. 88–89 °C (Found: C, 56.7; H, 4.9. C₁₀H₁₀O₅ requires C, 57.1; H, 4.8%); ν_{\max} (KBr) 3 550, 3 440, 3 380, 1 860, and 1 780 cm⁻¹; n.m.r. see Table.

Reaction of the Alcohol (8a) with Maleic Anhydride in Diethyl Ether.—A solution of maleic anhydride (0.5 g, 5 mmol) in diethyl ether (5 ml) was added to a solution of the alcohol (8a) (0.94 g, 5 mmol) in diethyl ether (5 ml). The *adduct* (9) precipitated from the solution instantaneously and was filtered off, washed with diethyl ether (3 ml) and dried (1.1 g), m.p. 114–116 °C (decomp.) (Found: C, 50.05; H, 5.3. C₁₂H₁₄O₈ requires C, 50.3; H, 4.9%); ν_{\max} (KBr) 3 400, 1 870, and 1 790 cm⁻¹; n.m.r. see Table.

Preparation of the Intermediate Esters (6a–c).—(a) *Ester (6a).* To a stirred solution of furfuryl alcohol (1a) (2.0 g, 20 mmol) in diethyl ether (20 ml) cooled to 0 °C was added BuⁿLi (1.5M; 20 mmol). An exothermic reaction set in and a solid precipitated from the solution. The slurry was stirred for 1 h and a solution of maleic anhydride (2.0 g, 20 mmol) in diethyl ether (20 ml) was then added. The reaction mixture was allowed to warm to 25 °C and was then stirred at 25 °C for 12 h, quenched with water (50 ml), and extracted with diethyl ether. The organic phase was discarded, and the aqueous layer was cooled to 0 °C, acidified with 1.0M HCl, and rapidly extracted with diethyl ether. The extract was washed with water and dried. The ether was evaporated off under reduced pressure to give the ester (6a) as a viscous oil (2.4 g), δ (CDCl₃) 5.23 (s, CH₂O), 6.3 and 6.35 (2 × m, 3- and 4-H and CH=CH), 7.4 (m, 5-H), and 8.65 (OH).

A solution of the ester (6a) (2.0 g) in CHCl₃ (10 ml) was kept at 25 °C for 7 d to give, on work-up, the *adduct* (3a) (0.8 g), m.p. 123–124 °C (decomp.). Similar results were obtained using either acetone or diethyl ether as the solvent.

(b) *Ester (6b).* In a similar manner, the alcohol (1b) (2.2 g,

20 mmol) gave the ester (6b) (2.6 g), δ (CDCl₃) 2.1 (s, CMe), 5.15 (s, CH₂O), 6.2 (br, d, 4-H), 6.3 (m, CH=CH), and 7.22 (m, 5-H).

The ester (6b) is unstable and tended to polymerise when stored neat. Alternatively, extraction of the ester from the acidified aqueous layer with CHCl₃ (15 ml), drying of the CHCl₃ layer, and storage at 25 °C for 48 h afforded adduct (3b) (0.8 g), m.p. 123–125 °C.

(c) *Ester* (6c). Following the general method, the furfuryl alcohol (1c) (2.2 g, 20 mmol) gave the ester (6c) (1.5 g), δ (CDCl₃) 2.2 (s, Me), 5.15 (s, CH₂O), 5.9 (d, *J* 3 Hz, 3-H), 6.2 (s, CH=CH), and 6.25 (d, *J* 3 Hz, 4-H).

The ester (6c) was very labile and polymerised readily. Extraction of the ester with CHCl₃ did not prevent its decomposition.

Conversion of the IMDA Adducts into the Corresponding Phthalides.—(a) *With NaOMe.*—The procedure for the conversion of the adduct (3b) into compound (7b) is typical. The IMDA adduct (3b) (1.1 g, 5 mmol) was added at 25 °C to a stirred 3.0M solution of NaOMe in MeOH (5 ml). An exothermic reaction set in and the solution turned deep orange. The solution was stirred for a further 12 h at 25 °C. The excess of MeOH was evaporated under reduced pressure and the residue was dissolved in water (8 ml). The aqueous solution was cooled to 0 °C and acidified with concentrated HCl. After 1 h at 0 °C the reaction mixture was filtered and the precipitate was washed with water and dried to give the phthalide (7b) (0.7 g). The filtrate was extracted with CHCl₃ to give a second crop of the phthalide (7b) (0.2 g). The product was purified by precipitation from a CHCl₃ solution with diethyl ether, m.p. 174–175 °C (Found: C, 62.3; H, 4.4. C₁₀H₈O₄ requires C, 62.5; H, 4.2%); ν_{max} (KBr) 3 040, 2 990, 2 890, 2 740, 1 730, 1 630, 1 305, 1 250, 1 120, 1 050, 860, 790, and 750 cm⁻¹; δ (CDCl₃) 2.46 (s, CMe), 5.47 (s, CH₂O), 7.66 (d, *J* 9 Hz, 4-H), and 8.36 (d, *J* 9 Hz, 3-H).

(b) *With Bu^tLi.* The following procedure for the conversion of the adduct (3a) into compound (7a) is typical. To a stirred suspension of the adduct (3a) (0.98 g, 5 mmol) in diethyl ether (10 ml) cooled to -78 °C was added dropwise Bu^tLi (5.9 ml, 10 mmol). The mixture was stirred for 1 h at -78 °C and then for 12 h at 25 °C. It was then quenched with MeOH, and the reaction mixture was processed as described above to give the phthalide (7a) (0.8 g). Recrystallisation from acetone gave an analytical sample, m.p. 173–174 °C (lit.,¹⁶ 170–172 °C) (Found: C, 60.3; H, 3.45. C₉H₆O₄ requires C, 60.65; H, 3.4%); ν_{max} (KBr) 3 080, 2 980, 2 740, 1 730, 1 600, 1 300, 1 180, 1 110, 1 050, 790, and 760 cm⁻¹; δ (CDCl₃) 5.57 (s,

CH₂O), 7.79 (dd, *J*₁ 7, *J*₂ 1.6 Hz, 5-H), 7.90 (q, 7 Hz, 4-H), and 8.53 (dd, *J*₁ 7, *J*₂ 1.6 Hz, 3-H).

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