800. *Studies in Molecular Rearrangement. Part IX.* Oxotropic Rearrangements in the Five-membered Heterocyclic Series.*

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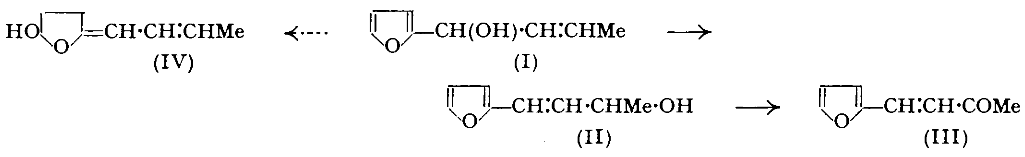
The synthesis of the isomeric 1-2′-furyl-3-methylallyl and 3-2′-furyl-1-methylallyl alcohols (I, II) and their thienyl analogues (V, VI), and the acid-catalysed rearrangements of (I) to (II) and of (V) to (VI) are described. 3-2′-Thienyl-1-methylallyl alcohol has been dehydrated to 1-2′-thienylbuta-1 : 3-diene (VII). The light-absorption properties of the various derivatives are recorded and discussed.

In earlier papers (Braude, Jones, and Stern, *J.*, 1946, 396; 1947, 1087; Braude, Fawcett, and Newman, *J.*, 1950, 793) oxotropic rearrangements of a series of 1-arylallyl alcohols have been described. It was demonstrated that aryl groups have a strong activating influence and cause almost complete displacement of the equilibrium to one side, owing to the resonance stabilisation associated with the conjugated 3-arylallyl systems. It was of interest to extend this work to some heterocyclic derivatives, in order to demonstrate the conjugating properties of the heterocyclic groups and, more particularly, for quantitative study of the effects of such groups on reactivity (cf. following paper). This paper describes the synthesis and rearrangement of 1-2′-furyl- and 1-2′-thienyl-3-methylallyl alcohol. Attempts to obtain the corresponding 2′-pyrryl derivative have, so far, been unsuccessful.

The alcohol (I) was readily obtained from 2-furylmagnesium iodide and crotonaldehyde. On treatment with dilute mineral acid, it underwent rearrangement in the expected manner to the isomer (II), which was also prepared from β-2-furylacraldehyde and methylmagnesium bromide and was characterised as the *p*-nitrobenzoate. The constitution of (II) was further confirmed by oxidation with acetone and aluminium *tert.*-butoxide to furfurylideneacetone (III), characterised as the 2 : 4-dinitrophenylhydrazone. Comparison of the ultraviolet light absorption properties of (II) and of the rearrangement product of (I) showed that the isomerisation is over 98% complete. An alternative mode of rearrangement, involving migration of the hydroxyl group into the ring to give (IV), can be envisaged, corresponding to that observed in the case of 2-furyldiphenylmethanol and similar derivatives (Ushakov and Kutcharov, *J. Gen. Chem. Russia*, 1944, **14**, 1073, 1080, 1087; 1950, **20**, 1885; cf. Braude, *Quart. Reviews*, 1950, **4**, 423), where migration in the side chains is not possible. No trace of (IV) was detected, however, under the conditions employed and this is not surprising since the propenyl group will be more susceptible than the furan ring to nucleophilic attack by a water molecule which constitutes the rate-determining step of the reaction (Braude, *loc. cit.*). Moreover, if any of the isomer (IV) were formed, the ensuing equilibrium between (IV) and (II) would be expected to lie far on the side of (II) which possesses a considerably higher degree of resonance stabilisation derived from the intact furyl system.



(IV) (I) (II) (III)

The alcohol (V) was similarly obtained from crotonaldehyde and 2-thienylmagnesium iodide, or, more conveniently, 2-thienylsodium (Schick and Hartough, *J. Amer. Chem. Soc.*, 1948, **70**, 287). Rearrangement under the influence of dilute hydrochloric acid gave exclusively the isomer (VI), which was also prepared from β-2-thienylacraldehyde and methylmagnesium bromide and characterised as the *p*-nitrobenzoate. As with the furyl analogue, spectral measurements showed that the isomerisation of (V) to (VI) is quantitative. Dehydration of (VI) with potassium hydrogen sulphate under very carefully con-

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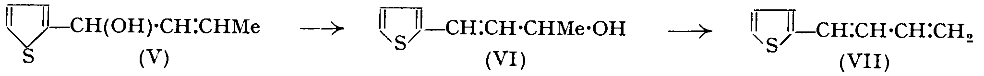
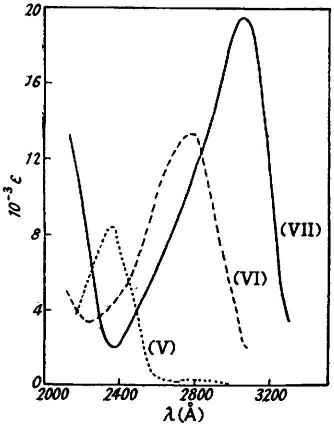
trolled conditions afforded the highly unstable thienylbutadiene (VII). Attempts to prepare this diene by the dehydration of other 2-thienylbutenols have since been described by Gmitter and Benton (*J. Amer. Chem. Soc.*, 1950, **72**, 4586) who were only able to isolate it in the form of Diels–Alder adducts.



Ultra-violet light absorption data for the main derivatives described and for the phenyl analogues are collected in the Table. The alcohols (I) and (V) show bands near 2200 and 2400 Å respectively, which are due to the unconjugated furyl and thienyl groups and may be compared with the "E"-band near 2100 Å associated with a monoalkylated phenyl group (cf. *Ann. Reports*, 1945, **42**, 108; Bowden and Braude, *J.*, 1952, 1068). The isomers (II) and (VI) exhibit new bands at longer wave-lengths which are due to the conjugated vinylfuran and vinylthiophen systems (cf. Laitinen, Miller, and Parks, *J. Amer. Chem. Soc.*, 1947, **69**, 2707; Kuhn and Dann, *Annalen*, 1941, **547**, 293; Jackman, Bolen, Nachod, Tullar, and Archer, *J. Amer. Chem. Soc.*, 1949, **71**, 2301) and may be compared with the band near 2500 Å associated with a styryl group. Lastly, the thienylbutadiene (VII) exhibits highly characteristic absorption at still longer wave-lengths which may be compared with that of phenylbutadiene (see Table and Fig.). It is noteworthy that the wave-length displacements of the bands of the conjugated with respect to the unconjugated derivatives are of the same order in the phenyl and the heterocyclic derivatives; this indicates that what may loosely be called the "extent of conjugation" with an ethylenic bond is similar for the phenyl, furyl, and thienyl groups.



Ultra-violet light absorption data (Å) (*ethanol solutions*).

	X·CH(OH)·CH:CHMe		X·CH:CH·CHMe·OH			X·CH:CH·CH:CH$_2$		
	$\lambda_{max.}$	ε	$\lambda_{max.}$	ε	Δλ †	$\gamma_{max.}$	ε	Δλ †
X = Phenyl [1]	2100	10,000	2510	19,500	410	2800	28,000	700
X = 2-Furyl *	2200	10,200	2650	18,000	350	—	—	—
X = 2-Thienyl	2360	10,000	2800	13,500	440	3070	22,000	690

* Main bands only (cf. Experimental section).
† Shifts with respect to first column.
[1] Braude, Jones, and Stern, *J.*, 1947, 1087.

EXPERIMENTAL

M. p.s are uncorrected. Light-absorption data were determined on a Hilger Spekker instrument and refer to ethanol solutions unless otherwise stated.

1-2'-*Furyl*-3-*methylallyl Alcohol*.—Ethyl bromide (0·5 g.) and then 2-iodofuran (47 g.; Gilman and Wright, *J. Amer. Chem. Soc.*, 1933, **55**, 3307) in ether (100 ml.) were added during 1 hour to magnesium filings (7·5 g.) in ether (500 ml.), with stirring under nitrogen. The resulting solution was decanted and to it freshly distilled crotonaldehyde (14·5 g.) in ether (50 ml.) was added during 1 hour at 0°. After a further 2 hours' stirring, excess of aqueous ammonium chloride was added and the ethereal layer was separated, dried (Na_2SO_4–K_2CO_3), and fractionated from a trace of potassium carbonate, to give the *alcohol* (12 g., 36%), b. p. 48—50°/0·02 mm., n_D^{23} 1·5018 (Found: C, 69·3; H, 7·1. $C_8H_{10}O_2$ requires C, 69·7; H, 7·3%). Light-absorption: $\lambda_{max.}$ 2200, 2690, 2780, and 2890 Å; ε 10,200, 1200, 1100, and 900, respectively.

3-2'-*Furyl*-1-*methylallyl Alcohol*.—(*a*) β-2-Furylacraldehyde (52 g.; Kornig and Hey, *Ber.*, 1925, **58**, 2559) in ether (300 ml.) was added dropwise to a stirred solution of methylmagnesium bromide (from magnesium, 10 g., and methyl bromide, 42 g.) in ether (500 ml.) at −10°. After 2 hours, excess of aqueous ammonium chloride was added and the products were worked up as above, giving the *alcohol* (32 g., 55%), b. p. 58°/0·02 mm., n_D^{18} 1·5291 (Found: C, 69·6; H, 7·4.

$C_8H_{10}O_2$ requires C, 69·7; H, 7·3%). Light absorption: $\lambda_{max.}$ 2580, 2650, and 2780 Å; ε 17,500 18,000, and 13,000 respectively. The p-*nitrobenzoate* separated from aqueous methanol in crystals, m. p. 59—60° (Found: C, 63·0; H, 4·7; N, 4·9. $C_{15}H_{13}O_5N$ requires C, 62·7; H, 4·5; N, 4·9%). Light absorption: $\lambda_{max.}$ 2660 Å; ε 31,000.

(*b*) 1-2′-Furyl-3-methylallyl alcohol (4 g.) was dissolved in a 0·001M-solution of hydrogen chloride in 60% aqueous dioxan (100 ml.). After 4 hours at room temperature, water was added and the oil which separated was distilled, giving 3-2′-furyl-1-methylallyl alcohol (3 g.), b. p. 52—53°/0·01 mm., n_D^{20} 1·5320, $\lambda_{max.}$ 2580, 2650, and 2760 Å (ε 18,000, 18,500, and 14,000, respectively) which formed a *p*-nitrobenzoate, m. p. 59°, undepressed on admixture with the authentic specimen described above.

2-*Furfurylideneacetone* (4-2′-*Furylbut*-3-*en*-2-*one*).—The above alcohol (4 g.), aluminium *tert.*-butoxide (6 g.), acetone (60 ml.), and benzene (60 ml.) were refluxed for 24 hours. Excess of dilute sulphuric acid was added and the product isolated with ether, giving 2-furfurylideneacetone (2·8 g.) which crystallised from pentane in needles, m. p. 36°, undepressed on admixture with an authentic specimen, b. p. 125°/25 mm., m. p. 37—38°, prepared by the method of Leuck and Cejka (*Org. Synth.*, Coll. Vol. I, 2nd edn., p. 283). It formed a 2 : 4-*dinitrophenylhydrazone* which crystallised from pyridine in crimson rods, m. p. 248° (Found: C, 52·7; H, 4·0; N, 17·7. $C_{14}H_{12}O_5N_4$ requires C, 53·1; H, 3·8; N, 17·7%) ($\lambda_{max.}$ 3130 and 4010 Å; ε 18,000 and 36,500, in chloroform).

3-*Methyl*-1-2′-*thienylallyl Alcohol*.—(*a*) 2-Iodothiophen (40 g.; Minnis, *Org. Synth.*, Coll. Vol. II, p. 357) in ether (150 ml.) was added dropwise to a stirred suspension of magnesium filings (4·8 g.) in ether (50 ml.) at 0° under nitrogen. Reaction was complete after 0·5 hour and crotonaldehyde (13·3 g.) in ether (40 ml.) was then added at 0°. After 2 hours, excess of aqueous ammonium chloride was added and the products were worked up as above, giving the *alcohol* (23·5 g., 80%) as a colourless liquid, b. p. 63—65°/0·2 mm., n_D^{20} 1·5530 (Found: C, 62·6; H, 6·6; S, 20·7. $C_8H_{10}OS$ requires C, 62·35; H, 6·5; S, 20·8%).

(*b*) Bromobenzene (30 g.) in ether (100 ml.) was slowly added to a well-stirred mixture of thiophen (24 g.), finely divided sodium amalgam (from sodium, 9 g., and mercury, 4 g.) and ether (100 ml.) (cf. Schick and Hartough, *J. Amer. Chem. Soc.*, 1948, **70**, 287), and the mixture was then slowly heated to the b. p. and refluxed for 3 hours. After this had cooled, crotonaldehyde (20 g.) in ether (30 ml.) was added dropwise at 5°. After a further hour, ethanol (20 ml.) was carefully added, followed by water (100 ml.). Isolation of the product with ether and fractionation from a trace of potassium carbonate gave the alcohol (28 g., 65%), b. p. 64°/0·1 mm., n_D^{26} 1·5495.

β-2-*Thienylacraldehyde*.—Thiophen-2-aldehyde (25 g.; Dunn, Waugh, and Dittmer, *J. Amer. Chem. Soc.*, 1946, **68**, 2118), freshly distilled acetaldehyde (20 g.), and 2% aqueous sodium hydroxide (200 ml.) were stirred together for 12 hours at room temperature. Isolation of the products with ether and fractionation afforded the *acraldehyde* (17 g., 55%), b. p. 55°/0·05 mm., n_D^{20} >1·68 (Found: C, 60·9; H, 4·5. C_7H_6OS requires C, 60·8; H, 4·4%). Light absorption: $\lambda_{max.}$ 3200 Å; ε 22,500. The *semicarbazone* crystallised from aqueous acetic acid in needles, m. p. 216° (decomp.) (Found: C, 49·0; H, 4·9; N, 21·2. $C_8H_9ON_3S$ requires C, 49·1; H, 4·7; N, 21·5%). Light absorption in dioxan: $\lambda_{max.}$ 3300 Å; ε 37,500. The 2 : 4-*dinitrophenylhydrazone* crystallised from ethyl acetate in dark red plates, m. p. 243° (decomp.) (Found: C, 48·5; H, 3·1; N, 17·2. $C_{13}H_{10}O_4N_4S$ requires C, 49·0; H, 3·2; N, 17·6%). Light absorption in chloroform: $\lambda_{max.}$ 3240 and 4060 Å; ε 13,500 and 39,000.

1-*Methyl*-3-2′-*thienylallyl Alcohol*.—(*a*) The above aldehyde (5·8 g.) in ether (20 ml.) was slowly added to a stirred solution of methylmagnesium bromide (from magnesium, 1 g., and methyl bromide, 4 g.) in ether (100 ml.). After 2 hours, excess of aqueous ammonium chloride was added and the product isolated as above, giving the *alcohol* (4·5 g., 63%), b. p. 72°/0·05 mm., n_D^{17} 1·5898 (Found: C, 62·6; H, 6·5; S, 20·1. $C_8H_{10}OS$ requires C, 62·35; H, 6·5, S, 20·8%). Treatment of the alcohol (0·5 g.) with *p*-nitrobenzoyl chloride (0·7 g.) in dry pyridine gave the p-*nitrobenzoate* which crystallised from aqueous methanol in needles, m. p. 67° (Found: N, 4·8. $C_{15}H_{13}O_4NS$ requires N, 4·6%). Light absorption: λ_{max} 2650 and 2810 Å; ε 26,000 and 22,000.

(*b*) 3-Methyl-1-2′-thienylallyl alcohol (3 g.) was dissolved in a 0·1M-solution of hydrogen chloride in 60% aqueous acetone (150 ml.). After 24 hours at room temperature, water (500 ml.) was added and the product isolated with ether. Fractionation from a trace of potassium carbonate gave 1-methyl-3-2′-thienylallyl alcohol (1·7 g.), b. p. 80—81°/0·5 mm., n_D^{18} 1·5885, which formed a *p*-nitrobenzoate, m. p. 66°, undepressed on admixture with the authentic specimen described above.

1-2′-*Thienylbuta*-1 : 3-*diene*.—The foregoing alcohol (4 g.) and finely powdered potassium hydrogen sulphate (0·8 g.) were heated to 70° for 15 minutes *in vacuo* (1 mm.) in a small flask with a wide side-arm fitted with a receiver cooled in solid carbon dioxide. Rapid distillation gave a product (2 g.) which was at once diluted with peroxide-free ether (10 ml.) and dried (K_2CO_3). Fractionation of the ethereal solution gave the *diene* as a colourless liquid, b. p. 73°/0·4 mm., n_D^{22} 1·5977 (Found: C, 70·5; H, 5·8; S, 23·7. C_8H_8S requires C, 70·6; H, 5·9; S, 23·6%).

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