Reaction of Allyl and Benzyl Alcohols, and their Toluene-p-sulphonates, with Furan

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2-Allyl- and 2-benzyl-furans may be prepared from allyl or benzyl alcohols which are capable of generating stable carbonium ions. The tosyl derivative of the alcohol is refluxed with furan in acetonitrile. The reaction is catalysed by lithium perchlorate. Some alcohols can react directly with furan under acidic conditions. Alcohols investigated include 2-benzylallyl alcohol (8), E-α-methylcinnamyl alcohol (2) and its p-nitro- and p-methoxy-derivatives, (1) and (3), benzyl alcohol, p-nitrobenzyl alcohol, and p-methoxybenzyl alcohol. Both geometrical isomers of α-methyl-p-nitrocinnamyl alcohol, (1) and (13), were prepared and their stereochemistry established by chemical and spectroscopic methods. Only the E-isomer (1) reacts with furan, however. The mechanism of the reaction is discussed and attempts to achieve a 1,3-dipolar cycloaddition are described.

REPORTS of allylfurans in the literature are rare. This is probably because these compounds are very difficult to obtain and are somewhat unstable, although recently a new method of synthesis was described by Hoffmann and Janes.[1] These workers treated substituted furans with allyl iodides under the influence of silver trichloro-acetate at −50° in liquid sulphur dioxide. We now report that some 2-allylfurans as well as 2-benzyl-furans, may be prepared by treating furan in aceto-nitrile solution with the appropriate allyl or benzyl tosylate, or in some instances by simply treating furan with the appropriate alcohol in ethanolic solution con-taining hydrochloric acid.

The reaction proceeds particularly well with β-aryl allyl tosylates. Thus when the tosyl derivative of E-α-methyl-p-nitrocinnamyl alcohol (1) was refluxed in acetonitrile solution containing 20% furan, the corresponding 2-allylfuran (4) was obtained in 60% yield. The much more reactive tosylates of E-α-methylcinnamyl alcohol (2) and E-α-methyl-p-methoxy-cinnamyl alcohol (3) reacted at room temperature to give 2-allylfurans (5) and (6) respectively, as also did the tosylate of *trans*-cinnamyl alcohol to give 2-cinnamyl-furan (7). The aryl residue in conjugation with the double bond of the allyl group in these tosyl derivatives markedly affects the ease of reaction with furan. Thus the tosylate of 2-benzylallyl alcohol (8), the uncon-jugated isomer of (2), remained largely unchanged after being refluxed for 74 h in acetonitrile–furan solution, and only a trace of new product could be detected by t.l.c. examination of the reaction mixture. When the reaction was carried out in an autoclave at 120°, or in a sealed tube, the desired product 2-(2-benzyl-allyl)furan (9) could be obtained. It was discovered, however, that addition of anhydrous lithium perchlorate to the reaction mixture markedly increased the rate of reaction and this enabled (9) to be obtained much more conveniently using ordinary refluxing conditions.

The tosyl derivatives of benzyl alcohols may also react with furan in acetonitrile to give the correspond-ing 2-benzylfurans. Benzyl tosylate behaves like the tosylate of alcohol (8) in that it only reacts in presence of lithium perchlorate, to give 2-benzylfuran (11), but the very unstable p-methoxybenzyl tosylate reacts rapidly at room temperature to give 2-p-methoxybenzyl-furan (12). On the other hand, 2-p-nitrobenzylfuran

(10) could not be obtained at all by this method, even in the presence of lithium perchlorate. Both allyl and 2-methylallyl tosylates also failed to undergo reaction with furan under a variety of conditions. Small amounts of new compounds were formed, as


(1) R = NO₂
(2) R = H
(3) R = OMe

(4) R = NO₂
(5) R = H
(6) R = OMe

(7)

(8)

(9)

(10) R = NO₂
(11) R = H
(12) R = OMe
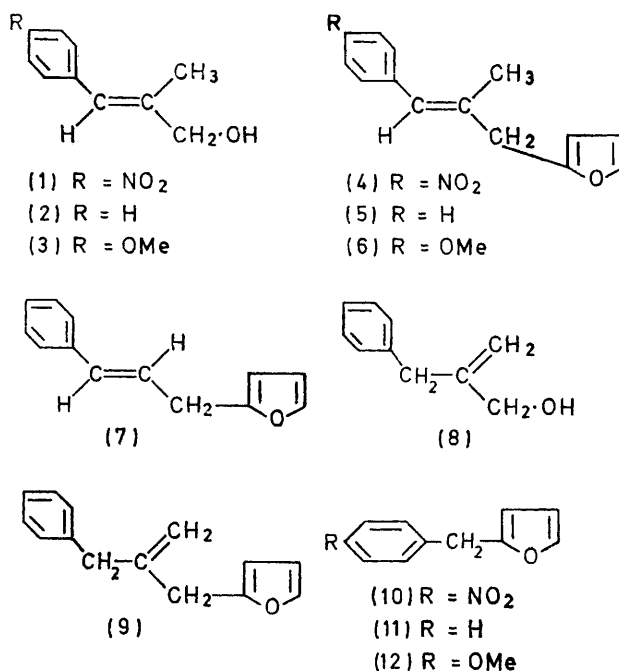
evidenced by t.l.c., but no allyl or methylallylfuran could be isolated and intractable brown polymeric material comprised the bulk of the product.

It was hoped to prepare the geometrical isomer of compound (4) from the tosylate of Z-α-methyl-p-nitro-cinnamyl alcohol (13). Alcohol (13) was obtained by u.v. irradiation of its geometrical isomer (1) in ether solution. Surprisingly, however, this tosylate failed completely to react with furan, even in presence of lithium perchlorate. This unreactivity may be attri-buted to steric inhibition of planarity in the derived allylic carbonium ion or ion pair. Models of the planar carbonium ion show a severe interaction between an *ortho*-hydrogen atom of the aromatic ring and the s-cis-hydrogen atom of the methylene group. A

[1] H. M. R. Hoffmann and N. F. Janes, *J. Chem. Soc.* (C), 1969, 1456.

further constraint on the reaction is that the bulky *cis*-aryl group sterically shields one side of the allylic methylene group so that the attacking furan molecule must approach the intermediate ion-pair from the same direction in which the tosylate anion is departing.

(13)

(14) R = Substituted allyl or benzene

(15)

(16)

(17) X = OMe
(18) X = OBu^t
(19) X = Cl
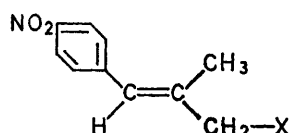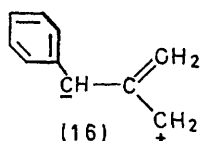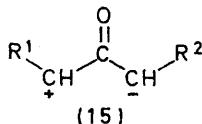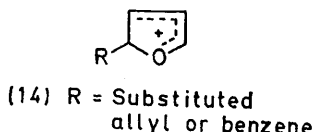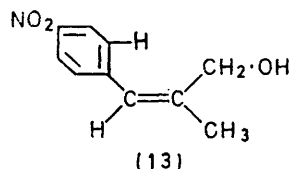
2-(*E*-α-Methyl-*p*-methoxycinnamyl)furan (6) could be prepared in good yield directly from the alcohol (3) by treatment of the latter with furan in ethanolic solution containing hydrochloric acid, at room temperature. *p*-Methoxybenzyl alcohol similarly afforded 2-*p*-methoxy-benzylfuran (12) together with di-*p*-methoxybenzyl ether as a by-product. Cinnamyl alcohol and α-methyl-cinnamyl alcohol (2) also reacted with furan under these conditions, but very slowly. Benzyl alcohol, *p*-nitrobenzyl alcohol, and alcohols (1), (8), and (13) did not react at all, although alcohol (1) gave *E*-α-methyl-*p*-nitrocinnamylbenzene when refluxed with toluene-*p*-sulphonic acid in benzene solution. When α-methyl-*p*-methoxycinnamyl alcohol (3) was treated with a 1 : 1 furan–ether solution which had been satur-ated with dry hydrogen chloride, di-(α-methyl-*p*-meth-oxycinnamyl) ether was obtained in addition to the furan derivative (6).

The double bond in the allyl compounds described in this study showed little tendency to migrate under the reaction conditions used, and no products containing the vinyl furan system were encountered. This was particularly surprising in compound (9) where the double

bond remained isolated and did not move into con-jugation with either the furan or the benzene ring. The position of the double bond in (9) was evident from its n.m.r. spectrum which showed signals at τ 3·80 and 4·05 due to two vinylic protons. There was no sign of a resonance due to a vinylic methyl group. The double-bond position in compounds (4)—(7) was assigned on three grounds; (i) the 3-furyl proton of these compounds resonates in the n.m.r. at τ 4·0—4·1. This is in agreement with the chemical shift of 3-H in 2-alkyl,[2] 2-benzyl,[3] and 2-furfuryl[4] furans, but is at appreciably higher field than would be expected for 3-H of a 2-vinyl furan;[2,5] (ii) u.v. spectra show no sign of a vinylfuran chromophore at 270 nm.,[6] (iii) i.r. spectra show no absorption in the region 1520—1570 cm.$^{-1}$ 2-Substituted furans having a double bond conjugated with the furan ring generally exhibit a C=C stretching vibration here.[7] In addition, compounds (5), (6), and (9)—(12), although not (4) or (7), show a peak at $M - 81$ in their mass spectra, corresponding to loss of $-CH_2-C=CH-CH=CH\cdot O$; in (6) this is the base peak. In (4), cleavage occurs at the same place but the positive charge is carried by the furfuryl fragment which appears at 81 as the base peak. All these compounds except (5) also display a molecular ion.

The stereochemistry of the double bond in the 2-allyl-furan derivatives (4)—(7) is taken to be the same as in the corresponding alcohols from which the furan com-pounds were prepared. This assumption is reasonable in view of the known high rotational barriers for allyl cations. For example, the non-interconversion of *cis*- and *trans*-allyl cations under solvolytic conditions was demonstrated by Young, Sharman, and Winstein[8] who showed that hydrolysis of *cis*- and *trans*-crotyl chlorides gave the corresponding alcohols with over 99% preservation of the geometry of the double bond. The stereochemistry of the double bonds in the alcohols (1)—(3) and (13) was assigned on the basis of the chemical shift of the vinyl proton in their n.m.r. spectra.[9] The assignment for (1) was confirmed rigorously by a chemical method, as follows. The alcohol (1) was ob-tained by sodium borohydride reduction of α-methyl-*p*-nitrocinnamaldehyde, which was prepared by base-catalysed condensation of *p*-nitrobenzaldehyde and pro-pionaldehyde.[10] The α-methyl-*p*-nitrocinnamaldehyde was oxidised to the methyl ester of the corresponding acid using activated manganese dioxide in methanol in presence of cyanide ion. This procedure, due to Corey,[11] converts αβ-unsaturated aldehydes into methyl esters with preservation of stereochemistry of the double bond.

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[3] F. Bohlmann, H. Jastrow, G. Ertingshausen, and D. Kramer, *Chem. Ber.*, 1964, **97**, 801.
[4] P. H. Boyle, W. Cocker, T. B. H. McMurry, and A. C. Pratt, *J. Chem. Soc.* (C), 1967, 1993.
[5] Varian Catalogue 235, 152; also ref. 2 and M. H. Gianni, E. L. Stogryn, and C. M. Orlando, jun., *J. Phys. Chem.*, 1963, **67**, 1385.
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[11] E. J. Corey, N. W. Gilman, and B. E. Ganem, *J. Amer. Chem. Soc.*, 1968, **90**, 5616.

The methyl ester was hydrolysed to the known [12] E-α-methyl-p-nitrocinnamic acid. Re-esterification of this acid with sulphuric acid and methanol gave the same ester, showing that no *cis–trans* isomerisation occurred during the ester hydrolysis. Direct oxidation of E-α-methyl-p-nitrocinnamaldehyde with chromium trioxide also gave E-α-methyl-p-nitrocinnamic acid. The assignment of E-stereochemistry to the double bond in alcohol (2) [13] was confirmed by its method of preparation, from E-α-methylcinnamaldehyde [14] by sodium borohydride reduction.

In the formation of 2-allyl- and 2-benzyl-furans described above, the initial step is most probably generation of the allyl or benzyl carbonium ion by heterolysis of the tosylate, possibly proceeding through ion pairs. The intermediacy of ion pairs is well established for many S_N1 reactions, particularly when carried out in poorly ionising solvents. The marked effect of lithium perchlorate on the reaction of tosylates with furan may constitute another example of Winstein's 'special salt effect', in which the perchlorate anion acts as a scavenger for the solvent-separated ion-pair, preventing its reversion to starting material (*i.e.* external ion-pair return) and accelerating the reaction rate.[15] After initial formation of allyl or benzyl carbonium ion (or ion pair) the reaction probably proceeds by electrophilic attack on furan, to give an intermediate of type (14), which with loss of proton would lead to the observed products. One cannot eliminate the possibility of an alternative mechanism [equation (1)] in which the allyl carbonium ion undergoes cycloaddition to the
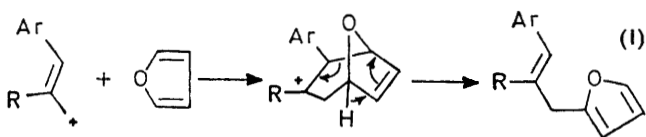
diene system of furan.[16] A fragmentation reaction with loss of proton from the resulting cationic cyclo-adduct would also lead to the observed products. This mechanism would be very unlikely for reaction with the benzyl tosylates, however, since the resonance energy of benzene would be lost in the cycloadduct, and it is perhaps unnecessary, therefore, to invoke it for reaction with allyl tosylates in the absence of evidence to the contrary.

Cycloaddition reactions have been achieved [17] between dienes and the 1,3-dipolar species (15), often postulated as an intermediate in the Favorskii reaction, and generated by reaction of an α-halogenoketone with base. Treatment of suitable allyl tosylates by base could, in principle, lead to proton removal followed by

loss of tosylate anion to generate a similar 1,3-dipolar species of type (16) which should be considerably stabilised by resonance. No cycloaddition products of a species such as (16) with furan could be obtained, however. Treatment of the tosylate of (1) with furan in refluxing acetonitrile in presence of the non-nucleophilic base, 2,6-lutidine, gave only the furan substitution product (4). Treatment of the same tosylate with furan in methanolic sodium methoxide or in a potassium t-butoxide–t-butyl alcohol system gave only the corresponding methyl or t-butyl ethers, (17) and (18) respectively. The methyl ether (17) was independently synthesised from the alcohol (1) by conversion of the latter into its chloride (19) with hydrogen chloride in ether and treatment of the chloride (19) with sodium methoxide in methanol. When the alcohol (1) was treated with thionyl chloride a mixture of (19) and its allylic isomer was obtained. Reaction of the tosylate of (1) with furan in dimethyl sulphoxide containing potassium t-butoxide resulted in a complex black mixture of decomposition products. Similar efforts to obtain a cycloadduct from furan and the tosylate of alcohol (8) also failed. On treatment of this tosylate in furan solution with basic alumina at room temperature, di-(2-benzylallyl) ether was obtained.

The common method used for preparing tosylates, with toluene-p-sulphonyl chloride in pyridine, was found to be unsuitable for preparing the allyl and benzyl tosylates used in the above work. The most successful methods were found to be either refluxing the alcohol with toluene-p-sulphonyl chloride in benzene solution over solid sodium hydroxide using Dean and Stark conditions, or else treating the alkoxide, formed from the appropriate alcohol and sodium hydride, with toluene-p-sulphonyl chloride in ether.[18]

EXPERIMENTAL

* For details see Notice to Authors No. 7 in *J. Chem. Soc. (A)*, 1970, Issue No. 20.

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[14] N. E. Hoffman, A. T. Kanakkanatt, and R. F. Schneider, *J. Org. Chem.*, 1962, **27**, 2687.

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[16] H. M. R. Hoffmann, D. R. Joy, and A. K. Suter, *J. Chem. Soc. (B)*, 1968, 57.

[17] R. C. Cookson, M. J. Nye, and G. Subrahmanyam, *J. Chem. Soc. (C)*, 1967, 473; A. W. Fort, *J. Amer. Chem. Soc.*, 1962, **84**, 4979.

[18] J. K. Kochi and G. S. Hammond, *J. Amer. Chem. Soc.*, 1953, **75**, 3443.

2-Benzylallyl alcohol (8) was prepared by the method of Hawthorne.[19] *E*-α-Methyl-*p*-nitrocinnamaldehyde was prepared by base-catalysed condensation of *p*-nitrobenzaldehyde and propionaldehyde,[10] m.p. 110—112° (lit.,[10] m.p. 112—114°), ν_{max} 1670 (C=O) and 1612 (C=C) cm^{-1}, λ_{max} 300 nm (log ε 4·29) [lit.,[10] 301 nm (log ε 4·29)].

E-α-*Methyl*-p-*nitrocinnamic Acid Methyl Ester.*—*E*-α-Methyl-*p*-nitrocinnamaldehyde (0·63 g) with sodium cyanide (0·82 g), glacial acetic acid (0·30 g), and active manganese dioxide (5·75 g) was stirred in methanol for 24 h at room temperature. Work up in the usual way[11] gave a yellow crystalline solid (0·41 g), m.p. 109·5—110° (from ethanol), ν_{max} 1700 (C=O) and 1611 (C=C) cm^{-1}, λ_{max} 207, 226, and 301 nm (log ε 4·35, 4·20, and 4·44), m/e 221 (M^+) (Found: C, 59·75; H, 5·0; N, 6·3. $C_{11}H_{11}NO_4$ requires C, 60·3; H, 5·15; N, 6·3%).

Hydrolysis of the ester with methanolic potassium hydroxide gave *E*-α-methyl-*p*-nitrocinnamic acid, m.p. 204—205° (from water), (lit.,[12] 205—207°), ν_{max} 1668 (C=O) and 1610 (C=C) cm^{-1}. The same acid was obtained by oxidation of the *E*-aldehyde with chromium trioxide in acetone.

E-α-*Methyl*-p-*nitrocinnamyl alcohol* (1) was prepared by sodium borohydride reduction of the corresponding aldehyde, m.p. 41—43° (lit.,[10] 44—46°), ν_{max} 3150 (OH) and 1640 (C=C) cm^{-1}, λ_{max} 224 and 312 nm (log ε 4·07 and 4·20) (lit.,[10] 221 and 311 nm, log ε 4·06 and 4·09) (Found: C, 62·2; H, 5·7; N, 7·25. $C_{10}H_{11}NO_3$ requires C, 62·3; H, 5·7; N, 7·1%).

Z-α-*Methyl*-p-*nitrocinnamyl Alcohol* (13).—*E*-α-Methyl-*p*-nitrocinnamyl alcohol (1) (3·5 g) was dissolved in ether (250 ml) and photolysed in a Pyrex cell for 3 h. The solvent was evaporated under reduced pressure and the resulting oil was chromatographed on silica (600 g); initial elution with ether–light petroleum (1 : 1) gave (1) (2 g) and (13) (1·2 g), b.p. 140° at 0·6 mmHg, ν_{max} 3490 (OH) and 1650 (C=C) cm^{-1}, λ_{max} 209, 224, and 308 nm (log ε 4·13, 4·18, and 4·27) (Found: C, 61·8; H, 5·85; N, 7·0. $C_{10}H_{11}NO_3$ requires C, 62·3; H, 5·7; N, 7·1%).

E-α-*Methyl*-p-*methoxycinnamyl alcohol* (3) was prepared by sodium borohydride reduction of the corresponding aldehyde,[20] m.p. 64·5—66° (from ethanol–light petroleum), ν_{max} 3300 (OH), 1650 (C=C), 1275 (C–O), and 1030 (C–O) cm^{-1}, λ_{max} 209 and 257 nm [log ε 4·23 and 4·29 (*c* 0·009 mg/ml)]; m/e 178 (M^+, 14%), 161 (62%), and 57 (100%).

The tosylates were prepared by one of two general methods.

Method A.—The alcohol (0·023 mol) was dissolved in benzene (250 ml) with toluene-*p*-sulphonyl chloride (0·024 mol), and sodium hydroxide (0·3 mol) was added. The heterogeneous mixture was refluxed using a Dean and Stark apparatus for azeotropic removal of water. The reaction was examined periodically by t.l.c. and reached completion after *ca.* 8 h. The mixture was allowed to cool and filtered to remove the solid inorganic layer. Evaporation of the filtrate gave the crude product.

Method B. The procedure was based on that of Kochi and Hammond.[18] The alcohol (0·027 mol) was dissolved in super-dry ether (25 ml) in a rigorously dried three-neck flask under an inert atmosphere. Sodium hydride (0·027 mol) (as a 1 : 1 dispersion in oil) was added and the mixture

was refluxed with stirring for 0·5 h; it was then cooled to −15° in an ice–salt bath. A solution of purified[21] toluene-*p*-sulphonyl chloride (0·027 mol) in super-dry ether (25 ml) was added slowly, with stirring. The mixture was allowed to warm slowly to 0° and a sintered glass filter was attached to the flask. The mixture was forced through the filter under pressure of dry nitrogen into a similar flask in a solid CO_2–acetone bath at −70°, thus removing precipitated sodium chloride. The original flask was washed twice with 10-ml portions of super-dry ether which were transferred similarly to the second flask. A solution of the desired tosylate at −70° was thus obtained.

E-α-*Methyl*-p-*nitrocinnamyl toluene*-p-*sulphonate* was prepared by method A giving crude material, m.p. 78—80°. Recrystallisation from ethyl acetate–light petroleum gave crystals (2·3 g, 30%), m.p. 82°, ν_{max} 1684 (C=C), 1365 (S=O), 1160 (S=O), and 1180 (S=O) cm^{-1} (Found: C, 59·2; H, 4·9; N, 3·9; S, 8·9. $C_{17}H_{17}NO_5S$ requires C, 58·9; H, 4·8; N, 4·0; S, 9·2%).

Z-α-*Methyl*-p-*nitrocinnamyl toluene*-p-*sulphonate* was prepared by method A. The crude material was recrystallised from ether–light petroleum to give pale yellow crystals, m.p. 91·5—92° (yield 45%), ν_{max} 1655 (C=C), 1380 (S=O), 1180 (S=O), and 1190 (S=O) cm^{-1}, m/e 347 (M^+) (Found: C, 58·8; H, 4·95; N, 4·1. $C_{17}H_{17}NO_5S$ requires C, 58·9; H, 4·8; N, 4·0%).

2-Benzylallyl toluene-p-*sulphonate* was prepared by method A. The crude material was recrystallised from cold ether–light petroleum to give white crystals, m.p. 56°, yield 60%, ν_{max} 1670 (C=C), 1380 (S=O), 1180 (S=O), and 1190 (S=O) cm^{-1}, m/e 302 (M^+) (Found: C, 67·2; H, 56·5; S, 10·9. $C_{17}H_{18}O_3S$ requires C, 67·5; H, 6·0; S, 10·6%).

Methylallyl tosylate was prepared by method A. The crude material was separated by column chromatography to give a colourless oil, b.p. 116—120° at 1 mmHg (lit.,[22] 136—138° at 2 mmHg), yield 20%. Allyl tosylate[23] was prepared by method A.

Cinnamyl toluene-p-*sulphonate* was prepared by method B. The ethereal solution of the tosylate at −70° was evaporated to dryness under a stream of dry nitrogen to give white crystalline material. A small sample was withdrawn but it decomposed to a red oil within 5 min on warming to room temperature, ν_{max} 1647 (C=C), 1378 (S=O), 1182 (S=O), and 1166 (S=O) cm^{-1}.

The toluene-p-sulphonates of α-methyl-*p*-methoxycinnamyl alcohol and α-methylcinnamyl alcohol were prepared by method B, but could not be successfully isolated and were used directly in ether solution.

The toluene-*p*-sulphonate of *p*-methoxybenzyl alcohol[18,24] was also prepared by method B, and used directly in solution.

The toluene-*p*-sulphonates of benzyl and *p*-nitrobenzyl alcohols were prepared as described by Kochi and Hammond.[18]

2-(E-α-*Methyl*-p-*nitrocinnamyl)furan* (4).—The toluene-*p*-sulphonyl ester of (1) (0·144 mol) was dissolved in a 20% solution of furan in acetonitrile (10 ml) and refluxed for 10 h; the cool mixture was diluted with ether, washed with water, dried (MgSO$_4$) and evaporated under reduced

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[23] H. Gilman and N. J. Beaber, *J. Amer. Chem. Soc.*, 1925, **47**, 518.
[24] H. C. Brown, R. Bernheimer, C. J. Kim, and S. E. Scheppele, *J. Amer. Chem. Soc.*, 1967, **89**, 370.

pressure to give a black oil. The oil was chromatographed on 50-g of silica; elution with light petroleum gave (4) as the only isolable product, b.p. 120° at 0·3 mmHg (yield 57%), $\nu_{max.}$ 1640 (C=C), 1150, 1107, and 1017 (C–O–C), $\lambda_{max.}$ 309 and 223 nm (log ε 5·63 and 6·01); m/e 243 (M^+, 78%), 115 (76), and 81 (100) (Found: C, 67·5; H, 5·5; N, 5·25. $C_{14}H_{13}NO_3$ requires C, 69·1; H, 5·3; N, 5·8%).

2-(α-*Methylcinnamyl)furan* (5).—A 20% solution of furan in acetonitrile (25 ml) was added to an ethereal solution of α-methylcinnamyl toluene-*p*-sulphonate (0·0233 mol) at −70°. The mixture was allowed to warm to room temperature, and was then set aside for 1 h, after which no further reaction occurred as evinced by t.l.c. The mixture was worked up as for (4) to give a trace of toluene-*p*-sulphonyl chloride (4% of starting amount) and (5) as the only isolable products. The overall yield of (5) was 17%, b.p. 66° at 0·2 mmHg, $\nu_{max.}$ 1646 (C=C) 1143, 1075, and 1010 (C–O–C), $\lambda_{max.}$ 246 and 211 nm (log ε 4·10 and 4·09) (c 0·91 mg/ml) m/e 77 (100%), 106 (86), 105 (85), 117 (14, M − 81) (Found: C, 84·8; H, 7·1. $C_{14}H_{14}O$ requires C, 85·0; H, 7·0%).

2-(E-α-*Methyl*-p-*methoxycinnamyl)furan* (6) was formed in 15% yield by reaction of α-methyl-*p*-methoxycinnamyl toluene-*p*-sulphonate with 20% furan in acetonitrile in the manner described for (5), b.p. 118° at 1·2 mmHg, $\nu_{max.}$ 1645 (C=C), 1150, 1078, and 1012 (C–O–C), $\lambda_{max.}$ 254 and 210 nm [log ε 4·04 and 4·03 (c 0·046 mg/ml)] m/e 228 (M^+, 3%), 147 (M − 81, 100), 162 (M − 66, 100) (Found: C, 78·7; H, 7·1. $C_{15}H_{16}O_2$ requires C, 79·0; H, 7·0).

2-trans-*Cinnamylfuran* (7).—An ethereal solution of *trans*-cinnamyl toluene-*p*-sulphonate (1·44 mol) at −70° was evaporated by passage of a stream of dry nitrogen, and a 20% solution of furan in acetonitrile (100 ml) was added to the residue. The mixture was allowed to warm to room temperature and was then set aside for 0·5 h. The mixture was worked up as described for (4) to give 2-cinnamylfuran as the only isolable product, b.p. 82° at 0·2 mmHg, (lit.,[25] 138—140° at 10 mmHg), yield 24%, $\nu_{max.}$ 1650 (C=C), 1150, 1080, and 1016 (C–O–C) cm⁻¹, $\lambda_{max.}$ 213 (shoulder 217) and 251 nm [log ε 3·83 and 3·79, (c 0·017 mg/ml)], m/e 184 (26% M^+), 77 (66), 67 (66), and 40 (100).

2-(2-*Benzylallyl)furan* (9).—2-Benzylallyl toluene-*p*-sulphonate (1·441 mol) was refluxed in 20% furan–acetonitrile (50 ml) for 24 h with lithium perchlorate (3·4 g). The cooled mixture was diluted with ether, washed with water, dried, and evaporated to give 2-(2-benzylallyl)-furan in 31% yield as the only non-polymeric product, b.p. 60° at 0·2 mmHg, $\nu_{max.}$ 1650 (C=C), 1150, 1076, and 1010 (C–O–C) cm⁻¹, $\lambda_{max.}$ 268, 251, and 222 nm [log ε 2·85, 2·86, and 3·91 (c 0·78 mg/ml)], m/e, 198 (M^+, 2%), 40 (100), no other abundance greater than 18%, 117 (M − 81, 8) (Found: C, 85·0; H, 6·95. $C_{14}H_{14}O$ requires C, 84·8; H, 7·1%).

2-*Benzylfuran* (11).—Benzyl toluene-*p*-sulphonate (1·441 g) was refluxed in 20% furan–acetonitrile containing anhydrous lithium perchlorate (3·4 g) for 2 h. Work up as for (9) gave 2-benzylfuran (24%), b.p. 90° at 8 mmHg (lit.,[26] 92° at 8 mmHg), m/e 158 (M^+, 100%), 129 (90,) 91 (68), and 105 (52).

[25] Y. I. Tarnopol'skii, I. S. Shraiber, and V. N. Belov, *Khim. geterotsikl. Soedinenii*, 1967, 10.
[26] V. Ramanathan and R. Levine, *J. Org. Chem.*, 1962, **27**, 1216.

2-(p-*Methoxybenzyl)furan* (12).—This compound was prepared from *p*-methoxybenzyl toluene-*p*-sulphonate as described for compound (5) (44% yield), b.p. 80° at 0·7 mmHg (lit.,[27] 97—99° at 1 mmHg).

Reaction of Cinnamyl and Benzyl Alcohols with Furan: General Conditions.—The alcohol (0·01 mol) was dissolved in ethanol (15 ml), with furan (0·02 mol) and concentrated hydrochloric acid (1 ml), and was then set aside until the reaction had proceeded to completion (t.l.c.). The mixture was diluted with ether, washed with water, dried (Na_2SO_4), and evaporated under reduced pressure. The resulting oil was separated by column chromatography with 15% ether–light petroleum.

α-Methyl-*p*-methoxycinnamyl alcohol (3) when treated in this way gave 60% of (6) after 6 h; starting alcohol (20%) was also recovered.

α-Methylcinnamyl alcohol (2) when treated likewise gave 52% of (5) after 7 days; starting alcohol (23%) was recovered.

Cinnamyl alcohol after 4 days of reaction as above yielded 57% of (7) and 40% starting alcohol.

p-Methoxybenzyl alcohol gave 32% of (12), together with di-*p*-methoxybenzyl ether, 34%, b.p. 120° at 0·2 mmHg (lit.,[28] 100—106° at 0·1 mmHg), and starting alcohol 10%.

In all cases a certain amount of intractable polymer was formed.

Reaction of the Alcohol (3) *with Furan and Gaseous* HCl.— α-Methyl-*p*-methoxycinnamyl alcohol (3) (750 mg) was dissolved in 50% furan–ether (100 ml) which was saturated with dry HCl gas. After 8 h the reaction was worked up in the usual manner to give (6) (43%) and di-(E-α-methyl-*p*-methoxycinnamyl) ether (38%), m.p. 63—64°, $\nu_{max.}$ 1670 (C=C), 1250, and 1036 (C–O–C) cm⁻¹, m/e 338 (M^+, 10%), 261 (62), and 186 (100).

E-α-*Methyl*-p-*nitrocinnamylbenzene*.— α-Methyl-*p*-nitrocinnamyl alcohol (1) (2·5 g) was refluxed in benzene (250 ml) with toluene-*p*-sulphonic acid monohydrate (2·5 g) for 3 h. The mixture was allowed to cool and was then washed with water, dried ($MgSO_4$), evaporated under reduced pressure, and chromatographed on silica (200 g); elution with 30% ether–light petroleum gave E-α-*methyl*-p-*nitrocinnamylbenzene* in 70% yield, b.p. 90° at 0·3 mmHg, $\nu_{max.}$ 1636 (C=C), 1508, and 1338 (C–NO₂) cm⁻¹, m/e, 253 (M^+, 100%), 192 (74), and 91 (62) (Found: C, 76·3; H, 6·3; N, 5·4. $C_{16}H_{15}NO_2$ requires C, 75·9; H, 5·9; N, 5·3%).

E-α-*Methyl*-p-*nitrocinnamyl Chloride* (19).—E-α-Methyl-*p*-nitrocinnamyl alcohol (1) (100 mg) was dissolved in ether which was saturated with dry hydrogen chloride for 96 h. The solution was diluted with ether, washed with water, dried (Na_2SO_4), evaporated under reduced pressure, and chromatographed on silica (200 g), elution with 10% ethyl acetate–light petroleum, gave the chloride (19), 68%, b.p. 136° at 0·6 mmHg, $\nu_{max.}$ 1640 (C=C), 1510 and 1342 (C–NO₂) (Found: C, 57·1; H, 5·0; N, 6·4; Cl, 16·3. $C_{10}H_{10}NO_2Cl$ requires C, 56·8; H, 4·7; N, 6·6; Cl, 16·8%).

Methyl E-α-*Methyl*-p-*nitrocinnamyl Ether* (17).—E-α-Methyl-*p*-nitrocinnamyl chloride (19) (80 mg) was refluxed for 4 h in methanol (10 ml) containing sodium (9 mg), to give 63% yield of ether (17), b.p. 140° at 0·3 mmHg, $\nu_{max.}$ 1648 (C=C), 1508 and 1342 (C–NO₂), and 1102 (C–O) cm⁻¹ (Found: C, 63·8; H, 6·3; N, 6·8. $C_{11}H_{13}NO_3$ requires

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[28] E. F. Pratt and P. W. Erickson, *J. Amer. Chem. Soc.*, 1956, **78**, 76.

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C, 63·8; H, 6·3; N, 6·8). The ether (17) was also obtained by refluxing *E*-α-methyl-*p*-nitrocinnamyl toluene-*p*-sulphonate with either methanolic sodium methoxide or with methanol.

t-Butyl E-α-*Methyl*-p-*nitrocinnamyl Ether* (18).—*E*-α-Methyl-*p*-nitrocinnamyl toluene-*p*-sulphonate (500 mg) was dissolved in furan (50 ml) and a solution of potassium t-butoxide (250 mg) in t-butyl alcohol (45 ml) was added to the solution. After being refluxed for 11 h, the mixture was diluted with ether, washed with water, dried (Na$_2$SO$_4$), and evaporated. The residue was chromatographed on silica; elution with 5% ethyl acetate–light petroleum gave the *ether* (18) as the only non-polymeric product (38% yield), b.p. 100° at 0·1 mmHg, ν$_{max.}$ 1652 (C=C), 1508 and 1340 (C–NO$_2$), and 1104 (C–O) cm^{-1} (Found: C, 67·1;

H, 7·5; N, 5·35. C$_{14}$H$_{19}$NO$_3$ requires C, 67·5; H, 7·6; N, 5·6%).

Di-(2-*benzylallyl*) *Ether*.—2-Benzylallyl toluene-*p*-sulphonate (730 mg) with basic alumina (19 g) was stirred in furan (30 ml) for 48 h at room temperature; the mixture was filtered, evaporated under reduced pressure, and chromatographed on silica (60 g); elution with light petroleum gave (9) (7 mg) and *di*-(2-*benzylallyl*) *ether* (236 mg), ν$_{max.}$ 1660 (C=C) and 1095 (C–O–C) cm^{-1} (Found: C, 85·9; H, 8·1. C$_{20}$H$_{22}$O requires C, 86·3; H, 8·0%).